

Migration and transformation behavior of volatile phenol in the vadose zone

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ABSTRACT

Research on the migration and transformation of phenol with space and temporal variability in the vadose zone is hindered by monitoring technology in field experiments. Four column experiments were conducted to investigate the effect of porous media size, volatilization, biological effects, and oxidation on the transport of phenol in the vadose zone. The initial inflow phenol concentration of each column was 500 mg/L, and the final outflow concentrations were 0, 348, 240, and 365 mg/L. More than 90% of reduction of phenol concentration occurred at the top of the simulation column. Results show that volatilization and oxidation are the main factors that could lead to the decrease of phenol concentration in an open system. However, these two processes cannot be accurately separated. The migration rate of phenol was larger in coarse sands (6.06 cm/d) than in fine sands (4.55 cm/d). Phenol biodegradation did not occur under experimental conditions. However, mercury (as biological inhibitor) could react with phenol to generate a mercury–phenol complex, which could lead to the reduction of phenol concentration to 21.6% in the simulation experiment.

Key words | influence factor, migration and transformation, phenol, underground environment

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INTRODUCTION

Oil prices are reaching record levels as energy demand continues to rise; oil shale becomes a domestic alternative source that helps meet the energy demand (Jiang *et al.* 2007; Bussell 2009; Liu *et al.* 2006). However, the development and utilization of oil shale resource could produce a number of pollutants. These pollutants are mainly divided into three categories, namely, volatile phenols, petroleum hydrocarbon contaminants, and heavy metals (Preis *et al.* 1997). The pollutants produced during the development and utilization of oil shale resource could cause local environmental issues in air, water, and soil, affecting the growth of plants and animals as well as human life activities (Gavrilova *et al.* 2010; Blinova *et al.* 2012). Volatile phenol is a toxic and mordant chemical substance and is considered to be one of the contaminants included on the superfund priority list of hazardous substances in the United States (USEPA 1987; Reichardt *et al.* 2003).

Phenol is an aromatic compound with one hydroxyl group attached to its benzene ring; hydroxyl hydrogen can be ionized and is mildly acidic in the solution (Pardeep 2010). Phenol is found not only in the oil-shale industry but also in oil refinery, petrochemical, and wood preservation

plants. The wastewater-containing phenol is discharged into the environment, moves down through the vadose zone, and subsequently leaches to the groundwater. However, the unsaturated zone, which is the connection bridge between groundwater and land surface, contains air and water and has a complicated hydrological structure (Joseph & Robert 1984a). In addition, a certain amount of mineral particles and some organic materials are present on the medium surface of the vadose zone (Winiarski *et al.* 2013). A hydrogeochemical reaction may occur during the migration of phenol in the unsaturated zone. However, the migration and transformation mechanisms of phenol in the vadose zone are unclear.

Predicting the migration behavior of phenol is challenging because of the complex geochemical reactions between phenol and the medium (e.g. adsorption-desorption and biodegradation). Some research has been conducted on the long-term leaching behavior of phenol in cement/activated-carbon solidified/stabilized hazardous waste. These studies indicate that the leaching behavior of phenol in a co-disposal scenario is unpredictable due to inadequate ionization of HAc in the HAC–NaAc buffer

solution (Liu *et al.* 2006, 2013). Varank *et al.* (2011) reported the migration behavior of phenol transported through alternative composite liners and found that 35 to 50% of organic contaminants (phenolic compounds) could transport through the landfill liners to the groundwater. Joseph & Robert (1984b) reported the influence of vadose zone conditions in groundwater pollution. Phenol can be biodegradable by many bacterial colonies (e.g. *Acinetobacter* and *Pseudomonas*) in a certain concentration range, which has been proven by many previous works (Kanekar *et al.* 1996; Mette *et al.* 2000; Spence *et al.* 2001; Shibata *et al.* 2006; Cordova-Rosa *et al.* 2009). However, whether the biodegradation reaction could occur during the migration of phenol through the vadose zone requires further study.

Limited studies have been performed regarding the migration and transformation of pollutants in the underground environment. Furthermore, few reports exist on the migration of phenol transport through the vadose zone. This paper aims to study the migration and transformation of phenol in the vadose zone by designing a series of simulation experiments. The influencing factors, such as different geological media, redox conditions, and biotic degradation, have been studied in the experiments, and the major controlling factors for phenol migration in the vadose zone have been analyzed and discussed.

EXPERIMENT MATERIALS AND METHODS

Chemicals

Phenol, mercuric chloride, 4-aminoantipyrene, potassium ferricyanide, sodium phosphate, and fluorescein double acetate, which are of analytic grade, were purchased from commercial suppliers. Nitrogen, which is a high purity gas, was purchased from Changchun JvYang Gas Co., Ltd. Deionized water prepared with Milli-Q water was used as experimental water. Oxygen needs to be removed in deionized water by injecting nitrogen for 2 h to prevent the oxidization of phenol by dissolved oxygen.

Porous media and columns

The porous media were derived from near-surface sediments of Yitong river in Changchun city, and then screened using standard sieves. The properties of the porous media are listed in Table 1.

Phenol transport was studied in five columns (1, 2, 3, and 4). The size of the column was 75 mm × 1,000 mm (inside diameter × height). The plexiglass column was covered by a black plastic bag to prevent the photocatalytic degradation of phenols. Columns were filled with sand. In addition, a layer of quartz sand, which was 2 cm thick, covered the top and bottom of each column to ensure proper liquid distribution and discharge at the inlet and outlet of the column. Six sampling ports were located at distances of 10, 30, 50, 70, or 90 cm from the bottom of the column. The solution was added to the column by a peristaltic pump. A schematic description of the packed column system is given in Figure 1.

Analytical methods

Phenol was measured at 510 nm by UNIC 7200 visible spectrophotometer by using 4-aminoantipyrene then stand light spectrophotometry (*Standard Methods for the Examination of Water and Wastewater* 1998). Biological activity was determined by the FDA fluorescent chromogenic method.

Methods

The factors influencing the transport of phenol in the vadose zone may include the following: porous media size, volatilization, biological effects, and oxidation. Table 2 lists the domain of variation of the four main experimental parameters. Four column simulations were set up to study the migration and transformation rule of volatile phenol in the vadose zone. In the open system, the simulation column was not sealed, and the top of the column was exposed to air. In the closed system, the simulation column was sealed to avoid volatilization during experiment. Mercury

Table 1 | Physical and chemical properties of the media in simulation experiments

Medium	Partical size mm	pH	Fe ³⁺ (mg/kg)	Ca ²⁺ (mg/kg)	Mg ²⁺ (mg/kg)	Cl ⁻ (mg/kg)	Organic matter (%)
Coarse sand	0.5–2.0	7.06	20.39	8.46	3.36	0.31	0.24
Fine sand	0.1–0.25	6.89	21.56	3.23	1.99	0.25	0.43

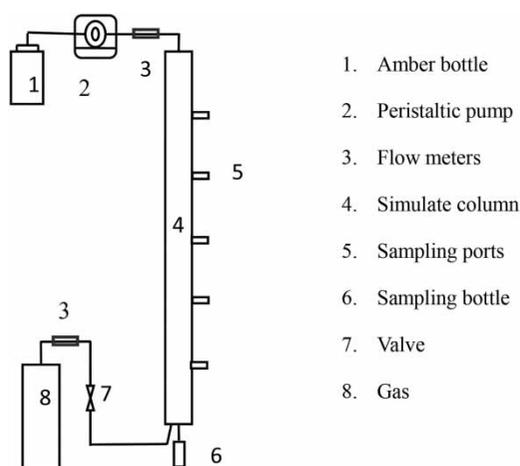


Figure 1 | Schematic diagram of experimental apparatus.

chloride was added in column 3 to inhibit biotic degradation. The experiments on columns 1 and 2 were performed in different system statuses to investigate the effect of volatilization. Biotic degradation can be studied by comparing columns 2 and 3. The influence of different media can be discussed by comparing columns 2 and 4. The initial concentration of phenol was 500 mg/L in experimental solution. Table 2 shows the experimental parameters of the simulation columns.

Another column simulation was designed for different inlet flow rates and conditions with or without dissolved oxygen (Table 3). The influence of flow rate can be analyzed

Table 2 | Factors considered in the experiments

	Medium	Quality Kg	Flow rate mL/d	System status	Solution type
Column 1	Fine sand	5.4	60	Open	Phenol
Column 2	Fine sand	5.4	60	Closed	Phenol
Column 3	Fine sand	5.4	60	Closed	Phenol + HgCl ₂
Column 4	Coarse sand	6.34	60	Closed	Phenol

Table 3 | Different flow rates and redox conditions in the experiment

	Time	Medium	Filled gas	System status	Flow rates
Stage 1	0–21 days	Fine sand	Nitrogen	Closed	60 mL/d
Stage 2	22–29 days	Fine sand	Nitrogen	Closed	100 mL/d
Stage 3	30–36 days	Fine sand	Air	Closed	100 mL/d

in the process of phenol pollution in the vadose zone by comparing the results of stages 1 and 2. The influence of oxygen can be analyzed in the process of phenol pollution in the vadose zone by comparing the results of stages 2 and 3.

RESULTS AND DISCUSSION

Volatilization effects

Column 1 is an open system; thus, phenol can be volatilized. Column 2 is a closed system; thus, no volatilization occurred. Phenol was not detected in the outlet of column 1. However, in column 2, the outlet phenol concentration was as high as 348 mg/L (Table 4 and Figure 2). By comparing the results of columns 1 and 2, we determined that volatilization is an important reducing process for phenol migration in the vadose zone. The volatilization of phenol is more important than oxidation because of the weak oxidation in the experiment (see ‘Influence of oxygen’ section). Volatilization played a dominant role in the process of phenol migration in the unsaturated zone.

The decrease in phenol concentration between inlet and outlet in columns 1, 2, and 3 was 500, 152, and 260 mg/L, respectively. Table 5 shows the phenol concentrations at different sampling ports from the top to the bottom of the column. The initial inlet phenol concentration for the three simulation columns was 500 mg/L. The phenol concentrations decreased from the top to the bottom sampling ports because of volatilization (Figure 3). The volatilization reaction mainly occurred on the top of the column. The phenol concentration decreased significantly, and more than 90% of the reduction in phenol concentration was observed at the top of the simulation column. The concentrations of the phenol nearly did not change in the middle

Table 4 | Results of the simulation experiment

	V	t/2	C	ΔC
Column 1				500
Column 2	4.55	22	348	152
Column 3	4.88	20.5	240	260
Column 4	6.06	16.5	365	135

V: migration velocity of phenol in the vadose zone, cm/d.

t/2: time that the relative concentration value phenol is 0.5 in water sample at the bottom of simulation column, d.

C: the average value of phenol concentration, mg/L.

ΔC: the decreased value of phenol concentration, mg/L.

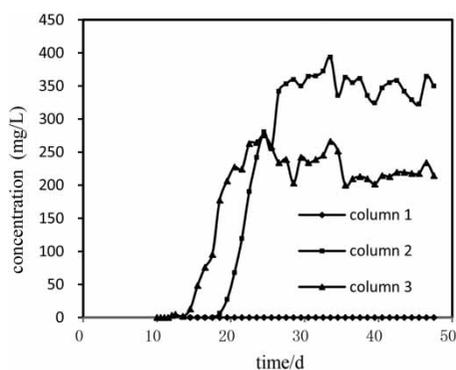


Figure 2 | Experimental results of volatile phenol under different conditions.

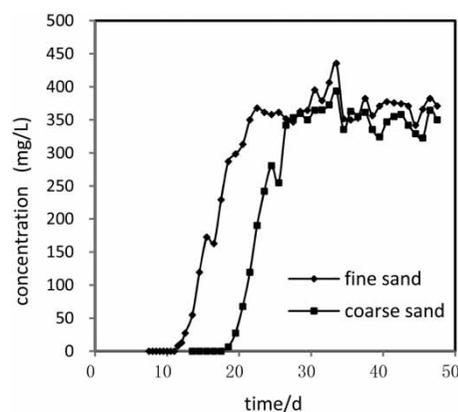


Figure 4 | Simulated experimental results of volatile phenol concentration in different media.

Table 5 | Concentration of phenol at all ports

Port	1	2	3	4	5	6
Column 1	54	0	0	0	0	0
Column 2	360	358	356	355	355	348
Column 3	260	254	249	246	245	240

Port 0: initial concentration; port 1: at the bottom of simulation column.

Port 2, 3, 4, 5 and 6: from the bottom to the top at the side of simulation column.

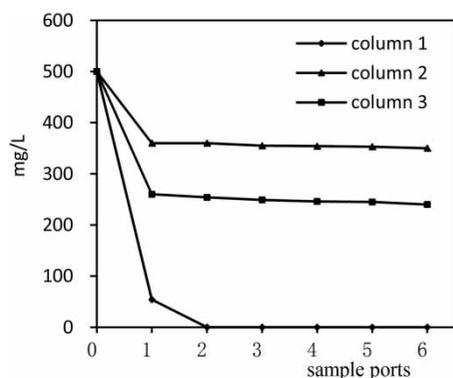


Figure 3 | Concentration of volatile phenol in each sample port.

to the bottom of the simulation column due to bad ventilation.

Influence of different media

Figure 4 shows the simulation results with different media. In the coarse-sand column, the phenol migration rate in the unsaturated zone is about 6.06 cm/d, which is faster than the migration rate (4.55 cm/d) in the fine-sand column. The decreases of outlet phenol concentration are 135 and 152 mg/L in coarse and fine sands, respectively.

This finding indicates that the phenol migration rate is larger in the coarse medium than in the fine medium. However, the difference of stable outlet phenol concentration for coarse sand and fine sand column is not significant, which means that the reaction effects of different media used in the experiment are similar (Figure 4).

Biodegradation effects

Phenol is bioavailable in aerobic and anaerobic conditions, as attested by previous works (Spence *et al.* 2001; Shibata *et al.* 2006). However, no evidence has been found for the biological reactions observed in this laboratory simulation experiment. The influence of biodegradation for phenol migration in the column experiments is very small and can be neglected. Therefore, the degradation strains of phenol might not exist, or the phenol concentration was 282 mg/L, which may suppress the biological activity in the experiment (Pardeep 2010).

Although the biodegradation effect was not evident in the simulation experiments, the phenol concentration in column 3 was lower than that in column 2. The simulated solution was added with mercury bichloride in column 3. The stable concentration of column 3 was lower by more than 108 mg/L than that in column 2. These findings illustrate that heavy metal Hg could affect the hydrogeochemical change of phenol and decrease the concentration of phenol. Moreover, this reaction led to the reduction of phenol concentration to 21.6% of the initial concentration. Ravichandran (2004) reported that phenol can react with mercury and produce mercury-organic complex, thus influencing the mobility and solution of phenol in the vadose zone (Drexel *et al.* 2002). Therefore, the concentration of

phenol will decrease in the unsaturated zone when mercury exists in the reaction system.

Influence of flow rates

At room temperature, with the increase of the inflow rate from 60 to 100 mL/d, the outlet phenol concentration changed from 282 to 304 mg/L (Figure 5). Therefore, increasing the flow rate will lead to an increase of phenol concentration. Thus, the larger the inlet flow rate, the easier it is for phenol to migrate in the vadose zone.

Influence of oxygen

In stage 3, oxygen exists in the column compared with stage 2 (without oxygen). The phenol concentration also decreased from 304 to 273 mg/L in stage 3 (Figure 5). This finding indicates that oxygen could react with phenol and lead to the decrease of phenol concentration. However, the reaction was weak. According to Lefevre et al. (2011) and Arena et al. (2010), phenol can be oxidized to catechol and hydroquinone or benzoquinone under the presence of oxidants, such as oxygen.

CONCLUSIONS

Phenol, as one of the main pollutants in oil shale distillation or other industries, was discharged into the environment and will gain access to the aquifer through the vadose zone. During the discharge of phenol through the vadose zone in the experiment, the phenol concentration in the water (500 mg/L) reduced to 0, 348, 240, and 365 mg/L. The migration rate in coarse sand was 6.06 cm/d, which is larger than that in fine sand (4.55 cm/d). Phenol will be oxidized in the underground environment when oxygen exists

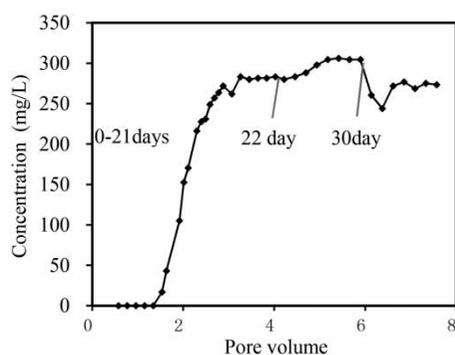


Figure 5 | Result of simulation experiment under different conditions.

in the vadose zone. However, the oxidation reaction during phenol migration is weak and slow. Volatilization is the main factor that could lead to the decrease in phenol concentration. More than 90% of reduction of phenol concentration occurred at the top of the simulation column. The phenol concentration hardly decreased when the phenol solution entered the deep underground environment. In the simulation experiment, phenol biodegradation did not occur under the experimental conditions. However, mercury, as a biological inhibitor, could react with phenol, thus generating mercury–phenol complex. This complex affects the hydrogeochemical reactions in the unsaturated zone. In addition, the larger the inlet flow rate, the easier it is for phenol to migrate in the vadose zone.

ACKNOWLEDGEMENTS

This research project was supported by the Geological Survey Projects of China (grant no. 1212011140036) and National Production Potential of Oil and Gas Resources in cooperative innovation projects (grant no. OSP-01 and OSR-01), and the authors are grateful to the Analysis and Testing Foundation of the Key Laboratory of Groundwater Resources and Environment, Ministry of Education.

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First received 9 March 2014; accepted in revised form 6 June 2014. Available online 19 June 2014