Migration characteristics of atrazine in porous media during managed aquifer recharge

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ABSTRACT

To study the influences of sand and gravel layer and groundwater velocity of Yufuhe River on atrazine migration, adsorption-desorption and sand column experiments were carried out. Results show that the adsorption capacity of montmorillonite, raw sand and washed sand to atrazine sequentially weakens. In different media, the time for atrazine concentrations to peak in washed sand with montmorillonite (WSM), raw sand and washed sand is 60, 135 and 105 minutes respectively, and the peak concentration accounts for 84, 90 and 95% of the initial concentrations. Under different flow rates, the peak time in washed sand at flow rates of 100, 150 and 200 mL/min is 135, 105 and 75 minutes, and the peak time in WSM is 90, 60 and 45 minutes, respectively. Results from this study indicate that increasing flow velocity and suspended colloids concentrations can promote the migration of atrazine in aquifers, while the presence of clay minerals in sand and gravel layers can reduce atrazine migration. Thus, during Yellow River water recharging, the sand and gravel layer of Yufuhe River is helpful to protect the aquifer, but the colloids-associated migration of atrazine can contaminate groundwater in underlying karst aquifer.

Key words: atrazine, flow velocity, managed aquifer recharge, migration, porous media

HIGHLIGHTS

- Migrations of atrazine in porous media are related to clay minerals and colloids.
- Sand and gravel layer can retard the atrazine migration during managed aquifer recharge (MAR).
- Increasing groundwater velocity would accelerate atrazine migration.
- This study is significant to maintain the long-term operation of the MAR.

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INTRODUCTION

Yellow River water is the main source of water supply for most cities in Shandong province (Gao et al. 2015). However, the Yellow River has high silt concentrations, high organic matter contents, and serious pollution. In settling basins, 85% of the suspended particles in Yellow River water are removed, and the turbidity is 3–5 NTU, but fine suspended particles (including clay minerals colloids) with particle size less than 74 μm, trace organic matters and odorous substances still remained (Chien et al. 2018; Hou et al. 2021). Montmorillonite, which accounts for 43% of clay mineral colloids in Yellow River water, can adsorb trace organic matter. Atrazine is one of the eight priority pollutants in Yellow River water with a content of 135.6 ng/L (Ali et al. 2016; Rong et al. 2016). Conventional water treatment technologies have insufficient treatment capacity to remove it, and activated carbon adsorption and ultrafiltration membrane filtration are costly and are not suitable for large-scale treatment (Saiers & Hornberger 1996). In the Yellow River Alluvial Plain, the managed aquifer recharge (MAR) - seepage method is used to improve the water quality of the slightly polluted Yellow River. As one of the main water sources of Yufuhe River recharge project, the Yellow River water stored by the Yellow River Diversion Reservoir is transported to the upper reaches of Yufuhe River by pumping station to recharge karst groundwater. The advantage of the Yufuhe River recharge project is that the Quaternary sand and gravel layer contacts directly with the underlying limestone, which not only has good permeability (20.7 m/d), but also protects the water quality of the karst aquifer. The thickness of the gravel layer is about 20 m, in which the upper gravel layer contains a small amount of clay and the lower gravel layer is pure gravel. The disadvantage is that the excessively high groundwater velocity makes the pollutants quickly migrate, affecting the whole karst aquifer in the area (White 2018). Therefore, the effects of the contents and characteristics of colloids on the
migration of atrazine and the adsorption-desorption characteristics of atrazine in different porous media and different flow rates are studied, which is of great significance to maintain the long-term operation of the MAR project and protect the karst groundwater.

Atrazine is a kind of herbicide with strong mobility in the soil-water environment, which can easily contaminate groundwater. Colloidal particles with high mobility as pollutant carriers in soil and groundwater can promote the diffusion of adsorbed pollutants in groundwater systems (Roy & Dzombak 1997; Kersting et al. 1999). For example, Grolimund et al. (1996) used sand column experiments to demonstrate that for strongly adsorbed pollutants, colloids became the main way for pollutants to migrate in non-calcareous soils with silt loam texture. Zhao et al. (2020) investigated the migration of antimony and arsenic in four kinds of soils by lysimeter experiments; the results showed that antimony and arsenic migrated faster when colloids existed in soils, and arsenic combined more easily with organic matter colloids, resulting in long-distance pollution. The co-migration levels also depend on the physical and chemical properties of the soil and the stability of the colloid. Barton & Karathanasis (2003) studied the effect of colloids on the migration of atrazine in silt sand; the results showed that colloids promoted migration of atrazine mainly by repulsion rather than adsorption. What’s more, TOC, clay properties, iron oxide content and pH value are the key parameters affecting the adsorption and desorption of atrazine in soil (Huang et al. 2013). The application of dissolved organic matters and surfactants can reduce the adsorption and improve the desorption capacity of atrazine in soil (Tian et al. 2019). However, atrazine exists in aquifers for a longer time than in soil, especially in quiet water, and the risk of accumulation is greater (Schwab et al. 2006). Zheng et al. (2018) studied the adsorption and migration of atrazine in washed sand with and without montmorillonite by sand columns, and suggested measures should be taken to reduce the colloids from Yellow River water into the aquifer in MAR schemes. Based on the work of Zheng et al. (2018), this study further explored the effects of clay minerals and groundwater flow velocity on atrazine migration, so as to provide references for recharge projects.

METHODS

Adsorption-desorption experiments

Based on the work of Zheng et al. (2018), isothermal and dynamic adsorption experiments of raw sand as well as isothermal desorption experiment were further studied.

Isothermal adsorption curves. Washed sand (5 g), raw sand (5 g) and montmorillonite powder with nanometer size (0.2 g) were placed in conical flasks (250 mL) respectively. The atrazine solution (20 mL) with concentrations of 5, 10, 15, 20, and 30 mg/L was also added to the conical flasks. Because atrazine is difficult to dissolve in water, the corresponding mass of atrazine was weighed with an electronic balance and dissolved in methanol. Then the solution was transferred to a 1000 mL volumetric flask and diluted with deionized water to volume. The solution was mixed for 24 h at 25 ± 1 °C in a shaker. At the end of the reaction, the supernatant was centrifuged and filtered with a 0.45 μm filter membrane. Raw sand was directly excavated from Yufuhe River, having the following different sizes of similar fractions: effective grain size (D10) of 0.31 mm, average particle size (D50) of 3 mm, and non-uniformity coefficient (D60/D10) of 19.35. Washed sand is raw sand washed by deionized water and filtered with a sieve. The weight of washed sand after drying is 83% of the raw sand. The particles less than 0.074 mm account for 1.24% and 0.1% in raw sand and washed sand respectively. Consequently, it can be considered that the clay minerals were removed from the raw sand by washing. That is, clay minerals account for 17% of the raw sand. Gradation curves of raw sand and washed sand are shown in Figure 1.

Isothermal desorption curves: after the isothermal adsorption experiment, in order to maintain the constant solid-to-liquid ratios, CaCl2 solution (10 mL) with a concentration of 1 mol/L was added to the above mixed solutions of atrazine and washed sand, atrazine and raw sand as well as atrazine and montmorillonite powder. The experimental steps of mixture, centrifugation and filtration were set similarly to the isothermal adsorption experiment.

Dynamic adsorption curves: washed sand (5 g), raw sand (5 g) and montmorillonite powder with nanometer size (0.2 g) were placed in conical flasks (250 mL) respectively. The atrazine solution (20 mL) with concentrations of 20 mg/L was also added to the conical flasks. The solution was placed on a vibrator and shaken back and forth for 2, 4, 6, 8, 12, 24, and 25 h. At the end of the reaction, the supernatant was centrifuged and filtered with a 0.45 μm filter membrane.

Calculation of atrazine adsorption amount:

\[ C = (C_0 - C_e) \times V / m \]  

(1)
where $C$ is adsorption amount of atrazine by media, mg/kg; $C_0$ is the initial concentration of atrazine, mg/l; $C_e$ is the concentration of atrazine in liquid phase after adsorption, mg/l; $V$ is solution volume, ml; $m$ is the mass of the medium, g.

**Calculation of atrazine desorption amount:**

$$C_w = \frac{(C_1 - C_2) V}{m}$$

where $C_w$ is the desorption amount of atrazine by media, mg/kg; $C_1$ is the concentration of atrazine in liquid phase after desorption, mg/l; $C_2$ is the concentration of atrazine in liquid phase before desorption, mg/l.

**Sand column experiments**

On the basis of the research of Zheng et al. (2018), the influence of raw sand on the atrazine migration was studied. Additionally, the effects of different flow rates on the migration of atrazine were explored, too.

A 1.3-m-long plexiglass column with 0.14 m inner diameter (Figure 2) was packed with raw sand or washed sand to 1.0 m thick. A layer of 1–2 cm gravel was filled at the bottom, and then covered with a filter screen to prevent the water outlet being blocked. The peristaltic pump was turned on to saturate the sand column and keep the inflow velocity equal to the outflow velocity.

Firstly, the tracer experiment was carried out. As control for subsequent experiments, salt solution was selected as tracer due to it not reacting with raw sand and washed sand. Salt solution (10 L, 360 g/L) was injected into the washed sand and raw sand respectively at 150 ml/min flow rate. The conductivity of outlet was measured every 5 minutes by conductivity meter. After the conductivity of outlet solution reached the peak and was stable for a period of time, the sand column was rinsed with deionized water until the conductivity of outlet close to zero. In order to be consistent with the following, the conductivities of the solution were taken as the concentrations in the results.

To study the influences of different porous media on the atrazine migration, three comparative experiments were set up. In the first and second experiments, atrazine solution (50 L, 20 mg/L) was injected into the sand column packed with washed
sand and raw sand. In the third experiment, atrazine solution (50 L, 20 mg/L) mixed with montmorillonite with nanometer size (5 NTU) for 2.5 h was injected into a sand column packed with washed sand, which was referred to as the washed sand with montmorillonite (WSM). The atrazine concentrations of the outlet were measured every 15 minutes by HPLC. After the outlet solution concentration reached the peak and was stable for a period of time, the sand column was rinsed with deionized water until the concentration of the outlet was close to zero.

To study the effects of different flow rates on the migration of atrazine, the sand column was packed with washed sand and WSM respectively, and injected with atrazine solution (20 mg/L) at three flow rates of 100, 150 and 200 ml/min. The other steps were the same as above.

RESULTS AND DISCUSSION

Adsorption-desorption experiments
Through adsorption-desorption experiments, the isothermal adsorption curves, isothermal desorption curves and dynamic adsorption curves of atrazine in washed sand, raw sand and montmorillonite were plotted (Figure 3). As shown in Figure 3(a), the adsorption capacity of montmorillonite to atrazine is the strongest, followed by raw sand and washed sand. As shown in Figure 3(b), the desorption capacity of washed sand to atrazine is the strongest, followed by raw sand. Because of the large adsorption amount of montmorillonite, the desorption amount of montmorillonite is larger than that of washed sand and raw sand. As shown in Figure 3(c), the adsorption of atrazine by the three media reaches equilibrium within 24 hours, and the adsorption capacity in 0–5 hours is relatively large, especially in the first 2.5 hours, reaching 42, 56 and 73% of the maximum adsorption capacity respectively.

The adsorption mechanisms of organic pollutants in soil include ion exchange, hydrogen bond, charge transfer, covalent bond, van der Waals force and so on. For soils or sediments, the adsorption of organic pollutants is actually the result of the interaction of clay minerals and organic matter (Cheng et al. 2021). In this study, the raw sand of the sand-gravel layer from Yufuhe River is selected, with low organic matter content, so clay minerals play an important role in the adsorption of atrazine. Clay minerals include montmorillonite, illite, kaolinite and so on. Ion exchange properties are important for clay minerals to adsorb organic pollutants (Awad et al. 2019). Compared with washed sand, there are more clay minerals in raw sand, thus the raw sand has stronger adsorption capacity for atrazine.

As a typical clay mineral, montmorillonite has a double-layer crystal structure and high cation content. The adsorption capacity of montmorillonite for organic compounds is stronger than kaolinite (Polati et al. 2006). Laird et al. (1992) pointed out that the adsorption of atrazine by montmorillonite is related to its surface charge. The higher the surface charge density, the lower the affinity for atrazine. Additionally, the type of montmorillonite also affects the adsorption capacity for atrazine. Sawhney & Singh (1997) claimed that Al-saturated montmorillonite can adsorb much higher amounts of atrazine than Ca-saturated montmorillonite due to the stronger H-bonding between the more polarized H2O and the trivalent Al ion. Therefore, the differences of adsorption and desorption effects between montmorillonite and raw sand are mainly caused by the differences of the characteristics of clay minerals. Compared with raw sand, montmorillonite is a nano-clay mineral with smaller particle size, and larger specific surface area, so it has stronger adsorption capacity than raw sand.

On the contrary, desorption is the reverse process of adsorption. Consequently, the desorption capacity of raw sand is larger than washed sand.

Figure 3 | The (a) absorption curves, (b) desorption curves and (c) dynamic adsorption curves on three porous media.
The migration of salt solution

The obtained experimental data were used to plot breakthrough curves (BTCs) of the salt solution. The ordinate of the BTC is the relative concentration of the salt solution; that is, the ratio of the salt solution concentration at the outlet to the initial concentration, \( C'/C_0' \), and the abscissa is time, in minutes. The BTCs can be used to observe the migration characteristics of salt solution in the porous media intuitively.

The BTCs of tracer in the raw sand and washed sand can be seen in Figure 4. It is basically symmetrical in the washed sand without obvious tailing, but slightly tailing at the end of the BTC in the raw sand. The relative concentration of the peak value in the washed sand and raw sand is 1, which indicates that the salt solution is not adsorbed by washed and raw sand. The salt solution moves faster in the washed sand than in the raw sand, and the time for the outlet solution concentrations to reach the peak value is about 55 minutes and 85 minutes respectively. The main reason is that the porosity of the two media is different. The larger porosity of the washed sand provides a more convenient channel for the migration of the salt solution.

The migration of atrazine in different porous media

The BTCs in different media were drawn in the same method to study the migration characteristics of atrazine in raw sand, washed sand and WSM (Figure 5).

The BTCs in different media are asymmetrical and with the phenomenon of trailing, indicating atrazine is adsorbed and desorbed in the three media. From the shape of the curves, before the peak value, the BTC of WSM is steepest and has the fastest change rate of the atrazine concentrations at the outlet; the raw sand has the slowest curve and change rate. After the peak value, the BTC of WSM has the greatest tailing. The BTC of washed sand has the least tailing and fastest rate to reach stability. From the ratio of peak concentration to initial concentration, the ratio of WSM, raw sand and washed sand is 84, 90 and 95% respectively. From the speed of migration, the migration speed of WSM, washed sand and raw sand is from fast to slow, and the time when the solution reaches the peak value at the outlet is 60, 105 and 135 minutes respectively.

Figure 4 | BTCs of tracer in washed sand and raw sand.

Figure 5 | BTCs of atrazine in three media.
Comparing the peak values of BTCs, the peak value of WSM is the lowest, which is due to the adsorption of montmorillonite. Atrazine and montmorillonite were mixed for 2.5 h before injecting to the column, so the adsorption of atrazine by montmorillonite reaches 73% of the maximum adsorption capacity. Therefore, atrazine was adsorbed continuously by montmorillonite during the migration in the sand column, but a small amount of montmorillonite retained with atrazine adsorbed onto it inside the column, causing the lower peak and subsequent earlier decrease of \( \frac{C}{C_0} \) in WSM. Comparing the migration speed of atrazine in washed sand with WSM, the results reveal that montmorillonite as a colloid, with a larger specific surface area and more adsorption sites, can adsorb more atrazine and promote its migration. Comparing the migration speed of atrazine in washed sand with raw sand, the results demonstrate that the larger porosity of the washed sand provides a convenient channel for its migration and has a smaller retardation than in the raw sand. The absorption capacity of endogenous fine particles in raw sand is limited, and the retardation on atrazine migration is greater than the acceleration. Comparing the migration speed of atrazine in WSM with raw sand, the results indicate that the properties of clay minerals also affect the movement of atrazine.

In summary, the migration of atrazine in the porous media is not only related to the characteristics of the media itself, such as porosity, and colloids content, but also related to the characteristics of clay minerals. Adsorption is the main factor in the migration of pollutants in soil (Smernik & Kookana 2015). Colloids as pollutant carriers provide the rapid transport pathway and promote the migration of adsorbing contaminants (Simunek et al. 2006). Inorganic colloids such as clay and organic colloids such as humus are both responsible for the migration of pollutants (Sun et al. 2020). Novikov et al. (2006) confirmed that colloids as carriers can promote the long-distance transport of plutonium. Therefore, colloids suspended in the water have great adsorption capacity for atrazine, although they can reduce the concentration of atrazine in solution, they associate atrazine and promote its migration to an aquifer, which would pollute more places in a short time. While the endogenous fine particles in the sand layer retard the migration of atrazine and play a role in protecting the aquifer. Schematic diagrams are provided in Figure 6 of the predicted migration patterns of atrazine involving its adsorption and desorption in an aquifer with colloids.

The migration of atrazine under different flow rates

The BTCs under different flow rates were drawn in the same method to study the migration characteristics of atrazine at the rates of 100, 150 and 200 mL/min (Figure 7).

As shown in Figure 5(a), when the flow rate in washed sand is 100, 150 and 200 mL/min, the time for the atrazine concentrations at the outlet to reach the peak is 135, 105 and 75 minutes respectively. The higher the flow velocity, the shorter the time to reach the peak value, the less the tailing, and the peak concentration has no obvious change, which indicates that the increasing flow velocity promote the migration of atrazine but has no effects on the adsorption capacity of washed sand to atrazine. As shown in Figure 5(b), when the flow rate in WSM is 100, 150 and 200 mL/min, the time for the atrazine concentrations at the outlet to reach the peak is 90, 60 and 45 minutes respectively. Similarly, the higher the flow rate, the shorter the time to reach the peak value, the less the tailing, and the higher the peak concentration. It illustrates that increasing flow velocity promotes the migration of atrazine and reduces the contact time between atrazine and porous media, resulting in insufficient adsorption. Consequently, there is more atrazine in solution, which increases peak concentrations.

Comparing (a) with (b), at the same flow velocity, the time to reach peak concentration is shorter, the peak concentration is lower, and the tailing is less in WSM. This is because montmorillonite has a stronger adsorption capacity for atrazine, which can promote the migration of atrazine and reduce its desorption capability, being consistent with the results in different media.

Thus, for the migration of atrazine in a saturated zone, compared with colloids-associated migration, the flow velocity is the dominant factor. Although increasing flow velocity can reduce the adsorption of suspended colloids on atrazine, it can increase the concentrations of atrazine in solutions and contaminate groundwater.

Figure 6 | Predicted migration patterns of atrazine involving its (a) adsorption and (b) desorption in an aquifer.
CONCLUSIONS

The adsorption-desorption experiments show that the adsorption capacity of montmorillonite, raw sand and washed sand to atrazine increases sequentially, while the desorption capacity decreases sequentially. The adsorption mainly occurred in the first 2.5 hours. The results imply that the adsorption and desorption characteristics of atrazine in three media are related to the properties and content of clay minerals.

Through the sand column experiments, the influences of different porous media and different flow velocities on the migration of atrazine are analyzed. In different media, the time of peak values of BTCs shown in WSM, washed sand and raw sand is 60, 105 and 135 minutes respectively, and the ratio of peak value to initial concentration is 81, 95 and 90%, respectively. Under different flow velocities, when the flow rate in washed sand is 100, 150 and 200 mL/min, the time for the atrazine concentrations at the outlet to reach the peak is 135, 105 and 75 minutes respectively, and in WSM the time is 90, 60 and 45 minutes.

Therefore, compared with exogenous montmorillonite, endogenous clay minerals contained in raw sand can retard the migration of atrazine and protect the groundwater. However, colloids have more ability to promote the migration of atrazine and so contaminate aquifer in short time. Larger flow velocity can accelerate the migration of atrazine, reducing the contact time with porous media and adsorption. Consequently, during the process of MAR projects in Yufuhe River using the Yellow River water, the clay mineral colloids in the Yellow River water promote the migration of atrazine in the aquifer. However, the fine particles in the quaternary sand gravel layer of the Yufuhe River retard the migration of atrazine, playing an important role in protecting the groundwater quality, and could reduce the impact of exogenous clay mineral colloids on the water quality in Jinan.

Next, what should be explored in the future is the effects of different amounts of montmorillonite on the migration of atrazine in porous media. How the montmorillonite influences the migration of atrazine will be studied by increasing the concentration of montmorillonite.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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