

Experimental Validation of Retardation of Tritium Migration in the Chinese Loess Media

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Abstract Retardation of tritium migration in the Chinese loess media was studied through column experiments by comparison of the migration velocity with other three “non-adsorptive” tracers of Br^- , ^{99}Tc , and ^{131}I . Results showed that the transport peak of Br^- was 1.25 times earlier than that of tritium when the tracers were simultaneously injected into the column, and the migration of ^{99}Tc was even 1.60 times faster than ^3H when the tracers were simultaneously injected. For iodine, it was only 1.02 times faster than that of tritium, but it should not be ignored. It reflected that the transport of ^3H , compared to that of Br^- , ^{99}Tc , or ^{131}I in the loess media, was retarded. In order to validate the adsorption behavior of tritium on loess, batch tests were carried out using Chinese loess soil. The experimental results indicated that the adsorption of tritium was actual existence, and the distribution

coefficient of tritium is influenced by initial activity of tritium, pH, water/solid ratio, and the content of humic and fulvic acids.

Keywords Tritium · Loess · Retardation · Column experiment · Distribution coefficient · Experimental validation

1 Introduction

Tritium (^3H), with a half-life of 12.323 years, has usually been considered an ideal substance to trace groundwater movement (Brady and Kozak 1995). Tritiated water acts very much like normal water in groundwater flow systems, though it is a radioactive isotope as a low-level β emitter (Leap 1992). Tritium, as a conservative tracer, has also been used to define the breakthrough curves in column or field experiments to characterize the hydrogeological parameters of media (Brustad and NjØs 1980; Gaber et al. 1995; Maraqa et al. 1999; Martin-Garina et al. 2002; Hu and Brusseau 1995; Li et al. 2009). In addition, in terms of radioactivity, tritium is the most abundant residual radionuclide from underground nuclear testing (Garland 1980); after a nuclear explosion, tritium is probably present in free radical form, intimately mixed with and incorporated in the vaporized water at temperatures sufficiently high to cause dissociation of the water molecules (Hu et al. 2008).

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As a “non-adsorptive” tracer, like other applied tracers of Br^- , Tc, and ^{131}I (Van Loon et al. 2003; Szántó et al. 2002), the transport rate of ^3H is generally considered the flow velocity of the groundwater (Zhang et al. 1995; Johansson et al. 2001). Retardation of ^3H by the medium particles is usually neglected when ^3H is applied in determining the flow rate of the groundwater (Gunnar et al. 2000); even though ^3H may be retarded in soil, it is commonly considered a result from volatilization of ^3H . However, some research has observed that tritium can actually be adsorbed on some minerals, causing the retardation of ^3H in some geological media. Fordor-Csanyi et al. (1985) found that migration of tritium became slower in soil media with increasing clay content. In migration experiments with ^{32}P and ^3H , Gupta et al. (1999) observed that the migrating velocity of ^{32}P was larger than that of ^3H by a factor of 4. Van Loon and Jakob (2005) accounted tritium adsorption on clay minerals by a small but non-zero K_d value on the order of $10^{-5} \text{ m}^3 \text{ kg}^{-1}$, which was found to reproduce the data with acceptable precision. Using batch and column experiments to quantify the retardation of tritium in brine-saturated mudstone, halite, and carbonate rocks from the Palo Duro Basin in Texas, Voudrias et al. (1993) concluded that the retardation factor (R_d) of tritium was 1.0–1.1. Otherwise, adsorptions of both gaseous ^3H by soil (Garland and Cox 1980) and liquid ^3H (existing as $^3\text{H}_2\text{O}$ form) by cement (Ono et al. 1995) have been reported. All of the results warranted doubt about the conventional understanding of the transport rate of ^3H , the veracity of “non-reactive” tracer for estimation of flow rate, and groundwater dating.

As adsorption of tritium on the media actually exists, then what are the factors that could influence the adsorption, and what is the influenced extent? As Garland described: “tritiated water, absorbed during a brief exposure, its behavior was described by the diffusion equation, but unexplained discrepancies were found in apparent diffusion coefficients in field conditions” (Garland 1980). It is well known that the physical and chemical properties of soil, such as particle size, pH and E_h , as well as the contents of organic materials and microorganisms, may affect the movement of nuclide (Koch-Steind and Pröh 2001), so the above factors may result in the retardation of ^3H during its transport in the geological media.

There are other reports about the experimental factors which could influence the adsorption or retardation of tritium on some media. In order to determine the suitability of bromide as a substitute for tritium in groundwater tracer in fractured and fissured dolomite, breakthrough curves of both substances were researched by column tests. The results showed that tritium was actually more retarded than bromide in flow-through highly transmissive openings (Leap 1992). An improved agreement between tritium transport results and model curves of chloride transport was obtained by assuming a retardation factor of 1.35 for tritium. The tritium delay could be explained by weak interactions with altered fracture surfaces or by anion exclusion of chloride that was responsible for the faster chloride transport (Hölttä et al. 1996). Furthermore, Turner et al. (2009) found that tritium distribution appears to be influenced by its affinity for organic matter. Moreover, as the mechanism, the kinetic control of groundwater system also was important for the retardation and adsorption of tritium. For example, pore water velocity normally has the opposite effect on solute adsorption. The retardation factors for tritium and chloride have been observed to depend strongly on pore water velocity, with the retardation factor decreasing with an increasing velocity (Bajracharya et al. 1996), and immobile water within soil pore affects the soil saturation as well as nuclide behavior (Maraqa et al. 1997).

Some findings on the migration of ^3H in porous media in China have been reported from both laboratory and field experiments. The retardation coefficient (R_d) is a dimensionless parameter characterizing the retarding ability of adsorption on solute transport, closely related to distribution coefficient. When $R_d = 1$, it implies non-sorption. R_d of tritium in loess was obtained by Teng et al. (2007); the results, based on saturated soil column experiments, showed that the R_d value was from 1.95 to 2.05. Wang et al. (2003) carried out a migration experiment on tritium at 30 m below land surface on loess media. The results gave a distribution coefficient of 0.12 mL/g.

Loess is a special Quaternary deposit characterized by predominance of silt-sized particles enriched in carbonates and quartz. It covers about 10% of the land surface of the Earth, which is concentrated in the temperate zones and in semi-arid desert margin (Liu 1985). In China, loess is widespread in its northern and northwestern parts, and the distribution area is

over one tenth of the whole area of China. The best developed loess area, named Loess Plateau, lies between 34° E and 45° N, along the middle reaches of the Yellow River where the largest thickness (100–200 m) and the major size fraction of loess is 0.05–0.01 mm, which accounts for about 45–60%. The remainder is <0.005 mm fraction, accounting for about 15–25% (Lin and Wei 2006).

The objectives of the present work were to compare the migration velocity of four “non-adsorptive” tracers, ^3H , Br^- , ^{99}Tc , and ^{131}I in loess media by the column experiments and analyze the various factors influencing tritium adsorption on loess media by a distribution coefficient (K_d) from batch tests, and the major influencing factors included water/solid ratio, pH, the activity of tritiated water, and quality of organic matter.

2 Experiments

Experiments were composed of column experiments and batch tests. The column experiments were carried out to investigate the migration of tritium in the loess media by a comparison of the transporting velocity between tritium and some non-adsorptive tracer, like Br^- , ^{99}Tc , or ^{131}I , which have usually been applied as one of the perfect substances for tracing groundwater movement. Batch tests of ^3H were performed for validating the adsorption characteristic of tritium in loess media under some different initial conditions, such as the initial activity of tritium, water/soil ratio, pH value, and mass of organic matter.

2.1 Experimental Site

The site chosen in the China Institute for Radiation Protection (CIRP) field test site was in Yuci City, Shanxi Province, central northern China where the field site is a loess plateau with an elevation of 953 m. The average annual precipitation and evaporation is

about 434 and 326 mm, respectively, and the average annual temperature is 9.3°C. It is a typical loessial zone with thickness of unsaturated loess and unconfined aquifer of 31 and 6 m, respectively. The layer property and relative coefficients of the unsaturated and unconfined aquifer are listed in Table 1.

2.2 Sample Description

All groundwater and loessial samples were collected from the field experimental site. Groundwater samples were taken from shallow groundwater by pumping from the bore holes in the experiment field. The water table was about –8 m from the surface, and the sampling point was 1 m below the water table. The groundwater samples were collected and transported following the protocols given in “Technical Specifications for Environmental Monitoring of Groundwater in China” (Ministry of Environment Protection 2004). The samples were collected in polyethylene bottles of 5-L volume, one at a time, and were stored in a cool and dark place, and the analytical results are presented in Table 2. The mineral, clay, and elemental compositions of loess samples were analyzed by X-ray diffraction. The Chinese national standard of “X-ray diffraction analysis methods for the total amount of clay minerals in sedimentary rocks and common non-clay mineral” (1996) and “X-ray diffraction analysis methods for relative content of clay mineral” (1995) were applied in full clay mineral analysis and the relative clay mineral analysis of the soil samples separately. The results of the mineral composition and chemical composition of the samples in the aquifer medium are shown in Table 3.

2.3 Column Experiments

There were three group column experiments named tests A, B, and C, which were designed and operated for the retardation of ^3H . The mixed tracers of the three groups were tritium and bromide, tritium and

Table 1 Layer property and relative coefficients of the unsaturated and unconfined aquifer

	Bulk density (g/cm ³)	Total porosity	Effective porosity	Hydraulic conductivity (10 ^{–4} cm/s)	pH	<i>T</i> (°C)	Heterogeneous coefficient
Unsaturated loess	1.34	0.51	0.23	4.30	7.85	9.30	7.00
Aquifer medium	1.62	0.42	0.24	5.60	8.00	14.00	10.00

Table 2 Results of groundwater analysis

Constituents			Chemistry compositions (mg/L)												
pH	E_h (V)	T (°C)	K^+	Na^+	Ca^{2+}	Mg^{2+}	HCO_3^-	SO_4^{2-}	Cl^-	PO_4^{3-}	NO_3^-	F^-	Br^-	Al^{3+}	Si
8.21	0.449	13	0.75	81.2	26.7	30.9	249.6	56.9	17.31	0.33	17.78	0.81	0.16	0.032	<0.01

technetium-99, and tritium and iodide. In order to research the influence of the scale of experiments, different sizes of the column tests were applied. A detailed description is as follows:

3H vs. Br^- (test A)

The disturbed soil columns, three duplicates (2 and 2.5 cm of inner and outside diameter, 20 cm long) in a material of fine polypropylene, were packed with loess from the field test site of CIRP at a depth of 1–2 m. To avoid possible channel effect and to assure homogeneity in density of the undisturbed loess medium, the backfilled loess was compressed with a wooden tamper layer by layer; the amount of loess backfilled in each layer was controlled according to the density of the undisturbed loess. Two circular flanges constituted the top and bottom of the columns. Between the circular flange and soil pillar in the column, some space of about 2-cm height was filled with quartz sand. Then, the nylon mesh, which is tiled on the flanges tightly, ensured that the water flow and solute transport through the column had a steady uniform flow. At the beginning of the experiments, air in the loess column should be pushed out by ingoing water from the bottom, and then the columns become saturated. Groundwater was infiltrated from the top with a steady flow rate of 0.1 mL/s for 1 day by a peristaltic pump. When flow was steady within the column and inflow and outflow reached a relative steady state, the mixed tracer solution of 3H and Br^- was injected into the three loess columns at the top by

impulse method. Outflow from the bottom of the column was collected by an interval of 40 min. HTO was delivered by China Institute of Atomic Energy (~2 mCi/mL). Activity of 3H was measured with a liquid scintillation analyzer (Tri-Carb 2250 CA), while Br^- was measured in accordance with the Standard for Drinking Natural Mineral Water of China (GB 8538-87), which is described as follows: (1) prepare the standard solutions of Br^- with concentration of 0–3 $\mu\text{g/mL}$; (2) plot the calibration curve; (3) use a spectrophotometer for measuring and calculating the concentration of Br^- . The detection limit of Br^- is 0.5 $\mu\text{g/mL}$.

3H vs. ^{99}Tc (test B)

The disturbed loess column experiments with the mixed tracers of 3H and ^{99}Tc were the same as installed and operated in test A; the detailed difference was: the columns, with an inner diameter of 2 cm and length of 10 cm, and the outflow were sampled from the outlet with an interval of 2 h, which was analyzed immediately to obtain the dynamic curve of concentrations vs. time (Liu et al. 2001).

Technetium-99 was delivered by the Amersham International plc. in the form of ammonium pertechnetate in 0.1 M ammonium hydroxide (package no. PA4381-00). The NH_4TcO_4 solution and the HTO solution were diluted with appropriate amounts of groundwater to form a series of radioactive solutions. Radioactive solution/sample (1.0 mL) was mixed with 10 mL liquid cocktail (Ultima Gold

Table 3 Mineral and chemical compositions of the unsaturated loess and the unconfined aquifer

Mineral type and content (%)						Relative content of clay minerals (%)					
Quartz	K-feldspar	Plagioclase	Calcite	Dolomite	Hornblende	Illite/smectite mixed layer	Illite	Kaolinite	Chlorite	Chlorite/smectite mixed layer	
37.0	2.9	14.9	11.1	2.0	1.4	21.2	4.3	1.84	3.4	–	
Elemental compositions (%)											
Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	Fe_2O_3	LOI	FeO
2.06	1.78	11.91	65.59	0.12	2.31	5.45	0.56	0.06	3.80	6.49	0.93

LLT). The mixture was shaken for a while and the ^{99}Tc detected with a liquid scintillation analyzer (Tri-Carb 2750 TR/LL).

^3H vs. Γ (test C)

The column experiments with tracers of ^3H and ^{131}I were unsaturated experimental installation and included a platform, a trestle table, a soil column, an artificial rainfall system, a revolving set, and a γ radial measurement instrument, which is with low background level. For the single thin source measurement of cesium-137, with a measuring time of 1,000 min and under 95% of the confidence, the detection limit is 0.1 Bq. The installing of the instrument and measuring of the samples was in light of the Chinese National Criterion (Analytical Method for ^{131}I in Water, GB/T13272-91). The soil column for unsaturated tests of ^3H and Γ transport was made of Plexiglass with an inner diameter of 28 cm and length of 120 cm. The artificial rainfall system consists of a high position water pool, a water level controller, a filter, a flow meter, and an electromagnetic valve and a sprayer. The sprayer was designed to supply a uniform artificial rainfall of 4–10 mm/h. The asymmetry for different rainfall densities was measured as <15%, and the asymmetry for any single rainfall density in 8 h was measured as <8%. The artificial rainfall system was operated and adjusted to supply an artificial rainfall of 10 mm/h for a month. Iodine chemicals (KI, all with purity N99%) were purchased from Aldrich Chemical Co., Milwaukee, WI.

Procedures of the unsaturated test were: (1) to gradually introduce water into the soil column from the bottom to push out the air in the column; (2) to artificially sprinkle distilled water into the column from the top to form a steady flow field; (3) to instantly inject the mixed solution of ^3H and Γ at the top of the column and then to continuously sprinkle distilled water with a rate of 10 mm/day; (4) to start the revolving set and the soil column with a uniform rotate speed; (5) to determine the concentration of Γ within the column by vertically running γ radial measurement instrument; and (6) to measure concentrations of ^3H in the collected outflow sample from the bottom of the column. Breakthrough curves of ^3H and ^{131}I were generated in accordance with the measured results.

To compare the migration velocity of ^3H vs. Br^- , Γ^- , and ^{99}Tc , respectively, the transporting peak of

tracer were calculated using Eq. 1:

$$V = \frac{X_{\max}}{t} \quad (1)$$

where V is the transport rate of a tracer peak (cm/h), X_{\max} is the distance between injection spot and concentration peak spot of the tracer (cm), and t is the elapsing time (h) when the tracer arrives to X_{\max} .

2.4 Batch Tests

When an aqueous solution of a particular compound or isotope is brought into contact with a geologic material and the system is allowed to reach equilibrium, it is generally found that a part of the solute has been lost from the solution and transferred to the solid phase. The processes controlling this transfer are typically complex and dynamic, but in practice, it is generally assumed that the dominant process is adsorption and that the distribution of mass between the solid (sorbed) and liquid (dissolved) phases at equilibrium can be adequately described by a distribution coefficient (K_d). The distribution coefficient is defined as the ratio of sorbed mass concentration (expressed as the mass of sorbate per mass of sorbent) to dissolved mass concentration (usually expressed as mass of solute per volume of solution) after equilibrium has been achieved between the dissolved and sorbed phases. For example, for the case of tritium in a given soil, one would typically determine the K_d value from the results of batch tests using the classic formula (Eq. 2):

$$K_d = \frac{Q}{A} = \left(\frac{C_0}{C} - 1 \right) \frac{V}{M} \quad (2)$$

where Q and A are, respectively, the total sorbed mass concentration of tritium (Bq/g) on the soil and the total dissolved concentration in the batch supernatant (Bq/mL) at the end of the experiment; C_0 and C are the initial and the equilibrium concentrations in the liquid phase; V is the volume of the liquid (mL); and M is the mass of the fine particle soil (g).

Batch tests were carried out under constant temperature ($20 \pm 1^\circ\text{C}$), with an adsorption time of 36 h and a water/solid ratio of 20:1 (except for tests specifically aimed at the influence of solid/water ratio). The specific activity for each tritiated water is

105.5 Bq/mL (except for the different initial activities tests) at pH 6.5 (except for experiments specifically targeting the effects of pH variation). The experimental procedures were as follows: (1) 0.25 g loess was weighed and placed into acid polypropylene centrifuge tubes with lids, with a volume of 10 mL and which had been weighted and pretreated; (2) 5.0 mL deionized water was added into the tubes and then covered and oscillated for 24 h; (3) after that, the tubes were put stable standing on the shelves for 24 h. The final mixed solution was separated centrifugally (15 min at 3,000 rpm for the separation of solid phase from aqueous phase) and weighed; (4) 3.0 mL readied tritiated water was put into each centrifuge tubes and oscillated until the samples were taken, and then 0.1 mL supernatant liquid was taken from the centrifuge tube by pipette and was put into the scintillation bottles; and (5) 8.0 mL scintillation liquid was put into the bottles for testing.

Four group experiments were done to determine the influence of the varying initial activity, pH, water/solid ratio, and the mass of organic matter. The individual difference between the single test was listed below. (1) The initial tritiated activity was 80.5, 105, 119.2, 146.3, 303.8, 361.3, and 486.7 Bq/mL, respectively. (2) The water/solid ratio is 8:1, 12:1, 16:1, 20:1, 24:1, 28:1, and 32:1, separately. (3) Aqueous pH value was 1, 3, 5, 7, 9, 11, and 13, respectively. (4) The added mass of different organic matters (fulvic acid and humic acid) was 0.05, 0.10, 0.15, 0.20, and 0.25 g, separately, while the mass of the loess was 0.25 g.

3 Results and Discussion

3.1 Migration Velocity of Tritium

3.1.1 Comparison of Breakthrough Curves with Br^-

The breakthrough curves of tritium and bromine obtained from the column experiments are illustrated in Fig. 1. Here, it is obviously found that the physical migration model consistency for the pulses of tritium and bromide in the same loess column honors all the independently available experimental values. For the tritium tracer, about 15 h after injection, the migration concentration peak was detected, although the value of concentration was three orders of magnitude lower than the initial concentration, while for bromine, the

concentration peak was about 13 h after injection. It was deduced that the reason for the difference of the peaks was that the retardation of tritium existed more than bromide. From the data of migration of tritium and bromide, the flow rates of the groundwater relative to the coinstantaneous injection and the combined injection of ^3H and Br^- are respectively 0.57 and 0.50 m/day. Therefore, tritium was more retarded than bromide.

In prior work, results well similar to those found in these studies were obtained by Leap (1992, 1993) in fractured and fissured dolomite. The apparent relative retardation coefficients of bromide with respect to tritium were computed by the cumulative relative mass time method from breakthrough curves of both substances, and tritium was retarded slightly more than bromide. On another note, temporal moment solutions for one-dimensional advective–dispersive solute transport with linear equilibrium adsorption and first-order degradation for time pulse sources were applied to analyze soil column experimental data (Pang et al. 2003). Based on a comparison of the calculated velocity value of migration of tritium and bromide, the velocity of tritium was 0.87 m/day, while that of bromide was 0.93 m/day; it is similar to the results from this experiment. In Hebei Plain, Northern China, as the tracers tritium and bromide were used in estimating groundwater recharge in China (Wang et al. 2008), the results implied that the migration of bromide was generally faster than tritium in 15 monitor points in the field site.

3.1.2 Comparison of Breakthrough Curves with ^{99}Tc

The comparison of the breakthrough of ^3H and ^{99}Tc (coinstantaneous injection) is presented in Fig. 2. From

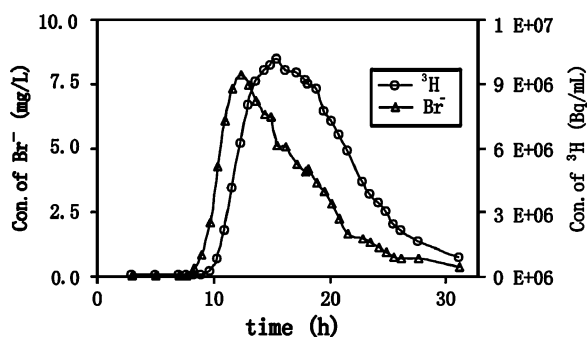


Fig. 1 Breakthrough curves of ^3H and Br^- (coinstantaneous injection)

the figure, although in the collective injection of ^3H and ^{99}Tc the concentration peak of technetium was earlier than tritium, the time of concentration peak from the breakthrough was about 18 h after injection, while for ^3H the time was 23 h after injection. Based on the data of the experimental analytical results, it is assured that tritium was more retarded than ^{99}Tc .

In the existing researches, in a field test, the migration of ^{99}Tc in a weak loess aquifer was investigated in situ with undisturbed aquifer medium columns (Liu et al. 2001). The columns were obtained horizontally at a depth of 32–36 m in an underground research facility. Quartz containing ^3H (HTO) and ^{99}Tc (in the form of $^{99}\text{TcO}_4^-$) was introduced into one end of the columns, and the columns were covered tightly. The breakthrough curves of ^3H and ^{99}Tc indicated that ^{99}Tc migrated a little faster than ^3H did in the aquifer. In another research in granite, concrete, and bentonite, Szántó et al. (2002) studied the diffusion behavior of ^3H , ^{99}Tc , ^{125}I , ^{36}Cl , and ^{85}Sr in a specially designed diffusion cell. The results reflected that the diffusion coefficient (D) of tritium was larger than ^{99}Tc . It also was explained that migration of tritium was a little slower than ^{99}Tc .

3.1.3 Comparison of Breakthrough Curve with $^{131}\text{I}^-$

Figure 3 presents the order of concentration peak of breakthrough of tritium and iodine ($^{131}\text{I}^-$) that were injected together in the same column. It is obvious that the concentration peak of iodine was a little earlier than tritium.

In prior works, the International Mont Terri Project aimed to investigate the geological, hydrogeological, geochemical, and rock mechanical properties of the Opalinus Clay (OPA) for assessing the feasibility and

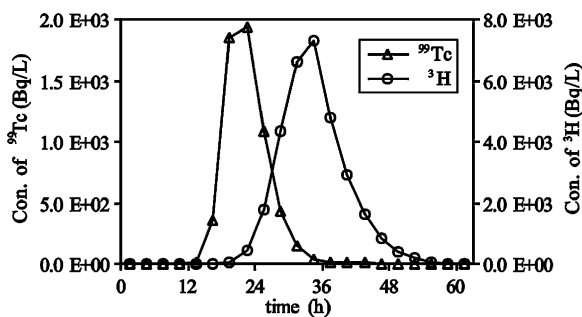


Fig. 2 Breakthrough curves of ^3H and ^{99}Tc (coinstantaneous injection)

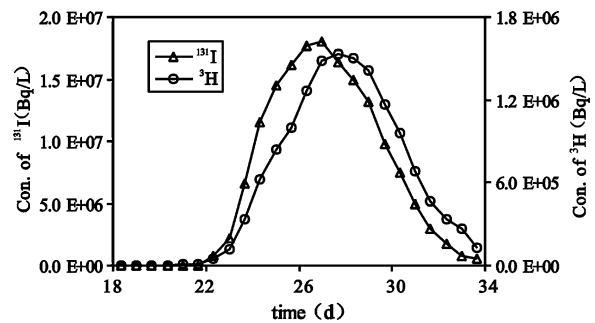


Fig. 3 Breakthrough curves of simultaneously injected tritium and iodine

safety of a repository for radioactive waste placed in this type of host rock. The investigated radionuclides were tritium and iodine. The effective diffusion coefficients were measured for tritiated water and iodine (as I^-), and it is larger for tritium ($1.7 \pm 0.4 \times 10^{-11} \text{ m}^2/\text{s}$) than for iodide ($2.7 \pm 0.3 \times 10^{-12} \text{ m}^2/\text{s}$; Yllera et al. 2001). In other study, Van Loon et al. measured and validated the results, where the D value of tritium is larger than iodide's, from calculating the diffusion coefficients and accessible porosities for HTO, $^{36}\text{Cl}^-$, and $^{125}\text{I}^-$ on OPA samples from the Mont Terri Underground Rock Laboratory (Wersina et al. 2004; Van Loon et al. 2003). Hu et al. (2005) considered the adsorption and transport of different iodine species in sediments from the Savannah River and Hanford Site. It is obvious, in the column experiments, that iodide transported faster than tritium, while iodate migrated slower than tritium.

3.1.4 Comparison of Migration Velocity of Tracers

Table 4 summarizes the results of mass recovery and the time of concentration peak and the velocity of tracers which included tritium, bromide, technetium, and iodine. From the results, the mass recovery of each analyte could ensure the experimental precision, and the transport rate of Br^- peak appeared earlier compared to the ^3H peak by 1.25 times when the tracers were simultaneously injected into the column. Moreover, the migration of ^{99}Tc was even 1.60 times faster than ^3H when the tracers were simultaneously injected. For iodine, it was only 1.02 times faster than transportation of tritium, but it should not be ignored.

3.2 Distribution Coefficient and Influencing Factors

In order to validate the adsorption and retardation of the migration of tritium on loess media, batch tests were

Table 4 Concentration peak and transport rates of ^3H , Br^- , I^- , and ^{99}Tc tracers

Test group	Mass recovery (%)		Time of peak occurring (t , h)		Peak transport rate (v , cm/h)		v_1/v_2
	^3H	$\text{Br}^-/^{99}\text{Tc}/\text{I}^-$	^3H	$\text{Br}^-/^{99}\text{Tc}/\text{I}^-$	^3H (v_2)	$\text{Br}^-/^{99}\text{Tc}/\text{I}^-$ (v_1)	
^3H or Br^-	96.2	96.7	15.42	12.33	1.3	1.62	1.25
^3H and ^{99}Tc	97.7	98.0	33.06	21.02	0.30	0.48	1.60
^3H or ^{131}I	94.5	94.9	585.36	571.68	0.21	0.21	1.02

applied to analyze the various factors influencing tritium adsorption on loess media. The characteristics of tritium adsorption on loess media were expressed by a distribution coefficient (K_d); the major influencing factors investigated included the activity of tritiated water, water/solid ratio, pH, and quality of organic matter.

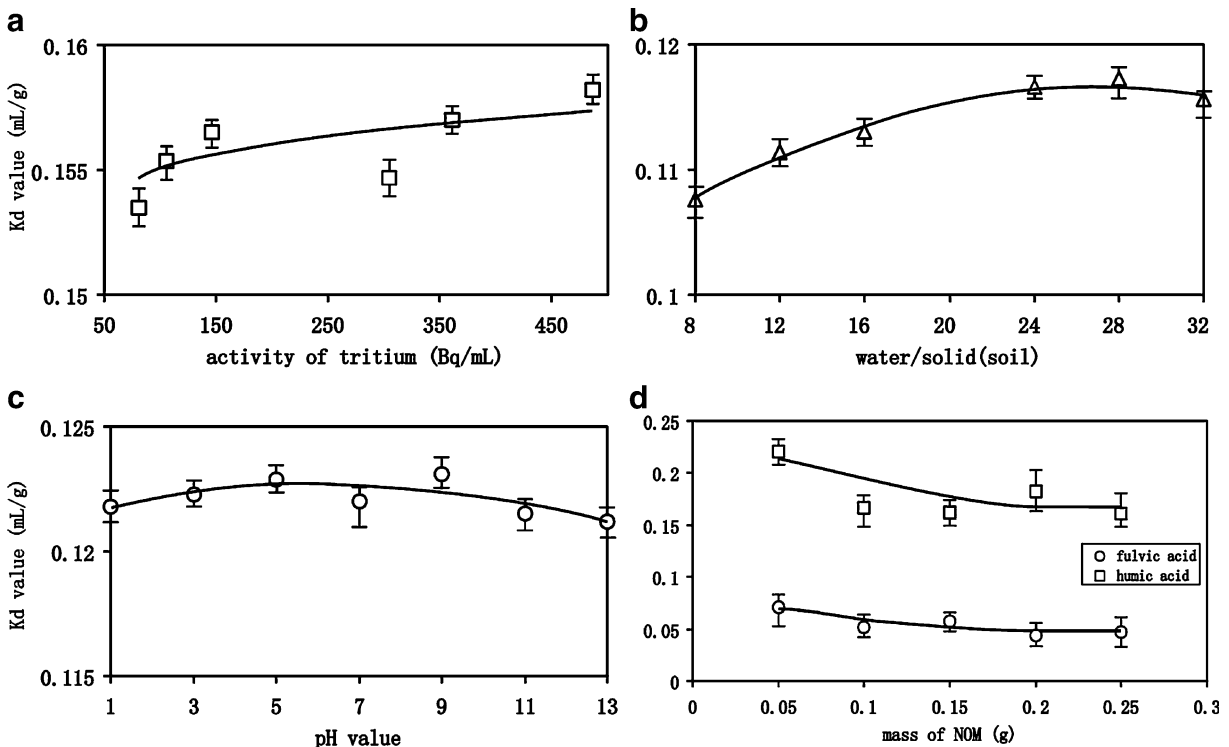
3.2.1 The Initial Activity

For investigating the influence of the activity of tritium in solution on its adsorption, the K_d value of tritium at a different initial activity of ^3H was tested. As shown in Fig. 4a, here, the distribution coefficients of tritium in loess media were non-zero, but there actually existed a

value of $K_d < 0.2$ mL/g, which changed only slightly as a function of a different initial activity. From Fig. 4a, we could see that the descending order of the distribution coefficient was fluctuatedly increasing with the corresponding activity.

3.2.2 Water/Soil Ratio

Figure 4b showed the influence of water/solid ratio on ^3H adsorption in the loess material as given by the experimental results. The water/solid ratio served to indicate the relative influence of loess and solution composition on the adsorption processes. From Fig. 4b, it was clear that the distribution coefficient of ^3H increases with increasing water/solid ratio for

**Fig. 4** Different factors influenced the K_d value on loess media

loess media. Such “solid concentration” effect has been reported in Cheng et al. (2006) and Limousin et al. (2007).

3.2.3 pH Values

The pH value commonly influences the mobility and adsorption process of radionuclides in soil media. The influence of aqueous pH value on the adsorption of tritium, as derived from the experiments targeting this issue, is shown in Fig. 4c. The results illustrate no clear influence of pH on the adsorption distribution coefficient of ^3H on loess media. The average K_d values for tritium on loess media were 0.12 mL/g. The results indicate that pH has a relatively slight effect on tritium adsorption on loess media.

3.2.4 Mass of Organic Matter

For the influence of different organic matters, including fulvic acid and humic acid, the K_d value of ^3H in a series of different organic matter solutions was investigated. The influence of organic matter on the adsorption of tritium in the analytical methods, which was on two groups of the same loess samples with a different mass of fulvic acid or humic acid (with the mass from 0.05 to 0.25 g), spiked with either fulvic or humic acids. When the acids were added, the tritium adsorption on loess media was larger with humic acid than fulvic acid, especially when there is only a little fulvic acid (0.05 g); the adsorption increased very significantly. With an increasing acid concentration, the adsorption decreases.

4 Conclusion

It is evident that migration of tritium in the loess, compared to Br^- , ^{99}Tc , and I^- transports, was retarded. In the saturated column experiments, the transport rate of Br^- was more rapid than that of ^3H by 1.25 times when ^3H and Br^- were synchronously injected into the column. Moreover, the migration peak of ^{99}Tc in saturated loess is 1.60 times earlier than that of ^3H . Result from the tests of ^3H and $^{131}\text{I}^-$ transportation shows that the peak time of ^3H was slightly slower than that of $^{131}\text{I}^-$. Retardation of ^3H is probably due to the adsorption of ^3H to the clay mineral particles, immobility of ^3H within the

immobile pore water, as well as changes of the physical and chemical properties of the loess.

Batch tests validate the adsorption of tritium on loess media, and the distribution coefficient is non-zero, but a value <0.2 mL/g. It could be summarized that tritium could be adsorbed by loess media. Experimental results of tritium adsorption on loess soil in different initial conditions indicate the following: the K_d value of tritium adsorption on soils was small but noticeable, and the effect of different factors, such as tritium activity, water/soil ratio, pH, fulvic acid, and humic acid, on the same sample is also observed.

Tritium was applied as a non-sorption tracer based on the same flow rate of ^3H and groundwater. It is therefore worthy to regard the fact that migration of ^3H is distinctly slower than the flow rate of the groundwater. Application of ^3H in determining the flow rate of groundwater may result in underestimations and unsafety.

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