

## Detection of tritium sorption on four soil materials

Yanguo Teng<sup>a,b</sup>, Rui Zuo<sup>a,b,\*</sup>, Jinsheng Wang<sup>a,b</sup>, Qinhong Hu<sup>c</sup>, Zongjian Sun<sup>a,b</sup>, Ni Zeng<sup>a,b</sup>

<sup>a</sup> College of Water Sciences, Beijing Normal University, Beijing 100875, China

<sup>b</sup> Engineering Research Center of Groundwater Pollution Control and Remediation, Ministry of Education, Beijing 100875, China

<sup>c</sup> Department of Earth and Environmental Sciences, University of Texas at Arlington, Arlington, TX 76019, USA

### ARTICLE INFO

#### Article history:

Received 2 December 2009

Received in revised form

22 November 2010

Accepted 6 December 2010

Available online 30 December 2010

#### Keywords:

Tritium

Adsorption

Distribution coefficient

water/solid ratio

pH

Humic substances

### ABSTRACT

In order to measure groundwater age and design nuclear waste disposal sites, it is important to understand the sorption behavior of tritium on soils. In this study, batch tests were carried out using four soils from China: silty clays from An County and Jiangyou County in Sichuan Province, both of which could be considered candidate sites for Very Low Level Waste disposal; silty sand from Beijing; and loess from Yuci County in Shanxi Province, a typical Chinese loess region. The experimental results indicated that in these soil media, the distribution coefficient of tritium is slightly influenced by adsorption time, water/solid ratio, initial tritium specific activity, pH, and the content of humic and fulvic acids. The average distribution coefficient from all of these influencing factors was about 0.1–0.2 mL/g for the four types of soil samples. This relatively modest sorption of tritium in soils needs to be considered in fate and transport studies of tritium in the environment.

© 2010 Elsevier Ltd. All rights reserved.

## 1. Introduction

Tritium ( $^3\text{H}$ ), with a half-life of 12.323 years, has usually been considered an ideal substance to trace groundwater movement, because it is a constituent of water and commonly assumed to behave conservatively (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  $\beta$  emitter (Leap, 1992). Tritium, as a conservative tracer, has often been used to define the breakthrough curves in column or field experiments to characterize the hydrogeological parameters of media (Gaber et al., 1995; Maraqa et al., 1999; Martin-Garina et al., 2002; Qian et al., 2009; Li et al., 2009). In addition, in terms of radioactivity, tritium is the most abundant residual radionuclide from underground nuclear testing (Hu et al., 2008).

However, several studies have observed the sorption of tritium and its retarded transport in geological media. Fordor-Csanyi et al. (1985) found that migration of tritium became slower in soil media with the increased clay content. In migration experiments with  $^{32}\text{P}$  and  $^3\text{H}$ , Gupta et al. (1999) observed that the migrating velocity of  $^{32}\text{P}$  was larger than that of  $^3\text{H}$  by a factor of 4. Van Loon and Jakob (2005)

accounted for tritium sorption on clay minerals by a small but non-zero value (0.01 mL/g) of distribution coefficient ( $K_d$ ). 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, reflecting the small, but non-negligible, sorption of tritium. The  $R_d$  value would be 1 if there is no sorption (i.e.,  $K_d$  value of zero) for tritium. Leap (1992) validated that tritium was more retarded than bromide in flow-through highly-transmissive openings from the fractured dolomite column. In another study, Hölttä et al. (1996) got a retardation factor of 1.35 for tritium with simultaneous transport of chloride and tritium, which was explained by its weak interactions with altered fracture surfaces or by anion exclusion of chloride that was responsible for the faster chloride transport. Non-zero  $K_d$  value, or retarded transport, of tritium in porous media in China have been reported from both laboratory and field experiments. The  $R_d$  value of tritium in loess from saturated-soil column experiments was measured to be 1.95 to 2.05 (Teng et al., 2007). Wang et al. (2003) carried out a migration experiment on tritium in loess at 30 m below land surface, and the results gave a distribution coefficient of 0.12 mL/g.

Other reports show that the experimental factors could influence the sorption or retardation of tritium on geological media. Turner et al. (2009) found that distribution coefficients of tritium appear to be influenced by its affinity for organic matter. The kinetic

\* Corresponding author. College of Water Sciences, Beijing Normal University, Beijing 100875, China.

E-mail address: [zuo1101@163.com](mailto:zuo1101@163.com) (R. Zuo).

**Table 1**

Particle-size distribution of four soil samples.

particle-size	Percentage ( % )			
	A	B	C	D
>1 mm	2.9	3.1	4.1	1.6
0.9–1 mm	9.6	7.9	10.5	5.5
0.45–0.9 mm	27.5	29.3	32.9	23.2
0.15–0.45 mm	25.3	18.6	28.1	23.3
<0.15 mm	34.7	41.1	24.4	46.3
Classification	Silty clay	Silty clay	Silty sand	Loess

control of groundwater system is also important for the sorption of tritium. The retardation factors for tritium and chloride have been observed to strongly depend on pore-water velocity, with the retardation factor decreasing with an increasing velocity (Bajracharya et al., 1996).

The objectives of the present work were to analyze the tritium sorption, and various influencing factors, on four soil samples from different sites in China. The major influencing factors investigated included adsorption time, water/solid ratio, pH, specific activity of tritiated water, and types of organic matter.

## 2. Materials and methods

### 2.1. Soil samples

Soil samples collected from four sites were used in this study. A silty clay sample, designated sample A, was collected from in An County in the southwestern China; another silty clay sample, named sample B, was collected from the terrace in Jiangyou County, also in Southwestern China. Both locations, where samples A and B were collected, could be considered the candidate sites for a Very Low Level Waste (VLLW) disposal. Sample C of silty sand was from the Beijing Normal University campus. Finally, a loess sample, sample D, was collected from a field experimental site in Yuci County in northern China, a typical Chinese loess region.

All samples were sieved using 2.0, 1.0, 0.9, 0.45, and 0.15 mm sieves to determine the mass percentages of particles in the different diameter ranges. The particle-size distribution results for the soil samples are shown in Table 1.

The major minerals, clay mineralogy and elemental compositions of four soil samples were analyzed by X-ray diffraction (RIPED, Petro-China) to obtain the relative and full clay mineral analyses (National Bureau of Quality and Technical Supervision, 1995; 1996); the results are shown in Tables 2 and 3.

### 2.2. Materials

All plastic- and glass-ware used for sampling, sample processing and experimental work were soaked in 5% Decon 90 (Decon Laboratories, Beijing, China) and 5% HNO<sub>3</sub> (AnalaR grade) successively for 24 h each before being rinsed with ultra pure water. AristaR or AnalaR grade reagents diluted in ultra pure water were used in the experiments. Tritiated water with a specific activity of 1  $\mu$ Ci/ml was purchased from the China Institute of Atomic Energy; the specific activity of tritium was measured by liquid scintillation after dilution using TRI-CARB 2900 TR (PerkinElmer, Massachusetts, USA).

### 2.3. Batch sorption experiments

#### 2.3.1. Batch sorption approach

In this study, the sorption extent and influencing factors for tritium in four soil samples were studied through batch-type experiments to determine the distribution coefficient ( $K_d$ ) value, which 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. A higher value of  $K_d$  means that the soil is able to sorb a greater mass, as a result of various physical and chemical interactions between tritium and the soil, and therefore the migration of

tritium will be retarded more efficiently. For the case of tritium in a given soil, the  $K_d$  value is determined using the classic equation (1):

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

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

#### 2.3.2. Experimental procedures

All of the experiments were conducted in triplicate measurements. Except for the tests specifically targeting for the individual influencing factor (e.g., adsorption time, water/solid ratio, initial activity, and pH), all sorption experiments were carried out under the following conditions: a constant temperature of  $20 \pm 1$  °C; an mixing time of 36 h; a water/solid ratio at 12:1 (3 mL:0.25 g); a specific activity for tritiated water at 105.5 Bq/mL; and a pH of 6.5. The experimental procedures were as follows: (1) a soil sample of 0.25 g was placed into acid-washed 10 mL polypropylene centrifuge tubes with lids; (2) for removal of the suspended and dissolved matter, 5 mL of deionized water was added in the tubes, the mixed solution was centrifuged for 15 min at 3000 rpm to separate the solid phase from the aqueous phase, then the solid phase sample was air-dried and stored for the next tests; (3) 3 mL of tritiated water were then added into each tube with the air-dried soil sample; and centrifuged after mixing for 36 h; then 0.1 mL of supernatant liquid was taken by pipette and placed into a scintillation vial, wherein 8 mL scintillation liquid was added for tritium counting; (4) the  $K_d$  value was calculated according to equation (1), and the uncertainties was evaluated after several repeated measurements with determination results for each time ( $i$ ), it is as follow: a) Calculate the mean value ( $\bar{L}$ ) and the deviation ( $V_i$ ) for  $L_i$  based on the measured  $K_d$ , and then get the  $V_i^2$ ; b) Calculate the root mean square error  $\sigma$  and limit error  $\Delta \text{lim}$ ; c) Calculate the root mean square error  $S$  and limit error  $\lambda \text{lim}$  for arithmetic mean value; d) obtain the relative limit error  $\delta \text{lim}$  for arithmetic mean value, and the  $K_d$  value could be described in  $L \pm \delta \text{lim}$ .

#### 2.3.3. Control experiment

Because of the radioactive decay of tritium, the specific activity of tritium in water samples will decrease with time even for samples to which no soil is added. Therefore, when calculating the distribution coefficient, the activity decrease from radioactive decay must be taken into account, both for the tritium dissolved in solution and for the tritium adsorbed in the soil samples. In the current study, the decay ratio of tritium in liquid scintillation with blank samples was taken as the background value of liquid scintillation.

The losses of evaporation and container adsorption of tritium were measured using the analytical method published by Turner et al. (2009) for distribution of tritium in estuarine waters. The principle of the method is to check for loss by evaporation, two samples were capped and left for 72 h before further aliquots were counted, while two were left uncapped in a fume cupboard for 48 h before further aliquots were counted, and adsorption to the container walls was evaluated by discarding two samples following a period of 48 h equilibration in capped tubes, and then were drained for 10 min, and rinsed with 10 mL of 1 M HCl. We observed that tritium loss of by evaporation and adsorptive to the container was only 0.2% and 0.4%, respectively, and the loss was not evident in sealed tubes; therefore, tritium loss was ignored in the  $K_d$  calculation process.

In our sorption experiments, tritium represents the total quantity of the isotope that is associated with soil particles and, therefore, subject to the same chemical controls as this phase. Particulate tritium is adsorbed, and present in hydration and structural waters, thereby encompassing all exchangeable and non-exchangeable forms (Turner et al., 2009). The sorption capacity of tritium on the soil is calculated from the difference in tritium activities before and after the addition of particles, and there are two control samples (with tritium, but no soil) to clarify uncertainty. Reductions in activities were typically between 1 and 2% based on water/soil of 12:1, and were significantly greater than activity losses incurred by entrainment or absorption of HTO in the control experiments.

#### 2.3.4. Design of individual sorption experiment

The sorption behavior of tritium in soils was investigated in five groups of batch experiments to determine the influence of sorption time, varying pH, and other

**Table 2**

Mineral components of the soil samples.

Sample	Mineral type and content ( % )					Relative content of clay minerals ( % )				
	Quartz	K-feldspar	Plagioclase	Calcite	Dolomite	Illite/Smectite mixed-layer	Illite	Kaolinite	Chlorite	Chlorite/Smectite mixed-layer
A	39.1	1.4	6.1	0.9	/	27.8	10.5	4.2	8.4	1.58
B	53.5	2.2	7.5	/	2	19.5	5.22	2.78	4.52	2.78
C	37	2.9	14.9	11.1	2	21.2	4.3	1.84	3.38	/
D	41.6	2.6	13.8	9.9	4.1	13.7	7.24	2.14	3.75	/

**Table 3**

Elemental composition of the soil samples.

Sample	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O	CaO	TiO <sub>2</sub>	MnO	Fe <sub>2</sub> O <sub>3</sub>	LOI	FeO
A	0.92	1.72	16.06	65.45	0.06	2.45	0.3	0.97	0.08	6.43	5.5	0.95
B	1.26	0.93	12.52	74.33	0.06	2.17	0.6	0.69	0.05	3.69	3.01	0.52
C	2.06	1.78	11.91	65.59	0.12	2.31	5.45	0.56	0.06	3.8	6.49	0.93
D	1.97	2.07	12.02	64.39	0.15	2.35	5.2	0.68	0.07	4.47	6.64	0.86

factors. Every individual sorption experiment was carried out according to the general steps and procedures given at Section 2.3.3, with the individual differences discussed below:

- (1) Sorption time: 10 h, 15 h, 20 h, 25 h, 30 h, 35 h, 40 h, 45 h, and 50 h.
- (2) Initial specific activity of the tritiated water: 80.5, 105, 119.2, 146.3, 303.8, 361.3, and 486.7 Bq/mL;
- (3) The water/solid ratio: 8:1, 12:1, 16:1, 20:1, 24:1, 28:1, and 32:1;
- (4) Aqueous pH: 1, 3, 5, 7, 9, 11, and 13. In each of these experiments the specific activity of the tritiated water was 74 Bq/mL. The solution pH of the aqueous solution was adjusted by adding HCl or NaOH, and the final water pH value of the experiment was determined from the supernatant.
- (5) Organic matter content: the natural organic matter in each soil sample was first removed by H<sub>2</sub>O<sub>2</sub> oxidation, and then the sample was spiked with either fulvic acid or humic acid (analytical reagents purchased from Sino-Pharm, China) in amounts of 0.05 g, 0.10 g, 0.15 g, 0.20 g, and 0.25 g for every 0.25 g soil, to study the effect of humic substances. The water/solid ratio in each of these experiments was 20:1, then the results of the batch tests was compared with that from the soils without organic matter for the  $K_d$  value of the tritium adsorption on media.

The procedures of H<sub>2</sub>O<sub>2</sub> oxidation method to remove organic matters in soil samples were as follows: (1) weigh a certain amount of the soil sample; (2) add 30% H<sub>2</sub>O<sub>2</sub> (the weight/volume ratio of soil to H<sub>2</sub>O<sub>2</sub> was 1:2); (3) repeatedly process them in a water bath at 90 °C; (4) after 30 min centrifugation at 4000 rpm and separation, wash the soil sample with distilled water several times, and then dry the samples.

### 3. Results and discussion

#### 3.1. Adsorption time

Fig. 1 shows plots of the distribution coefficient, for each of the four types of soils studied in this work, versus the batch reaction time. For samples A, C, and D, the distribution coefficient as determined for reaction times longer than 35 h virtually remains constant. For sample B (a silty clay from Jiangyou County), the distribution coefficient shows some random fluctuation for times greater than 35 h. Because there appears to be no clear trend of variation in the distribution coefficient as determined using reaction times greater than 35 h, this time was assumed sufficient to achieve equilibrium in all subsequent experiments.

As shown in Fig. 1, soil sample A (a silty clay from an county) exhibited the largest tritium  $K_d$  value among four soil samples,

which was followed by samples B, C, and D. That could be explained by natural variability of soil properties of different soil samples, it is shown from Table 3 (elemental composition of the soil samples), the percentages of Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> of sample A are 16.1% and 6.4%, which are greater than others; these sesquioxides could be a key factor in the tritium sorption process.

#### 3.2. Initial specific activity

As shown in Fig. 2, the distribution coefficients in four soils only slightly change as a function of different initial specific activity. It is clear that the impact of varying specific activity is small for tritium sorption on soils. The largest distribution coefficient is again associated with sample A, with a decreasing order of samples B, C, and D; the corresponding average  $K_d$  values are 0.17, 0.16, 0.15, and 0.12 mL/g, respectively.

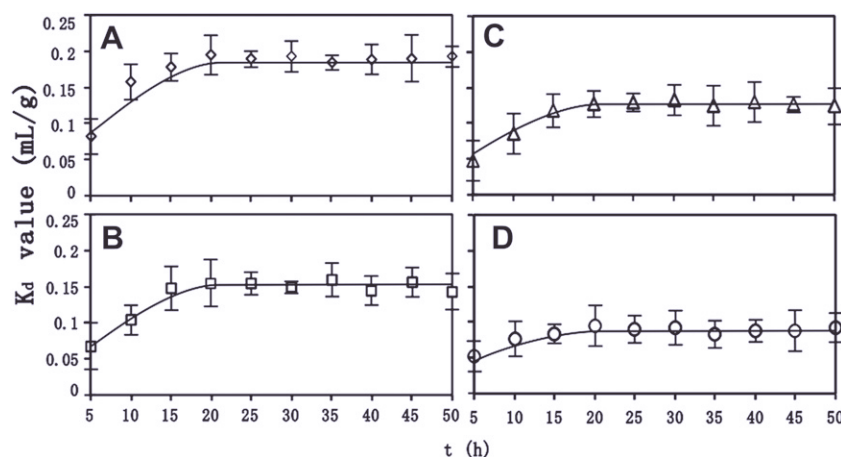
#### 3.3. Water/soil ratio

The water/solid ratio serves to indicate the relative influence of rock and solution composition on the sorption processes. From Fig. 3, it seems that the distribution coefficient of <sup>3</sup>H increases with increasing water/solid ratio for samples B, C, and D, while the trend of the  $K_d$  values for sample A seems to be slight. Such "solids concentration" effect has been reported in Cheng et al. (2006) and Limousin et al. (2007). The descending order of the distribution coefficient is A, B, D, C, with the corresponding average  $K_d$  value of 0.13, 0.12, 0.12 and 0.11 mL/g.

#### 3.4. pH value

The pH value commonly influences the mobility and adsorption process of radionuclides in soil. The influence of aqueous pH value on the sorption of tritium is shown in Fig. 4.

The results show no clear influence of pH on the sorption distribution coefficient of <sup>3</sup>H. The average  $K_d$  values for tritium on four soil materials, A, B, C, and D, were 0.16, 0.13, 0.12, and 0.11 mL/g, respectively.



**Fig. 1.** Time evolution of distribution coefficients.

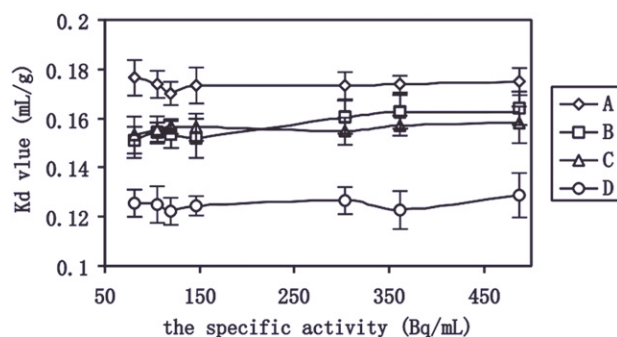


Fig. 2. Influence of initial specific activity on tritium sorption.

### 3.5. Organic matter

To study the influence of different fulvic acid and humic acid, the  $K_d$  value of  $^3\text{H}$  in a series of different organic matter solutions was investigated. The influence of organic matter on sorption of tritium included two kinds of analytical methods, (1) the  $K_d$  value of  $^3\text{H}$  on four different soil samples, with the same mass of fulvic acid or humic acid, with the mass from 0.05 to 0.25 g, (2) the  $K_d$  value of  $^3\text{H}$  on two duplicate soil samples from sample A, B, C, or D, spiked with either fulvic or humic acids.

#### 3.5.1. Different soil samples with the same organic acid

The results are shown in Fig. 5 and Fig. 6 for the influence of fulvic acid and humic acid, respectively.

As shown in Fig. 5, the distribution coefficients of tritium sorption on the four types of soil changed in different trend when the mass of fulvic acid changed. For samples A and B, the distribution coefficient is higher with the fulvic acid in the experiments than it without the humic substance, and when the input mass of fulvic acid was about 0.05 g, the  $K_d$  reached a maximum value;  $K_d$  values decreased as the fulvic acid amount was further increased. For sample A, compared with other experimental factors studied, such as pH and water/solid ratios,  $K_d$  value with the addition of fulvic acid increase significantly. On the other end, for samples C and D, the distribution coefficients decrease as the mass of fulvic acid increases, with the  $K_d$  value lower with any added fulvic acid.

Fig. 6 indicates that, under the addition of humic acid, the  $K_d$  value exhibits a similar variation tendency for all four soil samples. Values of  $K_d$  are larger than the conditions without humic acid, and also greater than the results from other influencing factors presented above. When the input mass of humic acid was 0.05 g, the  $K_d$  value is at maximum, and then, with the increasing mass of humic acids, there is a slight decrease of  $K_d$  value. Compared with the  $K_d$  increases from fulvic acid spiking, the distribution coefficient changes more for the humic acid. The reason of the  $K_d$  trend with increasing humic acid may

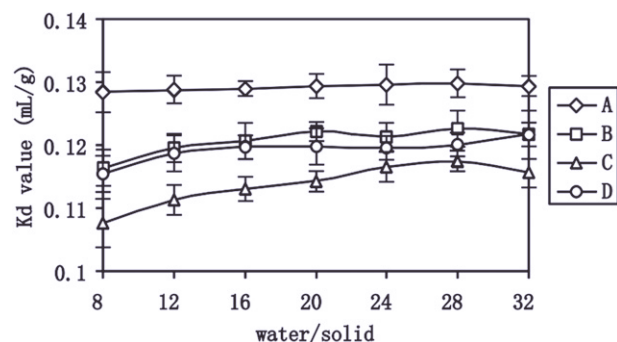


Fig. 3. Influence of water/solid ratio on tritium sorption.

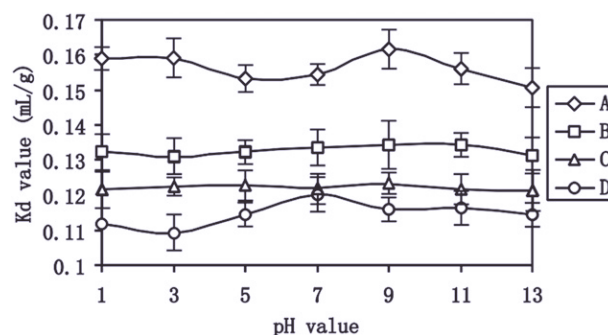


Fig. 4. Influence of aqueous pH value on tritium sorption.

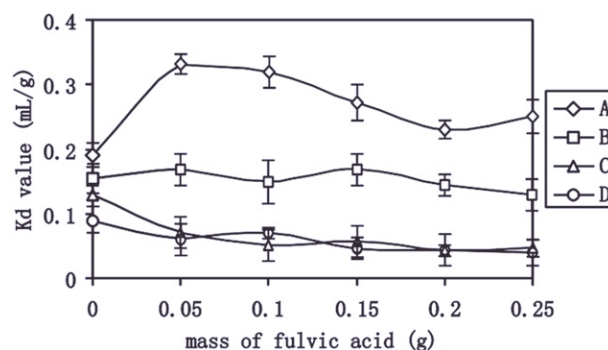


Fig. 5. Influence of fulvic acid addition on tritium sorption.

be that tritium rapidly equilibrates with dissolved organic ligands that are retained by a reverse-phase process, and with suspended sediment particles at first, and then  $K_d$  value fluctuates on the effect of a mass of existed humic substance; subsequent research should further address this question of the humic substance at which maximum sorption of  $^3\text{H}$  is observed in soil media.

#### 3.5.2. Different organic acids for the same sample

For every individual sample A, B, C, or D, an influence of humic and fulvic acids on tritium sorption was studied; the results are shown in Fig. 7.

When fulvic acid was added, the tritium sorption on sample A was larger than the other three samples, especially when there is only a little fulvic acid (0.05 g), the sorption increased very significantly. With an increasing fulvic acid concentration, tritium sorption became less. In contrast, the sorption of tritium on samples C and D were smaller. Though the mechanisms need to be further revealed, it is hypothesized that the phenomenon is related to the contents of  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  in sample A, which are higher than that

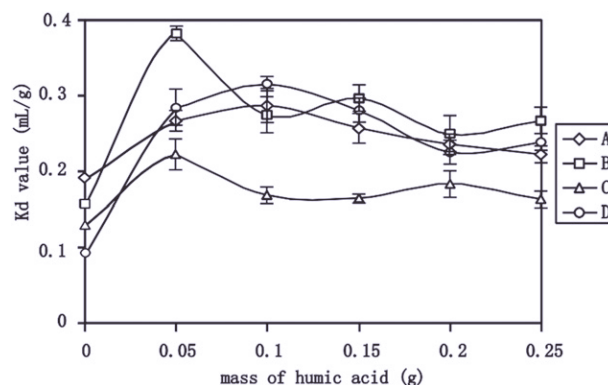


Fig. 6. Influence of humic acid addition on tritium sorption.



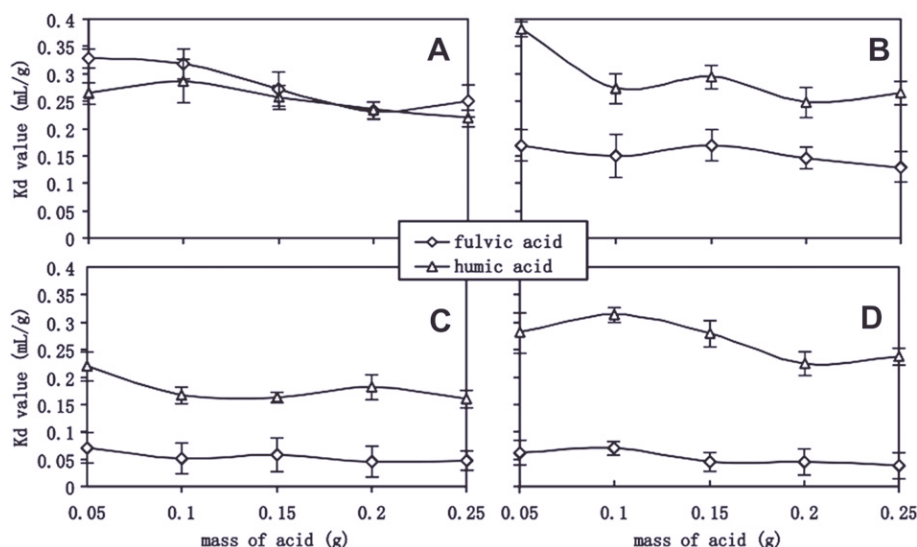


Fig. 7. Influence of fulvic and humic acids on tritium sorption.

of other soils. Overall, the effect of humic acid on four soil samples are apparent, especially on samples A and B.

#### 4. Conclusion

Batch sorption tests validate the adsorption of tritium on all of the four tested soil samples collected in China, and the distribution coefficient is found to be non-zero and less than 0.4 mL/g. Because of the differences of mineralogy, chemical composition and organic matter content in soils, tritium sorption of each soil is different. Experimental results of tritium sorption on four soils in different initial conditions indicate the following: the  $K_d$  value of tritium sorption on soils is small but noticeable, and the effect of different factors, such as adsorption time, water-soil ratio, tritium specific activity, pH, fulvic acid and humic acid on the same sample is also observed. Under the effect of fulvic acid, tritium sorption on sample A is stronger than other soil samples; the reason may be related to the higher contents of  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  in this soil sample. In a word, tritium has been accepted as a non-sorption tracer, based on the same flow rate of  $^3\text{H}$  and groundwater. It is, therefore, worthy to consider that, migration of  $^3\text{H}$  can be distinctly slower, from its sorption onto geological media, than flow rate of the groundwater.

#### Acknowledgement

This work was supported by the Specific Research on Public Service of Environmental Protection in China (No. 201009009) and National Natural Science Foundation in China (No.40773055).

#### References

- Bajracharya, K., Tran, Y.T., Barry, D.A., 1996. Cadmium adsorption at different pore water velocities. *Geoderma* 73 (3–4), 197–216.
- Brady, P.V., Kozak, M.W., 1995. Geochemical engineering of low level radioactive waste in cementitious environments. *Waste Manage.* 15 (4), 293–301.
- Cheng, T., Barnett, M.O., Roden, E.E., Zhuang, J.L., 2006. Effects of solid-to-solution ratio on uranium(vi) adsorption and its implications. *Environ. Sci. Technol.* 40 (10), 3243–3247.

- Fordor-Csanyi, P., Kasza, J., Feher, L., Berci, K., 1985. Movement of tritium-labelled water in soils. *Int. J. Appl. Radiat. Isot* 36 (3), 209–213.
- Gaber, H.M., Inskeep, W.P., Wraith, J.M., 1995. Nonequilibrium transport of atrazine through large intact soil cores. *Soil Sci. Soc. Am. J.* 59, 60–67.
- Gupta, A., Destouni, G., Jensen, M.B., 1999. Modeling tritium and phosphorus transport by preferential flow in structured soil. *J. Contam. Hydrol* 35, 289–407.
- Hölttä, P., Hakkanen, M., Hautajärvi, A., Timonen, J., Väättäinen, K., 1996. The effects of matrix diffusion on radionuclide migration in rock column experiments. *J. Contam. Hydrol* 21, 165–173.
- Hu, Q.H., Rose, T.P., Zavarin, M., Smith, D.K., Moran, J.E., Zhao, P.H., 2008. Assessing field-scale migration of radionuclides at the Nevada Test Site: “Mobile” species. *J. Environ. Radioact* 99, 1617–1630.
- Leap, D.L., 1992. Apparent relative retardation of tritium and bromide in dolomite. *Ground Water* 30 (4), 549–558.
- Li, M., Wang, T., Teng, S., 2009. Experimental and numerical investigations of effect of column length on retardation factor determination: a case study of cesium transport in crushed granite. *J. Hazard. Mater.* 162, 530–535.
- Limousin, G., Gaudet, J.P., Charlet, L., Szenknect, S., Barthes, V., Krimissa, M., 2007. Sorption isotherms: a review on physical bases, modeling and measurement. *Appl. Geochem.* 22 (2), 249–275.
- Maraqa, M.A., Wallace, R.B., Voice, T.C., 1999. Effects of residence time and degree of water saturation on sorption nonequilibrium parameters. *J. Contam. Hydrol* 36, 53–72.
- Martin-Garina, A., Gaudet, J.P., Charlet, L., Vitarta, X., 2002. A dynamic study of the sorption and the transport processes of cadmium in calcareous sandy soils. *Waste Manage.* 22, 201–207.
- National Bureau of Quality and Technical Supervision., 1995. X-ray Diffraction Analysis Methods for Relative Content of Clay Mineral (SY/T5163–1995) (in Chinese).
- National Bureau of Quality and Technical Supervision., 1996. X-ray Diffraction Analysis Methods for the Total Amount of Clay Minerals in Sedimentary Rocks and Common Non-clay Mineral (SY/T 6210–1996) (in Chinese).
- Qian, T., Li, S., Ding, Q., Wu, G., Zhao, D., 2009. Two-dimensional numerical modeling of  $^{90}\text{Sr}$  transport in an unsaturated Chinese loess under artificial sprinkling. *J. Environ. Radioact* 100 (5), 422–428.
- Teng, Y., Wang, J., Guo, M., 2007. Hysteresis of tritium transport in the Chinese loess. *China Environ. Sci.* 27 (3), 332–335 (in Chinese with English abstract).
- Turner, A., Millward, G.E., Stemp, M., 2009. Distribution of tritium in estuarine waters: the role of organic matter. *J. Environ. Radioact* 100, 890–895.
- Van Loon, L.R., Jakob, A., 2005. Evidence for a second transport porosity for the diffusion of tritiated water (HTO) in a sedimentary rock (Opalinus Clay-OPA): application of through- and out-diffusion techniques. *Transp. Porous Media* 61, 193–214.
- Voudrias, E.A., Means, J.L., Kittel, J., 1993. Retardation of tritium and cesium in brine-saturated mudstone, halite, and carbonate porous media. *Ground Water* 31 (4), 605–615.
- Wang, J., Guo, M., Liu, C., Li, S., 2003. Comparison of migration characteristic of  $^3\text{H}$  and  $^{99}\text{Tc}$  in loess. *Environ. Sci.* 24 (6), 48–53 (in Chinese with English abstract).