4.18 ADVECTIVE-DIFFUSIVE TRANSPORT OF D_2O IN UNSATURATED MEDIA UNDER EVAPORATION CONDITION

Jun KOARASHI[1], Mariko ATARASHI-ANDOH[2], Hiromi YAMAZAWA[3],
Hikaru AMANO[2] and Takao IIDA[3]

[1]Radiation Protection Division, Tokai Works, Japan Nuclear Cycle Development Institute,
Tokai-mura, Naka-gun, Ibaraki, 319-1194, Japan
[2]Department of Environmental Sciences, Japan Atomic Energy Research Institute,
Tokai-mura, Naka-gun Ibaraki, 319-1195, Japan
[3]Department of Nuclear Engineering, Nagoya University,
Furo-cho, Chikusa-ku, Nagoya, 464-8603, Japan

ABSTRACT

Advective-diffusive transport of HTO in unsaturated media was investigated empirically using deuterated water (D_2O) and columns filled with glass beads. The tortuosity factor was evaluated by numerical model calculations corresponding to first experiment for diffusion under no-evaporation condition. Temporal variations in depth profiles of D_2O concentrations in the columns were observed by second experiment, which considers the transferring and spreading of D_2O by pore-water flow caused by evaporation. Measurements and model calculations indicated that diffusion was about two times more efficient than dispersion for D_2O spreading process under this evaporation condition.

KEY WORDS: tritiated water (HTO), diffusion, advection, transport, unsaturated media

1. INTRODUCTION

Tritium is one of the major long-lived radionuclides which are discharged from nuclear facilities. The tritium released into the atmosphere could be mainly in chemical forms of tritiated water (HTO) and tritiated hydrogen (HT). It is well known that HTO is transferred from the atmosphere into the soil by washout with precipitation[1,2]. Although HT is 25000 times less radiotoxic than HTO, it can be rapidly oxidized by microorganisms in the surface soil layer to form HTO[3-7]. The tritium, entering the soil as the chemical form of HTO through these processes or direct application of HTO to groundwater, may cause a contamination of unsaturated soil and may be re-emitted from the soil to the

atmosphere, since it can move easily up and down through the soil column according to the soil moisture status and other related factors. Therefore, understanding and modelling of HTO transport in unsaturated soil is required to assess the emission potential of tritium and environmental safety[8-11].

In this study, two kinds of laboratory experiments were performed to investigate transport of HTO in unsaturated media. The first measurement was carried out on steady-state diffusive transport and the second one concerns advection and dispersion caused by water flow in pore space. Columns filled with glass beads and deuterated water (D_2O) were used in the experiments as an unsaturated media and a substitute of HTO, respectively. The experimental data were compared with calculation results of a numerical model including three major transport processes of diffusion, advection and dispersion. Some parameters in the model were obtained from separate experiments and relative importance of transport processes under evaporation condition was evaluated by the calculations.

2. EXPERIMENTAL METHODS

2.1 Column Preparation

Five columns made of polymethylmathacrylate with a base area of 5 cm × 5 cm and a height of 55 cm were used in the experiments. The upper end of the column was completely opened and the bottom tip has 61 small openings with 3 mm diameter. One side of wall can be detached from the column body if necessary. The column was filled with glass beads with weighing after absorbent cotton was laid on the bottom to avoid passing the beads from the small openings. The glass beads had a diameter of 0.2 mm, a bulk density of 1.36 g cm^{-3} and a particle density of 2.61 g cm^{-3}. The particle size is classified as fine sand in the soil classification system based on standard of International Soil Science Society[12]. The columns with beads were immersed in deionized water for half a day in order to prepare a steady-state depth profile of water content. Then the columns were drawn from deionized water and set in the containers to keep ground water level of 50 cm depth from column surface. The groundwater level was adjusted by pouring water into an inlet of the container. The amount of water evaporated from column surface was determined from the decrease in the weight of column and container once a day. After weighing, deionized water was supplied into the container until the groundwater level had reached the depth of 50 cm. It was considered that the steady-state depth profiles of water in the columns were established after 10 days because the evaporation rates almost became constant.

2.2 Experiment for D_2O Diffusion in Unsaturated Media

Column 1 was used to obtain background depth profiles of water content and D_2O concentration in column. For column 2, deionized water in container was replaced with D_2O-enriched water with a

concentration of approximately 1 % (i.e. 10000 ppm) after covering column surface with a film to suppress evaporation. After 288 h, water content and D_2O concentration in column 2 were determined by following method.

2.3 Experiment for D_2O Advection-Dispersion in Unsaturated Media

For columns 3, 4 and 5 with groundwater of deionized water, about 200 μl of D_2O with a concentration of 100 % were injected into the point of 38 cm depth from column surface. The glass beads were taken from these columns and analyzed by following method after 79 h for column 3, 199 h for column 4 and 312 h for column 5, respectively. During the experiment, the amount of water evaporated from column surface was determined and the groundwater level was adjusted by the same way as column preparation.

2.4 Determination of Depth Profiles of Water and D_2O

To determine water content and D_2O concentration in the column, the column was first pull out from the container and then the sidewall of the column was removed. The samples of glass beads were taken from the column every 5 cm from the surface up to a depth of 20 cm and every 3 cm between a depth of 20 cm to 50 cm for diffusion experiment, and every 5 cm up to a depth of 20 cm and every 2 cm below a depth of 20 cm for advection-dispersion experiment, respectively. Each beads sample was preserved in sealed vessel and was mixed well to homogenize the taken sample. The beads sample was divided into two portions for measuring water content and D_2O concentration. The water content was determined by oven-drying the sample at 105 °C. To measure D_2O concentration, the beads sample stored in a flask was heated to 105 °C, flowing high purity nitrogen gas (99.99 %) at 0.5 l min^{-1} for 4-5 h. The water vapor from beads sample was collected by a cryogenic trap with liquid nitrogen. For collected water sample, D_2O concentration was measured using a gas chromatography (GC; GC-14B, Shimadzu, Japan). Thereafter, for a water sample with a D_2O concentration lower than 300 ppm, the concentration was re-measured with an isotopic ratio mass spectrometry (IR-MS; MAT252 plus H/Device, Finnigan MAT Co.) to obtain accurate value. In the IR-MS, the ratio of the deuterium and hydrogen in the water sample was measured and compared with that in a standard sample[11,13].

3. MODEL DESCRIPTION

The transport of HTO in unsaturated media is caused by a combination of two movements that are a movement of water in the media and a movement of HTO within the water. The transport, under isothermal conditions, is described by a system of coupled equations that can be solved in tandem[11].

$$C_w(\psi_m)\frac{\partial \psi_m}{\partial t} = \frac{\partial}{\partial z}\left[K(\psi_m)\left(\frac{\partial \psi_m}{\partial z} - 1\right)\right] \tag{1}$$

$$\frac{\partial(\theta C)}{\partial t} = \frac{\partial}{\partial z}\left[D_e(\theta)\frac{\partial C}{\partial z}\right] - \frac{\partial}{\partial z}[q(\theta)C] \tag{2}$$

The first equation is Richards equation for moisture flow in unsaturated media, where ψ_m (m) is the matric head expressed as a unique function of volumetric water content θ (volume fraction), $C_w(\psi_m)$ the specific water capacity defined as $\partial\theta/\partial\psi_m$ and $K(\psi_m)$ (m s^{-1}) the unsaturated hydraulic conductivity. The second equation is the advection-diffusion equation that expresses solute transport in porous media without reaction with materials. In this equation, C (Bq l^{-1}) is HTO concentration in water and $D_e(\theta)$ (m^2 s^{-1}) is the effective dispersion coefficient of HTO in porous material. These two equations are linked by the advective water flux $q(\theta)$ (m s^{-1}) estimated by

$$q(\theta) = K(\theta)\left(\frac{\partial \psi_m}{\partial z} - 1\right). \tag{3}$$

The functions evaluated empirically by van Genuchten were used to describe the relation of θ and K to matric head ψ_m:

$$\frac{\theta - \theta_r}{\theta_s - \theta_r} = \left\{\frac{1}{1 + (a|\psi_m|)^n}\right\}^m \tag{4}$$

$$\frac{K(\theta)}{K_s} = \left(\frac{\theta - \theta_r}{\theta_s - \theta_r}\right)^{1/2}\left[1 - \left\{1 - \left(\frac{\theta - \theta_r}{\theta_s - \theta_r}\right)^{1/m}\right\}^m\right]^2 \tag{5}$$

where θ_s is the volumetric water content of saturated media, namely total porosity, θ_r the residual water content and K_s (m s^{-1}) the saturated hydraulic conductivity. The parameters a, m and n are the constants depending on the type of unsaturated media[14].

The effective dispersion coefficient in the pore is expressed as the following relationship, in which the first term refers to molecular diffusion in liquid phase, the second term to molecular diffusion in gaseous phase and the third term to hydrodynamic dispersion in liquid phase:

$$D_e(\theta) = \tau\theta D_w + \beta c(\theta_s - \theta)^d D_a + \alpha|q(\theta)| \tag{6}$$

where τ (dimensionless) is the tortuosity factor for diffusion in porous media, D_w ($m^2 s^{-1}$) the HTO diffusion coefficient in bulk water, 2.3×10^{-9} $m^2 s^{-1}$, β (dimensionless) the vapour-liquid distribution factor, D_a ($m^2 s^{-1}$) the HTO diffusion coefficient in bulk air, 2.2×10^{-5} $m^2 s^{-1}$, and α (m) the hydrodynamic dispersivity. Parameters c and d are constants in the relationship.

4. RESULTS AND DISCUSSION

The water-retention characteristics for all columns are presented in Fig.1, which shows the water content as a function of the depth from column surface. The columns used in diffusion and advection-dispersion experiments had an almost same distribution of water content.

Fig.2 shows the depth profiles of D_2O concentration obtained in diffusion experiment. Although advective flow of pore-water did not take place under no-evaporation condition in this experiment, D_2O was transported upward by molecular diffusion from watertable in the column 2. The concentration of 202 ppm was observed at the position of 37 cm depth, which was somewhat higher than the background concentration of about 150 ppm. In the simulations by numerical model, 50 cm deep column was divided into 50 layers with uniform intervals of 1 cm. No evaporation was applied to an upper boundary condition. As this condition conducts no advective water flux in the column, the depth profile of water content does not change during the objective period. A lower condition was defined as constant water content of 0.4 and constant D_2O concentration at groundwater level, which were obtained actually in the experiment. The parameters in water-retention characteristic curve,

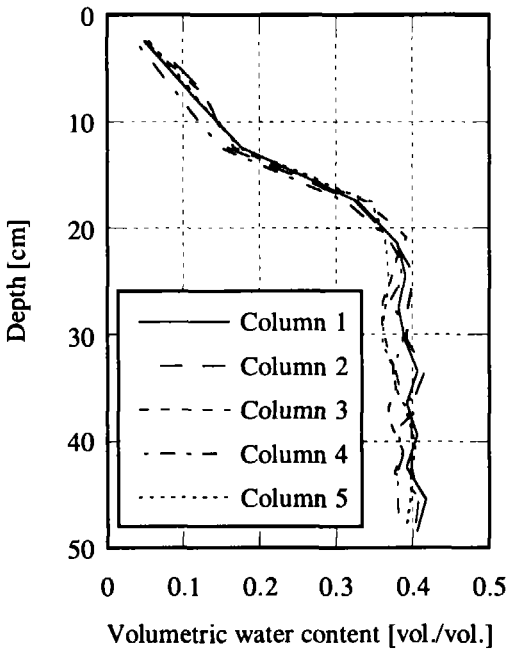

Fig.1 Water-retention characteristics of columns

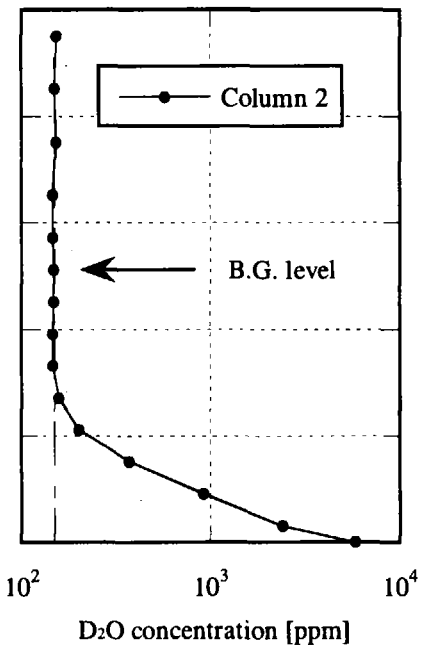

Fig.2 D_2O concentration profile in diffudsion experiment

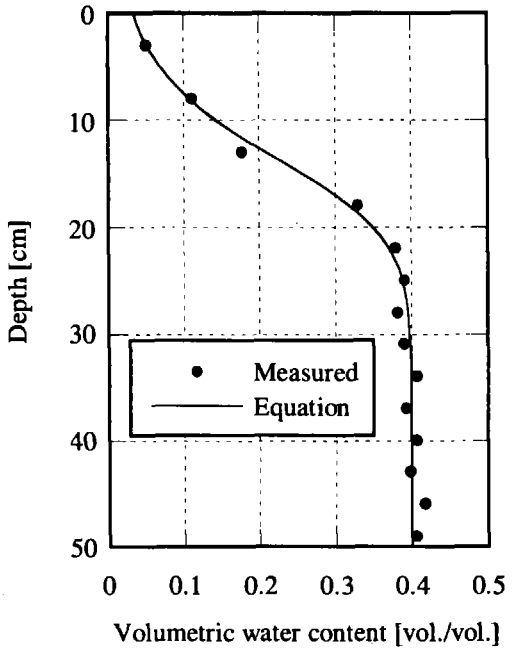

Fig.3 Water-retention characteristics curve used in the model.

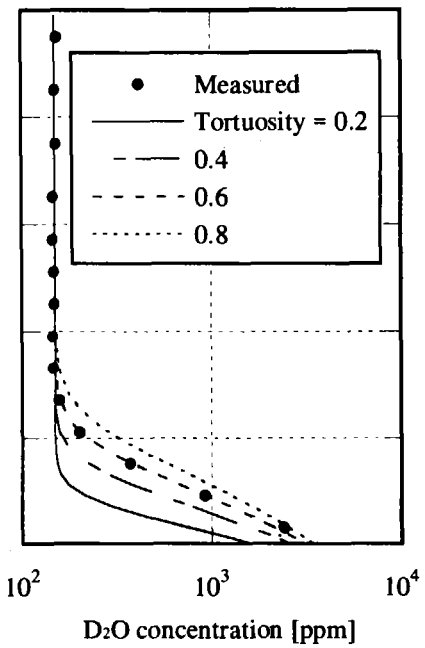

Fig.4 Measurements and calculations of D_2O concentration in diffusion experiment

equation (4), were determined by fitting to the observed water-content profile after setting θ_r to 0.02. The measurements and the curve used in the model calculations are shown in Fig.3. The effective dispersion coefficient was estimated with the values of $\beta = 1.1 \times 10^{-3}$, $c = 4.53$ and $d = 3.33$. The only parameters that determine the D_2O concentration profile are the tortuosity for diffusion in the pore space, because D_2O transport is independent of advection and dispersion processes under no-evaporation condition. The calculation results for diffusion experiment, which obtained by changing the tortuosity factor τ, are shown with experimental one in Fig.4. The D_2O profile calculated with $\tau = 0.6$ agreed well with the observations. The tortuosity factor estimated by considering only diffusion process was used in the following calculations.

With respect to the calculation for advection-dispersion experiment, the evaporation rates observed experimentally was used as an upper boundary condition. Since it is known that K_s has a wide range and is order of 10^{-4} cm s^{-1} for fine sand, the K_s of 1×10^{-4} cm s^{-1} was used in the calculation[12]. The hydrodynamic dispersivity of 5 cm was also used to estimate the dispersion coefficient[15]. Fig.5 shows the experimental data and calculated D_2O concentrations for columns 3, 4 and 5. Discrepancies of concentrations between measurements and calculations were observed near the watertable and the calculations generally underestimated the measured concentrations to some degree. Experimental procedure including the injection of D_2O into columns may produce the rapid downward transfer of D_2O into the watertable in experiment. An upward shift of peak of D_2O concentration and a spreading of D_2O were observed with elapsed time in the measurements. Evaporation conducts water flow and D_2O advection in the pore space, resulting in the upward shift of

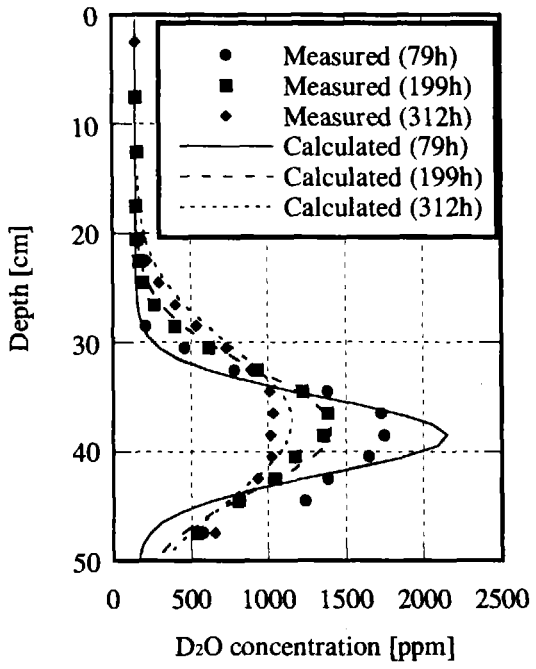

Fig.5 Measurements and calculations of D_2O concentration in advection-dispersion experiment

the peak. The model calculation provided the water flux of approximately 5.9×10^{-7} cm s^{-1} in the column. This was comparable to the flux of 4.6 to 9.3×10^{-7} cm s^{-1} by observations. The spreading of D_2O is, on the other hand, can be understood by a combination of diffusion and dispersion in the pore. The coefficients of diffusion and dispersion were estimated by model calculations to be 5.5×10^{-6} and 3.0×10^{-6} cm^2 s^{-1}, respectively. This indicates that the diffusion is predominant processes to D_2O spreading in column under this evaporation condition.

5. CONCLUSIONS

Laboratory experiments were performed to investigate HTO transport in unsaturated media, using D_2O and columns filled with glass beads. Profiles of water content and D_2O concentration were first measured as a function of depth under no-evaporation condition to evaluate tortuosity factor on D_2O diffusion in pore space. The comparisons between numerical model calculations and measurements provided the tortuosity of 0.6 for diffusion in this porous material. Furthermore, behavior of D_2O injected into column was observed by advection-dispersion experiment. Observations were compared with calculations of model including three major transport processes of molecular diffusion, advection and hydrodynamic dispersion. The results evaluated that the diffusion was about two times more efficient than the dispersion for D_2O spreading process under this evaporation condition.

REFERENCES

1. Chamberlain, A. C. and Eggleton, A. E. J., Washout of tritiated water vapour by rain, *International Journal of Air and Water Pollution*, **8**, 135 (1964).
2. Belovodski, L. F., Gaevoy, V. K., Golubev, A. V. and Kosheleva, T. A., Tritium oxide wash-out by drops, *Journal of Environmental Radioactivity*, **36**(2-3), 129 (1997).

3. Garland, J. A. and Cox, L. C., The absorption of tritium gas by English soils, plants and the sea, *Water, Air and Soil Pollution*, **14**, 103 (1980).
4. Sweet, C. W. and Murphy, Jr. C. E., Oxidation of molecular tritium by intact soils, *Environmental Science and Technology*, **15**(12), 1485 (1981).
5. Fallon R. D., Molecular tritium uptake in southeastern U.S. soils, *Soil Biology and Biochemistry*, **14**, 553 (1982).
6. Wu, L. F. and Mandrand, M .A., Microbial hydrogenases: Primary structure, classification, signatures and phylogeny, *FEMS Microbiol. Reviews*, **104**, 243 (1993).
7. Koarashi, J., Amano, H., Andoh, M., Iida T. and Koma, T., A new method for determining HT deposition velocity and dependence of the velocity on environmental factors, *Radiation Protection Dosimetry*, **93**(3), 237 (2001).
8. Murphy, Jr. C. E., Tritium transport and cycling in the environment, *Health Physics*, **65**, 683 (1993).
9. Golubev, A. V., Mavrin, S. V. and Sten'gach, A. V., Model of tritium dispersion by ground water, *Journal of Engineering Physics and Thermophysics*, **74**(4), 661 (2000).
10. Yamazawa, H., A one-dimensional dynamical soil-atmosphere tritiated water transport model, *Environmental Modelling and Software*, **16**, 739 (2001).
11. Koarashi, J., Atarashi-Andoh, M., Yamazawa, H., Amano, H. and Iida, T., Numerical modelling and laboratory experiments of tritium transport in unsaturated soil, *Fusion Science and Technology*, **41**, 464 (2002).
12. Tindall, J. A. and Kunkel, J. R., Unsaturated zone hydrology for scientists and engineers, Prentice Hall (1999).
13. Atarashi-Andoh, M., Amano, H., Kakiuchi, H., Ichimasa, M. and Ichimasa, Y., Formation and retention of organically bound deuterium in rice in deuterium water release experiment, *Health Physics*, **82**(6), 863 (2002).
14. van Genuchten, M. Th., A closed-form equation for predicting the hydraulic conductivity of unsaturated soils, *Soil Science Society of America Journal*, **44**, 892 (1980).
15. Forrer, I., Kasteel, R., Flury, M. and Flühler, H., Longitudinal and lateral dispersion in an unsaturated field soil, *Water Resources Research*, **35**, 3049 (1999).