How Heterogeneity Matters in Water-Soil Environmental Research

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How Heterogeneity Matters in Water-Soil Environmental Research

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Abstract - Recovery of water-soluble substances in air sparging was investigated and the prolonged tailing - linear decrease in double-log plots of concentration vs. time relationship - was observed in a simple sand-water-air system having no micropores. It was suggested that the configuration of gas and water phases brought about a kind of heterogeneity into a relatively uniform soil system.

I. Introduction

Subsurface environment, groundwater and soil have various kinds of heterogeneities and sometimes these heterogeneities hinder effective removal of pollutants, such as TCE, PCE, etc.

It is known that in groundwater remediation such as soil vapor extraction (SVE) and pump-up of polluted groundwater, the concentration of removed pollutants decreases gradually, and its time-concentration relationship often reveals approximate linearity in double-log plots.

Researchers have tried to make clear the mechanisms of this phenomenon - sometimes called prolonged tailing - and found that, in their modeling studies, they have succeeded in reproducing the trends only when they applied gamma-distribution or power law distribution to mass transfer rates or diffusion rates [1-3]. Also, Haggerty et al. have analyzed the relationship between the distribution of mass transfer or diffusion rates and the slopes in double-log plots of time-concentration relationship and found that power law distribution of mass transfer rates or diffusion rates was best fit to the liner relationship in double-log plots, as far as the absolute value of the slope in double-log plot, ? is smaller than 3, and the distribution of mass transfer or diffusion rates obeys the power law of ?$^{2-3}$ [3].

Researchers have ascribed the prolonged tailing to the distribution of diffusion rates in micropores (e.g. [4]). However, we think we cannot exclude the possibility that the heterogeneity of the distribution of water and gas in soil have caused the prolonged tailing. Also, we think that by applying the theory developed by Haggerty et al., we will be able to calculate the distribution of "diffusion distance" in water in the process that a dissolved substance is extracted to gaseous phase [3].

In this paper, we investigated the recovery of dissolved carbon dioxide from soil water in a system mimicking the air-sparging of groundwater, and tried to see if prolonged tailing occurs in the absence of micropores, and tried to calculate the distribution of diffusion distance of carbon dioxide in water phase.

II. Materials and Methods

A. *Experimental Apparatus*

Fig. 1 shows the experimental apparatus. A stainless column of 30 cm in inner diameter and 50 cm in inner height was prepared. Sand from Tedori river (obtained from a local constructor) was air-dried and sieved, and then 0.5 -- 2.0 mm fraction of it was packed into the column up to the height of 50 cm.

The column was connected to the water reservoir to enable to control the water table in the sand layer. Gas injection port was set 10 cm above the bottom of the column. The gas injection port were connected to nitrogen, helium and carbon dioxide cylinders via mass flow controllers.

B. *Experimental Procedure*

First, we set the water table in the column at the desired level. Then, nitrogen gas containing 2 -10 % of carbon dioxide and 5% of helium was supplied to the column. This process was continued for 10 - 20 hours. After the water was nearly saturated by the carbon dioxide, then, the supplied gas was changed to pure nitrogen. The outflow gas from the column was sampled with an automatic gas sampler (GL-Science, GS-5000A) and the concentration of carbon dioxide and helium was measured by gas chromatography (Hitachi GS-3000) with TCD and FID detectors and a methanizer (GL-Science MT221).

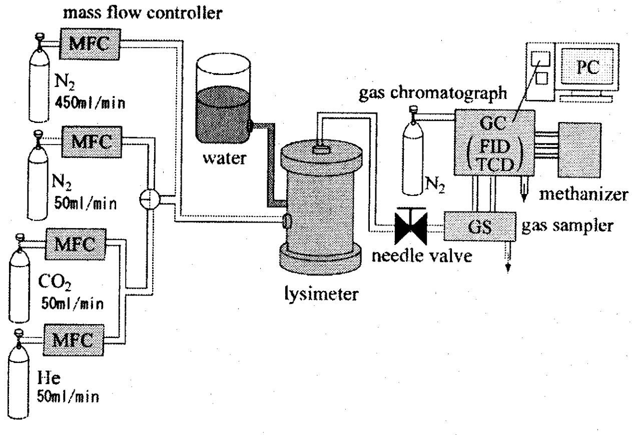

Fig. 1a Experimental apparatus.

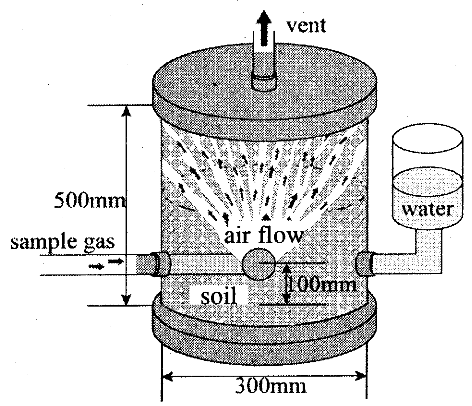

Fig. 1b Sand column.

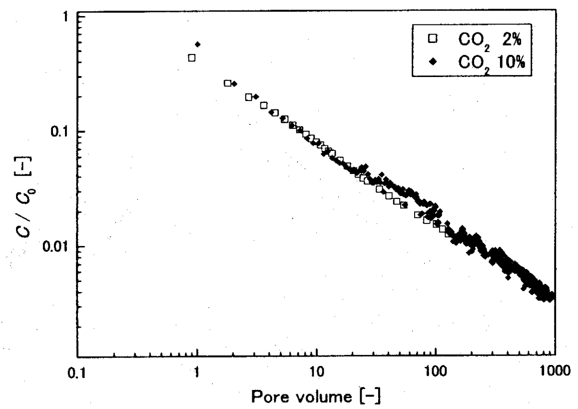

Fig. 2 Prolonged tailing obtained in the simple gas water soil system (water level: 45 cm). Carbon dioxide concentration had little effect on the prolonged tailing.

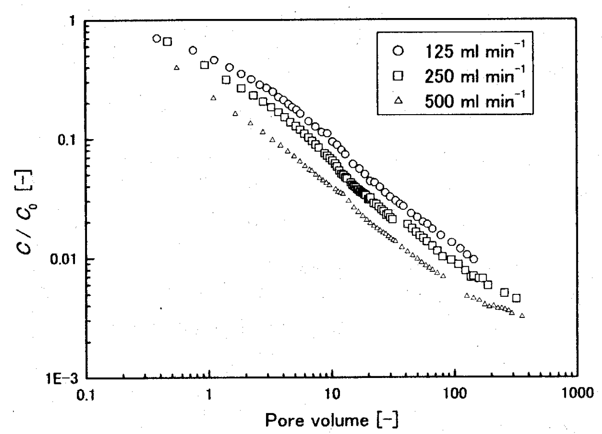

Fig. 3 Effect of flow rates on the prolonged tailing.

III. Results and Discussion

Fig. 2 shows the double-log plots of pore volume vs. concentration relationship at the water level of 45 cm. Pore volume was calculated by dividing real time by the average residence time of helium, and the concentration of carbon dioxide was normalized by its initial concentration.

It is clearly seen that the plots revealed approximately linear relationship in double-log plots, which lasted at least the pore volume up to 1000 (in this case it corresponds to approximately 66 hours). Also, Fig. 2 shows that the initial carbon dioxide concentration had little effect on the recovery rates.

In this system, we used sand of 0.5 - 2.0 mm particle diameters, in which there are not micropores in a significant amount. So, we see that the prolonged tailing can be seen in systems having little micropores.

Fig. 3 shows the effect of flow rates on the recovery of carbon dioxide. It is seen that as the flow rates increases, the plots move to the left, meaning that faster recovery rates at higher flow rates. However, the slopes in double-log plots are practically the same in these three flow rates.

We think that the configuration of water and air in this air-sparging apparatus caused the prolonged tailing, because the system was considered to have little micropores. As the air flows into the sand initially saturated with water, tree-like gas flow paths are established. In this kind of gas-water configuration, distance between two gas flow paths are short in somewhere and long in elsewhere, causing the distribution of size of water surrounded by the several gas flow paths.

The reason why the flow rates did not show significant effects on the slope in double-log plots is that once the flow paths has established, flow rates did not change the gas-water configuration so much.

The slope of the pore volume (time) vs. concentration plots in double-log in Figs. 2 and 3 were about 0.7 - 0.9. Haggerty et al. [3] have shown that if the absolute value of the slope ? is less than 3, the corresponding distribution of mass transfer coefficient k or diffusion rate (D_{eff}/a^2) is $f(k) \sim k^{?-3}$, or $f(D_{eff}/a^2) \sim (D_{eff}/a^2)^{?-3}$, where D_{eff} is the effective diffusion coefficients in water phase and a is the effective diffusion distance.

In our system, it is hard to consider that the mass transfer coefficient k has the distribution like $k^{(?-3)}$, also, the effective diffusion coefficient can be seen as constant throughout the system. Then, the only plausible explanation for $f(k) \sim k^{?-3}$ or $f(D_{eff}/a^2) \sim (D_{eff}/a^2)^{?-3}$ distribution is the distribution of diffusion distance a. That is, the diffusion distance a has the distribution like $f(a) \sim a^{1.1}$.

In traditional chemical engineering mass transfer analyses, the mass transfer coefficient k or the diffusion rate D_{eff}/a^2 was usually assumed as a constant. In chemical processes, they focus on the fastest parts of the mass transfer or the diffusion, occurring in relatively high concentrations of the substances, and the heterogeneity such as observed in this research does not matter. However, in soil and groundwater remediation, we usually are interested in the concentration around environmental quality standard, and then the heterogeneity in the air-water configuration in air-sparging really matters: Note that the time required for the system reaching the concentration below environmental quality standard depends on the slope of the time-concentration in double-log plots.

Fig. 4 shows the effect of water level on the prolonged tailing. It is clearly seen that the water level affected the slope in double-log plots. At different water level, the configuration of the water and air in the system will be different and that causes the difference in prolonged tailing.

The experimental results suggests that in real air-sparging processes, the prolonged tailing can be caused by at least two different kinds of mechanisms, micropore diffusion and heterogeneity brought about by the air flow. In real environment, heterogeneities can be seen everywhere, the permeability of water or gas are spatially non-uniform, pollutants exist non-uniformly in soil and groundwater. Also, what we have seen in this research is that even in the very simple systems, like packing of the sand having relatively uniform grain size distribution, revealed a kind of heterogeneity. This suggests that in some cases it may be not enough to apply spatially varying characteristics of the medium, such as permeability, but we also have to look at the configuration of water and air in subsurface environment, which apparently is another source of the heterogeneity.

Fig. 5 shows the hysteresis in gaseous diffusion coefficient in a sand fraction of 0.35 - 0.50 mm. It is well known that the soil water characteristics curves or retention curves reveal hystereses between drying and wetting processes. Fig. 5 clearly shows that not only the retention curves but also the gaseous diffusion coefficient reveals hysteresis. This is another example that the configuration of air and water brings about heterogeneities.

Percolation theory and network modeling might help our understanding of this kind of heterogeneity brought about by the configuration of air and water in the subsurface environment. The "size" of water lies between gas flow paths can be seen analogous to the percolation clusters in soil pore network. Also, the estimated power law distribution of diffusion distances suggests the some fractal nature of the gas-water interfaces, which is predicted in percolation theory: the peripheral of the clusters reveals fractal nature at the percolation threshold. In air-sparging, we can assume that the gaseous phase below water table will be near percolation threshold. In percolation theory, the percolation threshold is defined as the smallest occupation probability at which the sample-spanning cluster will exist. In air sparging, pressurized air is introduced into the groundwater and the air cluster will grow in a tree-like shape, and as soon as the front of the air phase reaches the soil air connected to the atmosphere, the volume of the air phase will not grow any more and retain the shape at the time the front hits the free soil air. Thus, the structure of the air phase in air sparging is analogous to the percolation threshold of a invasion percolation.

How heterogeneity matters in water-soil environmental research. This question is too big to answer in a short period of time and might be continually asked in different ways at different generations. In this paper, we only suggested that the configuration of water and gas phase in soil might bring about a kind of heterogeneity. The estimated power-law distribution of "diffusion distance" suggests that the possibility of the application of percolation theory to the analysis of the water-gas configuration. However, at this point, we do not know any further.

Heterogeneity really matters in the removal of pollutants from ground water and/or soil. The research in this field - how to deal with the heterogeneity - seems to be still in its infancy. More investigation will be necessary about how the gas and water configuration bring about heterogeneities and also how the coupling of gas-water configuration heterogeneity and other kinds of heterogeneities such as gas permeability, micropore diffusion, etc. affect the fate of pollutants

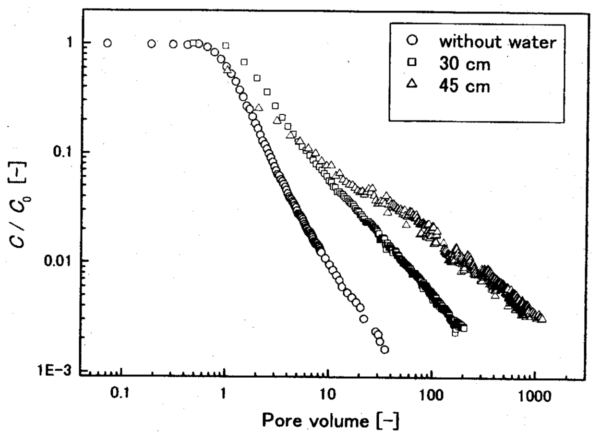

Fig. 4. Effect of water level on the prolonged tailing.

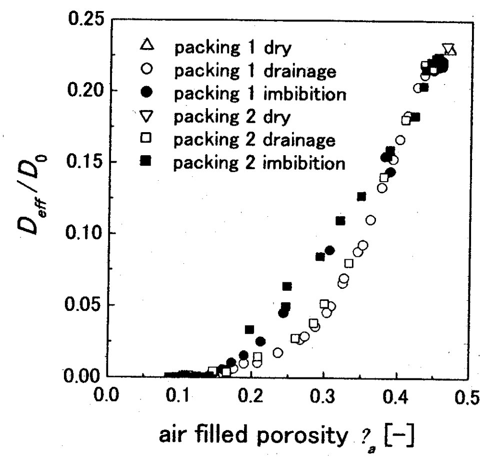

Fig. 5 Hysteresis in gaseous diffusion - air-filled porosity relationship in 0.35-0.50 mm fraction of Uchinada coastal sand.

IV. Conclusions

The mass transfer rates from water to gas in air-sparging was investigated. A prolonged tailing, the linear decrease in double-log plot of time-concentration relationship, is observed in a relatively simple sand-water-air system, having practically no micropores. From the tailing, the "diffusion distance", a, was estimated to have a power law distribution: $f(a) \sim a^{1.1}$. The results suggest that the air-water configuration caused by the gas injection has brought about a kind of heterogeneity.

Acknowledgements

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