Transfer of Boron and Tritiated Water Through Sandstone[1]

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ABSTRACT

The movement of tritiated water and boron were determined during unsaturated flow through undisturbed sandstone cores. From the displacement and slope of the breakthrough curves relative to 1 pore volume of effluent, adsorption coefficients and dispersion coefficients were calculated of 0.135 and 1.06 cm^2/day for boron, and 0.04 and 3.45 cm^2/day for tritiated water, respectively. The data were used to predict the downward movement of boron through a sandstone formation in the Four Corners area of New Mexico. With 20 cm annual rainfall and 10% of the precipitation contributing to recharge, it was calculated to take 1,628 years for the boron concentration at the ground-water table at 86 m to reach one-half the boron concentration at the soil surface.

Additional Index Words: breakthrough curves, dispersion coefficient, adsorption coefficient, ground-water pollution.

Pollution of ground-water resources from industrial wastes is of increasing concern in many parts of the country. Sources of possible ground-water pollution are storage reservoirs for radioactive wastes, wastes from mining and refining of metals, and irrigation with waste water containing heavy metals. A source of possible ground-water pollution in the Southwest US is waste from surface mining of coal for power generation or gasification. The coal used for these purposes may contain appreciable amounts of trace elements (22). When the ash from coal containing many trace elements is returned to pits from which the coal was taken, it is important to know whether, and how fast these trace elements may travel down to the ground-water table.

The movement of trace metals through soil is often severely retarded through adsorption of the metals on the soil material or by chemical reactions. Adsorption of boron on soil has been studied extensively (3, 9, 10, 11, 15, 17, 19) because boron is a micronutrient which becomes toxic at concentrations only slightly above optimum (9). The more recent literature on boron adsorption in soil indicates that the three major inorganic sites of adsorption are, (i) iron and aluminum-hydroxy compounds present as coatings on, or associated with, clay minerals; (ii) iron or aluminum oxides in soils; and (iii) micaceous-type clay minerals (17). Rhoades, Ingvalson, and Hatcher (17) found that arid zone soils can also have appreciable boron-sorption capacities in their silt and sand fractions in addition to their clay fractions, apparently due to magnesium-hydroxy clusters or coatings that exist on the weathering surfaces of ferromagnesian minerals.

Although there is a very extensive literature on mathematical modeling of solute movement and dispersion phenomena in soils (2, 4, 8), there are few studies on the prediction of the movement of adsorbed chemicals, including trace elements, through soil. Notable exceptions

are studies on pesticide movement through soil (7, 14, 23) and cation exchange (5, 12). Boron movement in soil was studied by Hatcher and Bower (10), who computed elution of boron from short columns by coupling the Langmuir adsorption isotherm with a chromatographic theory. Tanji (21) also combined the Langmuir adsorption isotherm and a chromatographic displacement theory in a computer model to successfully predict the leaching of boron from stratified soil columns.

The purpose of this paper is to present data on the movement of boron and tritiated water through an undisturbed sandstone core, and to show how these data may be used to predict transit times for boron to move to given depths in an unsaturated sandstone formation in the Four Corners area of New Mexico.

Theory

The movement of adsorbed chemicals through a porous medium under steady state soil-water conditions follows the differential equation

$$\frac{\rho}{\theta}\frac{\partial S}{\partial t} + \frac{\partial C}{\partial t} = D_o\frac{\partial^2 C}{\partial x^2} - v_o\frac{\partial C}{\partial x} \qquad [1]$$

where C is the concentration of the chemical in solution ($\mu g/cm^3$), S is the amount of chemical adsorbed per gram of soil ($\mu g/g$), D_o is the dispersion coefficient (cm^2/day), v_o is the average pore-water velocity (cm/day), ρ is the bulk density (g/cm^3), θ is the volumetric water content (cm^3/cm^3), x is the linear distance in the direction of flow (cm), and t is the time (days). The relationship between the amount in solution (C) and the amount adsorbed (S) can often be described with the Freundlich equation

$$S = KC^N \qquad [2]$$

where K is the adsorption constant and N a parameter. Differentiating Eq. [2] with respect to time gives

$$\partial S/\partial t = KNC^{N-1}(\partial C/\partial t). \qquad [3]$$

Equation [3] can be substituted into Eq. [1]. When $N = 1$, and adsorption and desorption are single valued we obtain

$$\frac{\partial C}{\partial t} = \frac{D_o(\partial^2 C/\partial x^2) - v_o(\partial C/\partial x)}{1 + (\rho K/\theta)}. \qquad [4]$$

The expression $1 + (\rho K/\theta)$ is often referred to as the retardation factor Rf. By making the following substitutions:

$$D_o' = D_o/\text{Rf} \text{ and } v_o' = v_o/\text{Rf} \qquad [5]$$

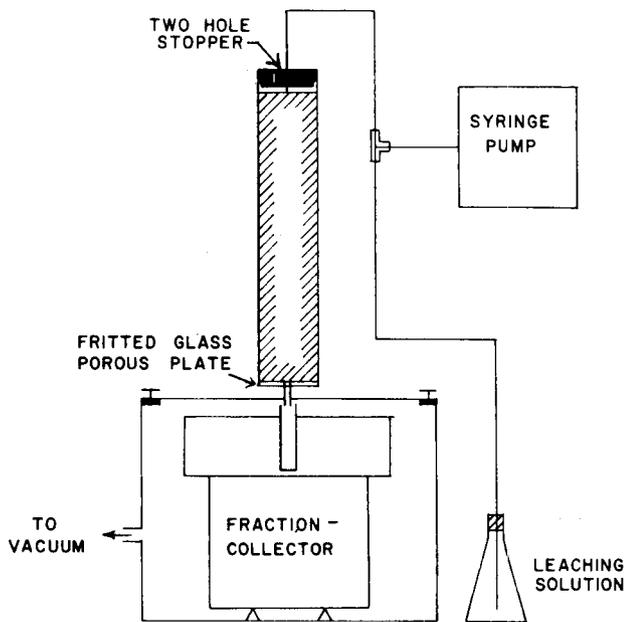we obtain the one-dimensional convective diffusion equation

Fig. 1—Schematic diagram of experimental set up during movement of boron and tritiated water through soil column.

$$\frac{\partial C}{\partial t} = D'_o \frac{\partial^2 C}{\partial x^2} - v'_o \frac{\partial C}{\partial x}. \qquad [6]$$

Consider a semi-infinite homogeneous medium of uniform water content. Solute is allowed to flow from a large reservoir at $x < 0$ into an initially solute-free column at a rate $v'_o \theta \, C_o$. The boundary and initial conditions then are as follows:

$$x = 0 \ \ t > 0 \ \ v'_o \, C_o = \lim_{x \to 0+} [v'_o C - D'_o(\partial C/\partial x)] \quad [7]$$

$$x > 0 \ \ t = 0 \ \ C = 0 \qquad [8]$$

The solution of Eq. [6] subject to conditions [7] and [8] for a semi-infinite medium is (Lindstrom et al., 13)

$$[C(x,t)/C_o] = 1/2 \, [L(x,t) - M(x,t)] + N(x,t) \quad [9]$$

where

$$L(x,t) = \text{erfc}\left[\frac{x - v'_o t}{(4D'_o t)^{\frac{1}{2}}}\right]$$

$$M(x,t) = \left[1 + \frac{v'_o(x + v'_o t)}{D'_o}\right] \times \text{erfc}\left[\frac{x + v'_o t}{(4D'_o t)^{\frac{1}{2}}}\right] \times \exp\left[\frac{v'_o x}{D'_o}\right]$$

$$N(x,t) = v'_o \left(\frac{t}{\pi D'_o}\right)^{\frac{1}{2}} \times \exp\left[\frac{v'_o x}{D'_o} - \frac{(x + v'_o t)^2}{4D'_o t}\right].$$

For long columns with $v'_o x/D'_o$ large, a direct evaluation of Eq. [9] fails on most computers. By using the approximations for erfc presented by Abramowitz and Stegun (1) the exponential and erfc functions in Eq. [9] can be combined. It can then be shown that the sum of the last 2 terms of Eq. [9] i.e. $N(x,t)-1/2 \, M(x,t)$ is small compared to the first term, and hence Eq. [9] may be

simplified to the "diffusion" solution of Danckwerts (6):

$$\frac{C}{C_o} = 1/2 \, \text{erfc}\left[\frac{x - v'_o t}{(4D'_o t)^{\frac{1}{2}}}\right]. \qquad [10]$$

In many practical situations the flux at the upper boundary changes with time or the profile is not homogeneous with depth. In these cases a numerical solution of Eq. [6] can provide more flexibility in obtaining the distribution of the chemical with depth. The numerical technique used in this paper is described extensively by van Genuchten and Wierenga (24).

METHODS AND PROCEDURES

Cores of undisturbed sandstone from the Pictured Cliffs Sandstone formation in the Four Corners area of New Mexico were used in the study. The Pictured Cliffs Sandstone is a thin- to massive-bedded gray to grayish-tan, fine- to medium-grained, cross-bedded variable indurated sandstone. The cores had an outside diameter of 5.34 cm and were broken in sections of about 30 cm in length. The cores were placed in plexiglass tubes of 5.40 cm inside diameter. The lower end of each tube consisted of a bottom plate enclosing a fine-fritted glass porous plate. A 3-mm layer of ground sandstone insured good contact between the sandstone core and the porous plate. The column was positioned vertically on top of and connected to a vacuum chamber enclosing an automatic fraction collector (Instrumentation Specialties Co., Lincoln, Nebraska). Through the vacuum chamber and the fritted glass porous plate a constant suction of 75 cm of water was maintained at the lower end of the sandstone column, using a vacuum regulator (Moore Products Co., Springhouse, Pennsylvania). The leaching solution was applied to the top of the column with a modified syringe pump (Sage Instruments, Cambridge, Massachusetts). With the pump, a constant inflow could be maintained over long periods of time. A diagram of the experimental set up is presented in Fig. 1.

Well water was obtained from a well in the Pictured Cliffs Sandstone formation from a depth of approximately 220 m below the soil surface. The pH of the well water was 7.54, the electrical conductivity was 3.80 mmhos/cm, and it contained 0.1 ppm boron. The column was leached with well water at a rate of 0.83 cm/day. After establishing steady-state flow conditions for several days, the leaching solution was replaced with well water to which 0.1144 g of H_3BO_4 and 20 mCi of tritiated water were added per liter (final concentrations 20 ppm B and 45,000 cpm, respectively). The effluent from the column was collected in 3- and 6-ml fractions in the fraction collector. The effluent samples were analyzed for boron using a colorimetric procedure (25), and for tritiated water by counting in a Packard Tricarb Model 3310 liquid scintillation counter using Aquasol as the counting medium. The average water content in the sandstone during displacement was determined by weighing the column before leaching and at several times during the leaching experiment.

RESULTS AND DISCUSSION

The results of the displacement experiment are presented in Fig. 2 for boron and in Fig. 3 for tritiated water. A procedure similar to the one described by Rose and Passioura (18), in conjunction with Eq. [10], was used to evaluate the dispersion coefficient D_o from the breakthrough data. For boron a value of 1.06 cm²/day was calculated. This value is comparable to the apparent diffusion coefficient of 0.68 cm²/day, as determined by Sulaiman and Kay (20) for boron diffusion in soil. If no adsorption of boron on the sandstone had taken place, the plot of the relative concentration vs. pore volumes of

effluent should have gone through $C/C_O = 0.5$ and V/V_O = 1.0. Instead, a relative concentration of 0.5 was observed after 2.55 pore volumes had passed the column. From this delay of the chemical in the effluent the adsorption constant K can be calculated by making use of Eq. [5] and the definition of the pore volume of effluent, i.e. $V/V_O = v_o t/L$.

It follows that

$$\left(\frac{V}{V_O}\right)' = 1 = \frac{v_o' t}{L} = \frac{v_o t}{L\mathrm{Rf}} = \frac{V}{V_O} \times \frac{1}{\mathrm{Rf}} = \frac{2.55}{\mathrm{Rf}}.$$

Thus $1 + (\rho K/\theta) = 2.55$, with $p = 1.92$, $\theta = 0.1669$, and $K = 0.135$. A boron breakthrough curve was calculated using Eq. [9] and the values of the adsorption coefficient and the dispersion coefficient. The dashed line in Fig. 2 represents the calculated effluent curve. Observed and computed data agree except near the end of the curve where the data show considerable tailing which may be due to interparticle and intraparticle diffusion.

The relative concentration of the tritiated water vs. pore volumes of effluent is plotted in Fig. 3. Using the procedure described above, a value of the absorption constant K of 0.042 was obtained, and a value of the dispersion coefficient D_O of 3.45 cm^2/day. The considerable horizontal displacement of the tritiated water effluent curve is probably due to exchange between the hydrogen isotope in the bulk water and the crystal-lattice hydroxyls of the sandstone. (G. L. Stewart, and J. H. Baker. Factors influencing the use of tritium as a tracer of soil water.
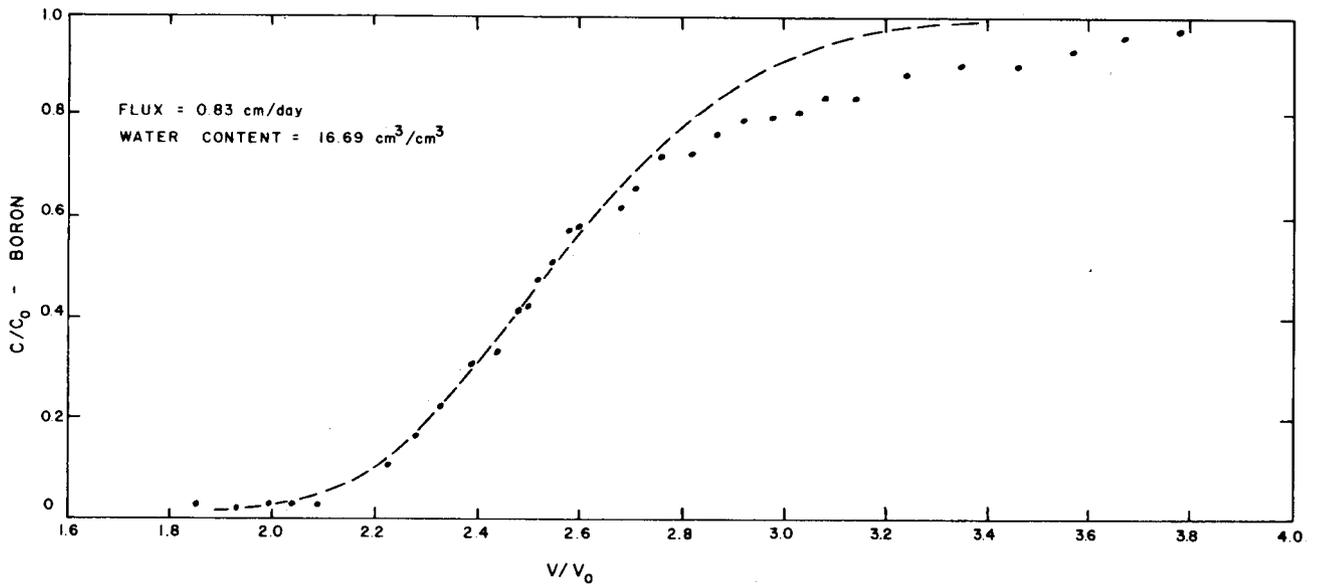

Fig. 2—Relative concentration of boron vs. pore volumes of effluent. The dashed line was calculated with Eq. [9], $K = 0.135$ and $D_O = 1.06$ cm^2/day.
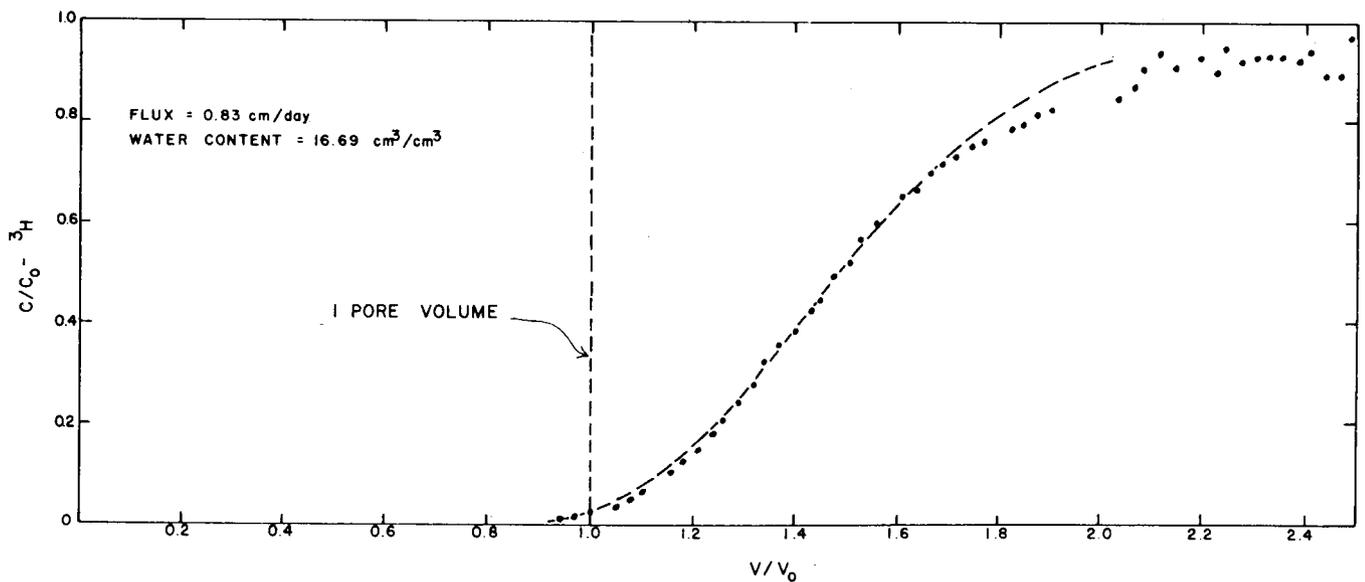

Fig. 3—Relative concentration of tritiated water vs. pore volumes of effluent. The dashed line was calculated with Eq. [9], $K = 0.042$ and $D_O = 3.45$ cm^2/day.

Agron. Abst.) Because the water content in unsaturated sandstone is small, and the density is large, a small value of K can give large values of the retardation factor, causing considerable displacement of the breakthrough curves (Eq. [4]). The use of tritiated water as a tracer for unsaturated water flow through sandstone can therefore lead to large errors.

The data obtained during the displacement study was used to predict transit times for boron movement (Eq. [10]) through Pictured Cliff Sandstone in the Four Corners Area of New Mexico. The average annual rainfall in the area is 20 cm/year. It was assumed that the average annual recharge is 10% of the average annual precipitation (16). The dispersion coefficient of (1.06 cm²/day) was assumed to be largely the result of diffusion and was therefore not expected to change appreciably with pore water velocity. The water content was taken as 12% by volume, which was somewhat higher than the water content of the cores obtained from the driller (10.2% by volume), but was below the water content of the column during the displacement experiment (16.69% by volume).

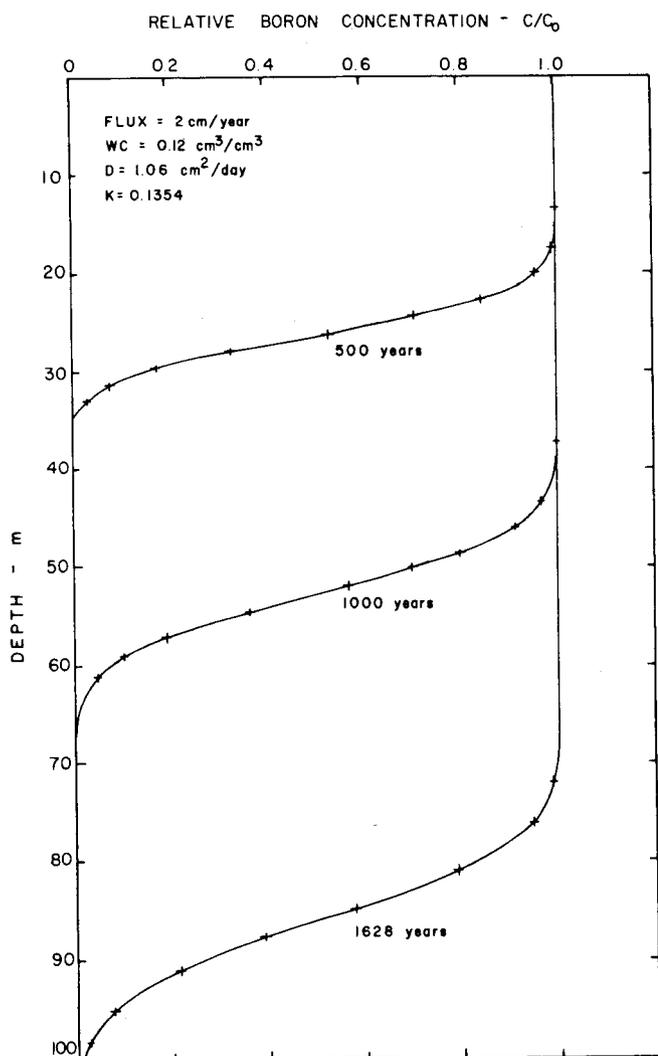RELATIVE BORON CONCENTRATION - C/C₀

Fig. 4—Relative boron concentrations in a sandstone profile as a function of time. The solid lines were calculated with Eq. [10]. The symbols were calculated using a numerical procedure.

The calculated relative boron concentrations as a function of depth below the soil surface at various times are given in Fig. 4. The data show that under the semiarid conditions of the Southwest it takes a very long time for adsorbed chemicals to travel downward to the ground-water table. For example, it takes 500 years for the boron front to reach a depth of 35 m. The ground-water table at the study site is at 86 m. Based upon this study it would take 1,628 years for boron at 86 m depth to reach one-half the concentration at the surface. If the percentage of the annual precipitation contributing to recharge increases, the transit times would decrease. Table 1 presents the time in years after which the boron concentration at 86 m would reach a concentration of one-half the concentration at the surface, for average annual recharges of 10, 25, and 100% of the average annual precipitation and water contents of 10.2, 12.0, and 16.7% by volume, respectively. These data emphasize the importance of the rate of downward water movement on the transit times for boron. A 10-fold increase in ground-water recharge reduces the transit times to one-tenth their original value.

The solid lines in Fig. 4 were calculated with Eq. [10]. The symbols were calculated with the numerical model of van Genuchten and Wierenga (24). Based upon their stability criteria, a layer thickness of 100 cm and an integration interval of 12.5 years was used in the calculations. The data from the analytical solution and the numerical solution agree very well. The numerical model may be used when the initial and boundary conditions are such that an analytical solution is not available.

In the calculations for the data in Table 1, it was assumed that the sandstone was physically and chemically homogeneous with depth, and similar to the sandstone used for the breakthrough study in the laboratory. This may not be true, and as such the data presented in Table 1 must be considered estimates of the transit times that may be expected under actual field conditions.

The data in Fig. 4 were calculated with Eq. [10] and a dispersion coefficient of 1.06 cm²/day, calculated from the boron breakthrough data presented in Fig. 2. The data in Fig. 2 show considerable tailing, which also may be expected to occur under actual field conditions. Equation [10] does not allow for tailing and therefore the calculated transit times for the relative boron concentration vs. depth (Fig. 4) to reach say 0.9 are underestimated. A more sophisticated approach, accounting for intraparticle diffusion of boron, is necessary to better predict the concentration of boron vs. depth in soil profiles.

Table 1—Calculated times (years) after which the boron concentration at the ground-water table (at 86 m) reaches a concentration of one-half the concentration at the surface

Ground water recharge	Water content	Time at which C/Co at 86 m is 0.5
cm/year	cm³/cm³	years
2	0.102	1,551
2	0.120	1,628
2	0.167	1,830
5	0.102	620
5	0.120	651
5	0.167	732
20	0.102	155
20	0.120	163
20	0.167	183

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