&EPA Project Summary

Transport of Macromolecules and Humate Colloids Through a Sand and a Clay Amended Sand Laboratory Column

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Laboratory experiments were conducted to determine if macromolecules or humate colloids would transport through sand columns and if they would exhibit any variations in their relative velocity based upon their molecular volumes and the pore size distribution of the column packing. Poly(ethylene oxide) standards ranging in molecular weights from 50,400 to 900,000 were investigated. Humate colloids were prepared from a humate muck as their calcium and sodium salts. Columns were packed with fine-grained Oil Creek sand (OCS) of uniform pore size ($\approx$ 20 μm in diameter) and the same sand amended with 4% each kaolinite and illite clays (amended OCS) resulting in a pore size distribution in which $\approx$ 10% of the pores had diameters less than 2 μm. The poly(ethylene oxides) and calcium and sodium humate colloids were transported virtually conservatively through the OCS, with no evidence of size exclusion phenomena. Calcium humate was retarded in the amended sand due to complexation with the clay fraction but moved through the column with 77% recovery of the humate mass. The mobilization of clays was observed as a temporary increase in column effluent turbidity and a significant shift in the particle size distribution of the effluent (150 to 450 nm).

The data presented here neither supports nor refutes the application of chromatographic principles to particle transport in soil columns. The relative velocities of macromolecules and colloids investigated were not described using a simplistic model discussed in this study. Subsequent studies may need to include diffusional non-equilibrium conditions and solid surface to particle interactions.

This Project Summary was developed by EPA's Robert S. Kerr Research Laboratory, Ada, OK, to announce key findings of the research program that is fully documented in a separate report of the same title (see Project Report ordering Information at back).

Introduction

Evaluating contaminant fate in any environment necessitates determining the compartments into which the contaminant will distribute. In saturated subsurface environments the partitioning of a contaminant between the mobile aqueous phase and the immobile aquifer solid matrix is often the controlling distribution. The association of a contaminant with immobile solids results in a reduction in the dissolved mobile concentration of the contaminant, sometimes by orders of magnitude. However, it has been suggested that mobile entities such as suspended organic and inorganic colloids and macromolecules may increase the "apparent" solubility of some contaminants. If this is the case, the predictions of contaminant transport based upon a two-phase system may seriously underestimate observed aqueous phase concentrations of contaminant in laboratory and field studies. The influence of these entities would need to be addressed by modeling systems as three

phases consisting of immobile sorbed, dissolved and mobile sorbed phases.

There is a good deal of research activity in the areas of colloid origination, chemistry, stability and mobility. Recently, colloidal entities such as macromolecules and viruses have been observed to be capable of eluting prior to conservative solutes in column and field studies. The intent of this study was to observe the transport of colloid-sized entities and examine the validity of two proposed mechanisms by which this phenomenon may occur in the subsurface.

For the most part, discussions of colloid and macromolecule transport have been confined to observations influenced by physical and chemical interactions that would retard their transport, relative to conservative species. As mentioned previously, there may be mechanisms by which macromolecules and colloids can elute prior to conservative species as has been observed in laboratory and field studies. Two mechanisms which have been proposed to account for this behavior are discussed. The first mechanism is that of particle exclusion from pores. Concepts from steric (size) exclusion chromatography have been examined with respect to applicability to classic dispersion/advection theory. A particle may be excluded from dead end pores and pores smaller than some critical diameter based upon the ratio of the particle diameter to pore diameter and flowrates (dynamic porosity). The exclusion from these pores is a function both of molecular volume and fluid velocity, that is, diffusional equilibrium into a pore is a function of the velocity of the fluid as it moves past the pore. This can result in an "effective" porosity for that particle (θ_ε) that may be both specific for the particle (i.e species) involved and less than the total porosity (θ_t). A solute diffusing through less than the total porosity would elute from a soil column prior to a smaller chemical specie like water.

The second mechanism by which the elution velocity of a particle may be a function of its size can be described by analogy to hydrodynamic velocity gradients in capillary flow. Hydrodynamic chromatography is an analytical technique used to separate particles based on their size and rate of transport through a bed packed with solid, non-porous particles. According to this theory, the rate of transport of conservative colloidal particles depends on the size of the colloid and the interparticle volume of the column packing. Larger particles move faster than the smaller ones, which in turn move faster than the molecules of the elution fluid. The rate of transport through a column bed is expressed by the quantity R_f, the average moving rate of a particle through the bed relative to the average flow rate of

the mobile phase $(\bar{v}_{p,w}/\bar{v}_w)$. R_f is analogous to the relative velocity of a contaminant in groundwater (i.e. velocity of the contaminant/velocity of the water). Hydrodynamic chromatography flow was first verified based on a model derived for rigid and flexible polymer molecules flowing in Poiseuille flow through a capillary tube. There exists across the flow channel a velocity gradient such that the velocity of the fluid is maximum at the center and diminishes toward the wall. The mean velocity of a particle is a function of the velocity gradient to which it is subjected, based upon the particle radius. A small molecule, such as water, can access the entire gradient; and hence, its average interstitial velocity is $1/2\, v_{max}$. A large particle will be subject to higher velocities than a relatively smaller particle. The velocity at a point r, v(r), from the center of the capillary in the radius of the tube is given by the equation:

$$v(r) = [(\Delta p r_o^2)/(4\eta\iota)]\,[1-(r/r_o)^2]$$

where

Δp = pressure drop across the capillary
r_o = radius of the cylinder
η = dynamic viscosity of the fluid
ι = total length of the cylinder

and the maximum velocity at r = 0 is

$$v_{max} = (\Delta p r_o^2)/(4\eta\iota) = 2\bar{v}_w$$

Since a particle of radius r_p will be subject only to the portion of the velocity gradient $\geq r_p$ from the wall, the average velocity of the particle $(\bar{v}_{p,w})$ can then be calculated as:

$$\bar{v}_{p,w} = \bar{v}_{max}[1 - 1/2(1-\alpha)^2]$$

where

α = radius of the particle/radius of the pore (r_p/r_o)

This then can be rewritten as:

$$\bar{v}_{p,w} = \bar{v}_w[1 + \alpha(2-\alpha)]$$

Based on the theories of size exclusion and hydrodynamic velocity in a system of conservative solutes, those particles not subject to physical straining should transport according to size and fluid velocities and the two mechanisms contributing to particle velocity would be operational. Assuming that the effective porosity is the total pore volume available to an excluded macromolecule and that corrections for the reduced fluid volume in which it travels is insignificant, then the elution

velocity of an excluded particle $(\bar{v}_{p,\varepsilon})$ can be approximated:

$$\bar{v}_{p,\varepsilon} = V_d/\theta_\varepsilon$$

where

$$V_d = \bar{v}_w * \theta_t$$

Since the average linear velocity of the excluded particle can be calculated by its hydrodynamic velocity as defined above $(\bar{v}_w = \bar{v}_{p,w})$ we now have:

$$\bar{v}_{p,\varepsilon}/\bar{v}_w = (\theta_t/\theta_\varepsilon)[1 + \alpha(2-\alpha)]$$

Using the guideline that straining will occur at a particle to pore diameter ratio (α) of 1 to 9 the limits placed on $\bar{v}_{p,\varepsilon}$ based on the hydrodynamic velocity will be:

$$\bar{v}_{p,\varepsilon}/\bar{v}_w = 1.20(\theta_t/\theta_\varepsilon) \text{ when } \alpha = 1/9 \text{ and}$$

$$\bar{v}_{p,\varepsilon}/\bar{v}_w = 1 \text{ as } \alpha \text{ approaches zero,}$$
$$\theta_\varepsilon \text{ approaches } \theta_t.$$

Procedure

Polymers and Colloids

Poly(ethylene oxide) polymers have the monomeric formula $(-CH_2CH_2O-)_n$. Standards were obtained as a kit containing eight high purity polymers ranging in average molecular weight from 14,200 to 900,000. Poly(ethylene oxides) were prepared in 0.01 M $CaCl_2$ and 0.1% by weight NaN_3. Sodium humate was prepared by weighing 100 grams of humate muck (25% solids by weight as determined by oven drying at 100°C for 24 hours) into 0.01 M $NaClO_4$ and bringing the solution up to a total volume of one liter. The initial pH was 3.92. The solution pH was then adjusted to match that of the background $NaClO_4$ solution, pH 5.76, using 1.0 M NaOH. After stirring overnight, the humate solution was allowed to settle for 24 hours. The supernatant was collected by vacuum suctioning, then centrifuged at 3,000 rpm for one hour and filtered in small aliquots through 0.45 μm Millipore filters. The calcium humate was prepared in the same manner, except the diluting solution was 0.01 M $CaSO_4$. The initial pH was 4.04 and was adjusted to 6.41.

Columns and Packing

The columns were specially fabricated of 316 stainless steel, 1 cm in length and 5.0 cm internal diameter. The columns were fitted with removable stainless steel porous endplates (0.078 cm thickness, 40 μm pore size) and Viton o-rings. Solutions were pumped into the columns by a proportioning

pump using tygon pump tubes. The columns were plumbed to the feed solutions and pump via teflon tubing. Flowrates were 9.6 ml/hour (0.474 cm/hr linear velocity) for all column experiments. The column packing material is a fine-grained sand referred to as Oil Creek Sand mined commercially in Oklahoma. It is comprised of 99.6% sand and 0.4% silt. The total organic carbon content of the sand is less than 0.01%. Where noted, the sand was amended with 4% each kaolinite and illite clay standard (8% total clay) obtained from the Clay Minerals Society for the purpose of adjusting the pore size distribution.

Analytical Methods

Humate concentrations were expressed as mg/L organic carbon determined using low temperature ultraviolet/potassium persulfate oxidation after acidification with concentrated phosphoric acid. The total organic carbon in column packings was determined by digestion in 10% perchloric acid with subsequent solids and filtrate analysis using low temperature ultraviolet/potassium persulfate oxidation. Fatty acid determinations (C_3 - C_7) were performed on column effluents as a qualitative indicator of presence or absence of microbial growth in poly(ethylene oxide) column experiments. The colloids prepared for column studies were examined for particle size distribution, stability of size distribution from one batch preparation to another and over time, and maintainence of distribution after transport through columns. Particle size distributions were determined on a Malvern Autosizer 2C. Tritium concentrations were analyzed on a liquid scintillation counter with automatic quench correction. Soil moisture characteristic curves were performed on both OCS and amended OCS using standard Tempe cells in which a drainage curve is established by pairing volumetric water content with matric pressure head (American Society for Testing and Materials, F316). From these curves, assuming spherical particles, pore size distributions were calculated using the equation:

$$2\pi r \gamma \cos\theta = r^2 \pi (h\rho g)$$

where

r = radius of the pore or capillary
γ = surface tension of water
θ = contact angle ($\cos\theta = 1$ for a wetted sample)
$h\rho g$ = hydrostatic pressure

Results and Discussion

The interparticle pore size frequency distribution for OCS is very uniform, with ≈74% of the pore radii between 13 to 8 μm and less than 1% ≤ 1.0 μm. When the sand was amended with 8% clay, ≈10% of the pores were less than 1.0 μm, which could be expected to provide a significant proportion of pore openings from which a large colloid would be excluded if size exclusion is functional.

The particle size distributions for the study polymers are given in Table 1. The poly(ethylene oxides) could only be estimated due to their non-spherical shapes. Nevertheless, the range of particle diameters (≈ 100 to 200 nm) can be used to estimate if there would be any significant effect of molecular volume on breakthrough velocity in either of the column packings used based on the theories described above. The calcium humate had a particle size distribution predominantly between 350 to 525 nm and a small contribution in the 200 to 250 nm range. The sodium humate had a significant particle population in the same size distribution as the calcium humate, but was bimodal with a significantly higher population in the range of 200 to 250 nm. The particle size distributions of both humates were stable over a period of five days. The reproducibility of the sodium humate from one batch preparation to the next was good, reaffirming that the bimodal distribution was not an artifact.

Experimental concentrations, recoveries and experimental R_f's for column breakthrough results for the study macromolecules are listed in Table 2 for reference.

Except for the 900,000 molecular weight fraction, all the poly(ethylene oxides) broke through the Oil Creek Sand after the tritiated water (R_f < 1.0). Recoveries of the 50.7K, 83.8K and 770K polymers were relatively high (84-98%) although some tailing was observed. The 900,000 molecular weight poly(ethylene oxide) eluted prior to tritium (R_f = 1.116). It is difficult to determine if this is real or an artifact, perhaps a reflection of inaccurate analysis as evidenced by the high recovery (109%). No polymer was detected in the effluent when transport studies of two of the polymers through an amended Oil Creek sand column was conducted. Batch sorption tests showed that due to sorption excessive quantities of the expensive polymers would need to be purchased to conduct further studies. For this reason the column elution studies were not pursued.

Both the sodium and calcium humates transported conservatively (≈100% recovery) through the OCS (Figure 1). The particle size distribution for the sodium humate effluent was virtually identical to that in the influent, however, a percentage of the particles in the calcium humate effluent shifted to significantly smaller particle diameters (Figure 2). This was probably due to calcium ion loss from the humate complex by the low cation exchange capacity of the sand causing disaggregation of the humate particles. The calcium humate was retarded in the amended OCS (Figure 3) in an apparently irreversible fashion. Approximately 77% of the humate mass was recovered. The effluent temporarily became turbid and the particle size distribution (Figure 3) showed a marked change from a primary particle size of 150 nm to ≈ 450 nm indicating that the elution species was probably a clay/humate complex. There was considerable scatter in the tritium data for this breakthrough curve which was probably due to interference by the clay particles. When calcium humate was pulsed a second time it was observed that the humate broke through with less retardation, possibly due to saturation of some fraction of the immobile clay sites (Figure 3).

Conclusions

The observation of column transport of the colloids and macromolecules present additional evidence for colloidal mobility. The ability to predict the rate at which these particles transport in media other than non-interactive is highly complex and may ultimately be of minor significance except under very specific circumstances.

The calcium humate colloid was retarded due to irreversible clay-humate interactions. Subsequent flow of calcium humate through the column showed significantly less retardation of the humate. Based on the theories of relative velocity presented here, it would be expected to see early breakthrough of the calcium humate colloid. However, this could not have been investigated without driving the system to saturation complicating the interpretation of results.

The behavior of the tritiated water was erratic as evidenced by data-scatter, breakthrough curve asymmetry and excessive tailing. This may have been due to the equilibrium of water molecules from the bulk phase to the hydrated colloid. If this is the case, then tritiated water may not be an appropriate conservative tracer for the transport studies.

Table 1. Particle Size Frequency Distribution for Study Macromolecules

Macromolecule	Conc. (ppm)	Primary Particle Size Frequency Distribution (nm)
Poly(ethylene oxides)		
50,700 MW [1]	1261	ND [2]
83,800 MW	1119	190
770,000 MW	1044	140
900,000 MW	961	201
Humates		
NaClO$_4$ / humate	327	200-250, 350-525
CaSO$_4$ / humate	285	350-525

[1] molecular weight
[2] Not determined

Table 2. Concentrations, Recoveries and Relative Velocities of Study Macromolecules

Macromolecule	Conc (ppm)	Column Packing	% Recovery	Observed Relative Velocity (R_f)[1]
Poly(ethylene oxides)				
50,700 MW [2]	1261	OCS	95	0.86
83,800 MW	119	OCS	98	0.98
770,000 MW	1044	OCS	84	0.96
900,000 MW	961	OCS	109	1.12
Calcium humate				
	285	OCS	107	1.01
	320	AOCS	100	–
Sodium humate	325	OCS	96	0.98

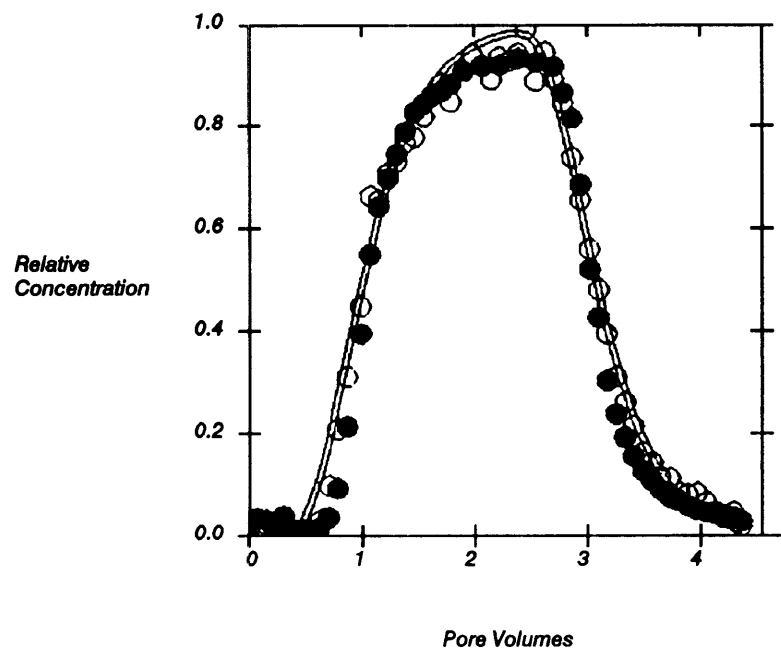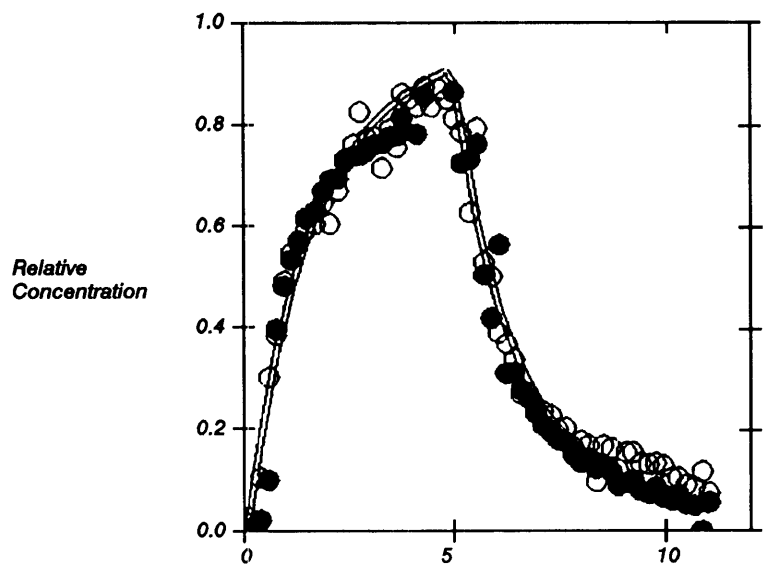[1] $R_f = (\bar{v}_p / \bar{v}_w)$
[2] molecular weight

Figure 1. Sodium humate (upper figure, closed circles) and calcium humate (lower figure, closed circles) transport through Oil Creek sand. Tritiated water data (open circles) fitted using a non-linear least squares procedure (double line). Porosity 0.32; Darcy velocity 0.47 cm/hr; dispersivity 0.09 cm for calcium humate and 1.2 cm for sodium humate.
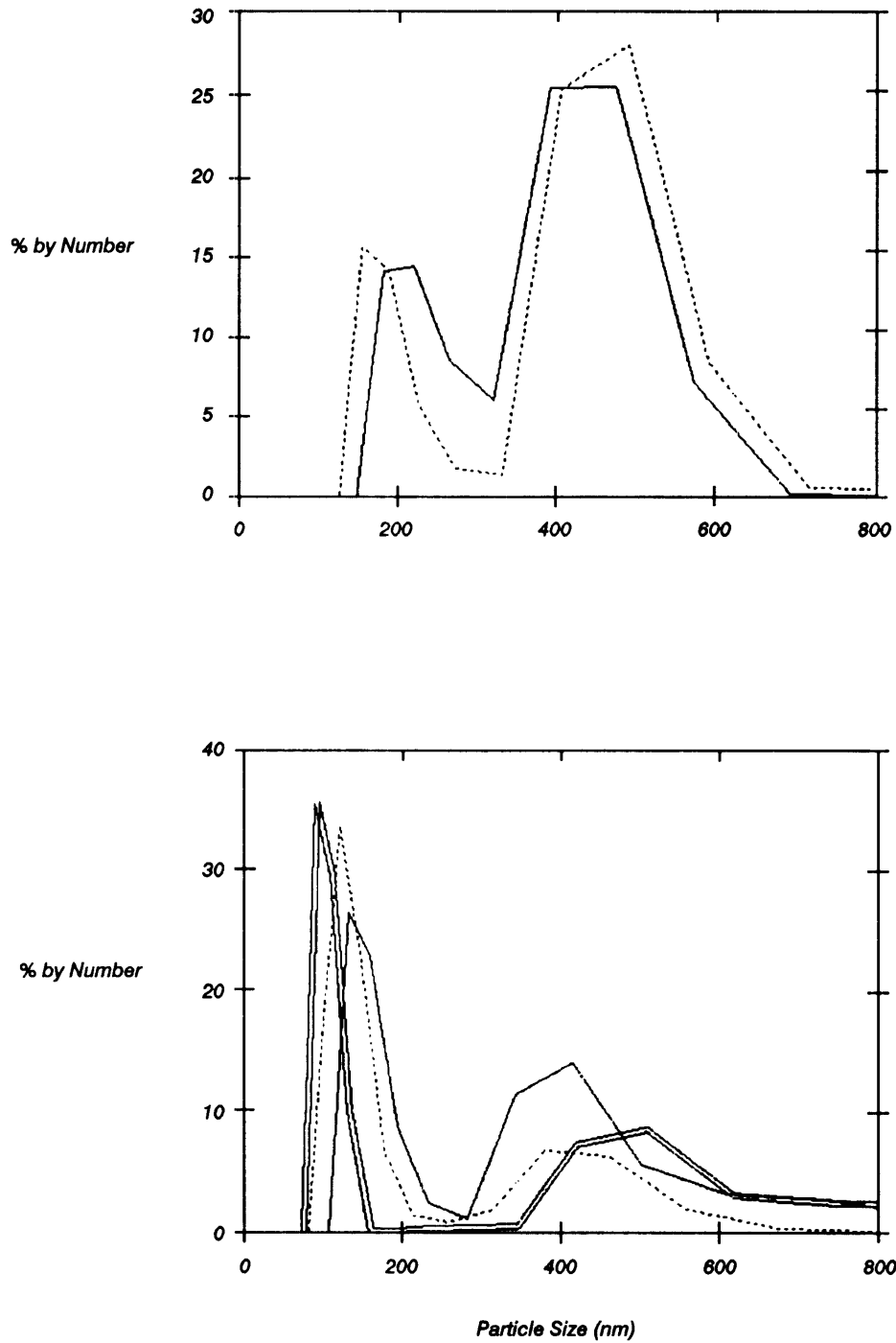
Figure 2. *Particle size distributions of humates transported through Oil Creek sand. Sodium humate (upper figure); influent, solid line and effluent, dashed line. Calcium humates (lower figure); influent, single line and effluents, double line (1.0 pore volume) and dotted line (1.9 pore volume).*
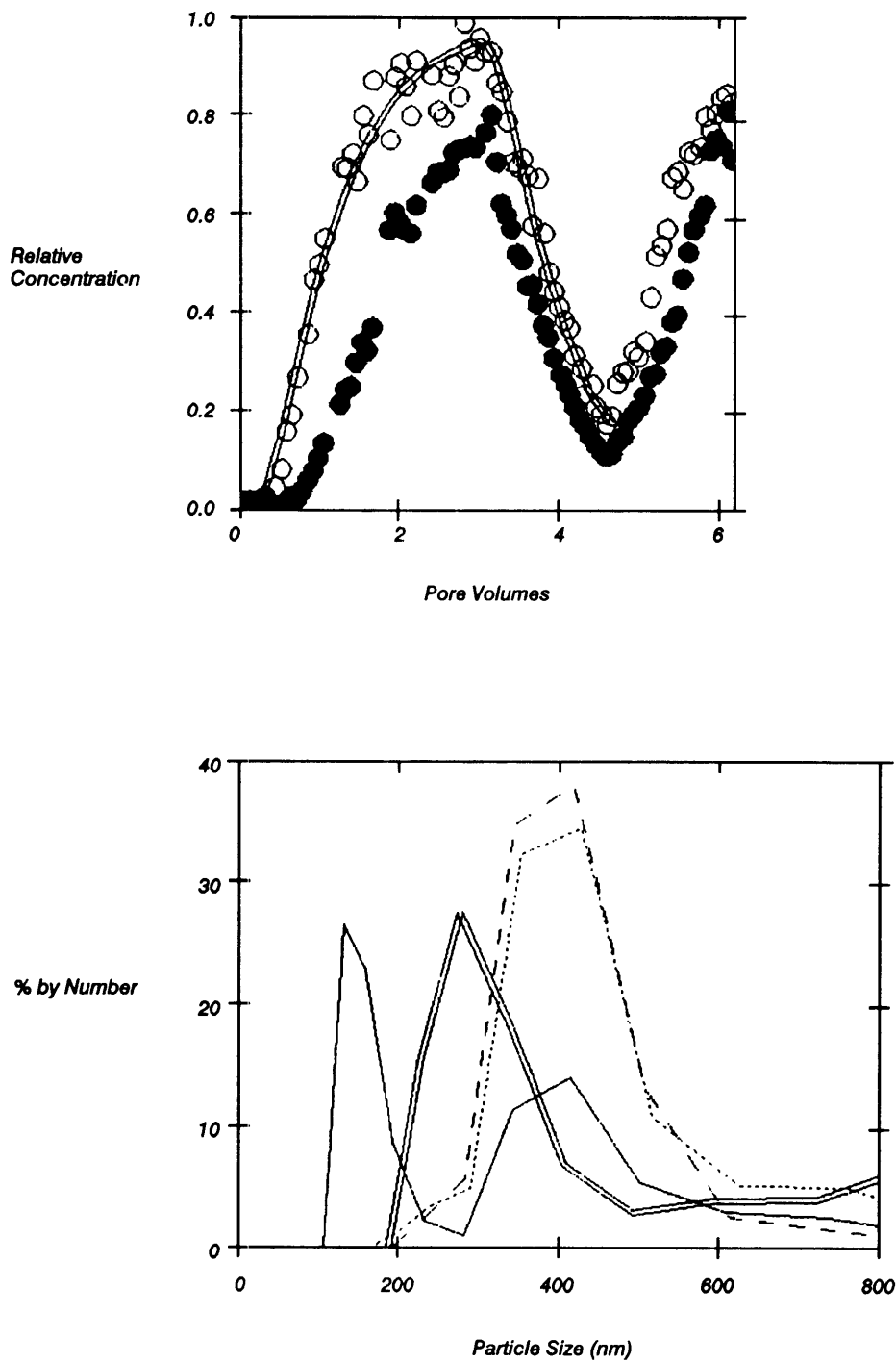
Figure 3. Upper figure: Calcium humate transport (closed circles) through amended Oil Creek sand. Tritiated water data (open circles) fitted using a non-linear sqares procedure (double line). Porosity 0.32; dispersivity 0.26 cm; Darcy velocity 0.47 cm/hr.

Lower figure: Corresponding particle size distribution. Influent, solid line. Effluents, 1.13, 1.73 and 2.27 pore volumes, double, dotted and dashed lines, respectively.

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Candida Cook West *is the EPA author and Project Officer (see below).*

The complete report, entitled "Transport of Macromolecules and Humate Colloids Through a Sand and a Clay Amended Sand Laboratory Column," (Order No. PB 90-219 205/AS; Cost: $17.00, subject to change) will be available only from:

> *National Technical Information Service*
> *5285 Port Royal Road*
> *Springfield, VA 22161*
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