

Sorption of Colloids, Organics, and Metals onto Gas - Water, Interfaces: Transport Processes and Potential Remediation Technology

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1.0 PROJECT OBJECTIVES

This research project has two objectives. The first is to improve basic understanding of contaminant interactions with gas - water interfaces, with emphasis on behavior of mixed contaminant systems. The second objective is to develop a sorptive microbubble fractionation remediation technique. Hypotheses supporting these objectives are: 1) contaminants and natural organics can sorb on and alter the interface hydrophobicity of the gas-water interfaces, and therefore influence sorption of colloids, metals, and radionuclides at gas-water interfaces; 2) surfactants can vastly increase sorption of colloids, metals and radionuclides selectively onto gas-water interfaces; 3) a sorptive microbubble fractionation remediation technique can be developed based on understanding of the previously mentioned processes. These hypotheses are being tested through quantification and visualization at both micro- and macro-scales.

2.0 OUTLINE OF PROGRESS TO DATE

2.1 Improve Understanding of Contaminant Sorption at Gas - Water Interfaces (Objective#1).

- Developed a sorptive bubble column method for quantifying surface excesses of contaminants under dynamic conditions
- ⁰ Related surface excesses measured with this new method to those measured using classic surface tension measurements
- Quantified humic acid sorption at air - water interfaces under dynamic conditions
- Obtained the first quantitative measurements of clay colloid sorption at air-water interfaces
- In progress: Quantification of metal - humic and metal - clay complexes on air - water interfaces

2.2 Develop a New Remediation Technique Based on Contaminant Sorption at Gas - Water Interfaces (Objective #2)

- Developed techniques for generating stable microbubbles (micrometer-scale):
 - spinning disk
 - ultrasonic probe

- Identified several surfactant combinations that provide microbubbles with different surface charge characteristics:
 - Span60Tween80
 - Span60/SDS
 - Span60/CTAB
- Optimized stability of microbubble suspensions typical microbubble suspension characteristics:
 - size: 1 - 2 μm
 - concentration: 10^7 - 10^8 per mL
 - interfacial area: ~ 3 - 13 cm^2 per mL
 - lifetime: in progress, one system now stable for at least 14 days
- Completed initial tests of microbubble transport in sand columns:
 - Slight microbubble retardation occurs during advective transport
 - Strong microbubble retardation/filtration occurs in hydrostatic columns
- Upcoming research activities:
 - Identifying microbubble surfactants that efficiently sorb metals and other contaminants
 - Microbubble sorptive extraction of contaminants in laboratory columns

3.0 POTENTIAL APPLICATIONS

In principle, sorptive bubble and microbubble separation techniques can be employed for removing any contaminants that partition favorably at gas - liquid interfaces, in environments that do not severely constrain bubble or microbubble movement. One main area of focus in our upcoming experiments is that of identifying surfactants that are highly selective for specific contaminants. In subsurface environments, the *in-situ* microbubble technique is expected to permit access to contaminated zones that are not pore size-restrictive. Thus, aquifer strata comprised of sands or gravel will be accessible. The lower grain-size limit is expected to be encountered in the fine sand to silt class. We also noted in our proposal that the sorptive, mobile gas - liquid interface might be useful in separations in waste tanks. In such an application, either microbubbles or bubbles could be used, since pore-size limitations do not exist. Factors that will determine applicability of this remediation approach include the level of contaminant-surfactant selectivity, microbubble (or bubble) stability and mobility, cost of surfactants, and development of microbubble (or bubble) collection-treatment methods.

4 . 0 DETAILED PROGRESS AND RESULTS

4.1 Sorptive Bubble Column Method for Quantifying Surface Excesses

Since groundwater systems are dynamic, heterogeneous, open environments, their gas - water interfaces can be in disequilibrium with respect to sorption of hydrophobic and surface active compounds. Thus, the traditional method of quantifying surface excesses by measuring changes in surface tension may only provide equilibrium-limit information. Furthermore, surface tension measurements are not sensitive to certain components that can be complexed with hydrophobic, surface-active species at the air - water interface. The nonfoaming bubble fractionation method provides an alternative approach to determining surface excesses. It was originally developed for industrial applications by Lemlich (1966, 1967) and Shah and Lemlich (1970) for separating surface-active agents from dilute solutions. The method is based on the preferential adsorption of the surface-active compounds onto the interface of rising gas bubbles. Gas is bubbled through a vertical column containing the dilute aqueous solution of the surface-active agent. The rising

bubbles adsorb and carry the surface-active agent to the top of the column, and release the sorbed component back to the solution when the bubbles burst. A concentration profile is established along the column length that, at steady-state, reflects the balance between upwards transport by sorption onto rising bubbles and downward transport by eddy dispersion. In this study, we further develop the bubble fraction column method in several ways. We first experimentally determined bubble column eddy dispersion coefficients, rather than assuming certain functional relations to column parameters. We then quantitatively compared surfactant partitioning in bubble columns with surface tension measurements. Finally, our main contribution is in applying the bubble fraction column method to the problem of quantifying partitioning of components at water - air interfaces, such as colloids and metals, which cannot be quantified by the surface tension method.

Before the bubble column method can be used reliably in quantifying surface excesses, an independent determination of the column dispersion coefficient is needed. It should be pointed out that no previous accounts of this method have included actual measurements of column dispersivities. Instead, previous researchers assumed certain functional relations and calculated dispersivities. The “measured” surface excesses in the bubble column method are very sensitive to errors introduced through assumed dispersivities. In our work, the eddy dispersivity was independently determined through electrical conductivity measurements of transient dispersion of NaCl pulses in bubble columns. Measured conductance time series were fit to the appropriate analytical solution of the diffusion equation, with the dispersivity as the fitting parameter. Our results show that previous researchers assumed dispersivities that were far too small.

It is important to understand whether or not steady-state concentration profiles in bubble columns reflect true equilibrium with respect to surface excesses on bubbles. For this purpose, we compared adsorption isotherms of surfactants Triton X-100, and sodium dodecyl benzene sulfonate at very dilute concentrations using both surface tension and bubble column methods. We found that surfactant partitioning at bubble interfaces in the dynamic column method amounted to only about 20% relative to equilibrium conditions (surface tension measurements). An article describing the bubble fraction column technique and applications is in preparation.

Our first environmental application of the bubble fractionation column involved measurements of humic acid partitioning at gas - water interfaces. Although several previous studies have investigated accumulation of humic substances at air - water interfaces via surface tension measurements, most of these previous experiments were conducted at concentrations that are much higher than those typically found in soil pore waters and groundwaters. Our recent bubble fraction column results quantify humic substance partitioning at moving air - water interfaces over a range of concentrations typical to subsurface environments. Figure 1 is an example of typical relative concentration profile along a column. In this example, the solution initial concentration is 10 mg/L of humic acid (IHSS Soil Standard Humic Acid), pH 5.7, and ionic strength 5.0 mM. The points are measured steady-state concentrations along the column from five repeated runs, and the curve is the model-predicted concentration profile. The model does not account for the very high humic acid concentration within the thin film at the top of the column. The large variation of data from the surface layer in repeated runs is probably due to different extents of mixing with the underlying bulk solution during sampling. The only fitting parameter is K, the steady-state adsorption isotherm constant. The K value is 8.5E-6 m in this case.

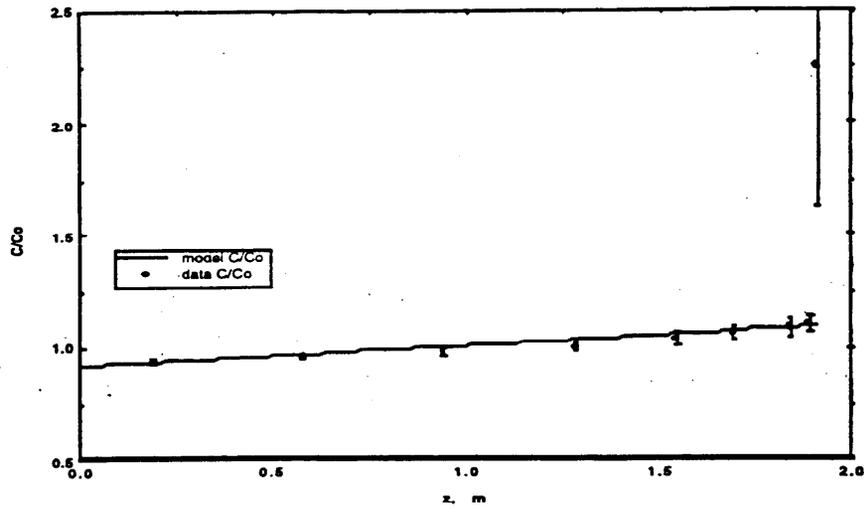


Figure 1. Steady-state relative concentration profile of humic acid in the bubble fraction column.

The bubble fraction column method has very recently been used to obtain the first quantitative measurements of clay mineral sorption at gas - water interfaces. This previously unrecognized phenomenon was first observed by Wan and Wilson (1994), and has considerable relevance in colloid-facilitated contaminant transport. The steady-state concentration profile of kaolinite clay in the bubble fraction column clearly reveals favorable partitioning at gas - water interfaces (Figure 2). It is important to note that such partitioning is probably impossible to determine through surface tension measurements. Upcoming experiments will determine the extent to which metals and organic contaminants partition at gas - water interfaces through complexation with humic substances and clays.

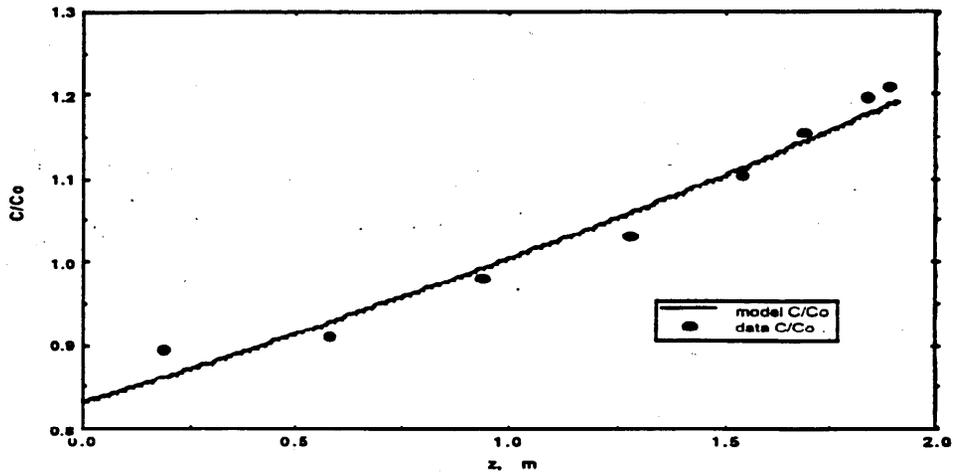


Figure 2. Steady-state concentration profile of kaolinite clay particles in the bubble fraction column.

4.2 Formation and Properties of Surfactant-stabilized Microbubbles

Success of the proposed remediation approach is based on the formation and stability of gas microbubbles. The lifespan of air microbubbles in pure water is relatively short. However, if the microbubbles are coated with surface-active agents (surfactants), the surfactant molecules will reduce gas diffusion from the bubbles toward the liquid phase and will also reduce coalescence among bubbles.

Surfactant-coated microbubbles were generated using a sonicator or a spinning disk. The microbubbles produced with the sonicator are fairly monodispersed with a diameter smaller than 1-2 μm (measured using a Coulter Multisizer II). The typical bubble concentration ranged from 5×10^7 to $9 \times 10^7 \text{ mL}^{-1}$. Larger volumes (1500 mL vs. 60 mL with the sonicator) and greater concentrations of bubbles (up to $2.3 \times 10^8 \text{ mL}^{-1}$) were prepared using the spinning disk. With this technique, however, two sizes are generated: microbubbles smaller than 3 μm and microbubbles ranging from 3 to 15 μm (Figure 3). The finer bubbles account for approximately 70 - 80% of the total bubble population.

The surfactants used to stabilize the microbubbles included nonionic surfactants (Tween 80, Triton X100, Span 60, and Span 40), anionic surfactants (sodium dodecyl sulfate or SDS, and sodium dodecyl benzene sulfonate), and a cationic surfactant (cetyltrimethyl ammonium bromide or CTAB). A single surfactant alone did not stabilize the gas microbubbles. In fact, as previously reported by Wheatley and Singhal (1995), one of the Span surfactants had to be present to stabilize the bubbles. Mixtures typically studied are SDS/Span 60, Tween 80/Span 60, SDS/Tween 80/Span 60, and CTAB/Span 60.

Stability of the bubbles is currently being determined as a function of surfactant type and concentration. Preliminary results have indicated that after an initial drop in microbubble concentration, bubbles remain stable for several weeks in the surfactant solution. Dilution experiments have shown that the bubbles are stable for up to 6 days. Experiments are underway to study the effects of ionic strength and hardness on the stability and size of the microbubbles. Additional experiments have also begun to determine the bubble surface charge using a Coulter DELSA 400SX.

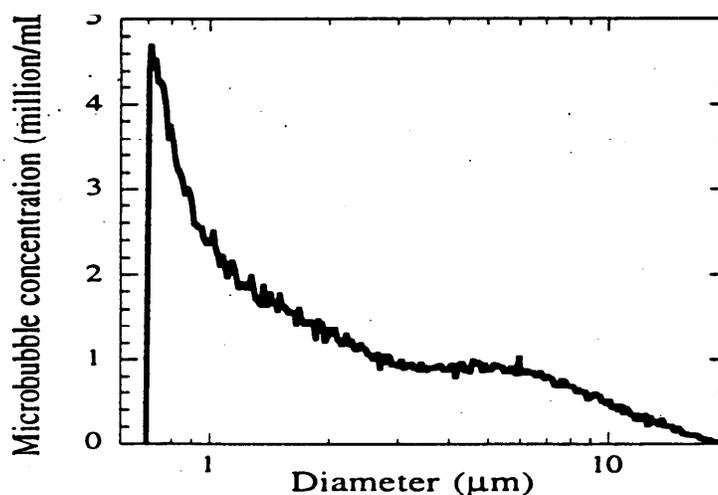


Figure 3. Concentration and size distribution of microbubbles-obtained using the spinning disk. Surfactants: SDS and Spa 60.

4.3 Microbubble Transport in Porous Media

The mobility and stability of microbubbles in saturated subsurface environments needs to be understood as part of the feasibility evaluation of the proposed remediation technique. In particular, the microbubble-based remediation approach requires the capability of efficient microbubble transport without significant decay. Transport is diminished by microbubble sorption onto mineral surfaces, while decay results from microbubble gas dissolution as well as coalescence into larger bubbles. Growth of larger bubbles at the expense of microbubbles is unfavorable because this results in a practically immobile distribution of gas bubbles (strained within finer pores) and lower available interfacial area for contaminant sorption. In this section, we show how the main features of microbubble transport in groundwater can be characterized in the context of filtration theory. We then provide brief descriptions of our initial, laboratory column studies on microbubble transport and upcoming experiments..

Studies of colloid transport in groundwaters borrow heavily from filtration theory (Tien and Payatakes, 1979). Since microbubbles are surfactant-encapsulated gas bubbles in the colloid size range ($\sim 10^{-8}$ to 10^{-6} m), we hypothesize that their transport in groundwater can be approximated by the colloid advection-dispersion equation, suitably modified to account for microbubble properties. Analyses of long-term transport requires consideration of microbubble dissolution as well as coalescence, sorption onto mineral surfaces, and buoyant rise. These last two factors dominate short-term transport of stable microbubbles, and relate to microbubble surface charge, size, mass density and interfacial mobility. Microbubble surface charge characteristics are expected to be surfactant- and solution-dependent, and will be quantified in upcoming studies. The buoyant rise of microbubbles is described by Stokes law. Modification of Stokes law to accommodate interfacial mobility and microbubble gas phase circulation is expected to be minor because of surfactant-encapsulation (Landau and Lifshitz, 1987). Buoyancy results in two main effects, microbubble rise relative to water, and (given attractive interactions) microbubble sorption on mineral grains. Note that buoyancy-initiated microbubble sorption at mineral surfaces is directly analogous to sedimentation-initiated colloid filtration, a process that has been extensively characterized in filtration theory. When collector-particle (sand-colloid) interactions are attractive, collection (sorption) efficiency depends strongly on the gravitational group, the ratio of sedimentation velocity to average pore fluid velocity. The fact that microbubbles in the 0.5 to 1 μm size range have buoyant rise velocities (in water) in the range of 10 to 50 mm d^{-1} , much slower than typical groundwater velocities, indicates that microbubble immobilization on aquifer grain surfaces may be minor. This is favorable for purposes of dispersing microbubbles over large volumes of contaminated groundwaters. However, it should be noted that groundwater flows are typically nearly horizontal, transverse to the vertically directed rise of microbubbles. All filtration studies of sedimentation effects have been conducted with vertical flow of suspensions. Our initial microbubble transport experiments are also conducted with vertical flow, in order to borrow from and build upon the wealth of existing research. At the end of this section, we briefly describe plans for near-future microbubble transport experiments in horizontal flow fields more typical of groundwater systems.

Our initial microbubble transport experiments were conducted in short, vertical, sand columns, under hydrostatic and steady-state flow conditions. Well-washed Unimin sand (425-500 μm) was packed into 24 mm ID glass columns. The columns' lengths differed for the hydrostatic and flow experiments, and are specified later. The bulk density, porosity, and hydraulic conductivity of these packings were 1.70 Mg/m^3 , 0.36, and $7.1 \times 10^{-4} \text{ m/s}^{-1}$, respectively.

Two hydrostatic microbubble transport experiments were performed, both in a 50-mm-tall sand column. In the first experiment, a Span60/Tween80 microbubble suspension was prepared. It had

a microbubble concentration of about 10^8 mL^{-1} in the $1 \pm 0.5 \mu\text{m}$ size range. In the second experiment, a Span60/SDS microbubble suspension was used. Experiments were initiated by injecting a microbubble suspension into a 19 mm deep reservoir at the bottom end of a water-saturated sand column. The upper end of the column was connected to a hydrostatic pool of water that was periodically sampled for microbubble breakthrough. No microbubble breakthrough was observed in either experiment, even after a period of 4 times the free rise travel time. These results indicate that sorption onto sand surfaces strongly retards microbubble transport under hydrostatic conditions.

Two microbubble transport experiments have been completed in 200 mm tall sand columns. In addition to the previously mentioned column properties, a dispersivity of 1 mm was determined in a separate NaCl breakthrough curve measurement. Span60/SDS microbubble suspensions were used for the transport tests, with concentrations in the range of 10^8 mL^{-1} , primarily in the 0.6 - 1.0 μm size range. For each experiment, one pore volume of this microbubble suspension was injected into the bottom of the water-saturated sand column, followed by further infusion with water. Flow was controlled by a syringe pump, with effluent diverted into a fraction collector. The microbubble suspension in the syringe was periodically agitated via a small enclosed magnetic stir-bar in order to maintain nearly constant inflow suspension concentrations. The two experiments were conducted at average pore water velocities of 6.0 and 0.6 m d^{-1} , corresponding to gravitational group numbers of 8×10^{-3} and 8×10^{-2} , respectively. Microbubble breakthrough curves were fit by an analytical solution to advective-dispersive transport with reversible sorption (van Genuchten and Alves, 1982). Breakthrough curve results (Figure 4) show essentially conservative microbubble transport with some sorption-induced retardation. These results are encouraging since they indicate that microbubbles can be effectively transported under both slow and typical groundwater velocities.

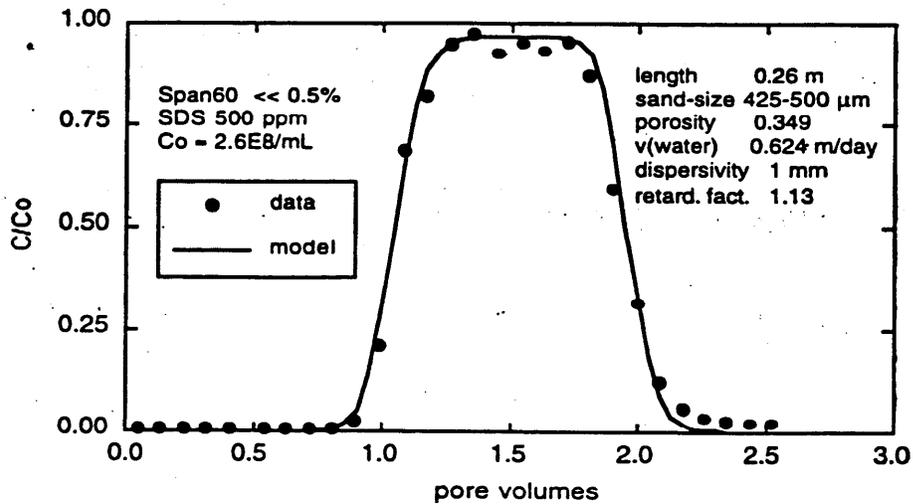


Figure 4. Breakthrough curve for Span60/SDS microbubbles transported through a sand column at low flow rate (pore water velocity = 0.624 m/day).

Upcoming studies on microbubble transport will focus on three areas. First, experiments in finer sands will be tested to determine grain-size limitations for microbubble transport. Second, microbubble transport experiments in 2-D sand packs under horizontal flow will be performed to determine the influence of flow transverse to the direction of buoyant rise. As noted previously, this is important since groundwater movement is typically nearly horizontal. Thirdly, microscopic

this is important since groundwater movement is typically nearly horizontal. Thirdly, microscopic visualization of microbubble transport will be conducted in vertically oriented glass micromodels (Wan et al., 1995), under both horizontal and vertical flows. These visualization studies will help in developing a mechanistic understanding of microbubble transport in porous media

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5.0 REFERENCES

- Landau, L.D., and E.M. Lifshitz, 1987. Fluid Mechanics, 2nd. Ed. Oxford Pergamon Press.
- Lemlich, R., 1966. A theoretical approach to nonfoaming adsorptive bubble fractionation. A.I.Ch.E.J., 12, 802-804.
- Shah, G. N., and R. Lemlich, 1970. Separation of dyes in nonfoaming adsorptive bubble columns. Ind. Eng. Chem. Fundam., 9, 350-355.
- Tien C., and A.C. Payatakes, 1979. Advances in deep bed filtration, A.I.Ch.E. J., 25,737-759.
- van Genuchten, M.Th., and W.J. Alves, 1982, Analytical solutions of the one-dimensional convective-dispersive solute transport equation. U.S. Dept. Agric., Tech. Bull. No. 1661, 151 p.
- Wan, J. and J.L. Wilson, 1994. Visualization of the role of the gas - water interface on the fate and transport of colloids in porous media, Water Resour. Res., 30, 11-23.
- Wan, J., T.K. Tokunaga, C.F. Tsang, and G.S. Bodvarsson, 1996. Improved glass micromodel methods for studies of flow and transport in fractured porous media, Water Resour. Res., 32,1955-1964.
- Wheatley, M.A., and S. Singhal, 1995. Structural studies on stabilized microbubbles: Development of a novel contrast agent for diagnostic ultrasound, reactive polymers, Reactive Polymers, 25,157-166.