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Project Title: **In Situ, Field Scale Evaluation of Surfactant Enhanced DNAPL Recovery Using a Single-Well, Push-Pull Test**

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In Situ, Field Scale Evaluation of Surfactant Enhanced DNAPL Recovery Using a Single-Well, Push-Pull Test

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RESEARCH OBJECTIVE: The overall goal of this project is to further develop the single-well, "push-pull" test method as a site characterization and feasibility assessment tool for studying the fundamental fate and transport behavior of injected surfactants and their ability to solubilize and mobilize DNAPLs in the subsurface. To address the three objectives, the research plan combines controlled intermediate-scale laboratory experiments in unique physical aquifer models with a parallel series of pilot-scale field experiments in existing monitoring wells at selected trichloroethylene (TCE) contaminated field sites.

RESEARCH PROGRESS AND IMPLICATIONS: Sorption to aquifer sediments can limit the effectiveness of surfactants injected to solubilize residual nonaqueous phase liquid contaminants in the subsurface. A study was conducted to evaluate the ability of the single-well, push-pull test to characterize sorption of linear alkylbenzene sulfonate (LAS) and hexadecyl diphenyl oxide disulfonate (DOWFAX) surfactants to natural aquifer sediment *in situ*. The results demonstrated

the ability of the push-pull test to characterize sorption of linear alkylbenzene sulfonate (LAS) and hexadecyl diphenyl oxide disulfonate (DOWFAX) surfactants to natural aquifer sediment under laboratory and *in situ* field conditions. Increased retardation and chromatographic separation of LAS homologs relative to Br^- observed during laboratory push-pull tests could not be accurately described by numerical transport simulations based on fitted sorption isotherms obtained from batch sorption experiments. Better agreement was obtained between simulated and observed breakthrough curves for DOWFAX; however, simulations predicted slight retardation for DOWFAX that was not observed in either laboratory or field push-pull tests. We attribute these differences to the inability of batch sorption isotherms to accurately represent *in situ* conditions. In particular, simulations based on batch sorption isotherms produced for a commercial surfactant mixture can not accurately describe surfactant transport when the composition of the surfactant mixture changes (e.g. due to chromatographic separation) during transport. Moreover, equilibrium sorption isotherms produced in batch experiments cannot describe the kinetically-limited sorption of a surfactant that potentially occurs during transport in the highly nonuniform pore water velocity field around an injection well.

However, generally close agreement was observed for extraction phase breakthrough curves for LAS and DOWFAX in laboratory and field push-pull tests. Retardation and chromatographic separation of LAS homologs observed in breakthrough curves and mass recovery plots from laboratory push-pull tests were clearly visible in breakthrough curves and mass recovery plots for field push-pull tests conducted *in situ*. Based on the results of this study, the single-well, push-pull test appears to be a useful method for obtaining site-specific information on the sorption behavior of injected surfactants (or other solutes). The method can be applied in existing monitoring wells without the need for sediment cores and appears

to provide results that are more representative of *in situ* conditions than laboratory batch sorption experiments. It should also be noted that the laboratory and field push-pull tests confirmed that information on sorption characteristics of an injected solute can be obtained from only the extraction phase breakthrough curves, without the need for observations at additional monitoring wells. The method should be particularly useful for selecting and evaluating surfactants as part of a feasibility assessment. In addition, the method can be used to perform small-scale pilot tests because the test conditions closely approximate those occurring in the vicinity of injection wells that will be used in full-scale surfactant-enhanced NAPL recovery systems. The method also provides a simple and rapid method for characterizing the *in situ* transport behavior of any solute without the need for sediment cores.

A second study was conducted to evaluate the ability of the push-pull test to characterize enhanced solubilization of trichloroethene (TCE) by a hexadecyl diphenyl oxide disulfonate (DOWFAX) surfactant. The results of intermediate-scale laboratory experiments indicate that the single-well, push-pull test method can provide quantitative information on the effectiveness of injected surfactants in enhancing liquid TCE solubilization in natural aquifer sediments. Push-pull test extraction phase breakthrough curves can be used (1) to examine surfactant transport behavior relative to that of a coinjected tracer; (2) to determine the recovery efficiency of an injected surfactant, and (3) to quantify the increase in aqueous TCE solubility due to injected surfactant.

Batch solubilization experiments indicated a linear relationship between TCE solubility and DOWFAX concentration characterized by weight- and molar-solubilization ratios of 0.26 and 1.25, respectively. Laboratory push-pull tests were performed in wedge-shaped physical aquifer models to simulate the alternating radially

divergent/convergent flow field in the vicinity of an injection/extraction well. Experiments were conducted in a TCE-free sediment pack and in a sediment pack initially containing liquid TCE with an initial saturation of ~ 5 % of the total pore volume. In an experiment conducted in the absence of DOWFAX, maximum TCE concentrations during the extraction phase were ~ 0.6 g/L. In contrast, in an experiment conducted with 13.5 g/L active DOWFAX, TCE concentrations during the extraction phase increased to ~ 3.2 g/L and TCE mass recovery increased by a factor of ~ 3. Two additional experiments conducted with DOWFAX in the same sediment pack yielded smaller maximum TCE concentrations and mass recoveries. The increased density of injected DOWFAX solutions due to TCE solubilization resulted in significant sinking of injected solutions and an accumulation of DOWFAX and TCE at greater depths in the sediment pack; however, no mobilization or sinking of liquid TCE was observed.

A third study was conducted to evaluate the influence of cation exchange on the solubilization of residual trichloroethene (TCE) by the surfactant sodium dihexyl sulfosuccinate (Aerosol MA 80-I). Laboratory transport experiments were conducted using natural aquifer sediment collected or obtained from a TCE-contaminated field site and a test solution consisting of 36,800 mg/L sulfosuccinate surfactant, 100,000 mg/L isopropanol, and 3,200 mg/L KBr. Laboratory experiments were designed to simulate conditions occurring during field push-pull tests. In batch experiments conducted in the presence of excess TCE, the test solution gave a Winsor Type I system with an enhanced aqueous TCE solubility of 26,700 mg/L and a solution density of 1.0000 g/cm^3. The sulfosuccinate surfactant was transported conservatively in sediment packs containing no

TCE; however, increased concentrations of Ca^{2+} and Mg^{2+} were observed, which resulted from cation exchange. Sulfosuccinate surfactant transport was strongly retarded in sediment packs containing 5 vol % residual TCE because cation exchange in the presence of liquid TCE resulted in the formation of a Winsor Type II system and resulted in the partitioning of the sulfosuccinate surfactant into the stationary TCE phase. Conservative sulfosuccinate transport was observed in a separate sediment pack containing 5 vol % residual TCE when a 130 mM NaCl pre-flush was used to reduce quantities of Ca^{2+} and Mg^{2+} in the sediment pack prior to sulfosuccinate injection. The results of this study emphasize the potentially detrimental effects of cation exchange on surfactant performance and enhanced TCE solubilization and demonstrate the utility of the push-pull test for predicting the effects of cation exchange on surfactant phase behavior in the presence of residual TCE.

In the final study of this project, we examined the ability of a modified push-pull test method for predicting cation exchange and the effects it will have on surfactant performance *without* the addition of surfactants to the subsurface. Our approach consists of injecting a simple salt solution to displace cations from the sediment, which simulates what would occur if a surfactant and its attendant salt were injected. A series of laboratory push-pull tests were performed in physical aquifer models designed to simulate conditions occurring near an injection/extraction well during a field test. Three physical models were packed with clean silica sand and two natural sediments. Injected test solutions contained 30 mM KBr to simulate the amount of salt typically added to the anionic surfactant Aerosol MA 80-I to promote Winsor Type I phase behavior and

optimal TCE solubility. Porewater samples were collected from the sediment pack and analyzed for Na^+, K^+, Ca^{2+}, Mg^{2+}, and Br^-. In addition, the collected samples were combined with surfactant (Aerosol MA 80-I) and liquid TCE and analyzed for aqueous phase surfactant and TCE concentrations. Samples collected during experiments conducted in clean silica sand, which had minimal cation exchange capacity, had low divalent/monovalent cation ratios and gave aqueous phase TCE concentrations essentially identical to those predicted from batch solubilization isotherms. In contrast, samples collected during experiments conducted in both natural sediments (which had similar cation exchange capacities of approximately 20 meq/100 gm) had divalent/monovalent cation ratios large enough to cause aqueous phase TCE concentrations to exceed those predicted from the batch isotherm. In previous work with these sediments and surfactant, the occurrence of TCE solubilization potentials larger than those predicted by the batch isotherm corresponded with the formation of Winsor Type II behavior and the partitioning of injected surfactant into the residual TCE phase. Thus, a push-pull test conducted with a low concentration of salt can be used as a low risk, low cost tool for predicting the deleterious effects of cation exchange on surfactant effectiveness.

PLANNED ACTIVITIES

This project will conclude in September, 1999. The remainder of project resources will be devoted to completing manuscripts in progress and in dissiminating research results to potential technology users.

PUBLICATIONS :

Field, J.A., T.E. Sawyer, M.H. Schroth, and J.D. Istok. 199X. Effect of Cation Exchange on Surfactant Enhanced Solubilization of Trichloroethene. Submitted to Journal of Contaminant Hydrology

Schroth, M.H., J.D. Istok, and R. Haggerty. 199X. In-Situ Evaluation of Solute Retardation Using Single-Well Push-Pull Tests". Submitted to Journal of Hydrology.

Field, J.A., J.D. Istok, M.H. Schroth, T.E. Sawyer, and M.D. Humphrey. 199X. Laboratory Investigation of Surfactant-Enhanced TCE Solubilization Using Single-Well, "Push-Pull" Tests. Ground Water (In Press).

Istok, J.D., J.A. Field, M.H. Schroth, T.E. Sawyer, and M.D. Humphrey. 199X. Laboratory and Field Investigation of Surfactant Sorption Using Single-Well, "Push-Pull" Tests. Ground Water (In Press).

Field, J.A. and J.D. Istok. 199X. Comment on Estimation of Nonaqueous Phase Liquid-Water Interfacial Areas in Porous Media Following Mobilization by Chemical Flooding. Environmental Science and Technology, Vol. 32, No. 2, pp. 3836-3837.