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

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OBJECTIVES

(1) **to develop a modified "push-pull" test for use in identifying and quantifying the effects of sorption, precipitation, and biodegradation on the fate and transport of injected surfactants**

(2) **to use the developed test method to quantify the effects of these processes on the ability of injected surfactants to solubilize and mobilize residual trichloroethene (TCE)**

(3) **to demonstrate the utility of the developed test method for performing site characterization and feasibility studies for surfactant enhanced DNAPL recovery systems**

Surfactant Enhanced DNAPL recovery

Inject surfactant to enhance solubilization of dense nonaqueous phase liquids (DNAPLs) and thus increase recovery efficiency

Effectiveness of technology is influenced by:

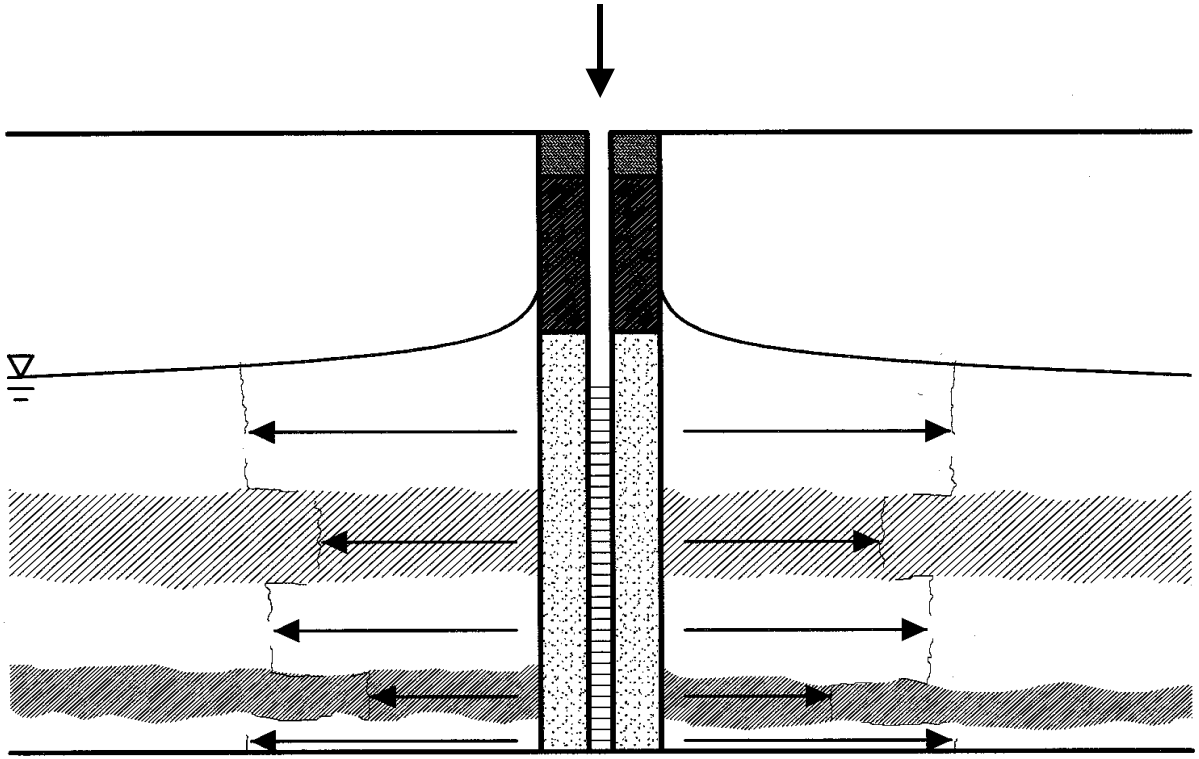
- **Surfactant phase behavior and solubilization potential**
- **Surfactant losses and changes in composition due to sorption and/or cation exchange**
- **Loss of hydraulic control of solubilized DNAPL**

Use push-pull tests to more efficiently move technology from the "flask to the field"

Small-scale laboratory	→	Pilot-scale field feasibility <u>push-pull tests</u>	→	Full-scale field demonstration

What is a “Push-Pull” Test ?

During the <u>injection phase</u>, a prepared test solution containing tracer and surfactant is injected into the saturated zone using an existing monitoring well



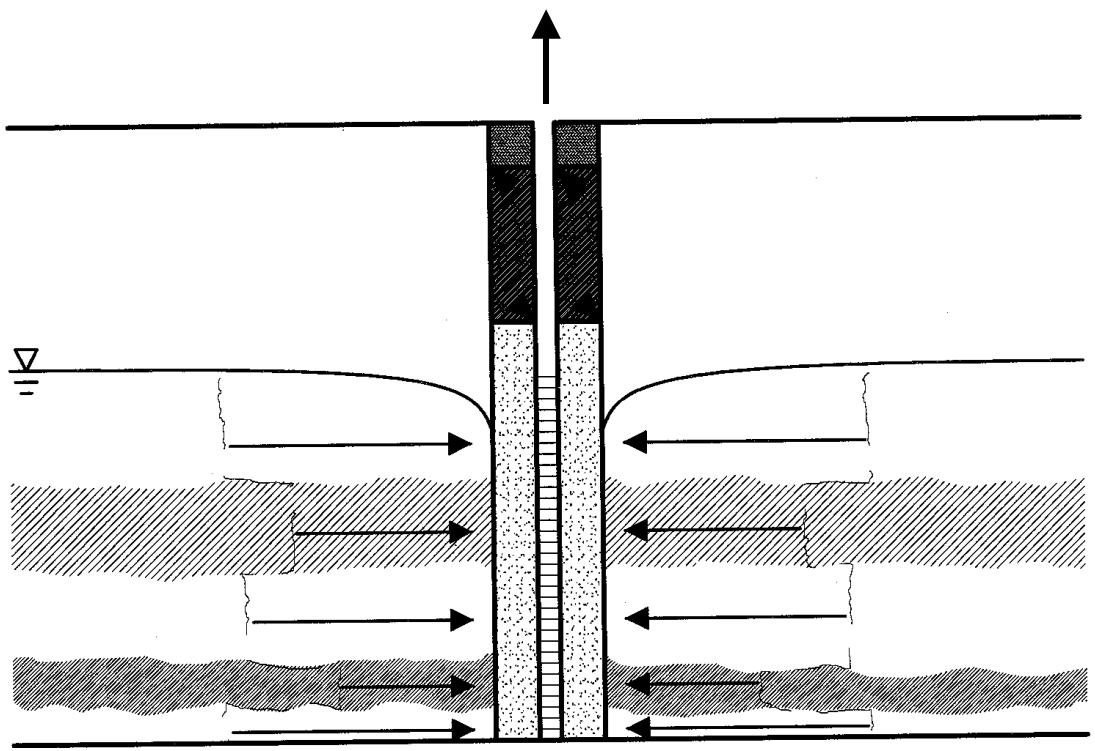
Using existing wells lowers costs and reduces risks of field experiments

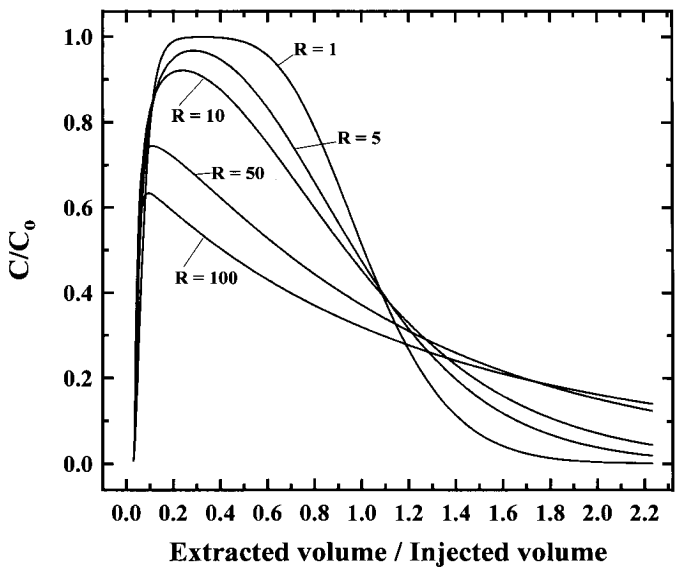
Injected volume is arbitrary and determines volume of aquifer interrogated during the test

Shape of interrogated zone is generally unknown

During the <u>extraction phase</u>, flow is reversed and samples of test solution/groundwater mixture are collected and analyzed to develop <u>breakthrough curves</u>

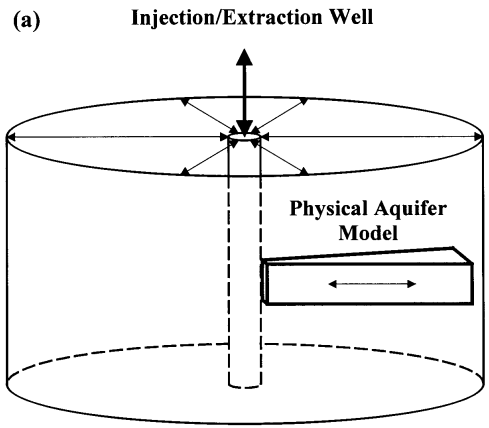
Solute physical, and chemical behavior is determined from extraction phase breakthrough curves





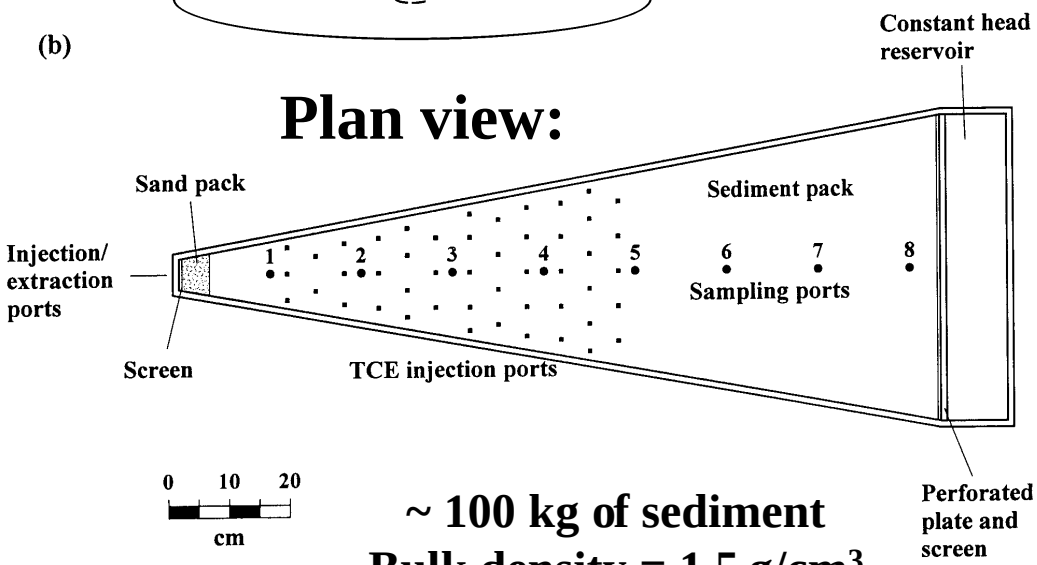
Multiple tests can be performed in a single day. Tests can be performed at multiple depths in a single well using packers

Physical Aquifer Models Used in Laboratory Push-Pull Tests

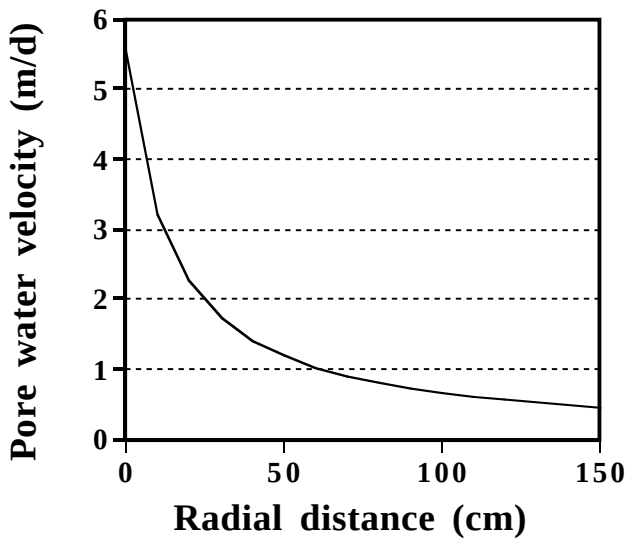


Physical models constructed in wedge shape to simulate radial flow near well during field push-pull tests

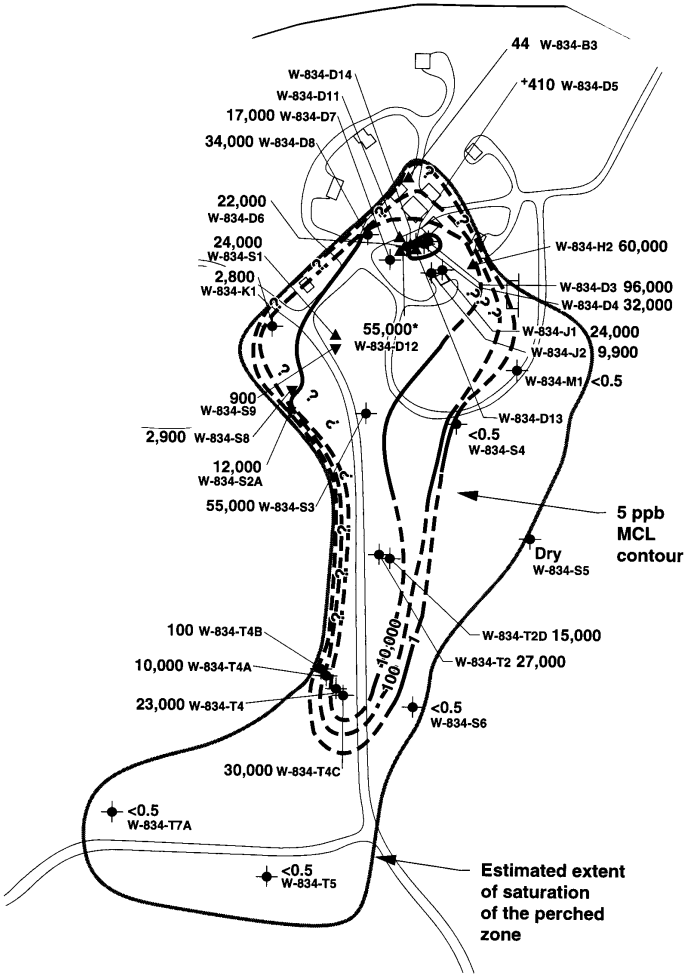
Note nonlinear velocity distribution with radial distance



~ 100 kg of sediment
Bulk density = 1.5 g/cm^3
Porosity = 0.39
Depth = 20 cm



Field Experiments Conducted at LLNL Site 300- Building 834 Complex



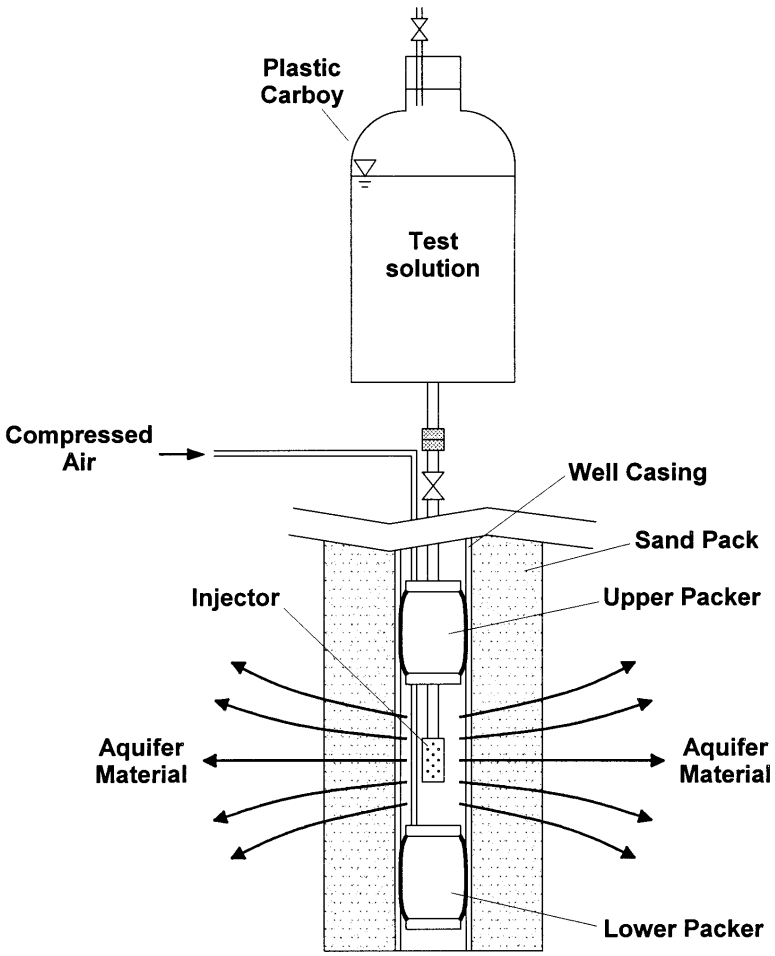
TCE used as heat transfer fluid during thermal testing of explosives

Site consists of unconfined, perched aquifer formed in alluvium. Sediment for laboratory experiments was collected from outcrops and consisted of 76.9% sand, 21.8% silt, 12.1% clay, a median grain diameter of 0.8 mm, a uniformity coefficient of 2.9, a particle density of 2.65 g/cm^3, an organic carbon content of 0.17 wt %, and a pH of 9

Field push-pull tests were performed in existing monitoring wells

Equipment Used in Field Push-Pull Tests

Equipment is simple and inexpensive



Surfactants

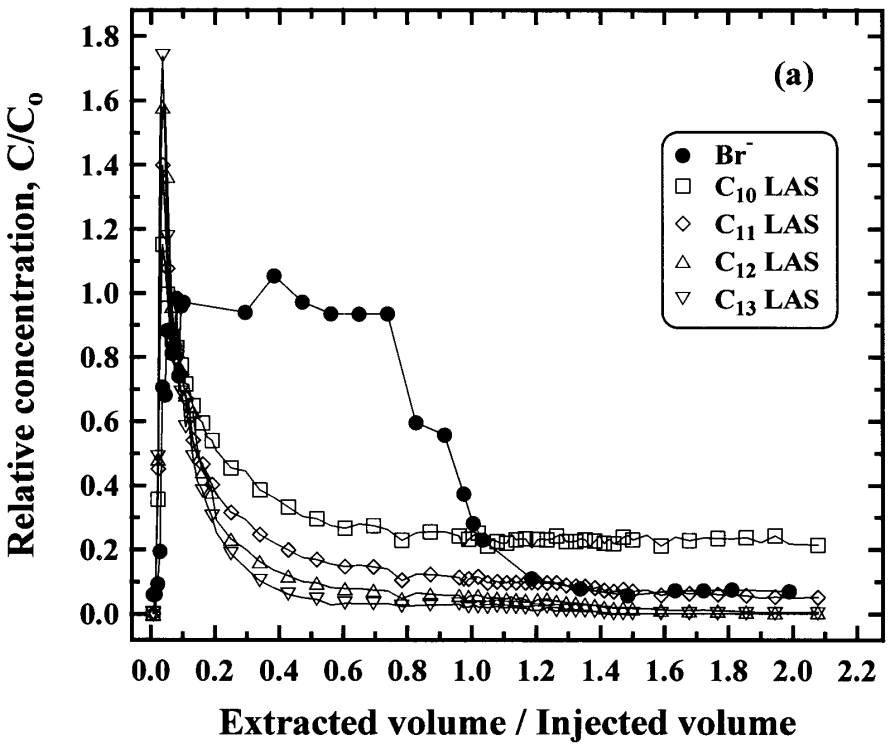
- **<u>Sodium linear alkylbenzene sulfonate (LAS)</u>**
  - **50 %active**
  - **22% C_{10}, 40% C_{11}, 30% C_{12}, 8% C_{13} alkyl chain homologs**
  - **CMC ~ 200 mg/L; C_o = 1924 mg/L (active)**
- **<u>Disodium hexadecyl diphenyl oxide disulfonate (DOWFAX)</u>**
  - **33 % active**
  - **90 % disodium hexadecyldiphenyl oxide disulfonate; 10% disodium dihexadecyldiphenyl oxide disulfonate**
  - **CMC ~ 125 mg/L; C_o = 13500 mg/L (active)**
- **<u>Sodium dihexyl sulfosuccinate (AEROSOL MA 80-I)</u>**
  - **80 % active; 5 %isoproponol**
  - **C_o = 36700 mg/L (active)**
  - **Injectate also contains 10 % isoproponol + 0.32 wt %KBr**

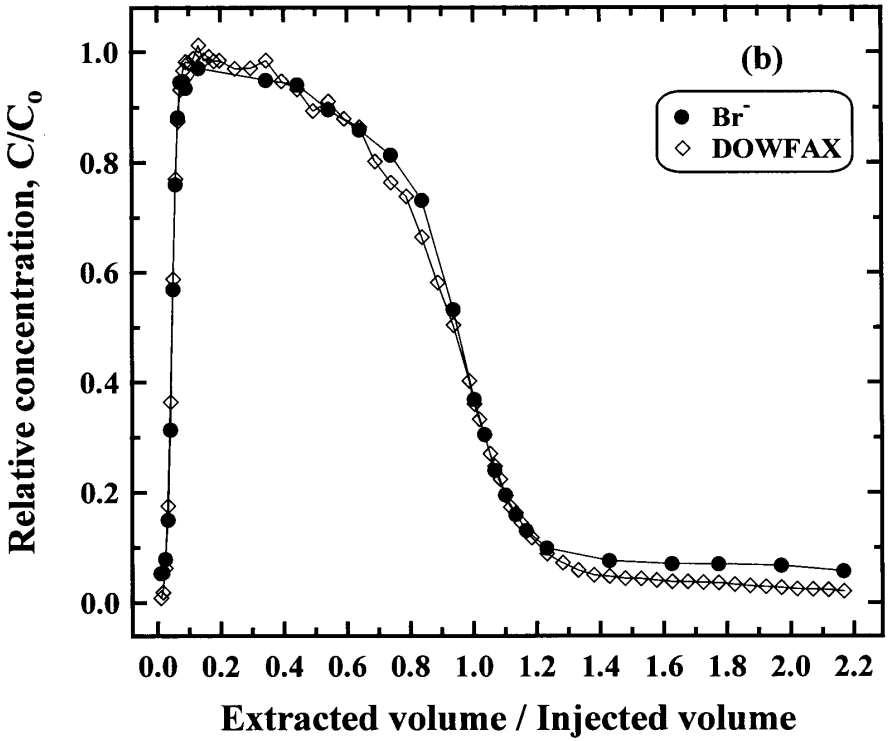
Characterization of Surfactant Sorption

The objective of this study was 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 aquifer sediment in situ. Batch sorption isotherms for both surfactants exhibited Langmuir-type sorption behavior with larger apparent sorption maxima for LAS than for DOWFAX. These same features are apparent in extraction phase breakthrough curves for both laboratory and field push-pull tests. However, numerical transport simulations based on batch sorption isotherms were unable to predict the retardation and chromatographic separation of LAS homologs and conservative transport of DOWFAX observed during laboratory and field push-pull tests, indicating that the single-well, push-pull test method can more accurately describe in situ surfactant sorption and transport behavior than batch sorption isotherms.

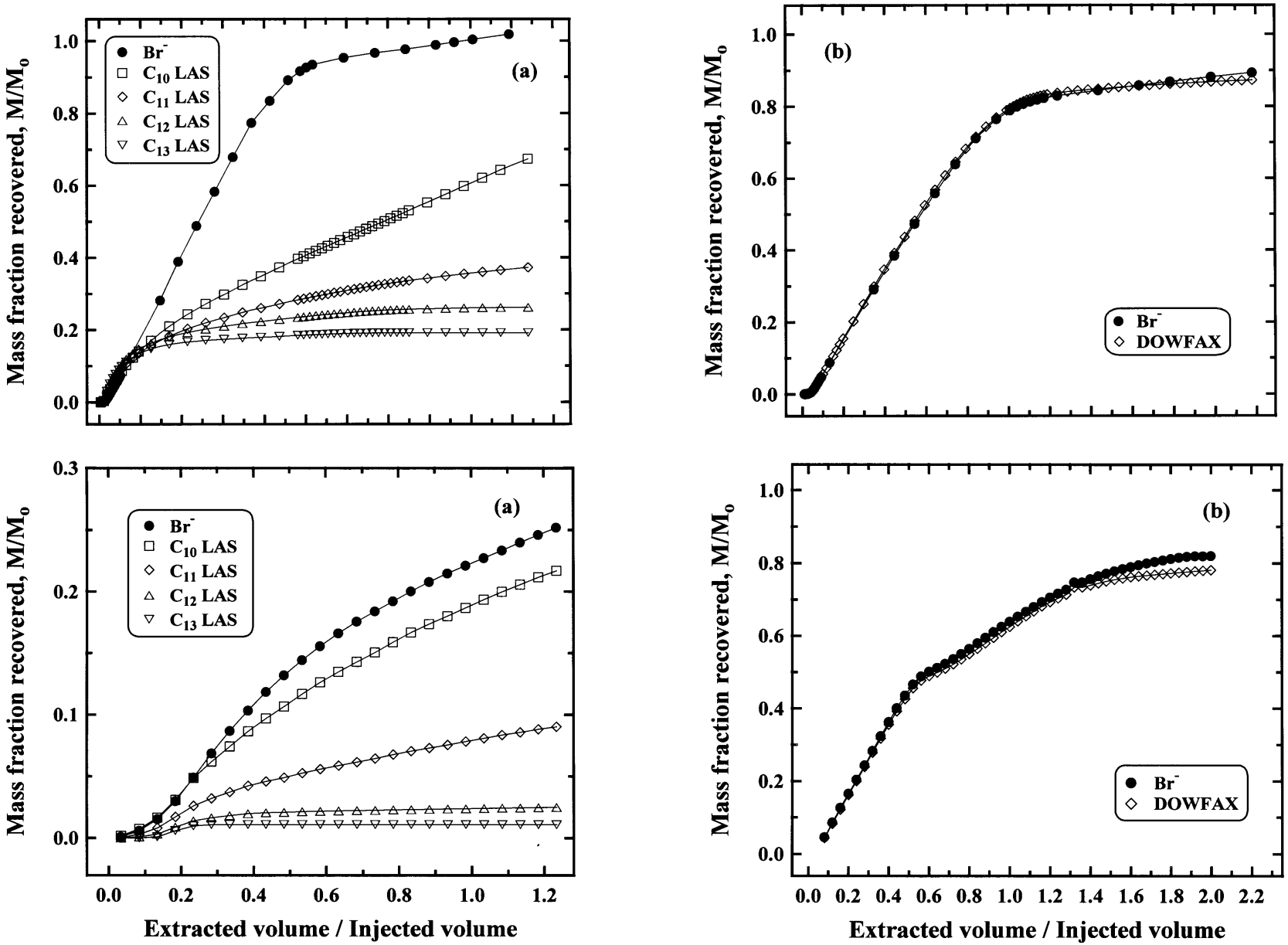
Effect of Sorption on Push-Pull Test Breakthrough Curves

(a) Extraction phase breakthrough curves for LAS showing preferential sorption and chromatographic separation of LAS components relative to Br^- tracer (b) Extraction phase breakthrough curves for DOWFAX showing conservative DOWFAX transport.





Comparison of laboratory (upper) and field (lower) mass recovery curves for LAS and DOWFAX

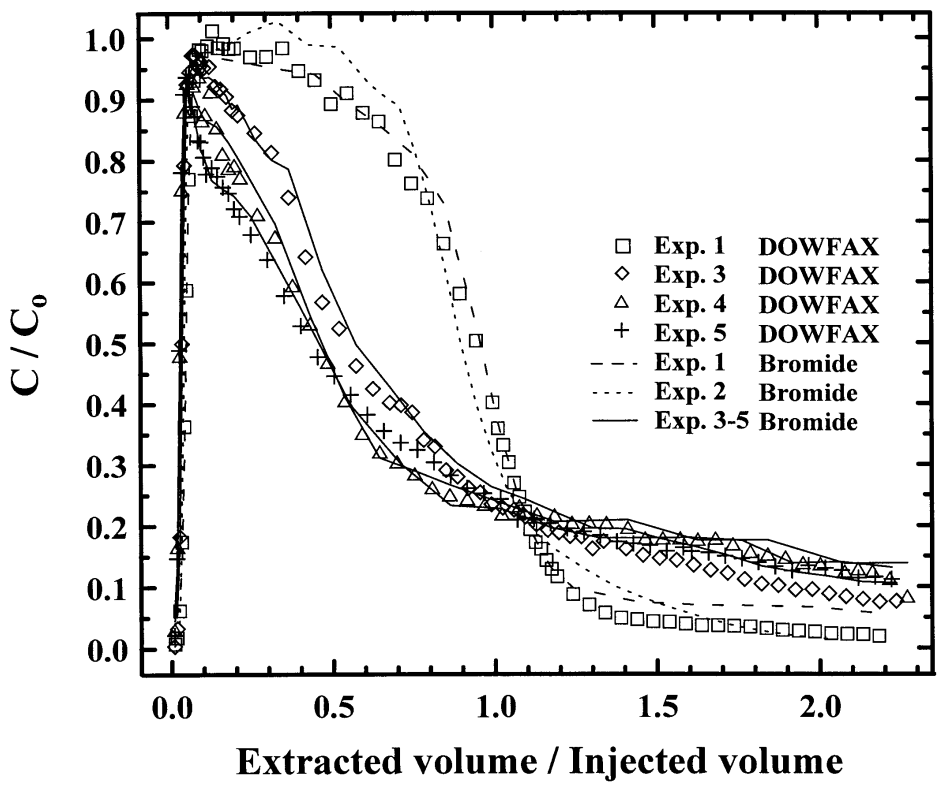


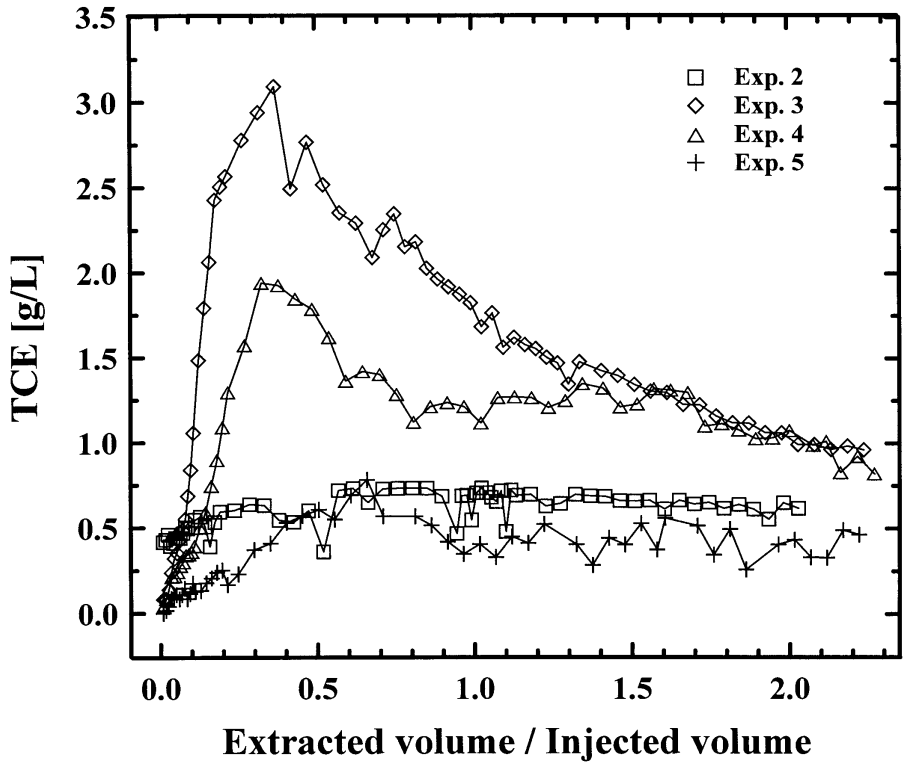
Solubilization of TCE by DOWFAX

Batch solubilization experiments indicated a linear relationship between TCE solubility and DOWFAX concentration (WSR = 0.26). Laboratory push-pull tests were conducted in a TCE-free sediment pack and in a sediment pack containing liquid TCE with an initial saturation of ~ 5 % of the pore volume. In 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 compared to tracer tests conducted without surfactant. 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.

Extraction Phase Breakthrough Curves With and Without TCE

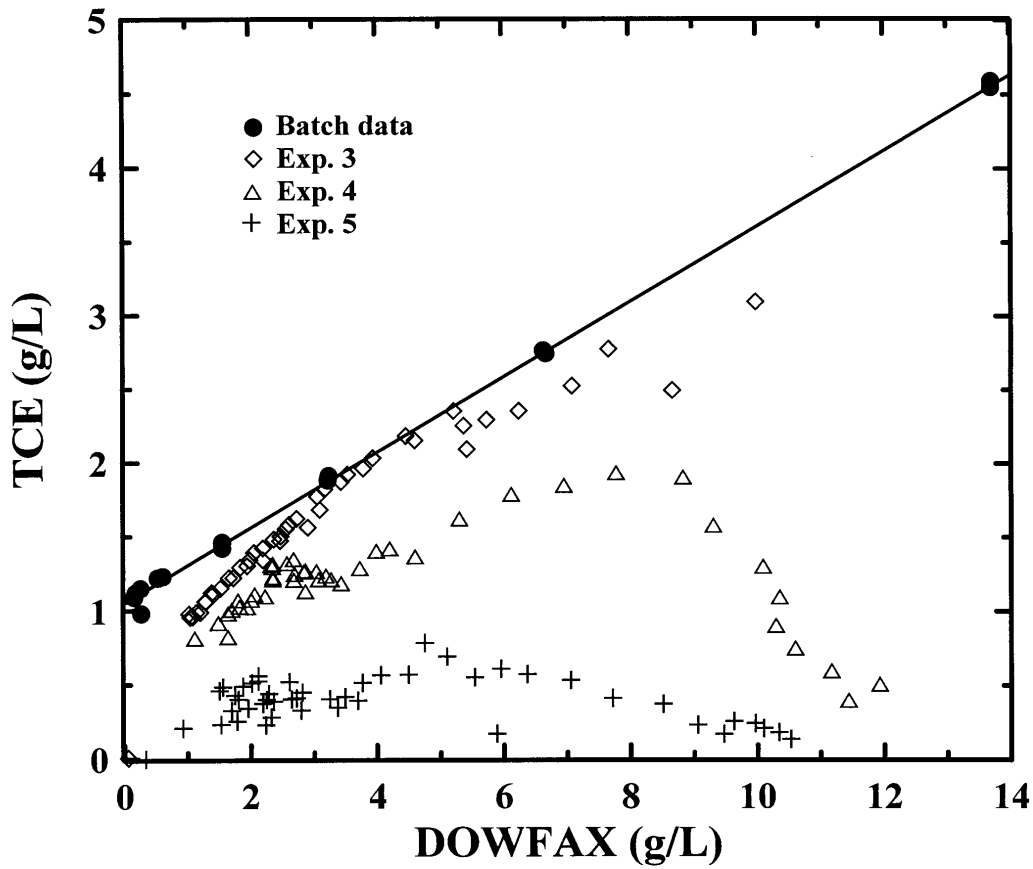
Experiment 1 = No TCE in sediment; Experiment 2 = tracer test
Experiment 3 = 1st push-pull test in sediment with 5 % TCE
Experiment 4 = 2nd push-pull test in sediment with 5 % TCE
Experiment 5 = 3rd push-pull test in sediment with 5 % TCE





Comparison of Batch Solubilization Isotherm with Push-Pull Test Results

Line shows fitted batch solubilization isotherm



Symbols are from extraction phase breakthrough curves

Exp. 3 = 1st push-pull test
Exp. 4 = 2nd push-pull test
Exp. 5 = 3rd push-pull test

Note reduced TCE solubilization with successive DOWFAX injections

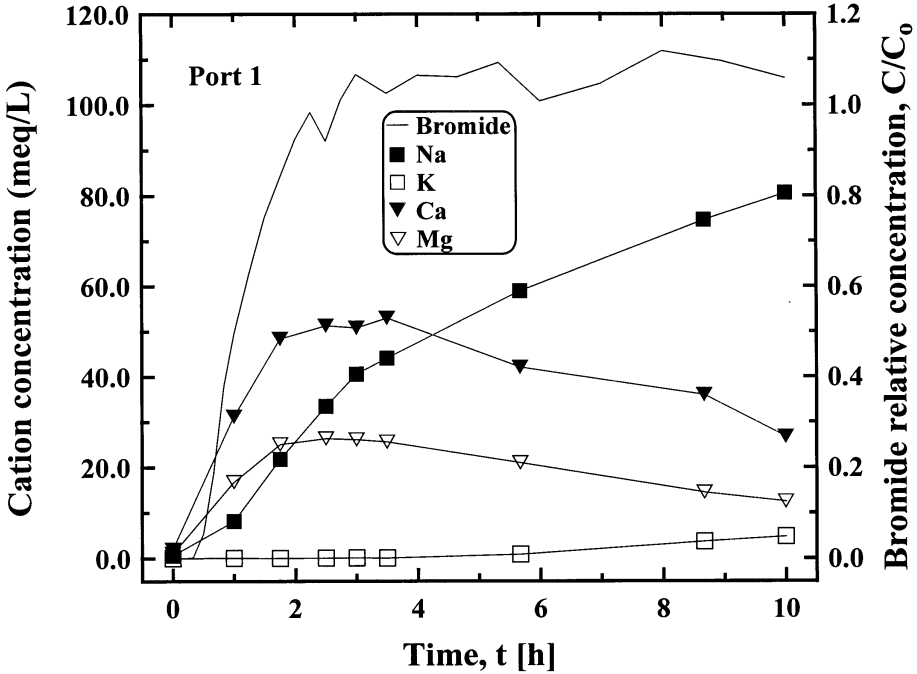
Effect of Cation Exchange on Surfactant Enhanced TCE Solubilization

Anionic surfactants are prepared as Na^+ and K^+ salts. When injected into the subsurface, cation exchange occurs between monovalent cations in surfactant micelles (m) and divalent cations on sediment (s). For example:

$$2Na^+(m) + Ca^{2+}(s) \longleftrightarrow 2Na^+(s) + Ca^{2+}(m)$$

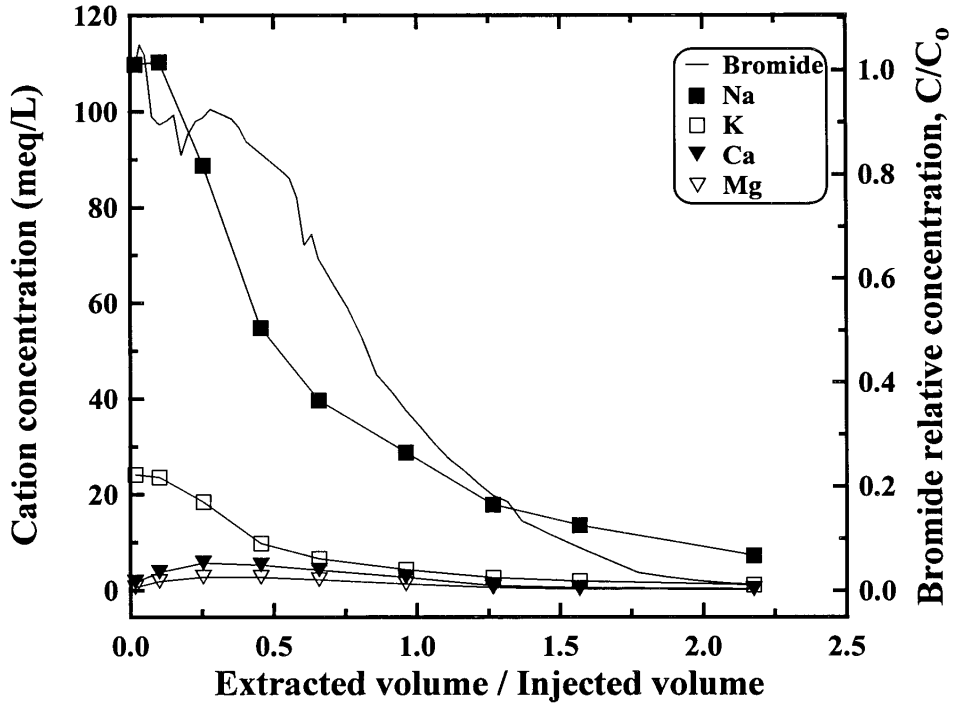
The effects of cation exchange can be substantial, affecting surfactant transport, phase behavior, and TCE solubilization.

Push-pull tests can be used to characterize the effects of cation exchange on surfactant transport, phase behavior and TCE solubilization



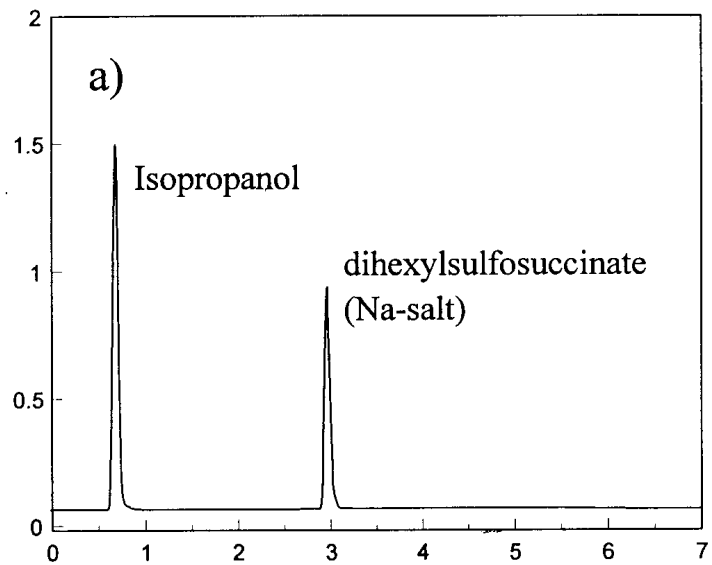
Injection phase breakthrough curves (left) showing exchange of divalent cations on sediment by injected monovalent cations in Aerosol MA 80-I injectate

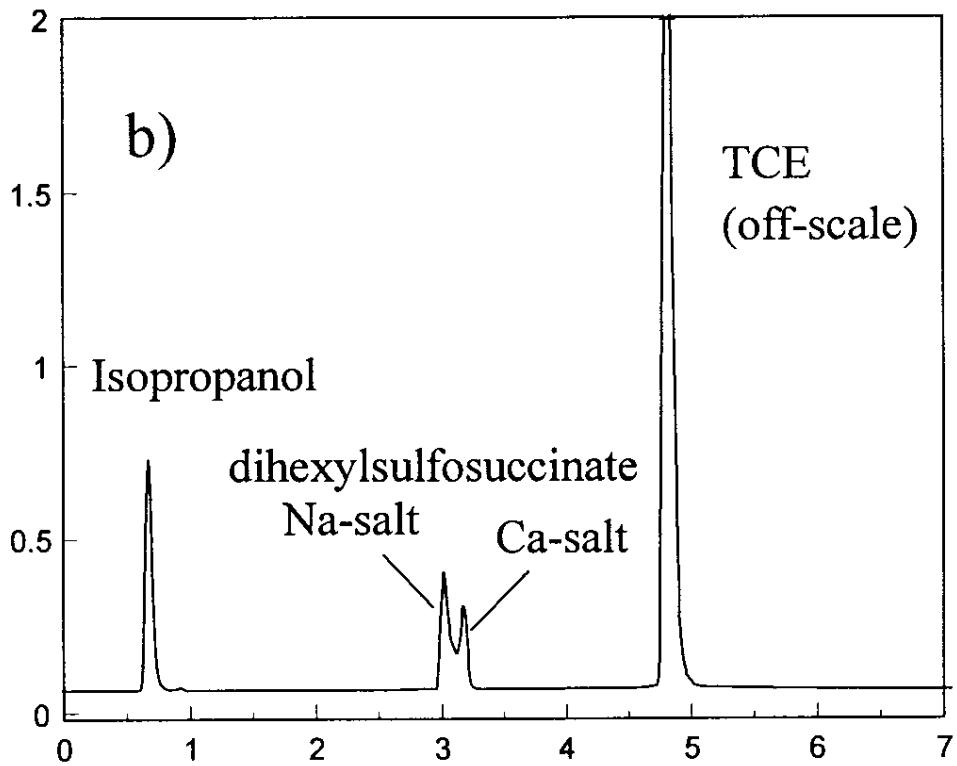
Extraction phase breakthrough curves (right) showing "retarded" Na^+ transport and small "pulse" of divalent cations exchanged from sediment (test performed with Aerosol MA 80-I in presence of TCE)

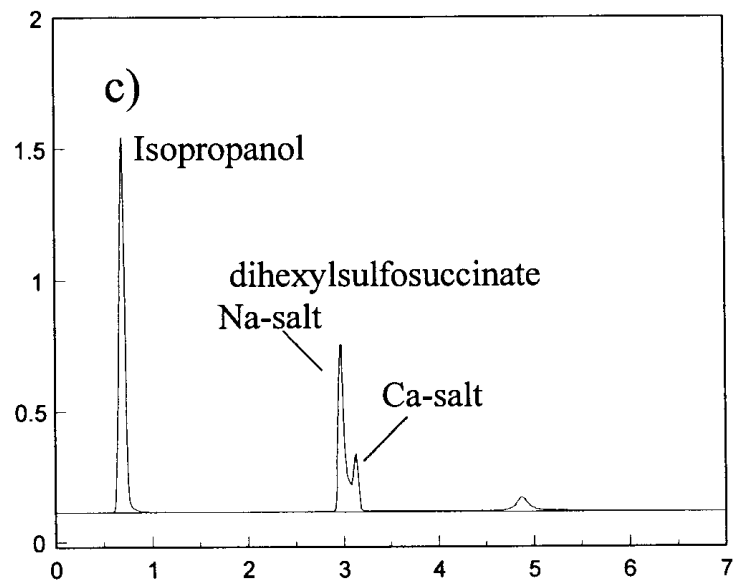


HPLC Chromatography

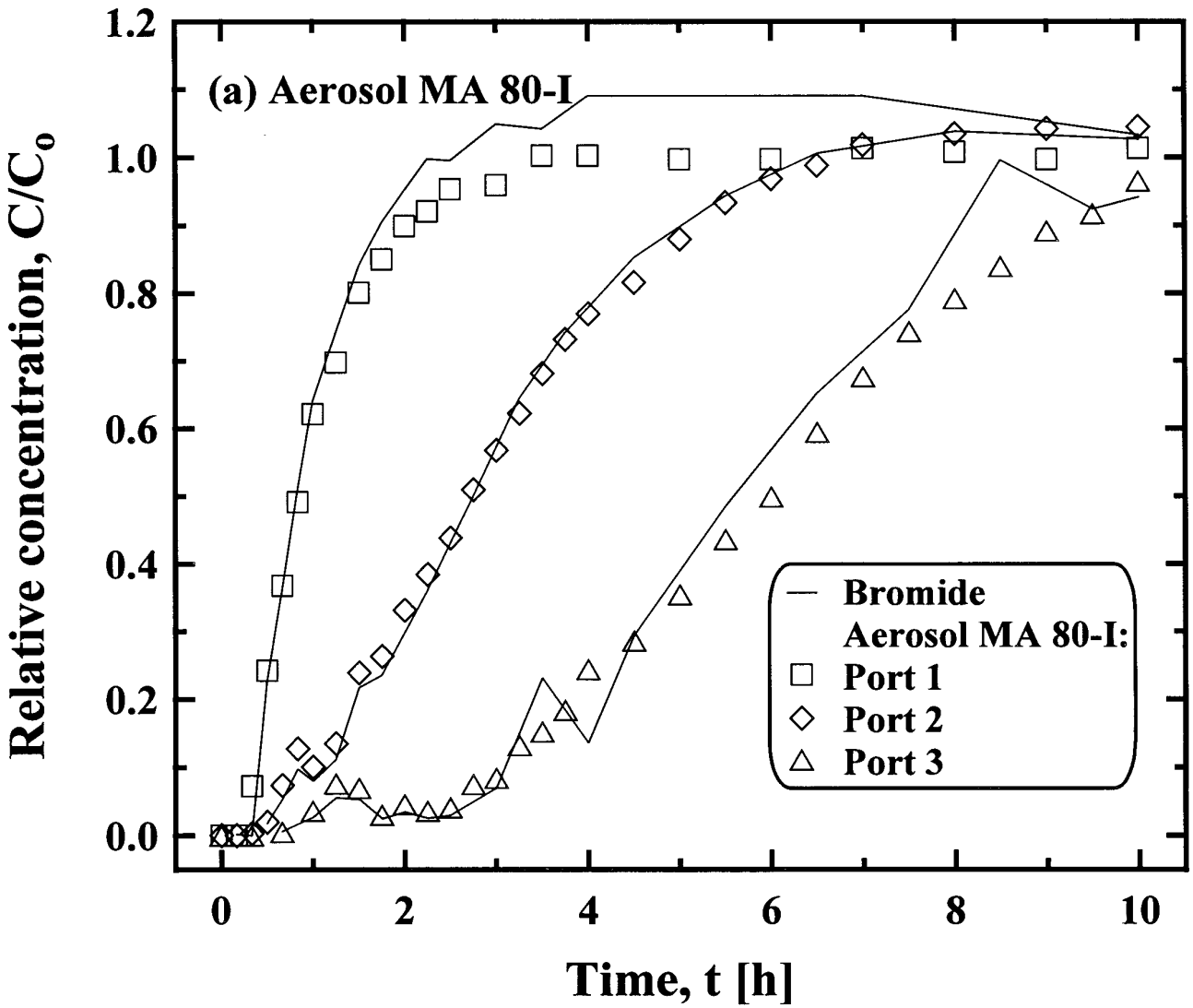
Chromatograms showing separation and identification of Na^+ and Ca^{2+} forms of Aerosol MA 80-I (a) Injectate, (b) Sample from port 2 after cation exchange, and (c) injectate plus added calcium



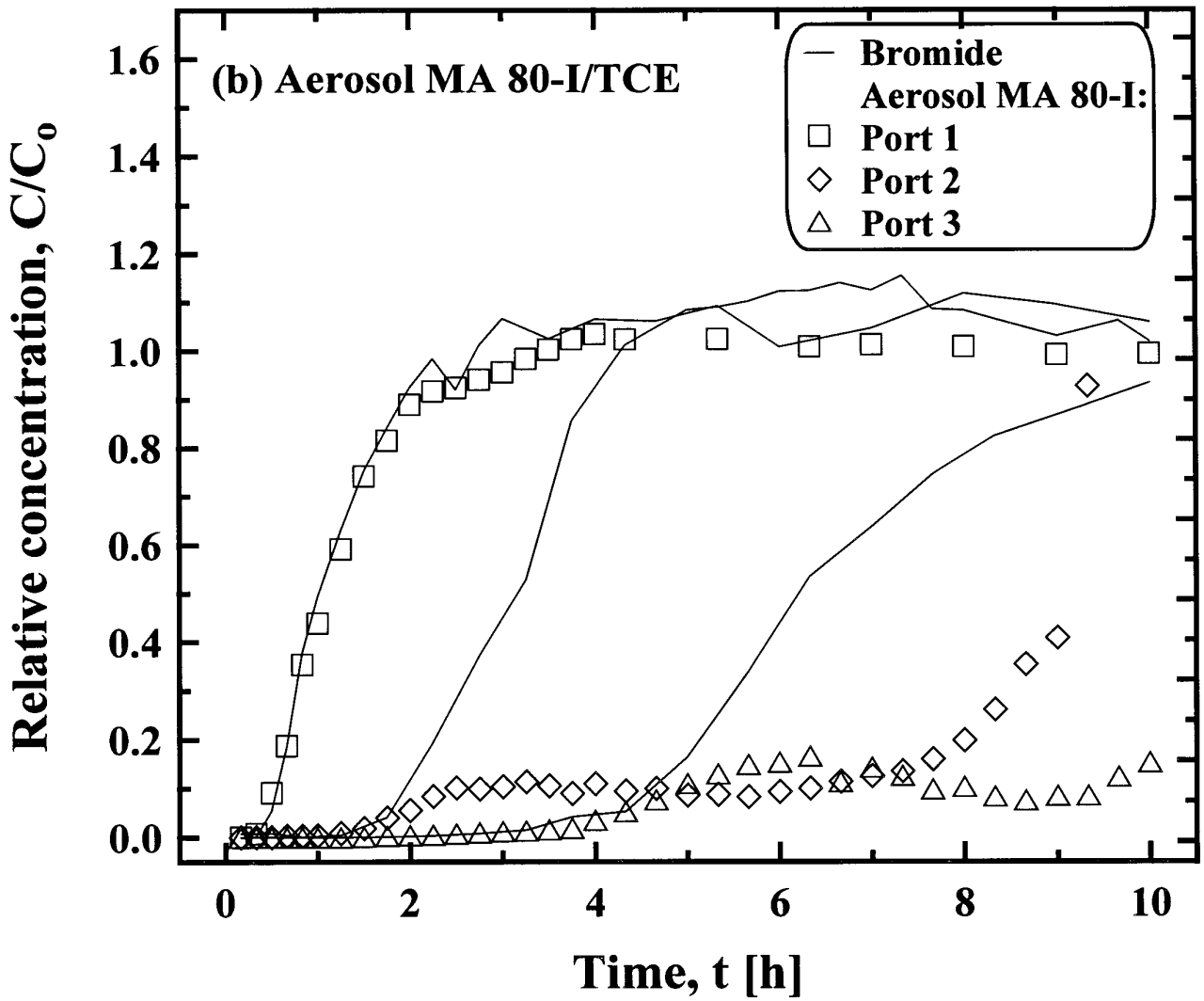




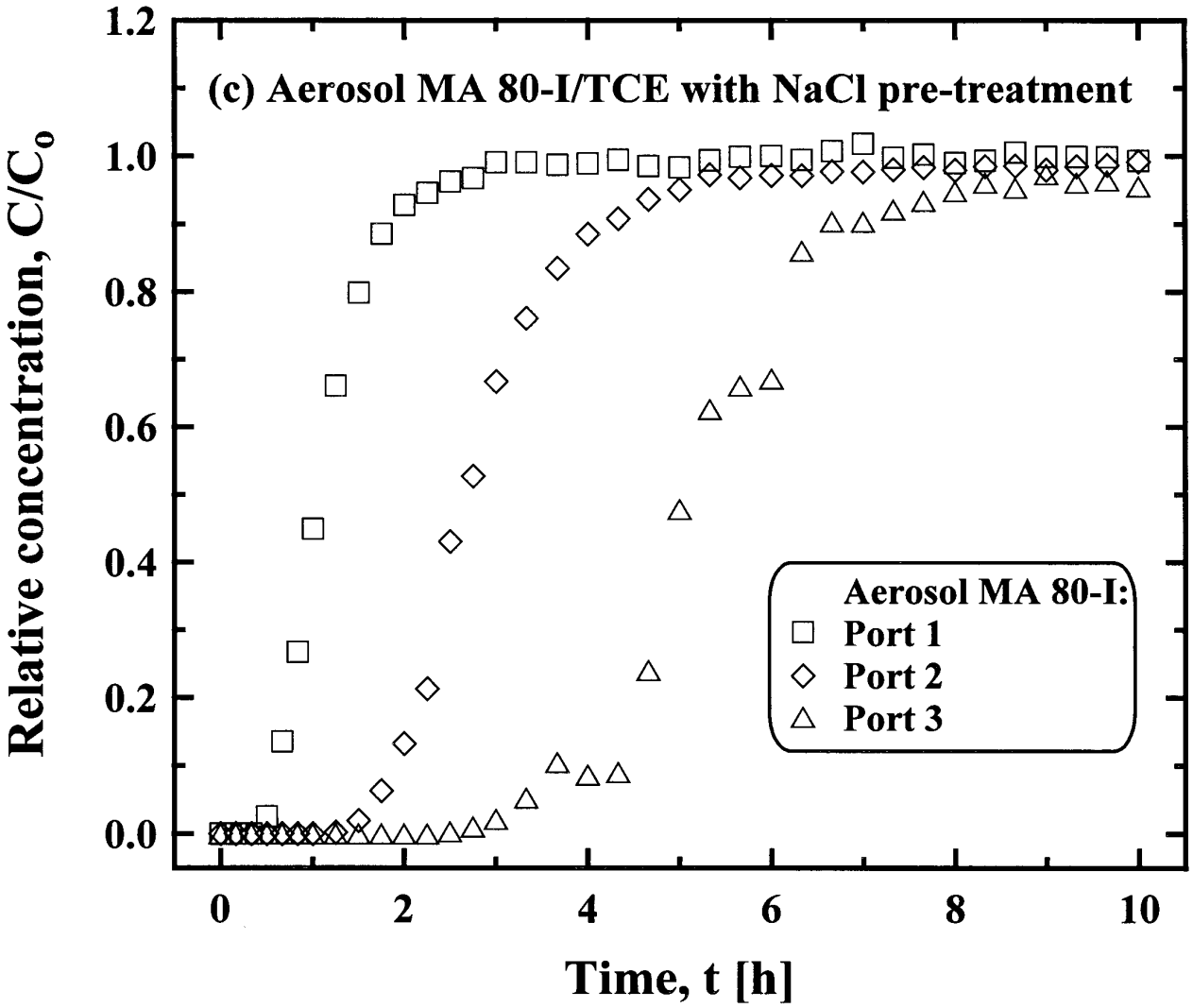
In the absence of TCE, Aerosol MA 80-I is transported identically to Br^- tracer. This is seen in injection phase breakthrough curves from laboratory push-pull tests.



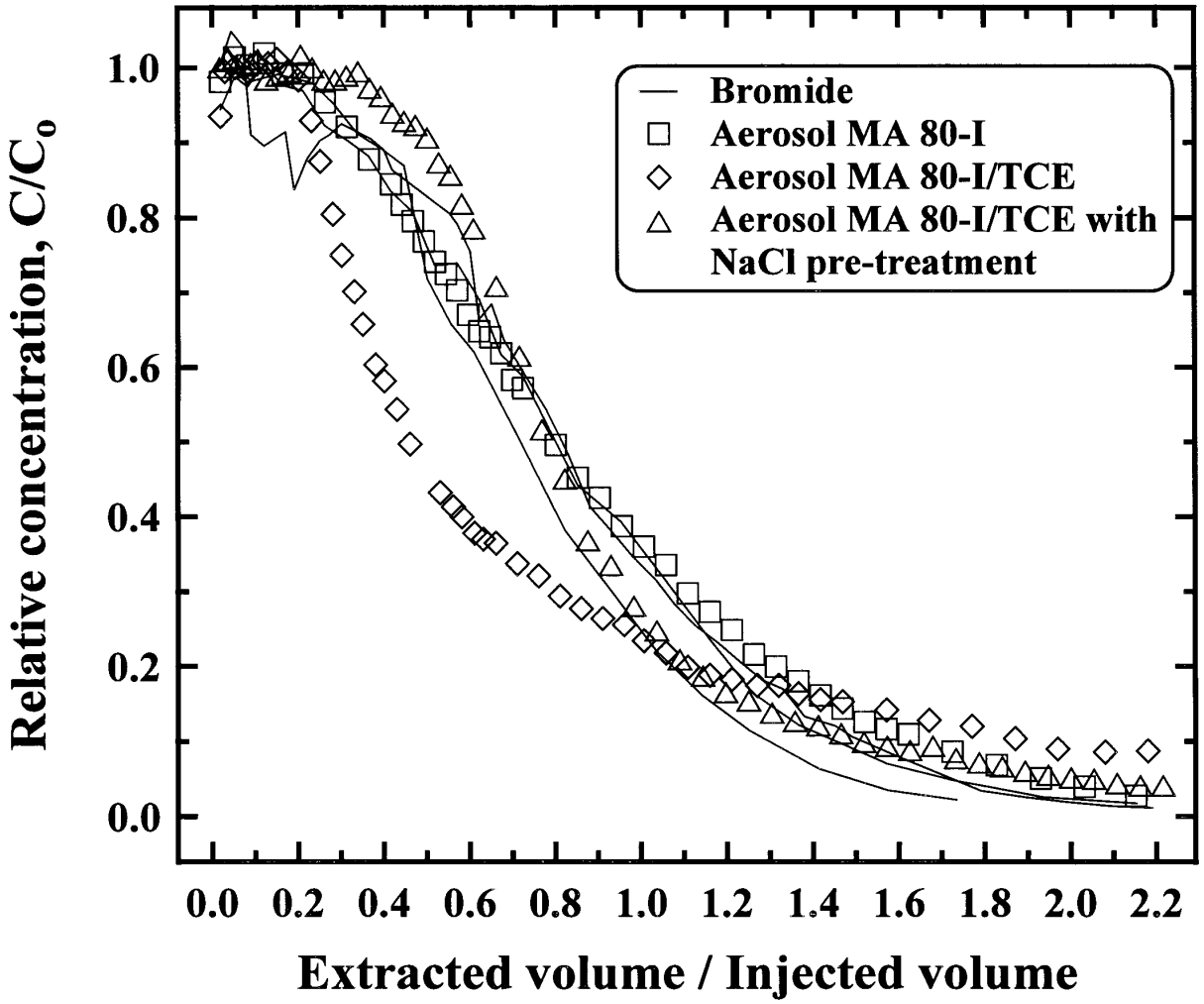
In the presence of TCE, Aerosol MA 80-I transport is retarded due to partitioning of Ca^{2+} form of injected surfactant into TCE NAPL phase.



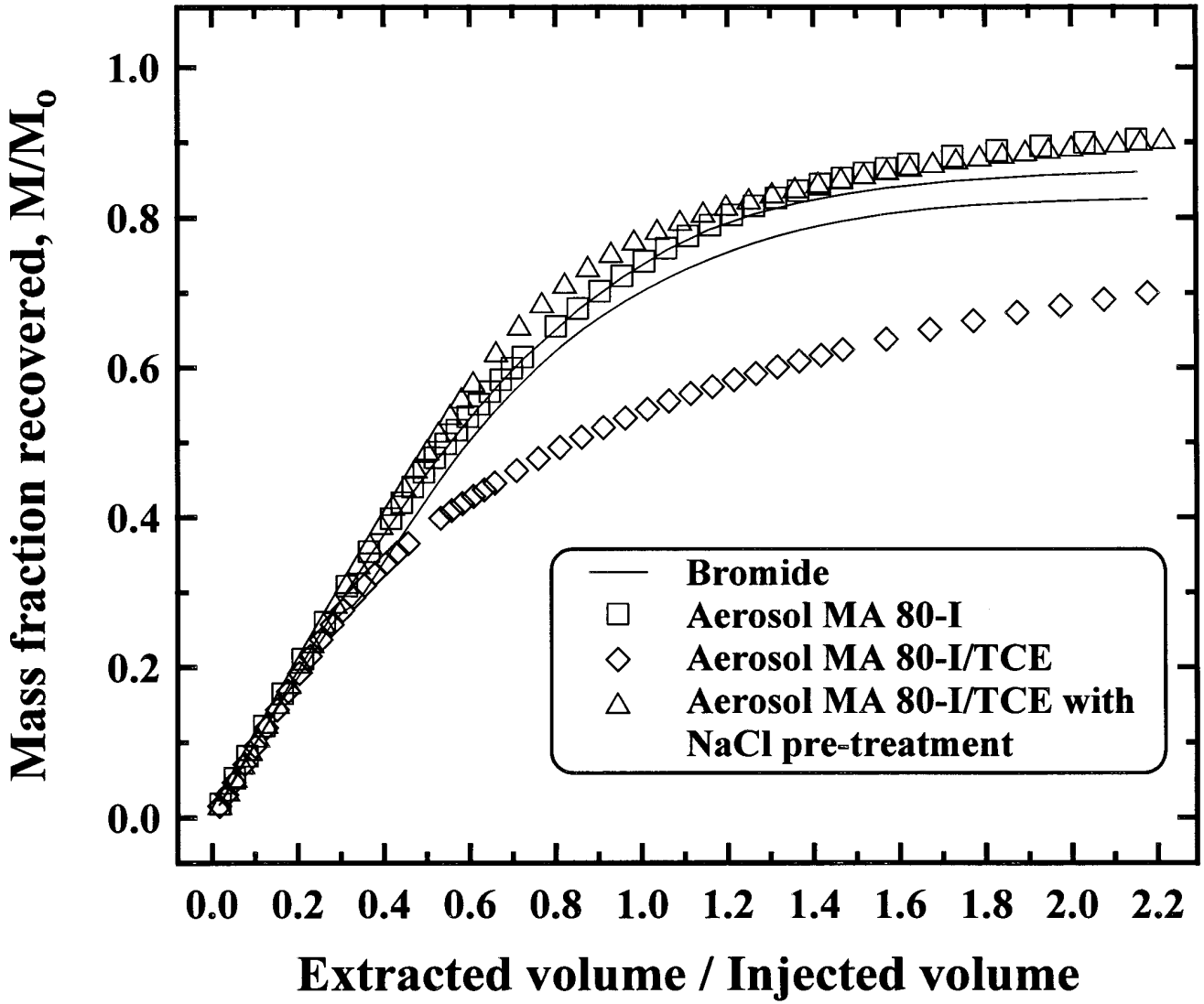
By pretreating sediment with ~ 10 pore volumes of 130 mM Na^+, conservative transport of Aerosol MA 80-I is restored.



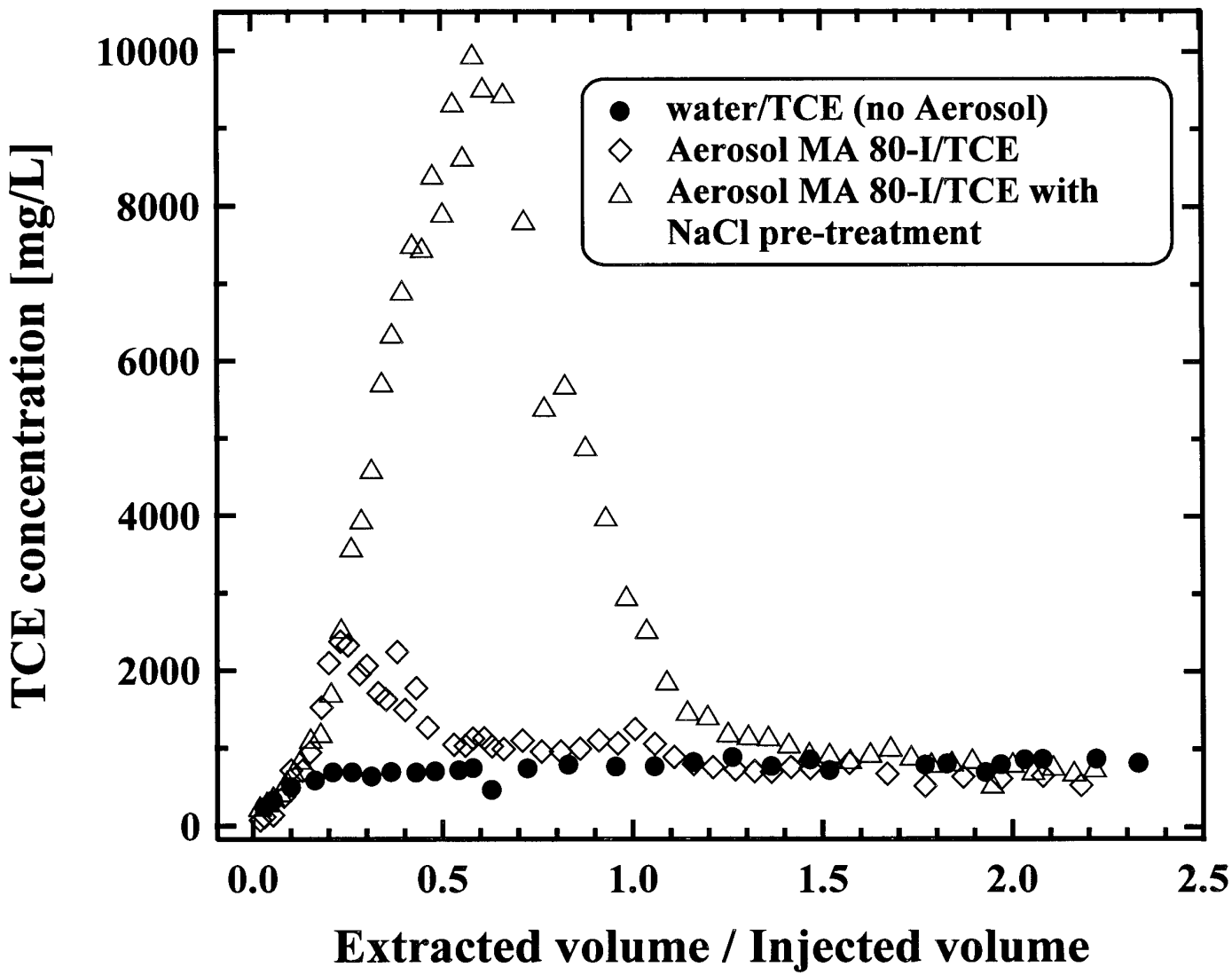
The same effects of cation exchange are apparent in extraction phase breakthrough curves. Aerosol MA 80-I transport is conservative in absence of TCE, retarded in presence of TCE, and conservative in Na^+ treated sediment.



The same effects of cation exchange on surfactant transport are apparent in mass recovery plots



Cation exchange greatly effects TCE solubility enhancement achieved by Aerosol MA 80-I



Solubilization potential was determined by adding ~ 300ul neat TCE to samples, shaking, and analyzing the aqueous phase for TCE and surfactant. Injectate reaching port 1 was initially dominated by divalent cations and only approached the injectate cation composition through time. When TCE was added to these samples, most of the surfactant partitioned into the TCE and the resulting aqueous phase TCE solubilization was very different from that of the original injectate.

Aqueous Aerosol MA 80-I

Time (hrs)	*before* TCE added (g/L)	*after* TCE added (g/L)	% remaining in aqueous phase	TCE (mg/L)
3.5	36.8	3.6	9.8	1915
6.0	36.8	6.7	18.2	4155
8.3	36.8	18.9	51.4	18137
9.3	36.8	16.8	45.7	25369
9.7	36.8	27.2	73.9	41309
injectate	36.8	35.4	96.2	26004

Similar data for the extraction phase breakthrough curve indicate that potential solubilization is closer to that predicted by the solubilization isotherm (data not shown). The extremely poor TCE recovery during the PAM experiment is difficult to reconcile with these data. The divalent cation dominated surfactant that did encounter liquid TCE partitioned into the TCE yielding the 25% mass loss of surfactant seen during the experiment.

Aqueous Aerosol MA 80-I

Ext./Inj. Vol.	*before* TCE added (g/L)	*after* TCE added (g/L)	% remaining in aqueous phase	TCE (mg/L)
.02	34.4	35.6	103.5	26196
.15	37.2	36.2	97.3	27750
.30	27.6	26.6	96.4	20751
.40	21.4	20.9	97.7	14096
.56	15.2	13.8	90.8	6737
.76	11.8	10.4	88.1	3604

Preprints (available on table)

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. Submitted to Ground Water.

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. Submitted to Ground Water .

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. and T.E. Sawyer. 199X. Quantification of Trichloroethylene and Anionic Surfactants Used for Surfactant Enhanced Aquifer Remediation by HPLC/DAD. Submitted to Ground Water Monitoring and Review.

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