BASIC RESEARCH STRATEGIES FOR RESOLVING REMEDIATION NEEDS IN CONTAMINATED FRACTURED MEDIA

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Abstract

This article describes a multidisciplinary endeavor to develop and employ basic research strategies for guiding remediation efforts in contaminated fractured subsurface media at the Department of Energy's Oak Ridge National Laboratory. Its intent is to provide a brief overview of research activities from the past 15 y that sought to provide an improved understanding and predictive capability of contaminant transport processes in highly &u&red, heterogeneous subsurface environments that are complicated by fracture flow and matrix diffusion. Our approach involved a multiscale (cm to ha) experimental and numerical endeavor to investigate coupled time-dependent hydrological and geochemical processes that control contaminant migration in unsaturated and saturated soil and rock Novel tracer techniques and experimental manipulation strategies were applied at laboratory, intermediate, and field scales to unravel the influence of multiple processes on contaminant fate and transport. The basic research strategies have significantly improved our conceptual understanding of time-dependent solute migration in fractured subsurface media. This information has proved useful in decision-making processes regarding the selection of effective remedial actions and the interpretation of monitoring results after remediation is complete.

Introduction

The disposal of low-level radioactive waste generated by the Department of Energy (DOE) during the cold war era has historically involved shallow land burial in unconfined pits and trenches. The lack of physical or chemical barriers to impede waste migration has resulted in the formation of secondary contaminant sources since radionuclides have moved into the surrounding soil and bedrock. At the Oak Ridge National Laboratory (ORNL), located in eastern Tennessee, USA the extent of the problem is massive, where thousands of underground disposal trenches have contributed to the spread of radioactive contaminants across tens of kilometers of landscape. Subsurface transport processes are driven by large annual rainfall inputs (-1400 mm.@) where as much as 50% of the infiltrating precipitation results in groundwater and surface water recharge (10 and 40%, respectively). This condition promotes the formation of secondary contaminant sources since lateral storm flow and groundwater interception with the trenches enhances the migration of waste constituents into the surrounding subsurface environment. The subsurface media at ORNL is comprised of fractured saprolite and shale bedrock which are conducive to rapid preferential flow coupled with significant matrix storage. Fractures are highly interconnected and

surround low permeability, high porosity matrix blocks. When storm flow infiltrates into the media, large hydraulic and geochemical gradients result among the various flow regimes causing nonequilibrium conditions during solute transport

In these systems, the soil and bedrock matrix (secondary sources) have been exposed to migrating contaminants for many decades, and thus account for a significant inventory of the total waste. A significant limitation in defining remediation needs of the secondary sources results from an insufficient understanding of the transport processes that control contaminant migration Without this knowledge-base, it is impossible to assess the risk associated with the secondary source contribution to the total off-site migration of contaminants. The objectives of our research were to help resolve this dilemma by providing an improved understanding of contaminant transport processes in highly structured, heterogeneous subsurface environments that are complicated by fracture flow and matrix diffusion. Our approach involves multiscale experimental and numerical basic research to address coupled hydrological and geochemical processes controlling the fate and transport of contaminants in fractured saprolite and shale rock Undisturbed soil columns (cm scale), in-situ soil blocks (m scale), and well instrumented field facilities (ha scale) were used in conjunction with novel tracer techniques and experimental manipulation strategies to unravel the impact of coupled transport processes on the nature and extent of secondary contaminant sources.

Laboratory Scale Assessment of Solute Migration in Fractured Media

Undisturbed columns are used in tracer transport experiments to assess the interaction of hydrology, geochemistry, and microbiology on the fate and transport of nonreactive and reactive solutes. The primary purpose of this research scale is to quantify transport mechanisms that are operative at the field-scale, but difficult to quantity at these larger scales. Undisturbed columns (typically 15 cm diameter x 40 cm length) are obtained in subsurface media identical to those used in the disposal of low-level radioactive waste on the Oak Ridge Reservation (ORR). This material is a weakly developed acidic Inceptisol that has been weathered from inter-bedded shale-limestone sequences within the Conasauga formation. The limestone has been weathered to massive clay lenses devoid of carbonate and the more resistant shale has weathered to an extensively fractured saprolite. Fractures are highly interconnected with densities in the range of 200 fractures/m (Dreier *et. al.*, 1987). Fractures surround low permeability, high porosity matrix blocks that have water contents ranging from 30-50%. Detailed information regarding the soil hydrodynamics, geochemistry, and mineralogy can be found in Watson and Luxmoore (1986),

Wilson and Luxmoore (1988), Wilsonet al. (1989, 1992, 1993, 1998), Jardine et al. (19881993 a,b, 1998), Luxmoore et al. (1990), Kooner et al. (1995), and Reedy et al. (1996).

At the column scale, several techniques are employed to assess nonequilibrium processes that result from the large difference in hydraulic conductivity of fractures vs. matrix blocks (Jardine et al., 1998). The techniques include (1) controlling flow path dynamics with manipulations of pore-water flux and soil-water tension, (2) isolating diffusion and slow geochemical processes with flow interruption, (3) using multiple tracers with different diffusion coefficients, and (4) using multiple tracers with grossly different sizes. For example, controlling flow-path dynamics by manipulation of the soil water content with pressure head variations is an excellent technique to assess nonequilibrium processes (Seyfried and Rao, 1987; Jardine et al., 1993 a,b). The basic concept of the technique is to collect water and solutes from select sets of pore classes in order to determine how each set contributes to the bulk flow and transport processes that are observed for the whole system. In heterogeneous systems, a decrease in pressure head (more negative) will cause larger pores, such as fractures, to dram and become nonconductive during solute transport. Since advective flow processes tend to dominate in large pore regimes, a decrease in pressure head, which will restrict flow and transport to smaller pores, will limit the disparity of solute concentrations among pore groups. By minimizing the concentration gradient in the system, the extent of physical nonequilibrium is decreased. Figure 1 conveys this concept by showing the breakthrough curves of a nonreactive Br^- tracer at three different constant pressure heads in an undisturbed column of the weathered fractured saprolite from the ORR. The increasing asymmetry of the breakthrough curves with increasing saturation (less negative pressure head) indicates enhanced preferential flow coupled with mass loss into the matrix. As the soil becomes increasingly unsaturated, breakthrough curve tailing becomes less significant due to a decrease in the participation of larger pores (fractures) involved in the transport process. These findings suggest that mass transfer limitations (nonequilibrium conditions) become increasingly negligible for these unsaturated conditions because fracture flow has been eliminated.

Another example of a useful technique for isolating diffusion or slow time-dependent geochemical reactions involves flow interruption during a portion of a tracer displacement experiment (Murali and Ayhnore, 1980; Brusseau *et. al.*, 1989; Ma and Selim, 1994; Hu and Brusseau, 1995; Reedy et al., 1996; Mayes et al., 1999). The technique involves inhibiting the

flow process during an experiment for a designated period of time, and allowing a new physical or chemical equilibrium state to be approached. When physical nonequilibrium processes are significant in a soil system, the flow-interruption method will cause an observed concentration perturbation for a conservative tracer when flow is resumed Interrupting flow during tracer injection will result in a decrease in tracer concentration when flow is resumed, whereas interruptingflow duringtracer displacement (washout) will result in an increase in tracer concentration when flow is resumed. The concentration perturbations that are observed after flow interrupts are indicative of solute diffusion between pore regions of heterogeneous media. Conditions of preferential flow create concentration gradients between pore domains (physical nonequilibrium), resulting in diffusive mass transfer between the regions. Therefore, during injection tracer concentrations within advection-dominated flow-paths (i.e., fractures, macropores) are higher than those within the matrix. Upon flow interruption, the relative concentration decrease that is observed indicates that solute diffusion is occurring from larger, more conductive pores, into the smaller pores. During tracer displacement or washout, the concentrations within the preferred flow-paths are lower than those within the matrix. Thus, solute diffusion is occurring from smaller pores into larger pores, and a concentration increase is observed when flow interruption has been imposed. The utility of the flow interrupt method for confirming and quantifying physical nonequilibrium can be observed in figure 2 , which shows Br^- breakthrough curves at two fluxes in an undisturbed column of fractured weathered shale from the ORR. The observed concentration perturbations on the ascending and descending limbs of the breakthrough curves are the result of prolonged flow-interrupt and the system approaching a new state of physical equilibrium. The concentration perturbations that are induced by flow interruption are significantly more pronounced at larger fluxes. This is because the system is further removed from equilibrium at the larger fluxes since a greater concentration gradient exists between advectiondominated flow paths and the soil matrix.

These and other techniques for assessing nonequilibrium processes in structured media are discussed by Jardine *et.* al. (1998). When combined, the techniques not only improve our conceptual understanding of time-dependent contaminant migration in subsurface media, they also provide the necessary experimental constraints that are needed for the accurate numerical quantification of the nonequilibrium processes that control solute migration.

Intermediate Scale Assessment of Solute Migration in Fractured Media

A logical progression from laboratory scale undisturbed columns is the use of intermediate scale m-situ pedons for assessing the interaction of coupled processes on the fate and transport of solutes in the fractured weathered shales (Fig. 3). This research scale, unlike the column scale, encompasses more macroscopic structural features common to the field (e.g. dip of bedding planes, more continuous fracture network, convergent flow processes), yet allows for a certain degree of experimental control since the pedon can be hydrologically isolated from the surrounding environment. Numerous undisturbed pedons have been constructed on the ORR for the purpose of monitoring contaminant fate and transport issues. The pedons are undisturbed blocks of soil 2m x 2m x 3m deep, with three excavated sides refilled with compacted soil and a concrete wall with access ports placed in good contact with the front soil face. The pedon is instrumented with a variety of solution samplers designed to monitor water and solutes through various pore regimes as a function of depth. Fritted glass plate lysimeters of varying porosity and bubbling pressures are held under different tensions to derive solutions from large, medium, and small pore regimes (e.g. Jardine et al., 1990s). Large pore samplers have very coarse fritted glass plates that are tension free in order to capture rapid drainage through macropores and fractures. Sampling medium sized pores, such as secondary fractures and mesopores, involves the use of coarse fritted glass plates maintained at tensions between 10-30 cm. Small pore samples (i.e. soil matrix) have fine fritted glass plates that are maintained at 250-500 cm tension and collect water and solutes from the micropore regime. The conductivity of the fine fritted glass is sufficiently low to minimize sampling contribution from medium and large pore regimes.

Numerous tracer experiments have been conducted using both nonreactive and reactive tracers with various steady-state infiltration rates or transient flow conditions driven by storm events (Jardine *et. al.,* 1989, 1990 a,b; Wilson, ORNL, unpublished data). The purpose of the experiments was to determine transport properties and mass transfer rates for the various pore regimes. An example of tracer mobility (Br^-) through the soil for two different infiltration rates can be seen in figure 4. At an infiltration rate of 30 cm/d, Br^- is transported exclusively through medium and small pore regimes indicative of secondary fractures and the soil matrix, respectively. Flow through the large pore regimes, indicative of primary fractures, is essentially excluded since the imposed infiltration velocity is not sufficient to accommodate their conductivity. Larger infiltration rates (e.g. 300 cm/d) did produce flow through the primary fractures, and thus three distinct breakthrough curves

can be observed for tracer movement through primary and secondary fractures, as well as the soil matrix. Large infiltration rates; however, create local-scale perched water tables within the soil, allowing small pore regime samplers to extract a portion of the larger pore water. This is why the ascending limb of the three breakthrough curves at 300 cm/h have diminutive differences. Nevertheless, the distinction of tracer migration through the different pore regions allows for quantitative estimates of distinct pore flow velocities, dispersion coefficients, and mass transfer rates between the pore classes at a scale one-step closer to the realities of the field scale.

Field Scale Assessment of Solute Migration in Fractured Media

Vadose Zone

Waste migration issues at the various DOE facilities throughout the USA are field-scale problems that are complicated by large scale media heterogeneities that cannot be replicated at the laboratory or pedon scale. For this reason, basic research efforts designed to assist with the remediation of contaminated sites must include solute fate and transport experiments at the field-scale. At ORNL, field facilities have been constructed for understanding storm-driven contaminant mobility in the unsaturated zone (Luxmoore and Abner, 1987; Wilson et al., 1993). The facilities contain buried line-sources for tracer release to simulate leakage of trench waste and are equipped with an elaborate array of water and solute monitoring devices. The Melton Branch Watershed field facility is situated on the Conasauga formation and contains the same subsurface material that was used in the disposal of low-level radioactive waste at ORNL. In fact, this field facility houses the intermediate scale pedon and is the location used for excavating undisturbed columns. The most unique feature of the facility is a set of subsurface weirs that collect lateral storm flow from a 2.5m deep by 16m long trench that has been excavated across the outflow region of the subwatershed (Fig. 5). Six massive stainless steel pans serve to intercept subsurface drainage from different portions of the landscape. The three upper pans intercept lateral drainage through the soil A- and B-horizons, and the three lower pans intercept lateral drainage that elutes through the soil C-horizon. Pan intercepted water, as well as overland flow and drainage under the pans, is routed into tipping bucket rain gauges situated in two H-flumes that are equipped with ultrasonic sensors for measuring water levels. The tipping buckets and ultrasonic sensors are equipped with computer data acquisition allowing for real-time monitoring of tracer fluxes during storm events. Besides the ability to

capture subsurface drainage, the field facility is equipped with numerous multilevel solution samplers, tensiometers, and piezometer wells, with the latter used to assess perched water table dynamics during storm events.

Two long-term, storm driven tracer studies have been conducted at this field facility for the purpose of addressing the rates and mechanisms of contaminant mass exchange between the various pore regions of the media An example of how this facility was used to quantify multiregion processes under field-scale transient flow conditions can be found in Wilson *et. al.* (1993), who released a Br^- tracer from the ridgetop buried-line source during a storm event and monitored its mobility through the subsurface for nearly 8 months. During the release they observed that a small portion of the total injected Br^- mass (-5%) migrated very rapidly through the hillslope via lateral storm flow with subsequent export through the weirs which were located 70m from the line source. Calculating the eluted Br^- mass through ail portions of the weir is possible since the total flux of water and the concentration of Br^- are measured with time. Subsequent storm events over the 8 month period resulted in the export of -25% of the injected Br^- mass (e.g. Fig. 6 a). While the actual tracer release revealed a rapid transport through the fracture network of the soil, the mass transfer into the low permeability matrix was significant since >50% of the applied tracer was found to reside within matrix porosity of the soil primarily at a depth of 1 - 1.5m, which is synonymous with where lateral storm flow occurs through the hillslope (Fig. 6 b). Strong evidence indicating matrix-fracture interactions during transient storm flow can be inferred from tracer breakthrough patterns at the subsurface weirs. Storm events that followed the release of tracer resulted in delayed tracer breakthrough pulses relative to the subsurface flow hydrograph (Fig. 6 b). This is caused by the time-dependent mass exchange of soil matrix Br^- with newly infiltrating storm water flowing along fractures. These observations are consistent with stable isotope ($^{18}O/^{16}O$) and solute chemistry (e.g. Si) analyses that revealed that subsurface flow was predominately new water at peak flow (i.e. minimal contribution from the soil matrix) and almost exclusively old water (i.e. significant contribution from the soil matrix) during the descending limb of the subsurface hydrograph. These results suggested that the storm driven export of Br^- through the weirs was the result of tracer mass transfer from the soil matrix into the fracture network with subsequent mobility through the hillslope. The field-scale endeavors provided an improved conceptual understanding of how transient hydrodynamics and media structure controlled the migration and storage of contaminants in the subsurface. The field-scale findings were consistent with the

multiregion conceptual framework established with laboratory and intermediate scale observations of flow and transport through these heterogeneous systems.

Saturated Zone

Lateral moving storm flow is not the only process contributing to the migration of contaminants from primary waste trenches into the surrounding soils. At ORNL, waste trenches were often excavated to depths that approached the bedrock-saprolite interface. Seasonally fluctuating groundwater levels coupled with storm derived perched water-tables allow contaminant to easily access the underlying bedrock. Further, the very nature of the trench design allows for rapid vertical infiltration of storm water and direct connection with the fracture network of the underlying shale bedrock. In an effort to understand the importance of secondary source formation in the shale bedrock, a field facility was established within the saturated zone of a contaminated fractured shale bedrock in Waste Area Grouping 5 (WAGS) on the ORR (Jardine et al., 1999). A transect of multilevel groundwater monitoring wells was established along geologic strike within a fast flowing fracture regime and a slow flowing matrix regime (Fig. 7). A sophisticated computer driven tracer injection system dispenses tracers into the fracture regime under natural gradient conditions. Two long-term steady-state natural gradient experiments, each with a duration of 1.5 to 2 y, have been conducted using multiple nonreactive tracers (Br, He, Ne) and multiple reactive tracers (^{57}Co(II)EDTA, ^{51}Cr(III)EDTA, and ^{109}CdEDTA). The multiple tracer technique takes advantage of the difference in the molecular diffusion coefficients as well as geochemical reactivity between the tracers. The experiments were designed to quantify the significance of fracture flow, matrix diffusion, and chemical reactivity on the formation and longevity of secondary contaminant sources in the shale bedrock.

Jardine *et.al.* (1999) showed the utility of multiple dissolved gas and solute tracers for assessing physical nonequilibrium processes in the fractured shale bedrock. The natural gradient injection of Br^-, He, and Ne was initiated for 6 months, followed by a 12 month washout. Spatial and temporal monitoring of the tracers was performed in the matrix and fracture regimes of the bedrock using the multilevel sampling wells instrumented downgradient from the injection source. Tracers migrated preferentially along strike, and their concentrations in the fracture regime quickly reached a consistent steady-state value. Thus, observed differences in tracer breakthrough into the matrix were a function of their molecular diffusion

coefficients. The breakthrough of the three tracers 6 m from the source and 0.8 m into the matrix relative to the fracture is shown in figure 8. The movement of He and Ne into and from the matrix was more rapid than Br^-, which is consistent with the larger molecular diffusion coefficients of the dissolved gases relative to Br^-. These results supported the notion that matrix diffusion contributed to the overall physical nonequilibrium process that controls solute transport in shale bedrock

At greater distances from the source, the contribution of matrix interactions are still prominent, and tracer breakthrough profiles remain suggestive of a diffusion mechanism, although at first glance this may not be apparent (Figure 8 b, c). At 13 m from the source and 0.6 m into the matrix, the three tracers break though nearly simultaneously, with the concentration of the gas tracers eventually surpassing Br^- (Figure 8 b). This is followed by tracer washout after the input pulse was terminated at 180 d. At 23 m from the source and 0.1 m into the matrix, the movement of Br^- into the matrix is actually more rapid than that of the noble gas tracers, which is exactly opposite of what was observed 6 m form the source. This apparent paradox is caused by the preferential loss of gas tracers to the rock matrix closer to the source. Thus, Br^- remains within the advective flow field (fracture regime) for a longer time period, allowing it to be transported greater distances. Having been transported further downgradient, Br^- experiences the first opportunity to begin diffusing into the matrix at greater distances from the source. Eventually, He and Ne arrive at the same locations and also begin to diffuse into the matrix, lagging behind Br^- (Figures 8 b, c). Because of the larger diffusion coefficients of the noble gases, the movement of He and Ne into the matrix is more rapid and, if given time, the He and Ne breakthrough curves will eventually cross over and surpass the Br^- breakthrough curves (see Figure 8 b as an example). The results of this study showed that secondary contaminant sources form within the bedrock matrix, and that the importance of this source increases with continued contaminant discharge through the bedrock fracture network. This is particularly important for reactive contaminant such as radionuclides, where matrix diffusion can enhance solute retardation by many orders of magnitude.

Geochemical processes also influence the behavior of radioactive contaminant in the subsurface environments. Low-level radioactive waste generated at DOE facilities was typically composed of inorganic fission byproducts mixed with various chelating agents such as ethylenediaminetetraacetic acid (EDTA) (Ayres, 197 1; Toste and Lechner-Fish, 1989; Riley and Zachara, 1992). The presence of the complexing agent alters the geochemical behavior of the disposed contaminant in

subsurface media Thus, afield experiment was conducted to assess the significance of fracture flow, matrix diffusion, and chemical reactivity on the migration of chelated radionuclides from waste trenches into the underlying bedrock The natural gradient injection of ^{57}Co(II)EDTA, ^{51}Cr(III)EDTA, and ^{109}CdEDTA was initiated at the WAGS field facility for 6 months, followed by a 12 month washout. The chelated radionuclides were significantly retarded relative to a nonreactive Br^- tracer (Fig 9) which is contrary to previous conceptual models that suggest chelated radionuclides move conservatively through shale bedrock Retardation mechanisms along fractures involved primarily geochemical processes, whereas retardation mechanisms within the matrix involved primarily physical processes (i.e. diffusion). Along fracture pathways, primary mineral coatings effectively dissociated the radionuclide-chelate complexes with the subsequent formation of $Fe(III)EDTA^-$. The dissociation reaction promotes the rapid stabilization of the free radionuclide as carbonate precipitates. By stabilizing the radionuclide in-situ, the off-site migration of the contaminants is significantly reduced. In many instances, the increased retardation provides sufficient time for short-lived radionuclides such as ^{90}Sr and ^{60}Co (-29 and 5 y, respectively) to decay, thereby eliminating the need for remediation.

Remediation Needs and Basic Research

There are several modes by which our basic research strategies improve remedial options at contaminated sites.

- Basic research provides an improved conceptual understanding of the geochemical and hydrological processes controlling contaminant migration from secondary sources. Such research can unravel complex, time-dependent coupled processes such as preferential flow, matrix diffusion, sorption, and redox transformations in heterogeneous media Basic research strategies designed around novel tracer techniques and experimental manipulations not only improve our conceptual understanding of time-dependent contaminant migration in subsurface media, they also provide the necessary experimental constraints needed for the accurate numerical quantification of the coupled nonequilibrium processes.

- Basic research provides a direct measure of contaminant migration rates along fracture flow paths and into the soil and rock matrix. Such information is critical to contaminant fate and transport modeling and risk assessment

modeling. Too often risk assessment models treat soil and bedrock as inert media or assume that they are in equilibrium with migrating contaminants. Failure to consider the time-dependent significance of secondary contaminant sources will greatly over-predict the off-site contribution of contaminants from the primary trench sources and thus provide an inaccurate assessment of pending risk Basic research provides the necessary information needed for more appropriate risk modeling strategies which can potentially translate into multi-million dollar savings by eliminating the need for certain remedial efforts.

- Basic research endeavors provide information that is necessary for improving our decision-making strategies regarding the selection of effective remedial actions and the interpretation of monitoring results after remediation is complete. Simple distinctions of how fracture networks operate to disseminate contaminants vs. matrix storage mechanistic are basic research issues that can drastically influence the type and cost of remedial effort that is mandated. Basic research endeavors provide a more thorough understanding of coupled transport mechanisms so that remediation concepts are not limited to a purely empirical approach. This will allow engineers to develop remediation strategies targeted at specific problems and with a higher probability of success.

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References

Ayers, J.A. Equipment decontamination with special attention to solid waste treatment. Surv. Rep. BNWL-B-90. Battelle Northwest Laboratories, Richland, WA, 1971.

Brusseau, M.L., P.S.C. 'Rao, R.E. Jessup, and J.M. Davidson. Flow interruption: A method for investigating sorption nonequilibrium. J. Contamin. Hydrol., 4, pp. 223-240, 1989.

Dreier, RB., D.K. Solomon and CM Beaudoin. Fracture characterization in the unsaturated zone of a shallow land burial facility, In: Flow and transport throughunsaturated rock D.D. Evans and T.J. Nicholson, eds., Geophysical Monograph 42, 51-59, 1987.

Hu, Q., and M.L. Brusseau Effect of solute size on transport in structured porous media. Water Resourc. Res., 3 1, pp. 1637-1646, 1995.

Jardine, P.M., G.V. Wilson, and R.J. Luxmoore. Modeling the transport of inorganic ions through undisturbed soil columns from two contrasting watersheds. Soil Sci. Soc. Am. J., 52, pp. 1252-1259, 1988.

Jardine, P.M, G.V. Wilson, R. J. Luxmoore, and J.F. McCarthy. Transport of inorganic and natural organic tracers through an isolated pedon in a forested watershed. Soil Sci. Soc. Am. J., 53, 3 17-323, 1989.

Jardine, P.M., G.V. Wilson, and RJ. Luxmoore. Unsaturated solute transport through a forest soil during rain storm events. Geoderma, 46, pp. 103-l 18, 1990a.

Jardine, PM, G.V. Wilson, J.F. McCarthy, R.J. Luxmoore, D.L. Taylor, and L.W. Zelazny. Hydrogeochemical processes controlling the transport of dissolved organic Con through a forested hillslope. J. Contamin. Hydrol., 6, pp. 3- 19, 1990b.

Jardine, P.M., G.K. Jacobs, and G.V. Wilson Unsaturated transport processes in undisturbed heterogeneous porous media: I. Inorganic contaminants. Soil Sci. Soc. Am. J., 57, pp. 945-953, 1993a.

Jardine, P.M, G.K. Jacobs, and J.D. O'Dell. Unsaturated transport processes in undisturbed heterogeneous porous media: II. Co-contaminants. Soil Sci. Soc. Am. J., 57, pp. 9.54-962, 1993b.

Jardine, P.M., R. O'Brien, Wilson, G.V., and J.P. Gwo. Experimental techniques for confirming and quantifying physical nonequilibrium processes in soils. p. 243-27 1. (In) H.M. Selim and L. Ma. Physical Nonequilibrium in Soils: Modeling and Application. Ann Arbor Press, Inc. Chelsea, Michigan, 1998.

Jardine, P.M., W.E. Sanford, J.P. Gwo, O.C. Reedy, D.S. Hicks, R.J. Riggs, and W.B. Bailey, Quantifying diffusive mass transfer in fractured shale bedrock Water Resour. Res, 35, pp. 2015-2030, 1999.

Kooner, Z.S., P.M. Jardine, S. Feldman. Competitive surface complexation reactions of SO_4^{2-} and natural organic carbon on soil. J. Environ. Qual. 24:656-662, 1995.

Luxmoore, R.J. and C.H. Abner. Field facilities for subsurface transport research. DOE/ER-0329. U.S. Department of Energy, Washington, D.C. p. 32, 1987.

Luxmoore, RJ., P.M. Jardine, G.V. Wilson J.R Jones, and L. W. Zelazny. Physical and chemical controls of preferred path flow through a forested hillslope. Geoderma. 46, pp. 139-154, 1990.

Ma, L., and HM. Selim. Predicting the transport of atrazine in soils: Second-order and multireaction approaches. Water Resourc. Res., 30, pp. 3489-3498, 1994.

Mayes, M.A., P.M. Jardine, I.L. Larsen, and S.E. Fendorf. Multispecies contaminant transport in undisturbed columns of weathered fractured shale. J. Contamin. Hyclrol. 2000 (in press).

Murali, V., and L.A.G. Aylmore. No-flow equilibration and adsorption dynamics during ionic transport in soils. Nature. 283, pp. 467-469, 1980.

Reedy, O.C., P.M. Jardine, G.V. Wilson, and H.M. Selim. Quantifying the diffusive mass transfer of nonreactive solutes in columns of fractured saprolite using flow interruption. Soil Sci. Soc. Am. J., 60, pp. 1376-l 384, 1996.

Riley, RG., and J.M. Zachara. Chemical contaminants on DOE lands and selection of contaminant mixtures for subsurface science research DOE/ER-0547T. U.S. Gov. Print Office, Washington, D.C., 1992.

Seyfried, MS., and P.S.C. Rao. Solute transport in undisturbed columns of an aggregated tropical soil: Preferential flow effects. Soil Sci. Soc. Am J., 51, pp. 1434-1444., 1987.

Toste, A.P., and Lechner-Fish. Organic digenesis in commerical, low-level nuclear wastes. Radioact. Waste Manag. Nucl. Fuel Cycle, 12, pp. 291-301, 1989.

Watson RW., and R.J. Luxmoore. Estimating macroporosity in a forest watershed by use of a tension infiltrometer. Soil Sci. Soc. Am. J., 50, pp. 578-582, 1986.

Wilson, G.V., and RJ. Luxmoore. Infiltration, macroporosity, and mesoporosity distributions on two forested watersheds. Soil Sci. Soc. Am. J., 52, pp. 329-335, 1988.

Wilson, G.V., J.M. Alfonsi, and P.M. Jardine. Spatial variability of saturated hydraulic conductivity of the subsoil of two forested watersheds. Soil Sci. Soc. Am. J., 53, pp. 679-685, 1989.

Wilson, G.V., P.M. Jardine, and J.P. Gwo. Modeling the hydraulic properties of a multiregion soil. Soil Sci. Soc. Am. J., 56, pp. 1731-1737, 1992.

Wilson, G.V., P.M. Jardine, J.D. O'Dell, and M. Collineau Field-scale transport from a buried line source in variable saturatedsoil. J. Hydrol., 145, pp. 83-109, 1993.

Wilson, G.V., J.P. Gwo, P.M. Jardine, and R.J. Luxmoore. Hydraulic and physical nonequilibrium effects on multi-region flow and transport. p. 3761 (In) HM Selim and L. Ma Physical Nonequilibrium in Soils: Modeling and Application. Ann Arbor Press, Inc. Chelsea, Michigan, 1998.

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Figure

Breakthrough curves for a nonreactive Br^- tracer as a function of pressure head (h) in an undisturbed column of fractured weathered shale. For conditions where h=0 cm, transport occurred under saturated flow and the entire fracture network was conductive. When h=- 10 cm the primary fracture network became non-conductive, and when h=- 15 cm primary fractures and a portion of the secondary fractures became non-conductive. The model-fitted curves used the classical convective-dispersive model with optimization of the dispersion coefficient to the observed data [modified from Jar-dine, P.M., et al., Soil Sci. Soc. Am. J., 57, 945-953, 1993a. With permission].

Figure 2

Breakthrough curves with flow interruption, at two specific discharges for a nonreactive Br^- tracer in an undisturbed column of fractured weathered shale. Flow interruption was initiated for 7 days after (a) approximately 4 and 11 pore volumes of tracer were displaced at a flux of 4 1 cm d^{-1} and (b) approximately 4, 5, and 10 pore volumes of tracer were displaced at a flux of 475 cm d^{-1}. The solid lines represent simulations using a two-region model with optimization of the mass transfer coefficient, a, that accounts for mass exchange between different pore regions [modified from Reedy, O.C., et al., Soil Sci. Soc. Am. J., 60, 1376-1384, 1996. Withpermission].

Figure 3

Cross-sectional diagram of the soil block (pedon) facility (2 m x 2 m x 3 m deep) that was used for tracer transport investigations in fractured weathered shale. The inset illustrates the fritted glass solution samplers that were installed laterally within the soil as a function of depth. Each depth interval contained a coarse, medium, and tine frit sampler that

were held at different tensions for the purpose of extracting pore water from primary fractures, secondary fractures, and the soil matrix, respectively. [modified from Jardine, P.M et al., Geoderma, 46, 103-l 18, 1990a. With permission].

Figure 4
Breakthrough curves for a nonreactive Br^- tracer in discrete pore regimes during two infiltration experiments on the fractured weathered shale soil block At an infiltration rate of 30 cm d^{-1} (a), only secondary fractures and the soil matrix are conductive, whereas at an infiltration rate of 300 cm d^{-1} (b), both primary and secondary fractures, and the soil matrix are conductive.

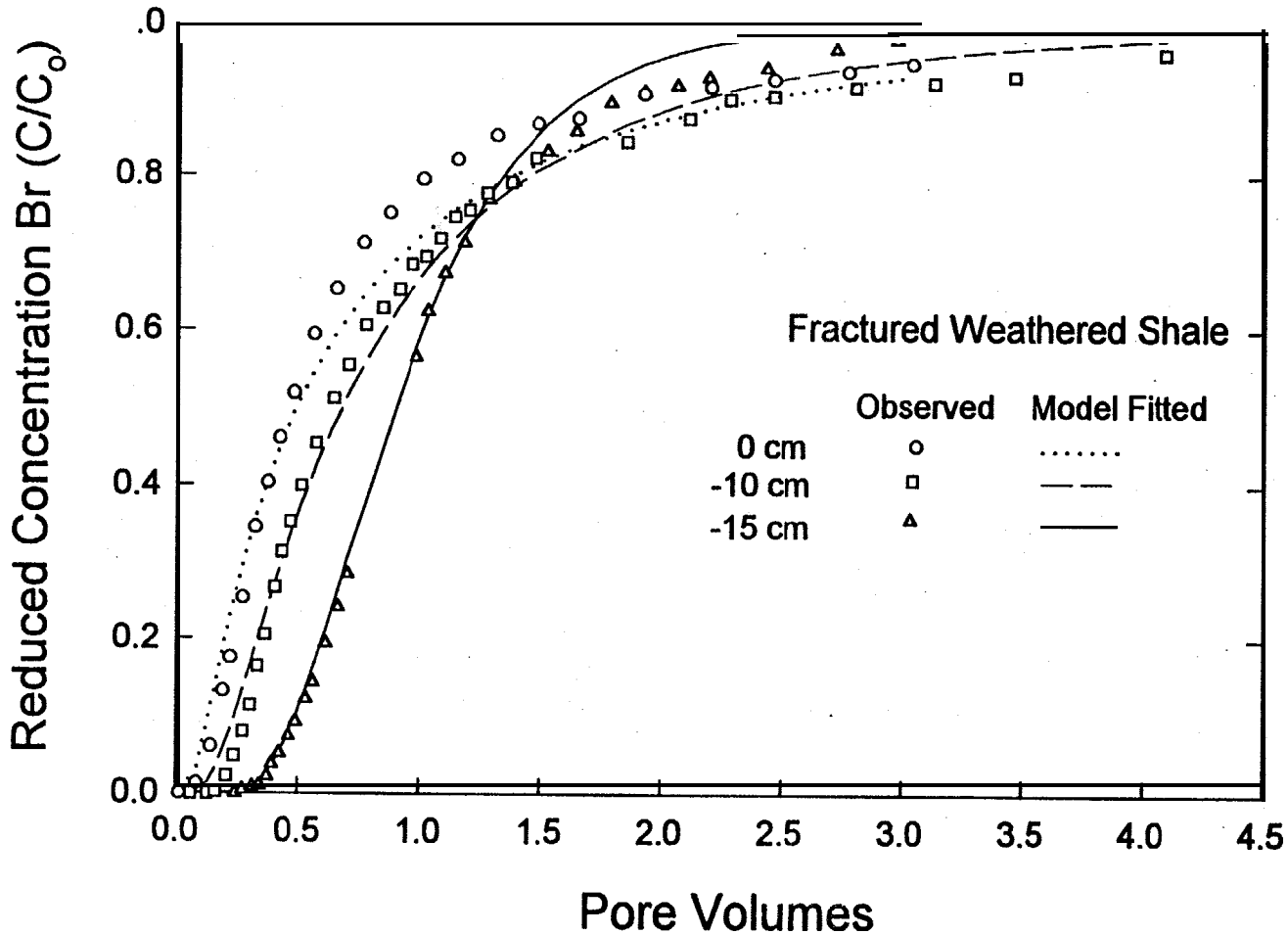
Figure 5
Schematic illustration of the subsurface weirs that intercept lateral storm flow from the subcatchment that is used for field scale tracer injection experiments in the fractured weathered shale soil. The upper illustration depicts the six stainless steel pans pressed against the trench face (-40 m^2 area) for collecting free-lateral flow, and the lower illustration shows the two H-flumes that contain tipping bucket rain gages and ultrasonic sensors for continuous monitoring of subsurface flow [from Wilson G.V, et al., J. Hydrol., 145, 83-109, 1993. With permission].

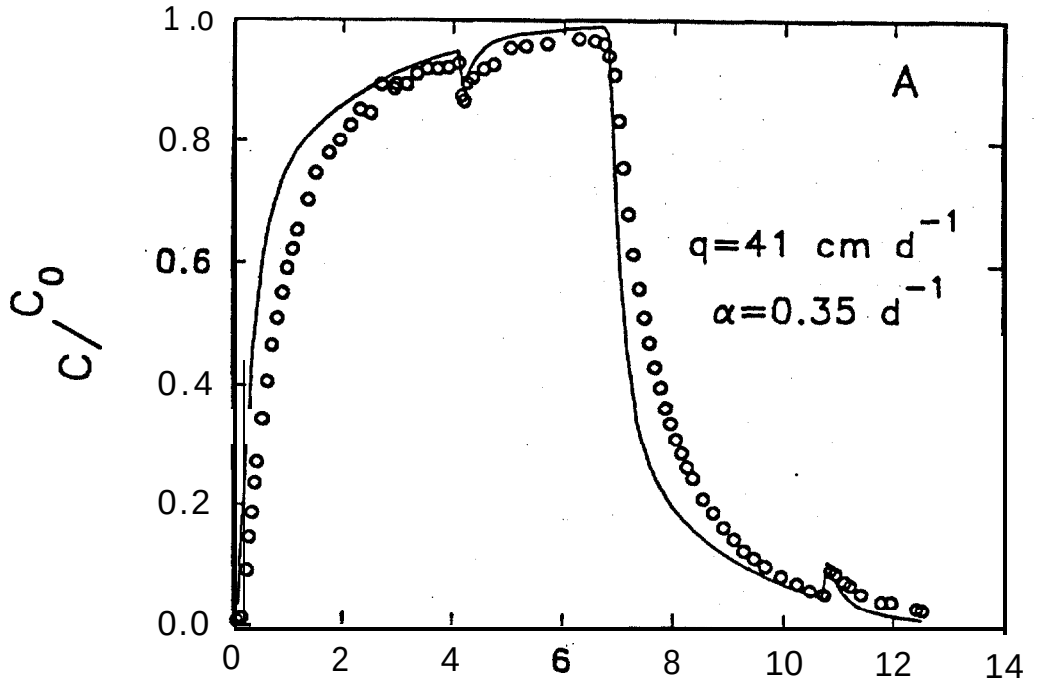
Figure 6
Storm flow and soil matrix tracer results following a release of Br^- at the field scale tracer injection facility in the fractured weathered shale soil. The upper graph (a) shows an example of a subsurface flow hydrograph (solid line) for the lower flume that resulted from a storm event, with the corresponding Br^- concentrations from the C-horizon (lower pans) and from flow beneath the lower pans. The lower graph (b) shows Br^- residence concentrations from the soil matrix as a function of depth for six sampling locations (see Wilson et al., 1993 for site coordinates) downslope of the line source where tracer was released [modified from Wilson, G.V., et al., J. Hydrol., 145, 83-109, 1993. With permission].

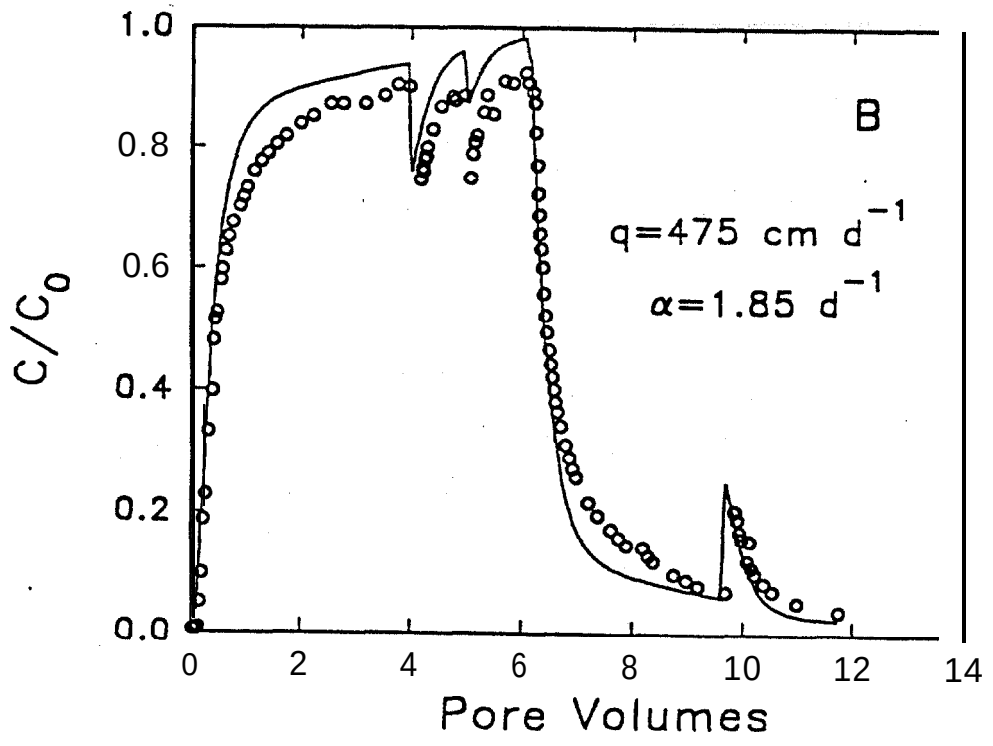
Figure
Cross-section of the experimental field facility in the saturated zone of a contaminated fractured shale bedrock showing the location and sampling depth of all groundwater monitoring wells, with well 40 14 serving as the tracer injection well. The wells form a strike parallel transect from the waste trenches to a seep that drains into a cross-cutting tributary. The approximate locations of the fracture and matrix regimes are also illustrated Numbers designate specific wells and letters designatemultilevel sampling ports within a given well [from Jardine, P.M et al., Water Resour. Res., 35, 2015-2030, 1999. With permission].

Figure
Observed breakthrough of three nonreactive tracers (He, Ne, and Br) within the matrix regime of the shale bedrock, at 6 m (well 8), 13 m (well 17a), and 23 m (well 18a) from the source (a, b, c, respectively). The three tracers have different free water molecular diffusion coefficients with He>Ne>Br [modified from Jar-dine, P.M. et al., Water Resour. Res., 3 5,201 5-2030, 1999. With permission].

Figure 9
Observed breakthrough of three reactive chelated radionuclides (^{57}Co(II)EDTA, ^{109}CdEDTA, and ^{51}Cr(III)EDTA) and the nonreactive tracer Br^- within the fracture regime of the shale bedrock 6 m from the source [Jardine, P.M. et al., ORNL., 1999, unpublished data].

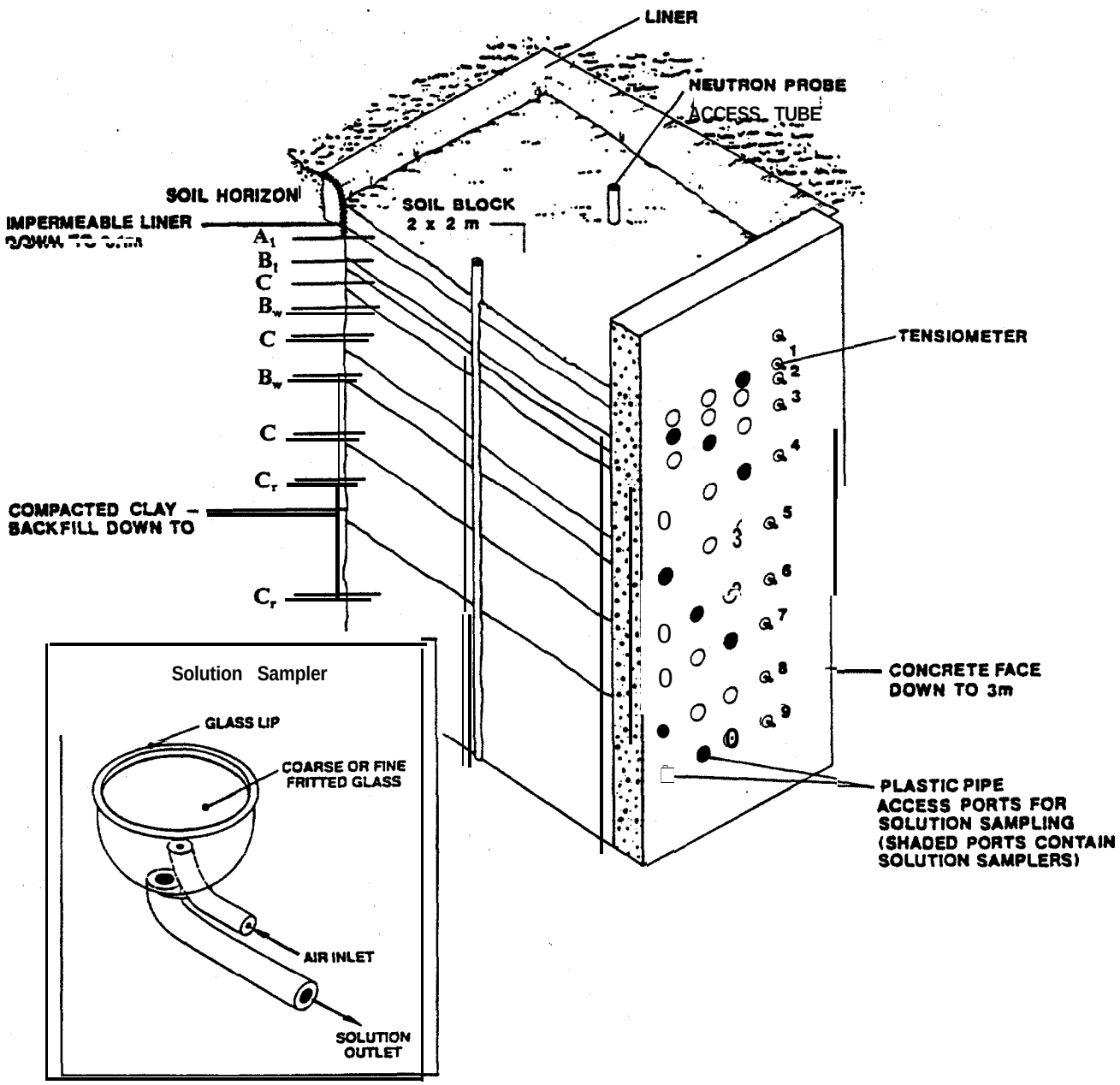

Reduced Concentration Br (C/C$_o$)
.0
0.8
0.6
0.4
0.2
0.0
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
Pore Volumes
Fractured Weathered Shale
Observed
Model Fitted
0 cm
-10 cm
-15 cm

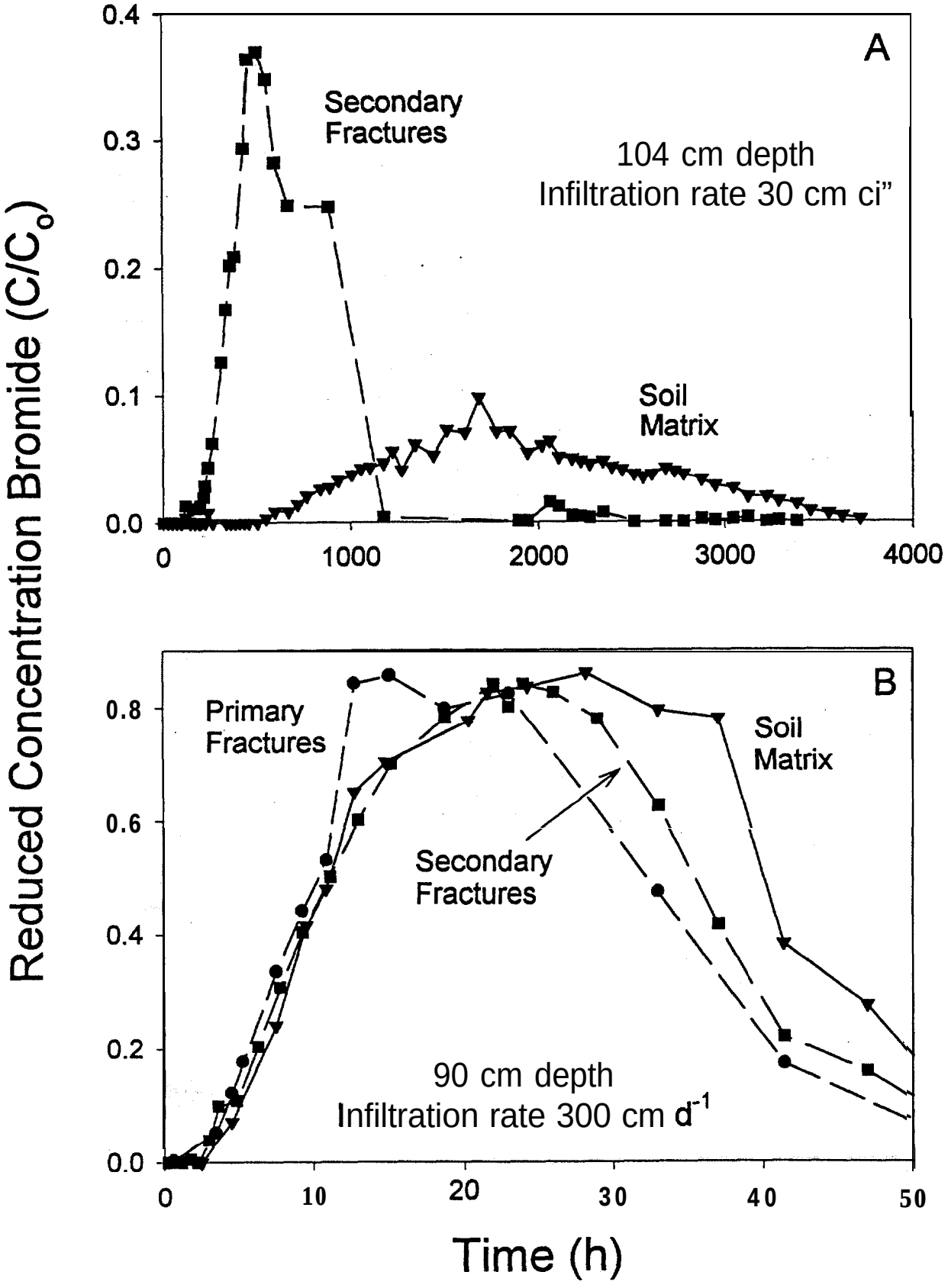

A
q=41 cm d^{-1}
α=0.35 d^{-1}
C/C$_0$
1.0
0.8
0.6
0.4
0.2
0.0
0
2
4
6
8
10
12
14


B
q=475 cm d^{-1}
α=1.85 d^{-1}
C/C$_0$
1.0
0.8
0.6
0.4
0.2
0.0
0
2
4
6
8
10
12
14
Pore Volumes

ORNL-DWG 88-1755

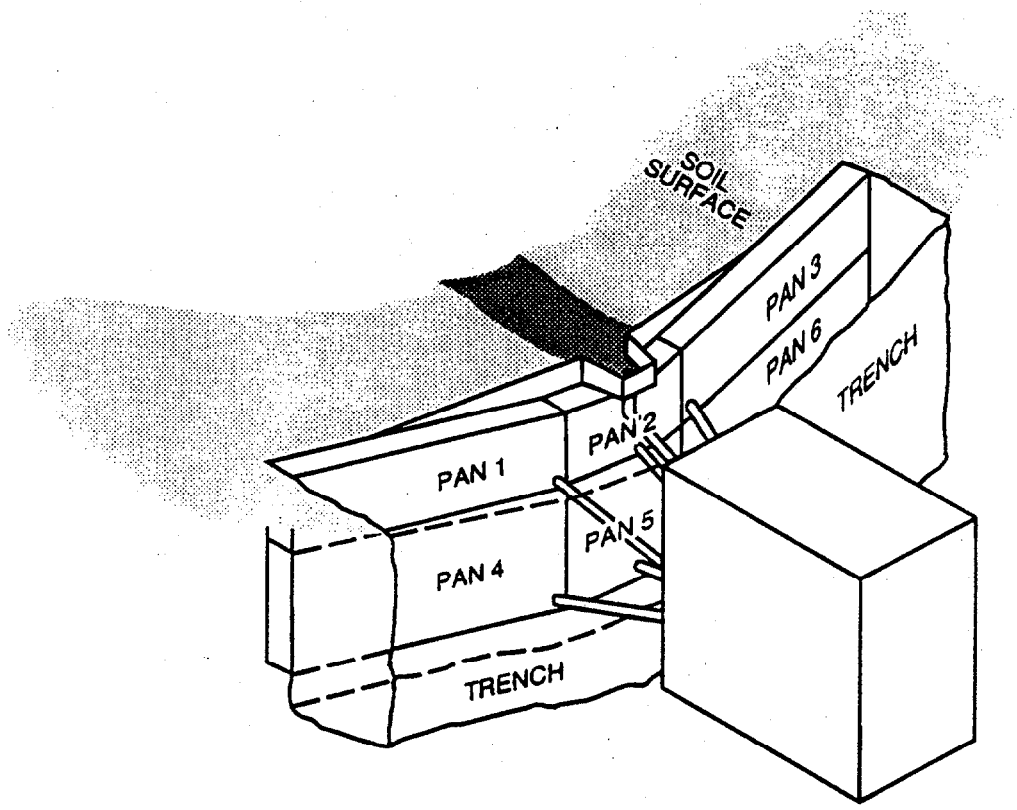
SOIL PEDON

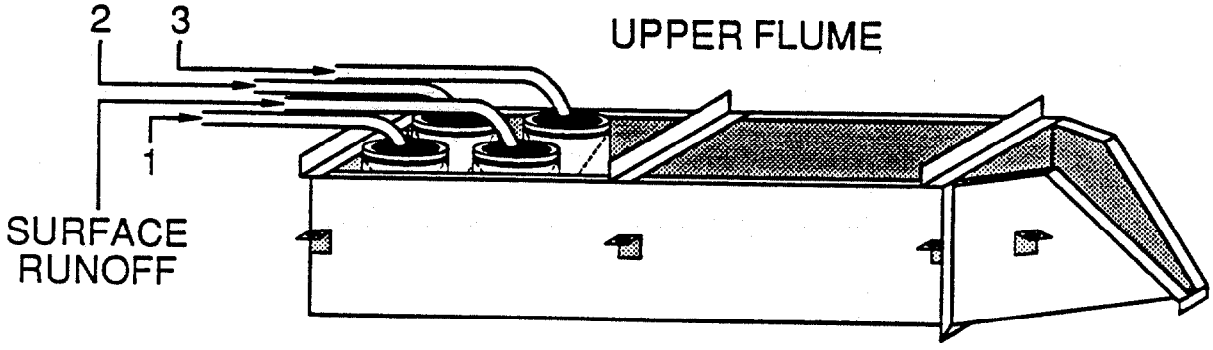


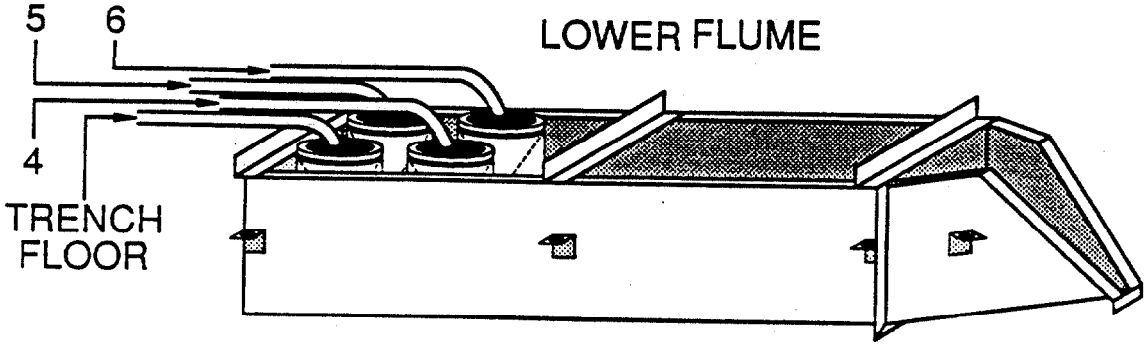

A
Secondary
Fractures
104 cm depth
Infiltration rate 30 cm ci"
Soil
Matrix
0.4
0.3
0.2
0.1
0.0
0
1000
2000
3000
4000
B
Primary
Fractures
Soil
Matrix
Secondary
Fractures
90 cm depth
Infiltration rate 300 cm d-1
0.8
0.6
0.4
0.2
0.0
0
10
20
30
40
50
Reduced Concentration Bromide (C/Co)
Time (h)

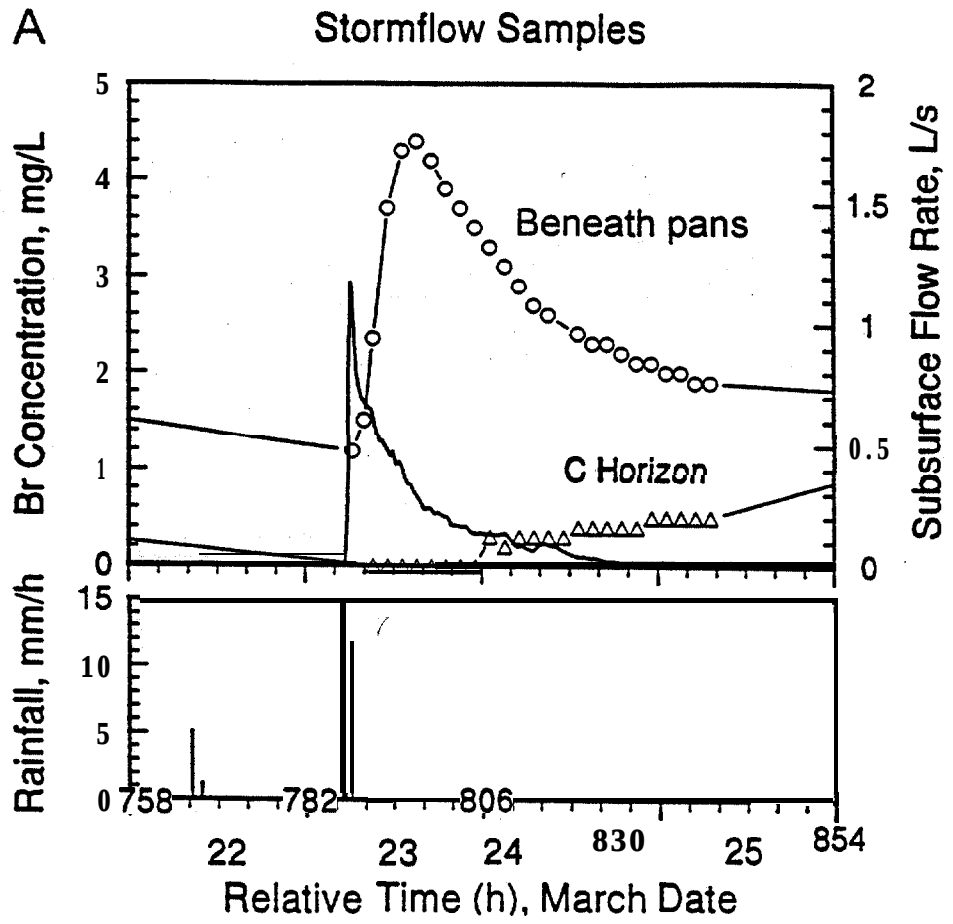
ORNL DWG 90M-4998

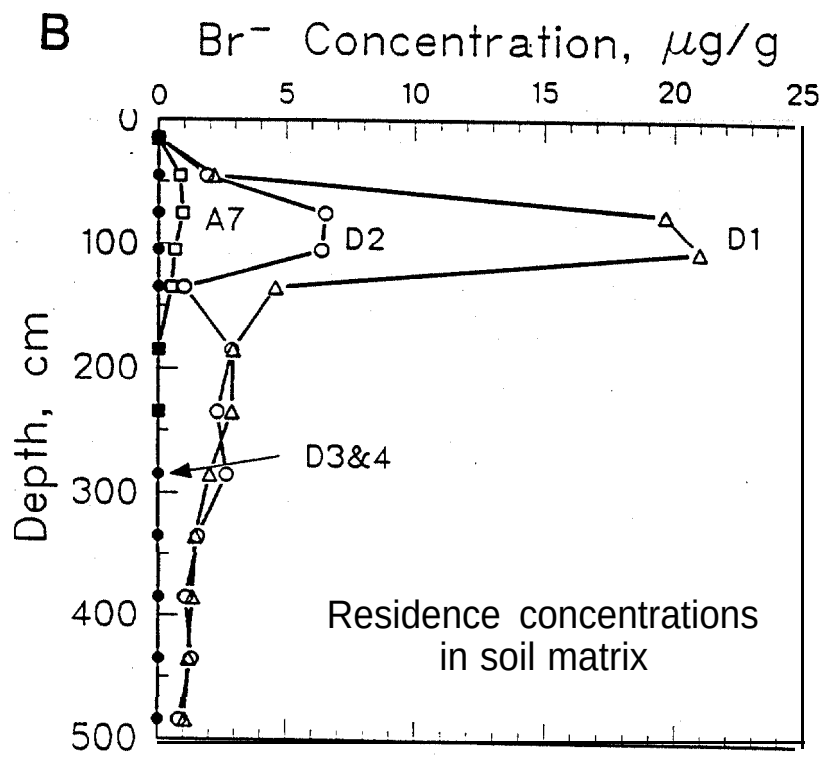
SURFACE- AND SUBSURFACE-FLOW WEIR AND MONITORING CELLAR

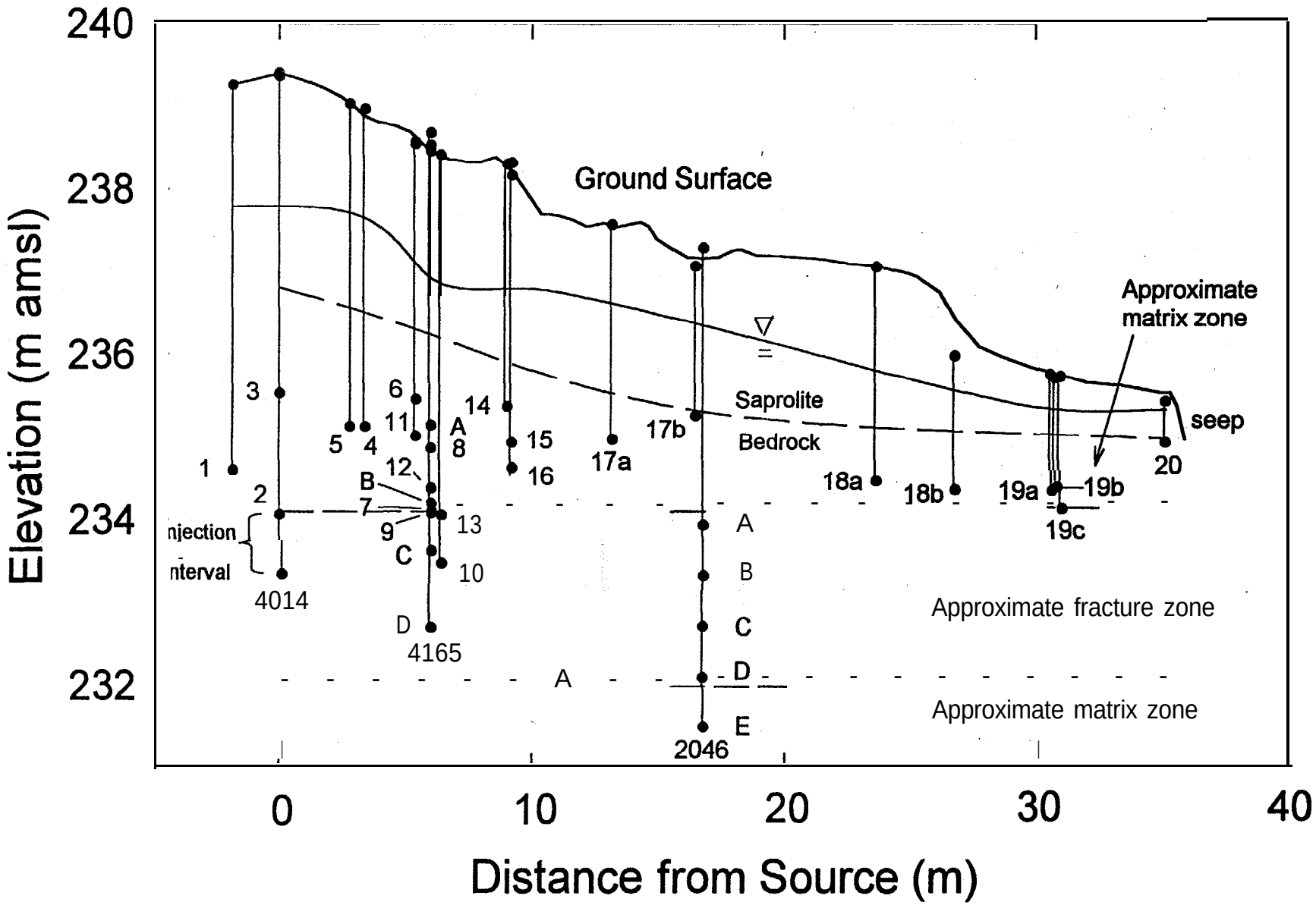


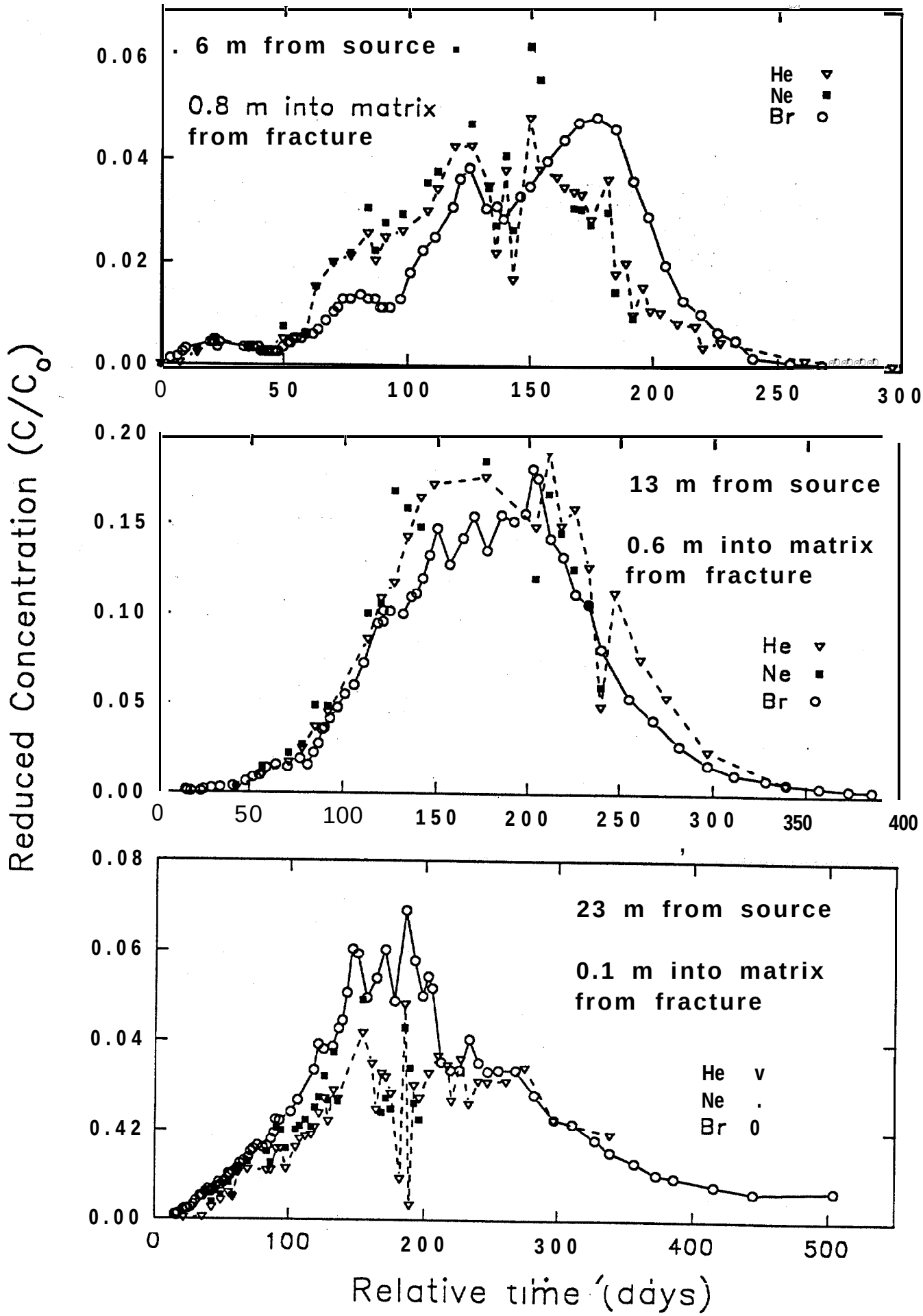


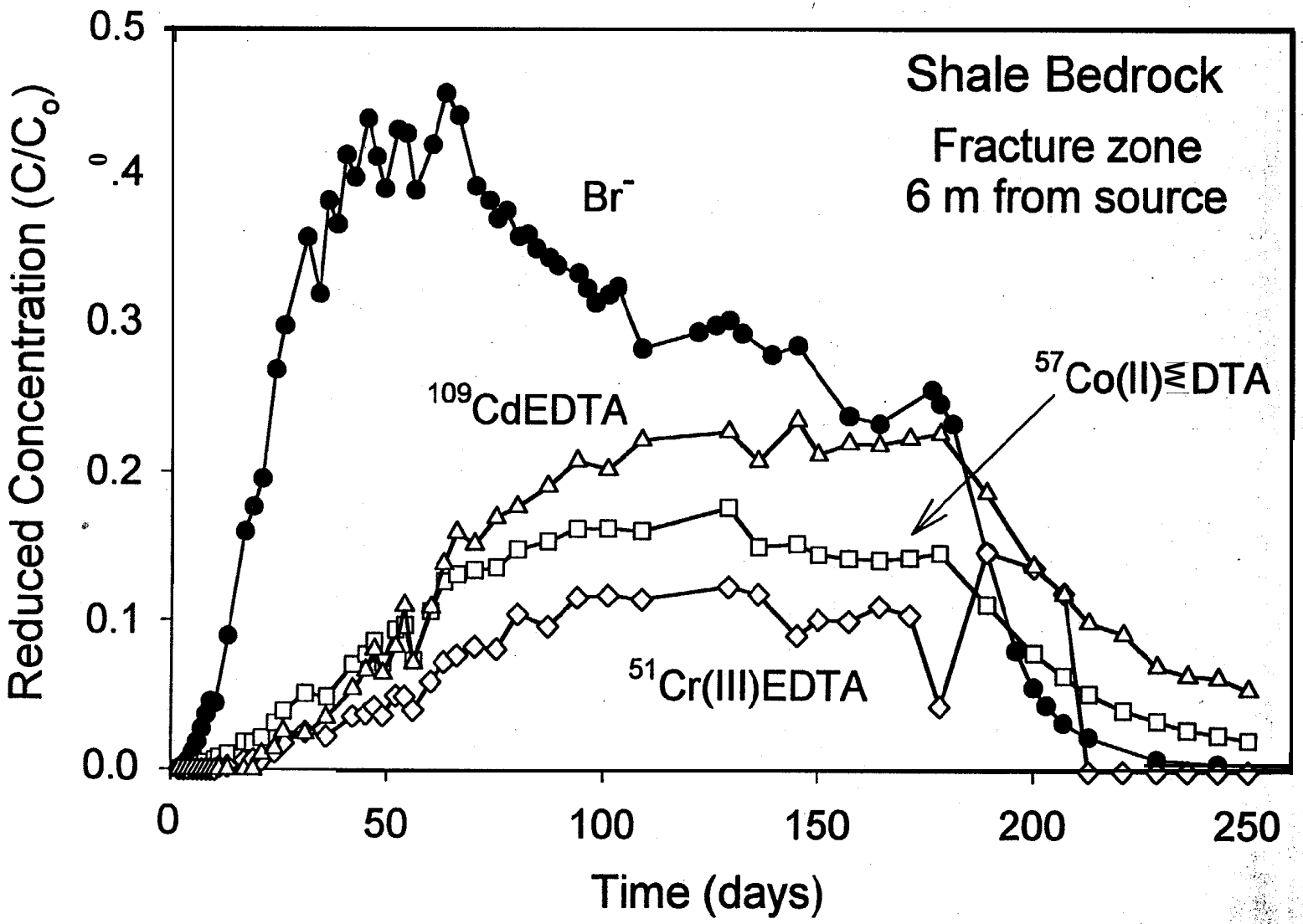



A
Stormflow Samples
Br Concentration, mg/L
Subsurface Flow Rate, L/s
Beneath pans
C Horizon
Rainfall, mm/h
758
782
806
830
854
22
23
24
25
Relative Time (h), March Date


B
Br⁻ Concentration, μg/g
Depth, cm
A7
D2
D1
D3&4
Residence concentrations
in soil matrix


Elevation (m amsl)
240
238
236
234
232
Ground Surface
Approximate matrix zone
Saprolite
Bedrock
seep
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17a
17b
18a
18b
19a
19b
19c
20
A
B
C
D
E
4014
4165
2046
Approximate fracture zone
Approximate matrix zone
0
10
20
30
40
Distance from Source (m)


6 m from source
0.8 m into matrix
from fracture
He
Ne
Br
13 m from source
0.6 m into matrix
from fracture
He
Ne
Br
23 m from source
0.1 m into matrix
from fracture
He
Ne
Br
Reduced Concentration (C/C$_o$)
Relative time (days)


Shale Bedrock
Fracture zone
6 m from source
Br⁻
109CdEDTA
57Co(II)EDTA
51Cr(III)EDTA
Reduced Concentration (C/Co)
Time (days)
0.5
0.4
0.3
0.2
0.1
0.0
0
50
100
150
200
250