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Vadose Zone Flow and Transport of Dissolved Organic Carbon at Multiple Scales in Humid Regimes

P. M. Jardine,* M. A. Mayes, P. J. Mulholland, P. J. Hanson, J. R. Tarver, R. J. Luxmoore, J. F. McCarthy, and G. V. Wilson

ABSTRACT

Scientists must embrace the necessity to offset global CO_2 emissions regardless of politics. Efforts to enhance terrestrial organic carbon sequestration have traditionally focused on aboveground biomass and surface soils. An unexplored potential exists in thick lower horizons of widespread, mature soils such as Alfisols, Ultisols, and Oxisols. We present a case study of fate and transport of dissolved organic carbon (DOC) in a highly weathered Ultisol, involving spatial scales from the laboratory to the landscape. Our objectives were to interpret processes observed at various scales and provide an improved understanding of coupled hydrogeochemical mechanisms that control DOC mobility and sequestration in deep subsoils within humid climatic regimes. Our approach is multiscale, using laboratory-scale batch and soil columns (0.2 by 1.0 m), an in situ pedon (2 by 2 by 3 m), a well-instrumented subsurface facility on a subwatershed (0.47 ha), and ephemeral and perennial stream discharge at the landscape scale (38.4 ha). Laboratory-scale experiments confirmed that lower horizons have the propensity to accumulate DOC, but that preferential fracture flow tends to limit sequestration. Intermediate-scale experiments demonstrated the beneficial effects of C diffusion into soil micropores. Field- and landscape-scale studies demonstrated coupled hydrological, geochemical, and microbiological mechanisms that limit DOC sequestration, and their sensitivity to local environmental conditions. Our results suggest a multi-scale approach is necessary to assess the propensity of deep subsoils to sequester organic C in situ. By unraveling fundamental organic C sequestration mechanisms, we improve the conceptual and quantitative understanding needed to predict and alter organic C budgets in soil systems.

Enhancement of soil carbon sequestration is a potential means for offsetting the adverse effects of the human-induced rise in atmospheric CO_2 (USDOE, 1999). The organic C pool in the upper 1 m of the world's soils is estimated to contain 1220 Gt organic C, which is nearly twice that of inorganic sources and about 1.5 times the total for standing biomass (Sombroek et al., 1993; Trumbore, 1997). This organic C pool within the upper soil layers (O and A horizons), is highly dynamic, being strongly influenced by changes in land use and manipulation (i.e., deforestation, agricultural practices, fertilization). Turn-over times of this soil organic C are on the order of years to decades (Sombroek et al., 1993; Balesdent and Recous, 1997; van Dam et al., 1997). Methods for protecting this C pool from oxidation and erosion provide an opportunity for sequestration. Widespread, highly developed mature soils such as Alfisols, Ultisols, and Oxisols have deep soil profiles that have a tremendous capacity to sequester organic C. The physical and chemical properties (acidic pH, abundant clay, and Fe oxides) of the lower horizons (B horizons) within these soils are ideal for maximizing organic C sorption to the solid phase (Sibanda and Young, 1986; Jardine et al., 1989a, 1989b, 1990a; McCarthy et al., 1993; Benke et al., 1999). This passive C pool is significantly less dynamic than the C in upper soil horizons since it is strongly stabilized on mineral surfaces with estimated turnover times of millennia and longer (Trumbore, 1997). The potential storage capacity of these lower horizons is estimated in the hundreds of gigatons (Brandt and Jardine, ORNL, unpublished data). Janssens et al. (2003) and Siemens (2003) suggested that DOC moving vertically through soil profiles is the "missing" C flux in the global budget.

There are examples of sustained subsoil organic C sequestration in the tropics where anthropogenically enriched Oxisol soils of the Amazon have maintained mineral stabilized organic C for a minimum of several centuries (Sombroek et al., 1993). In a similar manner, Humic Rhodic Eutrustox soils of the tropics are organic rich Oxisols with more than 16 kg C m^{-2} at depths greater than 1 m. This is several times higher than a typical Oxisol. Why? The Humic Rhodic Eutrustox soils are managed with low-input agriculture such that they have the opportunity to sequester organic C in deeper horizons. These soils support some of the largest human population densities in the world. However, many soil lower horizons are nowhere near saturation with respect to surface-bound DOC. So why is it that organic C sequestration in lower soil horizons is not typically observed in situ when laboratory studies (Tipping, 1981a, 1981b; Davis and Glour, 1981; Jardine et al., 1989b; Dunnivant et al., 1992; Baham and Sposito, 1994; Gu et al., 1995, 1996a, 1996b; Wan and El-Swaify, 1998) suggest that conditions are favorable?

We present a case study of DOC subsurface fate and transport at multiple scales. A variety of previously published site-specific studies from the laboratory scale to the landscape scale are interpreted in an effort to unravel the geochemical and hydrological mechanisms that control organic C mobility and sequestration in deep subsoils from high recharge humid regimes. We show how a multiscale experimental approach is critical to assessing the propensity of subsoils to sequester organic C in situ.

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Abbreviations: DOC, dissolved organic carbon; SSTF, Subsurface Transport Facility; S_t, sorption maxima.

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METHODS

Multiscale Approach and Site Descriptions

Our approach involves a multiscale experimental endeavor using laboratory-scale batch and soil columns (0.2 by 1.0 m), an intermediate-scale in situ pedon (2 by 2 by 3 m), a well-instrumented field facility on a subwatershed (0.47 ha), and empherial and perennial stream discharge at the landscape scale (38.4 ha) (Fig. 1). The study site is located on the Walker Branch Watershed in eastern Tennessee, USA, which is situated within the U.S. Department of Energy's Oak Ridge Reservation. The pedon and subwatershed infrastructures are known collectively as the Subsurface Transport Facility (SSTF) and are described in detail by Luxmoore and Abner (1987).

The Walker Branch mean annual temperature is 14.5°C, and mean annual rainfall is approximately 1400 mm yr^{-1}. About 50% of infiltrating precipitation contributes to surface water (40%) and groundwater recharge (10%). Watershed topography is characterized by broad ridges with relatively steep slopes (some exceeding 40%) and narrow stream valleys. Vegetation is second-growth deciduous forest dominated by oak (*Quercus* spp.) and hickory (*Carya* spp.), with scattered pine (*Pinus* spp.) on some of the ridge tops and mesophytic hardwoods such as tulip poplar (*Liriodendron tuliperfera* L.) and beech (*Fagus grandifolia* Ehrh.) in the valleys.

Soil depths range from a meter or less near the stream to about 30 m on the ridge tops. They are highly weathered Ultisols (fine loamy, siliceous, thermic Typic Paleudults), derived from Chepultepec dolomite. The dolomite is Lower Ordovician in age and is the lowest member of the Knox Group. In general, the soils have a 10-cm-thick A horizon above well-developed EB and Bt subsoil horizons. Solid phase organic C ranges from 3.5% in the A horizon to 0.1% in the lower B horizons (Jardine et al., 1989a). The soils have acidic (pH 4–5) B horizons with clay fractions dominated by kaolinite and lesser quantities of hydroxy-Al interlayered vermiculite. Clay material is often coated with 2 to 4% Fe oxides, primarily as hematite and maghemite (Arnseth and Turner, 1988; Jardine et al., 1988, 1989a). The bulk density of the B horizon is 1.4 to 1.5 g cm^{-3}.

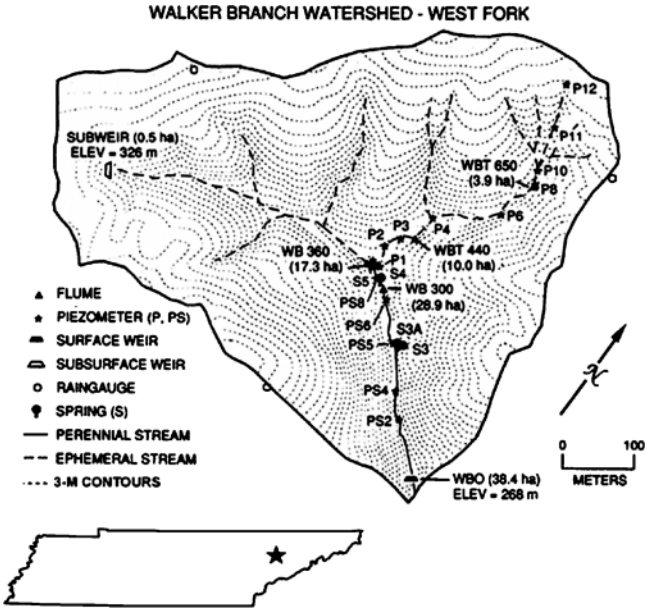

Fig. 1. Schematic of the West Fork portion of the Walker Branch Watershed showing the Subsurface Transport Facility (subweir on far left), collection points of ephemeral and perennial stream discharge (from Mulholland et al., 1990), and location of watershed in Tennessee.

Soils are highly structured and conducive to preferential flow and matrix diffusion. Subsoils consist of a complex continuum of pore regimes ranging from large macropores at the millimeter scale to small micropores at the submicrometer scale (Luxmoore, 1981; Wilson and Luxmoore, 1988; Wilson et al., 1989). The pore structure of the media is hydrologically interconnected where water and solute mass can move from one pore class to another via hydraulic and concentration gradients (Nkedi-Kizza et al., 1983; Seyfried and Rao, 1987; Jardine et al., 1988, 1990a, 1990b, 1993a, 1993b; Reedy et al., 1996; Mayes et al., 2003). Larger pores tend to carry solutes deeper into the soil profile, whereas smaller pores act as source–sinks and store solutes for relatively long time periods. Other select site-specific hydrological, physical, and chemical properties have been documented by Wilson and Luxmoore (1988), Jardine et al. (1990a, 1990b), Wilson et al. (1989, 1990, 1991a, 1991b), and Luxmoore et al. (1990).

Batch and Undisturbed Column Scale

Large undisturbed soil columns (0.2-m diam., 0.6-m length) and bulk soils were obtained from the SSTF on the Walker Branch Watershed. An additional 20 bulk soil samples of different series type were also collected by horizon throughout the 38-ha watershed. Bulk samples were air dried and passively ground to pass a 2-mm sieve. Organic C adsorption isotherms were performed at a constant ionic strength of 0.01 using NaCl, constant indigenous soil pH, and room temperature as described in Jardine et al. (1989a). The DOC source was obtained from a surface stream near a peat deposit in either Georgetown, SC, or Hyde County, NC. Both sources are very similar, and the chemical characteristics of these sources are described in Jardine et al. (1989a, 1989b), Dunnivant et al. (1992), McCarthy et al. (1993), and Gu et al. (1995).

Undisturbed columns were obtained as described by Jardine et al. (1988) and were used to investigate laboratory-scale saturated flow, fate, and transport of injected Georgetown DOC. The nonreactive tracer bromide was also coinjected with the DOC to track the movement of the aqueous phase. Constant-head miscible displacement experiments were performed as described by Jardine et al. (1988).

Intermediate Pedon Scale

The pedon used in this study is a well-instrumented, well-characterized soil block (2 by 2 by 3 m) located at the SSTF (Fig. 2 and 3). The pedon is hydrologically isolated so that tracer infiltration studies can be performed under controlled or rain-fed conditions. The face of the soil block has a concrete wall with PVC access ports for instrumentation. The other three sides were filled with compacted clay rich soil from the site. Water dynamics were monitored with tensiometers instrumented laterally within the pedon as a function of depth and with neutron probe access tubes extending vertically through the profile. Twenty-seven plate-type fritted glass solution samplers are also instrumented horizontally within the pedon, with three samplers installed at each of nine depths (Fig. 2). At any sampling depth down to 2.8 m, two coarse and one fine porosity fritted glass solution samplers were installed as described by Jardine et al. (1989b, 1990a, 1990b). The coarse porosity fritted glass samplers have bubbling pressures of about 30 cm and are designed to collect water and solutes from macropores and mesopores (preferential flow paths). The fine

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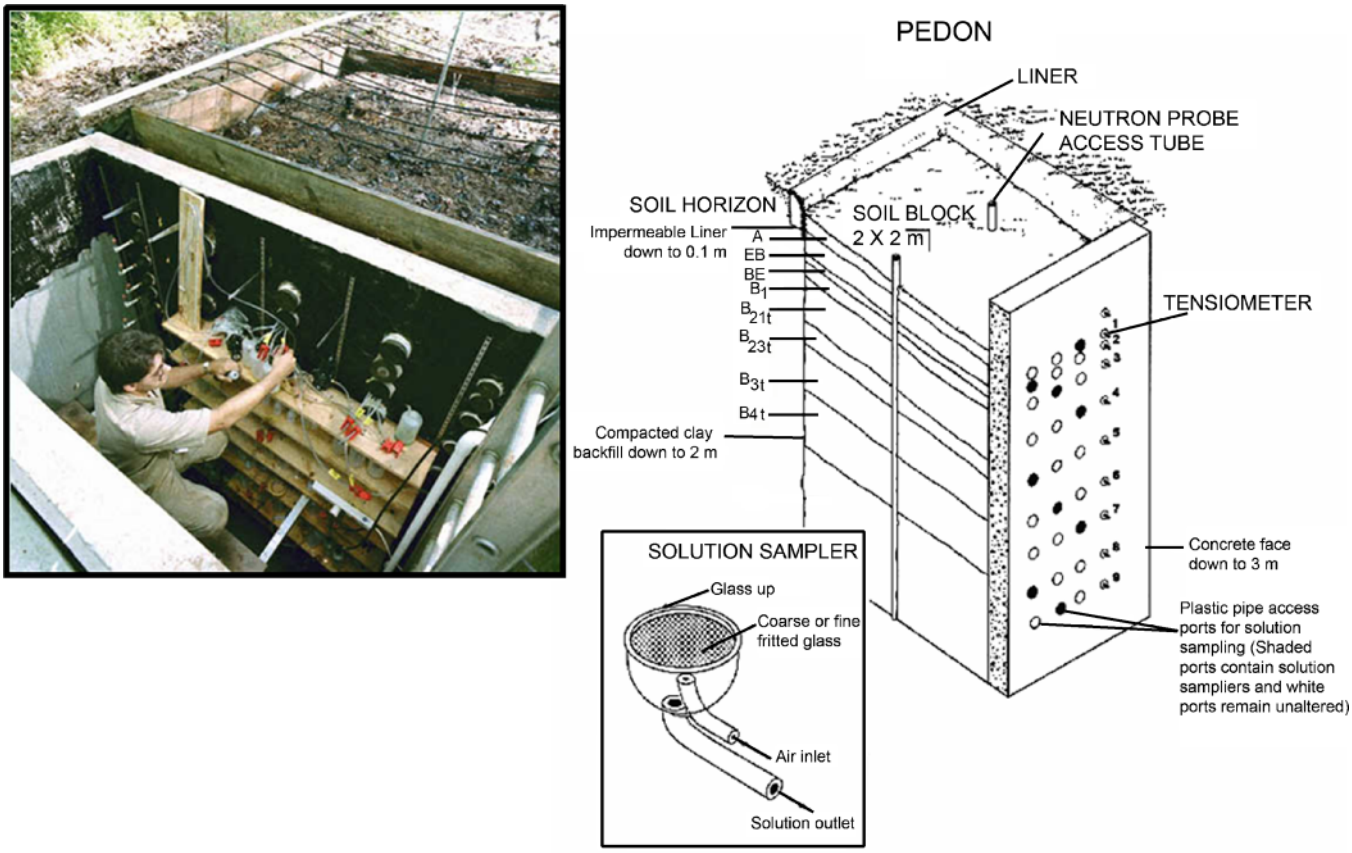

Fig. 2. Pictorial and schematic views of the pedon at the Subsurface Transport Facility. The schematic shows the location of solution samplers and tensiometers with depth and an example of a typical solution sampler instrumented laterally into the pedon.

porosity fritted glass samplers have bubbling pressures of about 500 cm and are designed to collect water and solutes primarily from the micropores of the soil matrix. The flow and transport processes of the pedon have been characterized using nonreactive and reactive tracers at different water contents (Jardine et al., 1990a, 1990b).

Two experiments were conducted on the pedon, one under satiated (near saturated) steady-state conditions and one under unsaturated transient-flow conditions. The former experiment involved steady-state injection of DOC obtained from Hyde County, NC, as described above. Nonreactive NO_3^- and reactive NH_4^+ were also injected, and the various solutes were monitored with time and depth as described by Jardine et al. (1989b). Unsaturated flow experiments involved monitoring the rain-fed transport of DOC as a function of time and depth as described in Jardine et al. (1990b).

Field Scale

The field-scale experiments were conducted at the SSTF by means of a subcatchment (0.47 ha) on the West Fork of the Walker Branch Watershed (Fig. 1, 3, and 4). It is located in the uppermost hillslope approximately 500 m from the upper portion of a perennial stream. Soils are highly weathered, well-structured Ultisols with profiles approximately 30 m thick. As with most well-developed, fine-textured soils, the clay content and bulk density of the material increase with depth. During appreciable storm events, infiltration through this lower subsoil can be restricted, causing transient perched water tables that initiate lateral subsurface flow (Wilson et al., 1990, 1991a, 1991b). In an effort to quantify lateral solution and solute fluxes through this system, a trench 13 m long and 2.5 m deep was dug across the outflow region of the subcatchment (Fig. 4). Six massive stainless-steel pans were braced against the upslope face of the trench (Fig. 3 and 4). The top three pans have their bottom edges in the lower portion of the $2B_t1$ horizon (≈1 m) and they serve to intercept drainage from the A, E/B, B_t, and $2B_t1$ horizons. The bottom three pans collect flow from the $2B_t2$ to the $4B_t6$ horizons. A surface collector monitors convergent overland flow, and drainage beneath the lower pans is also captured. Flow from the eight collectors is routed into tipping-bucket rain gauges interfaced for computer data acquisition. Thus, the total flux of solution and solutes can be assessed from the various landscape positions during storm events. The rain gauges are located within two H flumes, so that if flow exceeds the gauge capacity of the bucket, the total flow from the upper horizons and lower horizons can still be determined with ultrasonic flow sensors (Fig. 3 and 4). Thus, the weirs provide exceptional vadose zone flow and transport mass balance at the field scale, something that traditional point source measurements via monitoring wells cannot provide. The area above these subsurface weirs is also instrumented with 2 throughfall collectors, 45 suction-solution samplers, 75 tensiometers, and 45 piezometers at various depths. The piezometers are equipped with pressure transducers interfaced with the computer data acquisition system for continuous monitoring of perched water table dynamics. The physical, chemical, and mineralogic properties of the soils, including solid phase organic C, at this facility have been extremely well characterized in past efforts. The site hydrology is well known, as are storm-driven indigenous solute fluxes. The transport of DOC and other constituents were monitored for a variety of storm events as described in Jardine et al. (1990b).

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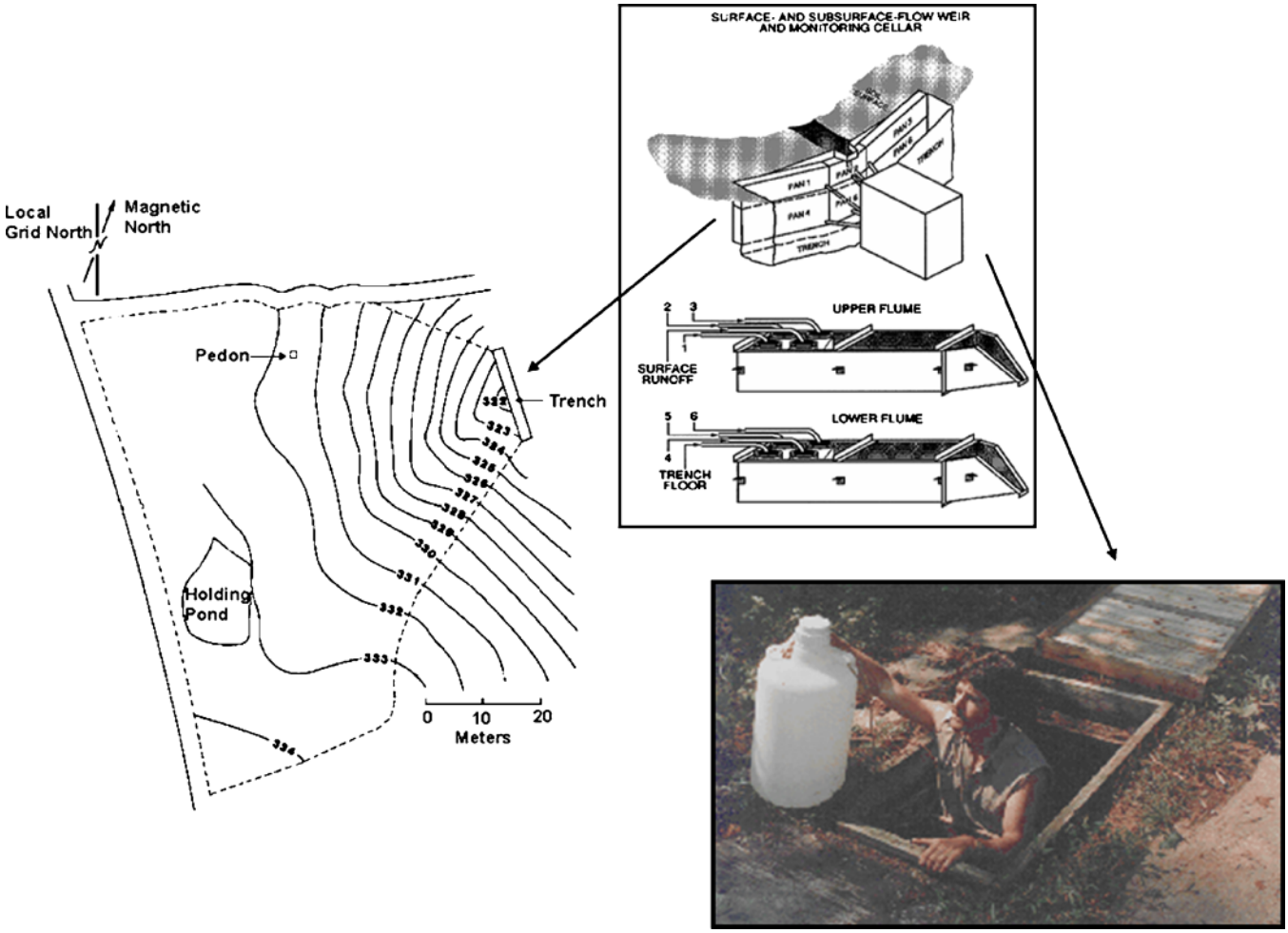

Fig. 3. Pictorial and schematic view of the Subsurface Transport Facility showing (a) birdseye view of the subwatershed, (b) schematic of the subsurface pans and weirs, and (c) an individual entering the weir from the ground surface.

Landscape Scale

This portion of the study was conducted in the West Fork of Walker Branch Watershed which is about 38 ha in size (Fig. 1). The adjacent East Fork is about 59.1 ha and was not considered in this study. The upper watershed is drained by a first-order stream that is fed by numerous springs and a network of ephemeral stream channels. Flow in the ephemeral stream channels occurs only in response to storm events and usually persists for a few days. Surface runoff from catchments ranging from 3.9 ha to the entire 38.4-ha watershed was monitored by a network of flumes and weirs installed on the ephemeral streams and perennial streams. The flumes were all downslope from the SSTF (Fig. 1). Groundwater levels were also monitored using shallow piezometers at numerous locations along the ephemeral and perennial streams. Water samples were collected and monitored for DOC and other solutes as a function of space and time for numerous storms as described in Mulholland et al. (1990). Storm sampling efforts were coordinated with storm monitoring activities at the SSTF where the subsurface weirs and pedon are located.

RESULTS AND DISCUSSION

Batch and Column Scale

Adsorption isotherms for DOC interaction with Walker Branch soils indicated that a significant quantity of DOC can be attenuated by the soil, with the potential for sequestration dependent on the solution concentration (Fig. 5). Soil samples from lower B horizons have significantly larger C sorption capacities relative to upper A, E, A/E, and B/E horizons. This is because B horizons are generally more acidic, clay and Fe oxide rich, and have lower indigenous surface-bound C, all of which promote enhanced sorption of added organic C (Jardine et al., 1989a). The B-horizon soils already contain 0.1% indigenous organic C (1000 mg C kg soil^{-1}) and Fig. 5 shows that these lower horizons have the potential to sequester an additional two to three times that amount. However, the amount of sequestration is dependent on the concentration of organic C in the pore water. The mechanisms of organic C adsorption on soils have been characterized in the laboratory where hydrophobic interactions, cation bridging, anion exchange, and ligand exchange reactions may all contribute to organic C solid phase association (Tipping, 1981a, 1981b; Davis and Glour, 1981; Jardine et al., 1989b; Dunnivant et al., 1992; Baham and Sposito, 1994; Gu et al., 1995, 1996a, 1996b; Wan and El-Swaify, 1998; Kahle et al., 2004). Hydrophobic interactions often dominate the sorption process, and this is supported by the preferential adsorption of hydrophobic organic species vs. hydro-

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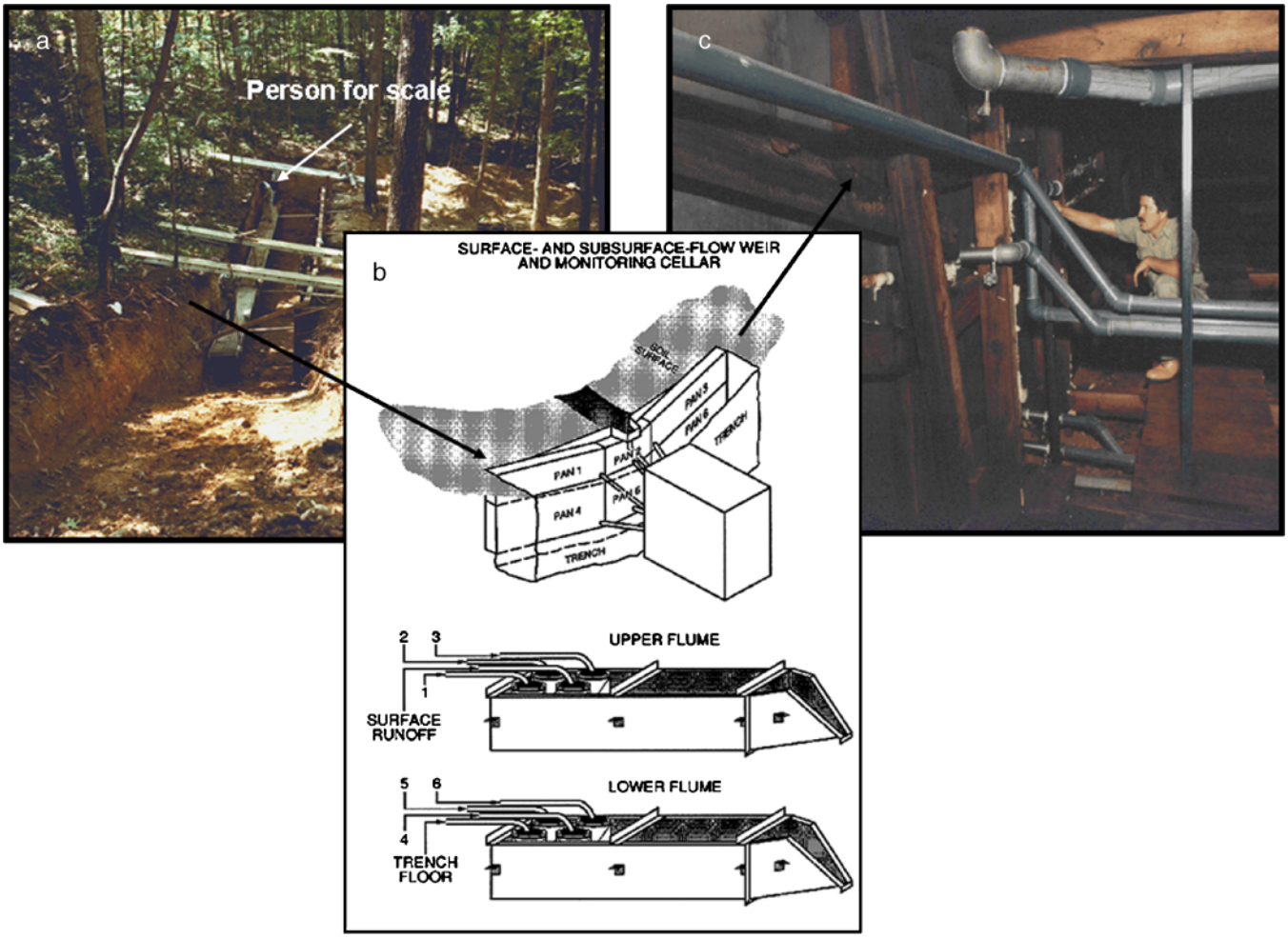

Fig. 4. Pictorial and schematic view of the Subsurface Transport Facility showing (a) excavation of the draw region before pan installation, (b) schematic of the subsurface pans and weirs, and (c) an individual next to the underground pans.

philic organic species (Jardine et al., 1989a; Dunnivant et al., 1992; Kaiser and Zech, 1997; Guo and Chorover, 2003; Ussiri and Johnson, 2004). Because weak positive sorbate–sorbent interactions overcome extremely weak solute–solvent interactions, the hydrophobic organic solutes are adsorbed by the soil through an entropy-driven process related to the destruction of highly structured water surrounding the solvated DOC macromolecule (Hassett et al., 1981).

Adsorption isotherms were modeled with the Langmuir equation in an effort to obtain estimates of the maximum organic C sorption (S_t) to a particular soil (Fig. 6). Data fits were generally excellent, with very good 95% confidence limits for the estimated S_t parameter. The S_t parameter was used in a multiple regression modeling strategy where soil physical and geochemical properties (e.g., particle size, Fe oxide content, clay content) served as the independent variables. It was noted that the clay content of the soils could explain 68% of the variability in the S_t parameter, suggesting that this particle fraction dominated the sorption process (Fig. 7). Similar findings were reported by Donald et al. (1993) and Moore and Turunen (2004); however, Percival et al. (2000) found that clay content was not related to the long-term C accumulation in New Zealand soils. The results for the Walker Branch soils also contrast similar efforts on a variety of Ultisol and Inceptisol soils from

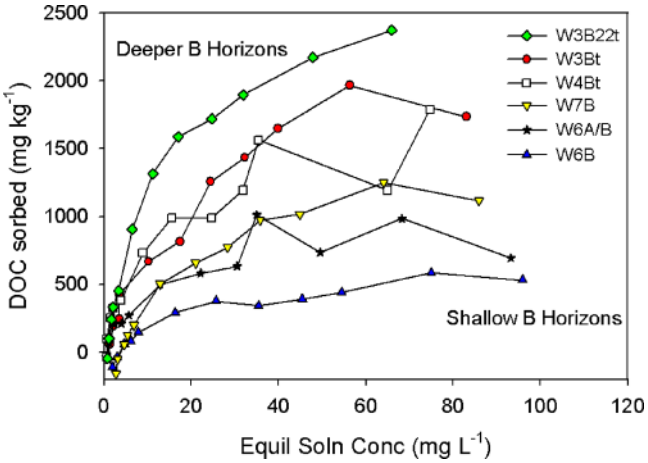

Fig. 5. Equilibrium sorption isotherms for dissolved organic carbon (DOC) adsorption on various soils from the Walker Branch Watershed at constant pH, ionic strength of 0.01 *M* NaCl, and 298 K. W3B22t through W6B represent B horizon soils of increasing depth within the Walker Branch Watershed.

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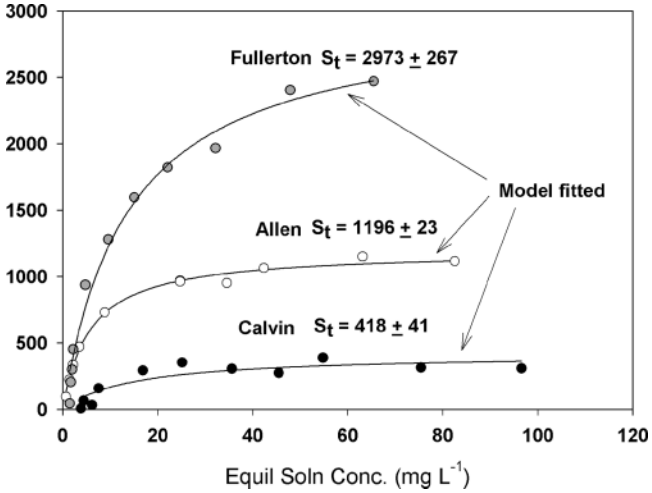

Fig. 6. Observed and model fitted equilibrium dissolved organic carbon (DOC) adsorption isotherms using the Langmuir equation. Model fitted parameter S_t is the maximum DOC sorbed by the soil with its corresponding 95% confidence interval.

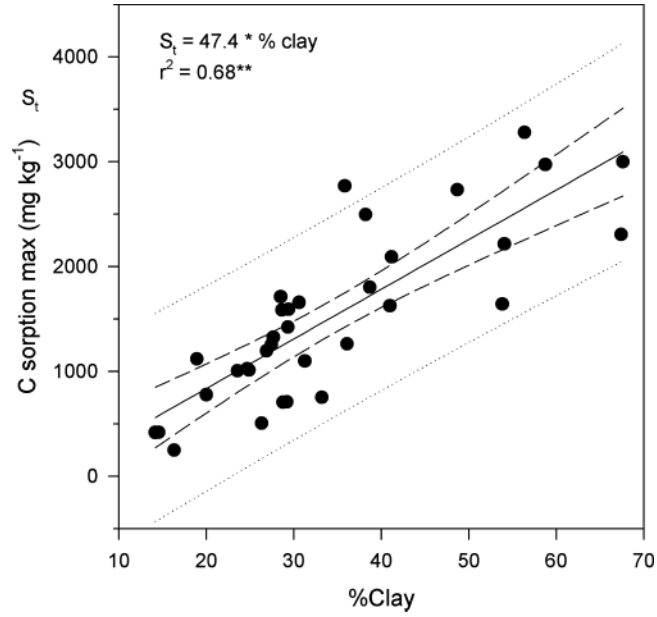

Fig. 7. Maximum dissolved organic carbon (DOC) sorbed (S_t) by a variety of Walker Branch subsoils as a function of clay percentage.

the southeast that showed Fe oxides controlled nearly 75% of the variability in organic C sorption (Fig. 8). More than likely, both clay content and Fe oxides control organic C sorption, as shown by Jardine et al. (1989a), with standard statistics possibly being insensitive to the contribution of each toward C sorption.

Saturated flow and transport of DOC was also investigated in undisturbed soil columns from the Walker Branch Watershed. Breakthrough concentration profiles were nearly identical to nonreactive tracers due to extreme preferential flow through the macroporous media of the soil (data not shown for the current study; Jardine et al., 1988). The hydrodynamics of the system were such that the residence time of DOC in the soil was too short for geochemical interactions to be of significance. Conflicting laboratory-scale results suggested the need for field studies of coupled hydrological and geochemical processes to determine if in fact the subsoils could truly serve as a sink for organic C being transported through the profile.

Intermediate Pedon Scale

The transport of nonreactive and reactive inorganic solutes and DOC was investigated through the upper 1.2 m of an isolated in situ pedon on the Walker Branch

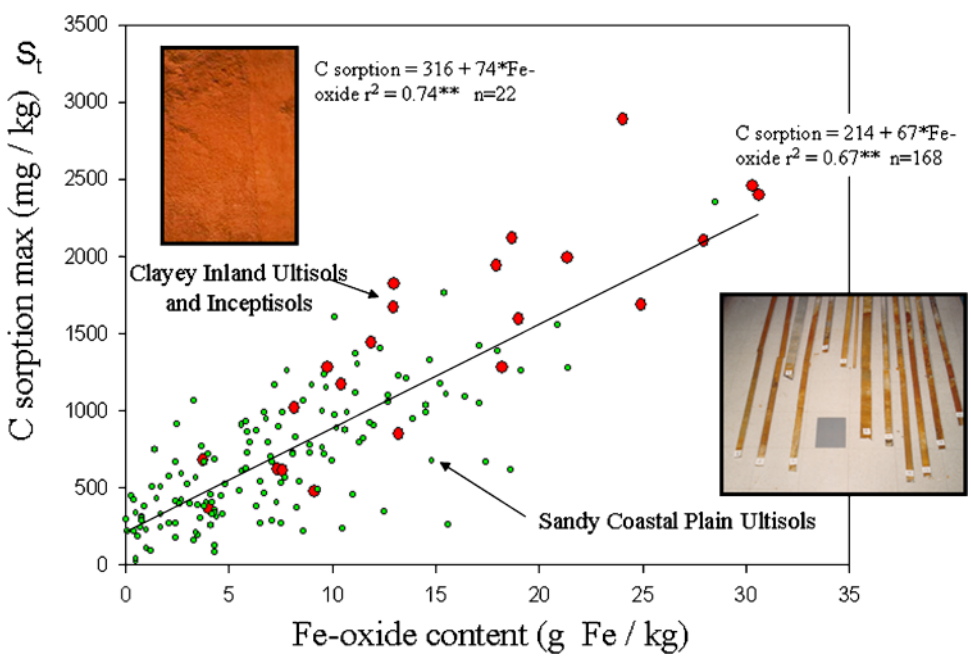

Fig. 8. Maximum dissolved organic carbon (DOC) sorbed (S_t) by a variety of soils on the Oak Ridge Reservation and the Coastal Plain of South Carolina as a function of Fe oxide content.

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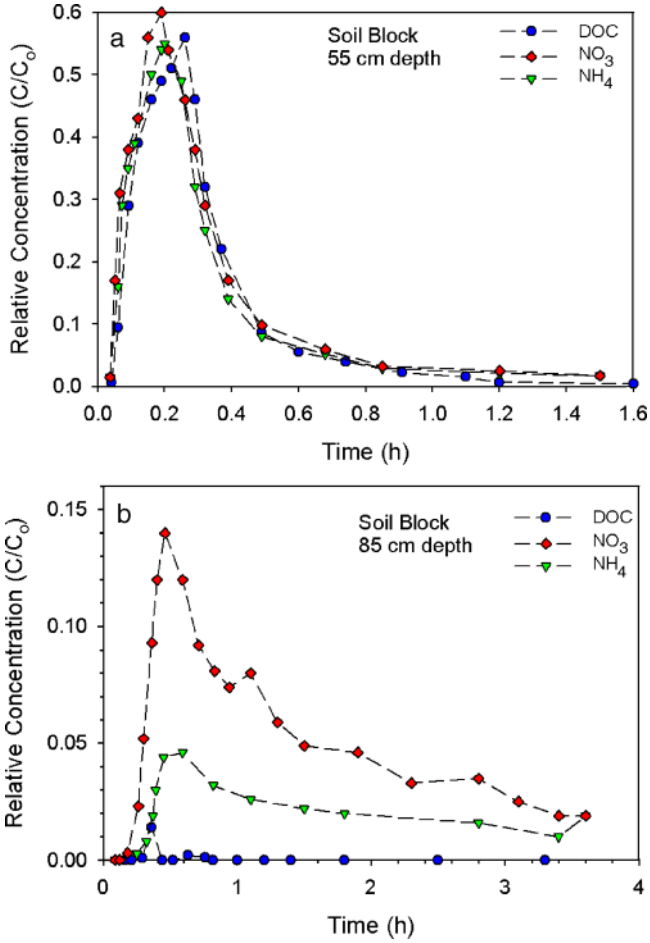

Fig. 9. Observed NO_3^-, NH_4^+, and dissolved organic carbon (DOC) effluent concentrations at the (a) 55-cm and (b) 85-cm depth locations in the pedon (from Jardine et al., 1989b).

Watershed (Fig. 2). The pedon provides an experimental scale-up closer to field conditions by encompassing new phenomena and allowing for multidimensional flow and transport (i.e., macroscopic geologic features are better conserved relative to core scale). It also allows for manipulation and control of solute transport behavior for defining coupled processes that operate at the field scale. Near-saturated and storm-driven C dynamics were investigated in two separate studies using the Walker Branch pedon (Jardine et al., 1989b, 1990b).

For near-saturated conditions, the steady-state injection of DOC was rapidly applied to the satiated pedon and allowed to infiltrate. The pulse was immediately followed with a steady-state continuous pulse of water for about 5 h. Nonreactive NO_3^- and reactive NH_4^+ were also injected in a separate identical experiment, and the various solutes were monitored with time and depth as described by Jardine et al. (1989b). Biological degradation of NO_3^- and DOC was not an issue due to the short duration of the experiments. Observed breakthrough curves for nonreactive NO_3^- transport through the pedon showed skewed pulses indicative of preferential flow (Fig. 9a and 9b). In all sampling locations except at the 55-cm depth, DOC and NH_4^+ had delayed and reduced breakthrough concentration profiles relative to NO_3^-, indicating that they were being sorbed by the soil. The sorption of DOC was dramatic at several locations where the pore water velocity was lower and the residence time of the solution was longer (Fig. 9b). However, where preferential flow was dominant, both DOC and NH_4^+ were nonreactive with the solid phase and essentially followed a similar path as nonreactive NO_3^- (Fig. 9a). Under conditions of rapid preferential flow, movement through the soil limits the solute residence time and decreases the amount of potentially reactive sites that can attenuate the solutes since the soil matrix is bypassed (Kalbitz et al., 2000). These findings were consistent with the laboratory investigations described above where DOC can be significantly retarded deep in the soil profile as long as advective preferential flow does not dominate the transport process.

A year after the above experiment was conducted, storm-driven organic C dynamics were investigated in the pedon and the transport of indigenous C was monitored as a function of depth (Jardine et al., 1990b). Since the system is unsaturated we were able to quantify the influence of pore size on organic C movement in these structured soils. Near the surface the concentration of DOC moving through large pores was consistently higher than that moving through small pores during rain events (Fig. 10). At lower profile depths (B horizons), where DOC reactivity with the soil was greater, the reverse is true. At these deeper depths, the concentration of DOC in small pores was two to three 3 times higher than small pore concentrations at shallow depths. This is consistent with the findings of Jardine et al. (1990a), who showed that small pores had a larger

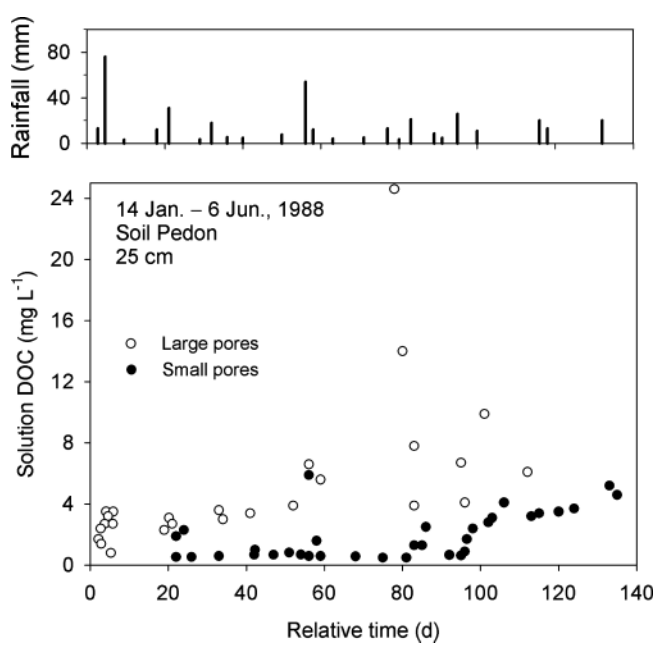

Fig. 10. Concentration of solution dissolved organic carbon (DOC) in large and small pores at the 25-cm depth in the pedon during a series of storm events. Sampling times are relative to time zero which 1200 h, 14 Jan. 1988 (from Jardine et al. 1990a).

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storage of inorganic solutes and thus acted as a source–sink for solutes being transported through larger pores. Zimmerman et al. (2004) and Wan and El-Swaify (1998) also noted elevated organic C concentrations in small pores where microbial degradation processes were limited. Thus, DOC being solubilized in the near surface pedon soil during storm events is transported to deeper profile depths, where it may have the opportunity to diffuse into smaller pores and/or be bound to the solid phase via interfacial geochemical reactions. Laboratory fractionation of pore water into hydrophobic and hydrophilic organic C species provided further evidence for enhanced attenuation of DOC in lower profiles. The results showed that the percentage of total hydrophobic DOC and hydrophobic acid DOC in solution decreased with depth (Fig. 11). This suggests that the hydrophobic organic solutes of the DOC were selectively adsorbed with depth as DOC was mobilized. These results agreed with laboratory studies on the same soils, which indicated that hydrophobic DOC is preferentially adsorbed by these soils, as compared with hydrophilic DOC (Jardine et al., 1989a).

Here we see the first influence of scale in understanding the mechanisms controlling organic C transport in soils. By maintaining the structure of the media, we were better able to define the mechanisms of organic C fate and transport. Not only are geochemical processes important in the retention of organic C, physical diffusive processes into small micropores also appear to be an important process controlling C sequestration in these soils. Small pore organic C sequestration may be an important C protection mechanism in that biodegradation of this C would be limited because microbes are too large to access this pore class (Mayer, 1994a, 1994b). By maintaining the structure of the media we also better define the role of preferential flow versus matrix diffusion on the movement of organic C through the soil profile. These are processes that would be difficult to observe in the laboratory, yet are critical to our understanding of organic C dynamics in subsurface systems.

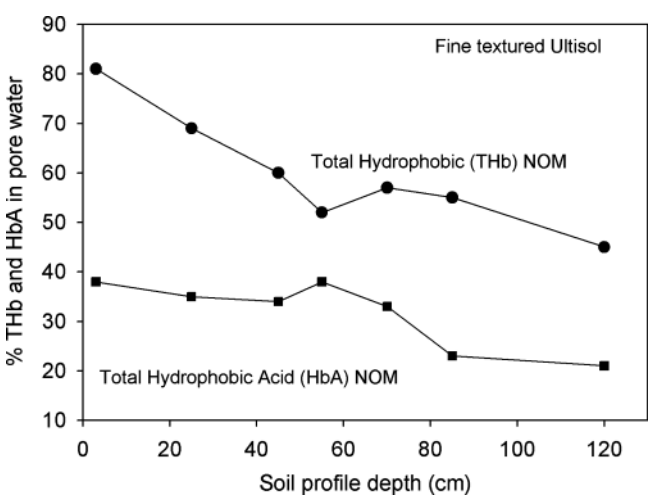

Fig. 11. Percentage of total hydrophobic organic solutes (Thb) and hydrophobic acid organic solutes (HbA) in solution as a function of depth for solution samplers in the pedon and on the subwatershed for a series of storm events during January 1989 to March 1989.

Field Scale

Although the mechanisms of C adsorption in soils have been fairly well characterized in the laboratory (Tipping, 1981a, 1981b; Davis and Glour, 1981; Jardine et al., 1989b; Dunnivant et al., 1992; Baham and Sposito, 1994; Gu et al., 1995, 1996a, 1996b; Wan and El-Swaify, 1998), only a handful of studies have demonstrated similar processes in the field (Jardine et al., 1989a, 1990a; McCarthy et al., 1993; Currie et al., 1996; Dosskey and Bertsch, 1997; McGlynn and McDonnell, 2003). Scaling up from columns and pedons to a subwatershed increases the degree of flow-path heterogeneity and results in the addition of new phenomena not represented at the smaller scales. For example, the boundaries imposed on the columns and pedon restrict lateral flow and convergent flow, which are known to occur at the field scale in humid environments (Wilson et al., 1990, 1991a, 1991b, 1993). Assessing the magnitude and extent of organic C accumulation in subsoils requires an improved understanding of the mechanisms controlling C dynamics in situ at a scale that is more representative of naturally occurring conditions.

Storm-driven organic C dynamics were investigated at the SSTF (Luxmoore and Abner, 1987), which consists of a well-instrumented subcatchment (0.47 ha) on the West Fork of the Walker Branch Watershed (Fig. 1, 3, 4). As described in the Materials and Methods section, the field site is equipped with a subsurface weir for capturing lateral storm flow through the soil profile. The weir setup provides exceptional flow and transport mass balance (Wilson et al., 1993), which is atypical for most other field studies that normally use spatially distributed point measurements (e.g., suction lysimeters, piezometers). Organic C transport was monitored for several different storm events of varying duration and intensity, with C dynamics being significantly different during small and moderate rain events versus large rain events (Jardine et al., 1990b).

Storm events with small to moderate amounts of rainfall (<50 mm) typically had higher DOC concentrations on the ascending limb of the subsurface hydrograph relative to the descending limb, with peak DOC concentrations occurring before peak flow (Fig. 12a). Because lateral flow is predominantly in the B_t2 and B_t3 horizons of the soil during storm events (Wilson et al., 1990), the total cumulative flux of DOC is typically much larger (>10 times) in the lower horizons than in the upper horizons of the soil profile. As described in Jardine et al. (1990b), a complex coupling of physical and geochemical processes controls the breakthrough of DOC, where reactive SO_4^{-2} competes for DOC sorption sites as they simultaneously move through the profile. These soils have been loaded with SO_4^{-2} for several decades due to historical coal-burning activities (Johnson et al., 1981). Since the source of DOC is nonlimiting (high supply) one would expect peak DOC concentrations at peak flow based on the pathlength-supply

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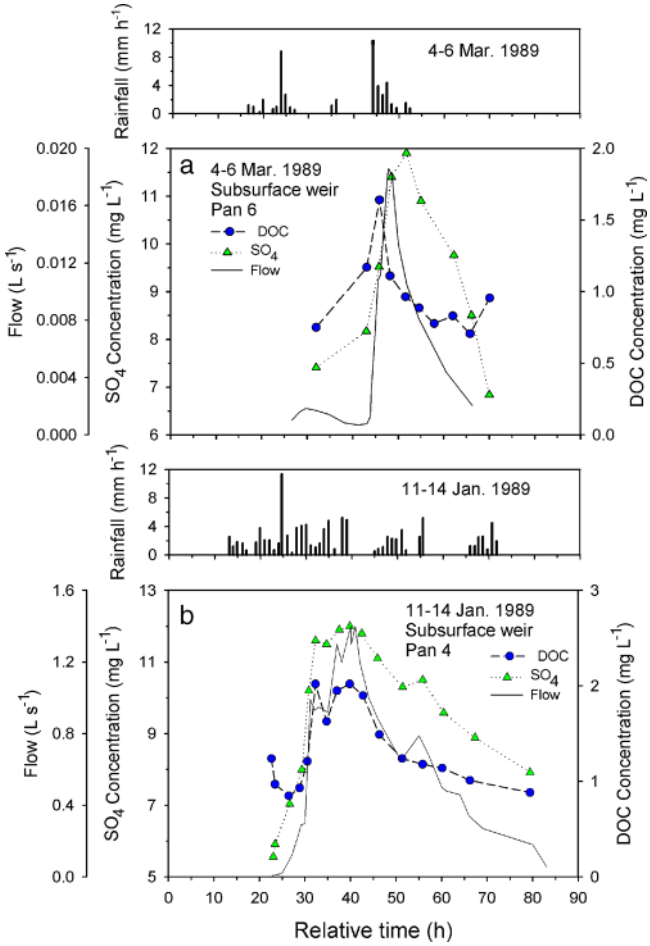

Fig. 12. Concentration of dissolved organic carbon (DOC) and SO_4^{-2} as a function of flow from the subsurface weir for (a) a small storm event in March of 1989 and (b) a large storm event in January of 1989. Relative time is used on the *x* axis to normalize and compare the two storm events.

hypothesis (see Appendix) proposed by Luxmoore et al. (1990). However, competition by SO_4^{-2} pushes DOC out ahead of peak flow, resulting in peak SO_4^{-2} concentrations after peak flow (Fig. 12). Competition of SO_4^{-2} for DOC sorption sites has also been noted by Guggenberger and Zech (1992) and Kooner et al. (1995).

Solute dynamics in the subwatershed were quite different for larger storm events (>50 mm) relative to small to moderate storm events. The cumulative subsurface lateral flow of water during a particularly large storm event (108 mm) was 8 to 1000 times greater than lateral flow for the smaller storm events discussed above. For the large storm event, the concentrations of DOC and SO_4^{-2} followed a similar path during subsurface flow, with lower concentrations along the ascending limb of the hydrograph and expressing maximum concentrations at peak flow (Fig. 12b). Soil solution pH values decreased during high flow, due to the large input of new water, resulting in nonequilibrium between mobile water and the soil matrix. Similar concentration profiles for DOC and SO_4^{-2} suggest chemical interactions are minimal during large storms because of the short residence time of water in the soil. These results are consistent with the pathlength-supply argument put forth by Luxmoore et al. (1990) where high-supply chemicals such as DOC and SO_4^{-2} may accumulate in soil water as the flow path increases. High-supply chemicals refer to a nonlimiting pool of soil material that can supply the pore water by desorption (e.g., SO_4^{-2}) and/or a continuous manufacture of new material (e.g., DOC). The pathlength argument for high-supply chemicals suggests that each unit of pore flow may possibly collect a unit of solute (from small pore sources), so that there is a higher solute concentration in the long-path water reaching the subcatchment relative to short-path water. Park and Matzner (2003) also suggested that DOC was a high-supply chemical since DOC is derived from both newly added litter and older organic horizons through complex interactions between microbial production and consumption and hydrologic transport. Thus, for large storm events, DOC and SO_4^{-2} concentrations should be similar on the ascending and descending limbs of the hydrograph and reach a maximum concentration at peak flow (Fig. 12b).

Once again we see the influence of scale in understanding the mechanisms controlling organic C transport in soils. Common features across scales persist, including preferential flow, matrix diffusion, and geochemical reactions. However, new important phenomena, such as lateral subsurface flow, develop at the field scale and can significantly influence the movement of organic C through the soil profile. Storm intensity and duration also influence C dynamics and the extent of lateral flow. These are processes that cannot be investigated at the laboratory or pedon scale. However, these field-scale studies lack information as to the extent of lateral vs. vertical flow and flux of organic C through the soil profile. Since we are unable to monitor deeper vertical flow, our knowledge of deep vs. shallow infiltration of organic C remains limited.

Landscape Scale

In an effort to quantify the extent of vertical vs. lateral flow for different storms of varying intensity and duration we monitored stream flow on the West Fork of Walker Branch Watershed (Fig. 1). As mentioned, the watershed is drained by a first-order stream that is fed by numerous springs and a network of ephemeral stream channels drains most of the upper portions of the watershed. Surface runoff from catchments ranging from 3.9 ha to the entire 38.4-ha watershed was monitored by a network of flumes and weirs installed on the ephemeral streams and perennial streams. Organic C transport was monitored for several different storms events of varying duration and intensity with C dynamics being significantly different during small and moderate rain events versus large rain events (Mulholland et al., 1990). We focus on discharge from ephemeral stream samplers WB 360 and WBT 440 and perennial stream sampler WBO (Fig. 1). Note that WB 360 is down gradient from the SSTF that contains the subsurface weirs.

Small to moderate storm events (<50 mm) typically resulted in the formation of temporary ephemeral

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streams and discharge enhancements of the perennial stream (Fig. 13). Organic C dynamics for the ephemeral streams showed peak C concentrations at the initiation of discharge, with C concentrations dropping rapidly to lower levels at peak flow and during the descending limb of the hydrograph (Fig. 13b). These results are consistent with subsurface discharge at the weirs that found organic C concentrations higher during the ascending limb of the hydrograph, with C concentrations decreasing at peak flow and during the descending portion of the hydrograph (Fig. 13a). It is this water that converges downslope to form the ephemeral stream. The dynamics of SO_4^{2-} in the ephemeral stream were a mirror image of the DOC dynamics, which again is consistent with discharge from the subsurface (Fig. 12a or 13a). It is interesting to note that both WB 360 and WBT 440 ephemeral streams showed similar discharge patterns for DOC

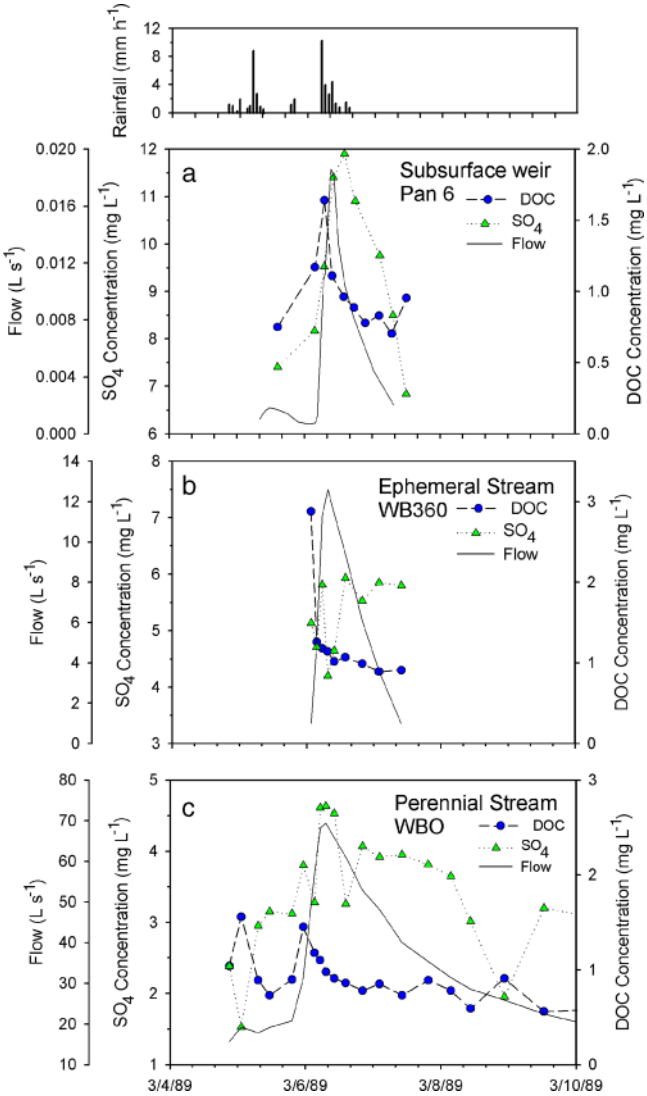

Fig. 13. Concentration of dissolved organic carbon (DOC) and SO_4^{-2} as a function of flow from (a) the subsurface weir (same as Fig. 12a), (b) the ephemeral stream collector WB 360, and (c) the perennial stream collector WBO during a small rain event in March of 1989. See Fig. 1 for locations.

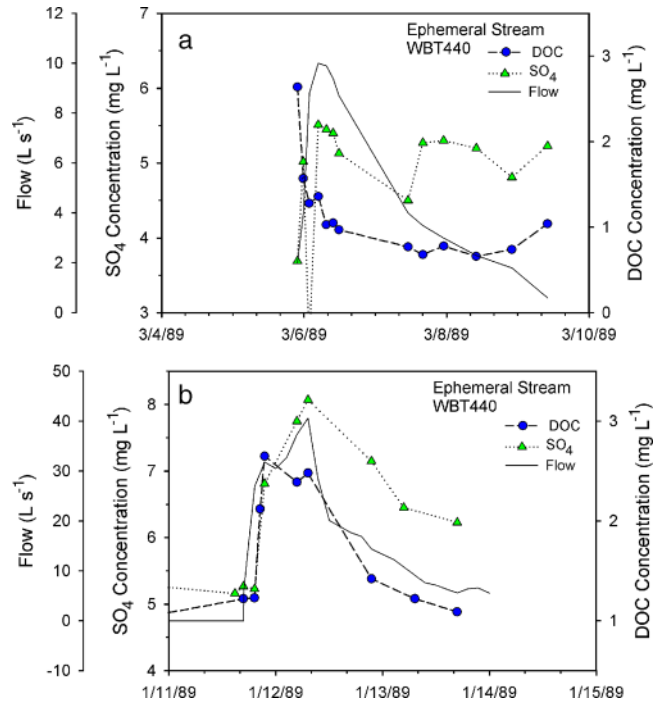

Fig. 14. Concentration of dissolved organic carbon (DOC) and SO_4^{-2} as a function of flow from the subsurface weir ephemeral stream collector WB 440 during a (a) small storm event in March 1989, and (b) a large storm event in January of 1989. See Fig. 1 for locations.

and SO_4^{-2} (Fig. 13b and 14a). Perennial stream DOC dynamics appeared similar to those observed for the ephemeral stream; however, perennial stream dynamics for SO_4^{-2} were somewhat different than those observed for the ephemeral stream during small storm events (Fig. 13c). Sulfate concentrations increased and decreased along the ascending and descending limbs of the hydrograph, respectively, with peak concentrations occurring at peak flow. Since ephemeral streams only form through converging lateral flow and perennial stream discharge can be a combination of lateral and vertical flow, difference between solute dynamics in the different stream types would suggest multiple source contributions to the perennial stream. These results suggest that the concentrations of SO_4^{-2}, and likely DOC, observed in the perennial stream were from multiple sources (e.g., discharge from lateral and vertical sources with the soil profile). A significant decrease in the concentration of SO_4^{-2} in water at the subsurface weirs versus that at the ephemeral and perennial streams also suggests that multiple sources of discharge are contributing to perennial stream flow. Lower solute concentrations in the streams suggest losses of these reactive constituents as they moved through the soil profile.

The flow and transport dynamics of DOC and SO_4^{-2} for large storm events (>50 mm) at the landscape scale were similar to those observed at the field scale (Fig. 15). For the large storm event, concentrations of DOC and SO_4^{-2} followed a similar path at the subsurface weirs, at the ephemeral stream, and at the perennial stream, with lower concentrations along the ascending and descending limbs of the hydrograph and maximum

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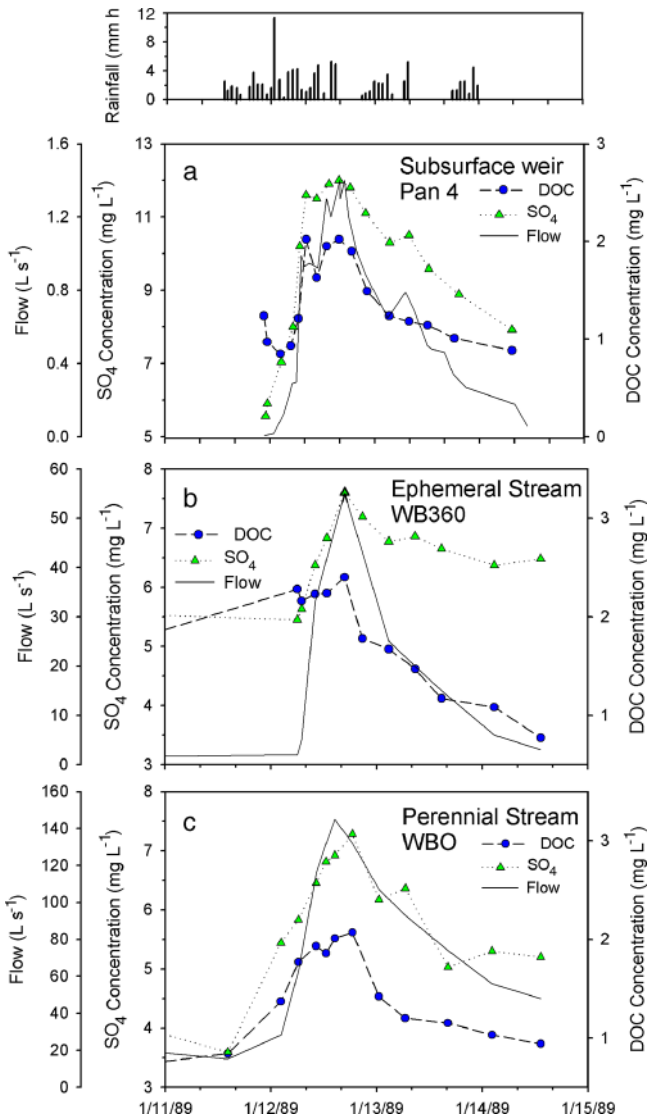

Fig. 15. Concentration of dissolved organic carbon (DOC) and SO_4^{-2} as a function of flow from (a) the subsurface weir (same as Fig. 12b), (b) the ephemeral stream collector WB 360, and (c) the perennial stream collector WBO during a large rain event in January of 1989. See Fig. 1 for locations.

concentrations at peak flow (Fig. 15). Both WB 360 and WBT 440 ephemeral streams showed similar discharge patterns for DOC and SO_4^{-2} (Fig. 14b and 15b). These results suggest that the lateral storm flow influences DOC dynamics more significantly than vertical transport during large storms. Similar concentrations of SO_4^{-2} and DOC in water at the subsurface weirs, the ephemeral stream, and the perennial stream also suggest the primary contribution of lateral storm flow through the soil profile to discharge at the perennial stream. These results are also consistent with the pathlength-supply argument put forth by Luxmoore et al. (1990), in which high-supply chemicals such as DOC and SO_4^{-2} may accumulate in soil water as the flow-path length increases.

Support for the rationalization of these observations was noted by Mulholland et al. (1990). For small to moderate storms, runoff per unit area increased with increasing catchment size, indicating that preferential flow was primarily vertical along relatively deep pathways that emerged in the lower portions of the watershed. However, for large storms, runoff was similar across catchment sizes, indicating that preferential flow was largely lateral along shallow paths (B_t2 and B_t3 horizons). Runoff generated by preferential lateral flow resulted in higher exports of DOC and SO_4^{-2} than an equivalent amount of runoff generated by preferential flow via deeper flow paths (Mulholland et al., 1990). This suggests attenuation of the DOC and SO_4^{-2} as they passed vertically through the soil profile. This finding is consistent with Janssens et al. (2003) and Siemens (2003), who postulated that DOC moving vertically through soil profiles is the "missing" C flux in the global budget.

A Conceptual Model of Subsurface DOC Migration in Humid Environments

The landscape-scale observations are completely consistent with results from laboratory, pedon, and field-scale observations. Combining landscape-scale observations with information at the other scales, we formulate the following conceptual model with regard to the mechanisms of DOC movement through soils in humid regimes. Small storms result in more vertical DOC transport relative to lateral transport. Residence times in the vertical direction can be orders of magnitude larger than in the lateral direction because of the thickness of the soil profile. As DOC moves vertically downward it has an enhanced opportunity to be sorbed by the solid phase or to diffuse into the soil matrix relative to lateral pathways. It is this organic C that may be the "missing" C flux in global budgets (Janssens et al., 2003; Siemens, 2003). These mechanisms account for the small export of DOC generated in runoff from deep sources that have passed through the entire soil profile. Large storms, on the other hand, result in more lateral flow, which has shorter residence times in the soil before converging and exiting the profile to create ephemeral streams. The short residence times discourage matrix diffusion and sorption of the DOC. These conditions, coupled with the fact that DOC is a high-supply source (nonlimiting), explain why larger exports of DOC are generated in runoff from shallow lateral moving sources vs. deep sources.

By monitoring organic C dynamics across scales we have provided credible evidence that supports the pathlength-supply hypothesis put forth by Luxmoore et al. (1990) for describing lateral solute transport processes in watersheds located in high recharge humid regimes. It is quite possibly the pathlength-supply mechanism that does not allow organic C to accumulate on the B horizon solid phase to the same extent that is observed in the laboratory. Fast flowing lateral storm flow with short residence times within the soil profile may deplete organic C from the soil matrix of the lower B horizon, whereas slower flowing lateral flow with longer profile residence times may replenish this organic C, thus resulting in a limited net gain or loss over time. Organic C accumulation due to preferential vertical flow may

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be another story (Janssens et al., 2003; Siemens, 2003). Deeper measurements of organic C accumulation could, if completed, identify whether deeper soil profiles are sequestering C. This would be an interesting area of research and an opportunity we put forward to the scientific community.

CONCLUSION

We conclude by emphasizing that laboratory-scale studies suggest that humid regime subsoils are potentially large sinks for organic C. Hydrologic conditions in these systems, however, limit the propensity for organic C sequestration by the solid phase. Efforts to enhance organic C sequestration in these lower horizons may be difficult, but historical evidence has shown that it is possible if they are managed appropriately. The necessity to reduce or offset global CO_2 emissions is a reality and one that the international scientific community must embrace regardless of politics (USDOE, 1999). We encourage resolution to the following questions: how does one mobilize active near-surface organic C pools and create passive subsurface organic C pools to create a state of long-term sequestration of organic C? How does one overcome the hydrologic constraints that exist in the humid vadose zone that impede subsurface organic C sequestration? Are manipulations available that can enhance surface and subsurface organic C pools? Will these efforts help with C sequestration in the near term and/or the long term? Is the DOC that moves vertically through soil profiles the "missing" C flux in global budgets? Resolution of these questions could have a significant impact on better defining soil organic C budgets and contribute to a reduction in net CO_2 emissions.

APPENDIX

The Pathlength-Supply Relationship

During storm events, the pathlength of lateral water flow through the subsurface tends to increase with distance downslope until it finally exits to form ephemeral streams. At the time of peak flow, water percolating along the longest path lengths contributes to the outflow along with the shorter-path water. The longer-path water has greater opportunity to interact with the surface area of preferential flow channels and with the soil matrix compared with the shorter-path water. High-supply solutes, such as DOC, are taken into the percolating water chiefly along lateral preferred flow paths and thus to a greater extent along the long flow paths vs. the short flow paths. Each unit of large pore flow tends to collect some solute from the adjacent soil matrix; thus, there is a higher solute concentration in the long-pathlength water reaching the ephemeral stream than in the short-pathlength water. Therefore, with significant lateral flow one would expect peak solute concentrations at peak flow. Low-supply solutes (e.g., Mn) have no immediate replacement following removal from the solid phase by percolating water. Thus, continued leaching becomes diluted by the incoming rain and the long-pathlength water does not gain additional solute as it percolates laterally through the profile. Thus, one would expect the minimum concentration of a low-supply solute during peak flow.

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