

Impacts of Sampling Dissolved Organic Matter with Passive Capillary Wicks Versus Aqueous Soil Extraction

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Quantitative characterization of dissolved organic matter (DOM) in soil and vadose zone solution is needed to interpret mechanisms of nutrient and C cycling as well as bio-weathering processes. Passive capillary wick samplers (PCaps) are useful for soil solution sampling because they can provide measures of water and associated DOM-constituent flux in the unsaturated zone, however potential impacts of the wick material on DOM chemical properties has not been investigated yet. We therefore conducted experiments where aqueous soil extracts were transported along PCap fiberglass wicks in flow-through experiments. Results indicated limited dissolved organic carbon (DOC) sorption and DOM fractionation, and related parameters (total dissolved nitrogen [TDN], DOM fluorescence components) also remained largely unaffected. We note that this experiment does not account for the extent to which soil hydrologic processes may be affected by PCap field installations. However, given that the wicks did not fractionate significantly DOM, we compared field-based PCap DOM solution collected in situ with laboratory-based aqueous soil extraction (ASE) of DOM from the same soils to assess differences in DOM quality. Spectroscopic analysis of DOM in ASE solutions showed lower O-H stretch/carboxylate band intensity ratios, more pronounced aliphatic C-H stretching (Fourier Transform Infrared analysis), higher specific ultraviolet-absorbance (SUVA₂₅₄) values as well as greater abundance of fluorescence components in the region attributed to fulvic acids. We conclude that difference in molecular properties of DOM derived from laboratory ASE vs. PCap field collection of the same soils is attributable to differential disturbance effects of the two methods of soil solution collection.

Abbreviations: ASE, aqueous soil extraction; CM, Cory and McKnight; DOC, dissolved organic carbon; DOM, dissolved organic matter; EEMs, excitation-emission matrices; Em, emission; Ex, excitation; FA, fulvic acid; FI, fluorescence index; FTIR, Fourier Transform Infrared; HA, humic acid; JRB-CZO, Jemez River Basin Critical Zone Observatory; PARAFAC, parallel factor analysis; PCap, passive capillary wick samplers; PV, pore volumes; TDN, total dissolved nitrogen.

Accurate analysis of DOM in soil solution is integral to critical zone science because pore water DOM, a product of ecosystem C and nutrient cycling, becomes a principal reactant in mineral weathering and aqueous or surface complexation reactions (Chorover, 2012). Soil solution DOM can be obtained by a variety of approaches such as in situ zero-tension and tension samplers (Weihermüller et al., 2007) or by performing soil extracts in the laboratory (Swift, 1996). Methods that permit measurement of both DOM composition and lithogenic solute flux are needed to quantify relations between DOM chemistry and geochemical weathering. Soil solution samplers that are potentially useful to determine such fluxes are in PCaps for which both the sample volume and the contributing area are known (Brandi-Dohrn et al., 1996; Jabro et al., 2008).

Soil Sci. Soc. Am. J. 76:2019–2030

doi:10.2136/sssaj2012.0061

Received 21 Feb. 2012.

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The PCaps extract soil solution from the vadose zone at a constant tension that is directly proportional to the vertical length of hydrophilic (silica-based) wick material. This wick material hosts a hanging water column that hydrates the wick-solution interface and extends into the pore domain of the fiberglass material where event-based water transport largely occurs (Biddle et al., 1995; Frisbee et al., 2010; Holder et al., 1991). As such, the samplers require minimal maintenance and are cost effective for collection of time-integrated samples in remote field sites. Solution held in the soil at potential values less negative than that imposed by the device are collected continuously and collection stops when the soil dries to the point where the gradient imposed by the sampler is less negative than the soil matric potential at the wick-soil interface. Potential disadvantages of PCap samplers are that installation may introduce artifacts, such as creation of preferential flow paths, as can occur with installation of many types of in situ samplers (Miro

et al., 2010; Peters and Durner, 2009). The extent to which samples thus collected are representative of a given field site depends also on how effectively they sample field-scale heterogeneities in water flow paths, hydraulic conductivities, etc. (Weihermüller et al., 2006). One concern with tension samplers in general is that they can impose unintended effects on potential distributions within the water flow domain (Mertens et al., 2007).

While virtually all sampling approaches pose potential soil physical problems, fiberglass PCaps raise unique concerns with respect to their sampling of solution chemistry because the reactive fiberglass interface may affect sample chemistry delivered into the collection carboy (Fig. 1). For example, prior studies have shown that certain mineral colloids (e.g., ferrihydrite, feldspatoids, montmorillonite, and kaolinite) are retained at the wick-water interface leading to incomplete colloid recovery (Czigani et al., 2005; Shira et al., 2006; Ilg et al., 2007). Goynes et al. (2000) com-

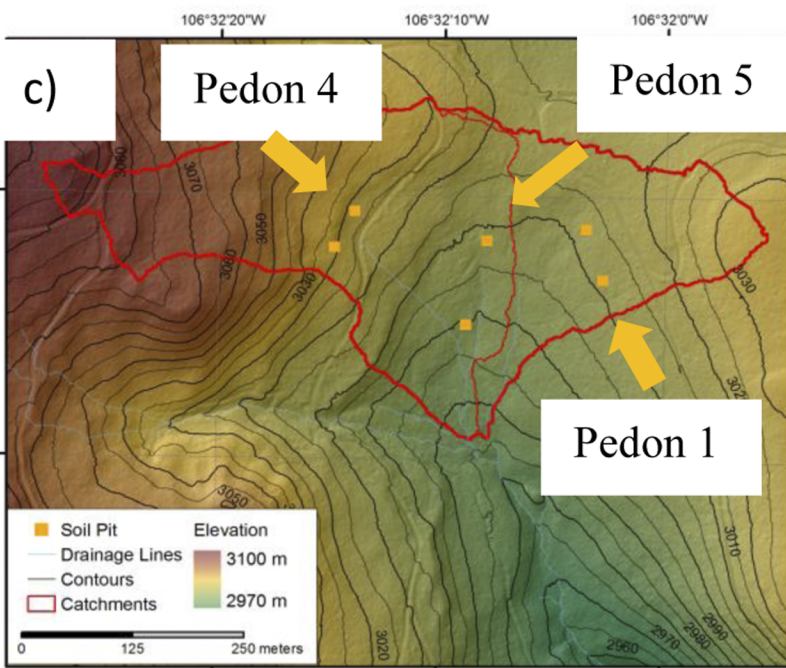
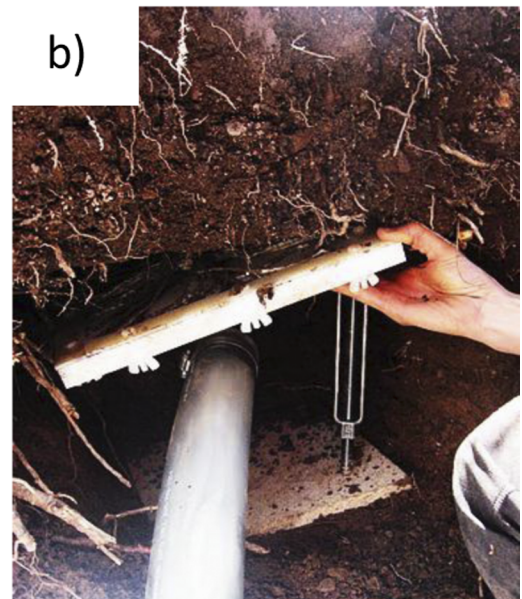
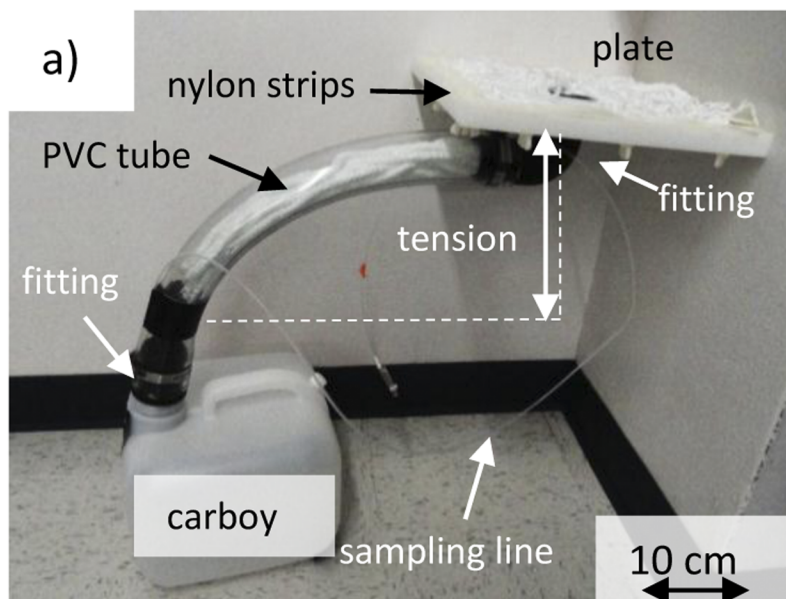


Fig. 1. (a) Passive capillary (PCap) design adapted to use only acid washable parts and abstain from glues and sealants. (b) The PCap installation under the sampling horizon using turnbuckles. (c) The PCap samplers were installed in planar (Pedon 1) and convergent (Pedon 5) sites. In situ and ex situ soil solution for the comparison was obtained from Pedon 4.

pared PCap samplers with zero-tension samplers at various depths in a deciduous forest soil and showed increased pH, dissolved inorganic C and alkalinity in PCap samples likely due to trace dissolution of the wick material. In addition to potential chemical effects of the wicks themselves, sealants and glues often used in the construction of the PCaps can also be problematic (Siemens and Kaupenjohann, 2003).

The potential impact of fiberglass wicks (as an integral part of the PCap design) on DOM chemistry has not been studied in detail and so their suitability for this application is unknown. Therefore, the first objective of this study was to test if collection of water over fiberglass wicks changes DOM chemical characteristics. For that purpose, fiberglass wicks were subjected to laboratory flow-through studies using a composite O- and A-horizon extract. Parameters pertaining to DOM chemistry including DOC and TDN concentrations, specific UV absorbance ($SUVA_{254}$), fluorescence excitation-emission spectra, and Fourier Transform Infrared (FTIR) spectra of the DOM solutions were monitored in effluent solutions.

Although it is generally preferred to obtain soil solutions in situ, if the research objective is to obtain a single-time measure of pore water chemistry for a given location, point sampling of solid phase material for subsequent laboratory-based ASE with deionized water is often employed (Swift, 1996; Notario del Pino et al., 2008; Hurraß, and Schaumann, 2006). In this case, local perturbations imposed on the soil between field collection and laboratory extraction, including disruption of aggregates comprising microbe–clay–organic associations, can potentially affect the extracted soil solution chemistry (Fest et al., 2008). In addition, drying of soils before extraction has been shown to impact extractable DOC concentration and composition (Bartlett and James, 1980; Fest et al., 2008; Kaiser et al., 2001) and soluble trace metal concentration/speciation (Koopmans and Groenenberg, 2011).

Despite the expected sensitivity of DOM quality toward different disturbances that may be imposed by laboratory- vs. field-based methods of soil solution extraction, it remains unclear whether DOM molecular properties will be differentially affected. Since both ASE and PCaps are being used to obtain soil solution chemistry datasets for a field-based study of C flux in the Jemez River Basin Critical Zone Observatory (JRB-CZO), the second objective of the current work was a comparison between DOM composition obtained from the same soils using field-based PCaps vs. laboratory-based ASE.

EXPERIMENTAL AND FIELD METHODS

Passive Capillary Design and Preparation

The PCaps constructed for this study were adapted from earlier published designs (Biddle et al., 1995; Holder et al., 1991) with modifications that have arisen from the dual goal of abstaining from organic glues and sealants and using only acid washable parts to minimize potential artifacts (Goynes et al., 2000; Siemens and Kaupenjohann, 2003). Each PCap consists of a 30.5 by 30.5 cm acid washed high density polyethylene (HDPE) sheet (1.9 cm thick) with a 5.1-cm hole in the center into which is threaded a

common polypropylene elbow fitting. Eight additional holes were drilled 1.2 cm from the outer boundary of the sheet as well as into 2.5 cm wide nylon strips so that the wicks could be fixed between the sheet and the strips using nylon screws (Fig. 1a).

A 45-cm long PVC tube with an inner diameter of 5.1 cm was inserted under the sheet using the push-on side of the elbow fitting and fixed to a two-way push-on coupling on the other side of the hose, connecting the PVC tube to a 5 L HDPE carboy. All connections were fixed with hose clamps for additional stability. A 2-m long Teflon sampling line was then introduced through a small incision in the PVC hose. Due to the thickness of the hose (1.2 cm) the incision was resealed after insertion of the sampling line and additionally protected with high strength adhesive tape (Gorilla Tape).

Fiberglass wick material was obtained from Pepperell and Braiding Co. (no. 1381, Pepperell, MA) and cleaned according to the procedure described in Goynes et al. (2000). Wicks measuring 70 cm in length were first combusted at 400°C for 4 h (Knutson et al., 1993), washed with a phosphate-free dilute detergent and rinsed several times with ultrapure water (resistivity 18.2 MΩcm⁻¹). Acid washing in 10 mM HCl was repeated twice, followed by daily rinses with ultrapure water using a flow through system until electrical conductivity (EC) and pH stabilized after several weeks.

According to Goynes et al. (2000), the appropriate number of wicks for each PCap was calculated based on Eq. [1]:

$$\text{Number of wicks} = \frac{(K_{\text{sat soil}})(\text{Plate area})}{(K_{\text{sat wick}})(\text{Wick}_{\text{cross-sectional area}})} \quad [1]$$

The plate area of the PCap is 7.8 E-02 m², the wick saturated conductivity ($K_{\text{sat wick}}$) is 1E-02 m s⁻¹ and the cross-sectional area for one wick is 1.27 E-04 m². For this field site, 10 wicks are used to match a soil K_{sat} of 1.6E-04 m s⁻¹. The pore volume for each PCap is approximately 400 mL.

Field Installation and Sampling

The field site is part of the JRB-CZO located in the Valles Caldera National Preserve (VCNP), northwest of Albuquerque, NM. On the south side of the largest resurgent dome (Redondo dome), a zero order basin (ZOB) within the larger LaJara catchment was instrumented in September 2010 with a range of aboveground and belowground sensors and sampling devices (Chorover et al., 2011). Three PCaps were installed as a function of depth (targeting O, A, and B horizons) in each of six excavated soil trenches as a principal approach for obtaining in situ soil solution. Wick-covered plates were inserted in excavated side windows and elevated to make contact with the overlying horizon using turnbuckles (Fig. 1b). The soil, classified as Vitrandric Haplustoll (Soil Survey Staff, 2011) has a loamy texture with ~ 25% clay, 36% silt, and 39% sand fraction. Total organic C is 234 g kg⁻¹ in the O horizon (0–5 cm) and 51 g kg⁻¹ in the A horizon (5–18 cm) and mineralogy is comprised predominantly of quartz, muscovite, albite, K-feldspar, kaolinite, and clinoptilolite.

Table 1. Sampling dates and depths and organic matter (OM) analysis results on passive capillary wick sampler (PCap)-aqueous soil extract (ASE) comparison. Samples obtained concurrently are ASE 2 and PCap 1 (4 Apr. 2011) as well as ASE 3 and PCap 4 (27 Apr. 2011, marked in bold italic).

Sampling parameters and analyses	ASE					In situ PCap				
	ASE 1	ASE 2	ASE 3	ASE 4	PCap sample 1	PCap sample 2	PCap sample 3	PCap sample 4	PCap sample 5	
Depth, cm	0–10	0–10	0–20	0–20	18	18	18	18	18	
Sampling date	3 Nov. 2010	4 Apr. 2011	27 Apr. 2011	24 June 2011	4 Apr. 2011	11 Apr. 2011	18 Apr. 2011	27 Apr. 2011	3 May 2011	
Season	post-monsoon	mid-snowmelt	late snowmelt	pre-monsoon	mid-snowmelt	mid-snowmelt	mid-snowmelt	late snowmelt	post-snowmelt	
DOC†, mgL ⁻¹	9.84	7.92	21.72	5.65	96.3	1360.1	1232.5	8013.8	4402.9	
TDN, mgL ⁻¹	1.21	0.05	2.11	1.02	1.7	252	172.4	1249.1	538.2	
DOC/TDN	8.11	161.63	10.30	5.53	55.52	5.40	7.15	6.42	8.18	
Avg/SD		46.39/66.6					16.53/19.5			
SUVA ₂₅₄ , L mg ⁻¹ C m ⁻¹	1.4	4.4	3.6	10.8	3.2	3.1	2.3	2.4	2.1	
Avg/SD		5.1/3.5					2.6/0.4			
FI	1.21	1.15	1.14	1.18	1.34	1.33	1.37	1.37	1.36	
Avg/SD		1.17/0.03*					1.35/0.02*			

* Parameters showing significant differences at the 95% confidence interval ($p = 0.05$).

† DOC, dissolved organic carbon; TDN, total dissolved nitrogen; SUVA₂₅₄, specific ultraviolet absorbance.

Water and DOC fluxes for snowmelt period 2011 were determined for two distinct PCap locations, Pedon 1 and Pedon 5, which are situated in planar and convergent hillslope locations, respectively (Fig. 1c). Flux values for DOC were determined by taking the product of water mass (kg) and DOC concentration (mg kg^{-1}) for each sampling date, summing these products across all sampling dates over the snowmelt period (April through May 2011), and normalizing the result to the cross-sectional area of the wick sampler plate. For the PCap-ASE comparison, a PCap on the E-facing slope of the ZOB was selected (Pedon 4) providing soil solution samples from 18-cm depth with a constant tension of around 30 cm. The PCap samples from Pedon 4 were collected five times during the 2011 snow melt in April (Table 1). Samples were filtered through combusted 0.7 μm glass fiber filters (GF/F, Whatman, Alameda Chemical & Scientific Inc., Oakland, CA) into acid washed HDPE bottles and transported in cool conditions ($\sim 4^\circ\text{C}$) to the laboratory within a maximum of 2 d after sampling. At selected time points, soil adjacent to the PCap was augered and composited to provide a depth integrated sample between 0 and 10 or 20 cm (Table 1). Because soil water availability in this semiarid site is limited to snowmelt and infrequent rainfall events, it was not possible to obtain PCap samples throughout the year, but two PCap and ASE sample sets were concurrent and allow for direct comparison.

Flow-Through Experiment

Cleaned, ultrapure water-saturated wicks were cut to 10-cm length and mounted in triplicate into acid washed and combusted glass columns of 14-cm length and 1.5-cm diam. Ashless Whatman 41 filters were cut to size and inserted at the column outlet to prevent particles larger than 20 μm from leaving the columns. Continuously stirred OA-horizon extract or an ultrapure water blank were supplied at a constant rate of 36 mL h^{-1} through acid washed PTFE tubing that delivered solutions drop-wise on to wicks. This mode of infiltration was chosen over direct pumping of effluent in a closed system to simulate unsaturated flow in the vadose zone and to reproduce realistic wick flow velocities. Effluents were collected into acid washed, combusted glass vials with an ISCO Foxy 200 fraction collector every approximately two wick pore volumes (PV). Each of three infiltration cycles of 3.5 h duration was interrupted by a 24 h stop flow period to simulate infiltration events. The wicks were not allowed to dry completely but drained gravitationally, losing approximately 3% of solution, to simulate field conditions between events. The feed solution was sampled daily, analyzed for the same analytes as the effluents, and means with standard deviation of chemical parameters are reported.

Aqueous Soil Extracts

Aqueous soil extracts of the O and A horizon (sampled as composite and referred to as OA) were used both for the comparison between PCap and ASE performance as well as the experimental solution for the flow-through experiment. Before extraction, soils were sieved field-moist to obtain the <2-mm fraction. Subsamples were oven dried for 24 h at 105°C and re-

sulting change in mass was used to calculate gravimetric water content. The field moist equivalent of 100 g of dry OA-horizon soil was then added to 1 L HDPE bottles and 500 g of ultrapure water were added to obtain a soil/water mass ratio of 1:5. The bottles were capped tightly and placed on a shaker at 180 rpm for 1.0 h. Suspensions were then centrifuged (7000 RCF for 30 min), before supernatant solutions were filtered through combusted 0.7 μm glass fiber filters and stored at 4°C in combusted 60-mL amber glass bottles before use in wick flow-through experiments or analysis. The soil extract used for the flow-through experiment was prepared <24 h before initiation of the experiment. The extract was diluted to give a about 6 mg L⁻¹ TOC concentration and stored at 4°C in a 2.5-L acid washed glass bottle wrapped in aluminum foil to shield from light.

Chemical Analysis

Dissolved organic C and N were determined by catalytic oxidation at 720°C followed by infrared and chemiluminescence gas detection using a Shimadzu TOC-VCSH with a TNM-1 N measuring unit (Shimadzu Scientific Instruments, Columbia, MD). Dissolved inorganic C was degassed beforehand by purging pre-acidified (pH 2) solutions. Samples for UV-visible spectroscopy (UV-vis) were placed in pre-rinsed 1-cm quartz cuvettes. The UV-vis absorbance spectra (250–665 nm) were collected using a Shimadzu 2501PC UV-vis spectrometer (Shimadzu Scientific Instruments, Columbia, MD). The specific UV absorbance (SUVA₂₅₄) was calculated by dividing absorbance at incident wavelength 254 nm by the cell path length (1 cm) and DOC concentration (mg L⁻¹). All samples were diluted as needed to give an absorbance below 0.3 at 254 nm. This dilution allowed for proper correction of the inner-filter effect (Ohno, 2002; Miller et al., 2010).

Fluorescence excitation-emission matrices (EEMs) were collected with a Fluoromax4 (Horiba Jvon, Irvine CA) at 5 nm increments over an excitation (Ex) range of 200 to 450 nm and an emission (Em) range of 250 to 650 nm. Water blank EEMs (resistivity: 18.2 M Ωcm^{-1}) were subtracted and fluorescence intensities were normalized to the area under the daily collected Raman peak at excitation 350 nm, and inner filter correction was performed based on the corresponding UV-vis values (Cory and McKnight, 2005). Two parallel factor analysis (PARAFAC) models were run to analyze the fluorescence excitation emission matrix data and assign PARAFAC components that can be linked to DOM characteristics. An original PARAFAC model was developed from 381 sample EEMs from JRB-CZO stream waters, soil solution and precipitation on machine uncorrected EEMs to include the region of Ex below 250 nm where important protein-like and fulvic acid (FA)-like fluorescence occurs (Chen et al., 2003). For this, the DOMFluor toolbox in Matlab was applied and the protocol of Stedmon and Bro (2008) was followed. Four unique components (C) were identified and validated and are indicated here as C1 (Ex 200–250, Em 255–415, region of “FA-like” fluorescence); C2 (Ex 200–230, Em 250–415, region of “protein-like” fluorescence); C3 (Ex 210–270, Em 250–455,

region of “FA-like” fluorescence) and C4 (Ex 230–450, Em 325–585, region of “humic acid (HA)-like” fluorescence). The regions were assigned after Chen et al. (2003). The second model was developed by Cory and McKnight (2005, referred to as CM model) and was fitted to instrument-corrected EEMs. This model does not include fluorophores in the region below Ex 250 and Em 350, but has a higher resolution for fluorophores above this region, thus complementing the original PARAFAC model. Six out of the 13 Cory and McKnight (2005) components (CM) were found abundant in the soil solutions: CM-1 and CM-3 (unknown components), CM-4 (“reduced hydroquinone”), CM-5 and CM-7 (“reduced quinone”) and C-11 (“oxidized quinone”). To facilitate comparison of PARAFAC components of the original and the CM-model, the components are displayed in the EEM space (Fig. 2a and 2b). From non-instrument corrected EEM data, fluorescence index (FI) values were calculated (FI = Em 450/Em 500 at Ex 370 nm, (McKnight et al., 2001)).

The FTIR spectroscopy was used to characterize the molecular structure and functional group chemistry of DOM. Spectra were recorded using a Nicolet 560 Magna IR Spectrometer (Nicolet, Madison, WI) equipped with CsI beam splitter and a DTGS detector. For sample introduction, 1.0 mL of each DOM sample was deposited onto a Germanium (Ge) transmission window (used because of its transparency to infrared [IR] incident radiation across a wide wavenumber range) and dried under vacuum overnight. All spectra were obtained by averaging 400 scans at 4 cm⁻¹ resolution over the spectral range of 4000 to 400 cm⁻¹. The dry, clean Ge window was consistently used for background correction. Data collection and spectral processing were performed using the OMNIC program (Thermo Nicolet Co., Madison, WI). Spectral analysis, including peak deconvolutions and integrations, were performed using the GRAMS/AI Spectroscopy Software Suite (Thermo Scientific, Waltham, MA). Sample splits were filtered through a nylon membrane (0.45 μm) and analyzed for Si by inductively coupled plasma mass spectrometry (ICP-MS) (ELAN DRC-II, PerkinElmer, Shelton CT) to monitor for any dissolution of fiberglass wick material.

RESULTS

Dissolved Organic Matter Solution Flow-Through Experiment

Dissolved Organic Carbon and Total Dissolved Nitrogen

The DOC and TDN concentrations of the feed soil solution as well as effluent solution (after percolation through the fiberglass wicks) are shown in Fig. 3a. Dissolved organic C concentration of the first effluent solution averaged 3.9 mg L⁻¹ and were notably lower than that of the influent solution (ranging from 5.7–6.4 mg L⁻¹). This can be attributed principally to dilution by water pre-existing in the wicks before DOC infiltration. Over the course of the first and second infiltration events, effluent DOC concentrations showed a steady increase but remained within or close to the range of influent DOC concentrations. Although stop-flow did not affect effluent DOC concentrations after the first infil-

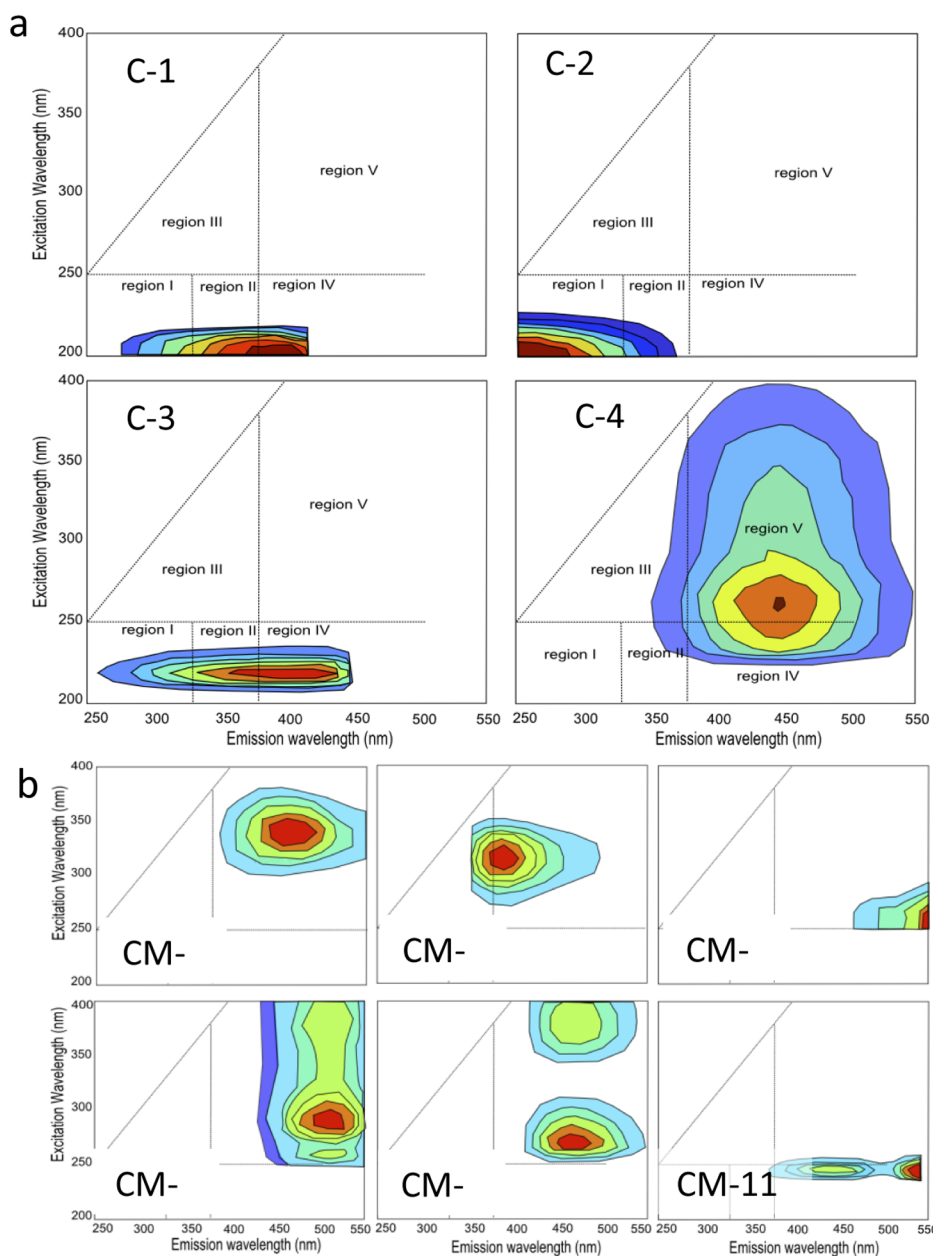


Fig. 2. Excitation Emission intensity of parallel factor (PARAFAC) components in raman units of (a) an original model and (b) the Cory and McKnight (2005) model with regions as assigned by Chen et al. (2003).

tration cycle, a drop in DOC concentrations was measured at approximately 47 PV corresponding to the start of the third infiltration event, after which concentrations increased again to reach influent values. Total N concentration of the first effluent solution also showed a dilution effect followed by steady-state release over the first infiltration cycle. The TDN concentrations were always within the range of influent solution concentrations and presented a steady effluent pattern over the course of the experiment. The exception was the occurrence of high effluent concentrations at the beginning of the second infiltration event.

Ultraviolet-vis, Fluorescence, and Fourier Transform Infrared Spectroscopy

The evolution of $SUVA_{254}$ and FI values during the flow-through experiment are shown respectively in Fig. 3b and 3c.

The $SUVA_{254}$ values of the first 2 PV were the lowest ($7.8 \text{ L mg}^{-1} \text{ C m}^{-1}$) whereas subsequent effluent sample $SUVA_{254}$ values at approximately 4 PV were higher ($10.4 \text{ L mg}^{-1} \text{ C m}^{-1}$, Fig. 3b). This initial fluctuation was followed by stable $SUVA_{254}$ values averaging $9.8 \text{ L mg}^{-1} \text{ C m}^{-1}$ and were within the range of feed solution values ($9.5\text{--}10.8 \text{ L mg}^{-1} \text{ C m}^{-1}$). The following infiltration cycles repeated the pattern with lower $SUVA_{254}$ values in the first effluent, followed by an increase in the following effluent and finally stabilization. Effluent $SUVA_{254}$ averaged $9.6 \text{ L mg}^{-1} \text{ C m}^{-1}$ over the experiment, which was not statistically different from the average feed solution ($10.0 \text{ L mg}^{-1} \text{ C m}^{-1}$).

Effluent FI values showed a different pattern with the first effluents of each infiltration cycle showing the highest FI values (1.22, 1.25 and 1.19 after the first, second, and third flow application, Fig. 3c), as opposed to an average of 1.14 during the rest of the run. With the exception of the high FI values in the first effluent, all FI values were in the range of the feed solution (1.12–1.18). The PARAFAC analysis of fluorescence EEMs on feed and effluent solution are shown in Fig. 3d and 3e. For the original PARAFAC model, the component with highest abundance in both feed and effluent solutions was C-1 (Fig. 3d). Influent C-1 (FA-like) abundance averaged 0.53 ± 0.01 and effluent C-1 abundances, ranging from 0.5 to 0.54, were close to feed solution abundances. The second most abundant component was C-3 (also FA-like), whose EEM-derived proportion of the feed solution averaged at 0.29 ± 0.04 . This variability was even greater in the abundance of effluent C-3, ranging from 0.20 to 0.36. The “protein-like” component C-2 feed abundance averaged 0.13 ± 0.06 , and effluent showed a broad range from 0.05 to 0.25. The least abundant component was C-4 (HA-like). This component showed a more narrow range in effluent abundances (0.02–0.08). Feed concentration averaged at 0.05 ± 0.02 . Results for the abundance of the CM model components are shown in Fig. 3e. The most abundant component was CM-3 (unknown fluorophore) with an average of 0.55, followed by CM-1 (unknown fluorophore, average 0.2 ± 0.01), CM-4 (hydroquinone-like, average 0.1 ± 0.01), CM-11 (oxidized quinone-like, average 0.04) CM-7 (reduced

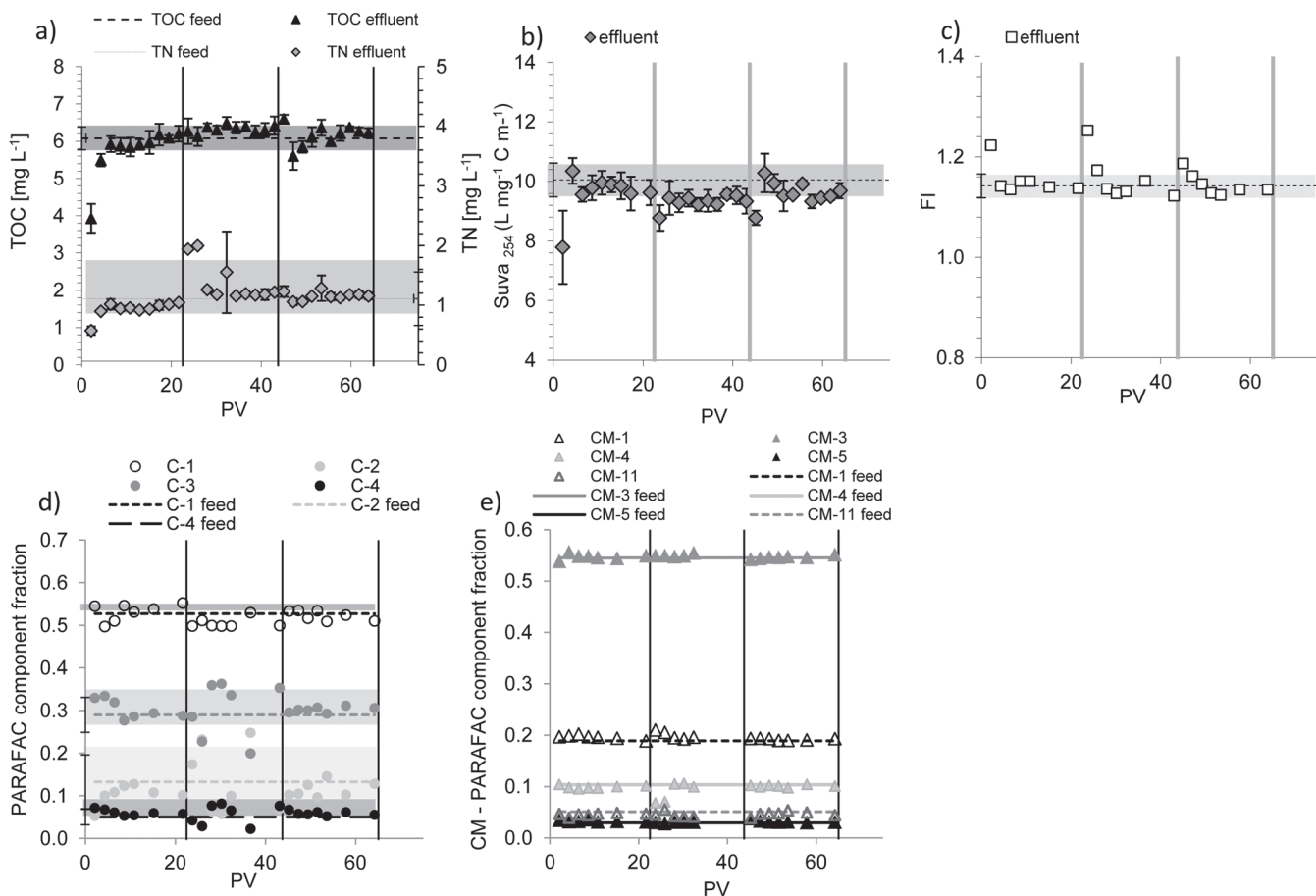


Fig. 3. Feed and effluent values for (a) total organic carbon (TOC) and total nitrogen (TN), (b) specific ultraviolet absorbance ($SUVA_{254}$), (c) fluorescence index (FI), (d) parallel factor (PARAFAC) component abundances, and (e) for the Cory and McKnight (CM) model. Mean values of feed solutions are indicated by dotted horizontal lines and respective standard deviations are highlighted in gray. Vertical lines indicate 24 h of stop flow.

quinone-like, average 0.04), and CM-5 (reduced quinone-like, average 0.03). No variation in feed solution concentration was observed and all effluent component abundances matched those of the feed solution. The only exception was the abundance of CM-1 in the feed solution, which was 0.19 and thus 3.6% lower than that of the effluent solution. Stop flow did not affect the abundances of PARAFAC components.

Transmission FTIR spectra of the feed solution, the first three effluents as well as the water blank are shown in Fig. 4. Several IR bands are represented in all spectra in the region 1700 to 1250 cm^{-1} , where amide and carboxylate vibrations occur. However, due to the low intensity and poor signal/noise ratio in the region, these bands could not be unambiguously assigned. All spectra showed a dominant band at 1010 cm^{-1} with a shoulder at 1084 cm^{-1} , except for the spectrum of the first effluent (2 PV) where the band at 1084 cm^{-1} predominated. The two bands are consistent with the stretching of phosphodiester (C-O-P) and polysaccharides (C-O-C, C-O), respectively (Omoike and Chorover, 2006),

however, since Si-O stretching also occurs at 1080 cm^{-1} (Smidt and Meissl, 2007; Farmer, 1974), increased intensity of that peak in early pore volumes can signal wick silica dissolution. That the latter contributes is substantiated by Si effluent values that spike in the first PV after re-application of flow (up to 15.8 $mg L^{-1}$), but much less Si release occurs during pseudo steady-state flow ($\sim 1.3 mg L^{-1}$).

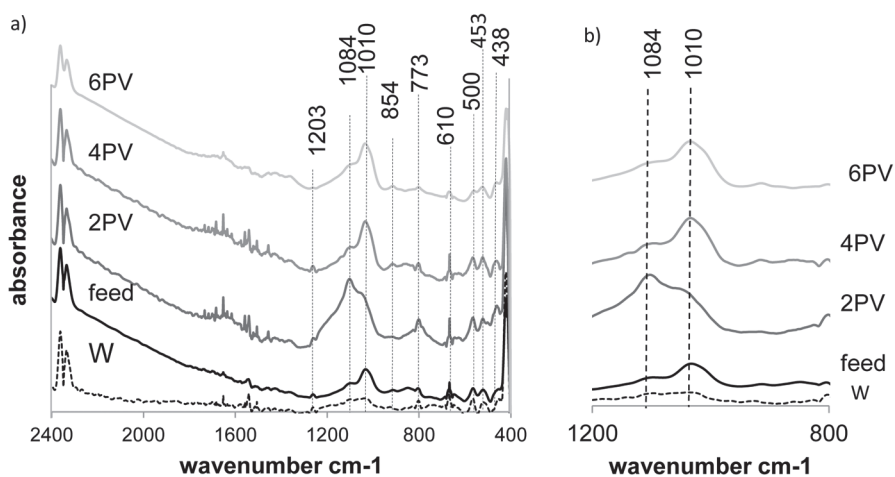


Fig. 4. (a) Fourier Transform Infrared (FTIR) absorbance spectra for the water blank (W), the feed solution (feed) and the first six pore volumes (PV). (b) Magnification of bands showing differences between the first 2PV and all other effluents.

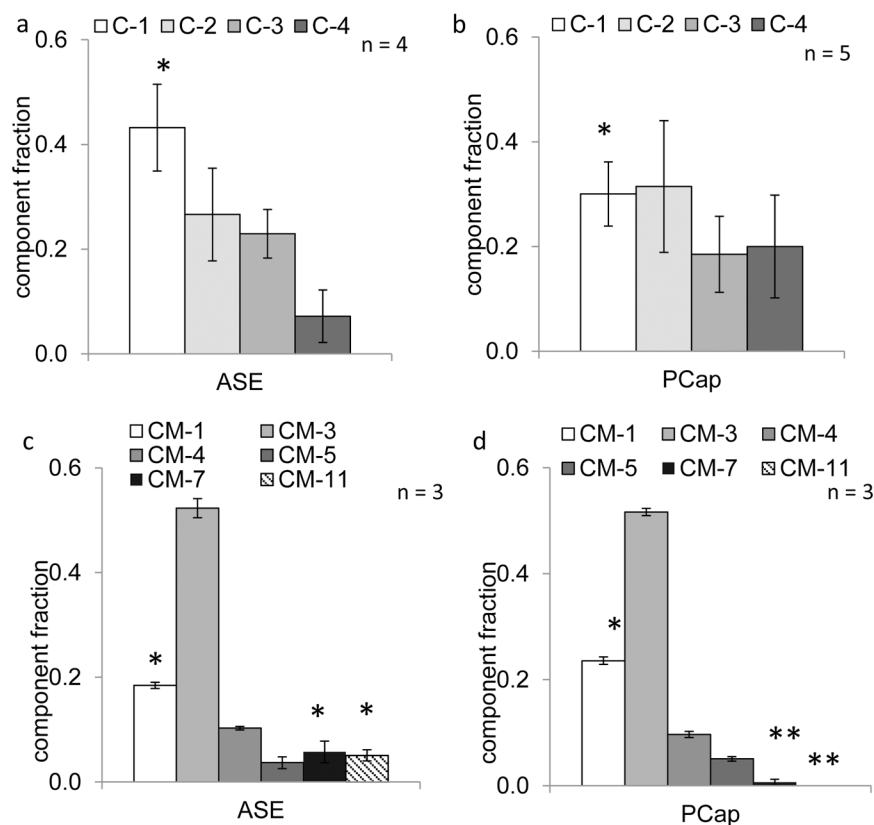


Fig. 5. Abundances of parallel factor (PARAFAC) components in aqueous soil extract (ASE) and passive capillary wick samplers (PCaps). *Components showing significant differences at $p = 0.05$, ** components showing significant differences at $p = 0.01$.

Comparison Between Field Passive Capillary Samples and Aqueous Soil Extraction

The DOC and TDN concentrations of ASE and PCap samples are given in Table 1. Since concentrations in the aqueous soil extracts depend on the mass ratio of soil to ultrapure water used during the extraction, the DOC/TDN ratio is also displayed to facilitate comparison. Samples were collected during both snowmelt and summer monsoon periods of the water year. The DOC/TDN ratios for both sample types were very high for the mid-snowmelt samples. Compared to those values, monsoon period samples were up to 30 times lower for ASE and 10 times lower for PCap samples. The $SUVA_{254}$ values showed a higher variability in ASE than PCaps (Table 1). Fluorescence index values showed small variations between snowmelt and post-monsoon samples for ASE but were consistently lower than those for PCap samples ($p = 0.05$). The abundance of original PARAFAC components for both sample types is displayed in Fig. 5. Component C-1 (FA-like) was most abundant in ASE, followed by C-2 (protein-like) > C-3 (FA-like) > C-4 (HA-like). In PCap samples the component fractions covered, on average, a narrower range from 0.31 (C-2) to 0.19 (C-3, Fig. 5b). The principal apparent differences between the sample types was, therefore, the abundance of C-1 and C-4, but only C-1 abundance was significantly different ($p = 0.05$). The abundances of the CM components in ASE decrease in the order CM-3 (unknown fluorophores) > CM-1 (unknown fluorophores) > CM-4 (hydroquinone-like) > CM-7 (reduced quinone-like) > CM-11 (oxidized quinone-like)

> CM-5 (reduced quinone-like, Fig. 5c) and in the order CM-3 > CM-1 > CM-4 > CM-5 > CM-7 for the PCap samples (Fig. 5d). The ASE samples had a significantly lower abundance of CM-1, a higher abundance of CM-7 and the only occurrence of C-11 (this component was not detected in PCap samples).

The FTIR spectra of ASE and PCap samples collected from (ASE2 and PCap1) are shown in Fig. 6. Spectra for both sample types showed a broad phenolic hydroxyl stretching band in the region 3330 to 3170 cm^{-1} (Table 2) as well as high intensity bands for asymmetric (ca. 1600 cm^{-1}) and symmetric (ca. 1400 cm^{-1}) stretching of carboxylate. Bands at approximately 1430 cm^{-1} (amide III), 1030 cm^{-1} (polysaccharides and phosphodiester) and below 900 cm^{-1} (aromatic C-H as well as inorganic metal-O stretches) were likewise present in both spectra. The principal differences between the spectra were greater O-H stretching abundance (3330 – 3170 cm^{-1}) in the PCap solutions, and greater intensity of aliphatic C-H stretching (2970 and 2935 cm^{-1}) in ASE solutions. Also, bands below 900 cm^{-1} were of higher intensity in PCap solutions. The peak intensity ratio of hydroxyl to carboxylate (symmetric plus asymmetric) stretching was 1.3 and 3.9 for ASE 2 and ASE 3, respectively. These values were significantly lower than corresponding ratios for PCap 1 and 4 solution samples collected at the same time from the same soils (5 and 4.8, respectively).

Water and Dissolved Organic Carbon Fluxes During Snowmelt 2011

The fact that precise hillslope location of PCap installation affects total water and C flux determinations is exemplified by measurement using PCaps installed in the field-site pedons in planar (Pedon 1) vs. convergent (Pedon 5) hillslope positions (Fig. 1c). Hence, as discussed in the introduction, soil physical and landscape parameters strongly impact field-based results. Data show a decrease in water and C flux with increasing depth at the planar site, whereas in the deepest depth for the convergent site, an increase in water and C flux is observed, presumably because of convergent flow regimes that deliver lateral flow at depth in Pedon 5 (Fig. 7). These data are included here simply to show the utility of PCaps for estimation of DOC and water flux in complex landscapes, and to highlight the fact that field site location of PCap installation can significantly influence the results obtained.

DISCUSSION

Experimental Constraints on Dissolved Organic Matter–Fiberglass Wick Interaction

The laboratory flow-through experiment was conducted to test whether interactions between influent DOM and wick ma-

material affect DOM molecular properties during transport along the wicks. Chemical processes occurring during water infusion to wicks that have been observed in previous studies include (i) solute release via wick dissolution (Goynes et al., 2000) or other PCap parts (Siemens and Kaupenjohann, 2003) and (ii) the retention of solutes/colloids onto the wicks (Czigani et al., 2005; Shira et al., 2006). Preferential sorption of specific dissolved organic compounds (i.e., fractionation) constitutes an additional process that, due to the heterogeneous nature of DOM, may impact the utility of PCaps for this aspect of critical zone research. Release of organic solutes from the wicks would translate into higher effluent concentrations compared to the feed solution. Neither TDN nor DOC showed this behavior (Fig. 3a and 3b) confirming that the pre-treatment of the wicks successfully removes any potential wick-derived organic C, as suggested already by Knutson et al. (1993).

However, FTIR spectra collected on the first two PV showed a difference in intensities of bands at ~ 1080 and 1010 cm^{-1} compared to the feed solution and subsequent PVs (Fig. 4b). Bands in this region result from stretching of phosphodiesteres (C-O-P) and polysaccharides (C-O-C, C-O). However, Si-O stretching also occurs at 1080 cm^{-1} (Smidt and Meissl, 2007; Farmer, 1974) and thus the unusual strong band at $\sim 1084\text{ cm}^{-1}$ in the spectrum of the first effluent can be attributed to inorganic Si-O stretching of silicic acid resulting from glass dissolution. The decreased intensity of this band in the 4 and 6 PV collections (Fig. 4) is consistent with progressively decreasing Si release to steady state early in the experiment. A pulse-like release of Si is further indicated by Si effluent values that spike in the first PV after re-application of flow (up to 15.8 mg L^{-1}) but less Si release during pseudo steady state flow ($\sim 1.3\text{ mg L}^{-1}$).

Solute sorption would be evidenced by lower values in effluent compared to feed solution. While sorption of mineral colloids (clays, iron oxides, silicon, and feldspathoids) on fiberglass wicks has been reported in experimental studies (Czigani et al., 2005; Shira et al., 2006), DOM sorption has not yet been investigated. Some sorption of DOM may contribute to the lower DOC concentration in effluent relative to feed solutions during the first infiltration cycle (Fig. 3a). However, pure water present in the wick material also led to decreased DOC concentrations in the first PV suggesting that this effect is likely a result of dilution and that sorption does not significantly affect effluent DOC sample concentration.

Prior studies have shown preferential sorption of aromatic DOM, primarily on hydrous metal oxide mineral surfaces and much lower sorptive affinity in general for silica surfaces (Chorover and Amistadi, 2001; Feng et al., 2005; Kaiser and Guggenberger, 2003; Kaiser and Zech, 1997; Meier et al., 1999). The $SUVA_{254}$, a surrogate for DOM aromaticity (Weishaar et al., 2003), was slightly higher in both the feed and effluent than is generally reported for surface water samples for which the index was initially developed. This could indicate the interference of other light-absorbing material such as Fe or nitrate or simply that soil extracts have higher $SUVA_{254}$ values. However, since the values for the feed and

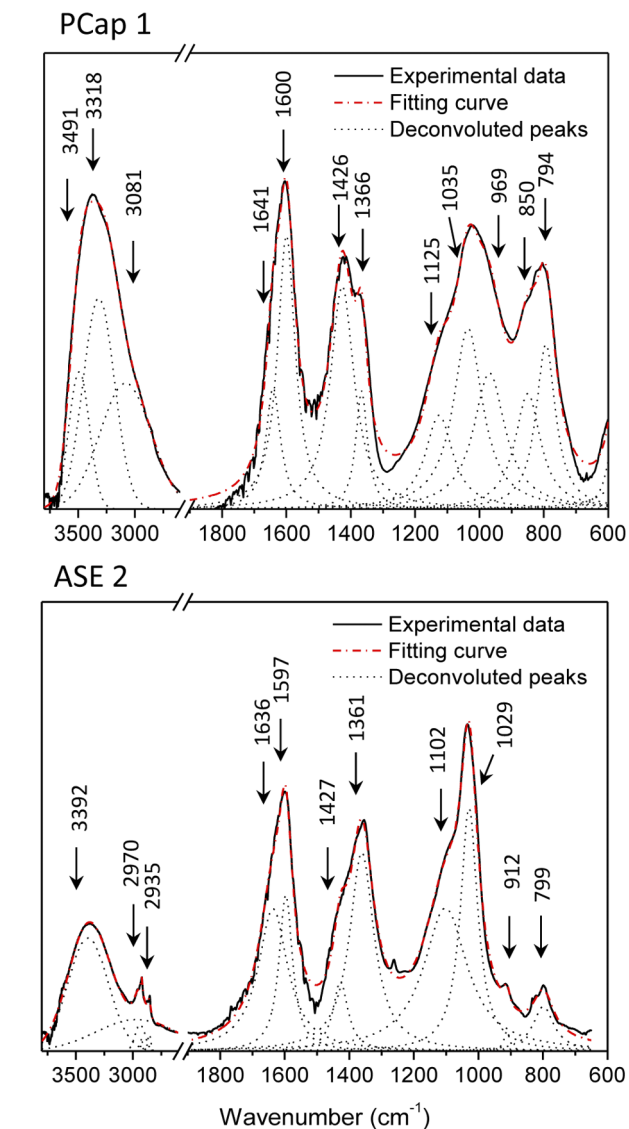


Fig. 6. Fourier Transform Infrared (FTIR) absorbance spectra with deconvoluted peaks for synchronous passive capillary wick (PCap) and aqueous soil extract (ASE) samples.

effluent are consistent throughout the experiment, the trend in $SUVA_{254}$ values is informative. The $SUVA_{254}$ showed a repeated pattern of low values in the first effluent PV following stopped-

Table 2. Band assignment based on Swift (1996)†, Senesi et al. (2003)‡, and Farmer (1974)§.

Band cm^{-1}	Assignment
3080–3490	OH stretch of phenolic OH†
2900–2850	Aliphatic C-H stretching†,‡
1690	Carbonyl vibrations of carboxyl groups, aldehydes, and ketones‡
1630–1640	C = O of amide groups (amide I) and quinone ketones‡
1600	Asymmetric-COO ⁻ stretch, aromatic C = C stretch†
1427	C-N stretching of primary amides (amide III)‡
1390–1410	Symmetric COO-stretch
1360	Symmetric-COO-stretch and/or-CH bending of aliphaticst
1100–1125	C-OH stretching of aliphatic OH‡
1080	Si-O of silicates‡
1080–1010	C-O stretching of polysaccharides, phosphodiesteres (C-O-P)§
900–600	Out of plane bending of aromatic C-H‡

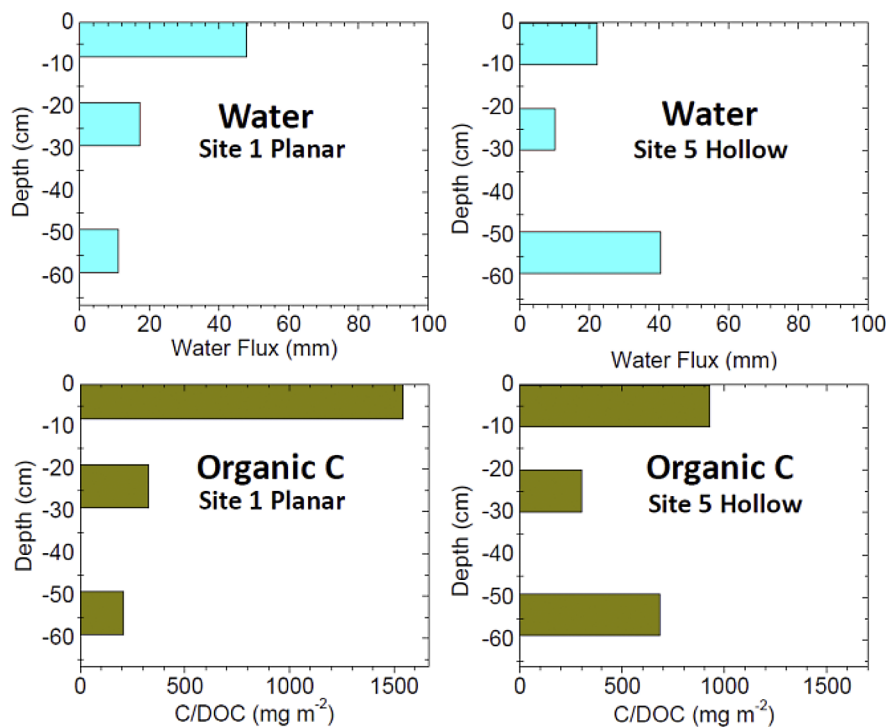


Fig. 7. Data on water and C flux as calculated for two pedons each equipped with three passive capillary wick (PCap) samplers. Results are plotted as a function of PCap plate installation depth and integrate the snowmelt 2011 period.

flow, consistent with preferential sorption of UV-absorbing moieties, followed by high values in subsequent PV before a stabilization with intermediate $SUVA_{254}$ values (Fig. 3b). The depression of $SUVA_{254}$ values following each stop flow event indicates that this effect is somewhat persistent, perhaps because of the production of new sorption sites during the 24 h stop-flow period, transformation of the wick surface material, and/or re-organization of sorbate fractions. Higher $SUVA_{254}$ values in subsequent PV indicate the desorption of UV-absorbing, putatively aromatic, DOM. Hence, the wicks appear to retard slightly the transport of more aromatic OM fractions via sorption. Overall, however, $SUVA_{254}$ values do not deviate significantly from the feed solution, indicating that the overall fractionation effects are minor.

Like $SUVA_{254}$, FI values provide an indication of DOM fractionation during transport along the wick surfaces. The FI values increased at the beginning of each infiltration cycle (Fig. 3c) and decreased subsequently to within the range of feed solution. The FI is an important DOM parameter since it is used for DOM sourcing (e.g., microbial vs. plant-derived DOM) based on the observation that microbial DOM is relatively depleted in lignin-derived polyphenols and a change in FI of 0.1 or more is considered significant (McKnight et al., 2001). Since $SUVA_{254}$ values decrease for the same initial samples for which FI is elevated, we interpret the higher FI values to be the result of sorptive retardation of aromatic polyphenols. Another possibility that cannot be excluded is that solute release from fiberglass dissolution quenches DOM component fluorescence through DOM-solute molecular interaction (Lakowicz, 2006). If intermolecular association were to lead to a blueshift in the EEM, the FI could be likewise affected.

Whereas FI provides a ratio of fluorescence intensities at two distinct wavelengths, PARAFAC analysis of the full EEM provides additional insight into sorptive fractionation that may be leading to differences between EEMs of feed and effluent solutions. Importantly, however, no systematic change in PARAFAC component abundance is evident from the data (Fig. 3d and 3e). This is consistent with relatively minor sorptive DOM fractionation effects of the wicks, and suggests that fiberglass wick PCaps can be used with minimal negative impact for quantitative collection of DOM solution from pore water in situ before subsequent qualitative spectroscopic analysis.

The TDN concentrations were always in the range of feed TDN concentrations and with the exception of high TDN concentration in the second infiltration cycle, TDN effluent concentrations were steady, suggesting that TDN moves conservatively through the wicks. The origin of the spiking effluent TDN concentrations is however unclear.

Care must be taken when translating laboratory results to the field scale. The experimental DOM solution was derived from an aqueous soil extraction that may or may not be fully representative of solutions percolating through field soil (also see next section) and this could impact results. For example, if in situ soil solution contains more or less aromatic OM than that used in the experiment, the relative impact of sorptive fractionation could potentially be affected. Nonetheless, based on the results of the current experiment, OA-horizon DOC concentrations measured using PCaps can be assumed to be representative within 5% error. The TDN concentrations are representative with a 2% error (when apparent outliers are excluded). The $SUVA_{254}$ shows variations imposed on effluent solutions on the order of 3 to 8%, depending on the flux associated with a given sampling event (higher error is expected for smaller events). Fluorescence index data suggest similar magnitude of potential error in that parameter for field collection, whereas PARAFAC analysis of fluorophores active below Ex 250 and Em 350 may be slightly more impacted (i.e., within 5% of the true values for all components) than fluorophores active above this region. The FTIR analyses from PCap samples are considered representative of pore water solutions, but investigators should be aware that Si-O stretching from soluble silica (which can of course derive from natural soil solution or from the fiberglass wicks themselves) may interfere with carbohydrate bands deriving from DOM.

Comparing Passive Capillary Wicks and Aqueous Soil Extraction

In respect to comparing PCaps to other methods of soil DOM collection, potential interaction between the fiberglass wicks and soil solution is one potential shortcoming of the for-

mer. However, the above-presented results indicate that DOM moves conservatively through the wicks. We contend, therefore, that fiberglass wick PCaps provide an accurate representation of soil DOM mobile in pore waters and can be used for the purpose of DOM collection from the unsaturated zone in field sites, and as a standard against which laboratory ASE can be compared. The ASE methods are commonly employed to obtain information about soluble DOM constituents (Swift, 1996) but destructive sampling of soil before laboratory extraction is likely to induce disturbances and a number of studies addressed the impact of specific procedures. Also, while parameters such as extraction solution, pH, and solid/liquid ratio are known to affect extracted solute concentration (Fest et al., 2008) it is still difficult to predict precisely how ASE extracts differ from solutions sampled during percolation through the soil. In the present study, we used the approach of comparing in situ PCap samples with ASE performed on soils collected at the same location and time, to elucidate the effects of disturbance and laboratory extraction on specific parameters used to characterize DOM.

The observation of higher variability in the ASE DOM parameters than in the PCap samples can be attributed, in part, to seasonal effects impacting DOM characteristics (Kalbitz et al., 2000) and the fact that not all ASE sampling dates also yielded PCap samples from flowing solutions. Therefore, we limit further discussion to those samples for which ASE samples and PCap solutions were taken in the same sampling campaign, and for which direct comparison is most valid. However it needs to be stated that due to the small sample number these results represent trends whose statistical significance is unclear, but that nonetheless provide direction for future studies. Results indicate no considerable difference between PCap samples and ASE for a number of parameters such as the TOC/TN ratio or $SUVA_{254}$ (Table 1). However, $SUVA_{254}$ values for PCap samples 1 and 4 were 25 to 30% lower than the corresponding ASE samples, indicating a lower concentration of UV-absorbing moieties, and suggesting greater aromaticity of ASE relative to PCap DOM, even after accounting for a potential error of 5% as discussed above. Likewise, higher FI values were observed for the PCap relative to ASE DOM samples, also consistent with a higher proportion of lignin-derived phenols in the latter. According to the flow-through experiment results, FI in PCap samples may be overestimated by 3 to 9%; however, even after applying this correction, PCap FI values remain substantially higher than the ASE values. Hence, both $SUVA_{254}$ and FI values are consistent with laboratory ASE yielding more aromatic DOM than PCap sampling in the field.

Differences in PARAFAC component fits to the two sampling procedures were also significant in that ASE solutions showed greater abundance of C-1 region (FA-like in the original PARAFAC model) as well as CM-7 and CM-11 (of the Cory and McKnight (2005) model) than did PCap solutions. In contrast CM-1 in the ASEs was found to have lower abundances than in PCap samples. Although it is difficult to assign specific structural characteristics to the mixture of fluorophores (and even more difficult to PARAFAC components), the trend

in $SUVA_{254}$ and FI suggests that PARAFAC component C-1 may be related to aromatic FAs. Most components of the CM model are already well constrained and the results indicate that ASE yield both higher abundance in “reduced” (CM-7) as well as oxidized quinone-like fluorescence (CM-11).

In contrast to the UV-Vis and fluorescence spectroscopy results, FTIR spectral deconvolutions showed lower (phenolic) hydroxyl/carboxylate intensity ratio for ASE relative to PCaps which would seem to contradict the asserted higher proportion of aromatic DOM in the case of ASE. However, this apparent contradiction may be explained, in part, by the higher abundance in PCaps of C-4 (HA-like) fluorescence (Fig. 5), which could be an important source of the phenolic hydroxyls that are prominently represented in the FTIR spectra (Fig. 6), and also the fact that contributions to O-H stretching in the FTIR spectra can derive from alcoholic OH, in addition to H_2O , and N-H stretching.

While the presented data confirms that fiberglass wicks in PCaps do not significantly alter DOM solution, it is important to point out that soil physical constraints imposed by PCap design (e.g., tension imposed at soil-PCap interface) can impact the sampled solution. In addition to the sampler tension, pit excavation and installation of the samplers constitute a disturbance wherein preferential flow paths can be created (Weihermüller et al., 2007). Numerical analyses have shown that flow can be disturbed by the device itself and specific designs have been proposed to minimize these effects (Mertens et al., 2007). Such perturbations can lead to a situation where the sample may not be representative of the soil solution targeted for isolation. While the present study limits itself principally to elucidating the impacts of PCaps on soil DOM chemistry, we also highlight the role of field heterogeneities by showing how the choice of hillslope sampling location affects quantitative results pertaining to C and water flux (Fig. 7). Hence, the influences of (i) soil landscape properties and (ii) potential installation-induced changes in local soil physics of a given field system are considered equally important in terms of sampler evaluation. Development of a better understanding of these relations between soil solution chemistry and the physics of field soil solution sampling is considered fertile ground for future research.

CONCLUSIONS

The experimental data presented here suggest that fiberglass wicks in PCap samplers do not significantly change DOM chemistry: DOM parameters such as TOC, TN, and fluorescence PARAFAC component abundances are not strongly impacted by DOM interaction with the fiberglass wick material. Although minor fractionation due to retention of lignin-derived polyphenols are indicated by $SUVA_{254}$ and FI evolution, wick effluent is considered to accurately represent DOM solution. Comparing DOM characteristics derived from ASE vs. PCap sample collection indicated that ASE yield higher amounts of UV-absorbing, presumably aromatic DOM, likely because of disturbances introduced during the extraction process.

ACKNOWLEDGMENTS

The Jemez-Santa Catalina Critical Zone Observatory is supported by the National Science Foundation, Grant no. EAR-0724958. Thanks to Mary Kay Amistadi, Scott Compton, Tim Corley, John Leedy, Allison Peterson, and Angelica Vazquez-Ortega for assistance with sampling and analysis.

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