

DIVISION S-2—SOIL CHEMISTRY

Artifacts Caused by Collection of Soil Solution with Passive Capillary Samplers

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ABSTRACT

Soil solution was collected with passive capillary samplers (PCAPS) and zero-tension samplers (ZTS) from A horizons of forested soils. The volume and chemistry of collected solutions were measured weekly during discrete seasonal collection periods. Acid-washed PCAPS increased alkalinity (3-fold), pH (1–3 units), and concentrations of Ca (2-fold), Na (8-fold), and Si (4-fold), relative to ZTS solutions. Aluminum concentrations were dramatically reduced in PCAPS compared with ZTS samples. Differences in solution chemistry were attributed to leaching and weathering of fiberglass wicking material utilized in the PCAPS. In addition, PCAPS collected greater volumes (normalized by sampler area) of solution relative to ZTS in weak-structured sandy loam soil due to a preponderance of matrix flow. The results indicate that the PCAPS used in this study are not suitable for aqueous geochemical studies of dilute soil solutions.

THE ANALYSIS OF SOIL SOLUTION is an essential aspect of soil science. Soil solution is the primary mediator of pedogenic processes and it influences groundwater and surface water quality. However, prior to analysis, soil solution must first be isolated from the soil. Numerous in situ devices have been employed over the years to collect soil solution, including zero-tension samplers or ZTS (Parizek and Lane, 1970; Haines et al., 1982; Jemison and Fox, 1992; Marques et al., 1996) and suction cup solution samplers (Parizek and Lane, 1970; Shaffer et al., 1979; Barbee and Brown, 1986; Chorover et al., 1994; Brandi-Dohrn et al., 1996a; Marques et al., 1996). Although these are the most commonly used samplers, both have inherent flaws in collecting solution.

The main limitation of ZTS is that they only sample that fraction of soil water flux occurring under saturated soil conditions or during macropore flow. In response to hydraulic gradients, flow lines are potentially diverted around the solution sampler when soil water content is below saturation (Boll et al., 1991; Jemison and Fox, 1992). Another constraint of ZTS is the large cross-sectional area requirement necessary for collection efficiency (Radulovich and Sollins, 1987). Also, stony soils do not allow for the practical installation of large ZTS such as those used by Jemison and Fox (0.465-m² cross-sectional area; 1992).

Although suction cup samplers may be used to collect solution under unsaturated conditions, they do not provide a reliable estimate of soil water flux (Shaffer et al.,

1979; Barbee and Brown, 1986; Grossmann and Udluft, 1991; Brandi-Dohrn et al., 1996a). The area or zone of sampling is unknown and may change with varying moisture conditions or suction applied. In addition, suction must be applied manually to the sampler several hours or days prior to solution collection. This is problematic because the magnitude of tension exerted on soil water gradually decreases over time. Lastly, because of the small cross-sectional area of the cup, multiple samplers are required to represent adequately soil variability (Barbee and Brown, 1986).

Brown et al. (1986) first introduced passive capillary samplers (PCAPS) to provide an alternative means of sampling soil water in the field. As a result of their high conductivity and the tension exerted, PCAPS collect matrix and macropore flow under both saturated and unsaturated conditions, thus providing a more representative soil solution sample and improved collection efficiency (Boll et al., 1991). The specific design of PCAPS varies slightly in the literature (Holder et al., 1991; Boll et al., 1991; Biddle et al., 1995; Brandi-Dohrn et al., 1996b) but the basic structure includes woven fiberglass ropes ("wicks") that create a hanging water column to produce a tension where the wicks contact the soil. Collected water is then transported along the length of the wicks into a collection container. The cross-sectional area of the samplers is easily manipulated for installation in stony soils.

The effects of wick material on the chemical composition of collected solutions is not well known. Holder et al. (1991) determined that fiberglass wicks did not adsorb Br⁻, NO₃⁻, Cd²⁺, ethylbenzene, toluene, naphthalene, or trichloroethylene. Boll et al. (1992) reported minimal retardation of FD&C no.1 blue dye in wicks. However, Biddle et al. (1995) found there was an initial contamination of solution from CO₃²⁻ at a level of almost 25 mol/m³ even after washing with 5% (v/v) phosphate-free enzyme-surfactant, rinsing with 5% (v/v) HCl, and then rinsing with deionized water. After leaching the wicks with 1.5 L of distilled water, the CO₃²⁻ concentration decreased to <80 mmol m⁻³ and soil solutions collected subsequently were considered unaffected by the wick material. Biddle et al. (1995) employed PCAPS to assess major ion and aqueous colloid chemistry in a field soil but they were unable to evaluate potential artifacts because no other kind of sampler was used for comparison. Other researchers have shown the utility of PCAPS for measuring transport of non-reactive species (e.g., bromide and nitrate) in soils (Holder et al., 1991; Brandi-Dohrn et al., 1996b). However, their application

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Table 1. Selected morphological and chemical data for Pottsville sandstone-derived and Mauch Chunk red shale-derived soils.

Subgroup	Horizon	Depth cm	Matrix color	Soil† structure	Textural‡ class	Particle size§			O.C.¶	pH#
						Sand	Silt	Clay		
						g/kg				
Pottsville Sandstone–Clymer Variant										
Typic Dystrachrept	O	3–0	10YR 2/1						288.0	4.48
	A	0–12	10YR 2/2	1 f sbk	SL	648	223	129	57.4	3.37
	B/A	12–30	10YR 5/3	1 f sbk	SL	630	226	144	17.5	3.86
Mauch Chunk Red Shale–Leck Kill Variant										
Typic Hapludult	O	1–0	2.5YR 3/2						377.8	4.08
	A	0–10	2.5YR 4/2	1 f/m sbk	SiL	114	749	128	58.1	4.02
	B/A	10–23	2.5YR 4/3	2 f/m sbk	SiL	152	615	258	30.6	4.08

† Grade (1 = weak, 2 = medium); size (f = fine, m = medium); shape (sbk = subangular blocky).

‡ SL, Sandy Loam; SiL, Silt Loam.

§ Particle size determined by pipette method.

¶ O.C., organic carbon, determined using SSM-5000A and TOC-5000A (Shimadzu Corp., Kyoto, Japan).

Soil pH determined using 3:50 (soil:water) for organic horizons and 1:1 for the mineral horizons.

to comprehensive geochemical studies of dilute soil solutions has not been tested.

Because of the high CO_3^{2-} concentrations observed by Biddle et al. (1995), we hypothesized that PCAPS could significantly alter measurement and speciation of soil solution chemistry in acid forest soils. We postulated also, that soil physical properties (e.g., soil texture and structure) could influence the efficiency of PCAPS to sample soil solution. Therefore, the objective of this work was to compare the chemistry—including cations, anions and dissolved organic constituents—and depth (volume normalized by sampler area) of soil solution collected using ZTS and PCAPS in two acid forest soils with contrasting physical properties.

MATERIALS AND METHODS

Construction of Solution Samplers

Zero-tension samplers were constructed from 0.64-cm-thick, acid-washed polyvinylchloride (PVC) sheeting to give a sampling area of 0.09 m². Flexible PVC tubing was used to connect the solution sampler to a 15-L acid-washed high density polyethylene (HDPE) container. The interior of each ZTS was filled with acid washed polypropylene pellets in the fall and winter seasons. These were replaced in the spring season with HDPE pellets rinsed with distilled–deionized water because of suspected contamination (see Data Structure and Statistical Analyses). Zero-tension samplers were forced against the top of the tunnel with wooden blocks and shims.

The PCAPS (0.027 m²) for both soil types were built to transmit an infiltration rate of 2.54 cm/h, typical of high intensity Pennsylvania storms, determined on the basis of Eq. [1]:

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

where K_{sat} of the soil horizon was estimated to be 2.54 cm/h. The K_{sat} of the 1.27-cm (diameter) fiberglass rope used in this study (no. 1381 from Pepperell Braiding Co., Pepperell, MA) had been previously determined to be 36 cm/h (Holder et al., 1991). An initial tension of 0.45 m was exerted on the soil at zero flux, through the total height drop of wicking material.

The fiberglass rope was combusted at 400°C for 4 h to remove organic impurities (Knutson et al., 1993). Preliminary tests showed that immersion of 3.15 g of wick material (about 7.5 cm of wick length) in 200 mL of ultrapure water increased the initial pH by 4 units because of carbonate dissolution.

Therefore, the wicking material was soaked in 0.01 M HNO_3 and the solution was changed every 24 h for 10 d until the pH stabilized at pH 2 for several days. This treatment was chosen because we postulated it would dissolve the carbonates but not destroy the integrity of the fiberglass rope. The fiberglass rope was then rinsed with deionized water, air-dried and solution samplers were constructed in a manner similar to Biddle et al. (1995). Turnbuckles were used to connect the upper plexiglas and plywood wick platform to the lower plywood platform at each of the four corners. The remaining fiberglass rope was passed through PVC pipe between the sampler and collection container. The turnbuckles were expanded as necessary, upon installation, to ensure adequate soil to wick contact.

Study Sites

The study sites were located on Laurel Hill anticline, Somerset Co., southwestern Pennsylvania, in the Allegheny Mountains of the Appalachian Plateau physiographic province. Two sites located on watershed divide positions, at about 700 m elevation and approximately 0.45 km apart, were chosen because they were in contrasting geologic units that give rise to soils with different physical properties. The “Pottsville” site was located on the Pottsville Group, a geologic unit composed primarily of sandstone. The “Mauch Chunk” site was located on the Mauch Chunk Formation, composed of red shale and siltstone. At each site three pits were excavated parallel to the slope, spaced approximately 4.5 m apart across the landform. Pottsville-derived soils are variants of the Clymer soil series, whereas Mauch Chunk–derived soils are considered Leck Kill soil series variants (Table 1). Both soils are moderately well-drained. The vegetative cover at both sites was comprised of a mixed oak (*Quercus rubra* L., *Quercus prinus* L., *Quercus alba* L., and *Quercus coccinea* Muenchh.) overstory.

Canopy Throughfall and Soil Solution Sampling

Canopy throughfall was sampled to assess soil input chemistry. In the fall of 1996, we used a single trough-style throughfall collector (Kostelnik et al., 1989) made of acid-washed PVC piping with a sampling area of 0.12 m² (1.63 m × 0.075 m). During the winter and spring seasons each trough-style sampler was replaced with three acid-washed plastic standard rain gauges, each with a sampling area of 8.11 × 10⁻³ m². Rain gauges were open at the top (i.e., funnels were removed).

Two soil solution samplers (1 PCAPS and 1 ZTS) were installed in August 1996, in each of three soil pits per site. Samplers were installed laterally from soil pits directly beneath

Table 2. Median anion, cation, alkalinity, pH, and dissolved organic constituent concentrations based on volume weighted mean concentrations for canopy throughfall and soil solution samples.

Solution† sampler	Pottsville sandstone															
	SO ₄	NO ₃	Cl	Alk.	DOC‡	DON§	Mg	Mn	Ca	K	Na	NH ₄	Al	Fe	Si	pH
A-ZTS	56.2a¶	4.94b	17.9a	-66.9a	1680b	85.8b	5.77a	1.75a	9.64a	14.8a	26.9a	0.00a	36.9a	3.59a	43.9a	4.16a
A-PCAPS	43.3b	4.54b	18.5a	77.2b	1450b	65.6b	15.7b	1.65a	28.0b	27.2a	151.6b	3.05b	1.9b	3.65a	62.2b	6.15b
	Mauch Chunk red shale															
Solution sampler	SO ₄	NO ₃	Cl	Alk.	DOC‡	DON§	Mg	Mn	Ca	K	Na	NH ₄	Al	Fe	Si	pH
A-ZTS	57.0a	36.7a	19.2a	-54.2a	903a	80.2a	9.88a	5.63a	28.1a	14.5a	20.9a	9.54a	17.7a	2.85a	30.3a	4.27a
A-PCAPS	63.8b	23.7a	28.2b	316b	989a	82.7a	28.6b	1.09b	33.7a	17.6a	324.3b	4.53a	0.6b	3.39b	290b	7.05b

† A, A horizon; ZTS, zero-tension sampler; PCAPS, passive capillary sampler.

‡ DOC, dissolved organic carbon.

§ DON, dissolved organic nitrogen.

¶ Median values within a column, for a given site, followed by the same letter are not significantly different ($\alpha = 0.05$) using Wilcoxon signed-rank test.

A horizons. Installation depths were 14 to 20 cm and 7 to 14 cm for the Pottsville and Mauch Chunk sites, respectively.

Throughfall and soil leachate were sampled five times from 30 Aug. 1996 to 6 Oct. 1996 (fall), five times from 17 Nov. 1996 to 16 Jan. 1997 (winter), and six times from 13 Apr. 1997 to 27 May 1997 (spring). Solutions were sampled on the same date at each site on a weekly basis. The volume of solution collected by each sampler was measured and normalized by the cross-sectional area of the sampler to give a measure of sample "depth", reported in centimeters. Although sampler equilibration time was relatively short in the soil, all samplers were installed in the soil within a few days of one another so that differences in solution chemistry could be related directly to the sampler type.

Upon collection, throughfall and soil solution samples were transferred into acid-washed HDPE bottles and packed on ice for transport to the laboratory where they were immediately refrigerated (4°C) prior to analysis.

Chemical Analysis

Solution pH, corrected for temperature, was measured by combination electrode on stirred, unfiltered samples within 24 h of collection. Samples were then filtered through pre-washed cellulose ester membrane prefilters and 0.45- μ m (nominal pore size) membranes in series. Samples for dissolved organic carbon (DOC) and cation analyses were acidified with nitric acid to pH 2. (Acid was added to the DOC samples to facilitate purging of inorganic carbon and no flocculation of DOC was observed.) Alkalinity was measured within 72 h by Gran titration with 0.01 M HCl as titrant (Morel and Hering, 1993). Anions (SO₄, NO₃, Cl, PO₄, F, and Br) were analyzed by ion chromatography (IC) (DX500, Dionex Corp., Sunnyvale, CA). Cations (except Si and NH₄) were analyzed by atomic absorption (AA) spectrophotometry (IL Video 22, Allied Analytical Systems, Waltham, MA) or graphite furnace AA (HGA-600 and Zeeman/5000 Furnace Module, Perkin-Elmer Corp., Norwalk, CT). Silicon was analyzed colorimetrically by autoanalyzer following molybdate blue reaction (Clesceri et al., 1989; modified by Technicon Instrument Corp., Tarrytown, NY). Ammonium was measured by ion selective electrode. Dissolved organic carbon was measured by high temperature combustion followed by detection of CO₂ by infrared absorption (TOC-5000A, Shimadzu Corp., Kyoto, Japan). Dissolved organic nitrogen was calculated from total-N (Kjeldahl) minus inorganic N.

Soil samples were obtained from genetic horizons concurrent with their description in the field. All samples were air dried and sieved through 2 mm mesh. Solid-phase organic carbon was measured on the TOC-5000A equipped with a solid sample module. Particle size analyses were performed on mineral samples using the pipette method (Gee and Bauder, 1986). Soil pH was determined in triplicate using a combination electrode with a 3:50 soil to water ratio for forest floor samples (Karam, 1993) and a 1:1 soil to water ratio for mineral samples (Thomas, 1996).

Speciation of Soil Solution

Soil solutions collected in the spring were speciated by MINTEQA2 (Allison et al., 1990). All measured constituents, except DON, were input to the model. Metal and proton binding with dissolved organic matter (DOM) was modeled using a pH-dependent composite ligand model (Dobbs et al., 1989) that was recently incorporated into MINTEQA2 (Allison and Perdue, 1994). We assumed a ligand site density of 9 μ mol/mg C based on DOM titration experiments performed

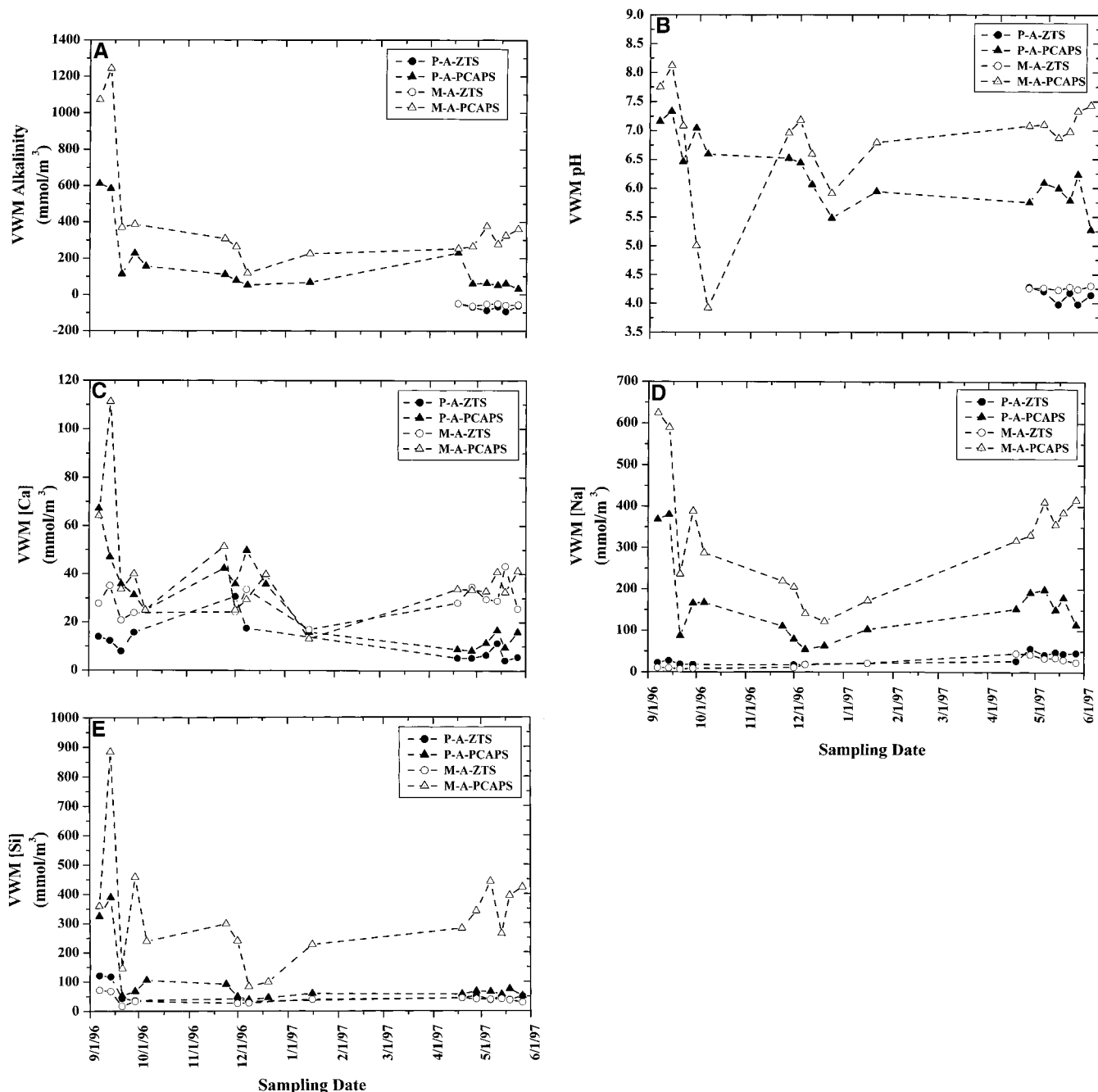


Fig. 1. Time series of volume weighted mean (VWM) solute concentrations in ZTS and PCAPS solutions collected under A horizons of Pottsville- (P) and Mauch Chunk-derived (M) soils: (a) alkalinity, (b) pH, (c) Ca, (d) Na, and (e) Si.

in our lab on northern hardwood forest floor DOM. This value is also in agreement with values reported by Cronan and Aiken (1985) and Perdue (1985). Means and standard deviations for DOM complex stability constants in MINTEQA2 are based on the work of Susetyo et al. (1991). The Davies equation was used to determine activity coefficients of ions in solution. Speciation was calculated for soil temperature values collected in the field. Speciation results are expressed as a percentage of the total measured component concentration for a particular sampler type averaged over the entire spring season.

Data Structure and Statistical Analyses

Volumes of solution (normalized by sampler area) collected from three replicate soil solution samplers were averaged and

this mean value was used in all statistical analyses. On two occasions, a single pit at the Mauch Chunk site was flooded and sampler data collected from the pit were discarded for those dates.

For each solute, the concentrations measured in replicate samplers were combined to create a volume weighted mean (VWM) for each collection date Eq. [2]:

$$VWM_a = \left(\sum_{i=1}^n C_{ai} V_i \right) / \left(\sum V_i \right) \quad [2]$$

where, C_{ai} is the concentration of Species a in Sample i , n is the number of samples and V_i is the volume of soil solution for Sample i .

Data for the three seasons were combined into a single

Table 3. MINTEQA2 speciation results Spring 1997 samples. Data presented as a percentage of total analyzed concentration for a given component.

Species	Solution sampler†			
	Pottsville sandstone		Mauch Chunk red shale	
	A-ZTS	A-PCAPS	A-ZTS	A-PCAPS
	%			
pH‡	4.2	6.0	4.3	7.2
H ₂ CO ₃	<0.1	64.6	<0.1	10.5
HCO ₃ ⁻	<0.1	35.4	<0.1	83.2
Al-DOM	89.0	50.3	78.0	5.4
Al ³⁺	10.1	0.3	19.2	1.0
AlOH ²⁺	<0.1	0.6	1.0	<0.1
Al(OH) ₂ ⁺	<0.1	19.2	0.4	5.1
Al(OH) ₃	<0.1	28.8	<0.1	84.1
Al(OH) ₄ ⁻	<0.1	<0.1	<0.1	4.1
Fe-DOM	86.6	4.7	65.7	6.2
Fe ³⁺	<0.1	<0.1	<0.1	<0.1
FeOH ²⁺	0.5	0.1	1.8	<0.1
Fe(OH) ₂ ⁺	12.4	93.9	32.4	74.7
Fe(OH) ₃	<0.1	1.0	<0.1	15.5
Fe(OH) ₄ ⁻	<0.1	<0.1	<0.1	3.4
Ca-DOM	6.0	41.0	10.0	36.9
Ca ²⁺	93.2	55.6	89.2	62.5
Mg-DOM	0.2	8.3	<0.1	7.4
Mg ²⁺	98.7	91.1	98.9	91.8
SI _{gibbsite} §	-3.28	0.32	-3.00	-0.79
SI _{ferrhydrite}	7.97	10.78	8.21	11.62

† A, A horizon; ZTS, zero-tension sampler; PCAPS, passive capillary sampler.

‡ Solution pH values, corrected for temperature, measured by combination electrode.

§ SI, Saturation Index = log (IAP/K_{sp})

data set to generate medians and for statistical analysis of differences between observations paired by sampler type and date. The nonparametric Wilcoxon signed-rank test ($\alpha = 0.05$) was executed by Minitab, Inc. (State College, PA) software. Tests were performed on VWM solute concentrations and solution depths to determine whether median differences between sampler types were significantly different from zero (Helsel and Hirsch, 1997). This statistical test was employed because the data were not normally distributed and samples collected from the same sampler at different times may not be statistically independent. Median values are reported for all samples collected, unless specified otherwise, to be consistent with the non-parametric statistical test employed. Because of trace nitric acid contamination of polypropylene beads during the fall and winter sampling periods, alkalinity, pH, and NO₃ data for ZTS are shown only for spring samples.

RESULTS AND DISCUSSION

Impact of Sampler on Solution Chemistry

Measurements of soil solution chemistry were dependent on the type of sampler employed (Table 2). Median alkalinity values were elevated in PCAPS relative to ZTS in both soil types. Alkalinity values of the PCAPS solutions were initially very high (>600 mmol/m³) but decreased rapidly during the first 5 wk the samplers were installed in the ground (Fig. 1a). (Note that values of alkalinity and pH in Fig. 1a and b are shown only for ZTS spring samples due to trace nitric acid contamination from the polypropylene beads used during the other two seasons.) However, alkalinity remained positive and never declined to the negative values obtained

Table 4. The median depth of solution (volume normalized by sampler area) for canopy throughfall and soil solution samples.

Solution† sampler	Depth of Solution	
	Pottsville sandstone	Mauch Chunk red shale
	cm	
TF	2.1a‡	2.1a
A-ZTS	0.43b*	0.84b
A-PCAPS	4.3c*	2.2a

† TF, throughfall; A, A horizon; ZTS, zero-tension sampler; PCAPS, passive capillary sampler.

‡ Median values within a column followed by the same letter are not significantly different ($\alpha = 0.05$) using Wilcoxon signed-rank test.

* Indicates median values within a row are statistically different ($\alpha = 0.05$) using Wilcoxon signed-rank test.

from ZTS in the spring season. Increased levels of alkalinity were apparently derived from dissolution of carbonate in the fiberglass wicks, a process that was also found to buffer solution pH (Table 2). Passive capillary sampler solution pH decreased only slightly through time in Mauch Chunk samples, but a steady pH decrease through time was observed in the Pottsville PCAPS (Fig. 1b). However, pH values remained much higher than those in ZTS solutions during the spring sampling period.

Median concentrations of Ca, Na, and Si were higher in PCAPS relative to ZTS (Table 2). Figures 1c, d, and e illustrate the initially elevated levels of Ca, Na, and Si, respectively, in Pottsville and Mauch Chunk PCAPS relative to ZTS in the same geologic unit. Calcium and Na concentrations in PCAPS solutions decrease concurrently with alkalinity, supporting the contention that the elevated levels may be attributed to wick dissolution. Calcium concentrations in PCAPS solutions are nearly equivalent to ZTS concentrations about 1 mo after installation and Si concentrations of PCAPS and ZTS solutions are almost identical in the Pottsville soil about 2 mo after installation. Figure 1d shows that the PCAPS data have much higher initial values of sodium, relative to ZTS, and remain higher throughout the study period. These data indicate that solution contamination from PCAPS may be mitigated with time but the requisite duration is solute dependent.

As a result of its impact on solution composition, the type of sampler also affects calculated speciation of some (but not all) dissolved constituents (Table 3). As expected, calculations indicate a relative enrichment of carbonate species (H₂CO₃ and HCO₃⁻) and Al and Fe hydrolysis products in the PCAPS solutions. Although Al-DOM and Fe-DOM predominated in the ZTS samples, these species may be underestimated in the PCAPS solutions because DOM complexation with hydroxy Al and Fe species is not modeled in MINTEQA2. According to our calculations, a higher proportion of Ca and Mg was complexed with DOM in the PCAPS solutions, relative to the ZTS solutions, because of increased total concentrations of these cations (Table 2) and greater dissociation of organic functional groups.

The concentration of Al in PCAPS solutions was dramatically reduced relative to ZTS solutions (Table 2). We attribute this reduction to Al precipitation after

interaction with the wick material. Average saturation indices [$SI = \log(IAP/K_{sp})$, where IAP is the ion activity product] with respect to microcrystalline gibbsite ($\log K_{sp} = 9.35$; Stumm and Morgan, 1996) were calculated after speciation of Al in ZTS and PCAPS solutions (Table 3). The SI values for ZTS solutions indicate an undersaturation of Al with respect to microcrystalline gibbsite in both soils. However, SI values for PCAPS indicate that dissolved Al is closer to equilibrium with gibbsite. Thus, we propose that the increase in pH caused by PCAPS neutralization of the acidic soil solution induces precipitation of Al and decreases the concentration of filterable Al.

In contrast, total iron concentration was less affected by sampler type (Table 2) indicating that significant Fe precipitation did not result from the increase in solution pH induced by PCAPS. Neutralization of acidic soil solutions, resulting in Fe oversaturation with respect to several Fe-containing solids, should first result in precipitation of ferrihydrite ($\log K_{sp} = 3.8$) (Schwertmann and Taylor, 1989; Langmuir, 1997). Values of Fe in all Spring 1997 samples from both ZTS and PCAPS were found to be highly oversaturated with respect to ferrihydrite (Table 3). Solutions from PCAPS exhibited a higher degree of oversaturation because of the pH shift. The fact that we did not observe a decrease in total Fe in PCAPS solutions may be due to slow precipitation kinetics, incomplete speciation, or microcolloidal Fe precipitates that were able to pass through the 0.45- μm filter.

Despite precautions taken to thoroughly cleanse the wicks, changes in soil solution chemistry and speciation still occurred. It is important to note that harsh cleaning treatments with more concentrated acid solutions resulted in complete wick dissolution. This indicates that an alternative cleaning treatment must be developed if the same fiberglass rope used in this study (no. 1381 from Pepperell Braiding Co., Pepperell, MA) is to be employed to create PCAPS for other studies of acid forest soils. Increasing the ionic strength of the wash solution (i.e., 0.1 M HNO_3) and designing a method to continuously leach solution through the fiberglass rope may aid in cleaning the wick material. In addition, alternative sources of wick material, such as those used by Knutson and Selker (1994), should be investigated and may prove to be less problematic.

Depth of Solution

Table 4 shows the median depth of solutions collected at 1-wk intervals during fall, winter, and spring seasons. Quantities of throughfall collected at both sites are equivalent, which allows a direct comparison of soil solution depths between the sites to be investigated. Lower quantities of solution collected by ZTS reflect the fact that these samplers collect water only under saturated conditions or when macropore flow is present. Unsaturated flow diversion around ZTS has been noted in other studies (Boll et al., 1991; Jemison and Fox, 1992). Conversely, the PCAPS sample at pressures heads ≥ -0.45 m. Hence, the increased depth collected

by PCAPS corresponds to the transmission of soil water at matric potentials between 0 and -4.41 kPa.

The PCAPS installed in the Pottsville soil collected a greater depth of solution relative to Mauch Chunk PCAPS, whereas Mauch Chunk ZTS collected more solution than Pottsville ZTS (Table 4). These differences correspond to physical properties of the soil measured in the laboratory and observed in the field (Table 1). A greater predominance of matrix flow is expected for the Pottsville soil because of weak structure, few observable macropores, and moderately coarse-texture. Conversely, macropore flow is likely to be more prevalent in the Mauch Chunk shale-derived soil, which is medium-textured and moderately structured with macropores present between the peds and elsewhere (i.e., old root channels and earthworm and insect burrows). Since PCAPS sample both matrix and macropore flow, they collect a greater depth of solution, relative to ZTS, in the Pottsville soil where matrix flow predominates. This effect is diminished in the macroporous Mauch Chunk soil. On the basis of median values, ZTS sampled 10 and 38% of the solution depth collected by PCAPS in the Pottsville and Mauch Chunk soils, respectively.

CONCLUSIONS

Although other studies have indicated that PCAPS constructed with fiberglass ropes have high potential for use in the collection and measurement of unreactive solutes, our results indicate they can be problematic when used to collect dilute soil solutions for complete geochemical investigations. Despite precautions to eliminate chemical contamination, the interaction of acidic forest soil solutions with the PCAPS wick material produced dramatic increases in pH and carbonate, Ca, and Na concentrations. However, the elevated concentrations of some solutes were diminished during the first couple of months as soil solution leached through the fiberglass wicking material in the field. Changes in pH induced Al precipitation and a large drop in soluble Al was observed. Although PCAPS *may* provide useful data pertaining to water fluxes, the chemical effects of the wicks hamper their utility in soil geochemical studies. As a result of their capacity to sample under unsaturated flow conditions, PCAPS collect greater depths of water than ZTS. Our results indicate that the magnitude of this difference is diminished in well structured, macroporous soils where matrix flow is diminished relative to macropore flow.

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