

Solute Response to Changing Nutrient Loads in Soil and Walled Ceramic Cup Samplers under Continuous Extraction

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ABSTRACT

This report evaluates a vacuum-assisted walled percolation sampler preconditioned in soil, and examines the dynamic response of leachate solutes. The 20-cm walled percolation sampler extracted soil water under continuous tension via a ceramic cup collector embedded in a silica flour layer, whose upper surface interfaced with field soil. In the laboratory, alternating solutions with high and low $\text{NO}_3\text{-N}$ (232 or 3.6 mg L^{-1}), molybdate-reactive P (MRP) (1.75 or 0.0 mg L^{-1}), K^+ (568 or 3.6 mg L^{-1}), and Br^- (9.6 or 0.0 mg L^{-1}) concentrations were delivered directly to the (i) sampler ceramic cup; (ii) silica flour bed surface, or (iii) 12-mm soil layer placed over the silica flour bed. For alternating input solutions delivered to the silica-flour bed surface, (i) solute breakthrough (95% equivalency) occurred in 4 pore volumes and was the same for both the high and low concentration input phases of the application, and (ii) concentrations of $\text{NO}_3\text{-N}$, Br^- , and MRP in cumulative extracted water volumes were within 5% of those in corresponding input volumes. Alternating nutrient loads from high to low levels in the fixed flow rate input waters caused excess MRP (1.6 times that in the high concentration MRP solution) to leach from the calcareous soil. The dynamic character of P transport in K-fertilized soils deserves further study and may have important environmental implications.

UNDERSTANDING THE DYNAMICS of soil solution chemistry is a prerequisite for redressing many environmental problems, but our ability to sample soil leachate is limited. Dynamic soil solution phenomena have not been investigated thoroughly because these processes are time-sensitive and most soil solution samples are collected manually, which limits the number and frequency of samples obtained (Lentz, 2006). Porous cups or plates installed alone in the soil under continuous suction extract soil water, but may not collect all macropore water (Wilson et al., 1995) and the rate of collection may be substantially different from the soil water percolation rate (Cochran et al., 1970; Van der Ploeg and Beese, 1977). These difficulties can be avoided by deploying the porous extractor in a walled percolation sampler (Duke and Haise, 1973) because the sidewall ensures that percolating macropore water cannot bypass the extraction device and collected percolation volumes are often less sensitive to suction applied to the bottom of the walled sampler (Corey et al., 1982; Montgomery

et al., 1987). Water flux and percolation volume measurement using walled samplers with ceramic extractors have been studied (Corey et al., 1982; Lentz and Kincaid, 2003), but the dynamic response of these systems to changes in solute concentration and associated effects on collected sample water quality is less known.

A number of researchers have investigated the effect of porous cups on extracted water chemistry. Solute sorption by porous ceramic cup samplers may alter the response of sample solute concentration to changes in drainage water chemistry, although reports in the literature are contradictory (Litaor, 1988; Grossmann and Udluft, 1991). Furthermore, since many investigations of ceramic cup solute effects were conducted using new unwashed or washed cups, but not ones preconditioned in soil environments, the reports give an incomplete understanding of cup behavior in the field (Grossmann and Udluft, 1991). Nagpal (1982), Hansen and Harris (1975), Bottcher et al. (1984), and Grover and Lamborn (1970) studied $\text{PO}_4\text{-P}$ adsorbed by new washed or unwashed porous ceramic cup samplers in the laboratory by passing an aqueous solution of known concentration through the cup. All reported that ceramic cups adsorbed $\text{PO}_4\text{-P}$. The P adsorption by the ceramic cups was (i) greater following nontension periods between extraction events (Nagpal, 1982) and (ii) less for ceramic cups having low air entry pressures (50 kPa) relative to higher air entry pressures (200 kPa) (Bottcher et al., 1984). However, when ceramic cups were compared with hollow fiber or fritted glass samplers installed in soil profiles, solutions collected from all samplers over 5- or 28-wk periods contained equivalent $\text{PO}_4\text{-P}$ concentrations (Levin and Jackson, 1977; Silkworth and Grigal, 1981).

The amount of $\text{NO}_3\text{-N}$ adsorbed by porous ceramic cups placed in solutions was minimal (Wagner, 1962; Hansen and Harris, 1975; Nagpal, 1982; Poss et al., 1995). Laboratory studies indicate possible desorption and/or adsorption of Ca^{2+} and Mg^{2+} from ceramic cups (Rasmussen et al., 1986; Peters and Healy, 1988); however, when ceramic samplers were installed in field soils and compared with fritted glass or polytetrafluoroethylene (PTFE) samplers or zero-tension soil water samplers with polyester mesh membranes, no consistent ceramic cup effects on leachate cation concentrations were observed (Levin and Jackson, 1977; Silkworth and Grigal, 1981; Rasmussen et al., 1986; Hendershot and Courchesne, 1991; Beier and Hansen, 1992). Both laboratory and field studies indicate minimal or no alteration of solution Na^+ concentrations when transmitted through ceramic cup samplers

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Abbreviations: CF-soil, cup-flour-soil sampler configuration; CPV, total pore volume of sampler configuration; MRP, molybdate-reactive P; PV, pore volumes extracted; SD, standard deviation; STAS, sequential tension autosampler.

(Silkworth and Grigal, 1981; Rasmussen et al., 1986; Peters and Healy, 1988; Beier and Hansen, 1992; Beier et al., 1992). The influence of adsorption and/or desorption effects of ceramic cups on sampled solutions has been measured under controlled laboratory conditions, but is less apparent in the field. This may be attributed to greater variability present in soils (Hendershot and Courchesne, 1991) or to a conditioning of cup surfaces in soil, resulting in the occlusion or occupation of adsorption sites and decreased adsorption capacity (Grugenberger and Zech, 1992). Comparisons between ceramic cup and PTFE, fritted glass, or zero tension samplers show greater equivalency when water samples are collected from >75-cm soil depths (Silkworth and Grigal, 1981; Hendershot and Courchesne, 1991; Beier et al., 1992). This may result from reduced spatial and dynamic variation in soil solution chemistry at greater depths compared to near surface conditions.

A soil water sampler was designed to continuously measure and collect water draining below 1.2-m depth in unsaturated soil (Fig. 1). Water was collected under tension from a 17-cm-long, 4-cm diam. ceramic cup placed in the bottom of a 20-cm diam. stainless steel container with 23 cm high sidewalls (Lentz and Kincaid, 2003). When supplied vacuum was adjusted for ambient soil conditions, the sampler intercepted macropore and matrix pore soil water draining through a known cross-sectional area (Duke and Haise, 1973; Lentz and Kincaid, 2003). We wished to evaluate this sampler design in the laboratory.

This study monitored solute concentration in samples collected from a walled percolation sampler during prolonged continuous extraction to (1) determine the response of sample solute concentrations when an input solution having high dissolved P, nitrate, and K concentrations is alternated with a low nutrient irrigation water, (2) evaluate potential effects of sampler com-

ponent materials and soil on that response; and (3) determine how the response in Objective 1 differs when the irrigation water is alternated with a water high in dissolved P, but lacking the elevated nitrate and K concentrations present in the original Objective 1 nutrient solution.

MATERIALS AND METHODS

Design details of the walled ceramic cup sampler used here are given by Lentz and Kincaid (2003). Water was extracted via tube through a porous ceramic cup, embedded in a 5 cm deep layer of silica flour in the bottom of the steel beaker. The ceramic cup had an air entry pressure of 50 kPa and a porosity of 50% (Soil Moisture Equipment, Goleta, CA). The silica flour was composed of primarily silt-sized (200 mesh sieve) particles. In field installations, the sampler is installed into the roof of a soil cavity dug into the sidewall of a pit. The lip of the beaker is inserted into a circular slot cut into the soil which forms the roof of the cavity. Thus, a continuous, undisturbed column of soil extends from the soil surface downward and into the steel beaker, where it makes hydraulic contact with the silica flour bed via a layer of moistened soil that was compressed between the two during installation. A sampler that had been installed in soil for 36 mo was exhumed for use in this experiment. The walled percolation sampler was set up on a laboratory bench top.

Experiment One

This experiment tested the effect of soil and percolation sampler components and changing inflow water nutrient load on solute concentration of continuously extracted water samples. We applied a nutrient solution (nutrient solution phase) followed by simulated irrigation water (irrigation water phase) to each of three sampler configurations while extracting water from the sampler under continuous suction. For each sampler configuration, extracted water was drawn under tension from the ceramic cup, but the input solution was either (i) applied directly to the cup via submergence in the solution (cup configuration); (ii) applied to the upper surface of the silica flour bed in which the ceramic cup was embedded (cup-flour configuration); or (iii) applied to the upper surface of a 12 mm deep soil layer placed over the top of the silica flour bed and ceramic cup (CF-soil configuration). We used a thin soil layer to reduce the time required for solute equilibration during each solution cycle, otherwise the observation periods would be impractically long. During the nutrient solution phase, a solution that simulated soil drainage water (Table 1, B), was applied to the sampler for 12 to 360 h followed immediately by an irrigation water phase, where simulated irrigation water (Table 1, A) was applied for 12 to 350 h. The nutrient solution contained elevated levels of $\text{NO}_3\text{-N}$, MRP, K^+ , and Br^- relative to that of the irrigation water (Table 1). Nutrient solution MRP and/or $\text{NO}_3\text{-N}$ concentrations approximated maximum levels observed in water percolating through furrow-irrigated field soils (Lentz and Westermann, 2001), whereas K^+ concentrations approximated those that might result from a heavy K fertilizer application to soils. Pneumatic suction was applied to the ceramic cup throughout each test, with sampling as necessary to describe solute response over time. Components of a single percolation sampler were used to create and test the three configurations. This process was repeated three times, with the initial configuration in each series selected randomly and other configurations tested in random order. Thus, each sampler configuration tested in a given series was prepared by deconstructing or upgrading a previous con-

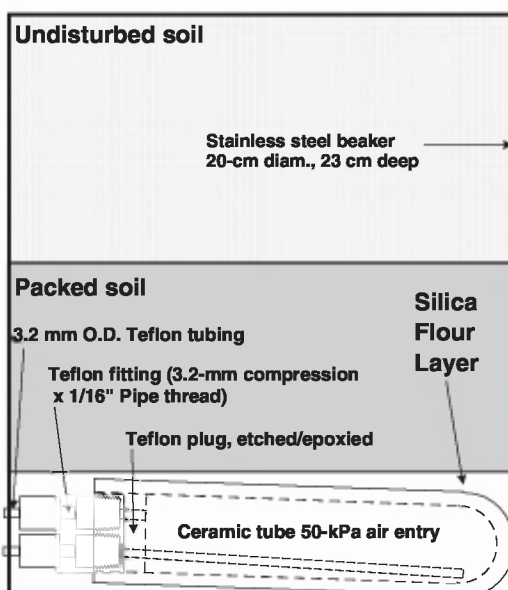


Fig. 1. Diagram of soil water percolation sampler showing the various components and their relation to soil in a field installation.

Table 1. Chemical characteristics of the low and high solute concentration solutions used to supply the soil water sampler.

ID-where used	Type	PH	EC	PO ₄ -P	NO ₃ -N	Br	Ca	K	Na	Mg	Cl	S	Si	Al	Fe	Mn	Zn
A. All exp.	Simulated irrigation H ₂ O	8.1	0.038	0.02	3.6	0.0	24.5	3.6	32.8	15.7	15.5	11.4	8.6	0.01	0.0	0.0	0.06
B. Exp. 1	Nutrient solution	7.7	23.7	1.75	232	9.6	28.8	568	33.5	14.5	27.5	11.2	7.25	0.01	0.0	0.0	0.10
C. Exp. 2	Nutrient solution	7.8	0.043	1.67	2.7	10.0	28.3	9.3	33.6	15.7	20.1	10.6	3.6	0.008	0.004	0.002	0.12

figuration using equivalent amounts of silica flour or soil for each respective configuration. Each series of tests was included as a replicate in the experimental design. Procedures used for each sampler configuration are detailed below.

Cup Configuration

The ceramic cup was removed from the percolation water sampler and flushed with simulated irrigation water, then placed in a 1-L glass cylinder containing about 500 mL simulated irrigation water (solution A, Table 1). The ceramic cup was equilibrated with the irrigation water by continuously drawing water through the sampler for at least 12 h. The ceramic cup was removed from the container, water in the cylinder was immediately replaced with nutrient solution (Table 1, B), and the ceramic cup was reinserted. Water extraction continued with samples collected every 1.5 or 2 h for 12 to 24 h. The nutrient solution was then replaced by irrigation water and the extraction continued for another 12 to 20 h, with sampling at 1- to 5-h intervals.

Cup-Flour Configuration

Depending on the sample configuration tested previously, either the ceramic cup was reinstalled in the walled sampler beneath the bed of silica flour or the soil layer was removed from the cup-flour-soil (CF-soil) sampler configuration to expose the silica flour bed. In the former case a thick silica flour slurry was poured over the cup in the sampler to ensure full contact. The silica flour bed had a bulk density of 1.52 g cm⁻³. The bed and ceramic cup were equilibrated with simulated irrigation water by ponding a 500-mL volume of water over the bed (2.34 kg dry wt.) and extracting it through the ceramic cup, followed by a continuous application and extraction of irrigation water for 48 h, using the standard rates. The nutrient solution (Table 1, B) was then applied to the silica bed for 40 to 50 h, with sample collection at 3- to 5-h intervals. This was followed immediately with simulated irrigation water (Table 1, A). The input solution flows were split and applied onto the flour bed surface at two locations, positioned midway between the buried cup and sampler wall. Solutions dripped onto a filter paper cover placed on the silica flour bed to help distribute the flow. Hence, water extracted from the sampler flowed only through the silica flour bed and ceramic cup.

CF-Soil Configuration

In addition in sampler components present in the cup-flour configuration, a 12 mm deep soil layer (590 g dry wt.) was placed over the silica flour bed in the walled percolation sampler. The air-dried, sieved (10 mesh, 2 mm), soil was topsoil from a Portneuf silt loam (coarse-silty, mixed, superactive, mesic, Durinodic Xeric Haplocalcids). The soil characteristics were as follows: 240 g kg⁻¹ sand, 560 g kg⁻¹ silt, 200 g kg⁻¹ clay, 8.8 g kg⁻¹ organic carbon, 62 g kg⁻¹ calcium carbonate equivalent, pH, 7.3; 0.4 S m⁻¹ electrical conductivity (EC) of saturated extract, and 15 cmol_c kg⁻¹ cation exchange capacity (CEC). The bulk density of the soil layer was 1.2 g cm⁻³. The sampler components were equilibrated with simulated irriga-

tion water via the same procedure used for the cup-flour configuration except that 1 L of irrigation water was applied initially. The nutrient solution (B) was applied for 150 to 250 h followed by a 270- to 340-h applications of simulated irrigation water (A), with sampling at 6- to 48-h intervals. Water extracted from the sampler passed via matrix flow through the soil, silica flour bed, and ceramic cup.

Experiment Two

This experiment was similar to Exp. 1, except applied input solutions were alternated between nutrient solution C and simulated irrigation water (Table 1). Solution C included the elevated MRP concentrations of solution B but lacked the elevated K⁺ and NO₃-N concentrations (Table 1). This protocol used only the complete sampler configuration, CF-soil, identical to that in Exp. 1. The same procedure as for CF-soil (Exp. 1) was used as well, except that nutrient solution C (Table 1) was substituted for solution B, and the nutrient solution monitoring period was extended. Solution C had elevated MRP and Br⁻ concentrations, but NO₃-N, K⁺, and EC concentrations were similar to those present in the simulated irrigation water. The objective was to evaluate the effect of reduced NO₃-N, K salt loading, and EC on phosphate solute response.

Solution Application and Sampling

Chemical characteristics of aqueous solutions used in the experiments are listed in Table 1. The laboratory's tap water is supplied from groundwater that contains solute concentrations roughly twice those found in the local irrigation water. Therefore, simulated irrigation water was prepared from a 1:1 tap/reverse-osmosis (RO) water mixture. Nutrient solutions were prepared by dissolving an appropriate quantity of KH₂PO₄, KNO₃, and KBr in simulated irrigation water. A syringe pump delivered solutions at 60 mL h⁻¹ to all sampler configurations and water was extracted from each configuration's ceramic cup at the same rate of 60 mL h⁻¹. This inflow/extraction rate matched the common water extraction rates for soil water samplers installed in a furrow-irrigated agricultural field and represented a percolation rate of 1.9 mm h⁻¹. Chemical analysis of extracted water samples determined how rapidly and completely the extracted water equilibrated with the supplied solution.

Continuous pneumatic suction was applied to the sampler's ceramic cup using an automated vacuum control system adapted from Lentz and Kincaid (2003). The vacuum control routine monitored the system suction, resetting it to the target value at the start of each minute. The extraction tension typically declined slightly (6 to 12%) between adjustment cycles. The target suction for the vacuum control was set to -160 kPa for all sampler configurations except for the cup. In this case, where the ceramic cup was placed directly into solutions, the tension target was set at -60 kPa. The pneumatic tensions applied in each experiment were sufficient to ensure a 60 mL h⁻¹ water withdrawal rate from each sampler configuration being tested.

A Sequential Tension AutoSampler (STAS) (Lentz, 2006) was used to sample the water extracted from the ceramic cup under continuous tension. Samples were collected over 60 to 90 min to obtain volumes of 60 to 90 mL. A biocide solution (62 g H₃BO₃ L⁻¹ RO water) was added to the STAS sample collection bottles (1 mL per 100-mL sample) before water collection and samples were stored at 5°C until analyzed. Flow injection analysis determined the following ion concentrations in water samples: NO₃-N using copperized cadmium reduction and modified Griess-Hoovay method (Keeney and Nelson, 1982); bromide using the phenol-red procedure; and chloride using the mercuric thiocyanate method (O'Brian, 1962). Molybdate-reactive P was determined on unfiltered samples using the Murphy and Riley (1962) procedure. Water samples extracted from the cup were clear and sediment free. The Mg, Ca, K, and Na concentrations in water samples were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES).

The times required for the outflow of MRP, NO₃-N, and Br⁻ concentrations to adjust to that of the inflows were evaluated. When nutrient solutions were input (nutrient solution phase), the time needed for the outflow concentrations to attain 95% that of the inflowing nutrient solution concentrations was determined. Similarly, after nutrient solution inflows were switched to irrigation water (irrigation water phase), we determined the time required for outflow concentrations to decrease 95% from the level observed in the outflow just after the switch. These breakthrough times were converted to equivalent pore volumes (PV), the ratio of effluent volume to the volumetric water capacity of the transport medium (Biggar and Nielsen, 1963 using Eq. [1]):

$$PV = T \times (CPV/IR)^{-1} \quad [1]$$

where T is the breakthrough time in hours, CPV is the total pore volume of all components included in the specified configuration in mL, and IR is the solution inflow rate, a constant 60 mL h⁻¹. Pore volume of the ceramic cup, silica flour bed, and soil was determined by saturating the components while installed in the sampler, then disassembling the components and weighing before and after drying.

Sampler Effects over Extended Periods

We wished to determine how percolation sampler components may influence the water quality of extracted samples under a condition similar to that in the field, where percolation water is accumulated in the sampler during a period of time before collection. The retrieved volume is then analyzed for various solute concentrations to estimate leaching losses. Using data from Exp. 1, we assigned each input nutrient solution phase and subsequent irrigation water phase as a "collection period." We determined solute concentrations in the cumulative water volumes extracted throughout each "collection period" and compared these to solute concentrations in the cumulative water volume that was input during the same period. Solute concentrations in the cumulative input water volumes or extraction volumes were calculated by integrating the area under the respective concentration versus cumulative volume curve, where cumulative volume is computed from time, using input rate = extraction rate = 60 mL h⁻¹. If solute concentrations between cumulative input and extracted volumes are equivalent, the net effect of included components on sampled water quality is null.

Statistical Analysis

The data were analyzed using a split-plot design with sampler configuration as main plot and solution phase as subplots, with

Table 2. Main and interaction effects of sampler configuration and solution input phase on time and pore volume required for solute concentration in outflow to equilibrate with that of the inflowing solution, Exp. 1.

Variable	Solute	Experimental factor		
		Sampler configuration	Irrigation phase	Interaction
Breakthrough time	BR	***	NS†	NS
	NO ₃ -N	***	NS	NS
	MRP	***	NS	NS
Pore volume	BR	NS	NS	NS
	NO ₃ -N	NS	NS	NS
	MRP	***	NS	NS

*** Significant at the < 0.001 level.

† NS, not significant at the 0.05 level.

3 replicates. Square root transformations were used to stabilize variances, and confidence intervals were constructed on the means ($P = 0.5$). Analysis of variance was conducted using the SAS PROC MIXED procedure (Littell et al., 1996). The relative concentration of the effluent (C/C_0), given as the ratio of effluent solute concentration (C) to the nutrient solution inflow solute concentration (C_0) was plotted as a function of the number of pore volumes eluted. The breakthrough curves were plotted for the nutrient solution input phase and the irrigation water phase that followed, and a representative curve from each of the treatments presented. We computed the mean relative concentration and standard deviations (SD) for selected eluted pore volume values from replicated runs made in each experiment. These are displayed in Fig. 2 to 5 to permit comparisons between breakthrough curves.

RESULTS AND DISCUSSION

The average CPV values (see Eq. [1]) obtained for sampler configurations were 72 mL for the cup, 682 mL for cup flour, and 877 mL for CF-soil. Thus, the mean time required to pass a single pore volume of solution through each sampler configuration was 1.2 h for the cup, 11.4 h for cup-flour, and 14.6 h for CF-soil.

Experiment One

The times required for outflow Br⁻, NO₃-N, and MRP solute concentrations to equilibrate with that of inflows differed significantly among sampler configurations, whereas the effect of solution input phase was not significant for the three solutes (Table 2). When break-

Table 3. Equilibration time required for solute concentration in outflow to attain that of the inflowing solution.

Sampler configuration	Inflow solution phase	Equilibration time†		
		MRP	NO ₃ -N	BR
		h		
Cup only	Nutrient solution	6.6 ^{CA} ‡§	5.6 ^{CA}	5.3 ^{CA}
	Irrigation water	6.8 ^{BA}	4.3 ^{CA}	4.4 ^{CA}
Cup-flour	Nutrient solution	44.0 ^{BA}	38.8 ^{BA}	32.2 ^{BA}
	Irrigation water	39.4 ^{BA}	39.7 ^{BA}	33.1 ^{BA}
CF-soil	Nutrient solution	298 ^{AA}	68.0 ^{AB}	60.4 ^{AB}
	Irrigation water	330 ^{AA}	57.9 ^{AB}	59.5 ^{AB}

† Outflow and inflow solute concentrations were considered equilibrated when concentration differences were <5%.

‡ Dissimilar lowercase letters indicate significant differences between treatments within columns.

§ Dissimilar uppercase letters indicate significant differences between nutrient equilibration times.

through times were analyzed in terms of equivalent pore volumes, the configuration effect was significant only for MRP and no effect of solution input phase was observed for any of the three solutes (Table 2).

The solute response, or breakthrough times increased with increasing complexity of the sampler configuration (Table 3), which introduced additional layers of transporting medium with varying dispersivity, tortuosity, sorption, and immobile-mobile domain characteristics along the water's flow path. Solution breakthrough times for the cup configuration did not differ between inflow irrigation or nutrient solution phase, or among MRP, $\text{NO}_3\text{-N}$, or Br^- solutes, and averaged 5.5 h. The solution breakthrough times for the cup-flour configuration also were similar, regardless of solution inflow phase or solute type, and averaged 37.7 h. Solute breakthrough times for MRP and the conservative Br^- tracer were similar for both cup and cup-flour configurations. This suggests that adsorption and/or desorption phenomenon had minimal effect on solute transport through the silica flour bed and ceramic cup under continuous extraction. Nevertheless, a slight upward trend in the breakthrough times occurred in the solute data, with the lowest times for Br^- and increasing times for $\text{NO}_3\text{-N}$, then MRP solutes. This suggests some retardation of MRP transport through cup and silica flour relative to Br^- , resulting from adsorption and/or desorption of MRP (Wierenga, 1995).

The breakthrough times of Br^- and $\text{NO}_3\text{-N}$ solutes for the CF-soil configuration did not differ with respect to solute type or solution input phase and averaged 61.5 h. Breakthrough times for the two MRP input phases did not differ significantly and averaged 314 h, nearly five times greater than that for Br^- and $\text{NO}_3\text{-N}$ solutes. The MRP added to soil can react with solid calcium carbonate via adsorption and precipitation reactions (Cole et al., 1953), or combine with exchangeable Ca^{2+} from the soil solution (Cho, 1991) to form calcium phosphate minerals. These reactions cause a flattening of the breakthrough curve and increase in breakthrough time (Biggar and Nielsen, 1963).

When breakthrough curve times were normalized by conversion to equivalent pore volumes, solute breakthrough times were found to be similar for all configurations, input phases, and nutrients, except for both input phases of the MRP response with the CF-soil configuration (Table 4). The average pore volume required for breakthrough of the MRP was 21.5, >5 times higher than $\text{NO}_3\text{-N}$ or Br^- (Table 4).

Breakthrough curves of different solutes and the three sampler configurations are presented in Fig. 2 through 4. The breakthrough curve for each input phase of the cup configuration was initially steep with some tailing (Fig. 2). The tailing was more pronounced for MRP than for $\text{NO}_3\text{-N}$ or Br^- . The ceramic of the cup included a range of pore sizes, which created immobile water regions and induced tailing of nonadsorbing transported solutes (Van Genuchten and Wierenga, 1977). Some tailing may also have resulted from the solution's short travel time through the thin ceramic wall, which reduced the time available for solute transfer between immobile and mobile pore water regions (Rao et al.,

Table 4. Pore volumes required for solute concentration in outflow to equilibrate with that of the inflowing solution.

Sampler configuration	Inflow solution phase	Pore volumes needed for outflow conc. to equilibrate with inflow†		
		MRP	$\text{NO}_3\text{-N}$	BR
Cup only	Nutrient solution	5.5 ^{bA} ‡§	4.7 ^{aA}	4.4 ^{aA}
	Irrigation water	5.6 ^{bA}	3.6 ^{aA}	3.7 ^{aA}
Cup-flour	Nutrient solution	3.9 ^{bA}	3.4 ^{aA}	2.8 ^{aA}
	Irrigation water	3.5 ^{bA}	3.5 ^{aA}	2.9 ^{aA}
CF-soil	Nutrient solution	20.4 ^{aA}	4.7 ^{aB}	4.1 ^{aB}
	Irrigation water	22.6 ^{aA}	4.0 ^{aB}	4.1 ^{aB}

† Outflow and inflow solute concentrations were considered equilibrated when concentration differences were <5%.

‡ Dissimilar lowercase letters indicate significant differences between treatments within columns.

§ Dissimilar uppercase letters indicate significant differences between nutrient equilibration times.

1980). Note that relative concentrations of Ca^{2+} , Mg^{2+} , and Na^+ in outflow rise above unity shortly after the nutrient solution input began, decreased to one, then dropped below unity shortly after irrigation water was reintroduced, followed by a rise toward unity, except Mg^{2+} (Fig. 2). This pattern suggests that K^+ from the inflowing solution replaced Ca^{2+} , Mg^{2+} , and Na^+ on the ceramic exchange complex via mass action, with the reverse reaction occurring when inflow was switched to irrigation water. The Mg^{2+} breakthrough curve rises above unity during the irrigation water phase because Mg^{2+} concentration in the irrigation water was slightly greater than that in the nutrient solution (Table 1, B).

Solute breakthrough curves of the cup-flour configuration (Fig. 3) were similar to those of the cup configuration (Fig. 2). While the breakthrough curves for the cup-flour configuration appear slightly flatter (i.e., slower rise to unity) than for the cup, an examination of corresponding relative concentrations on the two breakthrough curves does not support this contention. For example, the mean relative concentration value for MRP at 1.75 pore volumes was 0.73 (SD = 0.01) for the cup configuration (Fig. 2) and 0.66 (SD = 0.06) for cup-flour (Fig. 3), but the difference was not significant. Similarly, the relative concentrations of MRP in cup configuration samples, 0.35 (SD = 0.11), and cup-flour samples, 0.42 (SD = 0.02), collected at 1.25 pore volumes into the irrigation phase (11.25 effluent PV in Fig. 2 and 3) were not significantly different. Note that the Ca^{2+} , Mg^{2+} , and Na^+ response curves follow similar patterns as those observed for the cup configuration, presumably for similar reasons.

Breakthrough curves for CF-soil configuration were similar to cup and cup-flour configurations with respect to Br^- , $\text{NO}_3\text{-N}$, K^+ , and Na^+ solutes, but MRP, Ca^{2+} , and Mg^{2+} solute curves for CF-soil differed significantly from those in the other two configurations (Fig. 2, 3, and 4). For example, mean $\text{NO}_3\text{-N}$ relative concentrations at 1.75 or 2.74 PV were similar for cup, 0.92 (SD = 0.01), cup-flour, 0.83 (SD = 0.1), and CF-soil samples, 0.90 (SD = 0.05). The CF-soil MRP breakthrough curve was slightly delayed, and flatter, with greater asymmetry than for cup and cup-flour configurations. Such characteristics are indicative of a miscible displacement process

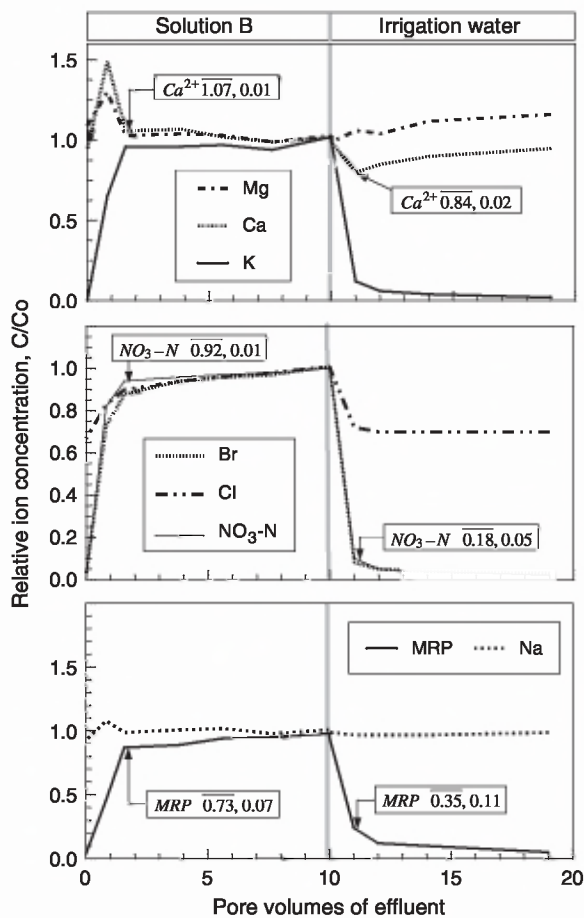


Fig. 2. Cup configuration, Exp. 1. Solute breakthrough curves for nutrient solution phase (solution B applied) and irrigation water phase (solution A applied). The vertical gray line indicates the start of the irrigation water application. The mean solute concentration and standard deviation at indicated pore volume values are included to allow comparisons among breakthrough curves.

where a nonadsorbed solute flows through an aggregated porous medium (Rao et al., 1980), or one in which the solute reacts with the porous material via adsorption or exchange (Biggar and Nielsen, 1963). The CF-soil MRP breakthrough curve also differed from other configurations in that, when the nutrient solution inflows were switched to simulated irrigation water, effluent MRP concentrations spiked to a value 1.6 times higher than that of the previously supplied nutrient solution. Mean relative concentration of MRP in samples collected 2.74 PV into the irrigation phase (12.74 PV in Fig. 3 and 19 PV in Fig. 4) was 0.12 (SD = 0.01) for cup-flour versus 1.64 (SD = 0.04) for CF-soil configurations. Furthermore, while Ca^{2+} and Mg^{2+} breakthrough curves in all three configurations were characterized by peaking concentrations early during the nutrient solution phase as well as depressed concentrations early in the irrigation input phase, the magnitude of the Ca^{2+} and Mg^{2+} response to these events was significantly greater for CF-soil than for cup and cup-flour configurations. Relative concentrations of Ca^{2+} in effluent at 1.75 PV were similar for cup, 1.07 (SD = 0.01), and cup-flour, 1.18 (SD = 0.05), but the relative concentration of Ca^{2+} for CF-soil was

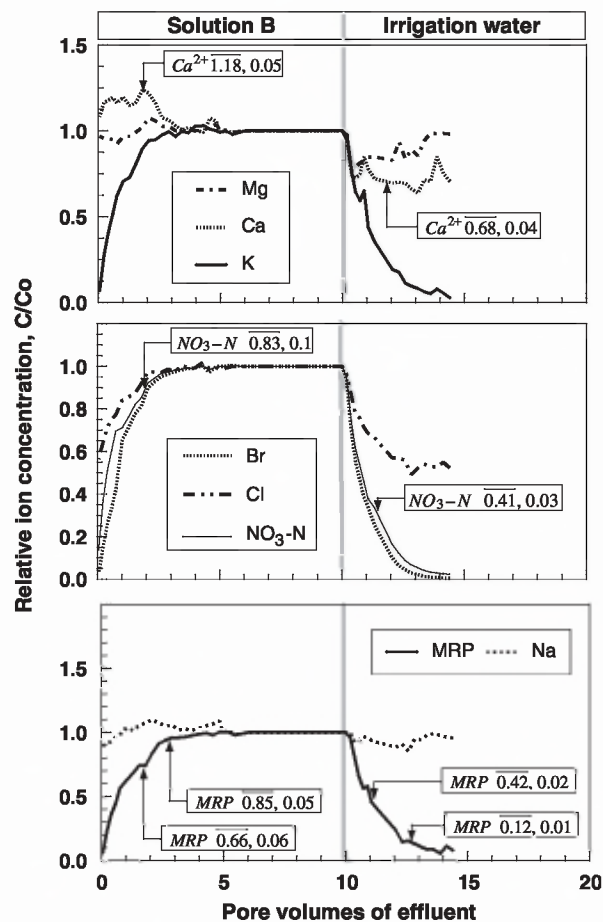


Fig. 3. Cup-flour configuration, Exp. 1. Solute breakthrough curves for nutrient solution phase (solution B applied) and irrigation water phase (solution A applied). The vertical gray line indicates the start of the irrigation water application. The mean solute concentration and standard deviation at indicated pore volume values are included to allow comparisons among breakthrough curves.

greater, 3.57 (SD = 0.84). Similarly, the depression in relative Ca^{2+} concentrations that occurred 1.7 to 2.7 PV after the switch to irrigation water (11.7 PV in Fig. 2 and 3, and 19.0 PV in Fig. 4) was less for cup configuration samples, 0.84 (SD = 0.02), and cup-flour samples, 0.68 (SD = 0.04) than for CF-soil samples, 0.39 (SD = 0.02).

The notable peak in the MRP breakthrough curve for the CF-soil configuration on switching to the irrigation water phase was not anticipated. We offer the following hypothesis to explain its occurrence. The soil media in the CF-soil configuration included an aggregated structure, free calcium carbonate, and ion exchange complex not present in the silica flour or ceramic cup components. The inflowing nutrient solution caused effluent Ca^{2+} , Mg^{2+} , and Na^{+} concentrations to rise, which resulted when abundant K^{+} from the inflowing nutrient solution substituted for the other cations on the soil exchange complex via mass action (Lehr and Van Wesemael, 1952; Sample et al., 1979). As the incoming nutrient solution displaced older soil water, the relative MRP concentrations in the soil solution and effluent increased, eventually rising to unity (Fig. 4). In response to higher MRP solute concentrations in the soil solution, the MRP was

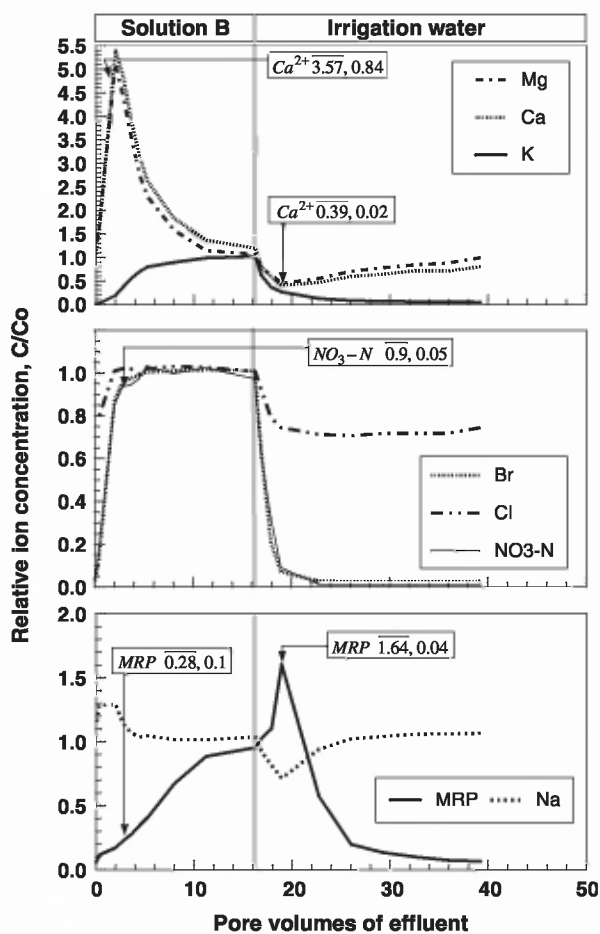


Fig. 4. CF-soil configuration, Exp. 1. Solute breakthrough curves for nutrient solution phase (solution B applied) and irrigation water phase (solution A applied). The vertical gray line indicates the start of the irrigation water application. The mean solute concentration and standard deviation at indicated pore volume values are included to allow comparisons among breakthrough curves.

adsorbed onto charged Fe and Al oxides, silicate clays (Borrero et al., 1988), and organically complexed Fe and Mn (Leytem and Westermann, 2003); adsorbed and precipitated onto the free calcium carbonate (Cole et al., 1953; Delgado and Torrent, 2000); or reacted with exchangeable Ca^{2+} or Mg^{2+} to form poorly soluble calcium or magnesium phosphates (Lindsay et al., 1962; Akinremi and Cho, 1991; Tunesi et al., 1999; Kumaragamage et al., 2003). Borrero et al. (1988) concluded that metal oxides and silicate clay in soil dominate the P sorption process in calcareous soils at low soil solution P concentrations ($\sim 1 \text{ mg L}^{-1}$).

When the switch to irrigation water occurred, the K^+ concentration of the inflowing water declined precipitously. This was accompanied by a decline in effluent Ca^{2+} , Mg^{2+} , and Na^+ concentrations, and an initial spike in effluent MRP concentrations (Fig. 4). The decreased inflow K^+ concentration caused K^+ to be displaced from the soil exchange complex and replaced by Ca^{2+} , Mg^{2+} , and Na^+ cations from the soil solution (the reverse reaction that occurred during the nutrient input phase). The decline in soil solution Ca^{2+} and Mg^{2+} concentrations increased the solubility of calcium phosphates

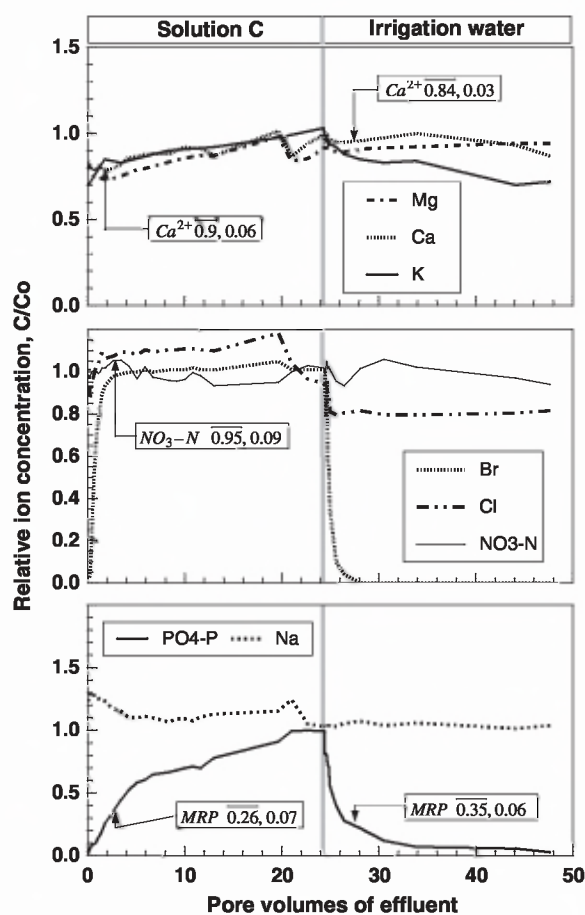


Fig. 5. CF-soil configuration, Exp. 2. Solute breakthrough curves for nutrient solution phase (solution C applied) and irrigation water phase (solution A applied). The vertical gray line indicates the start of the irrigation water application. The mean solute concentration and standard deviation at indicated pore volume values are included to allow comparisons among breakthrough curves.

(Lindsay, 1979), which resulted in a sudden rise of MRP in the soil solution and effluent and a sharp peak in relative MRP concentration (Fig. 4). In time, miscible displacement of soil water with irrigation waters lowered the soil solution MRP concentration, though this process was slowed by the reintroduction of MRP to the soil solution via desorption and solubilization reactions and the slow diffusion of MRP from mobile to immobile soil water regions. These reactions accounted for the changes observed in the MRP breakthrough curve, relative to cup and cup-flour configurations.

If K^+ from the inflowing nutrient solution did replace all cations on the soil exchange complex, the Ca^{2+} , Mg^{2+} , and Na^+ cations released to the soil solution would represent the equivalent of nearly 8.9 cmol_c ($0.59 \text{ kg soil dry wt.} \times 15 \text{ cmol}_c \text{ kg}^{-1} \text{ soil}$). This assumes that the entire soil mass participates in the reactions. The average amount of cations leached from the soil during the nutrient solution input phase (outflow – inflow contributions) was the equivalent of 3 cmol_c . Thus, it is feasible that the exchange of Ca^{2+} , Mg^{2+} , and Na^+ cations occurred, given that the entire soil mass likely did not participate in the reaction and that some cations

not leached away would have been available to react with P or carbonate, forming less soluble precipitates.

Experiment Two

Results from Exp. 2 provided an initial test of the hypothesis offered in above paragraphs. The influence of elevated K^+ and NO_3-N nutrient solution concentrations (solution B) on CF-soil breakthrough curves in Exp. 1 became apparent when breakthrough curves from Exp. 2 (Fig. 5) were compared with those from CF-soil configuration in Exp. 1 (Fig. 4). Because NO_3-N concentrations were nearly equal between input nutrient and input irrigation solution phases, the NO_3-N response curve was flat. The resulting MRP breakthrough curve was similar to the CF-soil (Exp. 1) curve with respect to the input nutrient solution phase; however, on switching to the input irrigation phase, instead of the effluent MRP concentration spiking upward as it did for CF-soil (Exp. 1), it declined relatively steeply and then subsequently tailed off. For example, relative concentration of MRP in Exp. 1 CF-soil samples, 1.64 (SD = 0.04), collected 2.7 pore volumes into the irrigation water phase (19.0 PV in Fig. 4) was significantly greater than that in Exp. 2 CF-soil samples, 0.35 (SD = 0.06), collected at an equivalent eluted volume (27.5 PV in Fig. 5). In addition, the Ca^{2+} and Mg^{2+} response curves from Exp. 2 lacked the peaks early in the nutrient solution phase and the depressions in the irrigation solution phase that were present for CF-soil (Exp. 1). Note the relative concentrations of Ca^{2+} at 1.8 PV into the nutrient solution phase (Fig. 4 and 5) and 2.7 PV into the irrigation water phase (18.7 PV in Fig. 4 and 27.7 PV in Fig. 5). These data are consistent with the concepts presented in the previous discussion to explain the MRP response peak. The Cl^- response also differed in Exp. 2, compared to that for CF-soil (Exp. 1). Its relative concentration in effluent during the nutrient input phase slightly exceeded unity in Exp. 2 but equaled unity for CF-soil (Exp. 1). The reason for this contrast is not fully understood, but it may be related to changes in anion supply and mobility. Cations leached from soil are accompanied by a mass of leached anions with an equal and opposite cumulative charge (Lehmann and Schroth, 2003). In Exp. 1, excess NO_3^- applied to soil in the nutrient solution likely provided the balancing anions for the leached cations. In Exp. 2 nitrate concentrations were low, and Cl^- anions may have assumed the charge balancing role (Montagnini et al., 1991), resulting in increasing Cl^- concentrations in extracted waters. The Na^+ response also differed slightly in Exp. 2 relative to that for CF-soil in Exp. 1. The relative Na^+ concentrations

rose slightly above unity only during the nutrient solution phase. This may have resulted from the displacement of Na^+ from the soil exchange complex by Ca^{2+} and K^+ cations, although the irrigation water phase does not show a corresponding and expected readsorption pattern. The Br^- response was no different from that of CF-soil (Exp. 1).

The realization that changing nutrient input loads can have pronounced effects on leachate MRP concentrations may have important implications for P management in calcareous soils. If similar enriched MRP pulses were induced in field soils, it is unclear how far they would be translocated through the soil, owing to sorption and precipitation processes in deeper soil layers. In this regard, the depth of penetration would likely be a function of the water transport characteristics, since mitigating effects of sorption and precipitation would be more important in soils dominated by matrix flow than in those dominated by macropore flow. Field soil water conditions can differ from the laboratory setting, with irrigation events commonly supplying fewer pore volumes and having shorter durations than included in this experiment.

Sampler Effects during Extended Periods

When water was extracted continuously over at least a 38-h period, the ceramic cup and silica-flour sampler components had minimal effect on solute concentrations in cumulative extracted water volumes relative to those in input volumes. In most cases, solute concentrations in cumulative input and extracted solution volumes differed by <5% for cup and cup-flour configurations (Table 5). In contrast, the presence of soil in the transport path altered mean MRP (-22%), Ca^{2+} (-44%), and Mg^{2+} (8.1%) concentrations in the cumulative extracted volumes relative to those in cumulative input volumes. This suggests that (i) this calcareous soil has a substantially greater impact on the water quality of percolating solutions than the ceramic cup or silica-flour sampler components and (ii) solute concentrations in water volumes extracted continuously during extended periods from a walled sampler installed in these soils should closely represent those in the soil percolation water (for solutes studied). These results corroborate those of several field studies, in which porous cup samplers installed in soils to sample soil water over extended periods did not alter PO_4-P (Levin and Jackson, 1977; Silkworth and Grigal, 1981) or Ca^{2+} , Mg^{2+} , and Na^+ concentrations relative to soil water (Levin and Jackson, 1977; Silkworth and Grigal, 1981; Rasmussen et al., 1986; Hendershot and Courchesne, 1991; Beier and Hansen, 1992).

Table 5. Mean difference between solute concentration in cumulative inflow volume and that in cumulative extracted volume during the combined nutrient solution and irrigation water phases, given as a percentage of the cumulative inflow volume concentration.

Sampler configuration	MRP	NO_3-N	BR^-	Cl^-	Ca^{2+}	Mg^{2+}	Na^+	K^+
Cup only	2.5 (6.0)†‡	0.1 (0.4)	3.2 (1.8)	1.0 (1.3)	-4.7 (1.4)	-1.4 (0.6)	-0.8 (0.9)	0.1 (0.4)
Cup/silica-flour bed	1.4 (5.0)	1.1 (1.2)	4.2 (1.6)	-0.6 (1.5)	-0.8 (3.2)	3.7 (0.9)	-6.5 (3.6)	-2.2 (3.2)
Cup/silica-flour bed/soil	-22 (19)	1.4 (1.4)	0.8 (2.8)	-4.4 (0.6)	-44 (19)	8.1 (8.3)	-2.6 (3.6)	2.7 (3.2)

† Calculated as $[(\text{Conc. in cumulative inflow volume}) - (\text{Conc. in cumulative extracted volume})] \times 100 / [\text{Conc. in cumulative inflow volume}]$.

‡ Standard deviation of the difference.

CONCLUSIONS

This laboratory study investigated solute effluent response in a preconditioned (in soil), walled, ceramic cup percolation sampler operating under continuous extraction at water withdrawal rates and solute concentrations similar to those observed in a furrow-irrigated agricultural soil. Results indicate that, when samplers are installed in the field, the $\text{NO}_3\text{-N}$, Br^- , and MRP effluent concentrations in extracted solutes should respond within minutes to a change in percolate solute concentration at the soil/silica-flour-bed interface, and attain 95% equivalency of the inflow concentration within 38 h or 4 pore volumes. Under continuous extraction, sorption phenomena played a minor role in the transport of $\text{NO}_3\text{-N}$, Br^- , and MRP through the silica-flour-bed and ceramic cup of the percolation sampler. The preconditioned walled sampler should provide reasonable estimates of solute concentrations in percolation water when cumulative water volumes are collected under continuous extraction during extended periods (2 to 5 d). Solute concentrations in water extracted during shorter periods will be representative of soil leachate only under static soil water chemistry conditions. Changing input irrigation waters from one with high $\text{NO}_3\text{-N}$, K^+ , and MRP concentrations to one with low concentrations caused an abrupt increase in soil MRP concentration in water extracted from these calcareous soils. Maximum MRP concentrations in the leachate averaged 1.6 times greater than that in the high concentration nutrient solution. This phenomenon may have significant implications for irrigated agriculture, particularly for confined animal feeding operations, where irrigation water nutrient loading can vary widely between alternate water sources. There is a need to better understand how changes in soil solution chemistry interact with soil exchange complexes to affect potential leaching of P. The walled percolation sampler coupled with the sequential tension autosampler provides a convenient tool for investigating the dynamic effects of infiltrating water chemistry on soil solute concentrations under continuous extraction.

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