COMPARISON OF METHODS FOR NUTRIENT MEASUREMENT IN CALCAREOUS SOILS: ION-EXCHANGE RESIN BAG, CAPSULE, MEMBRANE, AND CHEMICAL EXTRACTIONS

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Four methods for measuring quantities of 12 plant–available nutrients were compared using three sandy soils in a series of three experiments. Three of the methods use different ion-exchange resin forms—bags, capsules, and membranes—and the fourth was conventional chemical extraction. The first experiment compared nutrient extraction data from a medium of sand saturated with a nutrient solution. The second and third experiments used Nakai and Sheppard series soils from Canyonlands National Park, which are relatively high in soil carbonates. The second experiment compared nutrient extraction data provided by the four methods from soils equilibrated at two temperatures, "warm" and "cold." The third experiment extracted nutrients from the same soils in a field equilibration. Our results show that the four extraction techniques are not comparable. This conclusion is due to differences among the methods in the net quantities of nutrients extracted from equivalent soil volumes, in the proportional representation of nutrients within similar soils and treatments, in the measurement of nutrients that were added in known quantities, and even in the order of nutrients ranked by net abundance. We attribute the disparities in nutrient measurement among the different resin forms to interacting effects of the inherent differences in resin exchange capacity, differences among nutrients in their resin affinities, and possibly the relatively short equilibration time for laboratory trials. One constraint for measuring carbonate-related nutrients in high-carbonate soils is the conventional ammonium acetate extraction method, which we suspect of dissolving fine $CaCO_3$ particles that are more abundant in Nakai series soils, resulting in erroneously high Ca^{2+} estimates. For study of plant-available nutrients, it is important to identify the nutrients of foremost interest and understand differences in their resin sorption dynamics to determine the most appropriate extraction method. (Soil Science 2002;167:666–679)

Key words: Soil nutrient extraction, ion-exchange resin bags, capsules, membranes, chemical extraction, calcareous soils.

MEASURING plant–available soil nutrients with sensitivity to spatial and temporal variation in soil properties and other environmental conditions is an ongoing challenge for soil researchers. Nutrient bioavailability is a function of soil chemical, physical, and mineralogical properties that govern exchange reactions (Cooperband and Logan 1994; Dobermann et al., 1994), nutrient concentration, diffusion (Skogley et al., 1990; Abrams and Jarrell 1992; Skogley and Dobermann 1996), and biogeochemical processes such as mineralization. These factors are further affected by environmental conditions such as soil moisture and temperature (Binkley 1984; Skogley and Schaff 1985; Yang et al., 1991b).

Chemical extractions are conventional for measuring nutrient availability, but ion–exchange

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resins, demonstrated to be effective measures of soil nutrients in both terrestrial and aquatic ecosystems (Yang et al., 1991a; Abrams and Jarrell 1992; Dobermann et al., 1994), may be preferable in some studies (see Skogley and Dobermann, 1996 for review). Chemical extraction provides a static measure of potential nutrient supply (Gibson et al., 1985), in contrast to resins which, as ionic exchangers, represent an integration of bioavailable nutrient dynamics over a specified incubation period (Christensen and Posner 1980; Cooperband and Logan 1994; Skogley and Dobermann, 1996). In addition, resins are sensitive to environmental conditions (Binkley and Matson, 1983; Skogley, 1992), more efficient for measuring multiple soil nutrients than an equal number of chemical extractions (Schoenau et al., 1993), inexpensive, and nondestructive with respect to soil chemistry and mineralogy (Cooperband and Logan, 1994).

Resins have been used to simulate both soil colloids (e.g., Cooperband and Logan 1994; Skogley and Dobermann, 1996) and plant roots (e.g., Yang et al., 1991a and b; Qian et al., 1992). The acidifying effect of resins with desorption of a H^+ countercation is similar to that of plant roots, although whether it occurs in comparable rates and/or quantities is unknown. Also similar to root processes are the effects of cation uptake on that of anions and vice versa, due to charge-balance relations and shifts in soil equilibria (e.g., Yang et al., 1991a; Barber, 1995). The dynamic colloidal effects of resins, however, are very much like that of a soil. Hence, ion-exchange resins embody particular characteristics of both biological and mineral components of soil ecosystems.

Despite the application of ion-exchange resins for over 40 years (Amer et al., 1955) and their general acceptance as a method for detection of soil nutrient levels, methods of resin use are not uniform and the interpretive differences among varying methods are poorly understood. Major differences among different resin forms (resin bags, capsules, and membranes) are exchange capacity ($\sim$32.1 mEq of charge per bag compared with 2.2 mEq/capsule and 1.2 mEq/membrane), shape, and the mesh barrier containing the resin beads of bags and capsules. Theoretically, the spherical shape of resin capsules and bags allows for a geometrically consistent reactive surface area (Skogley et al., 1990), whereas the edges of a resin membrane may become saturated with high-affinity ions before the interior area, thereby decreasing the overall exchange rates. However, resin membranes, which are flat, should also maximize contact with the soil matrix

(Cooperband and Logan, 1994) and are the only resin method for which the reactive surface area can be accurately calculated; bags and capsules are filled with beads of varying surface area that is estimated. Additionally, the encasing mesh of bags and capsules may impose a diffusion barrier to the internal beads, allowing two different diffusion rates inside and outside of the mesh (Abrams and Jarrell, 1992; Cooperband and Logan 1994). Also, soil particles and fine roots often become embedded in or behind the mesh and are difficult to remove entirely, and can result in questionable results (Saggar et al., 1990).

Our overarching objective was to compare nutrient extraction data from different resin media and conventional chemical extraction techniques to determine which would be most appropriate for field studies. Although many chemical extraction techniques originally were designed for agronomic applications (e.g., Bohn et al., 1979), both resin and chemical approaches are widely used in ecological studies to quantify spatial and temporal variations in nutrient bioavailability. Our chemical methods were ammonium acetate (NH_4OAc), bicarbonate, DTPA, and KCl extraction of 12 plant-available nutrients. We performed these comparisons in three formats. The first was sand saturated with a nutrient solution of known concentrations. The second was a comparison of two different soil series in temperature-controlled environments. The third was a field-based comparison in the same soils that were used in the temperature-controlled experiments.

METHODS

Sand Saturated with Bolds Nutrient Solution

Resin bags were constructed with commercial nylon stockings filled with 8 g bipolar (H^+ and OH^- counterions) ion-exchange resin beads. Bipolar (H^+/OH^-) resin capsules were obtained (WECSA, Fort Collins, CO). Cation-exchange membranes (CEMs) (CR 67, Dynambio, Madison, WI) were cut to 3.5 × 5 cm and charged with H^+ by placing them in 0.2 M HCl for 2 h with the solution replaced halfway through the equilibration period. Anion-exchange membranes (AEMs) (AR 204, Dynambio), also 3.5 × 5 cm, were charged with OH^- in the same manner using 0.5 M NaOH.

Sand was sterilized in 1-L quantities. The sand was soaked for 5 min in 1.5 L of 1.0% acetic acid and rinsed of acetic acid with deionized (DI) water. Then, the sand was alternately washed and rinsed with 0.5% acetic acid and DI water, and

then rinsed with 2 L of boiling DI water. The sand was then autoclaved and dried in a 150 °C oven.

In 15 clear, acid-washed 9-oz plastic cups, 75 mL nutrient solution (Bold, 1957) was added to 250 g sterilized sand (nutrient quantities added are in Table 1). Sand was chosen to reduce the effects of cation exchange with clay colloids. Five replicates of each of the three resin forms were embedded in the saturated sand. AEMs and CEMs were placed back to back with a plastic membrane between them. Cups were covered with plastic wrap and allowed to equilibrate for 1 week. Ambient temperatures were 12 to 22 °C. At the end of the exchange period, all resins were collected, rinsed with DI water, and placed in a freezer at 0 °C until extraction. At the Soil and Plant Analysis Laboratory at Brigham Young University (SPAL), ions were desorbed from all resins in 2 M HCl for 1 h and all except inorganic N were measured by inductively coupled plasma spectrometry. NH_4^+-N and NO_3^--N were extracted by steam distillation in a H_3BO_3 indicator solution with MgO and Devarda alloy, and determined by titration with H_2SO_4 (Keeney and Nelson, 1982). Results were reported in μg resin^{-1} whether bag, capsule, or membrane, and converted to micromoles of ionic charge per resin (μmol$_c$ resin^{-1}). Five replicates of sand and nutrient solution with no resins were treated in the same manner and measured for NH_4OAc-extractable calcium, potassium, magnesium, and sodium at pH 8.5 (Ca^{2+}, K^+, Mg^{2+}, and Na^+, respectively; Normandin et al., 1998); DTPA-extractable copper, iron, manganese, and zinc (Cu^{2+}, Fe^{2+}, Mn^{2+}, and Zn^{2+}, respectively; Lindsay and Norwell, 1978); KCl-extractable inorganic nitrogen (NH_4^+-N and NO_3^--N); and bicarbonate-extractable phosphorus (HPO_4^{2-}-P; Olsen et al., 1954). Results were reported in ppm and converted to μmol$_c$ kg^{-1}.

Because the actual volume of soil subject to measurement by ion-exchange resins is unknown and the exchange capacity of the three resin forms differs, we converted all data to percentages of total ions of corresponding charge. Proportions were arcsin-transformed and analyzed among the four methods (chemical and three resin extractions) by multivariate analysis of variance (MANOVA). Na^+ was disregarded from the membrane data due to excessively high Na^+ data from initial charging with NaOH. Membrane Na^+ values were therefore estimated based on the mean proportion of Na^+ extracted by resin bags, resin capsules, and chemical methods, among

which there were no significant differences in proportional Na^+. In addition, nutrients were ranked according to net abundance as another means of comparison among methods.

Temperature-Controlled Comparison of Resin Forms in Canyonlands Soil

Soils from the Nakai and Sheppard series (Table 2) were collected from two sites within the Needles District of Canyonlands National Park (CNP) in southeast Utah (38.17°N, 109.98°W), an arid ecosystem averaging 11.6 °C and 214 mm annual precipitation (1965–1997; Miller, 2000). The soils were sieved (2 mm) and mixed with enough DI water to make a saturated paste (Rhoades, 1982). Within each soil type, 10 replicates each of resin bags, capsules, and membrane pairs were embedded in the saturated pastes, and cups were covered with plastic wrap. In February 2000, five replicates of each resin type and soil combination (for a total of 30 replicates) were placed in a cold frame at the Denver Botanic Gardens (DBG, Denver, CO) for the cold (average maximum and minimum temperatures for the incubation period were 23 and −4 °C, respectively) treatment. Five of each combination were placed in a seedling propagator room at DBG for the warm (average maximum and minimum temperatures were 34 and 18 °C, respectively) treatment. Samples were equilibrated for 1 week, at the end of which all resin media were removed, rinsed thoroughly with DI water, and stored at 0 °C. Extraction of resins and soils was as described above at SPAL.

Because nitrogen can undergo rapid microbial transformations and accurate Na^+ data were unavailable from resin membranes, NH_4^+-N, NO_3^--N, and Na^+ data were disregarded in calculating nutrient percentages. Data analysis was as described above.

Field Comparison of Resin Forms

On 11 March, 2000, resins were placed in the field at the same sites from which soil was collected for the temperature-controlled experiments (Table 2) (Walkley and Black, 1934; Rhoades, 1982; Day, 1965; Chapman 1965; Allison and Moode, 1965; Normandin et al., 1998; Lindsay and Norwell, 1978; Schoenau and Karamonos, 1993; Bremner, 1996; Olsen et al., 1954). At each site, five replicates each of resin bags, capsules, and membranes were placed in the A horizon at 5- to 7-cm depth. Soil moisture and temperature were recorded at 10-cm soil depth once per hour by climate stations close to the plots.

TABLE 1

Mean, SE, and percent nutrients added to and measured in a sand/nutrient solution*

| Nutrient | Added in solution | | Extracted | | | | | | | | | | | | | | | |
| | | | Chemical | | | | Resin bags | | | | Resin capsules | | | | Resin membranes | | | |
	μmol_c sample^{-1}	%	μmol_c sample^{-1}	SE	%		μmol_c bag^{-1}	SE	%		μmol_c caps.$^{-1}$	SE	%		μmol_c memb.$^{-1}$	SE	%	
Ca^{2+}	33.7	6.2	643.0	447	36.4	a	33.3	2.9	12.4	d	29.9	1.2	15.3	c	93.2	6.4	25.8	b
Cu^{2+}	0.9	0.2	1.7	1	0.1	d	2.2	0.1	0.8	b	2.6	0.3	1.4	a	1.6	0.1	0.4	c
Fe^{2+}	2.7	0.5	13.3	4	0.8	c	16.5	1.8	6.2	a	15.1	2.7	7.6	a	16.2	2.2	4.4	b
K^+	197.8	36.7	150.9	96	8.8	d	43.0	0.6	16.2	b	34.5	0.7	17.7	a	53.7	3.7	14.9	c
Mg^{2+}	45.5	8.4	165.3	25	9.6	a	17.1	1.0	6.4	c	13.9	1.0	7.1	b	33.7	2.6	9.3	a
Mn^{2+}	1.1	0.2	2.7	1	0.2	a	0.3	0.03	0.1	b	0.2	0.01	0.1	b	0.6	0.05	0.2	a
Na^+	252.4	46.9	727.3	93	42.7		113.5	2.3	42.7		90.1	4.0	46.2				[43.9]	
NH_4^+			21.1	24	1.3	c	39.9	1.3	15.1	a	8.8	0.8	4.6	b	3.0	0.4	0.9	c
Zn^{2+}	4.6	0.9	2.5	1	0.14	b	0.1	0.01	0.05	d	0.1	0.01	0.07	c	0.9	0.3	0.25	a
NO_3^-	219.9	65.1	9.6	3	20.6	a	3.1	0.4	6.8	c	4.5	0.6	14.8	b	4.5	0.5	14.8	b
HPO_4^{2-}	64.3	19.0	23.8	2	51.0		24.2	0.1	53.3		16.3	0.6	54.3		16.3	1.2	53.3	
SO_4^{2-}	53.7	15.9	13.4	6	28.5	b	18.2	0.6	39.9	a	9.3	0.6	30.9	b	9.8	0.6	32.0	b

*Percentages refer to the proportions of each cation or anion relative to total ions of the same charge. Na^+ data were exceedingly high from membrane data due to initial charging of AEMs with NaOH and were not included in proportional calculations. Because there are no significant differences in relative amounts of Na^+ extracted by the remaining extraction methods, cation percentages for membranes are based on the assumption that Na^+ represented 43.9% of all cations desorbed from membranes (the mean of the other three methods). Different letters indicate significant ($P < 0.05$) differences among extraction methods in arcsin-transformed nutrient proportions.

TABLE 2

Characteristics of two CNP soils used for resin comparisons.*

	Nakai	Sheppard	Nutrient	Nakai series	Sheppard series
USDA subgroup†	Typic Calciorthids	Typic Torripsamments	Exchangeable Ca (μmol_c kg^{-1})**	131,158	98,270
Bulk density (g cc^{-1})†	1.5	1.6	Cu (μmol_c kg^{-1})$^{\Psi}$	12.4	31.7
OM (%)‡	1.2	0.3	Fe (μmol_c kg^{-1})$^{\Psi}$	66.8	49.3
PH§	8.1	8.1	Available K (μmol_c kg^{-1})$^{\Delta}$	6331	954
EC (dS M^{-1})§	0.9	0.5	Exchangeable K (μmol_c kg^{-1})	7068	878
% Sand¶	61.6	85.6	Exchangeable Mg (μmol_c kg^{-1})	14,877	2908
% Silt	26.1	7.1	Mn (μmol_c kg^{-1})$^{\Psi}$	168	52.7
% Clay	12.3	7.3	Total N (ppm)$^{\partial}$	868	230
CEC (cmol$_c$ kg^{-1})‖	5.9	2.0	Exchangeable Na (μmol_c kg^{-1})	2806	2964
% CaCO$_3$ equiv.#	10.2	13.5	P (μmol_c kg^{-1})$^{\infty}$	463	28.3
			SO$_4$-S (μmol_c kg^{-1})$^{\Psi}$	283	140
			Zn (μmol_c kg^{-1})$^{\Psi}$	11.5	10.4

*Values are averaged from 6–10 replicates. Single-factor ANOVA showed that all differences in nutrients between soil types are significant ($P < 0.05$) except for Na$^+$ and Zn^{2+}.
†USDA & SCS 1991; ‡Walkley and Black (1934); §Determined with saturated paste (Rhoades, 1982); ¶Texture was determined by the hydrometer method (Day, 1965); ‖Chapman (1965); #measured by HCl neutralization (Allison and Moode, 1965) and includes any soil constituent that neutralizes acid; **All exchangeable nutrients were extracted with ammonium acetate at pH 8.5 (NH$_4$C$_2$H$_3$O$_2$; Normadin et al., 1998); $^{\Psi}$DTPA extraction (Lindsay and Norwell, 1978); $^{\Delta}$Schoenau and Karamonos (1993); $^{\partial}$Kjeldahl analysis (Bremmer, 1996); $^{\infty}$Olsen et al. (1954).

Soil temperature was measured with a Campbell CS615 water content reflectometer. Mean monthly soil temperatures for the March, April, May, and June equilibration periods at the Nakai soils site were 8, 15, 24, and 32 °C, respectively, and soil moisture was 12%, 6%, 4%, and 2% by volume, respectively. Mean monthly soil temperatures for the same periods at the Sheppard soils site were recorded as 10, 18, 24, and 31 °C, and soil moisture was 10%, 7%, 5%, and 3% by volume, respectively. Overall soil temperature and moisture means for the Nakai and Sheppard soils were 19.0 and 20.0 °C, and 6.4% and 6.6%, respectively. Precipitation events on 20 March, 27 March, and 7 May resulted in detectable but transient increases in soil moisture.

Resins were collected 94 days later on 13 June 2000. Nutrients were extracted at SPAL and data were analyzed as described above. Unless stated otherwise, all significance refers to $P < 0.05$.

RESULTS

Sand Saturated with Bold's Nutrient Solution

The measurement of nutrients added in solution to the sand medium varied widely by nutrient and by extraction method (Table 1). Cu^{2+} and Fe^{2+} were extracted by all methods in greater net quantities than they were added. This was despite prior sterilization with acetic acid and autoclaving, leaving us to conclude that the sand parent material contained some quantities of readily-extractable Cu^{2+} and Fe^{2+}. None of the methods measured the full supplement of K$^+$, Zn^{2+}, NO$_3^-$-N, HPO$_4^{2-}$-P, and SO$_4^{2-}$-S that were added, while Ca^{2+}, Mg^{2+}, Mn^{2+}, and Na$^+$ were measured in higher amounts by some methods and lower amounts by others than the net μmol_c that was actually added. Proportional to other ions of similar charge, all extraction methods detected high percentages of Ca^{2+}, HPO$_4^{2-}$-P, and SO$_4^{2-}$-S and low percentages of K$^+$, Zn^{2+}, and NO$_3^-$-N relative to that which was added.

Among methods in the sand/nutrient solution, chemical extraction represented Ca^{2+} and NO$_3^-$ in the greatest proportions and Cu^{2+}, Fe^{2+}, and K$^+$ in the least (Table 1). Resin bag extraction represented NH$_4^+$-N and SO$_4^{2-}$-S in greatest proportions and Ca^{2+}, Mg^{2+}, NO$_3^-$-N, and Zn^{2+} in the least. Capsules represented Cu^{2+} and K$^+$ in greatest proportions, and membranes represented Zn^{2+} in the greatest proportions. There were no significant differences among techniques with respect to proportional HPO$_4^{2-}$-P or Na$^+$.

In this sand/nutrient solution comparison, all methods determined Na$^+$ to be the most abundant nutrient (Table 3, Section 1). As suggested by proportional comparisons, the ranking of Cu^{2+}

TABLE 3

Descending order of inorganic nutrients measured by chemical and resin extractions*

Soil/experiment	Method			Order of representation
(1) Sand/Bolds	Chemical			Na Ca Mg K HPO_4 NH_4 SO_4 Fe NO_3 Mn Zn Cu
	Resin	Bags		Na K NH_4 Ca HPO_4 SO_4 Mg Fe NO_3 Cu Mn Zn
		Capsules		Na K Ca HPO_4 Fe Mg SO_4 NH_4 NO_3 Cu Mn Zn
		Membranes		Na Ca K Mg HPO_4 Fe SO_4 NO_3 NH_4 Cu Zn Mn
(2) CNP soil—Nakai series	Chemical			Ca Mg K Na HPO_4 SO_4 Mn Fe NO_3 Cu Zn Zn
	Lab resins	Bags	Cold	Ca Mg K NH_4 SO_4 Fe Na HPO_4 Mn NO_3 Zn Cu
			Warm	Ca Mg K NH_4 Fe SO_4 Na HPO_4 Mn NO_3 Zn Cu
		Capsules	Cold	Ca Mg K Na SO_4 Fe HPO_4 Mn NO_3 Zn Cu
			Warm	Ca Mg K NH_4 SO_4 Fe Na HPO_4 Mn NO_3 Zn Cu
		Membranes	Cold	Ca Mg K Na Fe SO_4 Mn HPO_4 NO_3 Zn Cu
			Warm	Ca Mg SO_4 NH_4 Fe Na K HPO_4 NO_3 Mn Zn Cu
	Field resins	Bags		Ca NH_4 Mg Fe Na K SO_4 NO_3 HPO_4 Mn Cu Zn
		Capsules		Ca Mg Na K SO_4 Fe NO_3 HPO_4 Mn Mn Zn Cu
		Membranes		Ca Mg NH_4 Na K Fe HPO_4 NO_3 Zn Cu
(3) CNP soil—Sheppard series	Chemical			Ca Na Mg K SO_4 Fe HPO_4 NO_3 Zn Cu
	Lab resins	Bags	Cold	Ca Mg NH_4 SO_4 K Fe HPO_4 Mn NO_3 Cu Zn
			Warm	Ca Mg NH_4 K SO_4 Fe Mn HPO_4 NO_3 Cu Zn
		Capsules	Cold	Ca Mg Na NH_4 K SO_4 Fe HPO_4 Mn NO_3 Cu Zn
			Warm	Ca Mg K NH_4 Na SO_4 Fe Mn HPO_4 NO_3 Zn Cu
		Membranes	Cold	Ca Mg SO_4 NH_4 K Fe Mn HPO_4 NO_3 Zn Zn
			Warm	Ca Mg SO_4 K Fe Mn HPO_4 NO_3 Zn Cu
	Field resins	Bags		Ca NH_4 Fe Mg K NO_3 HPO_4 Mn Zn Zn
		Capsules		Ca NH_4 Na Mg SO_4 NO_3 HPO_4 Mn Zn Cu
		Membranes		Ca Mg SO_4 K Fe NO_3 HPO_4 Mn Zn Cu

*Ranks are based on micromoles of ionic charge (μmol_c). Except for the comparison in sand/nutrient solution, Na^+ data for resin membranes and $NaHCO_3$-charged resins are disregarded. The term "Lab" is used to distinguish from field trials.

was particularly low in chemical extractions and of NH_4^+ was particularly high with bags. All methods desorbed anions in the consistent order HPO_4^{2-}-P > SO_4^{2-}-S > NO_3^--N.

Temperature-Controlled Comparison of Resin Forms in Canyonlands Soil

In temperature-controlled comparisons of CNP soils, there were significant effects of extraction method, temperature, and/or soil source on proportional nutrient representation among all ions but Fe^{2+}, which was not affected by any factor (Table 4). Regardless of soil source, Ca^{2+} was represented in significantly greater proportion and Mg^{2+} in the least proportion by chemical extraction when compared with resin methods (Table 5). SO_4^{2-}-S and Zn^{2+} were represented in the greatest proportions and K^+ and HPO_4^{2-}-P in the least proportions by membranes (Table 5). The proportional representation of other nutrients among methods differed by soil source. For example, in Nakai soils, chemical methods measured greater proportional HPO_4^{2-}-P than SO_4^{2-}-S, a trend that was reversed in the resin data. This reversal of HPO_4^{2-}-P and SO_4^{2-}-S trends did not occur in Sheppard soils. Significant temperature effects (Table 4) generally were due to greater ion sorption in warm conditions than

cold (Table 6). Exceptions include Cu^{2+} in Sheppard soils and NO_3^- in soils of either series, which were sorbed in greater quantities in colder temperatures.

All extraction methods reflected greater quantities of K^+, Mg^{2+}, Mn^{2+}, and HPO_4^{2-}-P in Nakai soils (Tables 2, 4, and 6). Some methods resulted in opposite trends between soils. For example, despite higher Ca^{2+} in Nakai soils extracted chemically (Table 2), all resins extracted more Ca^{2+} from Sheppard soils (Tables 4 and 6). Similarly, SO_4^{2-}-S values were greater in Nakai soils as determined by chemical methods (F = 3818, $P < 0.001$) and resin membranes (F = 14.3, $P = 0.001$) (Tables 2 and 6), but resin bags sorbed greater SO_4^{2-}-S from Sheppard soils (F = 10.5, $P = 0.005$).

Among resins only, pooling the effects of temperature and soil source, bags sorbed the most net ionic charge of most nutrients, generally with one of two slightly different patterns (Table 6): Bag > Capsule > Membrane (K^+, HPO_4^{2-}-P; F = 18.2 and 20.3, respectively; $P < 0.001$) or Bag > Capsule = Membrane (Ca^{2+}, Fe^{2+}, Mn^{2+}, NH_4^+-N, NO_3^--N, SO_4^{2-}-S; F = 22.5, 3.5, 8.0, 120, 4.0, and 196, respectively; $P < 0.05$). Mg^{2+} sorption also followed this Bag > Capsule = Membrane pattern, although statistical signifi-

TABLE 4

F values of MANOVA comparing arcsin-transformed proportions of nutrients extracted by four methods from saturated pastes that varied by soil source.

Nutrient	Resin and chemical extraction[a]						Resins only[b]			
	Extraction method		Soil series		Method × soil series		Temperature		Resin method × temperature	
Ca^{2+}	35.4	***	1725.5	***	19.2	***	1.0		0.1	
Cu^{2+}	77.7	***	132.9	***	80.8	***	19.8	***	0.8	
Fe^{2+}	1.7		1.0		1.4		3.6		1.4	
K^+	53.9	***	185.6	***	32.6	***	1.8		0.6	
Mg^{2+}	71.3	***	3254.2	***	43.4	***	0.1		0.0	
Mn^{2+}	3.2	*	14.1	***	0.2		66.4	***	12.5	***
NH_4^+							12.8	**	4.6	*
Zn^{2+}	25.6	***	3.3		5.6	**	10.6	**	2.0	
NO_3^-							31.1	***	1.4	
HPO_4^{2-}	137.9	***	658.9	***	59.3	***	0.1		0.3	
SO_4^{2-}							8.8	**	0.3	

[a]Proportions were calculated excluding Na^+ data, which were unavailable for resin membranes, and NH_4^+ and NO_3^- data, which were unavailable for chemical extraction. SO_4^{2-}-S and HPO_4^{2-}-P percentages are directly inversely related so only HPO_4^{2-}-P was included in the analysis. Resin data were pooled between temperatures.
[b]Equilibration temperature was manipulated for resin extractions only; NH_4^+ and NO_3^- were therefore included in the proportions calculated for this MANOVA.
*$P < 0.05$;
**$P < 0.01$;
***$P < 0.001$.

TABLE 5

Percentages of nutrients, specific to total positive or negative charge, extracted by conventional ("chemical") methods and by resin bags, capsules, and membranes equilibrating in saturated pastes under controlled environmental conditions*

Nutrient	Nakai series								Sheppard series							
	Chemical		Bags		Capsules		Membranes		Chemical		Bags		Capsules		Membranes	
Ca^{2+}	85.4	a	72.5	d	75.7	c	80.2	b	96.2	a	94.6	b	94.6	b	94.6	b
Cu^{2+}	0.008	b	0.009	ab	0.008	b	0.010	a	0.029	a	0.007	d	0.008	c	0.011	b
Fe^{2+}	0.04		1.72		0.30		0.49		0.05	b	0.38	a	0.42	a	0.34	a
K^+	4.7	ab	7.1	a	5.4	b	0.7	c	0.9	b	1.1	b	1.3	a	0.4	c
Mg^{2+}	9.8	b	18.4	a	18.3	a	18.3	a	2.8	d	3.8	b	3.4	c	4.5	a
Mn^{2+}	0.11		0.29		0.27		0.29		0.05		0.15		0.14		0.16	
Zn^{2+}	0.007	b	0.008	b	0.005	c	0.015	a	0.010	b	0.004	c	0.011	b	0.018	a
HPO_4^{2-}	61.8	a	25.6	b	28.9	b	17.5	c	16.6	a	12.7	ab	12.1	b	5.5	c
SO_4^{2-}	38.2	c	74.4	b	71.1	b	82.5	a	83.4	c	87.3	bc	87.9	b	94.5	a

*Percentages were calculated without Na^+, NH_4^+, or NO_3^- data (see Methods). Resin data (bags, capsules, and membranes) were pooled between two temperatures (see Methods). Different letters in a row indicate significant (P < 0.05) differences among methods within each series.

cance was borderline (F = 3.0, P = 0.06). Na^+ sorption by bags was also greater than by capsules (F = 4.4, P < 0.05). Exceptions to the above patterns are Cu^{2+} (Bag > Membrane > Capsule; F = 36.6, P < 0.001) and Zn^{2+} (Membrane > Bag = Capsule; F = 14.5, P < 0.001). The greater sorption capacity of bags was also apparent where there were statistical interactions (Table 4). For example, although greater net amounts of Ca^{2+} were sorbed from Sheppard soils (F = 13.0, P = 0.001), resin bags sorbed more Ca^{2+} ions from Nakai soils than capsules or membranes did from Sheppard soils (Table 6).

All extraction methods in this experiment determined Ca^{2+} to be the most abundant nutrient, and all but chemical extraction of Sheppard soils ranked Mg^{2+} immediately after Ca^{2+} (Table 3, Sections 2 and 3, chemical and lab trials only). SO_4^{2-}-S ranked relatively high in membrane extractions. Among methods, anions were generally extracted in the order SO_4^{2-}-S > HPO_4^{2-}-P > NO_3^--N. Exceptions to this order of anion extraction were cold membrane extraction in either soil, where NO_3^--N > HPO_4^{2-}-P, and chemical extraction of Nakai soils, where HPO_4^{2-}-P > SO_4^{2-}-S. HPO_4^{2-}-P ranked exceptionally low in chemical extractions of Sheppard soils. In Nakai soils, K^+ was the third-ranked nutrient by all methods except membranes in warm conditions. In Sheppard soils, chemical extraction ranked Na^+ higher than any other method.

The ratio of (Ca + Mg):K, an index of ionic competition with K^+ adsorption and activity in solution (Dobermann et al., 1995), was significantly greater (F = 224.6, P < 0.001) by mem-

brane determination (F = 189.8) than any other method (F = 52.4), and all methods determined the ratio to be greater in Sheppard than Nakai soils (F = 229.3). There were no significant effects of temperature on the index.

Field Comparison of Resin Forms

Proportional nutrient extraction was significantly different among chemical and resin methods in the field for all ions except Zn^{2+} (Table 7). Regardless of soil source, Ca^{2+} and HPO_4^{2-}-P were represented in significantly greater proportion and Mg^{2+} and SO_4^{2-}-S the least proportion by chemical extraction (Table 8). Cu^{2+} was generally extracted in greater proportion by bags and capsules (Table 8). As with the comparison in the controlled environment, proportional representation of most nutrients among methods differed by soil source (Table 7). Significant source effects were generally due to proportionally greater nutrients in Nakai than Sheppard soils, with the exceptions of Ca^{2+} by any method (F = 56.6, P < 0.001) and Cu^{2+} by chemical extraction (F = 150.3, P < 0.001), which were proportionally higher in Sheppard series soils.

Among resins only, pooled between the two soil series, there were several patterns of ion behavior among media according to net charge adsorbed (Table 9). Fe^{2+}, NH_4^+, and HPO_4^{2-}-P were sorbed in the order Bags > Capsules = Membranes (F = 12.4, 6.9, and 11.4, respectively; P < 0.01) (Table 9). SO_4^{2-}-S was sorbed in the order Bags > Membranes > Capsules (F = 42.2, P < 0.001). Ca^{2+}, Mg^{2+}, and Zn^{2+} followed the pattern Membranes > Bags = Capsules (F =

TABLE 6

Mean μmol_c resin^{-1} (SE) nutrients desorbed from resins equilibrating in CNP soil*

Nutrient	Nakai Series						Sheppard Series					
	Cold			Warm			Cold			Warm		
	Bag	Caps	Memb	Bag	Caps	Memb	Bag	Caps	Memb	Bag	Caps	Memb
Ca²⁺	1189 (174)	892 (82)	931 (20)	1258 (221)	1006 (91)	926 (21)	2517 (268)	1007 (76)	1096 (55)	2590 (145)	1117 (55)	1082 (15)
Cu²⁺	0.14 (0.01)	0.09 (<0.01)	0.12 (<0.01)	0.13 (0.01)	0.09 (0.01)	0.11 (0.01)	0.19 (0.02)	0.10 (<0.01)	0.13 (0.01)	0.16 (0.01)	0.08 (<0.01)	0.12 (0.01)
Fe²⁺	6.9 (2.0)	2.5 (0.2)	3.9 (0.5)	47.8 (28.1)	5.0 (0.5)	7.4 (0.5)	6.9 (0.8)	2.9 (0.2)	2.9 (0.1)	13.5 (2.6)	6.7 (0.5)	5.0 (0.3)
K⁺	89.2 (2.0)	48.5 (1.0)	9.5 (0.3)	140.1 (13.9)	87.6 (5.7)	7.8 (0.1)	23.7 (1.2)	11.6 (0.2)	5.4 (0.2)	33.8 (1.2)	18.6 (0.5)	4.1 (0.2)
Mg²⁺	289 (30)	200 (13)	203 (5)	331 (68)	260 (23)	221 (4)	92.3 (9.7)	34.2 (2.0)	48.6 (2.7)	110.9 (5.2)	43.1 (1.3)	54.1 (0.8)
Mn²⁺	3.6 (0.6)	2.2 (0.2)	0.9 (0.1)	6.5 (1.1)	4.7 (0.5)	5.8 (0.1)	3.4 (0.4)	1.1 (0.1)	0.7 (0.1)	4.8 (0.2)	2.0 (0.1)	3.1 (0.1)
Na⁺	17.4 (1.1)	15.5 (0.3)		17.2 (2.0)	14.9 (0.8)		13.8 (0.3)	13.2 (0.4)		14.5 (1.6)	12.1 (1.0)	
NH₄⁺	44.5 (7.6)	10.3 (1.6)	6.6 (0.6)	98.8 (7.8)	26.2 (5.5)	6.8 (0.7)	68.4 (2.2)	12.1 (0.2)	7.5 (0.7)	88.1 (3.7)	16.3 (1.0)	8.5 (0.2)
Zn²⁺	0.1 (0.02)	0.1 (0.01)	0.1 (0.01)	0.1 (0.03)	0.1 (<0.01)	0.2 (0.01)	0.1 (0.01)	0.1 (0.05)	0.2 (0.01)	0.1 (0.02)	0.2 (0.02)	0.03 (0.02)
NO₃⁻	5.0 (1.2)	2.0 (0.2)	2.4 (0.3)	1.5 (0.4)	0.7 (0.2)	0.4 (0.1)	1.3 (0.3)	0.7 (0.4)	1.1 (0.4)	0.7 (0.1)	0.5 (0.2)	0.4 (0.1)
HPO₄²⁻	8.4 (1.3)	4.3 (0.4)	2.2 (0.1)	7.1 (2.2)	4.7 (0.4)	2.0 (0.1)	4.2 (0.5)	1.3 (0.1)	0.5 (<0.1)	3.5 (0.3)	1.4 (0.1)	0.6 (<0.1)
SO₄²⁻	21.0 (0.9)	9.9 (0.5)	9.3 (0.2)	21.7 (2.2)	12.2 (1.0)	10.2 (0.2)	25.0 (1.6)	8.8 (0.4)	8.8 (0.4)	27.2 (0.8)	10.3 (0.3)	8.7 (0.1)

N = 5.

23.1, 8.4, and 21.0; $P < 0.01$) and Cu^{2+} and Mn^{2+} were sorbed in the order Membranes > Bags > Capsules (F = 33.5 and 25.0, $P < 0.001$). The only nutrients whose sorption patterns among resin forms in the field corresponded to that in the controlled experiments were Fe^{2+}, NH_4^+-N, and Zn^{2+}.

Similar to the other comparisons of extraction methods, resins in the field determined Ca^{2+} to be the most abundant nutrient (Table 3, Sections 2 and 3, chemical and field trials). The rank of K^+ was highest for chemical and membrane extraction and fell with increasing resin sorption capacity (rank of Bag_{K+} > $Capsule_{K+}$ < $Membrane_{K+}$). Similar to laboratory results, SO_4^{2-}-S ranked relatively high in membrane extractions, and NH_4^+-N ranked relatively low. Also, anions were usually extracted in the order SO_4^{2-}-S > NO_3^--N > HPO_4^{2-}-P, except for chemical extraction of Nakai soils, where HPO_4^{2-}-P > SO_4^{2-}-S. Again, HPO_4^{2-}-P was exceptionally low in chemical extractions of Sheppard soils.

Also similar to nonfield trials were trends of (Ca + Mg):K. The (Ca + Mg):K ratio was significantly ($P < 0.001$) greater for membranes than for bags or capsules (F = 37.4) and was greater in Sheppard than in Nakai soils (F = 121.6).

TABLE 7

F values of MANOVA comparing the proportional amount of nutrients extracted by resins in the field at CNP and conventional chemical extractions[a]

Nutrient	F values		
	Method	Soil series	Method × soil series
Ca²⁺	98.5 ***	514.2 ***	8.8 ***
Cu²⁺	9.6 ***	0.2	0.9
Fe²⁺	13.7 ***	0.0	0.1
K⁺	27.8 ***	88.9 ***	2.8
Mg²⁺	31.3 ***	449.4 ***	17.2 ***
Mn²⁺	14.9 ***	24.8 ***	7.6 **
Zn²⁺	2.7	4.3 *	0.8
HPO₄²⁻	375.0 ***	230.8 ***	177.9 ***
SO₄²⁻			

[a]Proportions were calculated excluding Na^+, NH_4^+-N and NO_3^--N data. SO_4^{2-}-S and HPO_4^{2-}-P percentages are directly inversely related so only HPO_4^{2-}-P was included in the analysis.
*$P < 0.05$.
**$P < 0.01$.
***$P < 0.001$.

TABLE 8

Percentages of nutrients, specific to total positive or negative charge, extracted by conventional ("chemical") methods and by resin bags, capsules, and membranes equilibrating in the field at CNP*

Nutrient	Nutrient percentages							
	Nakai Series				Sheppard Series			
	Chemical	Bag	Capsule	Membrane	Chemical	Bag	Capsule	Membrane
Ca^{2+}	85.4 a	62.0 c	69.0 b	72.0 b	96.2 a	83.2 c	85.0 c	94.2 b
Cu^{2+}	0.01 c	0.08 abc	0.09 a	0.04 b	0.03 b	0.08 a	0.07 a	0.02 c
Fe^{2+}	<0.1 c	7.7 abc	3.0 a	1.2 b	0.1 d	8.1 a	3.5 b	0.4 c
K^+	4.7 b	6.4 ab	8.7 a	2.7 c	0.9 c	1.9 b	3.9 a	0.7 c
Mg^{2+}	9.8 c	23.5 a	19.0 b	23.8 a	2.8 c	6.4 a	7.3 a	4.6 b
Mn^{2+}	0.1 b	0.3 a	0.1 b	0.2 a	0.05 b	0.17 a	0.13 ab	0.08 b
Zn^{2+}	0.01	0.08	0.12	0.09	0.01 c	0.06 a	0.05 a	0.03 b
HPO_4^{2-}	61.8 a	6.1 b	6.3 b	5.1 b	16.6 a	4.5 bc	7.7 b	4.2 c
SO_4^{2-}	38.2 b	93.9 a	93.7 a	94.9 a	83.4 c	95.5 ab	92.3 b	95.8 a

*Percentages were calculated without Na^+, NH_4^+, or NO_3^- data. Different letters in a row indicate significant ($P < 0.05$) differences among methods within each soil series.

DISCUSSION

Our results show that the four different extraction techniques are not comparable. Even a cursory comparison of nutrient rankings by their abundance reveals large differences among the methods (Table 3). Soil source affects this comparison, indicated by closer agreement of rankings among methods in Nakai series soils than in Sheppard series soils.

Methods varied not only in their net extraction of nutrients but in proportional extraction as well (Tables 1, 5, and 8), and soil source and/or experimental conditions also had an effect on extraction. For example, proportional HPO_4^{2-}-P was not different among methods in sand/nutrient solution (Table 1), but did show significant

differences among methods in both lab and field trials using CNP soils (Tables 4 and 7). Similarly, Zn^{2+} was not different among the methods in the field (Table 7) but was different among the methods in nonfield trials (Tables 1 and 4). Differences in equilibration time and in soil moisture (Yang et al., 1991a) probably contributed to the differences in laboratory and field results. Soil moisture in the field, never higher than 15.5% (in Nakai soils), was far less than that of the saturated pastes used in the temperature-controlled trials.

Exchange capacity (Bags > Capsules > Membranes) and ion affinities explain some of the patterns of net nutrient sorption among the resins as measured in μmol_c. Resin cation affinities occur in the order $Ca^{2+} > Mn^{2+} > Cu^{2+} >$

TABLE 9

Means (μmol_c resin^{-1}) and SE of nutrients sorbed by resins in field trials

Nutrient	Nakai series						Sheppard series					
	Bags		Caps		Memb		Bags		Caps		Memb	
	Mean	SE	Mean	SE	Mean	SE	Mean	SE	Mean	SE	Mean	SE
Ca^{2+}	132	31	79	9	361	72	135	10	106	20	958	35
Cu^{2+}	0.13	0.02	0.10	<0.01	0.17	<0.01	0.13	0.01	0.08	<0.01	0.19	0.01
Fe^{2+}	13.8	4.4	3.2	0.2	5.1	0.6	13.4	3.5	4.1	0.5	4.3	0.7
K^+	11.6	0.8	10.1	1.6	12.9	1.6	3.2	0.5	4.9	1.0	6.6	1.1
Mg^{2+}	51.4	13.2	21.4	2.4	121.8	26.8	10.6	1.3	9.2	1.7	46.9	3.9
Mn^{2+}	0.6	0.2	0.1	<0.1	1.1	0.1	0.3	<0.1	0.2	<0.1	0.8	0.1
Na^+	12.4	0.2	11.2	0.3			10.1	0.9	10.7	0.5		
NH_4^+	86.4	31.6	13.2	4.2	6.6	3.8	48.9	21.7	35.7	25.9	1.3	0.3
Zn^{2+}	0.1	0.03	0.1	0.04	0.4	0.06	0.1	0.01	0.1	0.02	0.3	0.02
NO_3^-	1.3	0.4	0.7	0.1	0.5	0.1	0.4	0.1	0.8	0.3	0.3	0.1
HPO_4^{2-}	0.8	0.1	0.2	<0.1	0.3	<0.1	0.4	<0.1	0.2	<0.1	0.3	<0.1
SO_4^{2-}	11.6	0.2	3.2	0.2	5.4	0.3	8.0	1.1	3.0	0.4	7.1	0.5

$Zn^{2+} \equiv Mg^{2+} > Fe^{2+} \geq K^+ > NH_4^+ > Na^+ > H^+$ (Skogley and Dobermann, 1996). In two of our experiments, higher affinity ions were sorbed in greater net amounts by nutrient membranes than the other two resin types: Ca^{2+}, Mg^{2+}, Mn^{2+}, and Zn^{2+} in the sand/nutrient solution trial (F = 74.8, 39.3, 40.4, and 408, respectively) (Table 1) and Ca^{2+}, Cu^{2+}, Mg^{2+}, Mn^{2+}, and Zn^{2+} in the field trial (F = 23.1, 33.5, 8.4, 25.0, and 21.0) (Table 9). We attribute the greater representation of these cations on membranes than on bags or capsules to their higher resin affinities, the lower exchange capacity of resin membranes, and sufficient duration for ionic affinities to differentiate. The low-affinity cations Fe^{2+} and NH_4^+-N were sorbed in the greatest quantities by resin bags (F > 3.5, Fe^{2+} and F > 6.9, NH_4^+) (Tables 6 and 9), where they should persist longer until replaced by higher affinity ions.

We observed an apparent relationship between Ca^{2+} and NH_4^+-N, whose sorption patterns among the three resin forms were opposite. In the sand/nutrient solution trial, Ca^{2+} constituted increasing proportions of total positive charge with decreasing exchange capacity (i.e., 12.4%, 15.3%, and 25.8% of the total positive charge of bags, capsules, and membranes, respectively) (Table 1). In the same experiment, NH_4^+-N represented decreasing proportions of the same (i.e., 15.1%, 4.6%, and 0.9% of bags, capsules, and membranes, respectively). Not only do the patterns of Ca^{2+} and NH_4^+-N sorption mirror each other in this trial, but their net differences in proportional representation between bags and membranes are approximately equal at 13% to 14%. The high resin affinity of Ca^{2+} (Skogley and Dobermann, 1996) is apparent in its high adsorption to resin membranes relative to their exchange capacity. Cation loading of exchange sites in bags and capsules probably had not approached capacity in the week-long equilibration, hence their lower representation of Ca^{2+}. NH_4^+-N is a cation of low resin affinity and its behavior among resin types can be explained by the same principle. Ca^{2+}-NH_4^+ trends were also opposite in both laboratory and field experiments with CNP soil except in Sheppard soils in laboratory experiments (Tables 5 and 8).

Nutrient sorption trends in nonfield analyses using CNP soils (Tables 4–6), however, cannot be universally explained using this argument of resin exchange capacity and ion affinities, probably due to insufficient equilibration duration (1 week) to allow ion affinities to become distinct. In this case, bags sorbed the greatest net amounts of most nutrients (Table 6). Our results are similar to the 16-h incubation of Saggar et al. (1990) and the 24-h incubation of Fernandes and Warren (1996), but contrast to Nuernberg et al. (1998), who found that resin bags and AEMs extracted roughly equivalent amounts of P from solution during incubations of 2 to 65 h.

Between soil series, only the trends of K^+ and Mg^{2+} were consistent among methods and experiments (Tables 2, 6, and 9), and resin-Ca^{2+} and -Na^+ trends between the two soils were contrary to those determined by chemical procedures. Ca^{2+} was higher in Nakai soils by chemical methods (F = 30.1, $P < 0.001$) (Table 2) and in Sheppard soils by resin methods (F = 4.5, lab; F = 13.0, field; Tables 6 and 9), a discrepancy of particular concern in this semiarid ecosystem that contains areas of exceptionally high soil Ca^{2+}. We suspect measurement error in the chemical extraction of Ca^{2+}. It is possible, for example, that the ammonium acetate extraction used to measure Ca^{2+} even at pH 8.5 (Normandin et al., 1998) dissolves some of the small particulate concretions of $CaCO_3$ that occur in finer-grained Nakai soils, resulting in an erroneously high estimate of exchangeable Ca^{2+}. This should be taken into account when considering NH_4OAc extraction of other carbonate-related nutrients, particularly in high-carbonate soils. In contrast, Na^+ by chemical methods was slightly higher in Sheppard soils (F = 4.7, $P = 0.06$) (Table 2) but higher in Nakai soils by resin extraction (F = 13.1, lab; F = 7.0, field) (Tables 6 and 9). This contradiction may be due to competitive displacement of low-affinity Na^+ by high-affinity and more abundant Ca^{2+} on resins in the Sheppard soils.

Our results generally show stimulation of ionic diffusion with higher equilibration temperatures, similar to the findings of Schaff and Skogley (1982), Skogley et al. (1990), and Yang et al. (1991b) with respect to Mn^{2+}, NH_4^+-N, SO_4^{2-}-S, and Zn^{2+} (Tables 4 and 6). An exception to this response is NO_3^--N (Tables 4 and 6), which showed greater adsorption at colder temperatures. This NO_3^--N response to cold temperatures corroborates Yang et al. (1991b) and Lundell (1989), and in these saturated soils could be due to increased denitrification with higher temperatures (Yang et al., 1991b). Temperatures over the 94-day field incubation approximately spanned the ranges tested in both cold and warm laboratory incubations, making it difficult to compare the effects of temperature in this experiment to those in the temperature-controlled experiment.

The lower temperatures and higher soil moisture of CNP during winter can result in higher CO_2 solubility and subsequent formation of carbonic acid ($CO_2 + H_2O \leftrightarrow H_2CO_3$) (Birkeland, 1984; Krauskopf and Bird, 1995). This in turn can affect the availability of $CaCO_3$-bound ions that typically peak during winter months (Schaff and Skogley, 1982; Lajtha, 1988; Lundell, 1989). Increasing formation of H_2CO_3 with decreasing temperature should account for some dissolution and increased sorption of carbonate-related ions such as Ca^{2+}, Mg^{2+}, Mn^{2+}, HPO_4^{2-}-P, and Zn^{2+} (Schaff and Skogley, 1982; Lundell, 1989), but this was not observed in this study. The sorption trends of Ca^{2+}, Mg^{2+}, and HPO_4^{2-}-P between temperatures were inconsistent and/or statistically insignificant among resins, and Mn^{2+} and Zn^{2+} were sorbed in greater quantities at higher temperatures (Tables 4 and 6). Lower carbonate solubilities and higher diffusion rates at high temperatures may counteract each other, yielding a lack of sensitivity to temperature, as Schaff and Skogley (1982) theorized with respect to Mg^{2+}. In contrast, it is possible that in an ecosystem with respiring roots and unrestricted gas exchange such as CNP, which supports wintertime growth, we would observe higher sorption of these ions at colder temperatures (e.g., Lundell, 1989).

As suggested above, multiple-element exchange with soil colloids and ion-exchange resins is saddled with interdependent dynamics (Curtin et al., 1987; Subler et al., 1995; Skogley and Dobermann, 1996) despite assertions to the contrary (Lajtha, 1988; Skogley et al., 1990; Yang et al., 1991a). In our soils, Ca^{2+} is by far the ion in greatest supply (Table 3) and, by virtue of its high affinity (Skogley and Dobermann, 1996), is an effective competitor for resin exchange sites. Resin membranes had significantly higher (Ca + Mg):K ratios than any other method in both field and laboratory trials, accounted for by Ca^{2+}-resin affinity and low membrane sorption capacity. This index of biological K^+ activity (Dobermann et al., 1995) is particularly important for biogeochemical measurements at CNP, where invasive species are associated with relatively high levels of exchangeable soil K^+ (Belnap and Phillips, 2001). Our comparisons of nutrient availability determined by different resin forms reinforce the proposition that sorption capacity and equilibration duration are interacting factors that need to be accounted for in experimental design.

While true that ion-exchange resins are dynamic nutrient exchangers (Christensen and Posner, 1980; Cooperband and Logan, 1994; Skogley

and Dobermann, 1996), sufficient duration of resin equilibration relative to its ion exchange capacity apparently allows ions of higher affinity to sorb preferentially to resin exchange sites. With respect to high-affinity ions, therefore, ion-exchange resins act as nutrient sinks (Lundell, 1989; Yang, 1991b). Different exchange capacities and ion affinities among resins should be taken into account in constructing research design and methods.

We also call attention to the possibility of inaccuracies of any extraction method measuring multiple nutrients, as demonstrated by comparisons between known amounts of nutrients added and those extracted (Table 1). If the goal is to represent plant-available nutrients in an ecosystem, it is advisable to identify which nutrients are of foremost interest and understand differences in their resin sorption dynamics, and to identify the appropriate resin-soil equilibration period, which will help determine the appropriate extraction method to employ. Resin bags, with their greater charge capacity, may create a diffusion gradient affecting strongly-sorbed nutrients such as Ca^{2+} and HPO_4^{2-}-P more than capsules or membranes (Saggar et al., 1990; Dobermann et al., 1995). In contrast, the larger exchange capacity of resin bags and capsules may simulate the strong nutrient sink created by a plant, but perhaps within a shorter equilibration time frame. Indeed, when used in the soils of plant communities, a small degree of nutrient competition may be expected between vegetation and ion-exchange resins, although this has not been observed to impede plant growth (Binkley, 1984; Lundell, 1989).

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