Comparison of Ion-Exchange Resin Counterions in the Nutrient Measurement of Calcareous Soils: Implications for Correlative Studies of Plant–Soil Relationships[#]

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ABSTRACT

For more than 40 years, ion-exchange resins have been used to characterize nutrient bioavailability in terrestrial and aquatic ecosystems. To date, however, no standardized methodology has been developed, particularly with respect to the counterions that initially occupy resin exchange sites. To determine whether different resin counterions yield different measures of

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soil nutrients and rank soils differently with respect to their measured nutrient bioavailability, we compared nutrient measurements by three common counterion combinations (HCl, HOH, and $NaHCO_3$). Five sandy calcareous soils were chosen to represent a range of soil characteristics at Canyonlands National Park, Utah, and resin capsules charged with the different counterions equilibrated in saturated pastes of these soils for one week. Data were converted to proportions of total ions of corresponding charge for ANOVA. Results from the different methods were not comparable with respect to any nutrient. Of eleven nutrients measured, all but iron (Fe^{2+}), manganese (Mn^{2+}), and zinc (Zn^{2+}) differed significantly ($p \leq 0.05$) as a function of soil $\times$ counterion interactions; Fe^{2+} and Zn^{2+} varied as functions of counterion alone. Of the counterion combinations, HCl-resins yielded the most net ion exchange with all measured nutrients except Na^+, $NH_4{}^+$, and $HPO_4{}^{2-}$, the three of which desorbed in the greatest quantities from HOH-resins. Conventional chemical extractions using ammonium acetate generally yielded high proportional values of Ca^{2+}, K^+, and Na^+. Further, among-soil rankings of nutrient bioavailability varied widely among methods. This study highlights the fact that various ion-exchange resin techniques for measuring soil nutrients may have differential effects on the soil-resin environment and yield data that should not be compared nor considered interchangeable. The most appropriate methods for characterizing soil-nutrient bioavailability depends on soil characteristics and likely on the physiological uptake mechanisms of plants or functional groups of interest. The effects of different extraction techniques on nutrient measures should be understood before selecting an extraction method. For example, in the calcareous soils used for this experiment, nutrient extraction methods that alter soil carbonates through dissolution or precipitation could compromise the accurate measurement of plant-available nutrients. The implications of this study emphasize the universal importance of understanding the differential effects of alternate methods on soil chemistry.

Key Words: Ion-exchange resins; Counterions; Calcareous soils; Nutrient extraction method.

INTRODUCTION

Measuring plant-available soil nutrients with sensitivity to variation in soil properties is an ongoing challenge. Chemical extractions are conventional for measuring nutrient bioavailability but ion-exchange resins, demonstrated to be effective measures of soil nutrients in both terrestrial and aquatic ecosystems,[1–3] may be preferable in some studies (see Skogley and Dobermann[4] for review). Chemical extraction provides a static measure of

potential nutrient supply,[5] in contrast to resins which, as ionic exchangers, represent an integration of bioavailable nutrient dynamics during a specified incubation period.[4,6,7] In addition, resins are sensitive to environmental conditions,[8,9] more efficient at measuring multiple soil nutrients than performing an equivalent number of chemical extractions,[10] inexpensive, and nondestructive with respect to soil chemistry and mineralogy.[7]

Resins have been compared to both soil colloids[4,7] and plant roots.[1,11,12] The acidification effect of resins with desorption of a H^+ counterion is similar to that of plant roots, although whether it occurs in comparable 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.[1,13] The dynamic colloidal effects of resins, however, are like that of soil. Hence, ion-exchange resins embody characteristics of both biological and mineral components of soil ecosystems.

Despite the application of ion-exchange resins for more than 40 years[14] and their general acceptance as a method for detection of soil nutrient levels, methods of resin use among researchers are not uniform and the interpretive differences among methods are poorly understood. The focus of this study is whether different resin counterions, which desorb from ion-exchange resins in exchange for nutrient ions of equivalent charge from the equilibrating solution, yield different nutrient measurement data. For example, different counterions have been identified as the best exchangers for solution P. These include bicarbonate (HCO_3^-)[15–17] OH^-[18–20] Cl^-,[6] and acetate (CH_3COO^-).[21] The soils used in the cited studies varied widely in their chemical, mineralogical, and physical characteristics, indicating that the best resin counterion for P exchange is a function of inherent soil properties.[15] For correlative ecological studies where among-soil variations in plant community composition are analyzed in relation to among-soil variations in soil nutrient bioavailability, it is critical to ascertain whether among-soil rankings of nutrient bioavailability are dependent on initial resin counterions.

We compared the results of soil nutrient measurements by three different resin counterion combinations in calcareous soils from the Canyonlands National Park (CNP), southeast Utah, USA. Carbonates are high in CNP soils (Table 1) and are sensitive to the changes in moisture, temperature, and pH[1,16,22] that can be induced by various extraction techniques. We included data from single measures (n = 1) of soil nutrients from conventional chemical extraction techniques. Although statistical tests with these data were precluded by the singular samples, it offers a useful comparison.

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Table 1. Soil characteristics of five sites from which soils were taken for resin counterion comparisons. Samples (n = 1) were taken from 0–10 cm depth. Soil group nomenclature is from the U.S.D.A. soil taxonomy. Data are from Miller.[23]

Site	Soil group	% sand	% silt	% clay	Texture class	Bulk density $(g\,cm^{-3})$	pH	EC $(dS\,m^{-1})$	Carbonates (% CaCO$_3$ equiv.)	CEC $(cmol_c\,kg^{-1})$	OM (%)
1	Mesic Ustollic Camborthid	77.3	17.0	5.7	Loamy sand	1.46	7.35	0.46	5.11	8.74	0.24
2	Mesic Typic Torripsamment	87.9	8.0	4.1	Sand	1.50	7.73	0.44	6.21	4.83	0.29
3	Mesic Typic Torripsamment	89.0	7.3	3.4	Sand	1.51	7.60	0.43	5.02	3.00	0.14
4	Mesic Ustollic Camborthid	82.2	12.8	5.0	Loamy sand	1.52	7.50	0.39	6.46	6.83	0.39
5	Mesic Ustollic Camborthid	79.8	15.0	5.2	Loamy sand	1.51	7.50	0.42	5.59	5.13	0.39

METHODS

Five sites representing a range of soil characteristics (Table 1) were selected for soil sampling in CNP ($\sim$ 1500 m a.s.l.), a cold semiarid ecosystem in eastern Utah averaging 214 mm annual precipitation and 11.6°C annual temperature.[23] Aggregate soil samples (0–10 cm) were collected from each site on 14 December 1999. At the Soil and Plant Analysis Laboratory (SPAL) at Brigham Young University (Provo, UT), soils were analyzed for ammonium acetate (NH_4OAc)-extractable calcium, potassium, magnesium, and sodium at pH 8.5 (Ca^{2+}, K^+, Mg^{2+}, and Na^+),[24] DTPA-extractable copper, iron, manganese, and zinc (Cu^{2+}, Fe^{2+}, Mn^{2+}, and Zn^{2+}),[25] KCl-extractable inorganic nitrogen (NH_4^+ and NO_3^-), and bicarbonate-extractable phosphorus (HPO_4^{2-}).[26] $N = 1$ for conventional chemical analysis.

Forty-five mixed-bed (bipolar) resin capsules (WECSA, Fort Collins, CO) originally charged with H^+ and OH^- ions were divided into three groups and charged with 0.5 M HCl, 0.5 M $NaHCO_3$, or nothing, in which case they remained charged with H^+ and OH^-. Capsules were ionically charged by shaking them in solution for 2 h with the solution replaced halfway through the shake period. Three replicates of resin capsules in each of the three ionic forms were equilibrated for 1 wk in saturated pastes[27] of the five soils. 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^+ and NO_3^- were determined by titration with H_2SO_4. Results were reported in μg capsule^{-1} and converted to μmol of charge capsule^{-1} (μmol$_c$).

Because the volume of soil subject to measurement by ion-exchange resins is unknown and each counterion combination extracts different quantities of ions, we converted all data to proportions of total ions of corresponding charge. For example, proportional NO_3^- was calculated as (μmol$_c$ NO_3^-)/(μmol$_c$ NO_3^- + μmol$_c$ HPO_4^{2-} + μmol$_c$ SO_4^{2-}). Sodium (Na^+) is over-represented on $NaHCO_3$-charged resins and sulfate (SO_4^{2-}) data were unavailable for chemical extractions; these were disregarded for proportional calculations. We arcsin-transformed proportional data and tested for differences in proportional nutrient representation among the resins charged with different counterions with multivariate ANOVA. No statistical comparisons between resin and chemical methods were made because there were no replicates of chemical extractions. All statistics were analyzed using SPSS Release 6.1.3. Unless otherwise stated, all significance refers to $p < 0.05$. To provide another, potentially clearer, way of interpreting the data, we constructed two rankings, one of CNP sites according to the nutrient quantities extracted by the different methods, and one of nutrients desorbed with each method.

RESULTS

Evaluating resin data only, all nutrients were extracted in significantly different proportions among different counterions (Table 2), and most showed significant interactions between counterion and site. There were significant differences among sites in the proportional representation of all nutrients except for Fe^{2+} and Zn^{2+}.

Among resins only, HCl-charged resins consistently extracted the greatest total amount of nutrient cations, even excluding Na^+ ($F = 390$, $p < 0.001$). HOH- and $NaHCO_3$-resins extracted decreasing amounts of cations (Table 3a–e). HCl-resins also extracted the greatest amounts of anions ($F = 178$, $p < 0.001$) with the exception of Sites 1 and 4, where there were no significant differences between anion extraction by HCl- and HOH-resins.

Patterns of net extraction of specific nutrients varied among resin forms. Mg^{2+}, Mn^{2+}, and SO_4^{2-} were extracted in the order HCl > HOH > $NaHCO_3$ at all sites ($F = 79.1$, 124, and 298, respectively; $p < 0.001$), as were Ca^{2+} and Cu^{2+} ($F = 318$ and 271; $p < 0.001$) except in Site 1 soils. Although differences were not always significant, K^+ and HPO_4^{2-} net

Table 2. F values of multivariate ANOVA comparing the proportional amount of nutrients extracted by resins with three counterion combinations from five different soil sources. All data were arcsin-transformed. Cation proportions were calculated excluding Na^+ data, which were unavailable for $NaHCO_3$ counterions. Chemical proportions were not included in this analysis because $N = 1$ for chemical extractions. $*p < 0.05$, $**p < 0.01$, $***p < 0.001$.

	Site	Counterions	Site × counterions
Ca^{2+}	134***	19.1***	2.5*
Cu^{2+}	19.5***	140***	2.6*
Fe^{2+}	1.5	30.7***	0.8
K^+	125***	64.6***	10.6***
Mg^{2+}	98.5***	25.0***	2.6*
Mn^{2+}	4.7**	92.6***	1.5
NH_4^+	37.3***	150***	14.0***
Zn^{2+}	0.8	20.6***	1.9
NO_3^-	18.5***	6.3**	4.6**
HPO_4^{2-}	7.6***	117***	2.8*
SO_4^{2-}	26.0***	54.7***	4.7**

Table 3. Mean, standard error (SE), and percent nutrients in CNP soils determined by chemical extraction and resin capsules charged with three different counterion combinations. Means are expressed in $\mu mol_c\,kg^{-1}$ for chemical extraction and $\mu mol_c\,capsule^{-1}$ for resin extraction. Percentages are relative to total positive or negative charge, disregarding Na^+ for cations and SO_4^{2-} data for anions. Different letters indicate significant differences ($p < 0.05$) among percentages for resin data only. $N = 3$ for resins. Dashes indicate that a value was not determined.

	Chemical		Resin capsule counterions											
			HCl				HOH				NaHCO₃			
Nutrient	Mean	%	Mean	SE	%		Mean	SE	%		Mean	SE	%	
a. Site 1														
Ca^{2+}	2940	86.1	1870	95.5	86.4	NS	923	96.4	82.3	NS	597	99.0	86.0	NS
Cu^{2+}	0.6	0.02	0.9	0.02	0.041	c	0.5	0.05	0.047	b	0.4	0.07	0.054	a
Fe^{2+}	1.3	<0.1	8.3	1.1	0.4	NS	4.2	0.7	0.4	NS	7.0	3.3	0.9	NS
K^+	324	9.5	35.6	13.6	1.7	b	46.0	2.6	4.1	a	25.5	1.0	3.8	ab
Mg^{2+}	138	4.0	204	19.4	9.5	NS	115	11.2	10.3	NS	56.3	7.6	8.2	NS
Mn^{2+}	2.8	0.1	36.3	6.6	1.7	a	20.7	2.0	1.9	a	4.0	2.6	0.5	b
Na^+	57.3	—	7.2	5.2	—		10.0	0.8	—		—	—	—	
NH_4^+	9.1	0.3	5.4	2.4	0.2	b	10.8	1.8	1.0	a	3.2	0.6	0.5	b
Zn^{2+}	0.2	0.01	0.3	0.02	0.01	b	0.2	0.01	0.02	b	0.2	0.02	0.03	a
NO_3^-	0.5	6.3	2.3	0.6	30.7	a	0.8	0.2	10.6	b	1.0	0.2	25.3	a
HPO_4^{2-}	6.7	93.7	5.0	0.6	69.3	b	6.6	0.8	89.4	a	2.9	0.5	74.7	b
SO_4^{2-}	—	—	12.7	0.3	—		8.6	0.8	—		5.3	0.7	—	
Total cations	3480		2160				1130				—			
Total anions	—		20.0				16.0				9.1			

(continued)

Table 3. Continued.

Nutrient	Chemical		Resin capsule counterions										
			HCl				HOH				NaHCO$_3$			
	Mean	%	Mean	SE	%		Mean	SE	%		Mean	SE	%	
b. Site 2														
Ca^{2+}	2520	90.7	1840	73.4	87.8	a	1130	60.5	86.0	b	525	5.7	86.8	ab
Cu^{2+}	0.3	0.01	0.8	0.03	0.040	c	0.6	0.02	0.043	b	0.3	0.01	0.048	a
Fe^{2+}	4.0	0.1	6.8	0.8	0.3	b	3.0	0.2	0.2	b	4.2	0.4	0.7	a
K$^+$	168	6.0	41.5	1.4	2.0	b	40.8	1.1	3.1	a	22.3	1.6	3.7	a
Mg^{2+}	76.1	2.7	174	8.7	8.3	a	107	6.4	8.1	a	44.8	1.8	7.4	b
Mn^{2+}	1.5	0.1	26.1	0.7	1.2	b	22.1	1.7	1.7	a	2.8	0.5	0.5	c
Na$^+$	52.9	—	3.4	0.8	—		11.1	0.6	—		—	—	—	
NH$_4^+$	9.7	0.3	6.3	0.1	0.3	b	11.4	1.1	0.9	a	5.2	0.3	0.9	a
Zn^{2+}	0.2	0.01	0.3	0.02	0.01	b	0.2	<0.01	0.01	b	0.2	0.01	0.03	a
NO$_3^-$	0.6	6.2	3.2	0.3	41.0	a	0.6	0.2	9.8	c	0.6	<0.1	20.0	b
HPO$_4^{2-}$	8.9	93.8	4.6	0.1	59.0	c	5.5	0.3	90.2	a	2.5	0.1	80.0	b
SO$_4^{2-}$	—	—	13.1	0.4	—		10.0	0.5	—		5.0	<0.1	—	
Total cations	2830		2100				1330				—			
Total anions	—		20.9				16.1				8.2			
c. Site 3														
Ca^{2+}	2500	93.3	2000	75.5	91.8	NS	1050	62.9	91.4	NS	434	13.5	92.0	NS
Cu^{2+}	0.3	0.01	0.8	0.02	0.036	b	0.5	0.03	0.043	a	0.2	0.01	0.048	a
Fe^{2+}	8.3	0.3	7.0	0.7	0.3	b	2.8	0.6	0.2	b	4.0	0.7	0.8	a
K$^+$	111	4.1	27.1	0.4	1.3	NS	15.6	2.1	1.4	NS	6.5	0.4	1.4	NS

Mg²⁺	50.7	1.9	110	4.0	5.0 a	54.6	4.1	4.7 b	21.5	0.7	4.6 b		
Mn²⁺	1.0	<0.1	26.0	1.6	1.2 a	15.3	1.9	1.3 a	1.8	0.5	0.4 b		
Na⁺	64.1	—	4.8	0.7	—	8.5	0.6	—	—	—	—		
NH₄⁺	8.8	0.3	8.2	0.1	0.4 b	10.0	1.2	0.9 a	3.7	0.6	0.8 a		
Zn²⁺	0.2	0.01	0.6	0.2	0.03 NS	0.2	0.02	0.01 NS	0.1	0.01	0.03 NS		
NO₃⁻	4.0	36.4	1.7	0.2	28.3 a	0.6	<0.1	12.6 b	0.5	<0.1	22.8 a		
HPO₄²⁻	7.1	63.6	4.2	<0.1	71.7 b	4.3	0.2	87.5 a	1.8	<0.1	77.2 b		
SO₄²⁻	—	—	13.0	0.5	—	8.7	0.3	—	3.7	0.1	—		
Total cations	2750		2180			1160			—				
Total anions	—		18.9			13.6			6.0				
d. Site 4													
Ca²⁺	2720	90.7	1810	156	87.1 a	1110	33.6	85.2 b	432	14.7	86.0 b		
Cu²⁺	0.4	0.01	0.8	0.05	0.041 c	0.6	0.01	0.047 b	0.3	0.02	0.059 a		
Fe²⁺	1.6	0.1	6.6	0.3	0.3 b	3.8	0.5	0.3 b	3.0	0.2	0.6 a		
K⁺	178	5.9	36.0	1.2	1.8 c	33.8	0.4	2.6 b	16.8	0.3	3.4 a		
Mg²⁺	89.7	3.0	186	20.0	8.9 a	116	3.5	8.9 a	38.2	1.5	7.6 b		
Mn²⁺	1.6	0.1	31.2	2.7	1.5 b	21.6	1.0	1.7 a	4.5	0.6	0.9 c		
Na⁺	50.2	—	2.0	0.2	—	10.3	1.0	—	—	—	—		
NH₄⁺	8.5	0.3	6.4	0.7	0.3 c	15.4	0.8	1.2 b	7.6	0.3	1.5 a		
Zn²⁺	0.2	0.01	0.3	0.02	0.01 b	0.2	0.03	0.02 ab	0.1	0.01	0.03 a		
NO₃⁻	4.3	40.1	2.5	0.1	34.4 a	2.5	0.3	25.7 b	1.3	<0.1	35.8 a		
HPO₄²⁻	6.5	59.9	4.7	0.1	65.6 b	7.2	0.3	74.1 a	2.4	0.1	64.2 b		
SO₄²⁻	—	—	12.4	0.9	—	9.9	0.3	—	4.2	0.2	—		
Total cations	3050		207			1310			—				
Total anions	—		19.6			19.6			7.9				

(continued)

Table 3. Continued.

	Chemical		Resin capsule counterions								
			HCl			HOH			NaHCO$_3$		
Nutrient	Mean	%	Mean	SE	%	Mean	SE	%	Mean	SE	%
e. Site 5											
Ca^{2+}	2700	90.2	1790	94.6	83.6 a	751	40.0	80.0 b	391	25.4	80.1 b
Cu^{2+}	0.4	0.01	0.9	0.03	0.041 c	0.5	0.02	0.050 b	0.3	0.01	0.055 a
Fe^{2+}	9.0	0.3	8.4	0.8	0.4 ab	2.7	0.1	0.3 b	2.8	0.1	0.6 a
K$^+$	189	6.3	80.2	1.5	3.8 b	68.9	1.6	7.4 ab	44.8	3.8	9.2 a
Mg^{2+}	86.3	2.9	215	12.9	10.0 a	83.3	6.3	8.9 b	36.9	2.4	7.6 c
Mn^{2+}	2.4	0.1	38.3	2.0	1.8 a	17.1	3.3	1.8 a	2.2	0.2	0.5 b
Na$^+$	51.7	—	10.4	0.2	—	11.9	0.3	—	—	—	—
NH$_4^+$	5.1	0.2	6.2	0.3	0.3 c	14.7	0.6	1.6 b	9.8	0.6	2.0 a
Zn^{2+}	0.2	0.01	0.3	0.01	0.014 c	0.2	<0.01	0.018 b	0.1	0.01	0.024 a
NO$_3^-$	0.3	3.4	2.7	0.3	36.0 NS	3.3	0.7	37.8 NS	1.7	0.3	40.4 NS
HPO$_4^{2-}$	9.0	96.6	4.7	<0.1	64.1 NS	5.3	0.4	62.2 NS	2.4	0.1	59.6 NS
SO$_4^{2-}$	—	—	13.0	0.7	—	7.9	0.1	—	4.4	0.2	—
Total cations	3040		2150			950			—		
Total anions	—		20.4			16.4			8.5		

averages were generally greater with H^+-resin extraction, the latter more with HOH- than HCl-resins. In soils from Sites 2–5, HCl-extracted Fe^{2+} was greater than that extracted with the other two forms (F = 21.0; $p < 0.001$) and HOH-extracted Na^+ exceeded HCl-extracted Na^+ (F = 14.5; $p < 0.001$). NH_4^+ was extracted in the greatest net quantities with HOH-resins in soils from Sites 2, 4, and 5 (F = 31.8; $p < 0.001$). NO_3^- patterns were inconsistent among sites, and no nutrient at any site desorbed in greatest net quantities from $NaHCO_3$-resins.

Relative to resin measurements, chemical extraction yielded high proportional K^+ except from Site 5 soils, and low Cu^{2+}, Mg^{2+}, and Mn^{2+} (Table 3a–e). Of all of the nutrients measured, chemical representation of proportional Ca^{2+} and Zn^{2+} was the most similar to the resin methods.

HCl-resins extracted proportionally more Cu^{2+} than chemical extraction, but less than the other resins. Except for soils from Site 3, HCl-resins extracted low proportional K^+. Except for soils from Site 5, HOH-resins extracted high proportional HPO_4^{2-} and low proportional NO_3^- relative to other resins. $NaHCO_3$-resins extracted relatively high proportions of Cu^{2+}, Fe^{2+} (except at Site 1), and Zn^{2+} (except at Site 3), and low Mn^{2+} relative to other resins. The representation of soil Na^+ on $NaHCO_3$-charged resins is unknown, but this cation represented an average of 1.8, 0.3, and 0.9 of all cations extracted by chemical means, HCl-resins, and HOH-resins, respectively.

Due to the relatively large number of nutrients compared among methods, we ranked nutrients in order of their net extraction within each site (Table 4) to offer a clearer picture of the data. All methods in all soils extracted Ca^{2+} in the greatest quantities (range 82.3–93.3%) and Zn^{2+} in the least (range 0.01–0.03%). K^+ was second-most abundant in all soils using chemical techniques (range 4.1–9.5%), and Mg^{2+} was second-most abundant in all resin analyses (range 4.6–10.3%) except by $NaHCO_3$-resins in Site 5 soils. Anions were extracted in the order $SO_4^{2-} > HPO_4^{2-} > NO_3^-$ by all analyses. As suggested by the proportional comparisons, and with the exception of $NaHCO_3$ extraction of Mn^{2+} from Site 5 soils, Mg^{2+} and Mn^{2+} ranked lower with chemical extraction (ranges 1.9–4.0%, Mg^{2+}; < 0.1–0.1, Mn^{2+}) than resin methods (ranges 4.6–10.3%, Mg^{2+}; 0.4–1.9, Mn^{2+}). In all soils, Fe^{2+} ranked relatively low with HOH-resin extraction, as did SO_4^{2-} except in Site 3 soils where the HOH-SO_4^{2-} ranking matched that of $NaHCO_3$. Similarly, in all soils, NH_4^+ ranked low with HCl-resin extraction, as did Na^+ except at Site 5 where HCl-Na^+ ranking matched that of HOH. Na^+ and HPO_4^{2-} ranked high with chemical extraction, except for HPO_4^{2-} in Site 3 soils. Mn^{2+} extraction ranked relatively high with both HCl- and HOH-resins.

We also ranked the CNP sites specific to nutrient and extraction method (Table 5) for greater clarity in interpreting the data. This ranking also shows

Table 4. Descending order of inorganic nutrients measured by chemical and resin extractions. Data are separated by site, indirectly accounting for site × counterion interactions. Ranks are based on µmol$_c$. Na$^+$ data for NaHCO$_3$-charged resins are disregarded and SO$_4^{2-}$ data for chemical extractions are unavailable.

Site	Method	Order of representation											
1	Chemical extraction	Ca	K	Mg	Na	NH$_4$	HPO$_4$	Mn	Fe	Cu	NO$_3$	Zn	
	Resin counterions:												
	HCl	Ca	Mg	Mn	K	SO$_4$	Fe	Na	NH$_4$	HPO$_4$	NO$_3$	Cu	Zn
	HOH	Ca	Mg	K	Mn	NH$_4$	Na	SO$_4$	HPO$_4$	Fe	NO$_3$	Cu	Zn
	NaHCO$_3$	Ca	Mg	K	Fe	SO$_4$	Mn	NH$_4$	HPO$_4$	NO$_3$	Cu	Zn	
2	Chemical extraction	Ca	K	Mg	Na	NH$_4$	HPO$_4$	Fe	Mn	Na	NO$_3$	Cu	Zn
	Resin counterions:												
	HCl	Ca	Mg	K	Mn	SO$_4$	Fe	NH$_4$	HPO$_4$	Na	NO$_3$	Cu	Zn
	HOH	Ca	Mg	K	Mn	NH$_4$	Na	SO$_4$	HPO$_4$	Fe	NO$_3$	Cu	Zn
	NaHCO$_3$	Ca	Mg	K	NH$_4$	SO$_4$	Fe	Mn	HPO$_4$	NO$_3$	Cu	Zn	
3	Chemical extraction	Ca	K	Na	Mg	NH$_4$	HPO$_4$	Fe	NO$_3$	Mn	Cu	Zn	
	Resin counterions:												
	HCl	Ca	Mg	K	Mn	SO$_4$	NH$_4$	Fe	Na	HPO$_4$	NO$_3$	Cu	Zn
	HOH	Ca	Mg	K	Mn	NH$_4$	SO$_4$	Na	HPO$_4$	Fe	NO$_3$	Cu	Zn
	NaHCO$_3$	Ca	Mg	K	Fe	NH$_4$	HPO$_4$	SO$_4$	Mn	NO$_3$	Cu	Zn	
4	Chemical extraction	Ca	K	Mg	Na	NH$_4$	HPO$_4$	NO$_3$	Fe ≡	Mn	Cu	Zn	
	Resin counterions:												
	HCl	Ca	Mg	K	Mn	SO$_4$	Fe	NH$_4$	HPO$_4$	NO$_3$	Cu	Zn	
	HOH	Ca	Mg	K	Mn	NH$_4$	Na	SO$_4$	HPO$_4$	Fe	NO$_3$	Cu	Zn
	NaHCO$_3$	Ca	Mg	K	NH$_4$	Mn	SO$_4$	Fe	HPO$_4$	NO$_3$	Cu	Zn	
5	Chemical extraction	Ca	K	Mg	Na	HPO$_4$ ≡ Fe	NH$_4$	Mn	Cu	NO$_3$	Zn		
	Resin counterions:												
	HCl	Ca	Mg	K	Mn	SO$_4$	Na	Fe	NH$_4$	HPO$_4$	NO$_3$	Cu	Zn
	HOH	Ca	Mg	K	Mn	NH$_4$	Na	SO$_4$	HPO$_4$	NO$_3$	Fe	Cu	Zn
	NaHCO$_3$	Ca	K	Mg	NH$_4$	SO$_4$	HPO$_4$	Mn	NO$_3$	Cu	Zn		

Table 5. Ranking of sites according to μmol$_c$ nutrients extracted by each method. A rank of 1 indicates that that site yielded the most nutrient quantity specific to the indicated method. Average deviations from the mean ranking are absolute (not standard). Na$^+$ data for NaHCO$_3$-charged resins are disregarded and SO$_4^{2-}$ data for chemical extractions are unavailable.

Nutrient	Method	Site 1	Site 2	Site 3	Site 4	Site 5	Sum
Ca^{2+}	Chemical	1	4	5	2	3	
	HCl	2	3	1	4	5	
	HOH	4	1	3	2	5	
	NaHCO$_3$	4	1	3	2	5	
	Avg. dev., resins only	0.89	0.89	0.89	0.89	0.00	3.56
	Avg. dev., all methods	1.25	1.25	1.00	0.75	0.75	5.00
Cu^{2+}	Chemical	1	3	3	2	2	
	HCl	1	2	2	2	1	
	HOH	2	1	2	1	2	
	NaHCO$_3$	1	2	3	2	2	
	Avg. dev., resins only	0.44	0.44	0.44	0.44	0.44	2.22
Na$^+$	Chemical	2	3	1	5	4	
	HCl	2	4	3	5	1	
	HOH	4	2	5	3	1	
	Avg. dev., resins only	1.00	1.00	1.00	1.00	0.00	4.00
	Avg. dev., all methods	0.89	0.67	1.33	0.89	1.33	5.11
NH$_4^+$	Chemical	2	1	3	4	5	
	HCl	5	3	1	2	4	
	HOH	4	3	5	1	2	
	NaHCO$_3$	5	3	4	2	1	
	Avg. dev., resins only	0.44	0.00	1.56	0.44	1.11	3.56

(continued)

Table 5. Continued.

Nutrient	Method	Rank (descending)					
		Site 1	Site 2	Site 3	Site 4	Site 5	Sum
	Avg. dev., all methods	0.38	0.50	0.50	0.38	0.38	2.13
Fe²⁺	Chemical	5	3	2	4	1	
	HCl	2	4	3	5	1	
	HOH	1	3	4	2	5	
	NaHCO₃	1	2	3	4	5	
	Avg. dev., resins only	0.44	0.67	0.44	1.11	1.78	4.44
	Avg. dev., all methods	1.38	0.50	0.50	0.88	2.00	5.25
K⁺	Chemical	1	4	5	3	2	
	HCl	4	2	5	3	1	
	HOH	2	3	5	4	1	
	NaHCO₃	2	3	5	4	1	
	Avg. dev., resins only	0.89	0.44	0.00	0.44	0.00	1.78

Method	Rank (descending)						Nutrient
	Site 1	Site 2	Site 3	Site 4	Site 5	Sum	
Avg. dev., all methods	1.00	0.75	1.25	0.88	1.50	5.38	
Chemical	1	1	1	1	1		Zn²⁺
HCl	2	2	1	2	2		
HOH	1	1	1	1	1		
NaHCO₃	1	1	2	2	2		
Avg. dev., resins only	0.44	0.44	0.44	0.44	0.44	2.22	
Avg. dev., all methods	0.38	0.38	0.38	0.50	0.50	2.13	
Chemical	4	3	2	1	5		NO₃⁻
HCl	4	1	5	3	2		
HOH	3	4	4	2	1		
NaHCO₃	3	4	5	2	1		
Avg. dev., resins only	0.44	1.33	0.44	0.44	0.44	3.11	

Mg²⁺

Method / Measure						
Avg. dev., all methods	0.88	0.50	0.00	0.50	0.38	2.25
Chemical	1	4	5	2	3	
HCl	2	4	5	3	1	
HOH	2	3	5	1	4	
NaHCO₃	1	2	5	3	4	
Avg. dev., resins only	0.44	0.67	0.00	0.89	1.33	3.33
Avg. dev., all methods	0.50	0.75	0.00	0.75	1.00	3.00

Mn²⁺

Method / Measure						
Chemical	1	4	5	3	2	
HCl	2	4	5	3	1	
HOH	3	1	5	2	4	
NaHCO₃	2	3	5	1	4	
Avg. dev., resins only	0.44	1.11	0.00	0.67	1.33	3.56
Avg. dev., all methods	0.50	1.0	0.00	0.75	1.25	3.50

$HPO_4{}^{2-}$

Method / Measure						
Avg. dev., all methods	0.50	1.00	1.00	0.50	1.38	4.38
Chemical	4	2	3	5	1	
HCl	1	3	4	2	2	
HOH	2	3	5	1	4	
NaHCO₃	1	2	4	3	3	
Avg. dev., resins only	0.44	0.44	0.44	0.67	0.67	2.67
Avg. dev., all methods	1.00	0.50	0.50	1.25	1.00	4.25

$SO_4{}^{2-}$

Method / Measure						
Chemical	3	1	2	4	2	
HCl	4	1	3	2	5	
HOH	1	2	5	4	3	
NaHCO₃						
Avg. dev., resins only	1.11	0.44	1.11	0.89	1.11	4.67

inconsistencies among methods. HOH- and NaHCO₃-resins appear to share the most similarities, but this agreement is not consistent among all nutrients. Chemical extraction of carbonate-related nutrients Ca^{2+}, Cu^{2+}, Mg^{2+}, and Mn^{2+} followed roughly similar patterns; K^+ also conformed to this among-site pattern. Importantly, in examining the most abundant nutrients (from Table 4), variation in the site ranking among methods is greater for carbonate-related Ca^{2+} and Mg^{2+} than for the non-carbonate related K^+ (Table 5).

DISCUSSION

Among five CNP soils, different nutrient extraction techniques yielded disparities in net quantities, ionic proportions, and abundance rankings of nutrients (Tables 2–5), indicating that the methods are not comparable. Importantly, which of the methods most closely represents actual plant-available nutrient levels is unknown and is certainly dependent on the characteristics of the local ecosystem. The soils used for this study were from Canyonlands National Park, a site with highly calcareous soils that are sensitive to fluctuations in moisture, temperature, and pH[1,16,22] that can be induced by various extraction techniques. The following discussion is in the context of the particular environmental conditions of CNP, but the implications of this study emphasize the universal importance of understanding the differential effects of alternate methods on soil chemistry.

H^+-containing resins, particularly HCl-resins, adsorbed more total soil cations and anions than did Na^+-containing resins (Table 3a–e). The especially low affinity of resins for $H^{+[4]}$ may explain the generally greater cation extraction with HCl- and HOH-resins, but it does not explain discrepancies in net nutrient sorption between HCl- and HOH-resins, found for Ca^{2+}, Cu^{2+}, Fe^{2+}, Mg^{2+}, Mn^{2+}, Na^+, HPO_4^{2-}, and SO_4^{2-}. Because the only difference between these two counterion combinations was the associated anion, different nutrient extraction patterns between HCl- and HOH-resins may be attributable to differences in Cl^- and OH^- dynamics.

Cl^- is less likely than OH^- to influence cation adsorption because OH^- has a greater capacity to affect pH and biogeochemical reactions. Many commonly used counterions, such as H^+, HCO_3^- and OH^-, can affect pH in the vicinity of the resins, which will in turn influence the solubility and/or soil release of certain elements.[1,4,7] In the pH range of the soils tested for this comparison (Table 1), resin release of OH^- induces more alkaline conditions in the resin environment and in turn should decrease the resin sorption of $HPO_4^{2-[7,28]}$ and other carbonate-related cations such as Ca^{2+}, Cu^{2+}, Mg^{2+}, and Mn^{2+}. There are counteracting processes in a mixed-bed system such as

ours, however, as simultaneous H^+ desorption can acidify the resin environment and actually promote the solubility of carbonate-related cations.[1] The pH buffer capacity of the soils used in this comparison (% $CaCO_3$ equiv. in Table 1) was not so high that it would preclude these reactions.[4] Because Cl^- does not have the same effect on solution pH as OH^-, we conclude that net acidification in the vicinity of the HCl-charged resin was largely responsible for greater solubility and subsequent adsorption of Ca^{2+}, Cu^{2+}, Fe^{2+}, Mg^{2+}, Mn^{2+}, and SO_4^{2-} from most of the soils by HCl-loaded resins. HOH-resin extraction of HPO_4^{2-} may be greater than HCl-resin extraction because resin affinity for Cl^- is greater than that for $OH^{-[4]}$ and OH^-/HPO_4^{2-} exchange is consequently easier. The reasons for greater extraction of Na^+ and NH_4^+ by HOH-resins remain unclear; one possibility is that HCl effected greater dissolution of $CaCO_3$ and the solubilized Ca^{2+}, which is a high-affinity ion,[4] competitively displaced Na^+ and NH_4^+ from HCl-resin exchange sites.

Resin counteranions could also affect cation adsorption in other ways. Exchange of HCO_3^-, for example, could result in precipitation of carbonate-associated ions[16] and reduce adsorption of Ca^{2+}, Cu^{2+}, Mg^{2+}, Mn^{2+}, HPO_4^{2-}, and Zn^{2+} on NaHCO3-resins. As a buffer, however, HCO_3^- desorption may also have the opposite effect and solubilize carbonates through a pH decrease, particularly in high-pH soils.[15] Desorption of OH^- from HOH-resins, via reactions with CO_2 ($\rightarrow HCO_3^-$), could have similar effects. This phenomenon could have indirect effects on other ions; for example, higher average HPO_4^{2-} sorption on HOH-resins could decrease that of SO_4^{2-}, as shown by their extraction data between HCl- and HOH-resins in all soils but those from Site 3 (Table 3a–e).

Because many of our field studies at CNP concern soil P status and dynamics,[23,29] this nutrient was of especial interest in these method comparisons. In all soils except for those from Site 5, our data show greatest proportional extraction of HPO_4^{2-} with OH^- (Table 3a–e), accountable by the greater resin affinity for Cl^- and HCO_3^- than for OH^-.[4,15] With the exception of Site 2 data, our results generally corroborate the anion-exchange resin bead studies of Bache and Ireland,[16] who found little difference between HCO_3^- and Cl^- as HPO_4^{2-} counteranions in a calcareous soil (pH 7.5), but are in contrast to the study of Sibbesen,[15] who found that HCO_3^- extracted more HPO_4^{2-} than Cl^-, also in a calcareous soil (pH 7.3).

We detected some consistent patterns among soils with respect to a method's preferential extraction of certain nutrients, such as proportionally lower extraction of Cu^{2+}, Mg^{2+}, and Mn^{2+} with chemical methods (Table 3a–e). Mg^{2+} was extracted with NH4OAc, which operates on the principle of cationic exchange between NH_4^+ and the target cations from soil exchange

sites. The theory that affinity for a soil exchange site occurs in the order $NH_4^+ > Na^+ \approx H^{+[30]}$ would predict higher proportional values of all nutrients extracted with NH_4OAc, i.e., Ca^{2+}, K^+, Mg^{2+}, and Na^+. Proportional Ca^{2+}, K^+, and Na^+ indeed were relatively high by chemical extraction in most soils (exceptions are Site 1 for Ca^{2+} and Site 5 for K^+), but proportional Mg^{2+} was noticeably lower (Table 3a–e), the reasons for which are unexplained. With respect to Ca^{2+}, it also is possible that the NH_4OAc extraction, even at pH 8.5,[24] dissolves some fine-grained $CaCO_3$ concretions, resulting in an erroneously high estimate of exchangeable Ca^{2+}. Either of these mechanisms should be taken into account when considering NH_4OAc extraction, particularly in high-carbonate soils.

Proportional Cu^{2+} and Mn^{2+}, also carbonate-related nutrients, were determined to be lower with chemical DTPA extraction, a procedure that also uses $CaCl_2$ to minimize the dissolution of carbonates.[31] In theory, the $CaCl_2$ may affect carbonate-related nutrients the least of the four options that we examined. The sensitivity of carbonates to biogeochemical alteration is difficult to gage with measures of Cu^{2+} and Mn^{2+}, however, as the opposing effects of carbonate dissolution by resin-H^+ and precipitation by resin-OH^- and resin-HCO_3^- are not evident in Table 3.

The inconsistent nutrient patterns among methods when compared from soil to soil (Table 3a–e) strongly suggest that the most appropriate method is specific to soil type. In calcareous soils such as CNP with substantial levels of carbonates and carbonate-related nutrients, we assert that a nutrient extraction technique that biogeochemically alters soil carbonates is inappropriate for measuring plant-available nutrients. Such alteration might occur with NH_4OAc- or H^+-induced dissolution of carbonates, or OH^- or HCO_3^--induced precipitation of the same. These analyses suggest that pH manipulation results in greater adsorption of several nutrients by HCl-resins, but that nutrient representation may also be affected by differing ion-resin affinities and interactions among ions. It is proposed that it is necessary to identify the nutrients of foremost interest to a study and to understand differences in their resin sorption and conventional chemical extraction dynamics in selecting a method of measurement. Studies of soil nutrient bioavailability should determine which method is most appropriate for particular soils and particular species or functional types.

Many extractions are conducted to determine the quantities of plant-available nutrients. It is difficult, however, to compare the ion affinities of resins with those of plant roots, to determine whether resin desorption of H^+ replicates that of plant roots, and whether this is in proportion to other ions sorbed. Because we do not know how accurately extraction methods represent biological uptake of any single nutrient, we also do not know the "best"

method to determine these quantities. Our study highlights the fact that various techniques for measuring soil nutrients with ion-exchange resins have differential effects on the soil-resin environment and yield data that should not be compared nor considered interchangeable. Studies of soil nutrient bioavailability should determine which methods are most appropriate for the particular soils, plant species and/or functional types of interest.

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