

## Repeated Use of Ion-Exchange Resin Membranes in Calcareous Soils

S. K. Sherrod,<sup>1</sup> J. Belnap,<sup>2,\*</sup> and M. E. Miller<sup>3</sup>

<sup>1</sup>University of Denver, Colorado

<sup>2</sup>U.S. Geological Survey, Forest and Rangeland Ecosystem Science  
Center, Canyonlands Field Station, Moab, Utah, USA

<sup>3</sup>National Park Service, Moab, Utah, USA

### ABSTRACT

This study compared the consistency of nutrient extraction among repeated cycles of ion-exchange resin membrane use. Two sandy calcareous soils and different equilibration temperatures were tested. No single nutrient retained consistent values from cycle to cycle in all treatments, although both soil source and temperature conferred some influence. It was concluded that the most conservative use of resin membranes is single-use.

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\*Correspondence: J. Belnap, U.S. Geological Survey, Forest and Rangeland Ecosystem Science Center, Canyonlands Field Station, 2290 S. West Resource Blvd., Moab, UT 84532, USA; E-mail: jayne\_belnap@usgs.gov.

## INTRODUCTION

Ion-exchange resins, used for over 40 years,<sup>[1]</sup> have been demonstrated to be effective measures of soil nutrients in both terrestrial and aquatic ecosystems.<sup>[2-4]</sup> Among different forms of ion-exchange resins such as bags, capsules, and membranes, only membranes are considered to be reusable because they do not have an encasing mesh like that of bags and capsules, which can trap soil particles and fine roots and result in questionable data.<sup>[5]</sup> However, it has also been stated that because ion desorption from resins is never complete,<sup>[6,7]</sup> no resins should be reused. The objective was to determine the integrity of data with repeated use of ion-exchange resin membranes. This study tested for differences in ion-exchange resin membrane performance in soils from two sources and at different equilibration temperatures.

## MATERIALS AND METHODS

Cation-exchange membranes (CEMs; CR 67, Dynambio, Madison, WI) were cut to 3.5 × 5 cm and charged with H<sup>+</sup> 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) were charged, also 3.5 × 5 cm, with OH<sup>-</sup> in the same manner using 0.5 M NaOH. Soils were collected from two sites within the Needles District of the Canyonlands National Park in southeast Utah (38.17°N, 109.98°W), an arid ecosystem averaging 214 mm annual precipitation (1965–1997) and 11.6°C.<sup>[8]</sup> Soils were Typic Calciorthiss from the Nakai series (“Nakai” soils) and Typic Torripsamments from the Sheppard series (“Sheppard” soils; USDA Soil Taxonomy). Soils were sieved (2 mm) and mixed with enough deionized (DI) water to make a saturated paste.<sup>[9]</sup> Within the saturated pastes of each soil type, we embedded 10 replicates of CEM–AEM pairs and covered the cups with plastic wrap. Five replicates of each soil were placed in a cold frame and five were placed in a seedling propagator room at the Denver Botanic Gardens (Denver, CO) for the cold and warm treatments, respectively (Table 1). Samples equilibrated for one week, at the end of which all membranes were removed, rinsed thoroughly with DI water, and stored at 0°C. At the Soil and Plant Analysis Laboratory at Brigham Young University, all ions were desorbed from resin membranes in 2 M HCl for 1 h and all but inorganic N were measured by inductively coupled plasma spectrometry. Ammonium (NH<sub>4</sub><sup>+</sup>) and nitrate (NO<sub>3</sub><sup>-</sup>) were determined by titration with H<sub>2</sub>SO<sub>4</sub>. Results were reported in μg membrane<sup>-1</sup> and converted to μmol<sub>c</sub> membrane<sup>-1</sup>.

**Table 1.** Equilibration temperatures for repeated resin membrane comparisons at either the Denver Botanic Gardens (DBG) or the University of Denver (DU).

Trial and month (2000)	Treatment	Location	Avg. max (°C)	Avg. min. (°C)
(1) February	Warm	Greenhouse, DBG	34	18
	Cold	Cold frame, DBG	23	-4
(2) July	Warm	Greenhouse, DU	33	21
	Cold	Refrigerator, DU	10	0
(3) September	Warm	Greenhouse, DU	31	19
	Cold	Refrigerator, DU	-2	-1

After desorption, membranes were recharged by the same methods that they were originally charged. The above methods were repeated twice more, for which the membranes were randomly placed in saturated pastes that varied by soil type and equilibration temperature (Table 1). Resins were not frozen in these latter two trials. Nutrients were extracted as described above.

The Na<sup>+</sup> was disregarded from the membrane data due to initial AEM charging with NaOH. Multivariate ANOVA was performed on nutrient data with trial, temperature, and soil source as factors. The nutrients were also ranked from most to least abundant as another means of comparison between cycles of membrane use.

## RESULTS

There were significant differences among trials and between equilibration temperature and soil source for most nutrients (Table 2). Interactions among factors were also apparent; for example, there were more significant differences overall between trials in Nakai soils equilibrating in cold temperatures than in warm temperatures (Table 3a), and the opposite was true for Sheppard soils (Table 3b).

In both soils, Ca<sup>2+</sup> and Mg<sup>2+</sup> retained comparable values among trials under cold conditions, but increased between Trials 2 and 3 under warm conditions (Table 3). Although differences were not always significant, average Cu<sup>2+</sup> values generally increased between Trials 1 and 2 and always significantly decreased between Trials 2 and 3. The only condition under which Mn<sup>2+</sup> showed significant differences was with warm equilibration in Sheppard soils. No nutrient retained comparable values when results from all treatments, trials, and soils were compared. There was also no pattern to

**Table 2.** F values of MANOVA comparing the amounts of nutrients extracted by ion-exchange resin membranes in repeated trials that varied by soil source and equilibration temperature.

Nutrient	Trial		Temperature		Soil Source		Trial X Temperature		Trial X Soil Source		Temperature X Soil Source		Trial X Temperature X Soil Source	
	F	p	F	p	F	p	F	p	F	p	F	p	F	p
Ca <sup>2+</sup>	11.2	***	26.3	***	56.3	***	21.0	***	0.5	0.2	0.1	0.2	4.5	*
Cu <sup>2+</sup>	73.8	***	0.1	***	0.2	***	1.4	***	6.2	**	2.4	4.5	2.1	*
Fe <sup>2+</sup>	89.9	***	82.1	***	3.3	***	7.6	**	32.4	***	11.4	2.1	11.4	***
K <sup>+</sup>	82.7	***	14.3	***	714.1	***	42.0	***	15.8	***	13.0	21.9	21.9	***
Mg <sup>2+</sup>	3.2	***	105.6	***	2538.2	***	20.0	***	1.7	***	7.3	34.3	34.3	***
Mn <sup>2+</sup>	17.2	***	129.3	***	4.1	*	18.7	***	5.9	**	7.2	0.2	0.2	**
NH <sub>4</sub> <sup>+</sup>	35.7	***	3.5	***	0.9	***	0.1	***	1.4	**	1.2	0.2	0.2	**
NO <sub>3</sub> <sup>-</sup>	7.2	**	49.7	***	21.9	***	0.6	***	0.1	0.1	0.8	5.8	5.8	*
HPO <sub>4</sub> <sup>2-</sup>	55.6	***	13.8	**	670.5	***	10.5	***	43.2	***	2.8	1.5	1.5	**
SO <sub>4</sub> <sup>2-</sup>	6.5	**	86.3	***	18.3	***	34.9	***	12.5	***	1.1	10.0	10.0	**
Zn <sup>2+</sup>	25.9	***	7.3	*	5.9	*	10.8	***	14.5	***	6.0	2.9	2.9	**

\**p* < 0.05, \*\**p* < 0.01, \*\*\**p* < 0.001.

**Table 3.** Mean and SE of nutrients desorbed from resin membranes in repeatability trials ( $\mu\text{mol}_c \text{ membrane}^{-1}$ ). Asterisks indicate significant differences between trials within temperature treatments.

Nutrient	Cold						Warm							
	Trial 1		Trial 2		Trial 3		Trial 1		Trial 2		Trial 3			
	Mean	SE	Mean	SE	Mean	SE	Mean	SE	Mean	SE	Mean	SE		
<b>(a) Nakai soils</b>														
Ca <sup>2+</sup>	931.2	19.6	899.6	29.3	869.6	44.0	925.5	21.4	952.7	16.6	**	1158.5	55.9	
Cu <sup>2+</sup>	0.12	<0.01	*	0.21	0.03	**	0.03	0.01	0.16	0.02	**	0.04	0.01	
Fe <sup>2+</sup>	3.9	0.5	3.2	0.3	***	1.0	0.1	7.4	0.5	**	3.3	0.6	1.9	0.2
K <sup>+</sup>	9.5	0.3	***	5.4	0.1	5.8	0.5	7.8	0.1	6.9	0.5	**	10.8	0.7
Mg <sup>2+</sup>	202.5	4.8	184.7	5.8	173.8	10.7	220.8	4.0	225.7	2.9	**	270.3	12.7	
Mn <sup>2+</sup>	0.9	0.1	0.9	0.1	1.1	0.1	5.8	0.1	3.5	0.9	1.3	0.4	0.4	
NH <sub>4</sub> <sup>+</sup>	6.6	0.6	***	1.5	0.6	**	4.4	0.3	3.5	1.2	5.3	1.0	5.3	1.0
NO <sub>3</sub> <sup>-</sup>	2.4	0.3	2.0	0.3	2.7	0.5	0.4	0.1	0.7	0.3	1.5	0.4	1.5	0.4
HPO <sub>4</sub> <sup>2-</sup>	2.2	0.1	*	1.7	0.1	***	0.8	0.1	1.7	0.1	*	1.3	0.1	
SO <sub>4</sub> <sup>2-</sup>	9.3	0.2	**	8.7	0.2	**	6.7	0.3	9.8	0.3	10.6	0.5	10.6	0.5
Zn <sup>2+</sup>	0.14	0.01	**	0.30	0.04	**	0.13	0.01	0.23	0.02	0.18	0.02	0.18	0.02
<b>(b) Sheppard soils</b>														
Ca <sup>2+</sup>	1096.1	55.3	1044.7	20.2	1039.9	34.0	1082.2	14.7	1057.2	34.9	**	1327.7	45.0	
Cu <sup>2+</sup>	0.13	0.01	0.13	0.01	0.05	0.01	0.12	0.01	0.17	0.01	***	0.08	0.01	
Fe <sup>2+</sup>	2.9	0.1	**	3.9	0.3	***	1.5	0.1	5.0	0.3	**	7.2	0.2	
K <sup>+</sup>	5.4	0.2	***	1.2	0.1	1.4	0.2	4.1	0.2	***	1.3	0.1	**	
Mg <sup>2+</sup>	48.6	2.7	43.0	1.5	39.4	3.2	54.1	0.8	55.1	0.6	**	64.5	1.9	
Mn <sup>2+</sup>	0.7	0.1	0.6	<0.1	0.6	0.1	3.1	0.1	4.3	0.1	***	1.6	0.5	
NH <sub>4</sub> <sup>+</sup>	7.5	0.7	**	3.2	1.0	3.6	0.8	8.5	0.2	***	2.9	0.8	4.9	0.6
NO <sub>3</sub> <sup>-</sup>	1.1	0.4	0.9	0.1	1.7	0.1	0.4	0.1	0.4	0.1	*	0.8	0.1	
HPO <sub>4</sub> <sup>2-</sup>	0.45	0.03	0.48	0.01	0.29	0.04	0.56	0.01	0.65	0.01	***	0.63	0.03	
SO <sub>4</sub> <sup>2-</sup>	8.8	0.4	*	7.8	0.1	7.7	0.2	8.7	0.1	**	8.0	0.1	***	
Zn <sup>2+</sup>	0.15	0.01	0.17	<0.01	0.13	0.01	0.26	0.02	0.19	0.01	**	0.13	0.01	

\**p* < 0.05, \*\**p* < 0.01, \*\*\**p* < 0.001.

**Table 4.** Descending order of inorganic nutrients measured by chemical and resin extractions. Ranks are based on  $\mu\text{mol}$ .

Soil	Temp.	Trial	Order of representation											
Nakai series	Cold	(1)	Ca	Mg	K	SO <sub>4</sub>	NH <sub>4</sub>	Fe	NO <sub>3</sub>	HPO <sub>4</sub>	Mn	Zn	Cu	
		(2)	Ca	Mg	SO <sub>4</sub>	K	Fe	NO <sub>3</sub>	HPO <sub>4</sub>	NH <sub>4</sub>	Mn	Zn	Cu	
		(3)	Ca	Mg	SO <sub>4</sub>	K	NH <sub>4</sub>	NO <sub>3</sub>	Fe	HPO <sub>4</sub>	HPO <sub>4</sub>	Zn	Cu	
	Warm	(1)	Ca	Mg	SO <sub>4</sub>	K	Fe	NH <sub>4</sub>	NH <sub>4</sub>	Mn	NO <sub>3</sub>	Zn	Cu	
		(2)	Ca	Mg	SO <sub>4</sub>	K	Mn	NH <sub>4</sub>	NH <sub>4</sub>	Fe	NO <sub>3</sub>	Zn	Cu	
		(3)	Ca	Mg	K	SO <sub>4</sub>	NH <sub>4</sub>	Fe	NO <sub>3</sub>	HPO <sub>4</sub>	Mn	Zn	Cu	
	Sheppard series	Cold	(1)	Ca	Mg	SO <sub>4</sub>	NH <sub>4</sub>	K	Fe	NO <sub>3</sub>	HPO <sub>4</sub>	HPO <sub>4</sub>	Zn	Cu
			(2)	Ca	Mg	SO <sub>4</sub>	Fe	NH <sub>4</sub>	K	NO <sub>3</sub>	Mn	HPO <sub>4</sub>	Zn	Cu
			(3)	Ca	Mg	SO <sub>4</sub>	NH <sub>4</sub>	NO <sub>3</sub>	Fe	K	Mn	HPO <sub>4</sub>	Zn	Cu
Warm		(1)	Ca	Mg	SO <sub>4</sub>	NH <sub>4</sub>	Fe	NH <sub>4</sub>	K	Mn	HPO <sub>4</sub>	Zn	Cu	
		(2)	Ca	Mg	SO <sub>4</sub>	Fe	Mn	NH <sub>4</sub>	NH <sub>4</sub>	K	NO <sub>3</sub>	Zn	Cu	
		(3)	Ca	Mg	SO <sub>4</sub>	NH <sub>4</sub>	Fe	Fe	K	Mn	HPO <sub>4</sub>	Zn	Cu	

nutrient values obtained from repeated use of the membranes. For example, extraction of some nutrients under some conditions increased with the 2<sup>nd</sup> use of the membrane and then decreased with the 3<sup>rd</sup> use ( $\text{Fe}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{SO}_4^{2-}$ ).

All cycles of membrane use in all treatments identified  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  as the first and second most abundant nutrients, respectively, and all identified  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  as the least abundant (Table 4). The  $\text{K}^+$  and  $\text{SO}_4^{2-}$  were alternately ranked as the 3<sup>rd</sup>- and 4<sup>th</sup>-most available nutrients in Nakai soils, while  $\text{SO}_4^{2-}$  was consistently identified as the 3<sup>rd</sup>-most abundant nutrient in all data from Sheppard soils. The variation in ranking of all the other nutrients was specific to soil source and equilibration temperature.

## DISCUSSION

Repeated use of ion-exchange membranes in these sandy calcareous soils resulted in inconsistent measures of all nutrients among cycles in at least one treatment (Table 3). Moreover, variation in the ranking of nutrients by abundance was detectable at levels of the 3<sup>rd</sup>-most abundant nutrient for Nakai soils and 4<sup>th</sup>-most abundant for Sheppard soils (Table 4). In contrast to our observations, the manufacturer of resin membranes claims that resins can be reused 5–20 times,<sup>[10]</sup> and other researchers have reused membranes between 3 and 500 times without any decline in performance.<sup>[5,11,12]</sup>

One methodological difference between trials was that resins were frozen after Trial 1, but not after Trials 2 or 3. This inconsistency could have affected results between the first two trials but does not account for differences between the second two. In fact, significant differences were more frequently shown between the 2<sup>nd</sup> and 3<sup>rd</sup> trials than between the first two (Table 3). Increases in resin adsorption between trials, such as observed with  $\text{Ca}^{2+}$  under warm conditions, could be due to ion buildup in resin interspaces that desorbed more effectively in subsequent elution steps (W. Jarrell, personal communication). Because our elution procedures were identical throughout, this seems improbable. Normal resin degradation could account for less effective sorption of other nutrients, but this was not expected after a single use. It was concluded that the most conservative use of resin membranes was single-use.

## ACKNOWLEDGMENTS

We would like to thank Robert (Buck) Sanford, Jr. for the use of his laboratory facilities and his review of this manuscript. We also thank Wes Jarrell, Earl Skogley, Gordon Warrington, and Sue Phillips for their

consultations. This work was funded by the Strategic Environmental Research and Development Program (Department of Defense).

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