

Differentiation of four northern Great Plains soils using resin extraction

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Olness, A., Weiser, H., Kunze, B., Lieser, M. and Rinke, J. 2004. **Differentiation of four northern Great Plains soils using resin extraction.** *Can. J. Soil Sci.* **84**: 31–42. Resin extraction of soils has revealed sensitivities of crops to the extractable V:(V + P) and Mg:(Mg + Ca) molar ratios. Consequently, we examined the Barnes and Buse soils in the northern Great Plains of North Dakota, South Dakota, and Minnesota. Svea and Langhei soils were included in the survey because of their close association. Samples of A or Ap horizons suspended in 20% ethanol were extracted with cation-(Na⁺) and anion-(NO₃⁻) exchange resin-extractors for a period of 5 d. After equilibration, extractors were eluted with 1 N HCl and eluates were analyzed using inductively coupled plasma-atomic emission spectroscopy. Analytical concentrations were log transformed and analyzed using SAS PROC GLM. Each soil produced a distinct suite of extractable ions. Mean pH values ranged from about 6.8 for the Svea soil to about 8.0 for the Langhei soils. Total resin extractable Ca ranged from about 150 to 28 000 nmol g⁻¹ soil and total resin extractable Mg ranged from 110 to 5500 nmol g⁻¹ soil; the least amounts were found in the Svea soil and the greatest amounts were found in the Langhei soil. The pH of the Barnes and Buse soils and the amounts of extractable Ca and Mg in the Barnes and Buse soils were intermediate to those of the Svea and Langhei soils. Trivial amounts of V were detected in extracts from a few samples of Buse soils. Large fractions of S, B, and As in the Langhei soil were extracted on cation exchange resins presumably due to complex formation with the much larger amounts of Ca and Mg. Amounts of Ba, Sr, Fe, Co, Cu, and Si, detected in the extracts differed between soils with more being extracted from the Langhei than from the other soils. Only resin extractable Li and K differed from the general trend in that the amounts associated with Langhei soils were among the least. Detectable amounts of Al, Ni, and Zn usually were obtained but without differences between soils. Resin extractable P was correlated with bicarbonate extractable P but slopes of the regression lines differed between soils and two groups of Barnes soils were clearly distinguished in these relationships.

Key words: Resin-extractable, nutrients, toxic elements, vanadium, sulfur, phosphorus

Olness, A., Weiser, H., Kunze, B., Lieser, M. et Rinke, J. 2004. **Différenciation de quatre sols du nord des grandes plaines par extraction à la résine.** *Can. J. Soil Sci.* **84**: 31–42. L'extraction à la résine révèle la sensibilité des cultures aux rapports molaires V:(V + P) et Mg:(Mg + Ca). C'est pourquoi les auteurs ont examiné les sols Barnes et Buse des grandes plaines du nord du Dakota Nord, du Dakota Sud et du Minnesota. Ils ont inclus les sols Svea et Langhei à l'étude en raison de leur étroite association aux sols précédents. Après suspension dans de l'éthanol à 20 %, les échantillons d'horizons A et Ap ont été traités avec un extracteur-résine échangeuse de cations (Na⁺) et d'anions (NO₃⁻) pendant cinq jours. Après équilibrage, ils ont dilué l'extracteur dans du HCl 1 N et analysé l'éluat au moyen de spectromètres par induction à plasma et à émissions atomiques. Ils ont ensuite établi la valeur logarithmique des concentrations relevées et analysé les résultats par SAS PROC GLM. Chaque sol produit une série distincte d'ions extractibles. Le pH moyen varie d'environ 6,8 pour le sol Svea à près de 8,0 pour les sols Langhei. La concentration totale de Ca extractible à la résine varie de 150 à 28 000 nanomoles par gramme de sol, contre 110 à 5 500 nanomoles pour le Mg. Les concentrations les plus faibles ont été observées dans le sol Svea et les plus fortes dans le sol Langhei. Le pH et la concentration de Ca et de Mg extractibles des sols Barnes et Buse se situent à mi-chemin de ceux des sols Svea et Langhei. On a dépisté une infime quantité de V dans quelques échantillons de sol Buse. Les résines échangeuses de cations ont permis l'extraction d'une grande quantité de S, de B et de As dans le sol Langhei, sans doute à cause de la formation de complexes avec le Ca et le Mg, en beaucoup plus grande concentration. La quantité de Ba, Sr, Fe, Co, Cu et Si extraite varie avec le sol, les sols Langhei en renfermant plus que les autres. Seuls le Li et le K extraits avec la résine s'écartent de la tendance générale en ce sens que leur concentration se situe parmi les plus faibles dans les sols Langhei. La concentration de Al, Ni et Zn est généralement décelable, mais ne permet pas de distinguer les sols. Quoique le P extractible à la résine soit corrélé au P extractible au bicarbonate, la pente de la fonction de régression varie avec le sol et a permis une nette identification de deux groupes de sols Barnes.

Mots clés: Extractible à la résine, oligoéléments, éléments toxiques, vanadium, soufre, phosphore

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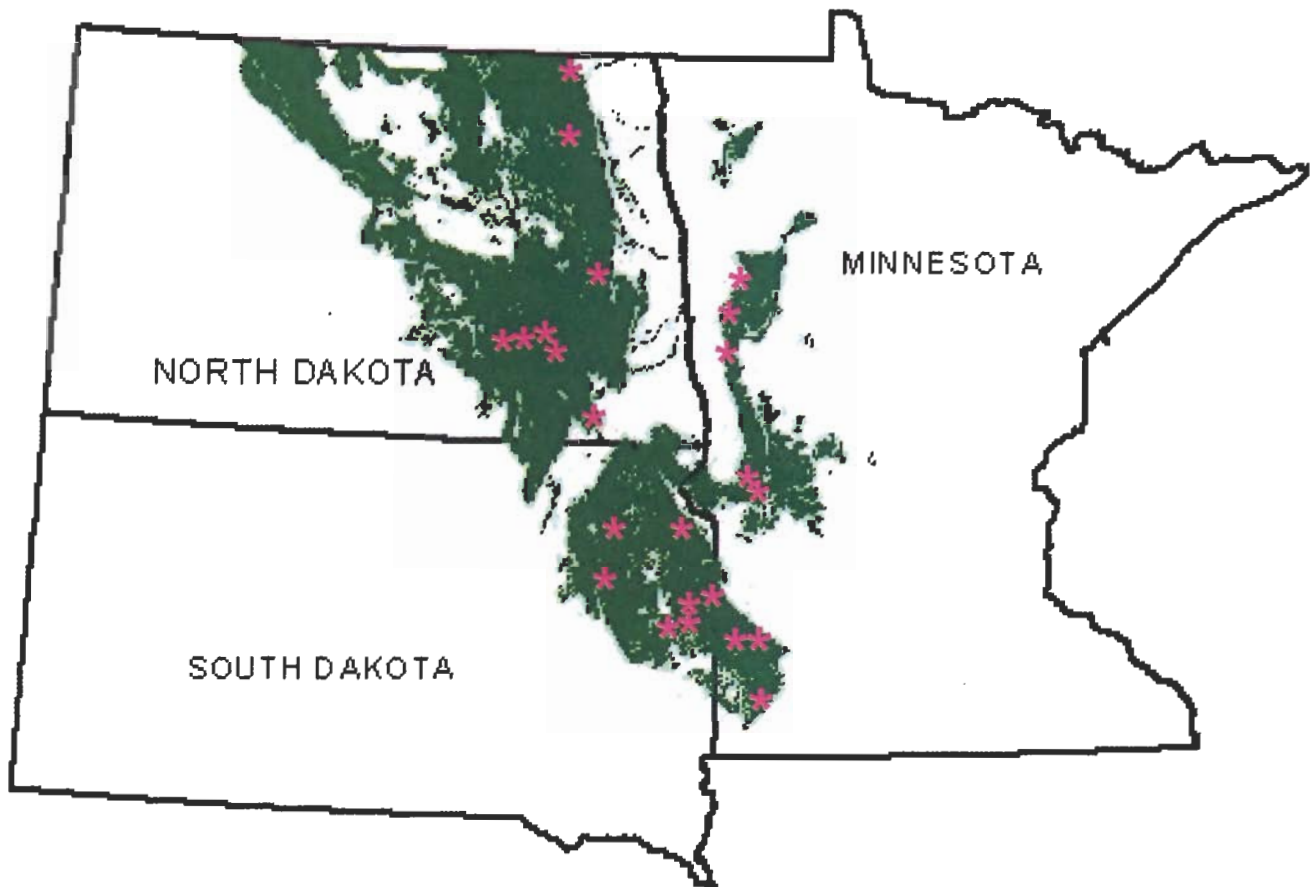


Fig. 1. The geographic extent of the Barnes and Buse soils in the Northern Great Plains. The * represents approximate locations at which samples were obtained.

Recently, Olness et al. (1999, 2000, 2001a, b) have shown differential sensitivity of maize (*Zea mays* L.) hybrids, soybean (*Glycine max* L.) and wheat (*Triticum aestivum* L.) varieties to resin extractable- (RE) V, K, and the V:(V + P) and Mg:(Mg + Ca) molar ratios in surface soils. These studies were conducted on the Barnes-Aasted Association's research farm at Morris, MN. Each soil provided a unique suite of RE elements. The Buse soil (fine-loamy, mixed, superactive, frigid Typic Calcudolls; Soil Survey Division 2001) had the largest RE-extractable V:(V + P), whereas the Barnes showed no evidence of extractable V. At the same time, the Barnes soil (fine-loamy, mixed, superactive, frigid Calcic Hapludolls; Soil Survey Division 2001) had the largest RE Mg:(Mg + Ca).

In the landscape, the Buse soil often lies immediately adjacent to the Barnes soil at the top of the topographic feature with convex slopes; they can occupy slope positions with up to 25% for the Barnes and 50% for the Buse (typically 5%). The Buse soils are located on convex shoulder positions, the Barnes soil on plane slopes, the Svea soil on concave foot slopes, and the Langhei soil on the steepest convex shoulders. The Langhei soil on less than 20 to 25% slopes is regarded as having formed from excessive water erosion of Buse soils on crop lands and formed naturally on slopes of greater than 20 to 25%.

Little has been observed regarding effects of V, a known inhibitor of plant growth, on agricultural production (Warington 1954, 1956; Singh 1971, Hara et al. 1976; Wallace et al. 1977). In the field study, RE-V (usually as VO_4^{3-}) was correlated with yield loss for wheat, soybean, and maize (Olness et al. 2000, 2001a; Olness 2001). Yield loss, apparently due to the RE-V:(V + P), resulted in as much as 20% of the yield potential, but varieties of soybean showed quite differing degrees of sensitivity to the presence of V. Soybean variety 9061 exhibited up to 20% yield loss compared with variety 9091, which showed only modest effects of V. At the same time, variety 9091 showed a 20% yield gain as the RE-Mg:(Mg + Ca) increased from about 0.17 to 0.8 (Olness et al. 2001b).

Results obtained for two maize hybrids also showed a differential response to the RE-Mg:(Mg + Ca) (Olness et al. 2002). Hybrid 2292 consistently showed a yield increase with increasing RE-Mg:(Mg + Ca). In contrast, hybrid 3895 seemed unresponsive to the RE-Mg:(Mg + Ca). Both hybrids were sensitive to RE-V and V:(V + P).

These observations led us to speculate on whether or not soil mapping could be used to predict potentially toxic levels of V and sites that might be responsive to changes in the RE-Mg:(Mg + Ca).

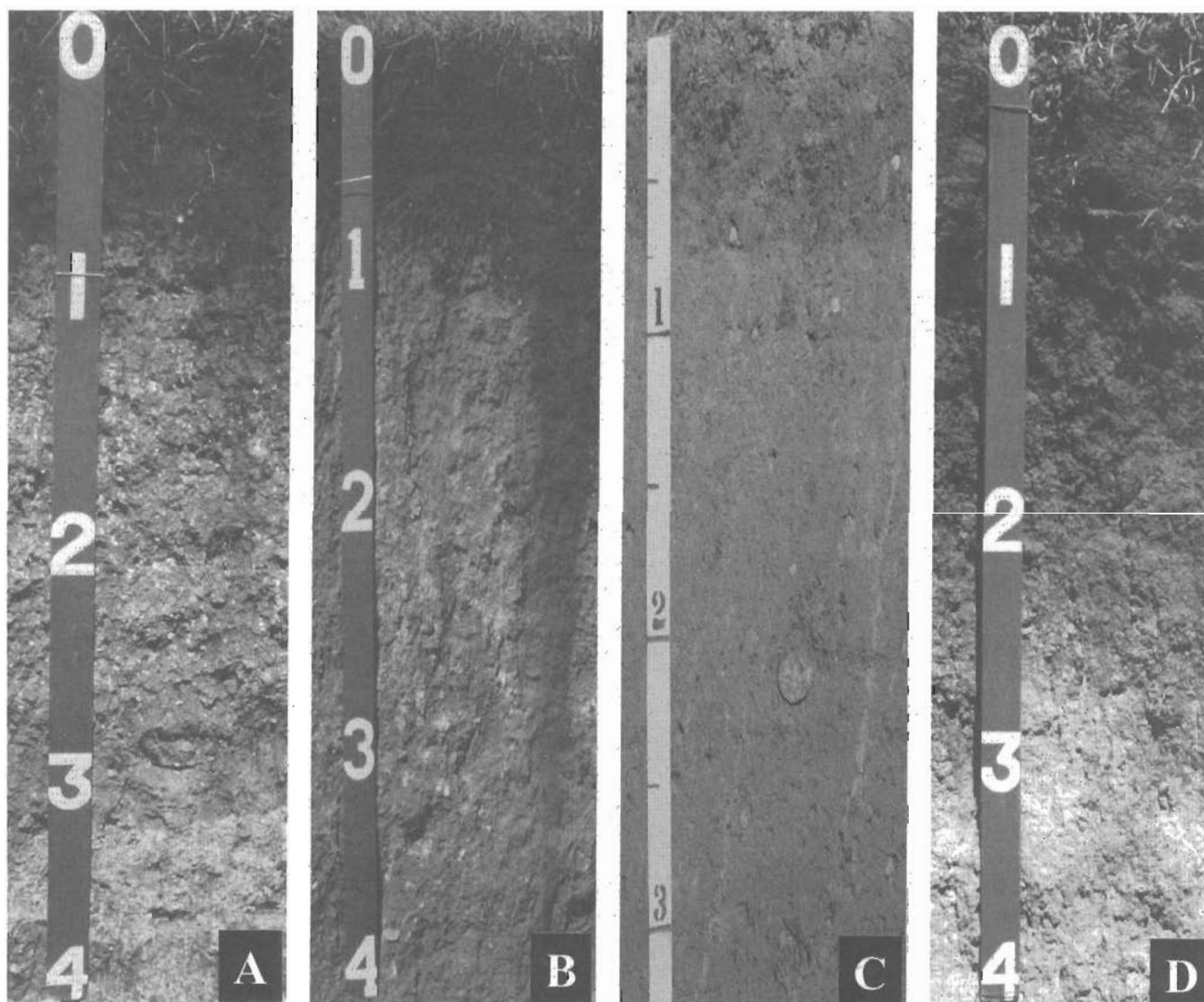


Fig. 2. Typical profiles of the Barnes (A), Buse (B), Langhei (C), and Svea soils (D)

MATERIALS AND METHODS

Twenty-three sites were selected within the mapped areas of the Barnes and Buse soils. Eight sites were selected in North Dakota and Minnesota and seven sites were selected in South Dakota (Fig. 1). In addition, either Langhei (fine-loamy, mixed, superactive, frigid Typic Eutrudepts) or Svea (fine-loamy, mixed, superactive, frigid Pachic Hapludolls) soils were sampled at most locations. The Langhei soils are located on convex slopes of 2 to 55% (14% typical) whereas Svea soils often occupy concave slope (< 2% typical) positions. Typical profiles of each soil are shown in Fig. 2.

At each site, five cores of each soil were collected usually to a depth of 60 cm, segmented by horizon, and each horizon was composited into a single sample at each site (Table 1). Soils were returned to the laboratory and dried (60°C), sieved (2-mm diam. mesh), and subsamples were crushed in a ceramic ball mill for chemical analyses. Soil samples (0.6 g) from A or Ap horizons were placed in a screw cap test tube with a teflon lined cap, 30 mL of 20% ethanol was

added, and a cation and an anion extractor (Olness and Rinke 1994) was inserted. Tubes were then secured in a plastic cylinder and placed on a rotary belt mixer, in a horizontal position, for 5 d at room temperature (about 25°C). Tubes were rotated at a rate of 12 times min^{-1} for 12 h each day. [At faster rates, the resin extractors are abraded by the soil particles. Although not researched, we believe that a slower rate (five rotations min^{-1}) would provide adequate mixing of the suspension.] After equilibration, samples were eluted with 10 mL of 0.1 N HNO_3 .

Resin extractors were prepared by washing IONAC® A-554, Cl^- type II (16–50 mesh) and Dowex® HCR-W2, H^+ form (16–40 mesh); Mallinckrodt J. T. Baker Inc., Phillipsburg, NJ) beads with water purified by reverse osmosis (Barnstead model EasyPure LF, Dubuque, Iowa). Resin beads were then washed first with 0.1 N HNO_3 and then with 0.1 N NH_4OH (J. T. Baker Ultrapure reagent) twice, rinsed with water and saturated using 50 mM NaNO_3 (Suprapure). The saturated beads were placed in resin extractors with 12 to 14 000 mole-

Table 1. Location and mean profile characteristics of collected soils

Site County	State	Soil A/Ap horizon depth (cm)		Status
1. Stevens	MN	Barnes	19.0 ± 2.85	Cropped
		Buse	18.3 ± 2.74	Cropped
		Langhei	16.0 ± 2.85	Cropped
2. Pope	MN	Barnes	28.5 ± 7.42	Cropped
		Buse	19.5 ± 4.00	Cropped
		Langhei	14.8 ± 2.40	Cropped
3. Ottertail	MN	Barnes	15.8 ± 1.68	Cropped
		Buse	15.5 ± 3.71	Cropped
		Langhei	17.5 ± 1.53	Cropped
4. Clay	MN	Barnes	14.5 ± 1.12	Cropped
		Buse	13.5 ± 2.85	Cropped
		Langhei	12.3 ± 2.56	Cropped
5. Mahnomen	MN	Barnes	18.0 ± 4.73	Cropped
		Buse	16.6 ± 3.00	Cropped
		Langhei	12.0 ± 3.26	Cropped
6. Cavalier	ND	Barnes	13.9 ± 2.18	Cropped
		Buse	11.0 ± 5.03	Cropped
		Langhei	8.3 ± 3.01	Cropped
7. Ramsey	ND	Barnes	13.3 ± 3.01	Cropped
		Buse	15.0 ± 1.77	Cropped
8. Stutsman	ND	Barnes	14.8 ± 1.85	Conservation Reserve Program
		Buse	16.8 ± 4.64	Conservation Reserve Program
		Langhei	14.5 ± 1.90	Conservation Reserve Program
9. Stutsman	ND	Barnes	10.0 ± 1.25	Permanent Pasture
		Buse	10.0 ± 2.93	Permanent Pasture
10. Barnes	ND	Barnes	15.5 ± 1.12	Cropped
		Buse	13.0 ± 2.09	Cropped
11. Dickey	ND	Barnes	14.8 ± 3.89	Cropped
		Buse	12.5 ± 2.50	Cropped
12. Steele	ND	Barnes	14.8 ± 1.85	Cropped
		Buse	13.5 ± 2.05	Cropped
		Langhei	16.0 ± 1.63	Cropped
13. Barnes	ND	Barnes	17.8 ± 3.11	Cropped
		Buse	14.3 ± 2.09	Cropped
14. Brookings	SD	Barnes	12.8 ± 1.49	Grass (previously tilled)
		Buse	12.5 ± 2.50	Grass (previously tilled)
		Svea ^z	15.0	Grass (previously tilled)
15. Kingsbury	SD	Barnes	11.8 ± 2.27	Cropped
		Buse	12.3 ± 2.05	Cropped
		Svea ^z	15.0	Cropped
16. Hamlin	SD	Barnes	15.0 ± 0.00	Cropped Alfalfa
		Buse	15.0 ± 0.00	Cropped Alfalfa
		Svea ^z	15.0	Cropped Alfalfa
17. Clark	SD	Barnes	14.3 ± 1.68	Conservation Reserve Program
		Buse	15.0 ± 1.77	Conservation Reserve Program
		Svea ^z	15.0	Conservation Reserve Program
18. Deuel	SD	Barnes	13.5 ± 1.37	Grassland
		Buse	14.5 ± 2.09	Grassland
		Svea ^z	15.0	Grassland

Table 1. Continued

Site County	State	Soil A/Ap horizon depth (cm)		Status
19. Day	SD	Barnes	16.3 ± 2.50	Grassland
		Buse	15.3 ± 2.85	Grassland
		Svea	15.0	Grassland
20. Roberts	SD	Barnes	13.8 ± 1.77	Grassland
		Buse	12.5 ± 2.93	Grassland
		Svea	15.0	Grassland
21. Lincoln	MN	Barnes	14.3 ± 1.68	Grassland
		Buse	13.1 ± 2.80	Grassland
22. Lyon	MN	Barnes	13.5 ± 3.79	Grassland
		Buse	13.0 ± 1.90	Grassland
23 Murray	MN	Barnes	21.3 ± 1.53	Grassland
		Buse	15.8 ± 3.91	Grassland

^aThe A/Ap horizons of Svea soils were ≥ 30 cm. Only the surface 15-cm increment was used to characterize resin extractable elements.

cular weight cut off Spectra/Por[®] dialysis membrane (Spectrum Laboratories, Inc., Rancho Dominguez, CA). Care was taken to insure that the beads contacted only Pyrex glass, polyvinyl chloride plastic, or Teflon throughout all manipulations and that the dialysis membrane was maintained moist during extractor preparation.

The 20% ethanol solution was used to inhibit microbial respiration during the extraction, and no evidence of inhibition or interference with the extraction was noted. Extracts were analyzed by inductively coupled plasma-atomic emission spectroscopy at the analytical research laboratory of the University of Minnesota at St. Paul. Detection limits (mg L^{-1}) were Al = 0.18, As = 0.036, B = 0.023, Ba = < 0.08, Ca = < 0.5, Cd = 0.006, Co = 0.012, Cr = 0.014, Cu = 0.026, Fe = 0.017, K = 0.707, Li = 0.02, Mg = 0.19, Mn = 0.003, Mo = 0.011, Ni = 0.022, P = 0.35, Pb = 0.084, Rb = 2.65, S = < 0.1, Si = 0.084, Sr = 0.003, Ti = 0.015, V = 0.018, and Zn = < 0.05. Data were logarithmically transformed to obtain normal distributions and then analyzed using SAS PROC GLM and ANOVA procedures (SAS Institute, Inc. 1989).

Particle size analyses were conducted using the Bouyoucos hydrometer method (Gee and Bauder 2002) without peroxide oxidation. Extractable P was determined after extraction with sodium bicarbonate (Kuo 1996) and K was determined after extraction with ammonium acetate (Helmke and Sparks 1996). Total carbon was determined through ignition and infrared detection using a LECO CN2000 furnace (LECO 1994a, b). Inorganic carbon was determined using the modified pressure calcimeter method of Wagner et al. (1998). Soil pH values were determined on a 2:1 soil water paste (Thomas 1996).

RESULTS AND DISCUSSION

Soil Characterizations

Each soil generally was distinguished by the pH of A or Ap horizons (Table 2). The Svea soils are considered productive soils and had pH values about 6.76 ± 0.64 ; this is near optimal for maximal microbial activity and nitrate production (Olness

1999). The Barnes soils had pH values of 7.33 ± 0.47 ; this soil is widely cultivated over the region. The Buse soils contained free carbonate at the surface and had pH values of 7.75 ± 0.26 . The Langhei soil, considered the least productive of these four soils, was rich in carbonates and had pH values of 8.03 ± 0.24 . Because of their relative landscape positions, the Langhei and Buse soils retain less rainfall on average; this is a major factor in relative productivity. Cultivation occasionally mixes the A-horizon with some calcareous subsoil and this probably has resulted in an increased variance in measured characteristics of the surface horizons on these sites.

Conventional soil test methods show that all four soils were relatively rich in extractable K and P (Table 2). Extractable K averaged about $250 \mu\text{g g}^{-1}$ and K additions for crop production would usually not be recommended. Likewise, the extractable P levels were quite high, averaging about $20 \mu\text{g g}^{-1}$, and fertilizer-P additions would be recommended for less than 25% of the sites. The rank order for extractable P was Svea ($24.9 \mu\text{g g}^{-1}$) \geq Barnes ($22.3 \mu\text{g g}^{-1}$) \geq Buse ($19.2 \mu\text{g g}^{-1}$) \geq Langhei ($14.1 \mu\text{g g}^{-1}$).

Total carbon was very similar in all soils, and ranged from $2.90 \pm 0.91\%$ in the Barnes soils to $3.56 \pm 1.23\%$ in the Svea soils (Table 2). Carbon in Svea and Barnes is organic as these soils contained only traces of carbonate carbon. By comparison, about 75% of the carbon in the Buse soil is organic ($2.49 \pm 1.22\%$) and the rest ($0.86 \pm 0.63\%$) is carbonate carbon. Only about 32% of the carbon in the Langhei soil is organic ($1.06 \pm 0.45\%$); the rest ($2.23 \pm 0.63\%$) is carbonate carbon. Consequently, the Langhei soil is likely to retain the least amount of water available for plant growth.

All soil types are loams (Table 2) and each of the soils has a similar amount of silt. Thus, conventional methods of analysis suggest very little potential ameliorative activities or management alternatives. Tillage and erosion may shift mean values slightly but they seem to have had little impact on soil texture.

Resin Extraction Characteristics

Arsenic, Boron, Sulfur, and Phosphorus

The bulk of the arsenic, boron, sulfur, and phosphorus oxyanions in the Svea and Barnes soils are mostly extracted

Table 2. Selected chemical characteristics of A/Ap horizons of Barnes, Buse, Langhei, and Svea soils

Soil	n		pH	Extractable		Carbon			Texture		
				P	K	Total	Inorganic	Organic	Sand	Silt	Clay
				(µg g ⁻¹)		(%)					
Svea	7	Min.	5.96	16	118	1.66	0.01	1.64	35.7	13.9	24.7
		Mean	6.76 ^c	25 ^a	248	3.51	0.05	3.51 ^a	42.2	18.6	34.9
		Median	6.77	23	182	3.60	0.01	3.59	43.1	19.8	37.3
		Max.	7.74	37	547	5.20	0.24	5.18	59.1	23.8	42.8
		Std. Dev.	0.64	8	151	1.23	0.08	1.27	7.1	3.4	5.9
Barnes	23	Min.	6.57	12	133	1.54	0.00	1.25	37.5	14.7	25.6
		Mean	7.33 ^b	22 ^{ab}	275	2.90	0.13	2.77 ^a	48.3	21.8	29.9
		Median	7.37	21	229	2.71	0.05	2.57	49.2	21.4	29.4
		Max.	8.08	41	579	4.38	0.73	4.37	58.2	33.0	37.6
		Std. Dev.	0.47	7	126	0.91	0.19	1.01	5.4	3.7	3.3
Buse	22	Min.	7.14	11	118	1.54	0.06	0.96	38.7	15.4	20.0
		Mean	7.75 ^a	19 ^{bc}	284	3.36	0.86	2.49 ^a	48.7	21.9	29.4
		Median	7.79	16	243	3.02	0.58	2.10	47.9	22.3	28.7
		Max.	8.13	39	636	5.13	2.20	4.64	58.9	32.5	39.5
		Std. Dev.	0.26	7	153	0.91	0.63	1.22	5.2	3.9	5.1
Langhei	8	Min.	7.55	9	126	2.44	1.54	0.41	35.3	18.3	23.6
		Mean	8.03 ^a	14 ^c	192	3.30	2.23	1.06 ^b	48.7	24.3	27.0
		Median	8.03	14	167	3.25	2.23	1.15	50.9	23.6	26.7
		Max.	8.40	20	377	4.03	3.26	1.69	52.4	32.0	32.6
		Std. Dev.	0.24	4	85	0.51	0.63	0.45	6.0	4.1	3.2

a–c Within columns, mean values followed by different letters are significantly different ($P > 0.05$).

by anion exchange resin (Table 3). However, about 60% of the boron and sulfur and over 90% of the arsenic in the Buse soil were extracted on the cation exchange resins. For the Langhei soils, > 83% of the boron and 99% of the sulfur appear on the cation exchange resins. Variance in amounts of extracted phosphate on the cation exchange resins was too great to distinguish differences and usually > 99% of the phosphate was extracted on the anion exchange resins (Table 3).

The appearance of boron and sulfur on cation exchange resins suggests that large fractions of these elements were extracted from Langhei and Buse soils as cationic complexes. Even arsenic, which was not extracted in large amounts from the Buse soils, appears to be complexed as well.

In terms of total amounts, the Langhei soils had the largest amounts of boron and sulfur and the least amounts of total extractable phosphorus. The Buse soils have the least amounts of extractable total sulfur and the largest amounts of extractable arsenic. At 2.6 nmols g⁻¹, extracts from the Buse soil contained only about 5 to 10% as much sulfur as was contained in extracts from the other soils.

Resin extraction has often provided close correlation of extracted amounts (concentrations) with plant response. In several instances, these relationships were superior to those of conventional methods (for example Møller and Morgensen 1953; Amer et al. 1955; Salomon and Smith 1957; Arnold 1958; Moser et al. 1959; Semb et al. 1959; Walmsley and Cornforth 1973; Sibbesen 1977; Adepoju et al. 1982; van Raij et al. 1986; Skogley et al. 1990). Assuming that resin extractions are proportional to the available amounts of these elements in the soil, we might expect economic returns to S applications on Buse soils. Bly

et al. (2001) recently observed responses to S fertilization of maize in the region.

Because we believe that this is the first observation of apparent measurable complexation of elements in a field study, we are unprepared to comment on the effect that complex formation may have on availability of B and S in the Langhei soil. However, if complexation limits their availability for plant growth, then it would seem that band applications, which effect much greater concentrations in a small soil volume, might be beneficial for crop production.

The extractions conducted were not exhaustive; the method is designed to extract only about 10% of the total available/extractable ions. This characteristic is shared to some degree by all resin extraction methods because both the soil and resin are competing sinks; in some cases, the resin sink has been relatively large. We would expect that correlation with plant response might be affected when the resin sink becomes saturated.

Some recent attempts to assess soil fertility with mixed bed resins have shown quite a bit of potential for their use (van Raij et al. 1986; Reith et al. 1987; Qian et al. 1992). Mixed bed resins provide estimates of total resin-extractable amounts; here, they would have been unable to identify the apparent complex formation effects.

Lithium, Potassium, Magnesium, and Calcium

Lithium is commonly found in northern prairie soils and it appears exclusively on cation exchange resins (Table 4). It is the lightest element and competes poorly for exchange sites. There were marked differences in RE-Li between the soils. Both Barnes and Svea soils, which are leached, contained the largest amounts of RE-Li. The Langhei soil, which shows lit-

Table 3. Anions extracted using anion- and cation-exchange resins from A/Ap horizons of Svea, Barnes, Buse, and Langhei soils

Soil	Arsenic		Boron		Sulfur		Phosphorus	
	Anion	Cation	Anion	Cation	Anion	Cation	Anion	Cation
Svea	0.005	0.001 ^b	0.184 ^b	0.000 ^d	24.00 ^a	0.00 ^c	57 ^a	0.40
Barnes	0.002	0.008 ^b	0.287 ^a	0.131 ^c	15.00 ^a	0.38 ^c	77 ^a	0.42
Buse	0.004	0.054 ^a	0.391 ^a	0.455 ^b	1.00 ^b	1.60 ^b	32 ^b	0.94
Langhei	0.008	0.000 ^b	0.469 ^a	2.349 ^a	0.23 ^c	33.00 ^a	11 ^c	4.30

a–d Within columns, values followed by the same letter are not significantly different ($P < 0.05$).

the evidence of leaching, contained very little RE-Li; this result is a little surprising as we expected proportionately at least as much Li in unleached as in leached soils. The ability to detect Li points to the sensitivity of the method.

The Buse soils were richest in RE-K and mean amounts appear to be near optimal for wheat production (Olness 2001). If previous observations indicate a potential toxicity to excess K (Olness 2001), then nearly half of the Buse soils would have excessive amounts of K and this condition has no known means of mitigation. The Barnes soils contain relatively large amounts of RE-K and a few may have excessive amounts. By comparison, the Langhei and Svea soils seem moderately deficient in having only 421 and 459 nmol g⁻¹ of RE-K, respectively.

These soils are typical prairie soils in that they are relatively rich in Mg and Ca. Each had measurably different amounts of extractable Mg and the rank was Langhei > Buse > Barnes > Svea. The Buse and Langhei soils averaged about 10-fold more RE-Mg than the Barnes and Svea soils; this is a very large difference for soils that lie immediately adjacent to each other. Also, while traces of cations appear on the anion exchange resins, more than 99% of the total for each cation was extracted with the cation exchange resin.

Extractable Ca concentrations followed the same pattern as those of Mg except that the amounts of RE-Ca on the Langhei and Buse soils were about 50 times more than those from the Barnes and Svea soils. It appears that Ca is the main complexing cation for several of the agronomically important anions. In the Langhei and Buse soils, RE-(Ca + Mg) exceeds the agronomically important RE anions by more than 1000:1. Bicarbonate, as indicated by pH and inorganic carbon measurements, was undoubtedly the main anion in these soils.

The RE-Mg:(Mg + Ca) to which some maize hybrids and soybean varieties are sensitive (Olness et al. 2001b, 2002) ranked in the following order Svea (0.42) ≥ Barnes (0.38) > Buse (0.20) ≥ Langhei (0.16). It would seem that even though the Buse and Langhei soils were richest in RE-Mg, they are relatively deficient in RE-Mg. The increase in yield of some genotypes of both soybean and maize was as much as 20% over the RE-Mg:(Mg + Ca) range of 0.17 to 0.75 (Olness et al. 2001b, 2002). Thus, some potential could exist for yield gain on the Buse and Langhei soils if sensitive genotypes were fertilized with MgSO₄ or MgNO₃. Because some hybrids and varieties are rather unaffected by the RE-Mg:(Mg + Ca), they would seem better suited for the Buse and Langhei soils.

Iron, Manganese, Cobalt, and Copper

Resin extraction of iron and manganese is sensitive to oxidation-reduction changes (Olness et al. 1990) and the amounts that are extractable may depend on antecedent climatic conditions. This also includes associated elements such as Ca that are contained in the amorphous oxide coatings (Olness et al. 1990). Iron was rarely and inconsistently found in resin extracts of the Svea soils (Table 5). Small amounts of iron were obtained with the cation exchange resins of most samples of the Barnes and Buse soils. For the Langhei soils an average of 1.25 nmols of Fe g⁻¹ were obtained in extracts with cationic exchange resins. When RE-Fe was present, the amounts extracted increased exponentially as the pH increased (data not shown). Except for the Langhei soils, nearly as much Fe was found on cation as on anion exchange resins; for the Langhei soils most of the RE-Fe was recovered on the cation exchange resins.

Most RE-Mn was recovered with cation exchange resins and the order was Langhei = Buse > Barnes > Svea. We were unable to find data on levels of toxicity or deficiency of Mn correlated with resin extraction, but excess Mn interferes with accumulation of several divalent cations, especially Mg and Ca (Isermann 1975; Heenan and Campbell 1981). Also, the effects of Mn supply are mitigated by environment (Heenan and Carter 1977; Rufty et al. 1979) and genetics (Edwards and Asher 1982; Horst 1988). From our results, it would seem that RE of soils might offer an efficient tool for evaluating effects of Mn on plant growth.

Detectable amounts of RE-Co were usually found only in the Langhei soils, and these were found on the cation exchange resins. Resin extractable-Co was found in extracts of Buse soils occasionally and rarely in those from Svea or Barnes soils. While it is a requirement for rhizobia, Co is not generally recognized as being either deficient or toxic in these soils.

While the soils differ with respect to RE-Cu, very little was obtained. Resin extractable-Cu was detected in only about half of the extracts from Langhei and Buse soils.

Barium, Strontium, and Cadmium

Amounts of RE-Ba, Sr, and Cd varied between each of the soils (Table 6). While none are regarded as nutrient elements, we speculate that their presence interferes with accumulation of nutrients such as Mg, Ca, etc. While some of the more toxic elements such as Cd, Pb, and Ni have received attention, Ba and Sr have been perceived as neither beneficial nor of manageable toxicity in crop production and, as a

Table 4. Cations extracted using anion- and cation-exchange resins from A/Ap horizons of Svea, Barnes, Buse, and Langhei soils

Soil	Lithium		Potassium		Magnesium		Calcium	
	Anion	Cation	Anion	Cation	Anion	Cation	Anion	Cation
	(nmol g ⁻¹)							
Svea	0.000	10.100a	0.106b	421c	1.11b	108d	0.059c	148d
Barnes	0.000	7.300a	0.211ab	702b	1.36b	361c	1.62b	592c
Buse	0.016	1.610b	0.320ab	1030a	2.04ab	2 130b	2.56b	8 320b
Langhei	0.000	0.089c	3.30a	459c	14.00a	5 380a	165.00a	27 900a

a-d Within columns, values followed by the same letter are not significantly different ($P < 0.05$).

Table 5. Redox sensitive and metal ions extracted using anion- and cation-exchange resins from A/Ap horizons of Svea, Barnes, Buse, and Langhei soils.

Soil	Iron		Manganese		Cobalt		Copper	
	Anion	Cation	Anion	Cation	Anion	Cation	Anion	Cation
	(nmol g ⁻¹)							
Svea	0.032	0.026c	0.936a	4.95c	0.000	0.000c	0.000	0.000c
Barnes	0.062	0.135b	0.595ab	9.49b	0.000	0.008c	0.003	0.006bc
Buse	0.156	0.172b	0.500ab	34.40a	0.000	0.074b	0.005	0.039b
Langhei	0.124	1.250a	0.294b	39.60a	0.004	0.305a	0.004	0.128a

a-c Within columns, values followed by the same letter are not significantly different ($P < 0.05$).

consequence, they often are ignored as production factors. Negligible amounts of Ba and Cd were extracted from these soils. Cadmium was undetectable in many extracts; so, concentrations in a few extracts, mainly from Langhei soils, were considerably greater than the mean concentration (Table 5).

By comparison, Ba was detectable in a larger fraction of the samples. It is generally accepted that Ba inhibits plant growth. Barium inhibits elongation of roots (Debnath and Mukerji 1982) and stops root growth at about 80 mM concentrations. If RE-Ba concentrations affect crop yield, we would expect to see evidence of chlorosis when Fe is in moderate to low supply. Here, the soils richest in RE-Ba are also richest in RE-Fe.

Very marked differences were observed in the amounts of Sr extracted from these soils, and the general order was Langhei > Buse >> Barnes > Svea. Like Ba, Sr is generally a plant growth inhibitor. For example, Sr inhibits cell elongation without affecting mitosis in pea (*Pisum sativa* L.; Burström 1983) and root extension was severely inhibited at 10 mM concentrations. The uptake of Sr by timothy (*Phleum pratense* L.) is correlated with the Sr:Ca in soil; this suggests an independent competition between Sr and Ca (Paasikallio 1979). From our results, it seems unlikely that Sr would have a large effect on plant growth in the Langhei or Buse soils, although studies of the effects of Sr in complex systems such as these remain to be done.

Silica and Vanadium

Silica, another element taken up in large amounts by several crops, is seldom studied. While not yet fully accepted as an essential element, it mitigates a number of nutrient effects, particularly poor internal Mn distribution within leaves (Williams and Vlamis 1957; Horst and Marschner 1978), P mobilization (Scheffer et al. 1982) and P induced Zn deficiencies (Marschner et al. 1990).

The order of RE-Si was Langhei ≥ Buse = Barnes ≥ Svea (Table 7). The amounts of extractable Si from the Langhei and Buse soils may mitigate the apparently readily available Mn in these soils and an evaluation of the vegetation on these soils seems warranted. For the Svea, Barnes and Buse soils, most Si was extracted with anion exchange resins in contrast to about 52% being extracted from the Langhei soils on the cation exchange resin (Table 7).

Assays for V were somewhat surprising in view of the amounts extracted locally. No RE-V was found in most sites and only trivial amounts were extracted in a few Buse soils. None of the amounts recovered would appear to have a measurable effect on crop growth. In addition to the Barnes-Aasted Research Farm, V has been extracted from different soils at other sites at some distance (data not given). In view of Shacklette et al.'s (1971) survey, we expected to find larger amounts of V; about 14% of their observations contained > 100 µg total V g⁻¹ of soil nationwide with a few observations having as much in this region. The complex nature of the chemistry of V in the environment (Crans and Tracey 1998; Pettersson and Elvingson 1998) may have prevented RE of this element from more sites.

Zinc, Nickel, and Other Elements

RE-Zn (range 3.80 to 10.5 nmol g⁻¹) and Ni (range 0.151 to 0.414 nmol g⁻¹) were easily detected, but we were unable to obtain measurable differences between soils. Similarly, RE-Al (range 0.149 to 218 nmol g⁻¹) was detected in several samples, but the variances were too large to support conclusions regarding differences between soils. We have been unable to detect Mo, Pb, Be, Ti, and Cr with this method.

The ability to detect Ni may be important to these soils because leaf Ni concentrations increase with pH (Chang and Donald 1952) and most soils in this region have pH values greater than 7.0. Nickel can induce Zn or Fe deficiency and produce typical symptoms of chlorosis in soybean (Anderson et al. 1973). While we recognize that a number of

Table 6. Barium, strontium, and cadmium extracted using anion- and cation-exchange resins from A/Ap horizons of Svea, Barnes, Buse, and Langhei soils

Soil	Barium		Strontium		Cadmium	
	Anion	Cation	Anion	Cation	Anion	Cation
Svea	0.235a	0.004c	0.019a	0.100d	0.000a	0.000b
Barnes	0.036b	0.060b	0.009a	0.271c	0.000a	0.000b
Buse	0.029b	0.142b	0.020a	2.800b	0.000a	0.001b
Langhei	0.016b	0.235a	0.022a	8.500a	0.002a	0.004a

a–d Within columns, values followed by the same letter are not significantly different ($P < 0.05$).

Table 7. Silica and vanadium extracted using anion- and cation-exchange resins from A/Ap horizons of Svea, Barnes, Buse, and Langhei soils

Soil	Silica		Vanadium	
	Anion	Cation	Anion	Cation
Svea	2.50 b [†]	0.063c	0.000	0.000
Barnes	8.06 ab	0.799b	0.001	0.002
Buse	7.12 ab	1.040b	0.008	0.000
Langhei	10.80a	11.600a	0.005	0.000

a–c Within columns, values followed by the same letter are not significantly different ($P < 0.05$).

nutrient problems contribute symptoms, chlorosis of soybean is commonly observed throughout the region.

Prospects for More Efficient Resource Use

The soils at each site were located, with one exception, in a single field that was under uniform land management. The differences between soils certainly suggest that crop yields could be improved with specific management practices applied to each soil. It is fashionable at the moment to evaluate “precision agricultural (soil)” management for a single element using a common soil test procedure. Most of these studies ignore the fact that several nutritional factors may be inadequate for maximal crop yield simultaneously; something the data in our study strongly support. The assumption that a conventional soil test adequately supports an evaluation of precision management seems particularly weak. Most of these tests evaluate a sample taken at a specific depth and the resulting variance in the correlation relationship should serve as a warning that (1) plants are not restricted to a shallow sampling depth and (2) complex interactions are probably occurring within the environment.

Using current soil-testing guidelines, most of the soils indicate adequate levels of K. Something missed by single element extraction is the impact of other readily extractable or soluble elements on the effective concentration of acetate-extractable K (Greer and Sulewski 2001). Crops grown on calcareous soils may respond to additions of K despite indications of sufficiency using conventional methods of determination.

The assumption also is invoked that a single test is equally valid on all sites. For P, soil-testing guidelines would fail to recommend P fertilization on most sites (Dahnke et al. 1992; Gerwing and Gelderman 1998). While correlation (calibration) tests have been conducted and have general application, soils vary considerably with regard to plant availability. This is illustrated in Fig. 3 where the RE-P is plotted against the bicarbonate-extractable P for each of the soils.

For the Barnes, and Buse soils, we found a general correlation with bicarbonate extractable P (Fig. 3). In the Barnes soils, two rather distinctly separated groups of soils are apparent ($R_1^2 = 0.76$ and $P < 0.05$; $R_2^2 = 0.79$ and $P < 0.05$); in both cases, the slopes of simple linear relationships are nearly identical ($S_1 = 5.63$; $S_2 = 5.26$ nmols μg^{-1} of bicarbonate-extractable P g^{-1} soil). Many of the soils probably have been fertilized and in two cases (not used in the regressions) it appeared that manure had been applied recently. Examination of the data failed to provide additional insights into a reason for the differences between these two relationships for the Barnes soils. Many of the grassland, CRP, and alfalfa (*Medicago sativa* L.) fields and many of the soils from South Dakota were associated with the relationship having a slope of 5.26 nmols of RE-P for each μg^{-1} of bicarbonate extractable P g^{-1} of soil. But the relationships are inadequate to support a conclusion that geographic location or present crop has affected the difference. For the Buse soils, the slope was 3.91 nmols of RE-P for each μg^{-1} of bicarbonate-extractable P g^{-1} of soil ($R^2 = 0.45$ and $P < 0.05$), but the variance precludes declaring that it is different from the Barnes soils.

We were unable to determine a relationship between RE-P and bicarbonate-extractable P within the Langhei and Svea soil groups (Fig. 3). This seems probably due to the small number of Svea soils surveyed. The Langhei soil shows very little evidence of change in RE-P even in soils quite rich in bicarbonate extractable P. The results strongly suggest that the Langhei soils will respond to P fertilization but that broadcast P applications would be impractical. Band applications might be able to achieve the potential economic gains suggested in the results. However, application of fertilizer P alone may be inadequate to realize an economic gain considering that these soils may also need S and B. Thus, several nutritional factors, not simply one or two elements, warrant careful consideration for management with-

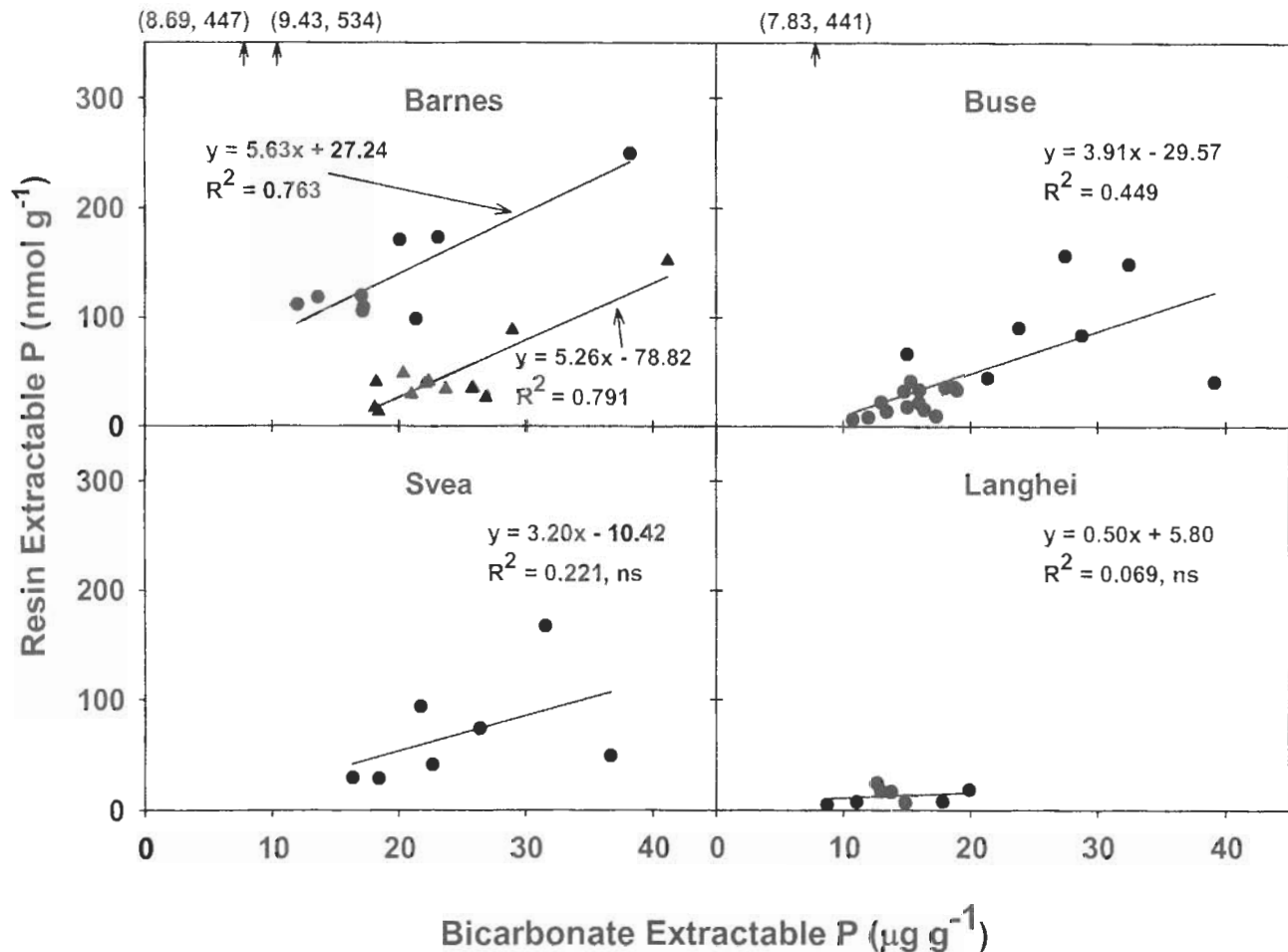


Fig. 3. The relationship between resin-extractable P and bicarbonate extractable P for the Barnes, Buse, Langhei, and Svea soils. Two data points for the Barnes soils and one data point for the Buse soils indicated by arrows were not used in the regression models.

in these soils. Finally, the Langhei soil contains much less organic carbon than the adjacent soils suggesting that these soils will retain less plant-available water, a yield-limiting factor in this region.

Soil mapping is a technical art that delineates repetitive segments of the landscape through use of aerial photography and identification of internal soil features. Soil composition within delineation is an approximation derived from samples observed. It is well understood that a natural body contains a certain amount of randomness of soil or landscape features. The aberrant features within the otherwise predictable soil continuum will result in occasional occurrences of soil with atypical characteristics. Still, the results presented here suggest that the mapping has been carefully conducted and provides some guidance in evaluating soils for more refined management.

CONCLUSIONS

Resin-extraction of four soils in the northern Great Plains has revealed that the suite of extractable elements is unique for each soil. Further, the initial inventory is relatively stable throughout the mapping region. Svea soils, which have received greater amounts of water in the form of rainfall

run-off from adjacent soils, exhibit more deeply weathered and somewhat leached profiles relative to the Barnes, Buse, and Langhei soils. Svea soils also have lesser amounts of extractable ions. The Langhei soils, for which leaching evidence is absent, show large amounts of extractable ions. Agronomically important anions such as B and S apparently are complexed with divalent cations such as Ca, Mg, and to much lesser extents, Sr in the Langhei and Buse soils.

Results suggest that band application of nutrients, some not currently recognized as deficient (for example, Mg), might be management options providing superior performance. The RE-Mg:(Mg + Ca) were least in the Langhei and greatest in the Svea soils; previous work has shown that some varieties and hybrids are sensitive to this ratio.

Among the inhibiting elements, RE-V generally was not found in the sites examined. Also, it was not found in amounts that have been recognized as yield limiting. Rather large amounts of Mn recovered in RE of Buse and Langhei soils may be mitigated by even larger amounts of RE-Si.

More than one factor in crop production often is affected by complex interaction of the active chemical matrix of the soil. As a consequence, conventional methods of soil analysis, which examine only the relative availability of a single nutri-

ent, and methods of mitigation may fail to provide support for differential or “precision” agricultural nutrient management on many soils.

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