# Salinity and salt contamination assessment using anion exchange resin membranes.

# K.J. Greer\* and J.J. Schoenau, University of Saskatchewan, Saskatoon, Saskatchewan

### Abstract

Exchange resins have the ability to sorb ions directly from the soil solution and, thereby show promise as a method to assess plant available nutrients. In salt affected soils, knowing the relative levels of various anions is useful in predicting the type of salts present and the potential for toxicity of specific anions, most importantly boron (B). The objective of this study was to apply the anion exchange membrane (AEM) burial technique to saline soils to rapidly assess anion composition and compare this to standard saturated paste extractions. Soils with a wide range in natural salinity levels were initially investigated. AEM extractable borate, chloride and sulfate were generally well related to the soluble levels found in saturated paste extracts ( $R^2$ =0.79, 0.81 and 0.75, respectively). Toxic limit for boron in the saturated paste extract corresponded to 0.12  $\mu$ g  $\text{cm}^2$  in the AEM test. AEM testing performed as well as the saturated paste method in distinguished between soils contaminated by native salinity and saltwater brine Spills. AEM testing is simple and rapid and show promise as an in-field method for spill site diagnosis.

Key words: Salinity, salt contamination, anion exchange membrane, testing.

### Introduction:

Salt accumulation in saline soils generally restricts growth by restricting water supply. However, concentration of toxic levels of borate anions, which often accompanies salinity, can be detrimental to plant growth even when.the total salt levels do not restrict yield. In Western Canada, sulfate rather than chloride is the dominant anion in naturally salt-affected soils. Industrially contaminated sites are characterized by high NaCl and KCL Therefore the relative abundance of Chloride is used a key indicator of contamination (Anonymous, 1988).

Anion exchange membranes (AEM) have been used to successfully quantify the levels of other nutrient anions, such as sulphate, nitrate and phosphate (Schoenau et al., 1993; Qian et al., 1992). Our objective in extending this testing procedure to saline soils was to develop a simple field method which could be used to characterize the levels of anions present in saline and brine contaminated sites.

### Materials and Methods:

*Description of Soils* 

Gravelly to clay loam Brown Chemozemic soil profiles were sampled in 1991 near Coronach, Saskatchewan. Soils were divided into 15 em depth increments up to a depth of 60 em and 30 em increments thereafter up to 120 em. Sampling was carried out to diagnose the extent of poor spring wheat productivity as a result of recent soil salinization.

Soils were well distributed among the conventional slightly, moderately, and severely saline ranges (Table 1). Soil pH, CEC, and saturation percentage were generally symmetrically distributed, with mean values differing only slightly among salinity categories.



Table 1. Basic properties of soils categorized by electrical conductivity of the saturated extract.

\* slightly, moderately and severely saline as classified by Richards (1954).

#### *Anion Analysis*

Soluble anions, pH, and EC were determined from extracts of saturated paste prepared using standard procedures (Richards, 1954). Anion Exchange resin extractions were performed by first saturating each 20 mm x 62 mm strip of membrane (BDH product no. 55164) with HCO<sub>3</sub>ions by overnight washing in a 1 M ammonium bicarbonate solution, followed by burial in 20 to 30 g of soil which was wetted to saturation and left for one hour. Strips were removed and adhering soil washed off with a stream of deionized water(approximately 200 ml). Anions adsorbed onto the AEM were eluted using a 1 hour shaking in 0.5 M nitric acid. Sulfate and borate concentrations in the eluate were determined using Inductively Coupled Plasma spectrophotometry. Chloride was determined colorimetrically using a Technicon autoanalyser. Level of each anion was expressed as the weight of anion per unit surface area of resin strip ( $\mu$ g cm<sup>-2</sup>).

# **Results and Discussion:**

Boron measured using AEM was generally well related to that measured in the saturated extract (Fig. 1). Despite being near the analytical detection limit, AEM borate levels show a good linear trend with saturated paste B in the range of 0 to 5 mg  $L^{-1}$ . Soils contaminated with greater than 5 mg  $L^{-1}$  appear to have similar AEM extractable B. This may be due to the nature of the borate ion, which can exist as various oxyanions with variable charge per B atom. It is possible that these complex ionic species, although measured in the saturated extract, are not adsorbed in proportion due to saturation of the exchange sites. Nevertheless, a AEM test level  $> 0.12$   $\mu$ g cm<sup>-2</sup> will clearly be above the typical toxic limit corresponding to 5 mg  $L^{-1}$  (Barth et al., 1987).



AEM extractable B  $(\mu g \text{ cm}^{-2})$ 

Figure 1. Relationship between anion exchange membrane (AEM) and saturated paste extract Bin non to extremely saline soils.

In Saskatchewan, saline soils are dominantly affected by S042- salts, with only minor accumulations of CI-. The relationship between AEM and saturated paste CI- was highly significant (P< 0.001, Fig.2). Under natural conditions, Cl- is typically highest on soils with high  $SO<sub>4</sub><sup>2</sup>$ . These severely saline soils, which typically contain greater than 8000 mg L<sup>-1</sup> of SO<sub>4</sub><sup>2-</sup> in the saturated extract, appear to saturate the AEM (Fig. 3). Hence some deviation at high CI- levels could be a result of anion exclusion.





Figure 2. Relationship between anion exchange membrane (AEM) and saturated paste extract Cl in non to extremely saline soils.





Sulfate adsorbed to the AEM showed good linear relationship in the lower concentration range. This agrees well with the other work assessing AEM  $SO_4$ <sup>=</sup> and plant nutrition (Schoenau et al. 1993). Gaining sensitivity in the higher concentration ranges is possible using shorter AEM testing times (Szmigielska and Schoenau, 1994 *this issue).* 

## **Assessing the nature of salt contamination**

Natural salinity in Western Canada is typically dominated by  $SO_4$ = salts. Industrial salt contamination from oil well or mine tailings are typically high in CI-. Therefore, it is the relative abundance of these anions which is used to determine the salinizing source (Anonymous, 1988). Currently, detailed ion analysis is performed on the saturated paste extracts of samples taken from contaminated and control sites (David Bromley Engineering, 1992}.

Extremely saline ( $EC > 16$  mS cm<sup>-1</sup>) soils were selected from the group of naturally salinized soils. Mean sulfate and chloride using each method were calculated and compared to those found on extremely saline brine contaminated soils (Figure 4).



Figure 4. Relative sulfate and chloride content of high EC ( $> 16$  mS cm<sup>-1</sup>) soils affected by native salinity and saltwater brine spill determined using saturated paste and AEM methods.

Ability to differentiate between brine spill and native salinity is clearly shown using either saturated paste extracts or AEM, as both show the preponderance of chloride in brine spill affected soils verses sulfate in the soils affected by native salinity. Testing using the saturated paste procedure requires a minimum of 2 days turnaround time (Richards, 1954; p.84). However, AEM testing requires less than 3 hours and shows the same trend in anion composition.

### CONCLUSIONS:

AEM extractable anions are generally well related to those measured in the saturated extract of salt affected soils. Toxic boron levels (greater than 5 mg  $L^{-1}$ ) in the saturated extract correspond to AEM levels greater than  $0.12 \mu g \text{ cm}^{-2}$  of borate-B. Sulfate and chloride extracted by AEM were similarly well related to the saturated extract values, except in extremely saline soils where sulfate appeared to saturate the exchange capacity of the resin. Altering the time of burial is likely to improve sensitivity in extremely saline soils.

Relative proportions of CI- and  $SO_4$ <sup>=</sup>, determined by either testing method, clearly differentiate type of salt contamination. However, AEM testing shows a significant advantage in time required. Potential exists for utilizing this AEM method to gain a rapid in-field diagnosis of brine spill sites.

## REFERENCES

- Anonymous, 1988. Field manual for treating saltwater contaminated soil. Esso Resources Canada Limited and Husky Oil Operations Limited. Calgary, Alberta.
- Barth, R.C., R.C. Severson, and G.Weiler. 1987. Boron. *in* R.D. Williams and G.E.Schuman (eds.) Reclaiming mine soils and overburden in the western United States. Analytic parameters and procedures. Soil Conservation Society of America. Ankeny, Iowa. pp. 135-153.
- David Bromley Engineering. 1992. Decommissioning and reclamation guidelines for small oil and gas sites in Western Canada. Canadian Association of Petroleum Producers. Edmonton, Alberta.
- Qian, P., J.J. Schoenau, and W.Z. Huang. 1992. Use of ion exchange membranes in routine soil testing. Commun. Soil Sci. Plant Anal. 23(15&16):1791-1804.

Richards, L.A. 1954. Diagnosis and Improvement of Saline and Alkali Soils. U.S. Salinity Lab. Staff. Agriculture Handbook No. 60. U.S.D.A. pp.84-85.

Schoenau, J.J., P. Qian, and W.Z. Huang. 1993. Assessing sulphur availability in soil using ion exchange membranes. Sulfur in Agriculture. 17: 13-17.

Szmigielska, A.M. and J.J. Schoenau. 1994. Determination of 2,4-D amine in soils using anion exchange membranes. Proc. Soils and Crops Workshop. Saskatoon, SK.

### ACKNOWLEDGEMENTS

Funding of this work through the Envirorimental Technology Development Fund, Sask. Environment and Public Safety is greatly appreciated.