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Potassium and magnesium in irrigation water quality assessment

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ABSTRACT

There is a growing trend of K replacing Na in wastewaters from agricultural industries to reduce the adverse effects of irrigation with these waters on soil hydraulic properties. However, problems with soil physical properties caused by wastewaters with high concentrations of K have been reported in both Australia and California. A review of the literature dating back to the 1930s supports the general conclusion that the relative order of deleterious effect on soil hydraulic properties of the four common cations in soils is Na > K > Mg > Ca. This paper explores the capabilities of the Cation Ratio of Structural Stability (CROSS), a generalized Sodium Adsorption Ratio incorporating all four cations, as an improved irrigation water quality parameter. This new parameter includes a coefficient for K that accounts for its relative deleterious effect as compared with Na and another coefficient for Mg that accounts for its relative beneficial effect as compared with Ca. Based on optimizing CROSS using threshold electrolyte concentration data for a Sodosol from the Riverina Region of Australia, the deleterious effect of K is estimated to be about one-third of that of Na, while the concentration of Mg needs to be about an order of magnitude larger than Ca to have the same beneficial effect.

1. Introduction

Wastewaters generated by agriculture and municipalities are being re-used increasingly for irrigation, both as a way to mitigate severe water shortages and as means of avoiding wastewater discharge to surface waters while producing economic value from wastewater streams (Bond, 1998; Arienzo et al., 2012). However, the sustainable use of wastewaters generated by agriculture poses significant challenges because they can contain high concentrations of K. This is especially the case for wastewaters generated by dairies, piggeries, wineries, and olive or tomato processing plants (Smiles and Smith, 2004a; Arienzo et al., 2009, 2012; Dellavalle, 2010, personal communication; Rengasamy and Marchuk, 2011). The change in water composition arises mainly as a result of moving from Na- to K-based products in the cleaning process and/or shifting animal diet, wherein cheese whey (K concentration: 1660 mg/L; Feigin et al., 1991) is used as part of the feed formulation (intensive piggeries). In many cases, the shift to K has been deliberate because of well-established concerns about negative effects of Na on soil physical properties (U.S. Salinity Laboratory Staff, 1954; Levy, 2012). However, recent studies have documented problems with water infiltration caused by high levels of K in applied waters (Rengasamy and Marchuk, 2011), particularly in Australia (Smiles and Smith, 2004a) and California (Nat Dellavalle, personal communication, 2010).

Generally, studies of the hydraulic properties of salt-affected soils have focused exclusively on the potential deleterious effects of two soil properties, exchangeable Na and soil water salinity (Quirk and Schofield, 1955; Bresler et al., 1982; Shainberg and Shalhevet, 1984; Sumner, 1993; Sumner and Naidu, 1998; Oster and Jayawardane, 1998; Levy, 2012). One reason the effect of K on soil hydraulic properties has not traditionally been taken into consideration is that Na concentrations in salt-affected soils and groundwaters are usually much higher than those of K, but the most important reason is that the authors of Handbook 60 (U.S. Salinity Laboratory Staff, 1954) concluded 60 years ago that “exchangeable K has only a slight or no adverse effect upon the physical properties of soils.” This conclusion was influenced by “measurements made recently at the Laboratory on samples of seven soils adjusted to various levels of exchangeable sodium and exchangeable potassium (Fig. 1)”. The figure in question displays the ratio of air permeability to water permeability as a function of exchangeable sodium percentage (ESP) and exchangeable potassium percentage (EPP). This ratio increases exponentially with ESP, whereas for EPP there

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is no increase observed for three of the seven soils examined, while the increase is small for the other four. Variations of this figure were published by Reeve et al. (1954) and Brooks et al. (1956), who stated: "Combinations of various levels of exchangeable sodium and potassium showed that exchangeable potassium, whether alone or in the presence of exchangeable sodium, had little if any effect in increasing the permeability ratio. . ." One may thus infer that the authors of Handbook 60 were confident in setting aside a premise stated long ago by de Sigmond (1928) and Magistad (1945), that exchangeable Na and K should be considered to have additive deleterious effects on soils. Even today, the potential impact of exchangeable K on soil properties is not mentioned in ASCE No. 71, a standard engineering manual related to salinity assessment and management (Wallender and Tanji, 2012).

2. Effects of K and Mg on soil hydraulic conductivity

Quirk and Schofield (1955), inspired by research on the effects of electrolyte concentration on the permeability of soils in California (Fireman and Bodman, 1939), reported what appears to be the first systematic investigation to document the effects of K on the saturated soil hydraulic conductivity. They equilibrated soil pads with concentrated Cl solutions of Na, K, Ca, or Mg, then leached them with a series of more dilute Cl solutions of the same cation. Their results showed decreases in the hydraulic conductivity over a five-hour period of leaching which depended on both the cation and the leaching solution concentration. The decrease in hydraulic conductivity followed the order: Na > K > Mg > Ca. Quirk and Schofield (1955) defined the cation concentration at which a 10–15% reduction in the saturated hydraulic conductivity occurred at the end of the leaching period as the threshold (electrolyte) concentration (TEC), reporting TEC values for Na, K, Mg, and Ca as 250, 67, 2.0 and 0.6 $\mathrm{mmol_c/L}$, respectively. They noted in particular for K that a concentration of 20 $\mathrm{mmol_c/L}$ produced turbidity in the soil percolate, and a concentration of 10 $\mathrm{mmol_c/L}$ resulted in clay deflocculation.

Since this early work, researchers have reported both positive and negative effects of K on soil hydraulic conductivity. Keren (1984), in his comprehensive review of the effects of K and Mg on soils, concluded that these mixed results indicate "the effect of exchangeable K on soil properties is not well understood." The same ambivalence was echoed recently in a brief review by Rengasamy and Marchuk (2011), who also noted that the need to solve this conundrum has grown more urgent because of increasing irrigation with wastewaters. Levy and van der Watt (1990), working with three South African soils, found little K effect on an Alfisol with kaolinite and iron oxide mineralogy (EPP of 6 or 13), a much larger effect on an Aridisol with illite and smectite mineralogy (EPP of 18.9), and an intermediate effect on an Alfisol with this same mineralogy. For two soils having an illite content of 10–11%, Chen *et al.* (1983) reported that the saturated hydraulic conductivity increased with increasing EPP < 20%, while for EPP > 20%, the conductivity decreased with increasing EPP. However, for a third soil which had an illite content of 16%, the hydraulic conductivity uniformly decreased with increasing EPP. Scanning electron micrographs showed that enrichment with K resulted in the formation of dense, continuous networks of clay particles filling the pore spaces between sand particles (Chen et al., 1983).

Marchuk et al. (2012) applied computed X-ray tomography to characterize changes in pore architecture as influenced by exchangeable Na, K, Mg, and Ca. Total porosity and pore connectivity were influenced by cation valence, as might be anticipated from the Schulze-Hardy Rule (Sposito, 2008). A well-developed pore structure was evident in soils having a sufficiently high concentration of exchangeable Ca and Mg, whereas soils dominated by Na and K had isolated pore clusters surrounded by pores filled with dispersed clay particles (Marchuk et al., 2012). Clay dispersion decreased in the order: Na > K > Mg > Ca and, correspondingly, hydraulic conductivity decreased in the reverse order, as reported originally by Quirk and Schofield (1955).

Magnesium has long been considered to have effects similar to Ca on soil physical properties (Keren, 1984; Levy, 2012), leading the U.S. Salinity Laboratory Staff (1954) to group these two bivalent cations together as promoting and maintaining good soil structure. Bresler et al. (1982) remarked that this customary grouping may not reflect the true status of Mg, which is masked by the typically two- to five-fold greater concentration of Ca over Mg in irrigation waters and soil solutions. Rengasamy et al. (1984) concluded that Mg has the greatest effect on the saturated hydraulic conductivity when the electrolyte concentration is low, a point also made by Keren (1984), Sumner (1993), and Levy (2012). Use of gypsum on silt loam soils with an exchangeable Mg saturation near 36% reduced runoff under surface irrigation conditions (Vyshpolsky et al., 2010). In experiments conducted on soils from the corn belt in the United States, Dontsova and Norton (2002) reported Mg-treated soils had half the final infiltration rate as Ca-treated soils for two of four soils they studied. In summary, the available literature supports the premise that, under certain conditions, both K and Mg can have deleterious effects on soil hydraulic properties, and when there are deleterious effects, they usually relate to clay particle dispersion, resulting in reduced soil permeability.

These trends, observed for soils of varying clay mineralogy, have to do with the fundamental relationship between soil particle flocculation and cation adsorption. If we think of the simplest theoretical approach to this relationship, diffuse double layer theory comes to mind (Sposito, 2008). This theory implies that only cation valence (Z) matters, and hence all cations of a given valence should behave in the same way, although monovalent cations should behave differently from bivalent cations. Therefore, one parameter to explain particle flocculation is cation valence, and this parameter alone suffices not only to understand the Schulze-Hardy Rule, but also to develop a semi-quantitative model of critical flocculation concentrations (Sposito, 2008). But such a model cannot explain Na–Mg systems as compared to Na–Ca systems, or K–Ca versus Na–Ca.

Two other parameters that have been used to account for cation adsorption phenomena are ionic potential (Z/R) and Misono softness (Sposito, 2008). The first one (ionic potential, Z/R) scales the valence by cation radius (R) and is a measure of the electrostatic binding energy of a cation, whereas the second one (Misono softness) involves the energy required to extract an electron from a cation and is a measure of the covalency of cation binding. Recently Marchuk and Rengasamy (2011) combined these two parameters into a single index for the degree of covalency of cation binding, then subtracted it from 1.0 to get what they termed the degree of non-covalency, or the ionicity index. This new index depends on cation valence and the energy required to extract an electron from a cation, but it does not depend on cation size. Thus it goes beyond diffuse double layer theory by saying that the degree of covalency in cation binding also is important, not just electrostatics, and in this way it distinguishes Na from K, and Ca from Mg. Table 3 in Marchuk and Rengasamy (2011) shows that the ionicity index is a very good predictor of both clay suspension turbidity and clay particle zeta potential for a wide variety of soil clays. In particular, it predicts observed differences in turbidity, a measure of clay dispersion, with the ordering: Na > K > Mg > Ca. We suggest, therefore, that the reason for the observed differences in soil response to applied water composition, summarized above, is related to both the valence of the cations and their ionicity index.