

# Changes in the cation composition of a Barossa Chromosol irrigated with wastewaters of contrasting monovalent cation concentrations

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## Abstract

Reusing wastewater, including recycled municipal water and winery wastewater, for irrigation has become increasingly commonplace as an efficient use of water and effective means of disposal. One of the major agricultural concerns related to the use of recycled water is the accumulation of exchangeable sodium (Na) in the soil profile and the potential impacts this has on soil structure. Potassium (K), like Na, has a high affinity for clay minerals and therefore has the potential to cause clay swelling and dispersion. Here, we describe the dynamics of cations in two contrasting wastewaters, a Na-rich municipal wastewater and K-rich winery wastewater (Na:K ratio ~ 1:1) following irrigation to a Barossa Chromosol. Accelerated annual irrigation, drying and rainfall cycles enabled long-term predictions to be drawn. With the passage of approximately 1000 pore volumes through the core over the course of 7 months, greater accumulation of K was evident in soils irrigated with winery wastewater irrigation, which is likely to be a result of adsorption to specific binding sites in the illite dominated clay. The high mobility of Na combined with the flow through nature of the columns has prevented accumulation of Na under both wastewater types despite the high initial Na concentration in both water sources. High Magnesium (Mg) concentrations in both wastewaters have led to a greater retention of Mg in favour of Calcium (Ca), conforming to Schofield's Ratio Law.

## Key Words

Winery wastewater, municipal wastewater, basic cations.

## Introduction

Agricultural land surrounding Adelaide is highly productive, while accounting for only 1.5 % of South Australia's total agricultural land, this region accounts for more than 18 % (A\$800 million) of the state's gross agricultural earnings (ABS 2003). Currently 2340 hectares of vines around Adelaide are irrigated with recycled water, however, interest has been expressed by the viticultural industry to utilise a greater percentage of recycled water from municipal and winery industry sources to overcome water shortages, rising mains water prices and enable the safe and sustainable disposal of wastewaters generated in the winery. Concern however is raised over the unfavourable concentration of salts in these waters and the ratio of monovalent cations (Na and K) to divalent cations (Ca and Mg).

A high concentration of monovalent Na in soils has the potential to disrupt soil structure, leading to changes in many key soil physical properties such as hydraulic conductivity, infiltration rate, bulk density and soil aeration (e.g. Rengasamy and Olsson 1991). Based on the large hydrated ion size and its affinity to clay minerals, high levels of exchangeable K in soil also has the potential to cause clay swelling and dispersion (Levy and Feigenbaum 1996). Research on the soil structural effects of K in irrigation wastewaters has received less attention due to the typically low abundance of K in most waters (Arienzo *et al.* 2008). Winery processing wastewater however tends to have elevated concentrations of both K and Na therefore posing a risk of clay dispersion when irrigated to land. Unlike Na, exchangeable K in soils is adsorbed by specific and non specific binding, the former being dependent on the soil clay mineral. Illite and other mica clay minerals are particularly abundant in specific binding sites for K within their structural layers (Arienzo *et al.* 2008).

In the Barossa Valley, South Australia, Municipal Sewage Wastewater and Winery wastewater are treated independently and distributed to growers for the irrigation of grape vines. Here, we investigate the effect of these two waters on the soil cation properties of a Barossa Chromosol containing illite clay mineral

## Methods

Intact columns (150 mm length x 100 mm width) of a duplex red chromosol soil profile were collected from the Viticultural Research Station in Nuriootpa, Barossa Valley, SA. This soil is described as a non restrictive duplex red chromosol with well structured topsoil and was selected due to its good representation of soils widely used for viticulture in the Barossa region and where winery wastewater is used for irrigation. Sixteen columns were used in this experiment and contained soil from 0-150 mm depth in the soil profile. In order to assess the bio-availability fraction of constituents applied in wastewater, ryegrass (Diplex Italian Hybrid) was established in each column. A fibre-glass wick was mounted at the base of each column to maintain a fixed tension and thereby create a 'hanging soil-water column' similar to field conditions.

Winery wastewater (WIN) was sourced from the North Para Environmental Control Treatment Plant (NPEC) in Barossa Valley and municipal wastewater sourced from the Tanunda Community Wastewater Management Scheme (CWMS). Irrigation of wastewater was applied to a depth of 60 mm per day for ten days and then allowed to drain for 4 days before applying a low ionic water solution, akin to rainfall, at a rate of 60 mm per day for 2 days. This schedule represents the volume of water applied to vineyard soils under drip irrigation over a 1 year period, thereby allowing us to apply the equivalent of 1 year's irrigation to soils in the space of 16 days. This cycle was repeated 9 times in continuous fashion, representing 9 years of irrigation. Care was taken to balance the time over which irrigation was applied each day, typically 8 hours, with the period of free draining, 16 hours, to ensure adequate diffusion of soluble ions throughout the soil matrix. For each treatment and replicate, a bulk sample of soil leachate was collected every 5 days of consecutive wastewater irrigation, approximately 8 pore volumes (p.v.), and every 2 days following rainfall irrigation (approximately 3.2 pore volumes). Analysis of basic cations was carried out on filtered (0.45 µm) samples using ICP-OES.

The sodium adsorption ratio (SAR) of the wastewaters is defined as  $\text{Na}/(\text{Ca}+\text{Mg})^{0.5}$  where the concentration of Na, Ca and Mg is in mmol<sub>c</sub> per litre, while the potassium adsorption ratio (KAR) is defined as  $\text{K}/(\text{Ca}+\text{Mg})^{0.5}$

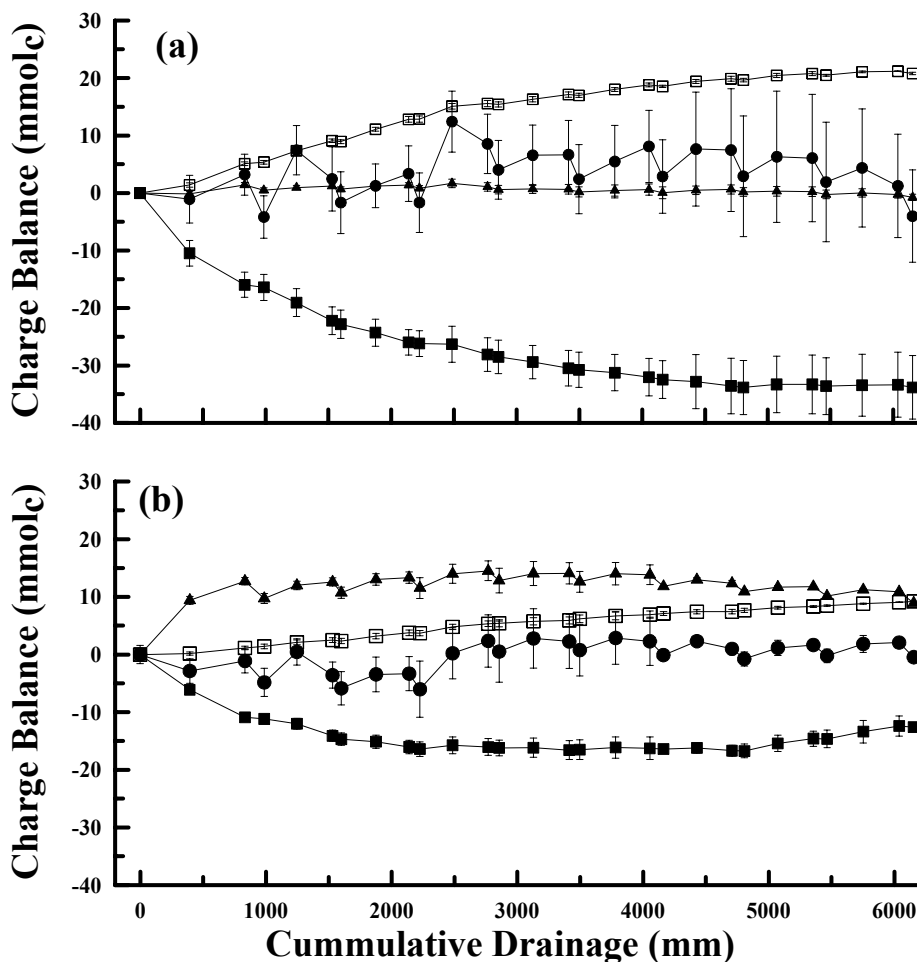
## Results

The composition of the two wastewaters, municipal CWMS and WIN, and rain water are shown in Table 1. It is evident that both wastewaters are dominated by monovalent cations. In the case of CWMS sodium is the dominant cation while in the WIN there is near equal concentrations of both sodium and potassium. The electrical conductivity of the two wastewaters is similar.

**Table 1. Chemical composition of Municipal CWMS water, NPEC winery wastewater and rainwater.**

Chemical parameter	Municipal CWMS Water		NPEC Winery Wastewater		Rainwater	
pH	<b>8.49</b>	± 0.31	<b>8.69</b>	± 0.20	<b>6.09</b>	± 0.20
Electrical Conductivity (dS/m)	<b>1.66</b>	± 0.15	<b>1.38</b>	± 0.13	<b>0.43</b>	± 0.03
Ca (mmol <sub>c</sub> /L)	<b>1.05</b>	± 0.24	<b>1.61</b>	± 0.24	<b>0.28</b>	± 0.11
Mg	<b>1.50</b>	± 0.11	<b>0.89</b>	± 0.08	<b>0.23</b>	± 0.07
Na	<b>13.64</b>	± 1.09	<b>7.50</b>	± 0.61	<b>0.79</b>	± 0.23
K	<b>1.19</b>	± 0.07	<b>3.94</b>	± 0.24	<b>0.05</b>	± 0.02
SAR			<b>7.0</b>		<b>1.72</b>	
KAR			<b>3.8</b>		<b>0.06</b>	

Cation balance for soils irrigated with CWMS water and WIN is shown in figure 1. On the basis of cation chemical charge balance, soils irrigated with CWMS displayed a net reduction in cations (i.e. chemical charges lost exceed those gained). This was principally due to the loss of Ca, despite relatively stable pH. In both soils, the loss of Ca occurred rapidly with the introduction of wastewater and changes after passing of the first 8 p.v. (first sampling point) accounted for 31 and 49 % of all Ca lost for CWMS and WW respectively. Such disproportional losses of Ca may reflect the solubilisation of CaCO<sub>3</sub> precipitates that have accumulated in these soils prior to trial commencement. Soils irrigated with winery wastewater showed a net increase in cations which is consistent with an increase in soil pH from 7.38 (initial) to 8.04 (final). Increase in pH noted here, is likely a result of the high bicarbonate content of winery wastewater (300 mg/L) and the effect of this on soil pH.



**Figure 1. Cation Balance for a Chromosol soil irrigated with (a) CWMS water and (b) winery wastewater. Data is expressed in terms of cumulative additions and losses of Ca (■), Mg (□), Na (●) and K (▲) within the soil profile based on net mmol<sub>c</sub> added in water source minus net mmol<sub>c</sub> removed by pasture and lost in drainage as a function of the cumulative volume of drainage.**

Magnesium is a divalent cation and is likely to have similar binding behaviour to Ca. Although not as effective as Ca in maintaining soil structure, Mg can mitigate the risk of soil dispersion posed by the high abundance of exchangeable monovalent cations. The retention of Mg has increased in soils irrigated with both CWMS and WIN in a similar linear fashion during the course of the experiment. Prior to irrigation, the ratio of soil exchangeable Ca to Mg was 9:1, while in the wastewaters this ratio was 0.68:1 in CWMS and 1.8:1 in WIN. Following irrigation, exchangeable cations undergo adsorption/desorption processes in order to maintain a common ratio between solid and liquid phase. Presumably therefore, Mg will continue to bind in favour of Ca until a Ca:Mg ratio similar to the given wastewater is reached.

In both soils, Na appears to be highly mobile and, given adequate percolation of water, does not appear to accumulate with on-going irrigation, despite the high Na concentration in both wastewaters. Due to the rapid loss of Na following irrigation, it is unlikely that this ion plays a role in the displacement of Ca, rather, the lesser valency, higher solubility and rapid percolation of water enable Na to pass through the column relatively unperturbed. Where evaporation (i.e. upward movement of water) exceeds downward movement (irrigation+rain) Na will have a greater propensity to build-up.

The retention of K in soils is markedly different between irrigation sources and is likely to reflect differences in the initial water concentrations. An accumulation of K is evident in soils irrigated with WIN, this appears to have occurred rapidly following commencement of irrigation. Clay content in the topsoil of this profile is approx. 17%, and is dominated by illite that contains specific binding sites for K within structural layers. With the introduction of K in WIN a considerable amount (10 mmol<sub>c</sub>) of K is likely to be retained on specific binding sites in the soil. Following the passage of approximately 16 p.v there is no further retention of K suggesting that specific binding sites are saturated after which time K appears to be readily leached through the column.

In instances where the level of specifically bound potassium in illitic clays is low, such additions of K may in fact improve structural properties of the colloid (Ravina and Markus 1975; Chen *et al.* 1983) and where flow through conditions occur there appears to be no risk of adverse K build up. Pasture irrigated with WIN also showed a corresponding increase in dry matter K concentration (not shown).

### **Conclusion**

Maintaining infiltration of wastewater and rainfall through the soil ensures adequate leaching of monovalent cations that may otherwise accumulate in soils and pose a risk of soil dispersion. It seems evident that although the initial concentration of Na in the CWMS water is high, greater mobility relative to other cations allows it to readily leach through soil. Potassium on the other hand is less mobile in soils and will be retained on both specific and nonspecific binding sites. Following saturation of specific binding sites K appears to be highly mobile. The loss of Ca we suggest is caused by a redistribution of exchangeable and soluble cations to equilibrate the high Mg:Ca ratio in both waters applied.

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