

no. 19  
**technical**  
report

**Winery wastewater irrigation**  
Effects of potassium and sodium on soil structure

S. Laurenson, N. Bolan, E. Smith and M. McCarthy



CRC for Contamination Assessment and Remediation of the Environment

Technical Report no. 19

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## **Effects of sodium and potassium on soil structure**

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November 2010



**Cooperative Research Centre for Contamination Assessment and Remediation of the Environment, Technical Report series, no. 19**

November 2010

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ISBN: 978-1-921431-23-4

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**This report should be cited as:**

Laurenson, S, Bolan, N, Smith, E & McCarthy, M 2010, *Winery wastewater irrigation: effects of sodium and potassium on soil structure*, CRC CARE Technical Report no. 19, CRC for Contamination Assessment and Remediation of the Environment, Adelaide, Australia.

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**Acknowledgement:**

CRC CARE acknowledges the contribution made by Seth Laurenson, Nanthi Bolan and Euan Smith (Centre for Environment Risk Assessment and Remediation, University of South Australia) and Michael McCarthy (Nuriootpa Research Centre, South Australian Research & Development Institute) towards the writing and compilation of this technical report.

## Executive summary

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Generation of wastewater is an inevitable component of the wine production process. Typically this wastewater has a high salt concentration, due mainly to chemical cleaning products and spent grape lees. Land application of winery wastewater is increasingly being advocated as a means to mitigate deteriorating water quality associated with surface water discharge. A major agricultural concern however, is the potential for monovalent cations, namely sodium ( $\text{Na}^+$ ) and potassium ( $\text{K}^+$ ) to accumulate in the soil profile and subsequently impact on soil structure.

Best management practice for managing nutrients in many wastewaters generally focuses on retaining constituents, such as nitrogen (N) and phosphorus (P), within the soil profile where they are assimilated into plant growth. However, the assimilation of  $\text{Na}^+$  by plants is low, and the best management approach to mitigate the potential effects of high soil  $\text{Na}^+$  concentrations is to leach this salt down the soil profile. Plant  $\text{K}^+$  requirements are generally high (i.e. similar to N), however, high loadings typical under winery wastewater (i.e.  $600 \text{ kg K}^+ \text{ ha}^{-1} \text{ yr}^{-1}$ ) far exceed plant requirements. Although the relative effect of  $\text{K}^+$  on soil structure is less than that of  $\text{Na}^+$ , an excess in the soil profile can contribute to a decline soil structure.

In many regions,  $\text{Na}^+$  and  $\text{K}^+$  are readily leached during winter rainfall events and, therefore, pose limited risk of accumulation or subsequent soil dispersion. In fine-textured soils that tend to drain poorly, or where loading rates of constituents are high, achieving adequate leaching may be problematic. A greater degree of management will, therefore, be required at locations where winery wastewater is applied to fine-textured soils with high clay content. Where accumulation of salts is likely, maintaining a sodium adsorption ratio (SAR) of winery wastewater below  $6 (\text{mmol}_c \text{ L}^{-1})^{0.5}$  and potassium adsorption ratio (PAR) below  $10 (\text{mmol}_c \text{ L}^{-1})^{0.5}$  is likely to prevent adverse soil structural changes.

There is a close relationship between winery wastewater electrical conductivity (EC) and soil dispersion, whereby adverse changes to soil structure under high net loading of  $\text{Na}^+$  or  $\text{K}^+$  is mitigated at higher EC. It is therefore valuable to include measurement of winery wastewater EC in routine analysis. Routine use of calcium ( $\text{Ca}^{2+}$ ) amendments including, yet not restricted to, lime, gypsum and calcium nitrate – either added directly to wastewater or to soils – will enable  $\text{Ca}^{2+}$  exchange and displacement of  $\text{Na}^+$  and  $\text{K}^+$ . Winter application of  $\text{Ca}^{2+}$  amendments will ensure its percolation down the soil profile, thereby ensuring good distribution of  $\text{Ca}^{2+}$  and raising soil EC that is otherwise lowered under rainfall.

Given the lesser effect of  $\text{K}^+$  on soil structure relative to  $\text{Na}^+$ , a switch to potassium-based sterilisers will lower SAR in the final stream. In addition to this, the greater PAR in winery wastewater will further prevent  $\text{Na}^+$  retention in soils.

The greatest volume of winery wastewater is generated immediately after vintage, during which time salt concentration tends to be at a maximum. The quantity of salt applied to soils with irrigation is influenced by the land area over which it is distributed. Because the period that winery wastewater is applied to land is relatively short, i.e. immediately following vintage, greater land area will be an effective means of minimising the net salt accumulation in soils. To avoid nutrient imbalances in crops grown with winery wastewater, loading rates could be determined based on meeting

the  $K^+$  demand of the crop. With adequate management (namely, prevention of high ESP and EPP during consecutive seasons) the risk of soil dispersion can be mitigated.

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# 1. Water for irrigation

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By global standards Australia is an extremely dry continent with a severe limitation of fresh water resources. In many parts of the country, continued rates of extraction for agriculture, declining rainfall trends and increased portioning of water for eco-system servicing have led to unsustainable levels of water consumption (Hamilton et al. 2005, 2007).

In Australia, a total of 24,000 GL of water is consumed per annum for industrial and domestic supply. Agriculture accounts for the vast majority (67%) of Australia's total water usage, which is mainly used for irrigation. This is followed by domestic supply that consumes 24%, while mining, manufacturing and service industries consume approximately 11% (ABS 2006). Despite the higher water usage in agriculture, gross value (i.e. economic return per unit of water) of water is substantially lower than in other sectors of the economy, in particular industry/manufacture sectors. The gross values of water in agriculture, for instance, range from AUD\$210 ML<sup>-1</sup> (rice) to \$1,750 ML<sup>-1</sup> (vegetables), while in the manufacturing industry, values range from AUD\$32,000 to \$680,000 ML<sup>-1</sup>, and in the service industry, from AUD\$2,137 to \$1,000,000 ML<sup>-1</sup> (ABS 2006). In the viticulture industry the gross value of water is approximately \$3,092 ML<sup>-1</sup> (ABS 2009a). Considerable pressure is now being placed on irrigators and agricultural producers to improve water-use efficiency and better utilise alternative water supplies such as storm water and recycled wastewaters for irrigation purposes (Government of South Australia 2004). This is particularly relevant given expectations that water usage within the horticultural industry alone is expected to increase by more than 50% by the year 2020 in order to meet greater production targets (Hamilton et al. 2005).

## 2. Irrigation of vineyards around Adelaide, South Australia

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Net profits from viticulture comprise a substantial proportion of South Australia's total farm gate profits, in particular the contribution from viticultural operations around Adelaide's urban fringe (van der Lee 2009). Although agricultural land area around Adelaide accounts for only 1.5% (800,000 ha) of South Australia's total agricultural land area, production on this land accounts for more than 18% (AUD\$800 million) of the state's gross agricultural earnings. In 2009 for instance, 10% of Australia's premium wine grapes were grown around the peri-urban areas of Adelaide, in the Barossa Valley, Adelaide Hills and McLaren Vale (ABS 2009b; van der Lee 2009).

Over the past 25 years, greater water usage associated with an expansion of vineyards has placed considerable stress on surface and groundwater resources. Ongoing reduction in water allocations around Adelaide is a key factor currently limiting the productivity of numerous vineyards. Typically this is associated with declining grape yield or quality, associated with greater soil salinisation, and subsequent lowering of the economic return per unit area of land (Anderson et al. 2008; Hamilton et al. 2005). This has fuelled a greater focus on alternative water supplies, such as treated municipal and winery wastewater that can potentially be used in place of scarce fresh water resources.

### 3. Characteristics of winery wastewater

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Approximately 50% of South Australia's grape crush is processed around Adelaide (PIRSA 2008) and approximately 875 ML of winery wastewater is generated annually as part of this process (Kumar & Christen 2009). Unlike municipal wastewater, winery wastewater is generally treated on-site, through treatment systems with low volume capacity only (South Australian EPA 2004). A recent survey of 45 Australian wineries showed a wide range of treatment methods between locations ranging from energy intensive aerobic systems to artificial wetland and land application systems (Kumar & Christen 2009). Land treatment of winery wastewater is increasingly being viewed as the most environmentally sound and cost effective means of final disposal (South Australian EPA 2004). In South Australia woodlots, fodder crops and vines are currently being irrigated with winery wastewater.

Generally winery wastewaters contain a significantly higher concentration of salts relative to many other waters conventionally used to irrigate grapes such as town supply and Murray River water (Table 1). The concentration of soluble salts in winery wastewater is similar to that of municipal wastewater, however unlike municipal wastewater in which the predominant salt is sodium ( $\text{Na}^+$ ), winery wastewater contains both  $\text{Na}^+$  and potassium ( $\text{K}^+$ ) cations. The concentration of  $\text{Na}^+$  and  $\text{K}^+$  in winery wastewaters is typically high relative to many other irrigation waters due primarily to widespread use of sodium hydroxide ( $\text{NaOH}$ ) and potassium hydroxide ( $\text{KOH}$ ) cleaners (Kumar & Christen 2009). A major agricultural concern when winery wastewater is used for irrigation is the potential for these cations to accumulate in the soil profile and subsequently impact on soil structure.

When the chemical composition of winery wastewater is deemed unsuitable for irrigating to soils, an upgrade of treatment facilities may be required in order to produce water fit for a given crop or soil type. This may not always be feasible for small scale operators and therefore disposal of wastewater to municipal wastewater treatment plants (WWTPs) or collective facilities handling wastewater from a number of wineries can be a suitable alternative. An example of this approach is the North Para Environmental Control Treatment Plant (NPEC) in the Barossa Valley that is a dedicated winery wastewater treatment facility collecting wastewaters from four major wineries. Treated winery wastewater is then distributed amongst seven vineyards in the immediate vicinity for irrigation purposes.

**Table 1. Selected chemical concentrations of waters and wastewaters generated around Adelaide, South Australia.**

	TDS	pH	NH <sub>4</sub> <sup>+</sup> & NO <sub>3</sub> <sup>-</sup>	Total P	Na <sup>+</sup>	K <sup>+</sup>	SAR <sup>a</sup>	PAR <sup>b</sup>
	(mg L <sup>-1</sup> )		mg L <sup>-1</sup>			(mmol <sub>c</sub> L <sup>-1</sup> ) <sup>0.5</sup>		
Mains water	338	7.3	0.3	0.01	62.1	4.4	3.0	0.2
River Murray water	344	7.4	5.5	0.5	73.6	7.0	2.9	0.1
Bolivar WWTP	1052	7.1	8.0	2.7	285.1	35.2	8.3	0.6
Christies Beach WWTP	843	7.4	29.2	9.1	190.8	23.5	5.8	0.4
Barossa CWMS	712	7.7	30.7	12.8	172.4	-	6.8	-
NPEC Scheme	858	8.0	8.1	5.3	173.0	129.0	7.4	3.2
Winery wastewater	1024	5.9	1.9	-	238	128	6.5	2.1

<sup>a</sup> SAR Sodium adsorption ratio =  $Na^+ / (Ca^{2+} + Mg^{2+})^{0.5}$

<sup>b</sup> PAR Potassium adsorption ratio =  $K^+ / (Ca^{2+} + Mg^{2+})^{0.5}$

Source: Laurenson (2010)

## 4. Variation in chemical composition with season

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The concentration of constituents, including salts, in winery wastewater fluctuates in response to winery operations and is highest during vintage periods when grapes are crushed and may range between 3.8 and 8.0 mmol<sub>c</sub> L<sup>-1</sup> (ANZECC & ARMCANZ 2000; Arienzo et al. 2009; Kumar & Christen 2009). This seasonal variation in SAR and PAR is evident in winery wastewaters reported by Kumar and Christen (2009) and shown here in Table 2.

**Table 2. Chemical composition of winery wastewater during the year in response to different stages of the wine production cycle.**

Month	Vintage	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	SAR	PAR	Na : K
		mmol <sub>c</sub>				(mmol <sub>c</sub> L <sup>-1</sup> ) <sup>0.5</sup>		
January	n	12.2	9.8	0.7	0.6	15.3	12.3	1.2
March	n	12.4	6.0	1.2	0.5	13.6	6.6	2.1
July	n	8.6	8.8	0.9	0.6	10.1	10.4	1.0
September	y	157.0	63.4	10.0	5.4	56.7	22.9	2.5
October	y	154.9	52.4	9.0	5.4	57.8	19.6	3.0
November	y	2.6	9.4	0.7	0.6	3.1	11.5	0.3

*Note: Vintage is the period of grape harvest and pressing*

Source: adapted from Kumar and Christen (2009)

## 5. Sodium in winery wastewater and its effect on soil structure

When continually applied to soils,  $\text{Na}^+$  can displace more desirable cations (i.e.  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ). An accumulation of exchangeable  $\text{Na}^+$  in soils may cause a breakdown of aggregates and subsequently lead to changes in many key soil physical properties such as hydraulic conductivity, infiltration rate, water-release potential and soil aeration. Resulting increases in clay dispersion and soil bulk density can affect the transformation, retention and movement of nutrients within the soil profile.

The sodium adsorption ratio (SAR) describes the ratio relationship between  $\text{Na}^+$  and divalent cations  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ , and is determined from the concentrations of these constituents in the winery wastewater, expressed in Equation 1 as  $\text{mg L}^{-1}$ :

$$SAR (\text{mmol}_c \text{L}^{-1})^{0.5} = \frac{[\text{Na}^+]/23}{\sqrt{[\text{Ca}^{2+}]/40 + [\text{Mg}^{2+}]/24}} \quad \text{Equation [1]}$$

The exchangeable sodium percentage (ESP) is used to gauge the build-up of  $\text{Na}^+$  in soils and is determined from the  $\text{Na}^+$  concentration divided by the sum of all cations (Equation 2). Similar to SAR, the ESP describes the abundance of  $\text{Na}^+$  in relation to other cations in the soil. Here, the exchangeable  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  concentration in soils is determined from routine soil testing and is expressed in  $\text{cmol}_c \text{kg}^{-1}$  (equivalent to  $\text{meq kg}^{-1}$ ). The ESP is:

$$ESP(\% \text{ of } CEC_e) = \frac{[\text{Na}^+]}{[\text{Ca}^{2+}] + [\text{Mg}^{2+}] + [\text{K}^+] + [\text{Na}^+]} \quad \text{Equation [2]}$$

Generally, physical soil properties such as hydraulic conductivity and aggregate stability are reduced as the ESP increases above 6% (Table 3). This however will depend greatly on the soil type, in particular the soil texture, and the salinity of the soil solution. Dispersion processes are confined to the clay fraction of the soil and therefore free-draining sandy soils with low clay content are at lesser risk of dispersion.

**Table 3. Critical limits for soil sodicity in relation to structural properties and clay dispersion (Cass 2002).**

Sodicity hazard	ESP	Soil structural stability
Non-sodic	0 to 6	Soil structure is generally stable
Sodic	6 to 15	Soil structure susceptible to damage by tillage and trafficking especially when wet
Very sodic	> 15	Soil structure may be damaged by tillage and trafficking and spontaneously by irrigation and rainfall (clay dispersion)

A high electrolyte concentration helps to flocculate soils with elevated ESP by compressing the thickness of the diffuse double layer (DDL), thereby mitigating adverse changes to the soil's hydraulic conductivity (Levy & Torrento 1995; Quirk 2001; Shainberg et al. 1981). The critical flocculation concentration (CFC) identifies a required electrolyte concentration associated with a given ESP that is necessary for maintaining soil permeability. This essentially describes the electrolyte concentration at which the thickness of the DDL is reduced beyond a critical level and therefore stabilises the clay domain. The CFC is often used when assessing the dispersion potential posed by particular irrigation waters (Curtin et al. 1994), and has been demonstrated in a number of studies to be strongly dependent on the exchangeable monovalent cation concentration (Quirk 2001; Rengasamy et al. 1984; Shainberg et al. 1981). Although it is possible to mitigate the effects of soil dispersion by raising soil EC, this will have a detrimental effect on vine growth and performance.

Cation selectivity co-efficients based on mass action law are frequently used to describe cation equilibria between exchangeable and solution phases based on knowledge of the SAR. The United States Salinity Laboratory (USSL) model (Richards 1954) for instance describes the relationship between SAR and ESP, and has subsequently been applied throughout the world to estimate soil ESP in a range of different soil types. In South Australia, guidelines relating to the application of winery wastewater to soil utilise the USSL SAR-ESP model (Richards 1954) to devise recommended SAR threshold values for the prevention of sodic conditions in irrigated soils (ANZECC & ARMCANZ 2000; South Australian EPA 2004). The graph in Figure 1 utilises the relationship between SAR of irrigation water (SAR) and ESP of the soil to predict the soil structural risk in relation to irrigation electrical conductivity (EC<sub>i</sub>).

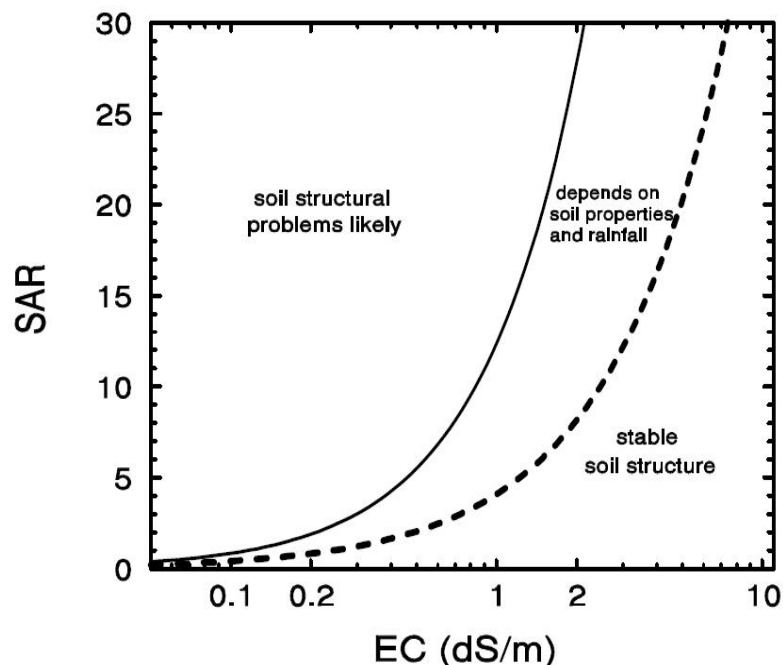


Figure 1. Relationship between irrigation sodium adsorption ratio (SAR<sub>i</sub>) and irrigation electrical conductivity (EC<sub>i</sub>) (ANZECC & ARMCANZ 2000).

The EC of winery wastewater ranges between 1.5 to 3.5 dS m<sup>-1</sup> (Table 1), and therefore soil structural problems are of concern only when SAR is above 20 (mmol<sub>c</sub> L<sup>-1</sup>)<sup>0.5</sup> (Figure 1). The soil dispersion risk in a Barossa chromosol soil, investigated by Laurenson (2010), is shown in Table 4 in relation to EC and SAR. When soil solution EC was higher than 3 dS m<sup>-1</sup> dispersed clay accounted for less than 1% of total clay content despite the SAR value (that ranged from 1 to 40 (mmol<sub>c</sub> L<sup>-1</sup>)<sup>0.5</sup>). At a SAR concentration of 1 (mmol<sub>c</sub> L<sup>-1</sup>)<sup>0.5</sup> dispersion was again < 1% even at the lowest EC (< 0.2 dS m<sup>-1</sup>). At SAR 5, the corresponding ESP of the soil was 7.8% at which point the onset of dispersion became apparent at an EC of < 0.2 dS m<sup>-1</sup>. Australian soils would be classified as sodic at an ESP above 6% (Northcote & Skene 1972) where they tend to show greater propensity to disperse upon wetting and exhibit hydraulic conductivity related issues (Rengasamy et al. 1984; Sumner 1995). However, at an EC of 0.62 dS m<sup>-1</sup> and SAR 5 dispersion was negligible. At higher SAR values, ESP is raised considerably and significantly greater EC is required to maintain flocculation of clays. At a SAR of 40 for instance, ESP is equivalent to approximately 35% of the total clay content and the CFC is greater than 1.30 dS m<sup>-1</sup>, at which point vine health would be severely affected (Cass 2002).

**Table 4. Clay dispersion risk in a Barossa chromosol soil equilibrated with solutions of known sodium adsorption ratio (SAR) and decreasing electrolyte concentration.**

SAR <sup>‡</sup>	ESP <sup>†</sup>	Electrical conductivity <sub>(1:5)</sub> (dS m <sup>-1</sup> )			
		< 0.2	0.2 – 0.65	0.65 – 1.30	1.3 – 3.0
1	2	LOW	LOW	LOW	LOW
5	8	HIGH	LOW	LOW	LOW
10	15	HIGH	MEDIUM	LOW	LOW
20	25	EXTREME	VERY HIGH	LOW	LOW
40	35	EXTREME	EXTREME	MEDIUM	LOW

Low = dispersed clay < 1% of total soil clay content

Medium = dispersed clay < 5% of total soil clay content

High = dispersed clay < 10% of total soil clay content

Very high = dispersed clay < 15% of total soil clay content

Extreme = dispersed clay > 15% of total clay soil clay content

<sup>‡</sup> SAR (sodium adsorption ratio) =  $Na^+ / (Ca^{2+} + Mg^{2+})^{0.5}$

Concentrations in mmol<sub>c</sub> L<sup>-1</sup>

ESP% (exchangeable potassium percentage) =  $[Na^+] / (CEC_e) \times 100$

## 6. Potassium in winery wastewater and its effect on soil structure

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The potassium adsorption ratio (PAR) describing the ratio of  $K^+$  to  $Ca^{2+}$  and  $Mg^{2+}$  (Equation 3) has been less widely adopted than SAR due to typically low amounts of  $K^+$  in most wastewaters. However, the PAR has shown to be an important first estimator of the soil dispersion hazard when  $K^+$  rich waters, such as piggery, meat processing and winery wastewaters, have been used for irrigation (Smith & Smiles 2004).

$$PAR (mmol_c L^{-1})^{0.5} = \frac{[K^+]/39}{\sqrt{[Ca^{2+}]/40 + [Mg^{2+}]/24}} \quad \text{Equation [3]}$$

Similar to ESP, the exchangeable  $K^+$  percentage (EPP) quantifies the exchangeable  $K^+$  cation comprising the soil CEC. Unlike  $Na^+$ , exchangeable  $K^+$  in soils is adsorbed by specific and non-specific binding, with the former being dependent on the soil clay mineral (Sawhney 1972). Illite and other mica clay minerals are particularly abundant in specific binding sites for  $K^+$  within their structural layers (Arienzo et al. 2009). Greater compaction between illite clay layers due to increased  $K^+$  adsorption can improve soil structural stability (Barré et al. 2008; Ravina & Markus 1975). In three South African soils however, Levy and van der Watt (1990) showed greater reduction in hydraulic conductivity in illite dominated clays relative to those dominated by kaolinite at EPPs less than 20%. Shainberg et al. (1987) however found no change in hydraulic conductivity of smectite clay with high charge density at an EPP of 20%, yet in low charge density smectite (montmorillonite) differences were evident at EPPs less than 15%. In Australia, limited research has investigated the behaviour of  $K^+$  in irrigation waters due to the relatively low  $K^+$  concentrations typical in most waters and soils.

$$EPP(\% \text{ of } CEC_e) = \frac{[K^+]}{[Ca^{2+}] + [Mg^{2+}] + [K^+] + [Na^+]} \quad \text{Equation [4]}$$

Potassium can impact on the structural stability of soils when EPP is high. Importantly however, when present in similar amounts, the relative effect of  $K^+$  on clay dispersion is less severe than  $Na^+$ . The dispersion of a Barossa heavy clay soil in response to an ESP or EPP of 40% is shown in Figure 2. Although dispersion is evident in both systems, dispersion is considerably greater at an ESP of 40% relative to an equivalent EPP.



**Figure 2. Clay dispersion in response to an exchangeable potassium percentage of 40% (right) or exchangeable sodium percentage of 40% (left).**

Clay dispersion reported by Laurenson (2010) was evident in soils equilibrated with PAR concentrations ranging from 1 to 40 ( $\text{mmol}_c \text{L}^{-1}$ )<sup>0.5</sup> when the electrolyte concentration was 10  $\text{mmol}_c \text{L}^{-1}$  or less and increased in response to increasing PAR concentration (Figure 2; Table 5). Although considerably less severe than the observed effect of  $\text{Na}^+$ , this indicates an effect of high  $\text{K}^+$  concentration on soil structure. As seen in Table 4, when the electrolyte concentration was beyond 0.65  $\text{dS m}^{-1}$ , no clay dispersion was evident regardless of solution PAR concentration. At an EC less than 0.2  $\text{dS m}^{-1}$ , the CFC (assuming negligible effect at < 1 % dispersed clay) was similar for PAR 1, 5 and 10 ( $\text{mmol}_c \text{L}^{-1}$ )<sup>0.5</sup>. For solutions of PAR 20 and 40 this was slightly higher at approximately 0.65  $\text{dS m}^{-1}$ .

**Table 5. Clay dispersion risk in a Barossa chromosol soil equilibrated with solutions of known potassium adsorption ratio (PAR) and decreasing electrolyte concentration (EC).**

PAR <sup>‡</sup>	EPP <sup>†</sup>	Electrical conductivity <sub>(1:5)</sub> ( $\text{dS m}^{-1}$ )			
		< 0.2	0.2 – 0.65	0.65 – 1.30	1.3 – 3.0
1	11	MEDIUM	LOW	LOW	LOW
5	24	HIGH	LOW	LOW	LOW
10	32	HIGH	LOW	LOW	LOW
20	39	VERY HIGH	MEDIUM	LOW	LOW
40	46	VERY HIGH	MEDIUM	LOW	LOW

Low = dispersed clay < 1% of total soil clay content

Medium = dispersed clay < 5% of total soil clay content

High = dispersed clay < 10% of total soil clay content

Very high = dispersed clay < 15% of total soil clay content

Extreme = dispersed clay > 15% of total soil clay content;

<sup>‡</sup> PAR (potassium adsorption ratio) =  $K^+ / (\text{Ca}^{2+} + \text{Mg}^{2+})^{0.5}$

Concentrations in  $\text{mmol}_c \text{L}^{-1}$

EPP % (exchangeable potassium percentage) =  $[K^+] / (\text{CEC}_e) \times 100$

## 6.1 Clay dispersion in response to potassium and sodium

The CFC for dispersion in a Na-Ca and K-Ca system reported by Laurenson (2010) as it relates to the electrical conductivity is shown in Figure 3. It is evident that the CFC increases with increasing SAR and PAR of the soil solution. As discussed by Laurenson (2010), greater binding affinity of  $K^+$  relative to  $Na^+$  results in higher EPP for a given PAR value relative to ESP at a corresponding SAR concentration. If the amount of dispersed clay relative to the ESP and EPP is considered, it is evident that at similar electrolyte concentrations, dispersion is far greater in the Na-Ca system relative to the K-Ca system.

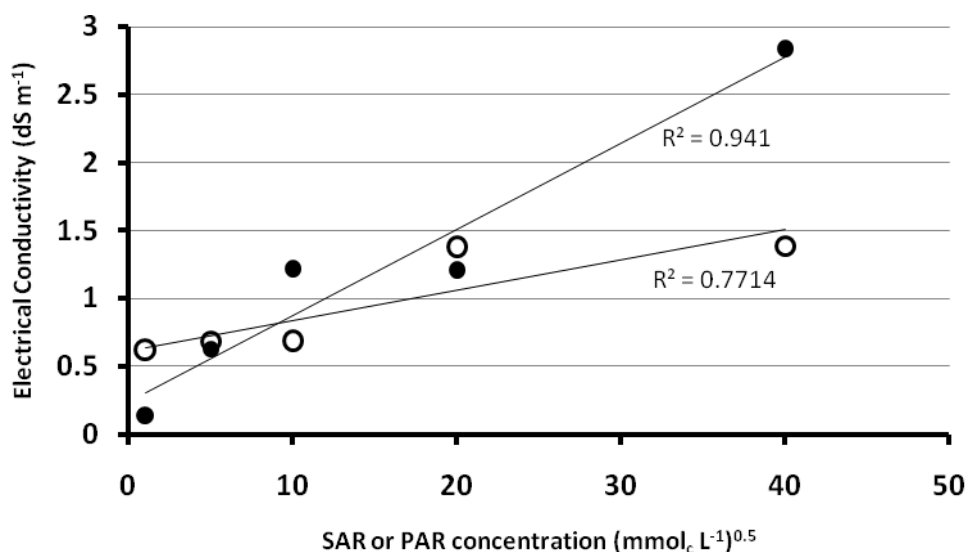


Figure 3. The critical flocculation concentration (CFC) required to prevent the dispersion of clay in a Barossa B horizon soil following equilibration with solutions of known SAR (●) and PAR (○) concentrations. Here, it is assumed dispersion below 1% of the total clay content is negligible (Curtin et al. 1994).

Grapevines are generally considered to be moderately tolerant of high soil salinity conditions (Cass et al. 2002). In soils with a high CFC, vine performance is likely to be affected at a salinity concentration lower than that required to maintain clay flocculation. In a Barossa chromosol soil irrigated with municipal wastewater high in  $Na^+$  and soil ESP of approximately 19% and EPP of 9%, Laurenson (2010) reported considerable clay dispersion (i.e. 50% of total clay dispersed) at a soil solution EC of  $1 \text{ dS m}^{-1}$  (EC determined on a 1:5 soil:water extract). Based on criteria provided by Cass et al. (2002), a severe decline (Table 6) in the performance of many grapevine cultivars, particularly those on own rootstocks, can be expected at a soil  $EC_{(1:5)}$  greater than  $1 \text{ dS m}^{-1}$ . Where winery wastewater was irrigated ESP and EPP were 11 and 19% respectively and clay dispersion was apparent only when soil solution EC decreased below  $0.4 \text{ dS m}^{-1}$ . The lower threshold point of clay dispersion reflects the lower ESP and the lesser effect of  $K^+$  on soil dispersion relative to  $Na^+$ . Most vine rootstock types are tolerant of salinity conditions of  $0.4 \text{ dS m}^{-1}$  and therefore clay flocculation can presumably be maintained without detrimental impact on vine performance (Cass 2002).

**Table 6. Criteria for soil salinity and potential yield reductions in vines (Cass 2002).**

Salinity hazard	Effects on grapevine growth	Electrical conductivity <sub>(1:5)</sub> (dS m <sup>-1</sup> )				
		Loamy sand	Loam	Sandy clay loam	Light clay	Heavy clay
Non-saline	Negligible effect on vines	<0.15	<0.17	<0.25	<0.30	<0.40
Slightly saline	Own-rooted vines start to be affected	0.16-0.30	0.18-0.35	0.26-0.45	0.31-0.60	0.41-0.80
Saline	Own rooted vines severely affected but some rootstocks are more tolerant	0.31-0.60	0.36-0.75	0.46-0.90	0.61-1.15	0.81-1.60
Very saline	Vines cannot be grown successfully	0.61-1.20	0.76-1.45	0.91-1.75	1.16-2.30	1.60-3.20
Highly saline	All grapevines will die	>1.20	>1.45	>1.75	>2.30	>3.20

## 7. Interaction of potassium and sodium in winery wastewater

The affinity of  $K^+$  to soils is substantially greater than  $Na^+$ , and when applied to soils in equal amounts  $K^+$  will bind preferentially. Potassium in winery wastewater can therefore be expected to increase the EPP of the soil following irrigation. Although  $Na^+$  will bind to soils, ESP will be lower for a given SAR especially in the presence of  $K^+$  due to its preferential binding.

Seasonal fluctuation in the Na:K ratio is likely to influence the subsequent retention of exchangeable  $Na^+$  in irrigated soils. The binding of  $Na^+$  and  $K^+$  in ternary Na-K-Ca systems was addressed by Laurenson (2010) using a combination of solutions with known SAR and PAR. It was demonstrated that soil ESP of a Barossa chromosol was substantially reduced in the presence of  $K^+$  (Figure 4) and was increasingly lowered at higher  $K^+$  concentrations. This suggests the sodicity risk associated with winery wastewater irrigation may be less during vintage periods when the  $K^+$  concentration increases.

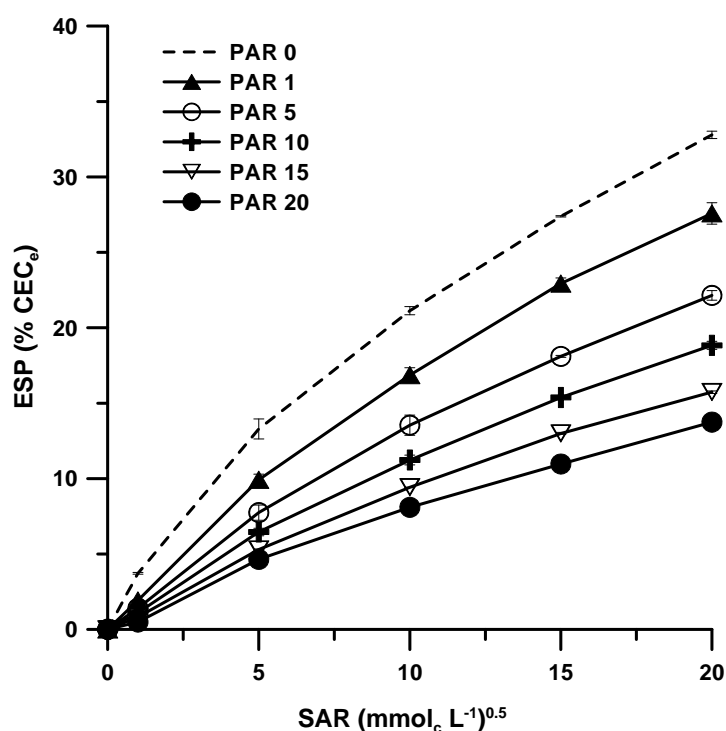


Figure 4. Exchangeable sodium percentage (ESP) measured at varying sodium adsorption ratio (SAR) values in the presence of increasing potassium adsorption ratio (PAR) values in a ternary system (Na-K-Ca). At PAR 0, the ESP-SAR relationship is described by the binary system (Na-Ca). Vertical error bars describing the standard deviation in SAR between replicates are generally smaller than the marker symbols.

When wastewaters, containing both a high concentration of  $\text{Na}^+$  and  $\text{K}^+$  as in the case of winery wastewater, are irrigated to soils, interactions between cations need consideration when predicting the resulting impact on soil physical properties. In soils irrigated with winery wastewater, the relationship between SAR and ESP is moderated due to the higher  $\text{K}^+$  affinity, in particularly at high  $\text{K}^+$  concentrations. It is expected therefore that soil ESP will be lower than predicted from the commonly used USSL SAR-ESP model (Richards 1954) when winery wastewater is used for irrigation. The risk of clay dispersion in response to soil ESP in the presence of  $\text{K}^+$  is provided in Figure 5.

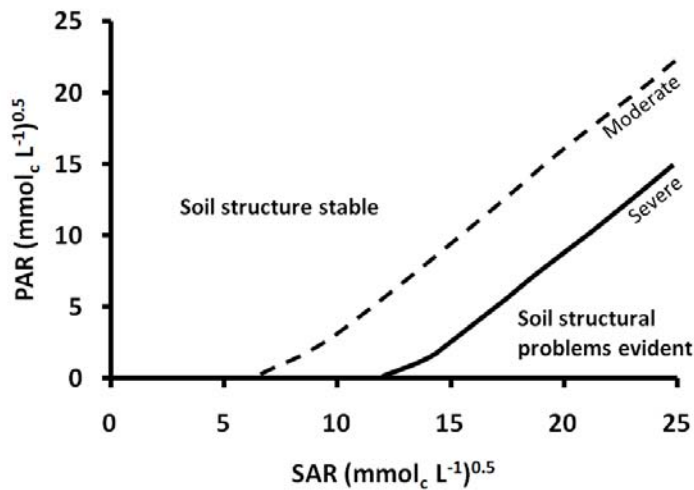


Figure 5. Clay dispersion risk in a Barossa chromosol soil when both the sodium adsorption ratio (SAR) and potassium adsorption ratio (PAR) in winery wastewater are considered and assuming optimal soil EC ( $0.65 \text{ dS m}^{-1}$ ) for plant growth in a heavy clay soil. Moderate and severe soil structural problems correspond to greater than 5 and 10 % s of total clay dispersed respectively.

## 8. Amelioration of soils with high exchangeable sodium and potassium percentage

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The reclamation of saline soils is generally achieved through the leaching of salts down the soil profile (Stevens 2002). Guidelines are typically used by viticulturalists to calculate the volume of water application necessary to achieve a certain reduction in salinity (ANZECC & ARMCANZ 2000). To alleviate sodic conditions in soils, a consideration of both water flow and chemical factors are required (Suarez 2001). Typically this involves:

- application of a required amount of  $\text{Ca}^{2+}$  in amendments/compounds such as gypsum ( $\text{CaSO}_4$ ) and lime ( $\text{CaCO}_3$ ) in order to replace exchangeable  $\text{Na}^+$  and reduce the ESP below approximately 6% (Chun et al. 2007; Graber et al. 2006; Grant et al. 1992; Hamza & Anderson 2003; Rengasamy & Olsson 1993)
- subsequent removal of monovalent cations such as  $\text{Na}^+$  and  $\text{K}^+$  through leaching with irrigation or rainfall (i.e. leaching fraction).

Calcium amendments such as calcite lime and dolomite generally result in a change in soil pH (Bolan & Hedley 2003; Bolan et al. 2003). Where there is pH-dependant charge, this is usually associated with an increase in cation exchange capacity and retention of  $\text{Ca}^{2+}$  thereby limiting movement of  $\text{Ca}^{2+}$  to lower depths in the soil profile (Greene & Ford 1985; McLay et al. 1994). Gypsum has little influence on soil pH, and in South Australia is likely to be more effective than other  $\text{Ca}^{2+}$  amendments such as lime, due to its greater ability to migrate to depth in the soil profile where clay content and monovalent cation retention tends to be greater (McIntyre et al. 1982; McLay et al. 1994). Interestingly, in a Vertisol soil irrigated with municipal wastewater, Hulugalle et al. (2006) report a reduction in exchangeable  $\text{Ca}^{2+}$  and increased clay dispersion under gypsum application relative to non-amended soils. These authors speculate this to be associated with inferior gypsum quality (i.e. containing high carbonate content that subsequently precipitates  $\text{Ca}^{2+}$ , as in the case of lime) and insufficient application rates relative to the  $\text{Na}^+$  loading under wastewater.

The rate of  $\text{K}^+$  leaching in soils is generally low and the potential for  $\text{K}^+$  to accumulate is therefore high (Arienzo et al. 2009). Although a number of studies have examined the value of gypsum to ameliorate high exchangeable  $\text{Na}^+$  in soils, its value in ameliorating high exchangeable  $\text{K}^+$  has not been widely documented. Using intact soil columns, Jalali and Rowell (2009) showed that gypsum was effective in displacing exchangeable  $\text{K}^+$  in a British sandy loam soil. In soils irrigated with piggery effluent, Smiles and Smith (2008) were able to reduce the exchangeable  $\text{K}^+$  concentration with surface applications of gypsum. Efficiency of gypsum amelioration will however be dependent on the ability of gypsum applied  $\text{Ca}^{2+}$  to penetrate soil aggregates (Smiles & Smith 2008).

The role of gypsum in raising soil solution EC and suppressing clay dispersion has been shown to improve soil-water infiltration of both sodic and non-sodic soils, particularly during rainfall cycles when soil EC tends to decline most significantly (Greene & Ford 1985; Suarez et al. 2008; Sumner 1995; Sumner et al. 1990).

Maintaining soil hydraulic conductivity will help facilitate percolation of water required to leach salts under field conditions, thereby overcoming the build-up in salinity that may otherwise occur under regular application of municipal and winery wastewater.

## 9. Influence of rainfall on soil dispersion

A reduction of the soil electrolyte concentration is likely to occur during rainfall periods or when soils are leached with comparatively good quality water (Suarez et al. 2008). In soils pre-treated with SAR solutions of 5 and 10 ( $\text{mmol}_c \text{L}^{-1}$ )<sup>0.5</sup>, Shainberg et al. (1981) reported a 10% and 20% reduction in hydraulic conductivity following application of deionised water. In two soil types, Suarez et al. (2006) demonstrated that irrigating with waters of SAR < 4 ( $\text{mmol}_c \text{L}^{-1}$ )<sup>0.5</sup> impacted on infiltration rates only when soil solution EC was drastically reduced during winter rainfall.

To some extent, the soil structural hazard associated with high exchangeable monovalent cation concentrations is likely to be greater in areas of high winter rainfall relative to areas of comparatively lower rainfall (Suarez et al. 2006). Where low rainfall prevents the leaching of salts, the adverse effects of monovalent cations on soil structure may be masked until salts are removed by greater rainfall volumes or when the irrigation source is replaced with waters of lower EC. In the Barossa Valley for instance, Na<sup>+</sup> related changes to soil hydraulic conductivity were prevalent only when bore water of high salinity was replaced by moderately saline water from the Murray River, whereby soil EC was reduced dramatically (Clark 2004). Winter application of gypsum to soils receiving wastewater can maintain a high soil EC to minimise the effect of rainfall dilution. A conceptual diagram describing the principal processes occurring under winery wastewater irrigation is shown in Figures 6 and 7.

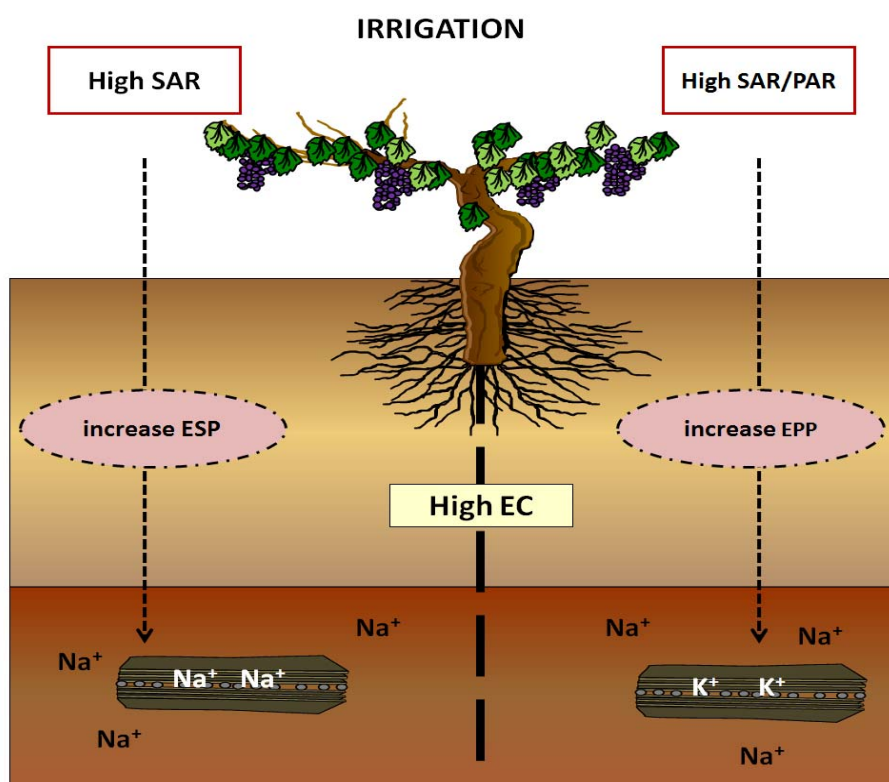
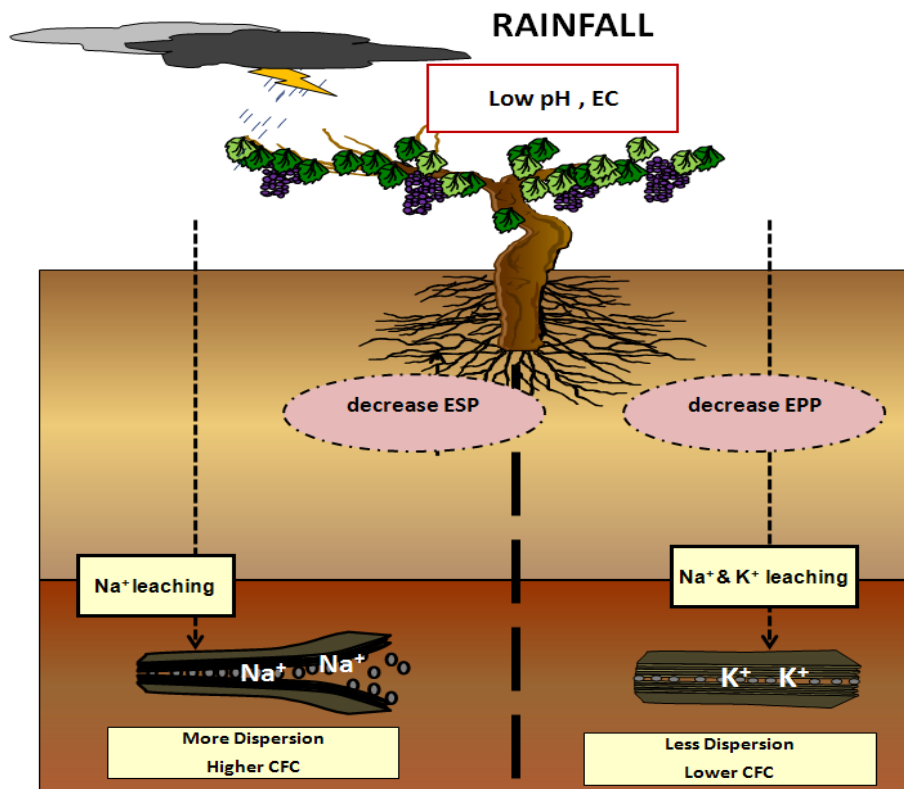


Figure 6. Schematic diagram showing the fate of Na<sup>+</sup> and K<sup>+</sup> in soils irrigated with wastewaters with high SAR and with high SAR and PAR.



**Figure 7. Effect of rainfall on the dispersion of soils irrigated with wastewaters with high SAR and with high SAR and PAR.**

In summer, high evapotranspiration rates concentrate the salt content in soils irrigated with winery wastewater. This in turn causes the SAR and PAR of the soil solution to increase. Where the SAR of the wastewater is high a subsequent increase in ESP will occur. When the PAR of the wastewater is high the retention of Na<sup>+</sup> is limited by the presence of K<sup>+</sup> and therefore only EPP increases. The high EC of winery wastewater and municipal wastewater enables soils to remain flocculated in both cases during irrigation.

During winter, a rapid decline in soil solution pH causes the dissolution of CaCO<sub>3</sub> and MgCO<sub>3</sub> precipitates. This in turn increases the EC of the drainage water from the 'A' horizon into the 'B' horizon. Monovalent cations displaced by divalent cations in the 'A' horizon are leached into the 'B' horizon. Soils with high EPP (i.e. under winery wastewater irrigation) require lower EC concentrations to maintain a state of flocculation relative to soils with high ESP (i.e. those irrigated with municipal wastewater). Higher drainage EC from soils irrigated with winery wastewater prevents dispersion of the 'B' horizon soils. Due to the higher accumulation of exchangeable Na<sup>+</sup> under municipal wastewater and greater dispersive potential of Na<sup>+</sup> relative to K<sup>+</sup>, the EC of the soil drainage is not sufficient to prevent soil dispersion during winter rainfall. Application of gypsum (not shown in this Figure) therefore is of greater necessity to maintain a higher EC.

## 10. Effect of potassium on vine performance

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Potassium is thought to be closely involved in the translocation of sucrose and other assimilates from vines to ripening fruit, and is important in balancing berry pH through exchange with hydrogen ions ( $H^+$ ) of malic and tartaric acids (Mpelasoka et al. 2003; Ruhl 1989). An excessive  $K^+$  level in fruit has a negative impact on wine quality through the formation of insoluble potassium bitartrate that decreases the available tartaric acid content. A lack of titratable acids causes berry pH to increase (Mpelasoka et al. 2003). In cool climates this may be beneficial, however in hot climates such as South Australia, wines with high pH typically have a flat taste and red wines have an undesirable brownish hue (Gladstones 1992; Ruhl 1989).

Although there is strong correlation between grape juice pH and  $K^+$  concentration, the association between  $K^+$  concentration of the berry and soil  $K^+$  supply is less certain. Boulton (1980), for instance, suggested that soil exchangeable  $K^+$  status has no direct bearing on berry  $K^+$  status, while other researchers such as Ruhl et al. (1989) and Garcia et al. (1999) identified a link between  $K^+$  supply and berry  $K^+$  concentration. Despite this, where vines have been irrigated with wastewaters rich in  $K^+$ , increased petiole- $K^+$  concentrations have been reported (Klein et al. 2000; McCarthy 1981; Neilsen et al. 1989; Paranychianakis et al. 2006). Deficiencies in  $Ca^{2+}$  and  $Mg^{2+}$  have been reported in rye grass pastures irrigated with wastewaters rich in  $K^+$  (Bolan et al. 2004; Laurenson et al. 2008). A decline in petiole- $K^+$  content was however reported by McCarthy (1981) in vines irrigated with municipal wastewater, although this was associated with greater  $Na^+$  uptake. To date however, the fate of  $K^+$  in soils and vines irrigated with winery wastewater has received limited attention.

Increased uptake of  $Na^+$  at the expense of  $Ca^{2+}$  and  $Mg^{2+}$  has also lead to nutrient deficiencies in vines (Grattan & Grieve 1998). The presence of  $Na^+$  in wine grapes can severely affect wine quality by lowering wine pH and increasing the abundance of undesirable phenolic compounds in white wine varieties (White 2003). Although in Australia there is currently no defined maximum limit for  $Na^+$  concentration in wines, concentrations are generally maintained below  $80 \text{ mg L}^{-1}$  in order to protect trade agreements set for Australian wines exported into the European Economic Community (OIV 2010; Walker et al. 1998).

In a study involving 1214 Australian grape juices (crushed grapes prior to fermentation), Leske et al. (1997) reported an average  $Na^+$  content of  $55 \text{ mg L}^{-1}$ . Although it is possible this may increase where municipal and winery wastewater is irrigated, root stock selection is likely to have an important role in mitigating excess  $Na^+$  uptake (Stevens 2009). Grafted rootstock types widely used in Australia for  $Na^+$  exclusion have, however, been found to enhance  $K^+$  uptake (Ruhl 1990), and may result in excessive grape  $K^+$  concentrations where winery wastewater is irrigated.

## 11. Conclusions

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This research has addressed concerns raised by growers over the long-term sustainability of irrigating with winery wastewater. From a soil structural viewpoint, quality of the wastewater, in particular the concentration of monovalent cations relative to divalent cations, is important when assessing suitability for irrigation use. A higher  $\text{Na}^+$  concentration in wastewater heightens the risk posed to soil structural degradation and will require a commitment to ongoing  $\text{Ca}^{2+}$  amendments such as gypsum or lime.

The use of winery wastewater introduces a considerable amount of  $\text{K}^+$  into the soil that is likely to cause soil ESP and EPP to increase. The retention of  $\text{K}^+$  in soils is far greater than for  $\text{Na}^+$  and therefore greater accumulation is likely. Despite the greater retention of  $\text{K}^+$ , dispersion will be considerably less than for  $\text{Na}^+$  and poses limited risk to soil structure until the EPP exceeds approximately 20% and EC decreases below  $0.4 \text{ dS m}^{-1}$ . The dissolution of carbonates and the high mobility of  $\text{K}^+$  in winter rainfall, however, is likely to maintain a sufficient solution EC and low EPP to prevent soil dispersion. The binding affinity of  $\text{Na}^+$  is lower in the presence of  $\text{K}^+$  and, therefore  $\text{K}^+$  in winery wastewater may in fact have an ameliorative role by preventing the retention of  $\text{Na}^+$  ions that are present in greater concentrations in this water source.

Given the lower clay content of sandy soils impacts of wastewater irrigation on soil structure of these soils are of limited concern. When wastewaters are irrigated to soils with high clay content, a higher amount of monovalent cations is retained. Under field conditions the continual evaporation of soil water may increase the ESP and EPP over time, thereby affecting soil structure.

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Established and supported  
under the Australian Government's  
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