Winery wastewater Irrigation

The effect of sodium and potassium on soil structure

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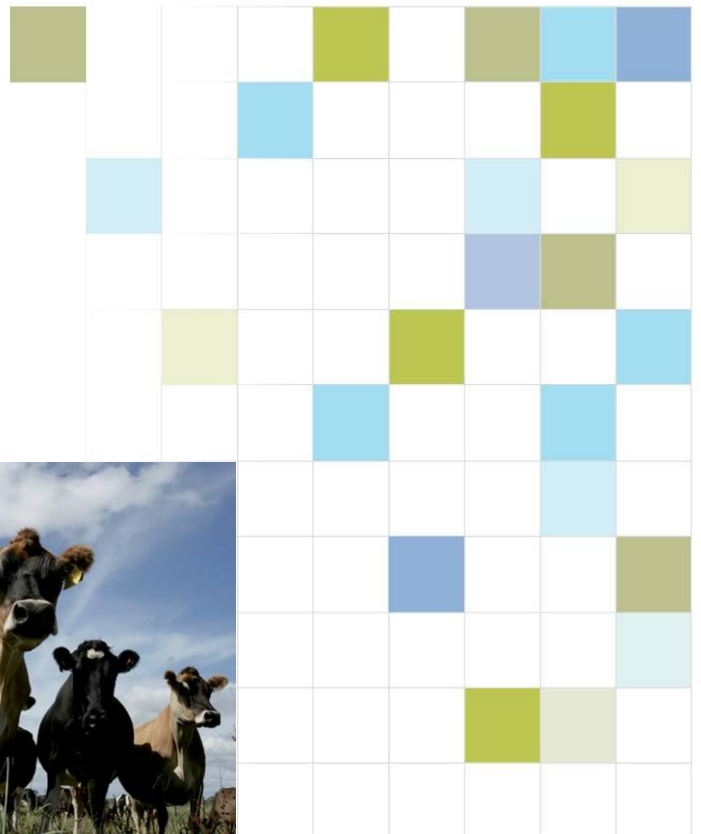
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Winery wastewater Irrigation- the effect of sodium and potassium on soil structure

Prepared for Marlborough District Council

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1.   Executive Summary

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 surface water quality associated with surface water discharge. A major agricultural concern however, is the potential for monovalent cations, namely sodium (Na^+) and potassium (K^+) to accumulate in the soil profile and subsequently impact on soil structure.

Best management practice for managing nutrients in many wastewaters, for instance farm dairy effluent, generally focuses on reducing leaching and runoff losses thereby retaining constituents, such as nitrogen (N) and phosphorus (P), within the soil profile where they are assimilated into plant growth. Although there is a need to manage high N concentrations in winery wastewater, particularly during vintage when concentrations peak, Marlborough District Council require loading to be maintained below 200 kg N ha yr^{-1} as stipulated by the Resource Consent. The assimilation of Na^+ by plants is however low and the best management approach to mitigate the potential effects of high soil Na^+ concentrations is to leach this salt down the soil profile. Plant K^+ requirements are generally high i.e. similar to N, however, high loadings typical under winery wastewater (i.e. 600 kg K^+ ha^{-1} yr^{-1}) far exceed plant requirements. Although the relative effect of K^+ on soil structure is less than that of Na^+, an excess in the soil profile can contribute to a decline in soil structure.

In many regions Na^+ and 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 slowly, 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 (i.e. fine textured clay dominated soils) maintaining a sodium adsorption ratio (SAR) of winery wastewater below 6 ($mmol_c$ $L^{-1})^{0.5}$ and potassium adsorption ratio (PAR) below 10 ($mmol_c$ $L^{-1})^{0.5}$ is likely to prevent adverse soil structural changes [N.B. assumes electrical conductivity (EC) of winery wastewater is approximately 1 dS m^{-1}].

There is a close relationship between winery wastewater EC and soil dispersion, whereby adverse changes to soil structure under high net loading of salts is mitigated at higher EC. It is valuable therefore to include measurement of winery wastewater EC in routine analysis. Routine use of calcium (Ca^{2+}) amendments including, yet not restricted

to, lime, gypsum and calcium nitrate either added directly to wastewater or to soils will enable Ca^{2+} exchange and displacement of Na^+ and K^+. Winter application of Ca^{2+} amendments will ensure its percolation down the soil profile thereby ensuring good distribution of Ca^{2+} and raising soil EC that is otherwise lowered under rainfall.

Given the lesser effect of K^+ on soil structure relative to 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 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, temporarily high hydraulic loading rates may be acceptable. Importantly however, 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. In many instances, however, this is likely to require considerably greater land area to that currently being utilised. With adequate management however, i.e. prevention of high ESP and EPP during consecutive seasons, the risk of soil dispersion can be mitigated.

2. Introduction

Rapid expansion of the viticultural industry in Marlborough has lead to an increase in wine production from 80 000 m^3 in 2000 to 285 000m^3 in 2009 (New Zealand Wine Growers 2009). Increased production has been coupled with the generation of significantly larger volumes of winery wastewater, an unavoidable component of the wine production process. In New Zealand, approximately 7.5 L of winery wastewater is produced per 750 mL bottle of wine (Gabzdylova *et al.* 2009) which equates to approximately 380 000 m^3 of winery wastewater annually. The wine industry and regional authorities are increasingly focusing on land application of winery wastewater as the most cost effective and environmentally sound means of disposal. This form of disposal does, however, raise concern over potential impacts on soil and crop health, and off-site environmental pollution associated with nutrient leaching and run-off. When the chemical composition of winery wastewater is deemed unsuitable for irrigating to soils, wastewater treatment facilities may require up-grading 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 (WWTP's) or collective facilities handling wastewater from a number of wineries can be a suitable alternative.

In Australia, winery wastewater has, in many regions, been successfully integrated into irrigation management (Stevens 2009). In New Zealand however, application of winery wastewater to land has not been a major focus of national water management strategies and has generally been treated via municipal waste streams and subsequently discharged to ocean. Precise estimates of quantity and quality of wastewater supply in the wine industry, their potential value as an irrigation source and expected adverse effect associated with their uncontrolled use/disposal are not well established. This, in part, reflects the abundance of fresh water in New Zealand and the lower volumes of winery wastewater generated.

Generally irrigating with winery wastewater accounts for a considerably greater salt loading than would be expected under more conventionally used water sources i.e. river and ground waters. A major agricultural concern is the potential for monovalent cations, namely Na^+ and K^+ to accumulate in the soil profile and subsequently impact on soil structure. A progressive decline in soil physical health would certainly undermine any eco-efficient benefit gained from applying wastewater to land as oppose to surface water discharge (Cameron *et al.* 1997).

3.   The Marlborough Grape growing region

Marlborough is the largest grape producing region of New Zealand. It has a Mediterranean climate where summers are usually hot and dry while winters tend to be wet. The average rainfall is 656 mm (Figure 1) with the majority (60 %) falling between May to October. Average annual evaporation (2004-10) is 1020 mm and exceeds the rate of precipitation during summer months thereby resulting in soil moisture deficits.
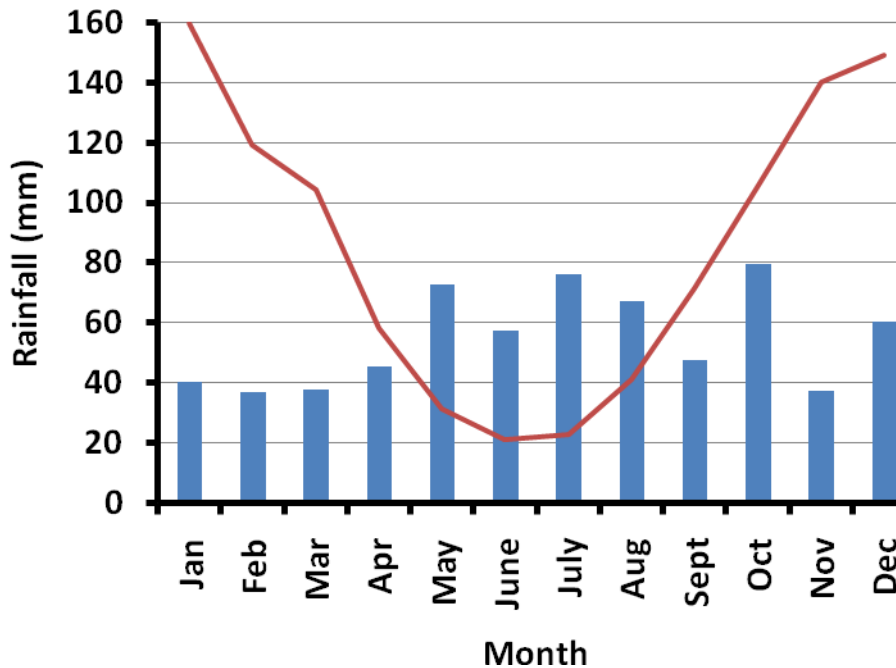

Figure 1. Monthly average rainfall (2004-2010) and evaporation measured at the NIWA Research Station in Blenheim. Monthly evaporation has been calculated using the Penmann-Monteith equation.

4.   Chemical composition of winery wastewater

The composition of winery wastewater varies considerably between wineries due to the waste stream and treatment process adopted and may require a management approach that is site specific when irrigated to land. In general, winery wastewater contains high salt concentrations (Table 1) thereby accounting for a considerably greater salt loading relative to irrigating with river, ground or mains supply (i.e. town) water. Specific ions, in particular Na^+ and K^+, originating from cleaning products, grape lees and spent juice may also have confounding effect on soils beyond that imposed by salinity alone. A high concentration of either Na^+ or K^+ in irrigated waters is undesirable and when continually applied to soils can displace more desirable cations (i.e. Ca^{2+} and magnesium (Mg^{2+}))

from the soil exchange complex (Bond, 1998; Pils et al. 2007) thereby raising the potential for adverse changes to the structure of the soil to occur. This chemically driven process of soil structural decline differs from those physical processes often reported under cattle grazing or heavy traffic (Houlbrooke et al. 2010). Generally, physical stress to soils results in a reduction of large macropores responsible for the rapid drainage of water and transmission of air. Chemical dispersion, however, tends to reduce the size and distribution of smaller meso- and micropores. The influence of mechanical stress on overall soil structure will, however, be exacerbated in soils with high monovalent cation composition.

The K^+ concentration in final wastewater varies depending on winery size, treatment process and season but generally is in the range of 150 to 410 mg L^{-1} during vintage periods (Arienzo et al. 2009). The effect of exchangeable Na^+ on soil structure has been widely publicised and in efforts to mitigate sodic conditions in soils, there has been a recent trend towards using potassium hydroxide (KOH) in replace of sodium hydroxide (NaOH) for cleaning and sterilisation purposes; this does of course raise the K^+ concentration in the final waste stream.

The presence of either ion in wastewaters can be described by the sodium adsorption ratio (SAR) (Equation 1) or potassium adsorption ratio (PAR) (Equation 2). These equations describe the molar ratio relationship between Na^+ or K^+ and di-valent cations, Mg^{2+} and Ca^{2+}, where concentrations of cations are expressed as mmol$_c$ L^{-1}.

$$SAR\ (mmol_c\ L^{-1})^{0.5} = \frac{[Na^+]}{\sqrt{[Ca^{2+}] + [Mg^{2+}]}} \tag{1}$$

$$PAR\ (mmol_c\ L^{-1})^{0.5} = \frac{[K^+]}{\sqrt{[Ca^{2+}] + [Mg^{2+}]}} \tag{2}$$

The SAR is a proven and widely adopted indicator for assessing the eventuating exchangeable Na^+ concentration in soils irrigated with a particular water source. The PAR has been less widely adopted due to typically low amounts of K^+ in most wastewaters. The PAR has, however, been shown to be an important first estimator when assessing the risk of soil dispersion posed by wastewaters of high K^+ concentration, such as piggery, meat processing and winery wastewaters, following irrigation (Smiles & Smith 2004).

Table 1. Chemical composition of winery wastewater from a number of different locations across Marlborough between 1996 to 2009.

Constituent	Average	Range
pH	5.2	(3.8 – 7.3)
	mg L^{-1}	
Na$^+$	120.2	(5.7 – 430.0)
K$^+$	179.1	(28 – 410)
Mg^{2+}	3.6	(1.8 – 5.8)
Ca^{2+}	21.4	(11.0 – 72.0)
	(mmol$_c$ L^{-1})$^{0.5}$	
SAR	5.9	(0.5 – 24.5)
PAR	6.4	(1.2 – 15.4)

Data supplied by Marlborough District Council. Figures represent average values collected from approximately six vineyards as part of routine monitoring conducted on an annual basis between 1996 and 2009.

5. Monovalent cation accumulation and soil structure

Structural attributes that promote soil aeration and water movement generally result in well developed crop roots and adequate water infiltration rates that allow for the amelioration of wastewater constituents (Houlbrooke et al. 2010). Greater soil bulk densities, associated with lower macroporosity, can however restrict the movement of air and water in the soil and lead to poor root growth and/or surface water run-off (Houlbrooke et al. 2010).

The relative effect of exchangeable Na$^+$ on soil structure has been widely documented (e.g. Halliwell et al. 2001) and, in soil, is often described by the exchangeable Na$^+$ percentage (ESP) that quantifies exchangeable Na$^+$ in relation to the cation exchange capacity (CEC) of the soil (i.e. ESP % = [Na$^+$] / (CEC) x 100). A soil is generally termed sodic when the ESP in the top 1 m of soil is greater than 6% (Sumner 1995). Often a decline in hydraulic conductivity is observed with increasing ESP beyond 6%, Menneer et al. (2001) for instance reported a 30 % decline in hydraulic conductivity of a silt loam soil irrigated with dairy factory effluent following an increase in ESP from 1 to 6%. Levy et al. (1988) also demonstrated a decline in infiltration rate by as much as 70% where ESP in repacked soil columns increased above 6%. This results from the dispersion of soils and the downward migration of clay particles that subsequently clog soil pores and

reduce hydraulic conductivity through the irreversible sealing of pore spaces (Levy et al. 1993; Shainberg et al. 1981; Shainberg et al. 1987b; Sumner 1995; Warrington et al. 2007).

Relative to Na^+, the influence of K^+ ions on soil structure is less widely documented (Levy & Torrento 1995). In New Zealand, limited research has investigated the behaviour of K^+ in irrigation waters due to the relatively low concentrations typical in most waters (Arienzo et al. 2009). Generally, dispersion is more pronounced in soils with high exchangeable Na^+ (Figure 2) due to the larger hydrated radius of Na^+ ions relative to K^+ ions (Chen et al. 1983; Levy and Torrento 1995; Rengasamy 2002). Similar to ESP, the exchangeable K^+ percentage (EPP) quantifies the exchangeable K^+ cation comprising the soil CEC (i.e. EPP % = $[K^+]$ / (CEC) x 100).

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

Levy and Torrento (1995) report soils with an EPP of 17% remained flocculated while those with an ESP of approximately 5% dispersed. Quirk and Schofield (1955), however, reported that exchangeable K^+ had an equally deleterious effect on soil structure and hydraulic conductivity to that of Na^+. In two Israeli soils, Chen et al. (1983) reported an improvement in hydraulic conductivity at EPP less than 20% due to a displacement of exchangeable Na^+ and subsequent lowering of the ESP. Notable differences in the relative effect of cations on soil structure were however evident between soils of differing clay mineralogy. Soils of higher illite content are more susceptible to dispersion under high K^+ loading due to specific binding and weaker attractive forces between clay platelets relative to clays with greater charge density include smectite. Brown soils generally contain illite clay minerals, however generally these are limited to the rolling hill slopes of the Marlborough region and are unlikely to be irrigated with winery wastewater (due to slope suitability for receiving wastewater).

Recent and Pallic soils, along the Awatere and Wairua River Valleys, are usually dominated by illite clay mineralogy and therefore may be more susceptible to K^+-induced dispersion. Careful monitoring of exchangeable K^+ concentrations is recommended particularly in slowly drained Pallic soils.

Figure 3 shows the relationship between SAR or PAR of winery wastewater and the resulting ESP or EPP in the soil following irrigation.
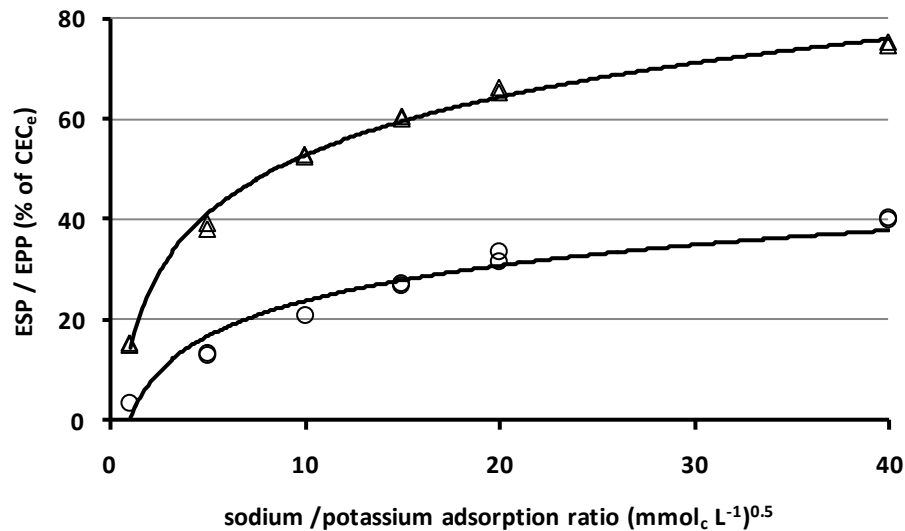

Figure 3. Soil exchangeable sodium percentage (ESP) (○) and exchangeable potassium percentage (EPP) (Δ) following equilibration with solutions of varying sodium adsorption ratio (SAR) or potassium adsorption ratio (PAR).

6.   Influence of salinity on clay dispersion

The salt content of winery wastewater is usually determined by measurement of electrical conductivity (EC) and is of interest in relation to soil structure and plant growth. Maintaining high salinity in the soil pore-water helps to flocculate clays with high ESP and EPP thereby mitigating adverse changes to the soil's hydraulic conductivity (Levy and Torrento 1995; Quirk 2001; Shainberg et al. 1981). The critical flocculation concentration (CFC) identifies a required salt concentration associated with a given ESP or EPP that is necessary for maintaining soil permeability. The CFC is often used when assessing the dispersion potential posed by particular irrigation waters (Curtin et al. 1994a), and has been demonstrated in a number of studies to be strongly dependent on the exchangeable monovalent cation type and concentration (Quirk 2001; Rengasamy et al. 1984; Shainberg et al. 1981). Essentially, soils irrigated with waters high in salt can sustain a higher ESP or EPP before changes in clay structure occur. Due to the

comparatively lesser effect of K^+ on soil dispersion, a lower EC is required to maintain clay flocculation relative to Na^+.

The general relationship between EC and the SAR or PAR of irrigation water equilibrating a soil is shown in Figure 4. This has been determined in a Barossa Chromosol soil from South Australia equilibrated with a range of solutions of varying SAR or PAR and then clay dispersion measured.
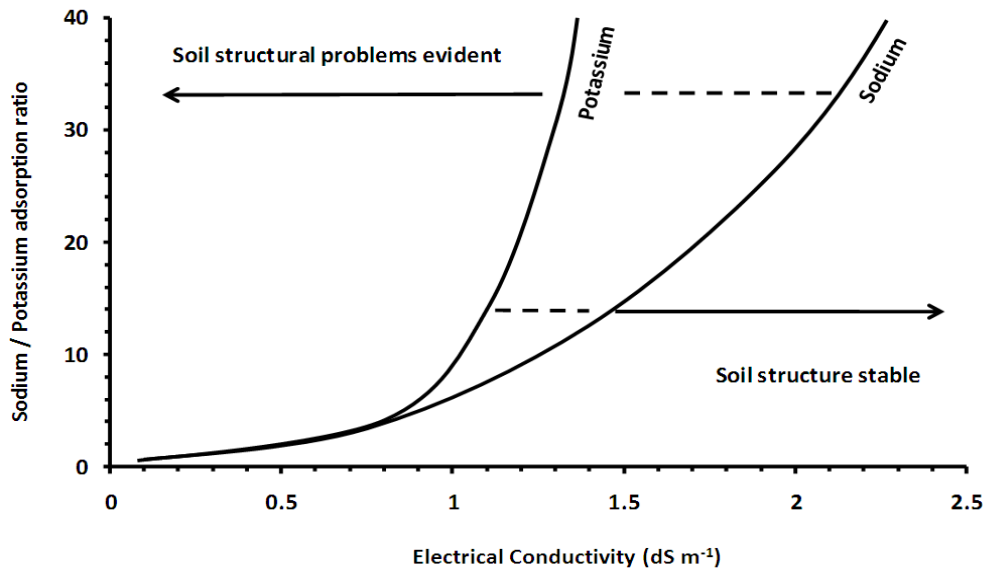

Figure 4. General relationship between irrigation sodium or potassium adsorption ratio (SAR or PAR) and irrigation electrical conductivity (EC) as determined by Laurenson (2010) on a Barossa Chromosol.

The EC of winery wastewater is not routinely monitored in New Zealand, however, in Australia EC ranges from 1.0 to 3.5 dS m^{-1} (ANZECC and ARMCANZ 2000). At the lower end of this range (i.e. 1.0 dS m^{-1}) dispersion of clays becomes apparent only when the SAR or PAR exceeds approximately 6 and 10 respectively; however this will be further complicated by clay content and EC of the soil and the rate of water percolation during summer and winter.

7.   Binding affinity of Na^+ and K^+ in soils

As shown in figure 3, soil affinity for K^+ is considerably greater than for Na^+ and therefore when applied at equal concentrations, exchangeable K^+ increases to a greater extent (Laurenson 2010; Levy & Feigenbaum 1996). Investigating the influence of differing PAR values on Na^+ binding, Levy and Feigenbaum (1996) showed that in the presence of K^+ the binding of Na^+ was substantially reduced, yet at similar

concentrations, Na^+ had no effect on K^+ binding. This essentially implies a preferential binding of K^+ over Na^+. In soils irrigated with winery wastewater, the retention of Na^+ is moderated by greater soil affinity for K^+ over Na^+. A generalised clay dispersion risk criteria, in response to various combinations of SAR and PAR in wastewaters is provided (Figure 5). Again, this data has been comprised by equilibrating a Barossa Chromosol soil with a range of solutions of differing SAR and PAR ratios under a constant EC of 0.65 dS m^{-1} that is suitable for plant growth (Laurenson 2010).

During vintage when K^+ concentration in winery wastewater is at its highest, the sodicity risk associated with winery wastewater irrigation is likely to be less. Given the comparatively greater effect of Na^+ on soil dispersion, the presence of K^+ and its subsequent influence on Na^+ leaching appears advantageous relative to when wastewaters of high in Na^+ only are irrigated. Subsequently a shift from Na^+-based cleaning agents to K^+-based products may be of merit.
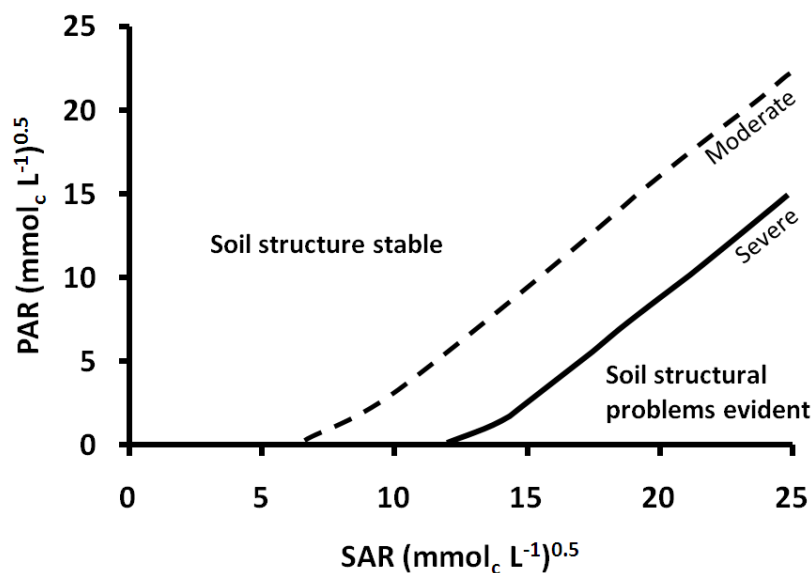

Figure 5.   Clay dispersion risk in a Barossa Chromosol soil when both the sodium adsorption ratio (SAR) and potassium adsorption ratio (PAR) in winery wastewater are considered and assuming optimal soil EC (0.65 dS m^{-1}) for plant growth in a heavy clay soil.

8.   Water movement in the soil profile

Soil texture has a strong influence on water percolation. Coarse textured soils with high porosity are generally well drained and when irrigated, water tends to move more vertically than in finer textured soils with higher clay content. This results in a piston-flow effect whereby irrigation input at the soil surface displaces and drains water situated deeper in the soil profile and in doing so leaches solutes including Na+ and K+ down the soil profile. Soils with high clay content generally have lower rates of hydraulic

conductivity and greater water holding capacities. The distribution of irrigation water in these finer textured soils is also less than more coarse textured soils, therefore at a single location in the soil profile where winery wastewater has been applied, the concentration of constituents tends to be greater. In addition to the water distribution characteristics of finer textured soils, greater clay content also increases the likelihood of soil dispersion relative to sand-dominated coarse textured soils.

During the Marlborough summer, high rates of evaporation and low rainfall are likely to concentrate the salt content of the soil, particularly in fine textured soils. This essentially raises the SAR or PAR in the soil solution and subsequent ESP or EPP. Wastewater applied during summer may therefore increase in concentration prior to the occurrence of winter rainfall. As shown in figure 3, the effect of SAR and PAR on soil dispersion is closely related to EC. A sudden decrease in soil solution EC during the onset of winter rainfall may result in soil dispersion if Na^+, and to a lesser extent K^+, has built up to a critical level during summer irrigation. In coarse textured soils, seasonal build-up during summer is often lower, as discussed above, and therefore critical concentrations at the start of winter less likely. Essentially this suggests that winery wastewater irrigation applied to coarse textured soils will require a degree of management considerable less than when applied to finer textured soils with poorer drainage characteristics, dominated by clay and lower bulk densities.

9. Soils of the Marlborough Region

In Marlborough, soils used for grape growing include both Pallic soils, immediately south-east of the Blenheim township, and Recent soils along the undissected older terraces near Renwick and regions of the younger terraces near to the Wairau and Awatere Rivers. A smaller region of organic soils occurs east of the Blenheim township and on the river escarpments of the lower Awatere Valley. Most viticulture in the Wairau Valley is sited on Recent soils and winery wastewater is routinely applied to these soils. While there are some discharges of winery wastewater to Pallic soils in the Awatere, these are relatively minor.

Recent soils, drain freely and monovalent cations will percolate more readily with annual rainfall and irrigation cycles due primarily to their low soil bulk density and clay content. It is likely, therefore, that accumulation of Na^+ and K^+ associated with winery wastewater irrigation will be low and the occurrence of structural decline less pronounced than in the heavier Pallic soils.

Many of the Pallic soils are characterised by imperfect or poorly drained profiles where C horizon soils may have bulk densities greater than 1.6 Mg m^{-3} (Gradwell 1984). A

minor change in the structure of these soils is likely to impact significantly on their hydrological properties. In these soils, percolation of water and soil-water constituents may be limited during winter and the propensity for Na^+ and K^+ ions to accumulate will be greater than the more free draining soils. Any subsequent decline in soil macroporosity due to clay dispersion may further reduce the drainage capacity of these soils if mitigation of high exchangeable K^+ or Na^+ is not carried out (Prior et al. 1992; Halliwell et al. 2001). Furthermore, high evaporative rates, common in Marlborough during summer (i.e. Figure 1) may concentrate the salts in the soil thereby increasing the SAR and PAR of the soil solution.

10. Amelioration of soils with high ESP and EPP

To alleviate sodic conditions in soils, a consideration of both water flow and chemical factors is required (Suarez 2001). Typically this involves:

- Application of a required amount of Ca^{2+} in amendments/compounds such as gypsum ($CaSO_4$), lime ($CaCO_3$) and calcium nitrate ($Ca(NO_3)_2$) to replace exchangeable Na^+ and K^+ thereby reducing ESP and EPP (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 Na^+ and K^+ through leaching with irrigation or rainfall (i.e. leaching fraction).

Calcium amendments such as calcite lime and dolomite ($CaMg(CO_3)_2$) generally result in a change in soil pH (Bolan & Hedley 2003; Bolan et al. 2003a). Where there is pH-dependant charge, this is usually associated with an increase in cation exchange capacity and retention of Ca^{2+}. This limits the movement of Ca^{2+} to lower depths in the soil profile (Greene and Ford 1985; McLay et al. 1994). Gypsum has little influence on soil pH and in high pH soils, is likely to more effective than other Ca^{2+} amendments such as $CaCO_3$, 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). Gypsum will also be preferred for soils already at optimum pH.

The hydrated ion size of magnesium (Mg^{2+}) is slightly larger than that of Ca^{2+}, therefore cohesion strength between clay layers tends to be lower (Curtin et al. 1994b). Magnesium-based amendments such as magnesium oxide (MgO) is therefore less effective in maintaining the structural stability of soils relative to Ca^{2+} (Shainberg et al. 1988). Emerson and Bakker (1973) for instance, report soils saturated with

exchangeable Na^+ and Mg^{2+} have lower hydraulic conductivity and disperse to a greater extent than soils saturated with exchangeable Na^+ and Ca^{2+}.

The efficiency of gypsum and lime to ameliorate soils with high exchangeable K^+ has not been widely documented. Jalali and Rowell (2009) showed that $CaSO_4$ was effective in displacing exchangeable K^+ in a British sandy loam soil. In soils irrigated with piggery effluent, Smiles and Smith (2008) were able to reduce a high exchangeable K^+ concentration with surface applications of gypsum. Efficiency of the Ca-amendment to ameliorate soils will, however, be dependent on the ability of the applied Ca^{2+} to penetrate soil aggregates (Smiles & Smith 2008).

In well drained soils where the accumulation of salts during the irrigation season is limited, Ca^{2+} contained in rainfall may be enough to instigate the exchange of Na^+ and K^+ i.e. directly leached. One consideration, however, is the decline in soil EC brought about by the dilution in soil concentration. In addition to its role in flocculating clays, $CaSO_4$ is effective in raising soil solution EC and suppressing clay dispersion thereby improving soil-water infiltration of both sodic and non-sodic soils, particularly during rainfall cycles when soil EC tends to decline most significantly (Greene and 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 winery wastewater.

Calcium products [$CaSO_4$, $CaCO_3$ and $Ca(NO_3)_2$] can be applied directly to the winery wastewater stream prior to its application to land. This essentially will reduce SAR and PAR by raising the Ca^{2+} concentration. Importantly however addition of ions will subsequently raise winery wastewater EC and will require consideration so as to prevent salinity stress to plants. The pH of the waste stream and method of application will influence the form of Ca^{2+} amendment used i.e. solubility and cost of these products descends in the order $Ca(NO_3)_2$ > $CaSO_4$ > $CaCO_3$ (N.B. solubility of $CaCO_3$ is extremely low and dissolution in wastewater is generally not practical, furthermore $CaCO_3$ also influences soil pH as discussed). Calcium amendments dissolved in the source water may however precipitation within irrigation infrastructure and can potentially be more problematic than application direct to soils. If Ca^{2+} products are applied directly to soils, the optimal application time is during winter when the soil EC is lowest due to rainfall dilution.

The quantity of $CaSO_4$ required to displace exchangeable Na^+ and/or K^+ and lower the soil ESP and/or EPP, can generally be calculated from soil analysis test results (a worked example of this is provided as Appendix 1). Approximate quantities of $CaSO_4$

required to lower the ESP from 15 to 6 % is approximately 4 t ha^{-1}, assuming a CEC of 20 cmol$_c$ kg^{-1}, depth of amelioration is 20 cm and bulk density is 1.3 Mg m^{-3}, see Appendix 1).

11. Changes in soil pH under wastewater irrigation

In Marlborough, winery wastewaters tend to be slightly acidic to slightly alkaline (Table 1). When applied to soils, a lowering of soil pH will alter the availability of nutrients and their subsequent uptake by plants, in particular phosphorous (Bolan & Hedley 2003). As previously mentioned CaCO$_3$ is often used to correct wastewater pH prior to land application.

Many winery wastewaters contain high concentrations of bicarbonate due to the use of alkaline cleaning agents, and application to soils with irrigation can increase soil pH (Suarez et al. 2006). At pH > 8, the formation of carbonate precipitates has shown to occur in soils irrigated with water and wastewaters with high bicarbonate content (Eshel et al. 2007; Wu et al. 2008). Both Mg^{2+} and Ca^{2+} can act as conjugate cations in this precipitation, however, Na$^+$ and K$^+$ do not precipitate to the same extent (Stumm & Morgan 1996; Suarez et al. 2006). This removal of divalent cations from the soil solution raises the SAR and PAR value and ESP or EPP that subsequently increases the potential for clay dispersion (Gardner 2004; Murray and Grant 2007; Suarez et al. 2008). Changes in pH of woodlot, pasture and vineyard soils irrigated with winery wastewater have been reported by Kumar and Christen (2009). These researchers report a 1 to 2 unit increase in soil pH$_{(1:5)}$ at most sites.

Changes in soil pH can alter the cation exchange capacity in variably charged components of the soil (Bolan et al. 1999; Bolan et al. 2003b; Goldberg and Forster 1990). Greater CEC reported by Laurenson (2010), was associated with a subsequent increase in exchangeable K$^+$ under winery wastewater due to the concentration of this cation in solution relative to other ions. Similarly, when soil pH and CEC was increased using sodium hydroxide, Bolan et al. (1996) reported a 2.5-fold increase in clay dispersion between pH from 6.0 to 7.0 due to increase exchangeable Na$^+$. When calcium hydroxide was used to equilibrate soils however, clays remained flocculated following similar increases in soil pH and an improvement in soil hydraulic conductivity was evident due to increased exchangeable Ca^{2+}.

12. Recommendations

Maintaining the percolation of water through the soil will prevent the accumulation of salts. This can be achieved under winter rainfall (usually well drained soil only). Where

accumulation of salts is likely (i.e. fine textured clay dominated soils), it is necessary to maintain a SAR below approximately 6 $(mmol_c L^{-1})^{0.5}$ and PAR below approximately 10 $(mmol_c L^{-1})^{0.5}$. [N.B. this assumes EC of winery wastewater is approximately 1 dS m^{-1}, where EC is higher than 1 dS m^{-1}, greater threshold values may be applicable].

Given the close relationship between EC and soil dispersion and the high net loadings of salts under winery wastewater irrigation, EC of this waste stream should be included in routine analysis.

Routine use of Ca^{2+} amendments including, but not restricted to, $CaCO_3$, $CaSO_4$ and $Ca(NO_3)_2$ either added to wastewater prior to its application to land or directly to soils. When applied to soils, winter application will ensure its percolation down the soil profile thereby ensuring good distribution of Ca^{2+} and raising soil EC that is otherwise lowered under rainfall. When Ca^{2+} amendments are applied to wastewater prior to land application, precipitation and blocking of irrigation hardware is of concern.

Given the lesser effect of K^+ on soil structure relative to Na^+, a switch to potassium-based sterilisers, or preferable (particularly for wastes disposed of to fine textured soils) utilisation of steam or water cleaning systems that will lower SAR in the final stream. In addition to this, the greater PAR in winery wastewater will further prevent Na^+ retention in soils.

The period during which winery wastewater is applied to land is relatively short i.e. immediately following vintage and, therefore, annual loading of salts is relatively low given suitable land area. To avoid nutrient imbalances in crops grown with winery wastewater, loading rates should be determined based on meeting the K^+ demand of the crop. In many instances, however, this is likely to require considerably greater land areas to those currently being utilised. With adequate management i.e. prevention of high ESP and EPP during consecutive seasons the risk of soil dispersion can be adequately mitigated.

13. Conclusions

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 introduces a considerable amount of Na^+ and K^+ salts to the soil. A high concentration of monovalent Na^+ and K^+ 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; Halliwell *et al.* 2001; Menneer *et al.* 2001; Stevens *et al.* 2003).

The retention of K^+ applied with winery wastewater is far greater than for Na^+ and therefore EPP under winery wastewater increases rather than ESP. Importantly, the likelihood of clay dispersion in response to K^+ is considerably lower relative to Na^+. Essentially it is advisable that both ESP and EPP be routinely monitored, particularly in fine textured soils. In many regions, Na^+ and K^+ are readily leached during annual winter rainfall and therefore pose limited risk of accumulation or soil dispersion. In fine textured soils or where loading rates of constituents is high, achieving adequate leaching may be problematic and will require greater management input including leaching with comparatively good quality waters, application of Ca^{2+} amendments such as $Ca(NO_3)_2$, $CaSO_4$ or $CaCO_3$ or reduced rates of loading.

14. Future Research

Current monitoring of soils where winery wastewater is applied indicate an increase in exchangeable K^+, however generally sampling has been carried out immediately after grape harvest when a high salt loading would be expected. Across several years there appears to be a general trend toward increasing EPP at some sites. Through comprehensive soil sampling at key periods of the year i.e. pre and post winter it would be possible to pick up temporal changes in salt content although this may be small given the reliable rainfall and pasture demands.

Much of the experimental work described in this report is based on soils in Australia that will differ slightly in mineralogy, clay content and salt content. While an indicative threshold value for SAR and PAR can be suggested, It would be of value to MDC to validate these measurements using the key soil types found in Marlborough. Experiments that investigate changes in hydraulic conductivity in response to winery wastewaters of varying cation composition would provide suitable information to better integrate Marlborough soils into the 'Effluent framework' approach devised by AgResearch and currently being adopted by the MDC.

Additional research may also address:

- How winery wastewater composition relates to operation (cleaning products, volume of grape crushed and treatment process)

- Effectiveness of various Ca^{2+} amendments to displace K^+, Na^+ and Mg^{2+} and it effect on soil and water pH

- Where winery wastewater is applied to pasture- an assessment of the feed quality in particular the K^+ content

15. Acknowledgements

16. References

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17. Appendix 1

Calculation of $CaSO_4$ requirement can be done by assuming the quantitative exchange of 2 cmol Na^+ per 1 cmol Ca^{2+} i.e. substitution of two monovalent cations per one divalent cation [N.B. cmol = meq/100g soil]. If for instance the soil ESP is 15 % then 0.15 x CEC ($cmol_c$ kg^{-1} soil) is Na^+. In a soil with a CEC of 20 $cmol_c$ kg^{-1} soil (this is equivalent to units of me/100 g often used on soil analysis reports) and ESP of 15 % is equivalent to 3 $cmol_c$ of Na^+. In order to lower the ESP to a desired level (i.e. ESP 6 % is generally the target), the Ca^{2+} requirement necessary to displace Na^+ can be calculated. Here, 1.8 $cmol_c$ Ca^{2+} kg^{-1} soil is required to lower the ESP to 6 % [i.e. 3.0 $cmol_c$ kg^{-1} - 1.2 $cmol_c$ kg^{-1} = 1.8 $cmol_c$ kg^{-1}].

Mass of 1 cmol $CaSO_4$ is 1.72 g [$CaSO_4.2(H_2O)$ = 0.40 + 0.32 + (0.16x4) + 2(0.2 + 0.16)], however each cmol of $CaSO_4$ contains two charges per Ca^{2+} (i.e. 2 $cmol_c$ Ca^{2+}). The $CaSO_4$ requirement necessary to displace 1 cmol of Na^+ therefore is calculated by:

$$g\ CaSO_4\ per\ cmol^{-1}\ Na^+\ displaced = \frac{formula\ wt.CaSO_4}{2\ cmol_c\ Ca^{2+}} = \frac{1.72}{2} = 0.86\ g$$

Given the target ESP of 6 %, 1.55 g kg^{-1} soil is required to lower the ESP from 15 % (i.e. 0.86 g x 1.8 $cmol_c$ kg^{-1} soil) [N.B. This assumes 100 % efficiency of $CaSO_4$]. On a per hectare basis this equates to approximately 4.03 tonne (assuming the depth of amelioration is 20 cm and bulk density is 1.3 Mg m^{-3} and therefore soil weight x volume is 2600 000 kg)).