Effect of Irrigation with Diluted Winery Wastewater on Cations and pH in Four Differently Textured Soils

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Environmental legislation requires the South African wine industry to find solutions for winery wastewater treatment or reuse. The feasibility of irrigation with diluted winery wastewater was assessed in a pot experiment under a rain shelter over four simulated irrigation seasons. Four soils varying in clay content were irrigated with winery wastewater diluted to 3 000 mg/L chemical oxygen demand (COD), whereas the control received municipal water. The rate of K^+ increase in the soil containing 20% clay was higher than in soils containing 13% clay or less. This suggests that heavy soils will aggravate the risk of high K^+ levels. The risk of Na^+ accumulation increased linearly with clay content. Low Ca^{2+} and Mg^{2+} concentrations in the diluted wastewater had no effect on the soil, irrespective of clay content. Irrigation with diluted winery wastewater increased soil $pH_{(KCl)}$ substantially in all the soils over the four simulated seasons. The soil pH increase was attributed to the addition of organic/bicarbonate salts to the soil. It must be noted that the results represent a worst case scenario, *i.e.* in the absence of rainfall or crops.

INTRODUCTION

Increased wine production in South Africa is putting more pressure on natural resources such as vegetation, water and soil. Changes in environmental legislation (Department of Water Affairs, 2013) put pressure on the wine industry to find solutions for the treatment or judicious use of winery wastewater (Van Schoor, 2001a). This initiated the development of guidelines for the management of wastewater and solid waste at wineries (Van Schoor, 2005). In many cases, a shortage of good-quality water leads to an increasing need to irrigate crops with poor-quality water, such as saline groundwater, drainage water and treated wastewater (Jalali *et al*., 2008). The impact of using untreated industrial and municipal wastewater for irrigation is well documented (Bond, 1998; Papini, 2000; Mulidzi, 2001; Arienzo *et al*., 2009a; Christen *et al*., 2010; Laurenson & Houlbrooke, 2011; Mosse *et al*., 2011; Arienzo *et al*., 2012; Laurenson *et al*., 2012; Howell & Myburgh, 2014a; Walker & Lin, 2008).

The disposal of winery wastewater through land application has been practised for many years (Mulidzi, 2001; Laurenson & Houlbrooke, 2011). Effective disposal of wastewater depends on the irrigation technology, as well as on soil properties (Oron *et al*., 1999). In an earlier study, Mulidzi (2001) confirmed that the impacts of using undiluted winery wastewater for irrigation differ substantially between soil types. Under some circumstances, irrigation with winery wastewater can have a beneficial effect. Papini (2000) observed improvements to the soil in terms of pH increases, water retention and the restoration and maintenance of soil micro-flora after the application of distillery wastewater. It was also suggested that using K^+-rich wastewater could enhance soil fertility (Mosse *et al*., 2011). On the other hand, this practice can also have a negative impact on soils. Irrigation with winery wastewater has been shown to result in the leaching of nitrate into the groundwater, increased soil sodicity and/or long-term detrimental effects on the soil physical and chemical properties of arable land (Bond, 1998). In Australia, continued irrigation of pastures with winery wastewater resulted in an accumulation of K^+ to levels that leached into the groundwater and other water resources (Christen *et al*., 2010). In addition, it was observed that using winery wastewater for the irrigation of poorly drained soils could lead to salinisation and water- logging, reducing the long-term sustainability of the land for agriculture (Christen *et al*., 2010).

The replacement of bivalent Ca^{2+} and Mg^{2+} by monovalent K^+ and Na^+ during continuous irrigation potentially can lead to the breakdown of the soil structure. Exchangeable Na^+ in soils tends to increase where wastewaters containing high levels of Na^+ are used for irrigation (Lieffering

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& McLay, 1996). Where wineries use Na^+-based cleaning agents, *e.g.* sodium hydroxide (NaOH), the accumulation of monovalent cations, such as Na^+, on the exchange sites has the potential to degrade the soil structure through clay dispersion and flocculation (Mosse *et al*., 2011). Consequently, soil hydraulic conductivity can be reduced where winery wastewater is used for irrigation (Laurenson *et al*., 2012). Indications of poor aeration and water infiltration observed in various soils where winery wastewater was used for irrigation were attributed to structural degradation caused by high Na^+ concentrations added to the soil (Mulidzi *et al*., 2009). This was confirmed when irrigation with diluted winery wastewater reduced the hydraulic conductivity of differently textured soils (Howell & Myburgh, 2014b). Using winery wastewater with very high K^+ levels for irrigation may also result in K^+ accumulation in the soil, resulting in the leaching of the flocculating cations Ca^{2+} and Mg^{2+}, thus increasing the instability of the soil structure in the long run (Mosse *et al*., 2011). Since K^+ has an affinity for clay minerals, high soil K^+ can cause clay swelling and dispersion where wastewater is used for irrigation (Arienzo *et al*., 2012). Similar to Na^+, K^+ in winery wastewater can reduce soil hydraulic conductivity (Arienzo *et al*., 2009b). However, knowledge regarding the negative effects of K^+ on soil structure stability is limited compared to that of Na^+.

Soil pH tends to increase when wastewater with high pH and Na^+ concentrations is used for irrigation (Liefferinq & McLay, 1996). A study carried out in the Western Cape showed that the disposal of grape-processing effluents changed the soil pH from acidic to alkaline (Papini, 2000). This pH increase was attributed to the initial removal of soluble organic matter through the volatilisation of CO_2 during biodegradation.

In contrast, the application of wine vinasse containing high bicarbonate slightly reduced the pH of a Mediterranean soil (Bueno *et al*., 2009). The pH reduction was attributed to the high electrical conductivity of the soil solution (EC_e), *viz.* 9.2 dS/m, and the transformation of organic sugars by microorganisms. These contrasting results of various studies imply that soil reactions to the application of winery wastewater cannot easily be predicted. The soils of the South African winelands are highly heterogeneous and can show a high degree of spatial variation in a relatively small area. Soils range in parent material, texture, structure, drainage, coarse fragment content and chemistry. Parent material is usually largely responsible for the physical and chemical makeup of a soil (Van Schoor, 2001b). In the Stellenbosch region, two of the dominant parent materials are shale and granite, while in the Breede River and Olifants River wine-growing regions, transported aeolian or fluvial sands are important parent materials (Bargmann, 2003). Due to the heterogeneity of the winelands soils, they are likely to respond differently to the application of winery wastewater; however, there has been little work done to determine these responses.

The objective of this study was to determine the effects of irrigation with diluted winery wastewater on selected chemical properties of four soils varying in parent material and clay content. This paper reports on base cations and pH.

MATERIALS AND METHODS

Soils

Four differently textured soils from three grape-growing regions in the Western Cape were included in the study, *viz.* (i) aeolian sand (Garies 1000) from Lutzville, containing 0.4% clay, (ii) alluvial sand (Longlands 1000) from Rawsonville, containing 3.3% clay, (iii) granite-derived soil from Stellenbosch (Cartref 1100), containing 13% clay, and (iv) shale-derived soil from Stellenbosch (Oakleaf 2210), containing 20% clay, with taxonomic soil classification at the family level according to the South African soil classification system (Soil Classification Working Group, 1991). A composite soil sample was collected from the topsoil layers of the four soils, *i.e.* approximately 0 to 30 cm deep. The soil samples were analysed to determine particle size distribution, water-holding capacities and initial soil chemical status.

Experimental procedures

Soils were packed into 3.54 dm^3 PVC pots to a bulk density of 1 400 kg/m^3 as described by Mulidzi *et al*. (2015). Control treatments were irrigated with water supplied by the Stellenbosch municipality. The winery wastewater treatments were irrigated with wastewater diluted to a chemical oxygen demand (COD) of 3 000 mg/L. The undiluted wastewater was obtained from the wastewater collection pit at a winery near Rawsonville. Treatments were applied over four simulated irrigation seasons, consisting of six irrigations each. Thus, 24 irrigations were applied over the four simulated seasons. The total irrigation amounted to 1 156 mm, 1 126 mm, 987 mm and 728 mm for the Rawsonville sand, Lutzville sand, Stellenbosch shale and Stellenbosch granite soils respectively. The pot experiment was carried out under a 20 m x 40 m translucent fibreglass rain shelter at ARC Infruitec-Nietvoorbij near Stellenbosch. Details of the pot experiment, wastewater dilution and the irrigation system are described in Mulidzi *et al*. (2015).

Water sampling and analyses

Water samples were collected prior to each irrigation. The COD in the water was measured using a portable spectrophotometer (Aqualitic COD-reactor®, Dortmund) and the appropriate test kits (COD, CSB, 0 to 15 000 mg/L). The pH and electrical conductivity (EC) were determined by a commercial laboratory (Bemlab, Strand) according to methods described by Clesceri *et al*. (1998). The water was analysed for Ca^{2+}, Mg^{2+}, K^+ and Na^+ by a commercial laboratory (BEMLAB, Strand) by means of atomic emission using an optical emission spectrometer (Varian ICP-OES). Total alkalinity was determined through titration with 0.05 N hydrochloric acid. The sodium adsorption ratio (SAR) of the water was calculated as follows (units in $meq.L^{-1}$):

$$SAR = Na^+ \div [(Ca^{2+} + Mg^{2+}) \div 2]^{½} \quad \text{(Eq. 1)}$$

Soil sampling and analyses

To make provision for destructive soil sampling, each experimental "plot" consisted of four pots. Following each simulated irrigation season, the soil in one of the pots was collected for sampling, *i.e.* after six, 12, 18 and 24 irrigations. Soil samples were collected from the 0 to 10 cm and 10 to 20 cm layers in the pots of all replications. Soil samples were air dried and passed through a 2 mm mesh sieve. All analyses were carried out by a commercial laboratory (Bemlab, Strand). The $pH_{(KCl)}$ was determined in a 1 M potassium chloride (KCl) suspension. The Ca^{2+}, Mg^{2+}, K^+ and Na^+ were extracted with 1 M ammonium acetate at pH 7. The cation concentrations in the extracts were determined by inductively coupled plasma optical emission spectrometry (ICP-OES), using a spectrometer (PerkinElmer Optima 7300 DV, Waltham, Massachusetts). For this study, the cations will be referred to as extractable calcium (Ca^{2+}_{extr}), magnesium (Mg^{2+}_{extr}), potassium (K^+_{extr}) and sodium (Na^+_{extr}). The extractable potassium percentage (EPP′) was calculated as follows:

$$EPP' = (K^+_{extr} \div \mathbf{S}) \times 100 \qquad \text{(Eq. 2)}$$

where K^+_{extr} is the extractable potassium (cmol$^{(+)}$/kg) and S is the sum of basic cations (cmol$^{(+)}$/kg).The extractable sodium percentage (ESP′) was calculated in the same way to obtain an indication of the sodicity status.

Statistical procedures

Each soil/water treatment was replicated three times in a completely randomised design. The four soils were randomly allocated within each block. The treatment design was a split-plot, with soil type as the main plot factor and soil depth as the sub-plot factor. Analyses of variance were performed separately for each season using SAS version 9.2 (SAS, 2008). The Shapiro-Wilk test was performed to test for non-normality (Shapiro & Wilk, 1965). Student's "t" least significant difference (LSD) was calculated at the 5% significance level to facilitate comparison between treatment means (Ott, 1998). Linear regressions were calculated using STATGRAPHICS® version XV (StatPoint Technologies, Warrenton, Virginia, USA).

Soil characterisation

Soils selected for this study were chosen because they represent dominant soils of the Western Cape wine-producing region. Furthermore, it was expected that the impacts of winery wastewater on soils would differ widely between differently textured soils. The Rawsonville soil was formed from the alluvium of the Breede River. The soils in this region are relatively young and often are stratified. The soils selected for this study showed no clear stratification and contained a mottled subsoil, thereby being classified as a Longlands soil form (orthic A-E horizon – soft plinthic B horizon). The topsoil texture of the soil was fine sand.

The soil was slightly acidic, with a $pH_{(KCl)}$ of 5.7. The geology of the Lutzville region is dominated by metamorphic rocks of the Nama Group in the north and sedimentary rocks of the Cape Super Group in the southern and south-western parts (Department of Water Affairs, 2011). However, the soils in this area are mainly derived from Aeolian-deposited sand (Saayman & Conradie, 1982). The soil was classified as the Garies form (orthic A – Red apedal B horizon – with dorbank as the underlying material). The topsoil texture was fine sand and the soil was neutral, with a $pH_{(KCl)}$ of 6.7. The Stellenbosch shale soil was located on the foothills of Simonsberg Mountain. The lower subsoil was derived *in situ* from shale, but the upper subsoil and A horizon were derived from colluvial material of shale origin. The soil was classified as a red Oakleaf soil form (orthic A – red neocutanic B horizon – unspecified material). The topsoil texture was a fine sandy clay loam and the soil was acidic, with a $pH_{(KCl)}$ of 4.2. The Stellenbosch granite soil was also located on the foothills of Simonsberg Mountain. The subsoil was derived *in situ* from granite, although the A and E horizons were derived from granitic colluvium. The soil was classified as a Cartref form (orthic A and E horizon – lithocutanic B horizon). Both the A and E horizons were highly leached and hard setting. The topsoil texture was coarse sandy loam. The soil was acidic, with a $pH_{(KCl)}$ of 4.4.

RESULTS AND DISCUSSION

Chemical composition of the water and amount of elements applied

The mean COD levels in the municipal water and diluted winery wastewater were 28 ± 4 and 3 210 ± 43 mg/L respectively during the four simulated seasons. The COD in the diluted winery wastewater was reasonably close to the target level of 3 000 mg/L. As expected, most of the other winery wastewater quality variables were considerably higher compared to the municipal water (Table 1). On most irrigation days, the winery wastewater pH was lower compared to the municipal water. The average SAR of the winery wastewater was close to 5 (Table 1), which is the upper permissible limit for irrigation with wastewater according to South African water quality legislation (Department of Water Affairs, 2013). Due to the differences in the chemical composition of the municipal and diluted winery wastewater, considerably more cations were applied to the soil *via* the wastewater compared to the municipal water (Table 2). Total irrigation amounts applied to the Rawsonville sand (1 156 mm), Lutzville sand (1 126 mm) and Stellenbosch shale (987 mm) over four simulated seasons were comparable, but the Stellenbosch granite (728 mm) received substantially less water. According to Mulidzi *et al*. (2015), this particular soil had a lower water-holding capacity and high coarse sand content compared to the other three soils.

Extractable potassium and EPP′

Where municipal water was applied, K^+_{extr} amounted to 0.21 cmol$^{(+)}$/kg, 0.42 cmol$^{(+)}$/kg, 0.35 cmol$^{(+)}$/kg and 0.31 cmol$^{(+)}$/kg for the Rawsonville sand, Lutzville sand, Stellenbosch shale and Stellenbosch granite respectively after the four seasons (data not shown). Since these values were comparable to the baseline values (Table 3), this indicated that irrigation with municipal water had no effect on the K^+_{extr}, irrespective of clay content. In contrast, irrigation with the diluted winery wastewater increased K^+_{extr} substantially over the four seasons. The K^+_{extr} in the 0 to 10 cm soil layer was slightly higher that that in the 10 to 20 cm layer, irrespective of clay content (Fig. 1). According to Arienzo *et al*. (2009b), a higher amount of exchangeable K^+ is retained by soils higher in clay content than soils low in clay content following winery wastewater irrigation. This may have resulted in the similar trend being observed in the four soils. Furthermore, K^+_{extr} in the four soils increased linearly with the cumulative amount of K^+ applied *via* the irrigation water (Fig. 1).

In the 0 to 10 cm layers, the degree of K^+ extraction was similar for the four soils, with an increase of 0.0002 cmol$^{(+)}$/

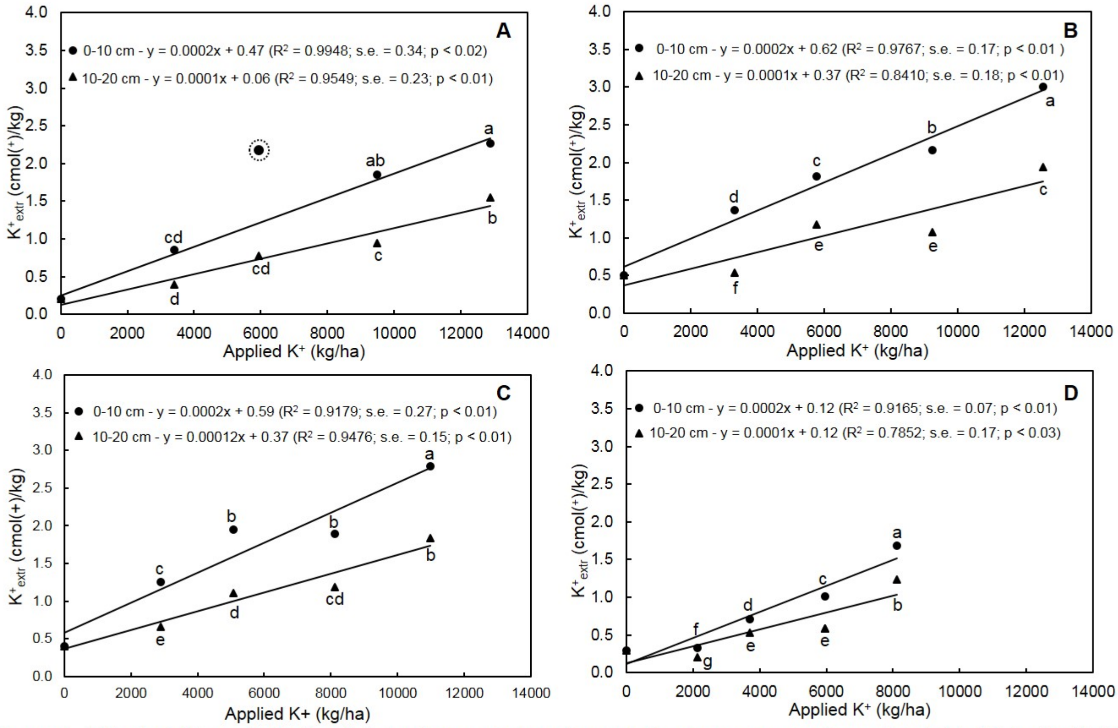

FIGURE 1

Effect of K^+ applied via diluted winery wastewater over four seasons on the extractable K^+ in the 0 to 10 cm and 10 to 20 cm layers of (A) Rawsonville sand, (B) Lutzville sand, (C) Stellenbosch shale and (D) Stellenbosch granite soils. The encircled data point was regarded as an outlier due to experimental error and was not included in the equations. Values designated by the same letter do not differ significantly ($p \leq 0.05$).

kg per kg K^+ applied. After the four seasons, EPP′ amounted to 4.6%, 11.5%, 13% and 9.5% for the Rawsonville sand, Lutzville sand, Stellenbosch shale and Stellenbosch granite soils respectively where municipal water was applied (data not shown). Similar to K^+_{extr}, the EPP′ values were comparable to the baseline values (Table 3), indicating that the municipal water irrigation did not affect EPP′. In contrast, irrigation with the diluted winery wastewater increased EPP′ over the four seasons (Fig. 2). The EPP′ in the 0 to 10 cm soil layer was slightly higher compared to that in the 10 to 20 cm layer, with the exception of Stellenbosch granite soil. In the case of the sandy soils and Stellenbosch shale soil, the EPP′ in the 0 to 10 cm layer showed a slower increase following the second season (Figs 2A, 2B & 2C). The EPP′ in the 10 to 20 cm layer showed an almost linear increase with applied K^+. These trends did not occur in the case of Stellenbosch granite, as EPP′ was comparable in both soil layers (Fig. 2D). After the fourth season, EPP′ was similar in both layers, which suggests that the granite soil was no longer retaining high amounts of K^+ in the 0 to 10 cm layer.

For healthy grapevine growth in soils with a pH below 6, it is recommended that a K^+ saturation of 4% is required at the exchange sites (Conradie, 1994). Prior to irrigation, the EPP′ was greater than 4% in all the soils, except for the Rawsonville sand, which had an EPP′ of 3.7%, which was close to the threshold (Table 3).

Thus, for the soils investigated, K^+ added *via* the wastewater did not represent a benefit in terms of nutrient balance and supply. In fact, high K^+_{extr} levels may cause excessive absorption by grapevines, which could result in high wine pH and eventually reduce the colour stability of red wines where winery wastewater was applied (Mpelasoka *et al*., 2003; Kodur, 2011).

Under normal cropping conditions there is a possibility that K^+ applied *via* wastewater can be beneficial if it can maintain optimum levels when K^+ is absorbed by the grapevines and/or inter-row crops, or if K^+ is leached by rainfall in winter. It should be noted that the observed K^+ accumulation occurred in the absence of rainfall or crops. Determining the effect of leaching by winter rainfall where diluted winery wastewater is used for irrigation is part of an ongoing study.

Extractable sodium and ESP′

Where municipal water was applied, Na^+_{extr} amounted to 0.15 $cmol^{(+)}$/kg, 0.17 $cmol^{(+)}$/kg, 0.16 $cmol^{(+)}$/kg and 0.25 $cmol^{(+)}$/kg respectively for the Rawsonville sand, Lutzville sand, Stellenbosch shale and Stellenbosch granite soils after the four seasons (data not shown). Being comparable to the baseline values (Table 3), this indicates that municipal water irrigation had almost no effect on the Na^+_{extr}, irrespective of clay content. On the other hand, irrigation with the diluted winery wastewater increased Na^+_{extr} substantially over the four seasons. In all the soils, the degree of Na^+_{extr} accumulation in the 0 to 10 cm layer was higher than in the 10 to 20 cm layer (Fig. 3). The difference between the layers was most prominent in the shale, followed by the granite and sandy soils (Figs 3C & 3D). These trends indicate that more Na^+ was extracted in the 0 to 10 cm layer of the heavier soils than the sandy soils. The increased extraction of Na^+ from the top layer may be as a result of less sorption of Na^+ to the soil and the evaporative concentration of Na^+ in the evaporating soil solution. In fact, previous studies have shown that the adsorption of Na^+ was reduced by the presence of high K^+ levels where winery wastewater was applied (Laurenson *et al*., 2012 and references therein).

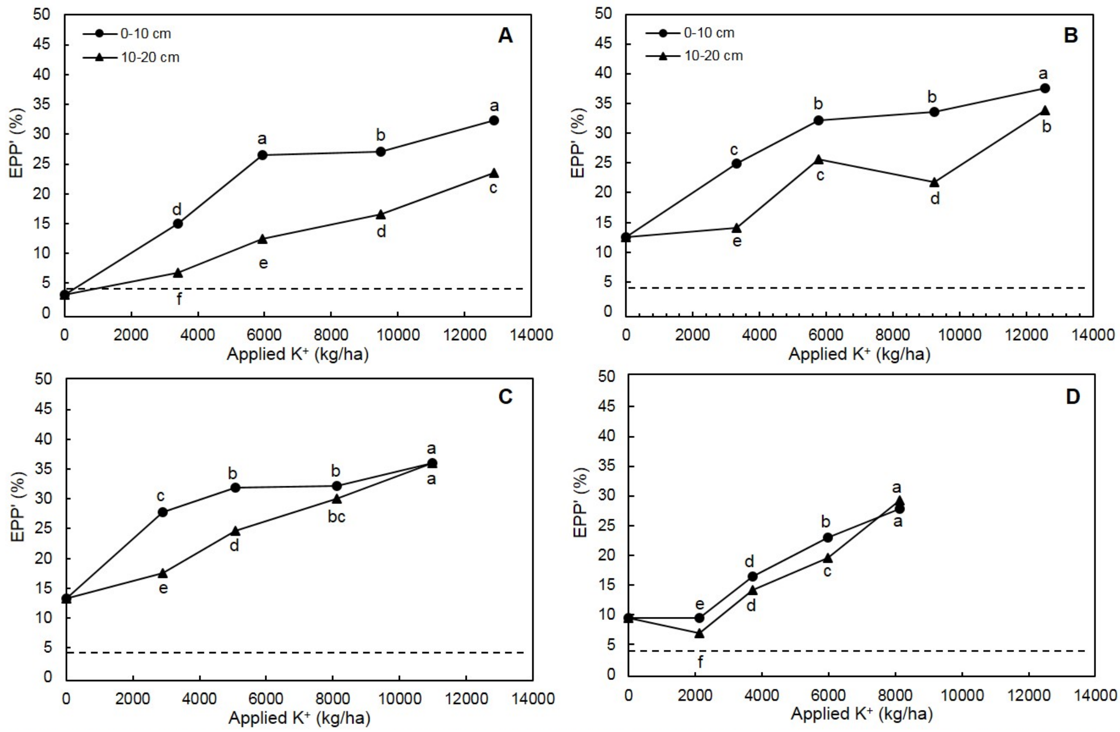

FIGURE 2
Effect of K^+ applied *via* irrigation with diluted winery wastewater over four seasons on the extractable potassium percentage (EPP′) in the 0 to 10 cm and 10 to 20 cm layers of (A) Rawsonville sand, (B) Lutzville sand, (C) Stellenbosch shale and (D) Stellenbosch granite soils. The dashed line indicates the critical EPP′ threshold for grapevines. Values designated by the same letter do not differ significantly ($p \leq 0.05$).

TABLE 1
Quality characteristics of municipal water and winery wastewater used for irrigation of four different soils.

	Season				
	1	2	3	4	Mean
Water quality variables	Municipal				
pH	7.7	7.5	7.7	6.9	7.4
EC (mS/m)	8.3	7.2	9.5	9.3	8.6
K^+ (mg/L)	0.8	0.7	0.9	1.6	1.0
Na^+ (mg/L)	7.4	7.2	8.1	8.5	7.8
Ca^{2+} (mg/L)	6.3	6.0	6.1	5.3	5.9
Mg^{2+} (mg/L)	1.3	1.1	1.5	1.8	1.4
SAR	0.7	0.7	0.8	0.8	0.8
HCO_3^-	32.6	22.4	18.4	26.0	24.9
	Winery				
pH	5.3	6.0	4.9	5.6	5.4
EC (mS/m)	94.2	109.8	94.6	119.0	104.4
K^+ (mg/L)	196.1	186.6	204.9	196.4	196.0
Na^+ (mg/L)	75.5	114.9	78.7	68.6	84.4
Ca^{2+} (mg/L)	14.1	18.0	20.0	22.4	18.6
Mg^{2+} (mg/L)	4.9	8.4	6.5	9.1	7.2
SAR	4.5	5.6	4.0	4.1	4.6
HCO_3^-	511.3	655.1	438.2	552.9	539.4

In all soils the Na^+_{extr} increased linearly with the cumulative amount of Na^+ applied *via* the irrigation water (Fig. 3). However, the rate of increase in Na^+_{extr} with increase in applied Na^+ (Na^+_{extr}/Na^+_{appl}) differed between the soils. The Na^+_{extr}/Na^+_{appl} increased with clay content in the 0 to 10 cm layer, but no correlation was observed in the 10 to 20 cm layer (Fig. 4). Where municipal water was applied, the ESP′ amounted to 3.2%, 4.4%, 2.9% and 4.3% in the Rawsonville sand, Lutzville sand, Stellenbosch shale and Stellenbosch granite soils respectively after four seasons. The ESP′ values were comparable with the baseline values, with the exception of the Stellenbosch granite soil, which had a higher baseline ESP′ (Table 3). Where winery wastewater was applied over four seasons, the ESP′ did not show a definite linear increase with the amount of Na^+ applied in any of the layers (Fig. 5).

In the case of the Rawsonville sand, the ESP′ exceeded the critical threshold of 15% for sustainable agricultural use from the second season onwards in the 0 to 10 cm layer (Fig. 5A). Wastewater irrigation increased the ESP′ above 15% from the first season in the Lutzville sand, but also only in the 0 to 10 cm layer (Fig. 5B). From the first season, the ESP′ exceeded 15% only in the 0 to 10 cm layer of the Stellenbosch shale soil (Fig. 5C). Although no infiltration problems occurred after four seasons, this does

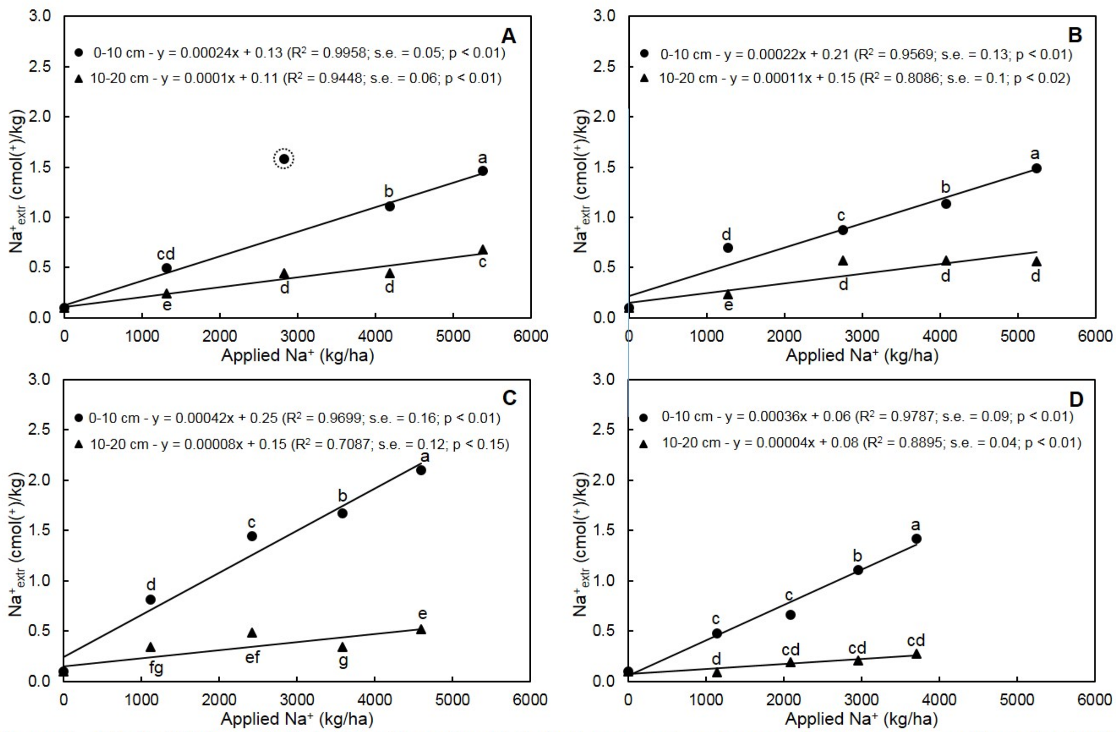

FIGURE 3
Effect of Na^+ applied *via* irrigation with diluted winery wastewater over four seasons on the extractable Na^+ in the 0 to 10 cm and 10 to 20 cm layers of (A) Rawsonville sand, (B) Lutzville sand, (C) Stellenbosch shale and (D) Stellenbosch granite soils. The encircled data point was regarded as an outlier due experimental error and was not included in the equation. Values designated by the same letter do not differ significantly ($p \leq 0.05$).

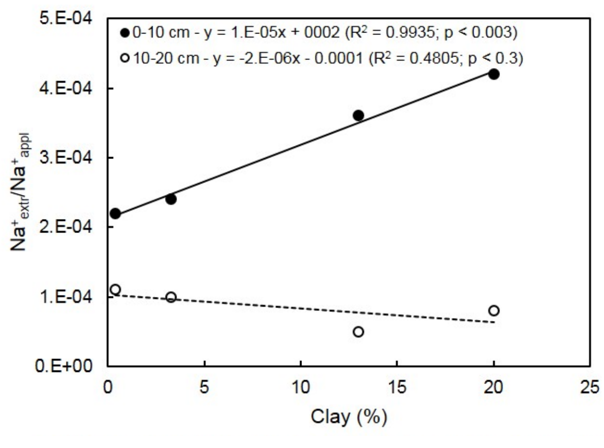

FIGURE 4
Relationship between the ratio of extractable sodium (Na^+_{extr}) to sodium applied per hectare (Na^+_{appl}) and clay content for four different soils.

TABLE 2
Amount of elements applied per simulated irrigation season *via* municipal water and diluted winery wastewater.

Element	Season	Amount applied (kg/ha)							
		Rawsonville		Lutzville		Stellenbosch shale		Stellenbosch granite	
		Municipal	Winery	Municipal	Winery	Municipal	Winery	Municipal	Winery
K^+	1	11	3414	11	3312	10	2895	7	2124
	2	12	2535	12	2472	10	2181	7	1587
	3	16	3538	15	3463	13	3034	10	2253
	4	29	3406	28	3312	24	2887	18	2157
Na^+	1	100	1315	97	1276	85	1115	62	818
	2	125	1514	121	1477	107	1303	78	948
	3	139	1358	136	1329	119	1165	89	865
	4	147	1189	143	1156	125	1008	93	753
Ca^{2+}	1	86	245	84	237	73	207	54	152
	2	104	270	101	263	89	232	65	169
	3	106	345	103	338	91	296	67	220
	4	92	388	90	378	78	329	59	246
Mg^{2+}	1	17	85	16	83	14	72	10	53
	2	19	114	18	112	16	98	12	72
	3	26	112	25	110	22	96	17	71
	4	32	158	31	153	27	134	20	100

TABLE 3
Initial extractable cations, extractable potassium percentage (EPP′), extractable sodium percentage (ESP′) and $pH_{(KCl)}$ in the four soils selected for the study.

Variable	Rawsonville sand	Lutzville sand	Stellenbosch shale	Stellenbosch granite
K^+_{extr} (cmol$^{(+)}$/kg)	0.2	0.5	0.4	0.3
Na^+_{extr} (cmol$^{(+)}$/kg)	0.1	0.1	0.1	0.2
EPP′	3.7	13.2	13.8	9.7
ESP′	1.9	2.6	3.4	6.5
Ca^{2+}_{extr} (cmol$^{(+)}$/kg)	3.5	2.4	1.6	1.8
Mg^{2+}_{extr} (cmol$^{(+)}$/kg)	1.6	0.8	0.8	0.8
$pH_{(KCl)}$	5.7	7.6	4.2	4.4

not rule out the possibility that sodicity could have negative effects on soil structure in the long run. In the case of the Stellenbosch granite soil, the ESP′ exceeded 15% after the third season, but also only in the 0 to 10 cm layer (Fig. 5D). Although the ESP′ in the two sandy soils seemed to have reached a plateau at c. 20%, it might induce negative effects on grapevine growth and yield if the ESP′ remains near the threshold over time. Given the higher ESP′ in the heavier soils, sodicity will have negative effects on plant growth and soil physical conditions if these soils are irrigated with winery wastewater, even when diluted. The Stellenbosch shale soil showed no visual signs of infiltration problems, but water infiltration into the Stellenbosch granite soil was considerably slower where wastewater was applied rather than municipal water. It should be noted that the infiltration problems occurred right from the first season, *i.e.* when the ESP′ in the top layer was around 15% (Mulidzi *et al.*, 2015). It is well documented that Ca^{2+} and Mg^{2+} can counter the negative effects of Na^+ on water infiltration, but the Ca^{2+}_{extr} and Mg^{2+}_{extr} in the Stellenbosch shale and granite soils were comparable (Table 3). It was previously reported that the saturated conductivity of a topsoil of a similar granitic soil at Nietvoorbij was 112 mm/h (Myburgh, 2015). Since the drip application rate was 115 mm/h (Mulidzi *et al.*, 2015), it could be that the infiltration rate of the granitic soil was exceeded, thereby causing the slow water infiltration. Another possible reason for the slow infiltration rate in the granitic soil is the dispersive nature of the bleached topsoil. Bleached topsoils are pale in colour due to the loss of Fe^{2+} from the horizon. Iron oxides play an important role in stabilising clays against dispersion (Tombacz *et al.*, 2004). The lack of Fe^{2+} in the granitic topsoil might make this soil more susceptible to clay dispersion and surface sealing when irrigated with wastewater containing high levels of Na^+ and K^+. The red Oakleaf soils in the Stellenbosch region have a high Fe^{2+} content (Le Roux, 2015). This may explain why infiltration in these soils was unhindered, despite the poor quality of the irrigation water.

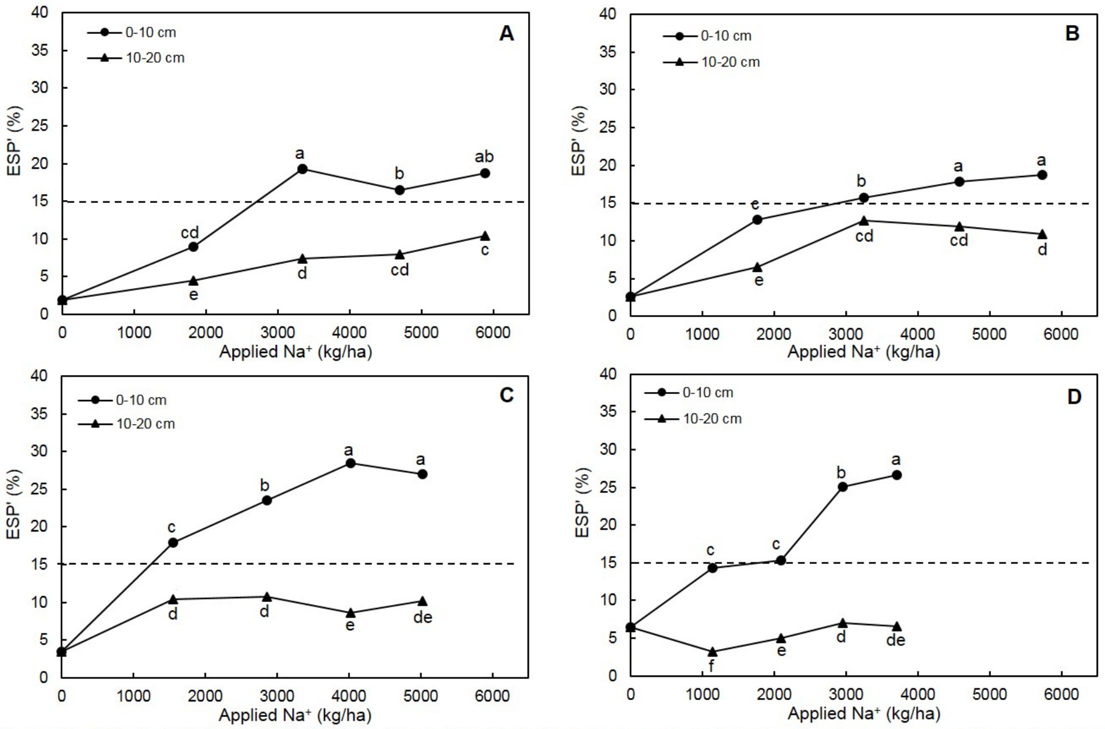

FIGURE 5
Effect of Na^+ applied *via* irrigation with diluted winery wastewater over four seasons on the extractable sodium percentage (ESP′) in the 0 to 10 cm and 10 to 20 cm layers of (A) Rawsonville sand, (B) Lutzville sand, (C) Stellenbosch shale and (D) Stellenbosch granite soils. The dashed line indicates the critical ESP′ threshold for grapevines. Values designated by the same letter do not differ significantly ($p \leq 0.05$).

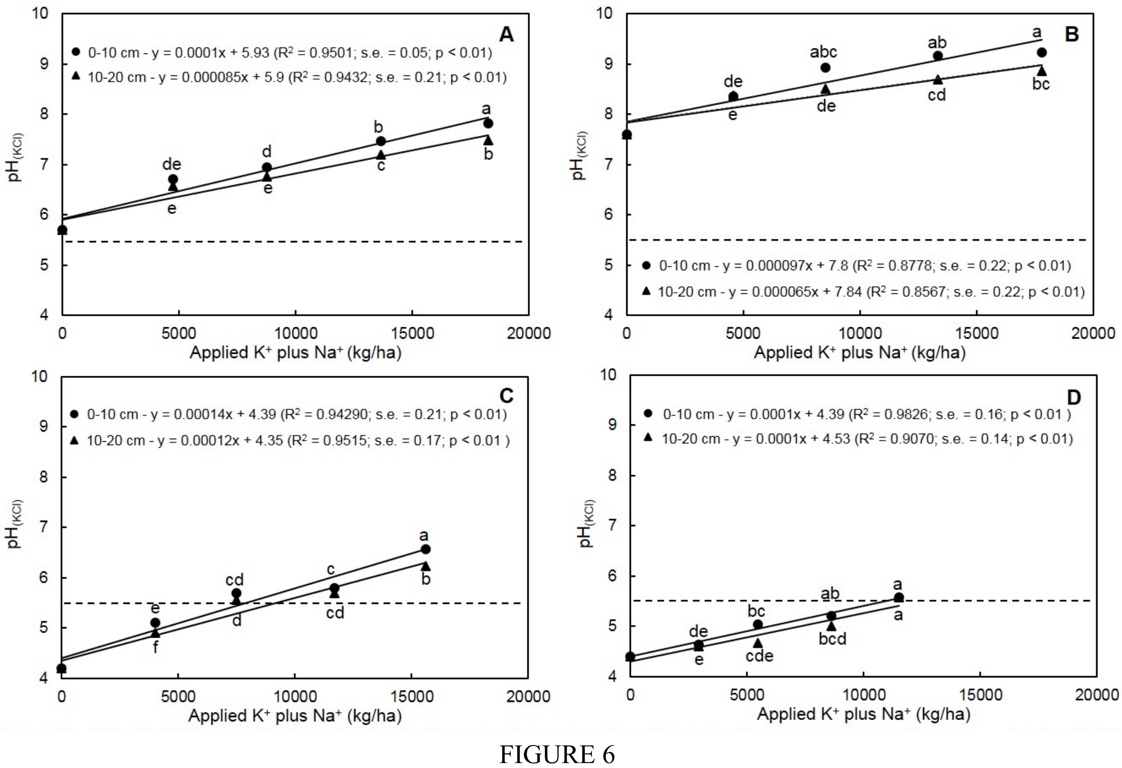

FIGURE 6
Effect of K^+ plus Na^+ applied *via* diluted winery wastewater over four seasons on the $pH_{(KCl)}$ in the 0 to 10 cm and 10 to 20 cm layers of (A) Rawsonville sand, (B) Lutzville sand, (C) Stellenbosch shale and (D) Stellenbosch granite soils. Dashed lines indicate a lower $pH_{(KCl)}$ threshold for grapevines. Values designated by the same letter do not differ significantly ($p \leq 0.05$).

TABLE 4
Effect of irrigation with municipal water and diluted winery wastewater on the extractable Ca^{2+} and Mg^{2+} in four different soils after four simulated seasons.

Soil	Municipal		Winery	
	0-10 cm	10-20 cm	0-10 cm	10-20 cm
	Ca^{2+}_{extr} (cmol$^{(+)}$/kg)			
Rawsonville sand	3.5a[(1)]	3.5a	3.1b	3.1b
Lutzville sand	2.7a	3.1a	2.9a	2.7a
Stellenbosch shale	1.9a	1.7a	2.0a	1.9a
Stellenbosch granite	2.4a	2.2a	2.1a	1.9a
	Mg^{2+}_{extr} (cmol$^{(+)}$/kg)			
Rawsonville sand	1.3a	1.4a	1.2a	1.2a
Lutzville sand	0.8a	0.7b	0.6c	0.5d
Stellenbosch shale	0.8a	0.7b	0.9a	0.9a
Stellenbosch granite	1.0a	0.5d	0.9b	0.7c

[(1)] Values designated by the same letter within each row do not differ significantly ($p \leq 0.05$).

Calcium and magnesium

After the four simulated irrigation seasons, Ca^{2+}_{extr} and Mg^{2+}_{extr} did not show any trends that could be related to the amounts of these elements applied *via* the municipal water and diluted winery wastewater respectively (Table 4). The lack of response could be expected in view of the small amounts of Ca^{2+} and Mg^{2+} applied through the irrigation water (Table 2). In fact, irrigation with the wastewater reduced the Ca^{2+}_{extr} in the Rawsonville sand after the four seasons. The Mg^{2+}_{extr} in the Lutzville sand showed a similar trend (Table 4). Where wastewater was applied to the Stellenbosch granite soil, Mg^{2+}_{extr} also was lower compared to Mg^{2+}_{extr} in the 0 to 10 cm layer of the municipal water irrigation. The foregoing implies that irrigation with winery wastewater is unlikely to have any benefits in terms of Ca^{2+} and Mg^{2+} supply to plants. Furthermore, if applied in such small amounts, these elements will not be able to counter possible structural problems caused by high levels of Na^+ applied *via* winery wastewater.

$pH_{(KCl)}$

The $pH_{(KCl)}$ of the soils prior to any treatment is given in Table 3. The Stellenbosch soils had a low $pH_{(KCl)}$ (4.2 to 4.4), while the Rawsonville and Lutzville sands had substantially higher values (5.7 and 7.6 respectively). Where municipal water was applied, soil $pH_{(KCl)}$ was 5.9, 7.6, 4.5 and 4.6 for the Rawsonville sand, Lutzville sand, Stellenbosch shale and Stellenbosch granite soils respectively after the four seasons (data not shown). In contrast, irrigation with diluted winery wastewater increased $pH_{(KCl)}$ substantially in all the soils over the four seasons (Fig. 6). In all the soils, $pH_{(KCl)}$ in the 0 to 10 cm soil layers tended to be very slightly higher than that in the 10 to 20 cm layer.

This means that, despite the wastewater having a fairly low pH (4.9 to 6.0), it actually increased the soil pH. The Lutzville, Rawsonville and Stellenbosch shale soils showed a pH increase of approximately 2 pH units, while the granite soil, which received less irrigation water, only showed a pH increase of 1 unit. Although this may seem counterintuitive, it is not an unusual phenomenon and has been recorded in numerous studies where organic substrates are added to a soil (Yan *et al*., 1996; Li *et al*., 2008; Rukshana *et al*., 2011; 2012). When salts of organic acids are added to a soil, decarboxylation and hydrolysis of the organic/bicarbonate anions increases the pH (Li *et al*., 2008). The winery wastewater used in this study had an extremely high total alkalinity (Table 1). It is likely that this alkalinity comprised a number of deprotonated organic acids as well as bicarbonate ions. The charge on these anions is largely countered by K^+ and Na^+ cations, thus when applied to soils this results in a pH increase due to decarboxylation and anion hydrolysis reactions, as described by Li *et al*. (2008). These authors found that Na^+ and K^+ organic salts are more effective at increasing soil pH than Ca^{2+} and Mg^{2+} organic salts. This would explain why the soil $pH_{(KCl)}$ increased linearly with the cumulative amount of K^+ plus Na^+ applied *via* the diluted winery wastewater (Fig. 6). Similar increases in pH were reported by Laurenson *et al*. (2012) when high alkalinity winery wastewater was applied to vineyard soils.

Initially, $pH_{(KCl)}$ in the Rawsonville and Lutzville sands (Table 3) was higher than the lower threshold of 5.5 for vineyard soils (Conradie, 1994). However, where these soils were irrigated with diluted winery wastewater, the high $pH_{(KCl)}$ levels (Fig. 6) could have detrimental effects on the availability of plant nutrients (Busman *et al*., 2002). Where the $pH_{(KCl)}$ initially was lower than 5.5 in the Stellenbosch shale and granite soils, irrigation with the diluted winery wastewater had a beneficial effect by raising the $pH_{(KCl)}$ to the optimum range after the first season (Fig. 6C and D). In sandy soils, where the pH is not well buffered, vineyard soils may become acidic under intensive irrigation, particularly drip irrigation (Myburgh, 2012). Such soils, *e.g.* the sandy vineyard soils in the Olifants River region, require frequent liming. Therefore, irrigation with diluted winery wastewater containing high levels of K^+ may reduce the rate of acidification in these poorly buffered sandy soils.

CONCLUSIONS

Irrigation with winery wastewater containing relatively high levels of K^+ and Na^+ affected the soil more than irrigation with municipal water, which served as the control. Since the K^+_{extr} increase with increasing amounts of K^+ applied was comparable for the four soils, it is suggested that clay content did not play a significant role. The EPP′ was above the critical level of 4% in all the soils before the experiment commenced. This means that, under the prevailing conditions, there is a high risk of K^+ accumulating to levels that could have negative effects on wine colour if the excess K^+ is not leached out in the winter or absorbed by inter-row crops in the summer. In the heavier soils the increase of Na^+_{extr} with increasing amounts of Na^+ applied was almost double than in the sandy soils. This indicates that the risk of Na^+ reaching excessive levels will be less when vineyards in sandy soils, compared to heavier soils, are irrigated with diluted winery wastewater. Although the ESP′ exceeded the threshold of 15% only in the 0 to 10 cm layer, Na^+ accumulation in the deeper layers could increase ESP′ to excessive levels in the long run. Due to low Ca^{2+} and Mg^{2+} concentrations in the diluted winery wastewater, their extractable concentrations in the soil were comparable to the initial levels after four seasons.

This indicates that these elements are not contained in the cleaning detergents used in wineries to the extent that they would accumulate in the soil, irrespective of clay content. The increase in soil $pH_{(KCl)}$, irrespective of clay content, could be attributed to organic anions added to the soil *via* irrigation with diluted winery wastewater. In the sandy soils, where the $pH_{(KCl)}$ approached 8 or even higher values, nutrient solubility and absorption could be reduced if winery wastewater was used for vineyard irrigation. It must be noted that the foregoing results represent a worst-case scenario, *i.e.* in the absence of rainfall or crops. Determining the effect of seasonal leaching by winter rainfall on the chemical status in soils irrigated with diluted winery wastewater is part of an ongoing study.

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