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Research Article

A California Winery Wastewater Survey: Assessing the Salinity Challenge for Wastewater Reuse

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Abstract: Over thirty percent of the United States is currently considered to be in a drought that is expected to have profound social, economic, and environmental impacts. Drought conditions are intensifying in the southern and western regions of the country, spurring interest in wastewater reuse in agriculture, including wine production. Presented here is the first data set of its kind to support California growers and vintners reuse of treated winery wastewater (WWW). The data provide a detailed description of California WWW, with particular emphasis on WWW salinity, required to assess benefits and risks of land application. Monthly samples were obtained over a twenty month period from eighteen participating wineries in Ukiah, Napa, Lodi, King City, and Paso Robles. Samples collected prior to (pre-) and after (post-) treatment were analyzed for pH, electrical conductivity (EC), cation and anion concentrations, specific ultra-violet absorbance ($SUVA_{254}$), dissolved organic carbon (DOC), and biological oxygen demand (BOD_5). The pH of WWW varied widely (3-12). Organic parameters ($SUVA_{254}$, DOC, and

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BOD_5) indicated that treatment effectively decreased organic carbon to levels that would not have negative effects on plant growth and soil. Cation concentrations (Na^+, K^+, Ca^{2+}, Mg^{2+}) observed in this study were not reduced by WWW treatment, indicating salts stayed in solution after treatment. These baseline data confirm that dissolved salts pose one of the greatest challenges to reuse of WWW. However, measurements of total salinity (electrical conductivity) of the WWW at participating wineries was found to be moderate (mean of 1.0 dS/m), and usually below thresholds for common wine grape rootstocks and soil salinity hazards. The conditions under which WWW could be recommended as a water management option in California are described.

Key words: sodium, potassium, salinity, drought, reuse, BOD, greywater

Introduction

The agricultural industry of the United States is vulnerable to social, economic, and environmental impacts of ongoing and intensifying changes in climate (NOAA 2013). Projected increases in fresh water demand and more frequent incidences of drought are raising interest in alternative sources of water (IPCC 2013). For the fast growing and dynamic California wine industry water reuse has emerged both as a management alternative and as a matter of great concern. Local legislation has placed tight limits on water use by agriculture. Regulations to meet habitat requirements for threatened wildlife have further reduced fresh water availability for irrigation in recent years. Policies for maintaining in-stream flows in Northern California [(e.g. AB2121) (North-Coast-Stream-Flow-Coalition 2009)] have existed for some time, but very recently (September 2014) new landmark groundwater legislation, AB1739 (SWRCB 2014), SB

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1168 and SB 1319 (CDFA 2014), was signed into law. These are among the key factors that have spurred interest in onsite reuse of winery wastewater (WWW).

During the wine making process most WWW is generated from cooling and cleaning inside the winery (Smyth and Russell 2009). Typically, because of additions of acidic grape juice and alkaline cleaners, WWW has widely fluctuating acidity (pH 3-11) and contains dissolved sugars measured as biological oxygen demand (BOD_5), or as dissolved organic carbon (DOC). The electrical conductivity (EC) of WWW typically ranges from 0.8-3.1 dS/m (Bustamante et al. 2005). Nitrogen (N) is also sometimes present (0-142 mg/L) and usually phosphorus (P) concentrations are in the range 3-188 mg/L (Bustamante et al. 2005). WWW is rich in potassium (K^+) and sodium (Na^+) salts due to the naturally occurring K^+ in grapes and K^+ and Na^+ introduced in cleaning agents. When applied via irrigation to land, K^+ and Na^+ ions in solution can detrimentally alter the soil chemistry and physical structure, and reduce HC (Ayers 1985). Although K^+ may be less detrimental to soil structure than Na^+ due to its smaller hydrated radius, currently there is no consensus on the impact of increasingly K^+-rich waters on soils and plant health (Boulton 1980, Morlat 2008).

The problems associated with Na^+ accumulation in soils are well recognized and agricultural guidelines defining conditions in which soils experience swelling, dispersion and subsequent reductions in infiltration have long been established (Ayers 1985). A variety of wastewater treatment methods are employed to produce effluent that, ideally, will be suitable for irrigation of landscaping or even grapevines (Hamilton et al. 2007). Available treatment methods include physicochemical or biological approaches, or a combination of the two. The physicochemical

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66 methods rely on natural evaporation in ponds, often combined with sprinklers or aerators to
67 enhance evaporation, as well as flocculating agents and filtration systems (Hamilton et al. 2007,
68 Mosse et al. 2011). Biological methods utilize microorganisms in suspension or immobilized for
69 anaerobic digestion and aerobic biological treatment (Laurenson et al. 2012, Oliver et al. 2008).

70 Management requirements for WWW are unique because the composition and volume of the
71 effluent stream is seasonally variable, with the bulk of the volume being produced during the
72 vintage, which usually falls between September and November in the Northern hemisphere
73 (Laurenson et al. 2012, Mosse et al. 2013b). The WWW is most often treated on-site and
74 provides a large potential alternative water source for vineyard and landscaping irrigation. A pH
75 adjustment and screening of gross solids is required prior to discharge to a municipal system.
76 WWW might also be discharged to a leachfield or small wineries may also use septic tanks
77 (Malandra et al. 2003). Any winery that produces more than 40,000 cases annually will likely
78 treat their wastewater on site, where aerated ponds are the simplest, most common, and
79 inexpensive method (Storm 2001). Pond systems are treated like any other fermentation process
80 and require appropriate temperatures, nutrients, and pH in order to remove organics, mostly in
81 the form of dissolved sugars. Clarifiers are used after pond treatment to remove settleable solids
82 and the settled sludge can be returned to the ponds to maintain an active inoculum (Storm 2001).
83 Aerated ponds usually succeed at reducing the biological oxygen demand (BOD_5) and total
84 solids of the effluent (Arienzo et al. 2009, Laurenson et al. 2012). Additionally, when used as a
85 tertiary treatment, wetland systems can remove all organics from WWW (98%). However, the
86 large initial investments and land required for wetland construction are sometimes deterrents

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(Shepherd et al. 2001). Anaerobic ponds and digesters are not common for WWW treatment due to the highly variable flow rate of WWW, as well as the odors often associated with anaerobic processes (Mosse et al. 2011).

None of these treatment options have been shown to remove salts (Christen et al. 2010). A review of treatment approach and efficacy describes electrodialysis, ion exchange, and reverse osmosis as possible physiochemical methods for removal of salts, but the disadvantages of these systems include requirements for specialized equipment and operator expertise, as well as high cost and energy inputs (Mosse et al. 2011). While previous studies have investigated the characteristics of WWW (Bustamante et al. 2005, Conradie 2014, Eales 2014, Hamilton et al. 2007, Mosse et al. 2013b), the objectives of this study were to evaluate the effectiveness of existing on-site WWW treatment options and to assess the salinity challenge for WWW reuse in California. This survey is the first of its kind in the state, examining WWW across a spectrum of production volumes and treatment options with consideration for application thresholds of common wine grape rootstocks and soil salinity hazards.

Materials and Methods

Sample Collection and Background Survey.

Eighteen California wineries were selected for this study based on site visits in the July, 2010. Background surveys covering general information about wine production and winery cleaning practices were conducted to ensure that the participating wineries represented diverse annual crush volume, production volume, effluent volume, percent red and white wine produced, cleaners used and WWW treatment and reuse approaches. Types of cleaners used by each winery

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were also tabulated (Supplemental Table 1). Treatment methods represented in this study include both physicochemical treatments (sumps, leach fields, and evaporation ponds) and biological methods (aerated ponds, bioreactors, wetlands and trickle towers). Additionally, for each monthly sampling event, wineries indicated winery activities at the time of sampling (e.g., floor washing, barrel washing, crush, harvest, racking, lees filtering, sanitation, wine spillage, bottling, and rain - Table 1). Events that occurred in 50% or more of the wineries in any given sampling month are indicated with an asterisk (Table 1).

Winery employees collected monthly pre- and post-treatment WWW samples for twenty months (consecutive months from November 2010 – June 2012). Duplicate 250 mL polypropylene bottles (SKS Science, Watervliet, NY, USA) were rinsed three times with sample water and then filled to the lip and sealed. Samples were then shipped on ice to UC Davis overnight. Upon receipt, samples were prepared for analysis of chemical (cation and anion concentrations, EC, pH) and organic characteristics (DOC, $BOD_{5,}$ $SUVA_{254}$).

Wastewater Parameter Measurements.

Sample pH (Thermo Scientific Orion 4 Star meter, Davis, CA, USA, Fisher Scientific Accumet Gel-filled Pencil-Thin pH Combination Electrodes-Mercury-Free 13-620-290, Davis, CA, USA. Method 150.1), EC (Thermo Scientific Orion 4 Star meter, Davis, CA, USA. Orion 013005MD conductivity cell, Davis, CA, USA. Method 120.1), and BOD_5 (Thermo Scientific Orion 4 Star meter, Davis, CA, USA. Thermo Scientific Orion 9708 Dissolved Oxygen probe, Davis, CA, USA) were measured on unfiltered samples immediately upon arrival (Burt and Staff 2014).The BOD_5 was measured according to EPA method, 5210 B (U.S. EPA 1979).

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Samples were then filtered through a 0.45 micron Whatman glass fiber filter. Filtrates were stored in two 50 mL Falcon tubes (Corning Life Sciences DL, Tewksbury, MA, USA). One tube was acidified (using 1 µL 12 mol/L HCl per 1 mL sample) for DOC analysis, and the other was not acidified and stored at 1.6 °C for $SUVA_{254}$, nitrate (NO_3^-) analysis. For DOC, samples were placed in combusted 20 mL glass DOC vials (National Scientific, Rockwood, TN) for analysis with a high temperature catalytic oxidation analyser (Shimadzu TOC-V, Davis, CA, USA). The mean of 3–5 injections of 100 µL is reported for every sample (Qian and Mopper 1996, Spencer et al. 2008). NO_3^- was measured using a colorimetric method (Doane and Horwath 2003). One mL of NO_3^- reagent was transferred into a 1 ml microcuvette (BrandTech Scientific, Essex, CT) and 0.05 mL sample was added. After 8-12 hrs color development, absorbance at $\lambda = 540$ nm was measured on a Thermo Scientific spectrophotometer (GENESYS 10S UV-Vis, Davis, CA, USA). For $SUVA_{254}$, UV-visible absorbance ($\lambda = 254$ nm) was measured at room temperature on a Thermo Scientific spectrophotometer (GENESYS 10S UV-Vis, Davis, CA, USA). $SUVA_{254}$ values were determined by dividing the UV absorbance measured at $\lambda = 254$ nm by measured DOC (Spencer et al. 2008).

Cation (Na^+, K^+, NH_4^+, Mg^{2+}, Na^{2+}) and anion (Cl^-, SO_4^-, Br^-, NO_3^-, PO_4^{3-}) concentrations were measured using a Ion Chromatograph (Dionex ICS-2000, Davis, CA, USA). Samples were prepared in duplicate and run according to ASTM cation determination method D6919-09 and EPA anion determination method 4110 (ASTM 2009, U.S. EPA 2007). Data were used to calculate values for several metrics of WWW quality, including the sodium adsorption ratio (SAR), the potassium adsorption ratio (PAR), the monovalent cation ratio (MCAR), and the

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cation ratio of structural stability (CROSS) (Jayawardane et al. 2011) (Eq. 1-4). Equations 1-4 are calculated with concentrations in mEq/L.

$$SAR = Na^{+}/ ((Ca^{2+} + Mg^{2+})/2)^{\wedge 1/2} \quad \text{conc. in mEq/L} \quad \text{Eq. 1}$$

$$PAR = K^{+}/ ((Ca^{2+} + Mg^{2+})/2)^{\wedge 1/2} \quad \text{conc. in mEq/L} \quad \text{Eq. 2}$$

$$MCAR = (Na^{+} + K^{+})/ ((Ca^{2+} + Mg^{2+})/2)^{\wedge 1/2} \quad \text{conc. in mEq/L} \quad \text{Eq. 3}$$

$$CROSS = (Na^{+} + 0.56K^{+})/ ((Ca^{2+} + 0.6Mg^{2+})/2)^{\wedge 1/2} \quad \text{conc. in mEq/L} \quad \text{Eq. 4}$$

SAR is a weighted ratio of Na^{+} to other cations in solution. PAR is calculated similarly. The MCAR equation (Eq. 3) considers the combined effect of all cations present in solution, including Na^{+} and K^{+} (Jayawardane et al. 2011). The CROSS equation (Eq. 4) considers the relative flocculating effects of Mg^{2+} and Ca^{2+} and the dispersive effects of K^{+} and Na^{+}, as described by Rengasamy (2002). Rengasamy (2002) determined the relative flocculating powers, where $Na^{+} = 1$, and thus the values are: $Na^{+} = 1$, $K^{+} = 1.8$, $Mg^{2+} = 27$, $Ca^{2+} = 45$. The CROSS equation uses these flocculation coefficients to estimate reductions in hydraulic conductivity (HC) at given cation ratios. The use of the CROSS equation could potentially provide more a more accurate risk predictor for saline waters and the potential hazards they present to soil HC (Jayawardane et al. 2011, Laurenson et al. 2012).

Data Analysis and Interpretation.

Statistical analyses were performed using JMP 10 (SAS Institute License 2013, Cary, NC, USA). In order to meet assumptions of normality and homogeneity of variance, the data was log transformed ($\log_{10}(x+1)$) prior to analysis (Shapiro-Wilk test with $W \geq 0.95$). An initial analysis of variance (ANOVA) was run using a mixed-effect model to test the significance ($P \leq 0.05$) of

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fixed (year, month, water treatment) and random (site) effects, as well as their interaction. For most variables, this procedure indicated absence of significant differences between sampling years, so data for year one and year two could be combined to generate monthly averages. For further analysis, another mixed-effect ANOVA was used to test the significance ($P \leq 0.05$) of fixed (month, water treatment) and random (winery = site) effects, as well as their interaction. For each measured parameter the effect of month and treatment were reported (Table 2) and, whenever interactions were significant, data were presented as pre- and post-treatment averages (pH/ BOD_5/ DOC/ $SUVA_{254}$). A final two-way ANOVA, with the main effect of month and random effect of site, was then used to examine temporal variation of all parameters on averages that removed any confounding interactive effects. When appropriate, a Tukey's HSD (Honestly Significant Difference) test was used to determine differences in the mean across months. For a select group of variables ($SUVA_{254}$/ Br^-/ NO_3^-/ NH_4^+), which did not conform to assumptions of normality and/or homogeneity of varience, an equivalent (non-parametric) multiple comparison (Steel-Dwass All Pairs) test was used.

Results and Discussion

This survey reflects a wide range of management practices and treatments already in use in California wineries to improve WWW quality. Significant differences in WWW chemistry between months can be explained by increased winery activities during different times of the year (e.g. the vintage, which falls between September and December in California).No significant differences were observed between the two years of sampling. Consistent improvement in WWW quality was observed in all cases as a result of treatments, despite

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192 substantial temporal variation in WWW chemistry (Supplemental Figures 1-8), indicating
193 effective management of a variable loads and successful reduction of BOD_5. From the analysis
194 of this data set and comparison to previous research, it is clear that treated WWW could be
195 reused for irrigation (Mosse et al. 2013a, Weber et al. 2014). A synthesis of the background
196 survey and baseline values for each measured parameter are presented below.

197 **Winery Wastewater Background Survey.**

198 The data collected on winery activities by month clearly show that harvest and crush activities
199 were indicated only between September and December in California (Table 1). Overall, the three
200 activities that were cited most often as contributing to WWW were barrel washing, sanitation,
201 and racking (Table 1). The data in Table 1 also suggest that larger quantities of WWW are
202 usually generated between September and December (vintage), but that floor and barrel washing,
203 racking, sanitation, and bottling occur throughout the year and continue to produce WWW, even
204 in the off-season. The offset between the time that WWW is generated and when additional
205 water may be required in the vineyard are important considerations for a sustainable water
206 management plan. The types of cleaners used by all wineries are summarized in the
207 supplemental information (Supplemental Table 1), and should also be considered when
208 implementing future best management strategies. Some specific parameters that could be used to
209 indicate safe WWW reuse and associated baselines for reference in future studies are described
210 as follows.

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Organics in Winery Wastewater.

The changes in BOD_5, DOC, and $SUVA_{254}$, were indicative of shifts in the composition of organic compounds with respect to month and WWW treatment (Table 2). Frequently, untreated WWW samples had high BOD_5, upwards of 15,000 mg/L, but all treatment methods represented in this study typically reduced BOD_5 to below 150 mg/L (Fig. 1). DOC showed the same trends as BOD_5 (Supplemental Figure 1). The efficacy of WWW treatment is reflected by the reduction in the labile fraction of organic carbon from pre- to post-treatment, measured as a reduction in BOD_5 and DOC concentrations (Table 3, 4, and 5). The US EPA BOD_5 limit for a normal secondary treatment facility is a monthly average of 30 mg/L dissolved oxygen, but most wineries are usually not classified as 'normal' secondary treatment facilities and their permitted BOD_5 limit may be greater than 65 mg/L (U.S. EPA 2004). Despite this, 30 mg/L is also the recommended maximum put forth by the EPA for any water source intended for reuse. If irrigation of a valuable cash crop, such as grapes, was the intended end use for treated WWW, it would behoove the grower to meet the suggested limit of 30 mg/L BOD_5.

For pH, BOD_5, DOC, and $SUVA_{254}$, the effects of month were examined separately from treatment, due to significant interactions between month and treatment (Table 2). For this WWW study, pre-treatment values for BOD_5 were highest between October and February (Fig. 1), when crush and harvest activities, including sanitation, spills, lees filtering, barrel washing, floor washing, and racking were all major contributors to WWW (Table 1) (Conradie 2014). The high BOD_5 seen in pre-treatment WWW in April is likely a result of racking and bottling and highs in July can be attributed to preparations in the winery for harvest and crush (Fig. 1) (Conradie 2014).

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234 Post-treatment BOD_5 increased to close to 100 mg/L in November and December, a time of year
235 of high activity for California wineries, indicating that efficacy of treatment systems were
236 reduced during this period (Fig. 1). The WWW generated during these months is stored and
237 mixed with WWW from other times of the year, and sometimes freshwater sources (Waisdorff et
238 al. 2005). This practice may contribute to the reduction seen in post-treatment BOD_5 (Fig. 1) to
239 close to 10 mg/L by early spring (March-April), and during the summer months (June-August).
240 These differences in BOD_5 concentrations seen throughout the year, confirm the high temporal
241 variability of WWW streams. Both the variability of organic and inorganic characteristics of
242 WWW and the volume of WWW generated at different times of year are critical factors to
243 consider when developing a sustainable water management plan. These considerations will be
244 unique to each winery, but, commonly, treatment and storage of WWW are necessary in order to
245 provide water suitable for land application at critical times of the year.

246 $SUVA_{254}$ is the mean absorptivity for the molecules constituting the DOC in water samples. It
247 serves as an indicator of the aromatic fraction of DOC and as a proxy for phenols and tannin
248 concentrations, which comprise the more recalcitrant constituents of WWW (Mosse et al. 2013b,
249 Weishaar et al. 2003). The mean annual $SUVA_{254}$ value for this study was 0.64 L/mg C/m.
250 $SUVA_{254}$ in this range indicates that about ≤10% of the DOC is aromatic (Weishaar et al. 2003).
251 An increase in $SUVA_{254}$ close to 6 L/mg C/m in January (after the vintage, for California
252 wineries) suggested a more recalcitrant carbon fraction becoming concentrated in the WWW
253 stream (Fig. 2). Overall, post-treatment $SUVA_{254}$, BOD_5, and DOC of treated WWW were below
254 maximum thresholds for concentrations that would be harmful to the soil and plants receiving the
255 treated WWW (Table 3 and 4) (Laurenson et al. 2012, Weber et al. 2014).

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Acidity of Winery Wastewater.

Like the organic parameters, WWW pH also differed by month (Supplemental Table 2) and with treatment, increasing after water treatment. Post-treatment pH also differed seasonally, increasing leading up to harvest and crush (July-August; Table 2 and Supplemental Table 2). Cleaning agents used in the winery and chemical compounds used in the wine making process affect the pH of WWW (Mosse et al. 2011, Sims and Morris 1984). The increase in post-treatment WWW pH is different from other findings, where low pH values have been observed in Spain and Greece (Bustamante et al. 2005, Vlyssides et al. 2005). High pH values are attributed to the use of alkaline cleaning agents [i.e., sodium percarbonate ($2Na_2CO_3 \cdot 3H_2O_2$), sodium carbonate (Na_2CO_3), sodium and potassium hydroxide (NaOH, KOH)]. The difference in the mean pH of WWW from California wineries suggests that larger quantities of alkaline compounds were introduced into WWW by these wineries compared to other wine regions (Mosse et al. 2011). In this study, WWW samples were taken from both pre- and post-treatment sites. This may make comparison to other studies difficult, since it is usually not specified where exactly in the WWW treatment stream samples were taken, but presumably WWW is sampled prior to treatment. With respect to existing studies from other world regions, these findings demonstrate how regional distinctions in practice influence WWW pH.

Chemical Characteristics of Winery Wastewater.

One of the biggest challenges when irrigating with treated WWW is effectively evaluating and mitigating salinity risk, both to plants and to soil. Total N concentrations in WWW are usually very low to moderate and can provide an additional source of N fertilizer. Total P can be of concern and is often between 3-188 mg/L. In this study, the mean PO_4^- concentration post-

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278 treatment was13.5 mg/L. Grapevines remove only about 4 kg P/ha/yr (Conradie and Saayman
279 1989). If P runoff is to be minimized, this would allow for the land application of close to 300,
280 000 L/ ha WWW. Total P concentrations do present a challenge to the reuse of WWW, but many
281 treatment approaches exist that effectively reduce P concentrations, such as biofilters of chemical
282 precipitation (Leverenze 2002).

283 The persistence of salts in solution can be seen by the similarity in pre- and post-treatment EC
284 values and ion concentrations (Table 3 and 4). The post-treatment EC of the WWW sampled for
285 this study was usually below 2 dS/m and the maximum was 4.66 dS/m. The pre- and post-
286 treatment mean EC were both close to 1 dS/m. Cation concentrations ranged from 1-3,100 mg/L
287 and also did not differ before and after treatment. Monthly differences, however, were apparent
288 for some compounds (Table 2). Concentrations for Na^+, Ca^{2+}, Mg^{2+}, Cl^-, PO_4^{3-}, and NO_3^- all
289 showed increases in November (Supplemental Figures 3-6, Supplemental Table 2). Unlike the
290 individual ion concentrations in this study, SAR did not show differences between months (Fig.
291 3). This was due to concurrent increases in monovalent and divalent ions, which buffered the
292 salinity risk presented by high Na^+ or K^+ concentrations and maintained a mean SAR close to 2
293 and PAR close to 1.5 (Table 2). PAR showed increases in July and September (Fig. 4). The
294 MCAR and CROSS equations are designed to reflect the nuanced effects of increasing
295 concentrations each of the major cations contributing to the total salinity of a solution. One study
296 observed that MCAR and CROSS values from 6-52 can negatively affect soil HC (Jayawardane
297 et al. 2011). The calculated MCAR (Eq. 3) and CROSS (Eq. 4) values for this WWW survey
298 were more synchronous with seasonal fluctuations of cation concentrations than SAR or PAR,
299 increasing in September and November and decreasing in January through March (Supplemental

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Figures 7 and 8). Throughout the year, the mean CROSS value was between 2 and 5 (Table 3 and 4). This indicates that the ratios of cations were not above the threshold value for reductions in soil HC.

Most anions were present at low concentrations. Chloride (Cl^-) is of greatest concern to growers, because of its potential toxicity if present at concentrations exceeding the Cl^- tolerance of a particular cultivar (Weber et al. 2014). Cl^- concentrations seen in this study were usually moderate, ranging from 2-541 mg/L post-treatment (Table 3), and increased in November (Supplemental Tables 3b). However, even the maximum post-treatment concentrations of chloride seen in this survey could only be harmful to the most salt sensitive grape rootstocks, namely Cardinal and Black Rose (Weber et al. 2014). Therefore, when reusing treated WWW in California, any potential Cl^- toxicity threat to grapevines can be avoided by monitoring and diluting the WWW appropriately (Weber et al. 2014). Dissolved salts can also be removed from solution by electrodialysis, ion exchange, and reverse osmosis, but these methods are not commonly used, due to expense and energy requirements (Mosse et al. 2011).

Despite the moderate total salt concentration indicated by the EC of WWW in this study, the data show that Na^+ and K^+ can sometimes be present at elevated concentrations sufficient to reduce soil HC via osmotic swelling (Fig. 5). Na^+ is a large monovalent ion and more effectively forces clay tactoids apart than Ca^{2+} or Mg^{2+} (Quirk 1986). Based on the water infiltration risk zones for Na^+, first established by Quirk and Schofield (1955) and later by (Ayers 1985), SAR values from 3-9 pose slight to moderate risk for reductions in infiltration at EC > 0.3-0.5, and are severely hazardous if EC < 0.3-0.5 dS/m (Ayers 1985). Therefore, considering the Na^+ and K^+

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concentrations seen in this study, the most common risk scenario for California wineries was for Na^+ concentrations to increase above 3 dS/m while total EC remained below 1 dS/m (Fig. 5). However, a recent study, including a Napa vineyard that was irrigated with recycled Napa Sanitation District water for seven seasons, has shown that even when consistently irrigating with water possessing SAR values slightly above the recommended limit of 3, Na^+ accumulation could be easily managed with gypsum applications and with no other negative effects to soil, plants, or fruit (Weber et al. 2014). In Figure 5 the risk zones have been superimposed onto the WWW survey post-treatment SAR-EC data. While most of the data points fall into the no- or moderate-reduction-of-infiltration zone, the points that are at risk of severe reductions in HC have total EC below 1 dS/m. The risk to HC in this zone is due to dispersion, which arises in dilute electrolyte solutions due to the electric double layer phenomena and will occur independently of Na^+ or K^+ concentrations of the soil solution when EC < 0.2 dS/m (Ayers 1985). Figure 6 depicts the calculated threshold electrolyte concentration (gray line) at different CROSS values, and includes points for all samples in this WWW study, showing that the electrolyte concentrations of the WWW samples usually fall above the threshold line, indicating that the water should not reduce soil HC.

The effects of salinity on soil HC sometimes differ from the established risk zones, depending on soil mineralogy (Buelow 2013). If the vineyard soil is predominantly montmorillonite or vermiculite, the HC may experience less of a reduction at elevated levels of K^+, than of Na^+. However, if the soil is dominated by kaolinite, it is possible that increases in K^+ concentrations could be equally as or more detrimental to the soil HC as increases in Na^+ (Buelow 2015,

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342 Buelow 2013). Therefore site specific assessment of water and soil prior to reuse of treated
343 WWW is recommended (Buelow 2015, Buelow 2013, Frenkel 1985, Frenkel et al. 1978).

344 Conclusion

345 This survey is the first WWW characterization study specific to wine regions in California. The
346 data presented here reflect seasonal variations alongside the effect of common treatment
347 approaches and will serve as a baseline. Findings from this WWW study and other published
348 work strongly suggest that WWW has great potential to be reused on site. Samples from this study
349 showed that BOD_5 and DOC concentrations were most often effectively reduced. It is common
350 practice to monitor BOD_5 and DOC, and these parameters can be used to ensure that soils are not
351 overloaded with organic carbon. Although total P may also be of concern from a regulatory
352 standpoint, it can be effectively reduced by treatment. Elevated salt concentrations are difficult to
353 remove and pose the greatest challenge to WWW resuse; however, in the current study the
354 salinity of wastewater samples from the 18 participating wineries was larelgey acceptable for
355 irrigation use. Additionally, the range of concentration of Cl^- found should not negatively impact
356 vine growth. Furthermore, the time of year when higher concentrations of salts were measured
357 did not coincide with the season when treated WWW would be utilized as an additional water
358 source in vineyards. This temporal offset allows for mixing of WWW streams and time for
359 mitigation of high salt concentrations. Despite measures taken to ensure that high concentrations
360 of Na^+ and K^+ are not introduced into agricultural soils, their variable impact on soils of differing
361 mineralogy highlights an area of further research. Currently, the data and risk assessment tools
362 available to winemakers and growers suggest that the reuse of treated California WWW is

363 possible and should be further pursued, although regular monitoring and establishment of
364 geographically specific guidelines still need to be developed for widespread use in irrigation.

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Table 1 Percentage of wineries that indicated a particular activity was occurring at the time of sampling (*greater than 50%). Harvest and crush activities extend into December in California. The month sum total does not include rain, and the bolded values indicate the 6 months with highest activity recorded in the winery. Barrel washing, racking, and sanitation were cited most often. California vintage = September-December; Off-season = January-August.

Month	Floor washing	Barrel washing	Crush	Harvest	Racking	Lees filtering	Rain	Sanitation	Spills	Bottling	Month Sum Total
Sep.	74*	56*	41	41	44	15	0	7	22	37	**400**
Oct.	38	75*	88*	63*	88*	75*	13	88*	25	13	**563**
Nov.	40	40	100*	100*	60*	60*	70*	90*	60*	10	**630**
Dec.	83*	92*	42	42	100*	50*	75*	92*	67*	33	**675**
Jan.	63*	88*	0	0	71*	33	50*	71*	38	17	**429**
Feb.	0	0	0	0	33	33	33	33	33	0	167
Mar.	43	71*	0	0	57*	0	71*	57*	29	14	343
Apr.	67*	87*	0	0	87*	20	67*	67*	13	53*	**460**
May.	55*	55*	0	0	45	10	45	45	20	30	310
Jun.	53*	87*	0	0	47	7	47	73*	20	33	367
Jul.	44	78*	0	0	72*	17	33	44	11	56*	356
Aug.	44	67*	0	0	33	11	11	50*	22	0.61*	300
Sum	604	**794**	270	245	**737**	331	515	**780**	360	357	

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Table 2 *P*-values for analysis of variance (ANOVA),* indicating differences ($p \leq 0.05$) from the whole model mean by month, treatment, and interactions. All data is log transformed, except where ◊ = not log transformed. ND = no data. n = 579.

	Units	Month	Treatment	Treat.*Month
BOD_5[a]	mg/L	<.0001*	<.0001*	0.0002*
DOC [b]	mg/L	0.0016*	0.0006*	0.0034*
SUVA[c]	L/mg C/m	<.0001*	0.1093	0.6244
◊ pH		0.0021*	0.0105*	0.3576
EC[d]	dS/m	0.0013*	0.4849	0.9712
Cl^-	mg/L	<.0001*	0.5746	0.5500
SO_4^{2-}		0.011*	0.2211	0.9523
Br^-		0.2546	0.0198*	0.1863
NO_3^-		N.D.	N.D.	N.D.
PO_4^{3-}		0.0032*	0.2222	0.7224
Na^+		0.0013*	0.4724	0.1999
K^+		0.0786	0.2456	1.0000
Mg^{2+}		0.0042*	0.1753	0.2662
Ca^{2+}		<.0001*	0.4519	0.1608
SAR[e]		0.0915	0.0442*	0.6389
PAR[f]	mEq/L	0.0012*	0.0495*	0.9865
MCAR[g]		0.0002*	0.0202*	0.9977
CROSS[h]		0.0004*	0.0208*	0.9847

a = Biological oxygen demand; b = Dissolved organic carbon; c = Specific ultra violet absorption; d = electrical conductivity; e = Sodium adsorption ratio; f = Potassium adsorption ratio; g = Monovalent cation ratio; h = Cation ratio of structural stability.

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Table 3 Comparison of pre- and post-treatment data during the off-season (January-August) from the California winery wastewater survey.

		Off-season - Pre-treatment (n=179)			Off-season - Post-treatment (n=142)		
	Units	Mean	Min	Max	Mean	Min	Max
DOC	mg/L	670	0.739	1.06×10^4	77.2	1.46	1.34×10^3
BOD_5	mg/L	1.39×10^3	3.93	4.10×10^4	107	1.61	3.33×10^3
SUVA	L/mg C/m	1.47	0.00	83.2	0.57	0	4.28
pH		7.12	3.59	11.3	8.01	4.38	11.0
EC	dS/m	0.97	0.137	3.26	0.88	0.198	2.4
Cl^-	mg/L	23.0	3.35	143	22.5	2.79	115
SO_4^{2-}		109	0.00	1.29×10^3	45.0	0.00	592
Br^-		4.22	0.00	95.3	3.39	0.00	209
NO_3^-		0.48	0.00	6.4	1.15	0.00	23.1
PO_4^{3-}		17.1	0.00	237	12.5	0.00	209
Na^+		86.6	5.40	714	65.9	9.93	409
K^+		133	1.31	1270	115	1.16	888
Mg^{2+}		27.4	1.96	1.17×10^2	43.8	6.90	393
Ca^{2+}		69.1	17.8	248	61.2	13.6	159
SAR		1.5	0.146	9.5	1.16	10.2	5.41
PAR	mEq/L	1.36	0.146	27.65	1.09	0.22	6.9
MCAR		2.85	0.100	27.6	2.24	0.32	12.3
CROSS		2.43	0.100	16.0	1.93	0.32	10.2

a = Biological oxygen demand; b = Dissolved organic carbon; c = Specific ultra violet absorption; d = electrical conductivity; e = Sodium adsorption ratio; f = Potassium adsorption ratio; g = Monovalent cation ratio; h = Cation ratio of structural stability.

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Table 4 Organic and chemical characteristics of winery wastewater, pre- and post-treatment, during the California vintage (September-December).

		Vintage - Pre-treatment (n=146)			Vintage - Post-treatment (n=112)		
	Units	Mean	Min	Max	Mean	Min	Max
DOC [b]	mg/L	808	1.63	9.14 $X10^3$	129	2.53	1.73 $X10^3$
BOD_5 [a]	mg/L	1.79 $X10^3$	6.09	1.54 $X10^4$	577	1.33	7.76 $X10^3$
SUVA[c]	L/mg C/m	0.15	0.00	2.44	0.37	0.000	3.08
pH		6.92	3.58	12.9	7.80	4.58	9.64
EC[d]	dS/m	1.32	0.37	9.70	1.17	0.32	4.66
Cl^-	mg/L	48.8	2.28	1.05$X10^3$	44.0	5.77	541
SO_4^{2-}		99.7	0.00	1.08 $X10^3$	58.7	1.73	374
Br^-		1.59	0.00	15.0	1.26	0.00	10.2
NO_3^-		3.03	0.00	15.8	5.04	0.00	48.8
PO_4^{3-}		17.0	0.00	100	17.5	0.00	67.7
Na^+		137	6.84	3.06 $X10^3$	99.5	12.5	351
K^+		176	3.18	772	162	1.91	568
Mg^{2+}		31.2	2.52	219	60.5	6.38	746
Ca^{2+}		75.5	7.84	356	79.5	21.4	268
SAR[e]	mEq/L	2.43	0.21	46.9	1.66	0.21	5.26
PAR[f]		1.87	0.04	11.8	1.48	0.028	6.61
MCAR[g]		4.21	0.28	52.5	3.12	0.31	9.41
CROSS[h]		3.65	0.20	51.9	2.68	0.31	8.19

a = Biological oxygen demand; b = Dissolved organic carbon; c = Specific ultra violet absorption; d = electrical conductivity; e = Sodium adsorption ratio; f = Potassium adsorption ratio; g = Monovalent cation ratio; h = Cation ratio of structural stability.

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Table 5 Analysis of variance (ANOVA) with main effect of month performed on pre- and post-treatment of parameters where interactions between month and treatment were observed. All data is log transformed, except where ◊ = not log transformed.

	Month Pre-treatment	Month Post-treatment
◊ pH	0.0876	0.0003*
BOD_5[a]	<.0001*	0.0003*
DOC[b]	0.0001*	0.2107
SUVA[c]	<.0001*	<.0001*

* = significance. n = 579.
a = Biological oxygen demand; b = Dissolved organic carbon; c = Specific ultra violet absorption.

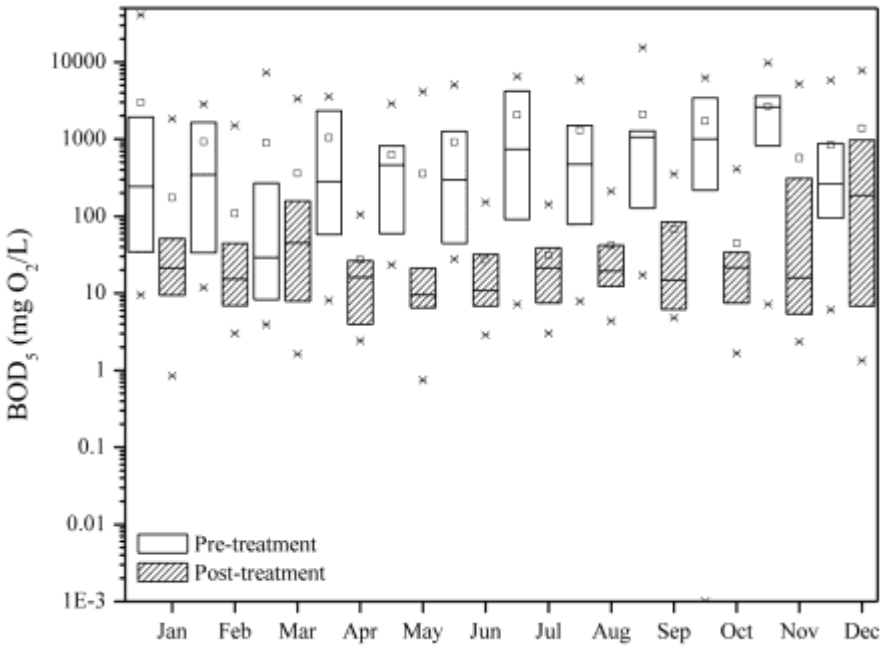

Figure 1 Biological oxygen demand (BOD_5) of all pre- and post- treatment samples. Note y-axis is on a log scale. × = 1st and 99th percentile; ▫ = mean (n= 36 for Oct.-Mar. / n = 18 for Apr.-Sep.)

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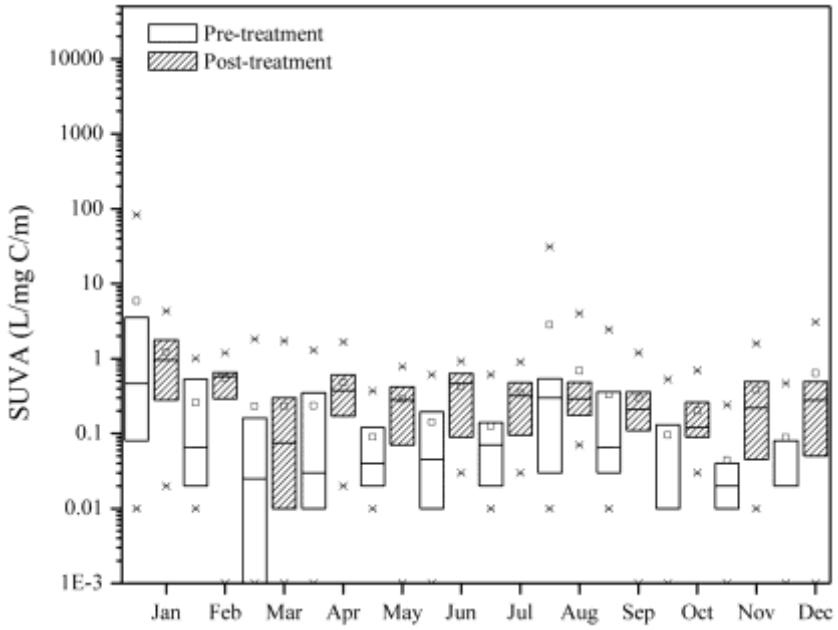

Figure 2 Specific ultra violet absorption ($SUVA_{254}$) of all pre- and post- treatment samples. Note log scale on y-axis. × = 1st and 99th percentile; ▫ = mean (n= 36 for Oct.-Mar. / n = 18 for Apr.-Sep.).

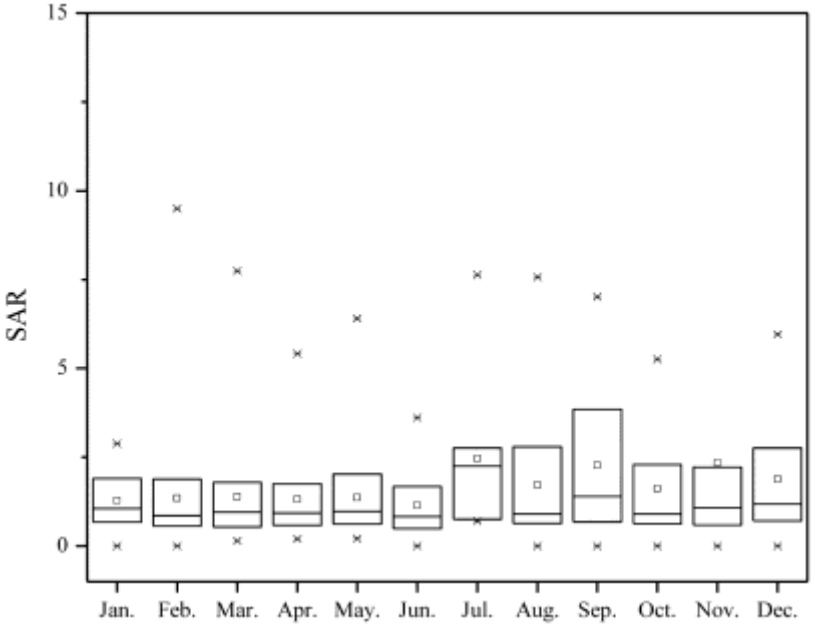

Figure 3 Post-treatment average monthly sodium absorption ratio (SAR) (n= 36 for Oct.-Mar. / n = 18 for Apr.-Sep.). × = 1st and 99_{th} percentile; ▫ = mean.

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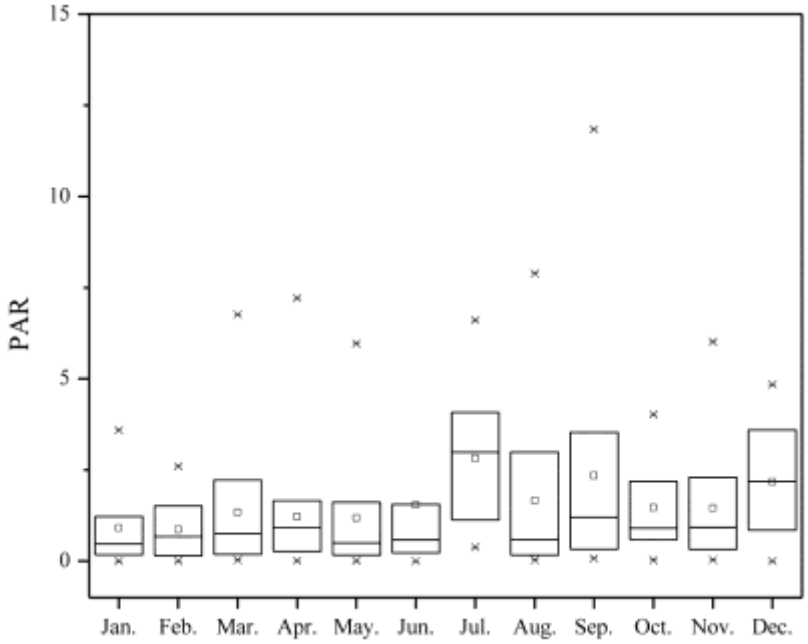

Figure 4 Post-treatment average monthly potassium absorption ratio (PAR) (n= 36 for Oct.-Mar. / n = 18 for Apr.-Sep.). × = 1st and 99th percentile; ▫ = mean.

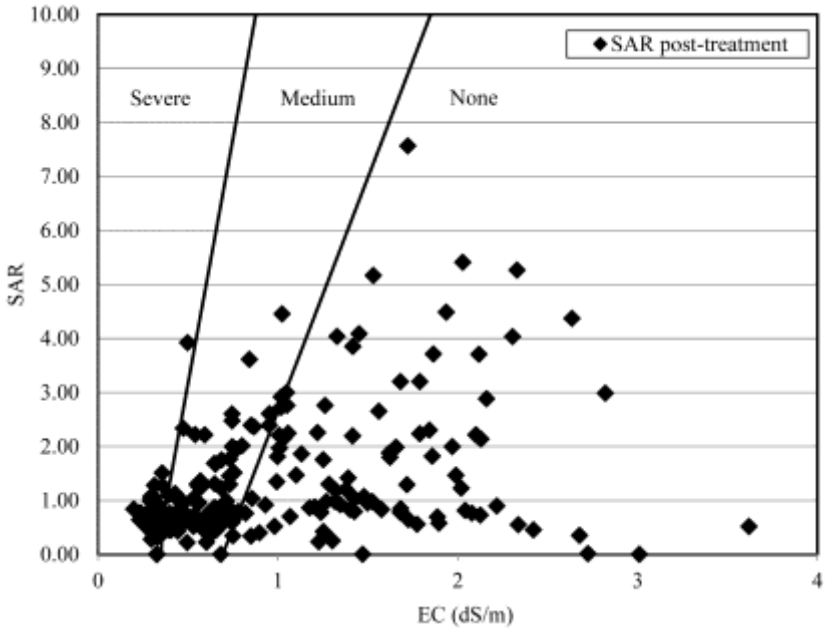

Figure 5 Post-treatment winery wastewater sodium absorption ratio **(**SAR**)** values plotted by electrical conductivity (EC). Risk zones adapted from Ayers and Westcot (1995).

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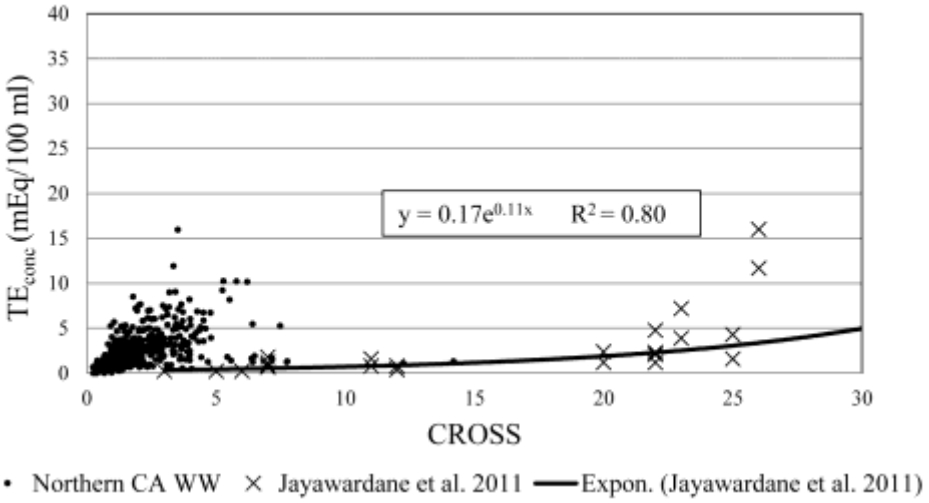

Figure 6 All measured electrolyte concentrations (EC in mEq 100 mL^{-1}) from current study plotted with an experimentally determined threshold electrolyte concentration (TE$_{conc}$) curve established by Jayawardane et al. (2011), using the cation ratio of structural stability (CROSS) values for a smectitic soil.

Supplemental Table 1 Chemical compounds used by the eighteen wineries participating in WW survey.

Compound	Chemical formula	# of Wineries Using	Total #of Wineries Using
Sodium Percarbonate	$2Na_2CO_3 \cdot 3H_2O_2$	5	Sodium based = 17
Sodium Hydroxide	NaOH	5	
Sodium Hypochlorite	NaClO	1	
Sodium Carbonate	Na_2CO_3	5	
Trisodium Phosphate	Na_3PO_4	1	
Potassium Hydroxide	KOH	6	Potassium based = 7
Potassium Bisulfate	$KHSO_4$	1	
Peracetic Acid	CH_3CO_3H	7	Other = 20
Chlorine based cleaner	Cl^-	3	
Citric acid	$C_6H_8O_7$	7	
Ozonated water	$H_2O \cdot O_3$	1	
Iodine	I	1	

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Supplemental Table 2 Winery wastewater parameters multiple means comparison
Results of Tukey HSD test, performed on two-way mixed-effects model ANOVA, fixed effect of month and random effect of site = winery for chemical parameters of WW, with no pre/post treatment division month 1 = Oct. ; month 12 =Sept.; LSM = least square mean (JMP 10 SAS Institute Liscence 2013-University of California Davis).

a) Response pH

Level				LSM
12	A			8.0858
11	A	B		7.9309
10	A	B	C	7.7576
9	A	B	C	7.6636
8	A	B	C	7.6307
5	A	B	C	7.5828
6	A	B	C	7.4415
7	A	B	C	7.3595
2	A	B	C	7.3035
4		B	C	7.2528
3		B	C	7.2310
1			C	7.1474

b) Response log Cl^-

Level					LSM
2	A				1.4933
1	A	B			1.4388
12	A	B	C		1.4084
3	A	B	C		1.3672
11	A	B	C	D	1.3236
8	A	B	C	D	1.3038
10	A	B	C	D	1.2685
5			C	D	1.2475
9		B	C	D	1.2283
4			C	D	1.2156
7			C	D	1.1887
6				D	1.1518

c) Response log EC

Level				LSM
1	A			3.0685
2	A	B		3.0415
12	A	B		3.0006
10	A	B		2.9562
11	A	B		2.9554
5	A	B		2.9329
3	A	B		2.9254
6		B		2.9091
9	A	B		2.9086
8	A	B		2.8946
7	A	B		2.8890
4		B		2.8873

d) Response log SO_4^{2-}

Level		LSM
1	A	1.5906
12	A	1.5850
4	A	1.5601
10	A	1.5502
8	A	1.5294
2	A	1.5029
9	A	1.3986
11	A	1.3924
7	A	1.3914
3	A	1.3101
5	A	1.3061
6	A	1.2429

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e) Response log DOC

Level				LSM
2	A			2.0258
1	A			1.9931
10	A	B		1.8488
9	A	B		1.8403
3	A	B		1.8063
7	A	B		1.7494
5	A	B		1.7391
6	A	B		1.7360
12	A	B		1.7072
11	A	B		1.5513
8	A	B		1.5495
4		B		1.4982

f) Response log Br^-

Level			LSM
10	A		0.3831
12	A		0.3534
7	A		0.3498
11	A		0.3382
2	A		0.3087
4	A		0.3000
8	A		0.2955
1	A		0.2791
9	A		0.2628
5	A		0.2525
3	A		0.1883
6	A		0.1860

g) Response log BOD_5

Level				LSM
2	A			2.4011
3	A	B		2.2795
12	A	B	C	2.1169
1	A	B	C	2.0877
11	A	B	C	2.0244
10	A	B	C	1.9339
4		B	C	1.9223
5		B	C	1.8809
7		B	C	1.8453
9		B	C	1.7886
6			C	1.7536
8			C	1.7373

h) Response NO_3^-

Level			LSM
2	A		1.9475
12	A	B	1.9122
3	A	B	1.8652
1	A	B	1.8252
8	A	B	1.7968
11	A	B	1.7776
9	A	B	1.7647
7	A	B	1.7460
4	A	B	1.6840
6		B	1.6474
10	A	B	1.6467
5		B	1.6278

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i) Response log SUVA

Level				LSM
4	A			0.3093
11	A	B		0.2083
5		B	C	0.1242
7		B	C	0.1121
12		B	C	0.0988
3		B	C	0.0951
9		B	C	0.0931
10		B	C	0.0852
6			C	0.0647
8		B	C	0.0613
2		B	C	0.0612
1			C	0.0438

j) Response log PO_4^{3-}

Level			LSM
3	A		1.0798
2	A		1.0421
11	A	B	0.9594
1	A	B	0.9008
10	A	B	0.8889
8	A	B	0.8742
9	A	B	0.8732
5	A	B	0.8690
7	A	B	0.8685
6	A	B	0.8407
12	A	B	0.8121
4		B	0.7115

k) Response log Na^+

Level				LSM
2	A			1.9475
12	A	B		1.9122
3	A	B		1.8652
1	A	B		1.8252
8	A	B		1.7968
11	A	B		1.7776
9	A	B		1.7647
7	A	B		1.7460
4	A	B		1.6840
6		B		1.6474
10	A	B		1.6467
5		B		1.6278

l) Response log SAR

Level		LSM
2	A	0.4249
12	A	0.4197
1	A	0.3841
11	A	0.3707
8	A	0.3566
3	A	0.3549
9	A	0.3477
7	A	0.3465
10	A	0.3265
4	A	0.3260
5	A	0.3154
6	A	0.3119

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m) Response log NH_4^+

Level		LSM
10	A	0.5108
8	A	0.4777
9	A	0.4296
1	A	0.3608
2	A	0.3570
3	A	0.3321
11	A	0.3316
7	A	0.3312
12	A	0.2966
5	A	0.2820
4	A	0.2786
6	A	0.2556

n) Response log PAR

Level				LSM
12	A			0.4241
10	A	B		0.4004
11	A	B	C	0.3707
2	A	B	C	0.3534
3	A	B	C	0.3416
1	A	B	C	0.3290
8	A	B	C	0.3224
7	A	B	C	0.3153
9	A	B	C	0.3145
6	A	B	C	0.2889
4		B	C	0.2523
5			C	0.2460

o) Response log K^+

Level		LSM
3	A	1.9817
2	A	1.9744
12	A	1.9344
1	A	1.8776
11	A	1.8767
10	A	1.8358
8	A	1.8114
9	A	1.8097
5	A	1.8037
7	A	1.7965
4	A	1.7876
6	A	1.7388

p) Response log MCAR

Level				LSM
12	A			0.6491
2	A	B		0.6113
11	A	B	C	0.5849
10	A	B	C	0.5721
1	A	B	C	0.5672
3	A	B	C	0.5477
8	A	B	C	0.5449
9	A	B	C	0.5223
7	A	B	C	0.5215
6		B	C	0.4823
4			C	0.4754
5			C	0.4749

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q) Response log Mg^{2+}

Level			LSM
3	A		1.4880
2	A	B	1.4813
1	A	B	1.4704
7	A	B	1.4264
11	A	B	1.4237
8	A	B	1.4202
12	A	B	1.4137
9	A	B	1.4055
4	A	B	1.3771
5	A	B	1.3675
6		B	1.3517
10	A	B	1.3450

r) Response log CROSS

Level			LSM
12	A		0.6044
2	A		0.5697
11	A	B	0.5404
1	A	B	0.5299
10	A	B	0.5201
8	A	B	0.5017
3	A	B	0.5015
9	A	B	0.4839
7	A	B	0.4813
4		B	0.4439
5		B	0.4423
6		B	0.4413

s) Response log Ca^{2+}

Level			LSM
2	A		1.8709
3	A		1.8577
8	A	B	1.7896
1	A	B	1.7863
7	A	B	1.7672
9	A	B	1.7565
5		B	1.7422
10	A	B	1.7405
6		B	1.7346
11		B	1.7103
4		B	1.7078
12		B	1.6668

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Supplemental Table 3 Results of Tukey HSD test, performed on two-way mixed-effects model ANOVA (JMP10 2013), fixed effect of month and random effect of site = winery, for parameters of WW showing effects of treatment (pH/ BOD_5/ DOC/ SUVA) with pre/post treatment division. The output of a Non-parametric Steel-Dwass All Pairs test for the non-normal SUVA data, divided by pre- and post-treatment, is also included. (JMP 10 SAS Institute Liscence 2013-University of California Davis)

Month = level; level 1 = Oct.; level 12 = Sept.; LSM = least square mean.

a) Response Pre-pH

Level				LSM
12	A			7.7164
11	A	B		7.2924
5	A	B		7.2667
9	A	B		7.2385
6	A	B		7.1350
8	A	B		7.0856
2	A	B		6.9744
4	A	B		6.9314
10	A	B		6.9278
3	A	B		6.8646
7	A	B		6.6978
1		B		6.4633

b) Response Post-pH

Level				LSM
10	A	B		8.5854
11	A			8.5679
12	A	B	C	8.4545
8	A	B	C	8.1734
9	A	B	C	8.0887
7	A	B	C	8.0205
5	A	B	C	7.8975
1	A	B	C	7.8306
6	A	B	C	7.7485
2		B	C	7.6304
3			C	7.5981
4			C	7.5732

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c.) Response log Pre-DOC

Level				LSM
2	A			2.5306
1	A			2.4969
7	A	B		2.3926
10	A	B	C	2.3539
9	A	B	C	2.3402
3	A	B		2.3210
5	A	B	C	2.1336
6		B	C	1.9622
8	A	B	C	1.9589
12		B	C	1.8652
11		B	C	1.8530
4			C	1.7743

c) Response log Post-DOC

Level			LSM
12	A		1.5031
1	A		1.4878
2	A		1.4825
6	A		1.4472
5	A		1.3210
10	A		1.3000
9	A		1.2912
3	A		1.2501
11	A		1.2165
4	A		1.1880
8	A		1.0949
7	A		1.0882

d) Response log g)
f) Pre-BOD_5

Level				LSM
2	A			3.0686
12	A	B		2.7739
1	A	B		2.7529
10	A	B	C	2.6870
11	A	B	C	2.6339
9	A	B	C	2.4968
8	A	B	C	2.4918
5	A	B	C	2.4881
7	A	B	C	2.4861
4		B	C	2.4166
3		B	C	2.4131
6			C	1.9020

e) Response log g)
g) Post-BOD_5

Level				LSM
3	A			2.1123
2	A	B		1.7088
6	A	B		1.6052
12	A	B		1.4455
4		B		1.4118
1	A	B		1.4053
11	A	B		1.4005
5		B		1.2575
7		B		1.1993
10		B		1.1775
9		B		1.0765
8		B		0.9744

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h) Response log Pre-SUVA

Level				LSM
4	A			0.3216
11	A	B		0.2438
12		B		0.0961
5		B		0.0839
7		B		0.0750
6		B		0.0628
9		B		0.0470
10		B		0.0468
8		B		0.0433
3		B		0.0305
1		B		0.0254
2		B		0.0153

i) Response log Post-SUVA

Level				LSM
4	A			0.2961
11	A	B		0.1736
5		B		0.1653
3	A	B		0.1612
7	A	B		0.1506
9		B		0.1407
10		B		0.1253
2		B		0.1093
12		B		0.1021
8		B		0.0799
6		B		0.0692
1		B		0.0649

j) Non-parametric Steel-Dwass All Pairs test

Response log Pre-SUVA

Level				Mean
4	A			0.3094
11	A	B		0.2130
5		B	C	0.1224
7		B	C	0.1093
12		B	C	0.0961
9		B	C	0.0928
10		B	C	0.0874
3		B	C	0.0843
6			C	0.0710
8		B	C	0.0594
2		B	C	0.0541
1			C	0.0477

k) Non-parametric Steel-Dwass All Pairs test

Response log Post-SUVA

Level				Mean
4	A			0.2964
5	A	B		0.1850
11	A	B		0.1742
3	A	B		0.1644
7	A	B		0.1542
9	A	B		0.1423
10	A	B		0.1291
6		B		0.1142
2		B		0.1078
12		B		0.1045
8		B		0.0815
1		B		0.0682

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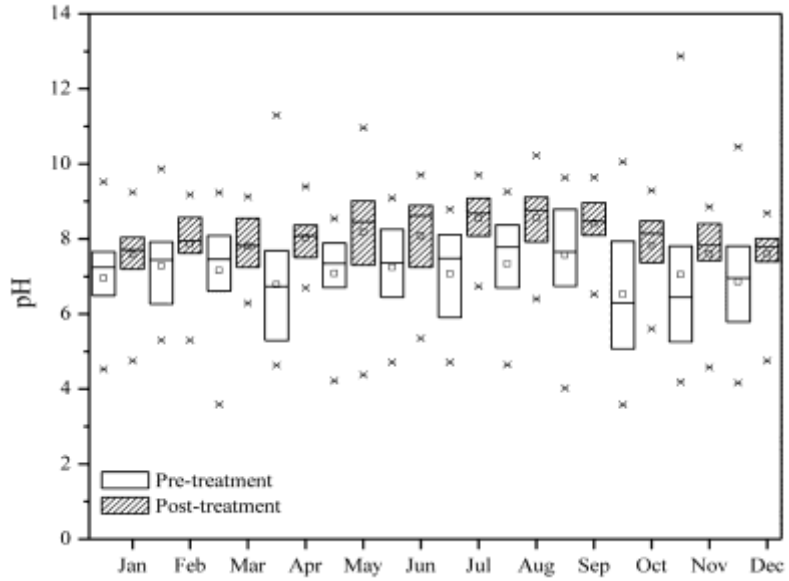
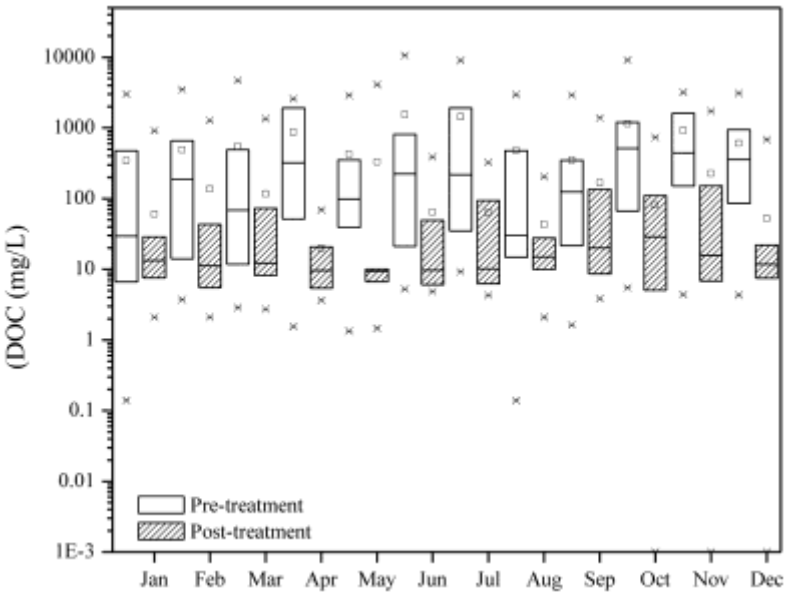


Supplemental Figure 1 pH of pre- and post- treatment samples. × = 1st and 99th percentile; ▫ = mean (n= 36 for Oct-Mar / n = 18 for Apr-Sep).



Supplemental Figure 2 DOC of all pre- and post- treatment samples. Note log scale on y-axis. × = 1st and 99th percentile; ▫ = mean (n= 36 for Oct-Mar / n = 18 for Apr-Sep).

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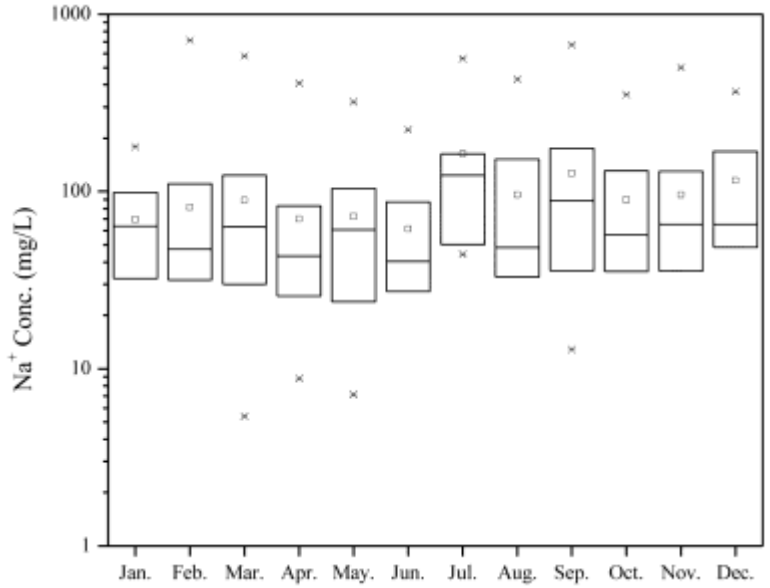
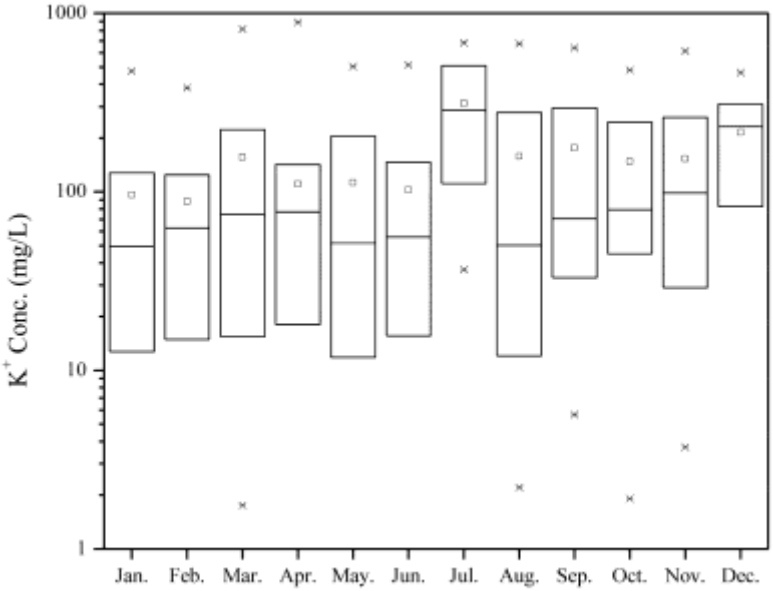


Supplemental Figure 3 Average monthly Na^+ concentrations (n= 36 for Oct-Mar / n = 18 for Apr-Sep). Note log scale on y-axis. × = 1st and 99th percentile; ▫ = mean.



Supplemental Figure 4 Average monthly K^+ concentrations (n= 36 for Oct-Mar / n = 18 for Apr-Sep). Note log scale on y-axis. × = 1st and 99th percentile; ▫ = mean.

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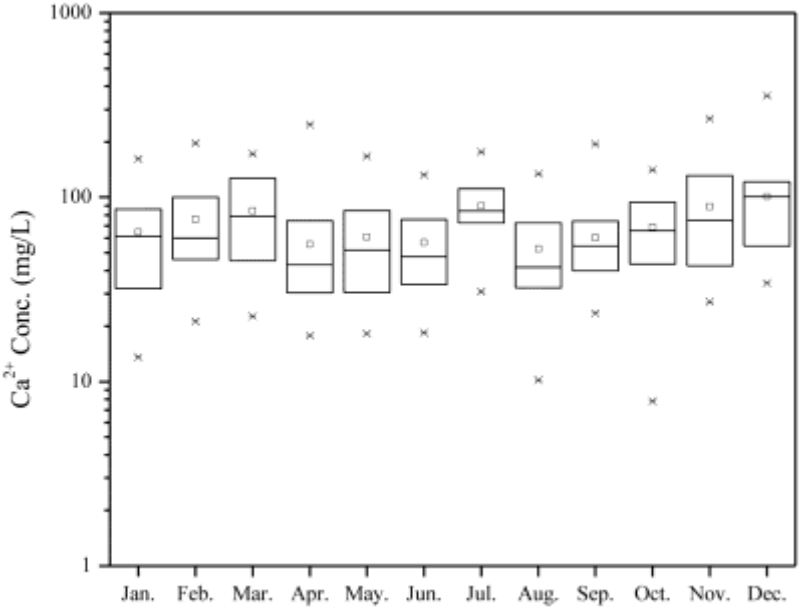
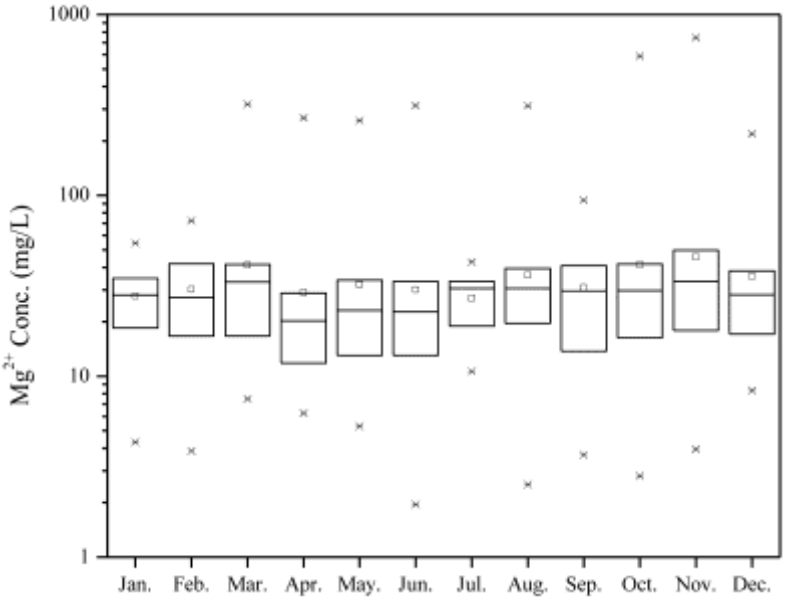


Supplemental Figure 5 Average monthly Ca^{2+} concentrations (n= 36 for Oct-Mar / n = 18 for Apr-Sep). Note log scale on y-axis. × = 1st and 99th percentile; ▫ = mean.



Supplemental Figure 6 Average monthly Mg^{2+} concentrations (n= 36 for Oct-Mar / n = 18 for Apr-Sep). Note log scale on y-axis. × = 1st and 99th percentile; ▫ = mean.

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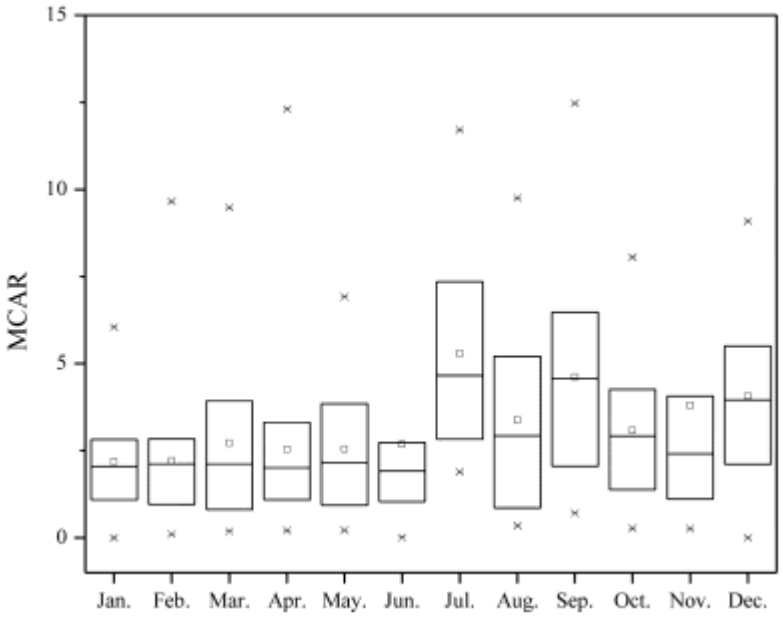
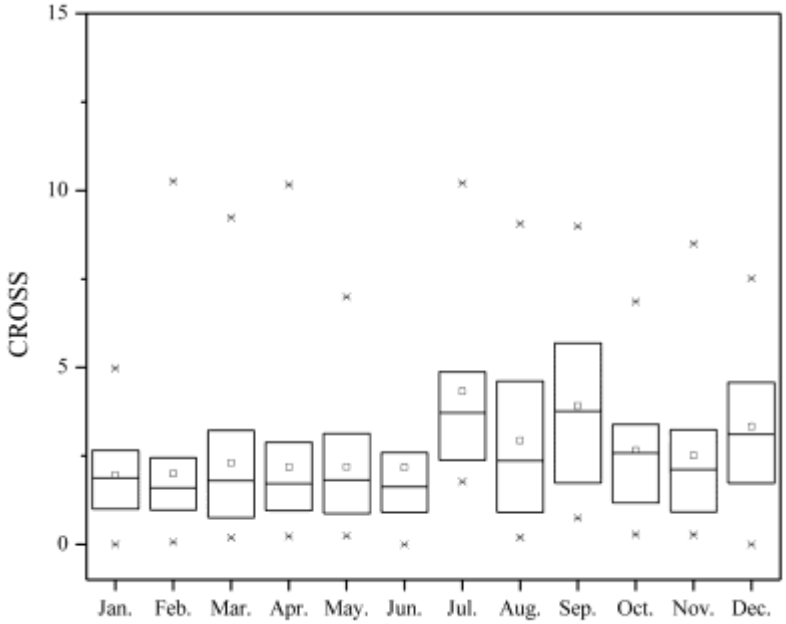


Supplemental Figure 7 Average monthly MCAR values (n= 36 for Oct-Mar / n = 18 for Apr-Sep). × = 1st and 99th percentile; ▫ = mean.



Supplemental Figure 8 Average monthly CROSS values (n= 36 for Oct-Mar / n = 18 for Apr-Sep). × = 1st and 99th percentile; ▫ = mean.