



Department of  
Primary Industries

# Managing acidity in grapevines and wines



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# Managing acidity in grapevines and wines

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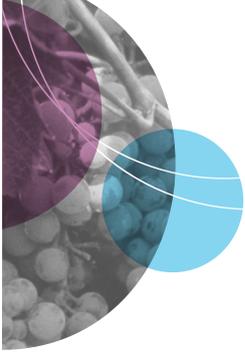
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# Managing acidity in grapevines and wines

## Introduction

Consistently producing high quality grapes from one season to the next in a changing climate is a significant challenge for viticulturists. Studies in Australia and overseas show that over the last 35 years, wine composition is changing; pH is increasing and titratable acidity (TA) is decreasing. Unfortunately wines with these characteristics often demonstrate instability and are more susceptible to microbial spoilage.

Both grape pH and TA influence the quality and ongoing vitality of wine. Grape growers across warm inland winegrowing regions of NSW wish to retain natural acid, thus lowering the fruit pH. This means that smaller acid additions can be made without increasing the palate hardness sometimes experienced in highly acidic wines. Consequently, management practices, both in the vineyard and the winery, need to be researched and implemented to ensure the desired fit-for-purpose wine quality outcomes can be achieved.

## Measuring acidity in grapes and wine

Acidity affects the sensory attributes of wine, for example, crispness or tartness. Knowing the acidity of wine can help winemakers with decisions about harvest time, acidity adjustments, treatments and the overall wine stability and qualities. There are several ways to measure wine acidity, including:

### pH

pH is a quantitative measure of the acidity or alkalinity of a solution and is determined by the hydrogen ion concentration. pH is a useful ripeness indicator for grapes and it influences various sensory properties of wine (Godden et al. 2015). A solution is considered to be:

- acidic when there are more H<sup>+</sup> ions than OH<sup>-</sup> ions present (pH < 7)
- alkaline when there are more OH<sup>-</sup> ions than H<sup>+</sup> ions present (pH > 7)
- neutral when there are equal number of H<sup>+</sup> and OH<sup>-</sup> ions present (pH = 7).

### Total acidity

Total acidity is a measure of all the acids in wine, both fixed organic and volatile acids. Measuring total acidity is difficult as it requires the ability to directly quantify organic acids. Total acidity is commonly but incorrectly assumed to be the same as titratable acidity. While titratable acidity does not measure all acids, it is easier to measure and is considered to be the better way to measure perceivable acidity in wines.

### Titratable acidity

Titratable acidity (TA) is an approximation of the total acidity and is measured by titration with a strong base to a fixed pH of 8.2. It is usually expressed in grams per litre (g/L) as tartaric acid equivalents. TA does not discriminate between the acids present in the juice of wine, but rather is a measure of the combined amount of the various acids. TA is often used as a ripeness measure of grapes, with TA falling with increasing ripeness (Godden et al. 2015).

A full description of this inter-conversion approach of acidity units, including a

calculator, is available on the [AWRI web site](https://www.awri.com.au/industry_support/winemaking_resources/frequently_asked_questions/interconversion-of-acidity-units/) ([https://www.awri.com.au/industry\\_support/winemaking\\_resources/frequently\\_asked\\_questions/interconversion-of-acidity-units/](https://www.awri.com.au/industry_support/winemaking_resources/frequently_asked_questions/interconversion-of-acidity-units/)).

### Acidity constant

The acidity constant is a quantitative measure of the strength of an acid in a solution. Organic acids are usually weak acids and only partially dissociate (separate into smaller particles). The extent of dissociation is measured by pKa, which is an index to express the acidity of weak acids; the lower the pKa value, the stronger the acid.

### Volatile acidity

Volatile acidity is the measure of acetic acid and other volatile acids (VA) in the wine.

### Fixed acidity

Fixed acidity is the difference between TA and VA.

## Acids in grapes and wine

There are many acids in grapes and wines and they are generally classified into the following categories as being most likely to occur:

- in the grape: tartaric acid and malic acid
- during yeast fermentation: citric acid and succinic acid
- during bacterial action (positive): lactic acid
- during bacterial spoilage: acetic acid.

### Tartaric acid

Grapevines are the only cultivated plant of European origin that accumulate significant quantities of tartaric acid. The acid is synthesised in both the berries and leaves. It is the strongest acid in wine based on pKa values. The maximum concentration at véraison can reach greater than 20 g/L, decreasing to 4–15 g/L at harvest. This decrease is more a consequence of the increase in berry volume and not degradation of tartaric acid.

Tartaric acid is a di-carboxylic acid containing two COOH groups (C<sub>4</sub>H<sub>6</sub>O<sub>6</sub>). Because of its isomerism, it is a chiral molecule with the isomers having different structural arrangements (Figure 1). At wine pH, there is a balance of tartaric acid and hydrogen tartrate due to its isomerism. The form in grapes and wine is L(+) tartaric acid. D,L-tartaric acid is a mixture of the two isomers.

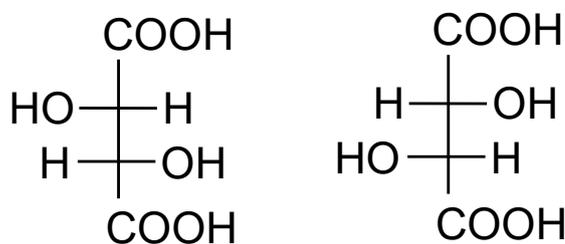


Figure 1. D(-) tartaric acid and L(+) tartaric acid.

### Malic acid

Malic acid (C<sub>4</sub>H<sub>6</sub>O<sub>5</sub>) is common in many plants, for example green apples. It is a di-carboxylic acid but is not as strongly acidic as tartaric acid. The metabolism for production proceeds by well-characterised pathways. Malic acid respire after véraison as an energy source for berry development. Although the mechanism of

this respiration is not properly understood, the outcome leads to loss of acidity in the berry that is more of a problem in warm climates.

### **Succinic acid**

Succinic acid ( $C_4H_6O_4$ ) is a di-carboxylic acid and is weaker in acidity than tartaric and malic acids. Its contribution is more to TA than pH. It is as a product of the fermentation process and the amount formed is dependent on the yeast strain used. However, there might also be other factors involved.

### **Citric acid**

Citric acid ( $C_6H_8O_7$ ) is a tri-carboxylic acid that is formed in small amounts during fermentation. It is frequently added to young wines to give an 'acid zest' character, although some countries place limits on the amount that can be added.

### **Lactic acid**

Lactic acid ( $C_3H_6O_3$ ) is a mono-carboxylic acid with a pKa value of 3.86, making it a milder acid than tartaric and malic acids. Lactic acid is formed from malic acid in malo-lactic fermentation. This process reduces the acidity, softens the taste and increases the complexity of wine.

### **Acetic acid**

Acetic acid ( $CH_3COOH$ ) is a weak mono-carboxylic acid with a pKa value of 4.79. A small amount is formed in fermentation, but most comes from oxidative spoilage resulting from the combination of oxygen/ethanol/*Acetobacter*. In wine, acetic acid exists as the neutral molecule making it a 'volatile' acid, meaning that if opportunity arises, it will assist in spoilage resulting in the aroma of vinegar.

## **Wine acidity trends**

Godden et al. (2015) examined changes in Australian wine composition of over 24,000 commercially bottled white, rosé and red wines from 1984 to 2014. The mean year-on-year TA for white and rosé wines combined and for red wines did not change significantly during 1984 to 2014. While there seems to be a trend for the TA to be decreasing in white and rosé wines (Figure 2) and increasing in red wines (Figure 3), so far neither of these is significant.

The mean year-on-year pH for white and rosé wines combined (Figure 4) and for red wines (Figure 5) also did not change significantly during 1984 to 2014. However, since 2000, red wine pH has been increasing (Figure 5).

Taken together, the trend for increasing TA and pH in red wines could be due to changes in climate, including the prolonged drought conditions experienced by much of Australia since 2000. However, given that the changes are not seen in white wines, perhaps it is more likely that these changes are consumer-driven trends towards more 'drinkable' wines, resulting in changes in varieties planted and producing wines with more acceptable and popular 'mouthfeel'.

Likewise, in a study of the acidity of wines from the Languedoc-Roussillon region in France from 1984 to 2013, Escudier et al. (2014) reported a decrease in TA coupled with an increase in alcohol content (Figure 6) and an increase in pH (Figure 7).

Escudier et al. (2014) were adamant that water stress and climate change caused the changes in the acidity parameters. However, the authors of the Australian study were more cautious in interpreting the changes found in their study, claiming that while it might be easy to relate these changes to climate and prolonged drought,

it is difficult to attribute any of the compositional trends specifically to change in climate or compressed vintages. They concluded that marketing influences are probably having the greatest influence on any changes, because as soon as a trend is evident, winemakers attempt to follow it. This could explain the trend towards higher pH wines as they are perceived as softer in mouthfeel (Gawel et al. 2014) and more consumer-friendly. Given that the changes in pH are different in Australia and France, perhaps it suggests that the changes are not directly attributable to climate alone.

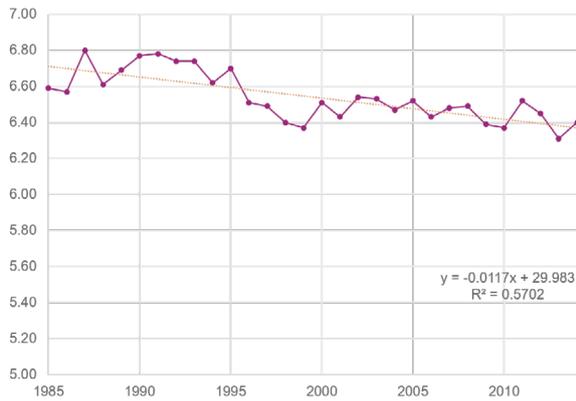


Figure 2. White and rosé wine titratable acidity from 1984 to 2014.

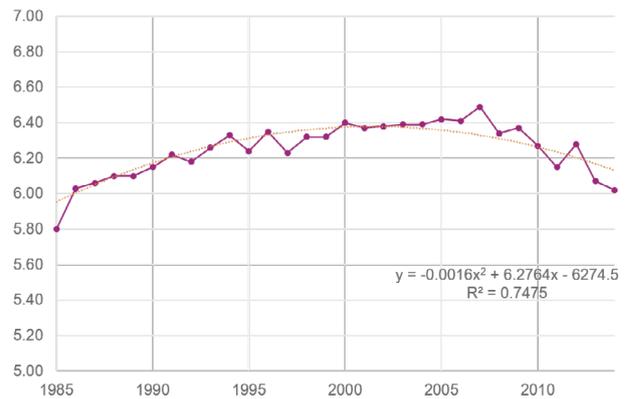


Figure 3. Red wine titratable acidity from 1984 to 2014.

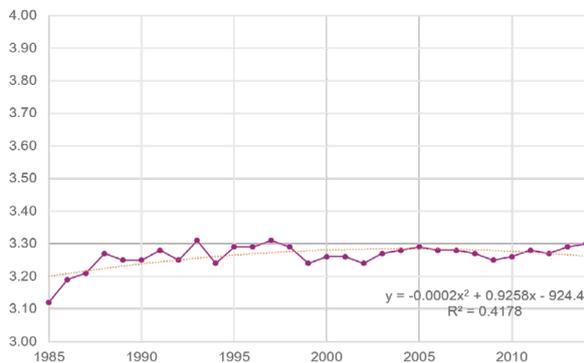


Figure 4. White and rosé wine pH from 1984 to 2014.

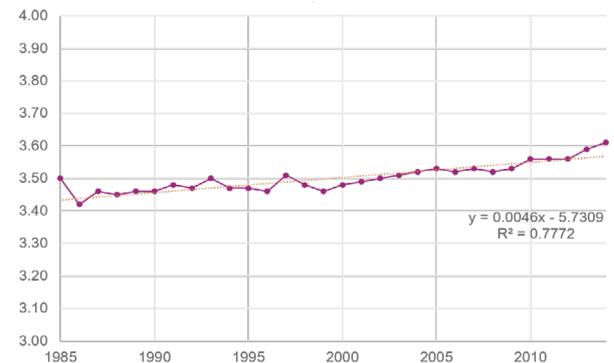


Figure 5. Red wine pH from 1984 to 2014.

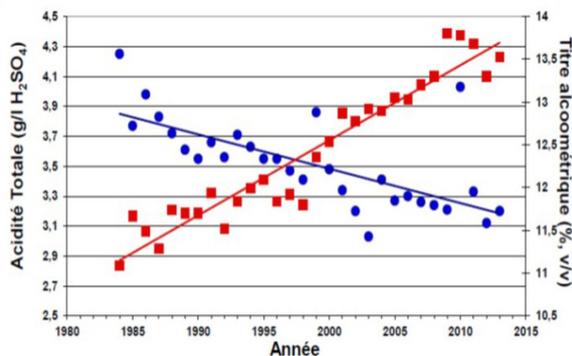


Figure 6. Decrease in TA (blue line) and increase in alcohol (red line) of French wine from 1984–2013. Source: Escudier et al. (2014).

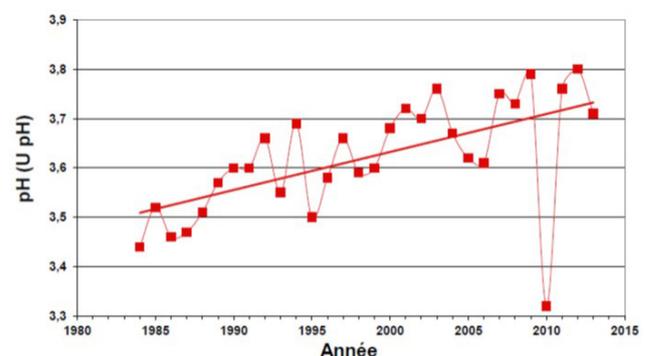


Figure 7. Increase in pH of French wine from 1984–2013. Source: Escudier et al. (2014).

A complete interpretation of the data from both these studies is inhibited by two main factors:

1. The data are for wine and not juice or must. For the Australian wines at least, pH adjustment might have occurred before analyses were performed.
2. There are no data available on the concentration of potassium, especially at the juice or must level.

The key point that is not resolved is the basis for the changes. Acidity management is one of the most important considerations for wine quality, especially for wine stability. Some of the significant stability concerns related to pH are:

- inhibition of spoilage organisms at low pH
- lower pH favours molecular sulfur dioxide (SO<sub>2</sub>), the anti-microbial form
- more red colour at low pH, going to 'blue' as pH increases
- oxidation rates decrease as pH decreases.

The contribution of acidity to the wine's sensory profile depends on the amount of each organic acid present as well as the interactions of the acids with other wine components. For example, the sweetness of ethanol and residual sugar can balance the acid taste.

Another issue that is not yet resolved is whether the decrease in TA is linked to a change in the profile of the organic acids. This is important because the TA value represents the total amount of acid, but does not give details of the individual acids.

### The changing nature of the organic acid profile

The Australian Wine Research Institute (AWRI) has recently completed an analysis of the organic acid profile of 277 red and white wines during 2010 to 2015 (Figure 8; Wilkes 2016). While the full provenance of the wines in this study is not known, tartaric acid dominates the contribution to the TA value (Table 1). The contribution of both malic and lactic acids are variable, reflecting vintage conditions and the use of malo-lactic fermentation. The malic acid contribution to TA is approximately 31% in white wine and 15% in red wine, while lactic acid contributes 7% to white wine and 16% to red wine (Table 1).

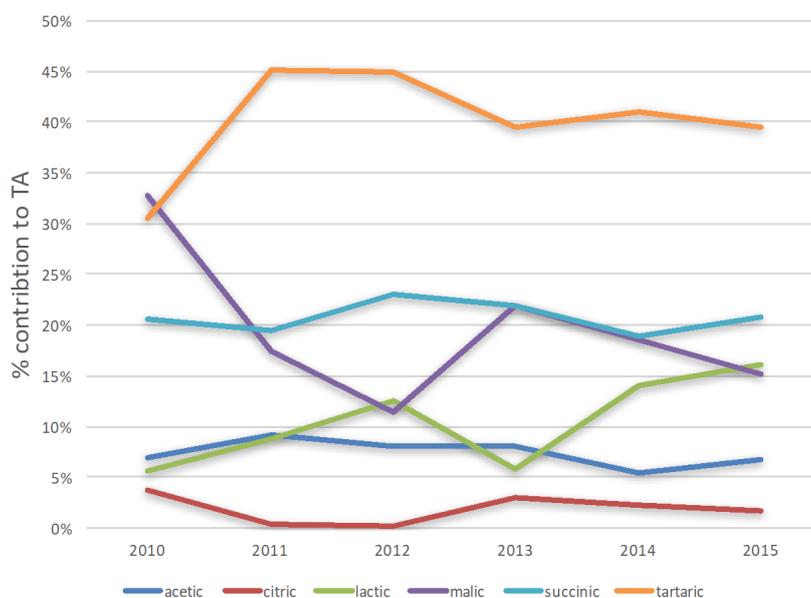


Figure 8. The relative contribution of organic acids to TA.

While the 4% vintage variation in the succinic acid concentration could be considered small, its concentration is such that it makes a significant contribution to the TA value. The contribution from succinic acid in red wine is higher than in white wine (21.4% to 13.6% respectively). Succinic acid is a relatively weak organic acid and thus contributes little to the pH value. It is chemically stable and does not precipitate as a salt as does tartaric acid. It is also microbiologically stable, so it does not degrade like malic acid.

Table 1. Relative proportions of organic acids to red and white wine.

Acid	Proportion of acid (%)	
	Red wine	White wine
Acetic acid	7.4	5.8
Citric acid	1.5	2.3
Lactic acid	15.6	7.3
Malic acid	14.8	30.8
Succinic acid	21.4	13.6
Tartaric acid	39.2	40.2

A higher concentration of succinic acid in wine could influence palate response. Its taste descriptors are 'sour, salty and bitter', creating a desire for some tasters to expectorate immediately. While it is recognised that some yeasts tend to favour succinic acid production, model ferments from Stellenbosch University (Redzepovic et al. 2003) suggest that the production of succinic acid is favoured by:

- a moderate to high fermentation temperature (20–28 °C)
- a sugar concentration between 200 and 240 g/L
- a moderate amount of metabolically available nitrogen
- the presence of flavonoids and unsaturated long-chain fatty acids
- aeration of the fermentation juice.

Accepting that the taste contribution of succinic acid is not always positive, a more detailed study of its production is required.

### Acidity adjustment – the traditional way

Adding tartaric acid to the wine has been the traditional way to adjust acidity. It is relatively easy to do and the amount to be added can be determined by bench tests or using web-based calculators. There are, however, some limitations with this method including:

- the procedure can be expensive as quality L(+) tartaric acid is costly
- the amount required to attain the desired pH decrease can be large
- losses of the added tartaric acid, via precipitation of potassium hydrogen tartrate (KHT), can be excessive, meaning further tartaric acid additions
- high juice potassium concentrations will exacerbate these losses
- in extreme cases, calcium tartrate might also precipitate, causing additional losses
- some countries have limits on the amount that can be added.

To minimise the cost, some winemakers have explored using DL-tartaric acid because it costs significantly less than L(+) tartaric acid. However, a limitation of the DL-form is that it can lead to unpredictable precipitation post-bottling; this is especially the case for calcium DL-tartrate.

## Acidity adjustment – alternative strategies

Alternative strategies to adjust wine acidity include:

- blending with higher acidity wines
- adding acids other than tartaric acid
- plastering
- using cation exchange resins
- bipolar membrane electrodialysis.

### Blending options

1. Blending grapes that have been harvested at different ripeness stages because grapes from early harvest have higher acidity. A potential issue with this could be 'green' characters. Additionally, the cost can be significant.
2. Blending across regions, for example selecting grapes from both cooler (more acid) and warmer (less acid) regions. Cost can also be significant with this method.
3. Blending with small portions of neutral, high acid cultivars. Some examples include:
  - Pinot Gris: holds acidity until late in ripening and has been considered as a sparkling wine base using grapes from warm regions
  - Furmint: the classic of Tokaj wines from Hungary has high acidity with TA of 10 g/L or more at 14% alcohol
  - Graciano: in La Rioja, Graciano is blended with Tempranillo to enhance acidity and colour.

### Adding acids other than tartaric acid

1. Adding malic acid, which can be added as L or DL forms. This process is similar to adding tartaric acid except that malic acid is a weaker acid, so a higher rate will be required. The consequence is an increase in TA value and problems with microbiological stability.
2. Adding lactic acid, but because this is the weakest acid of those permitted to be added, the addition rate needs to be higher to achieve the same pH decrease as malic or tartaric acids. Using lactic acid will give a more predictable pH decrease compared with using tartaric acid. Lactic acid additions are not affected by cold stabilisation as the potassium salt is soluble. There are other advantages allegedly claimed for lactic acid addition, including that it:
  - can be added just before bottling without cause for precipitation
  - produces a rounder and smoother mouthfeel than malic acid
  - increases the formation of lactic esters that contribute to a wine's aroma.However, results for these are anecdotal and further evidence to support this option is required.
3. Adding citric acid to white wine is effective as it generates a fresher mouthfeel. However, it is a substrate for bacteria so additions need to be limited to 0.15 to 0.2 g/L. Some countries have imposed limits on how much can be added. There is also a higher risk of bacterial spoilage if citric acid is added to red wine because of the lower sulfur dioxide level.

## Plastering

Plastering is an old practice that evolved in Spain to produce dry white fortified wine. It involves adding calcium sulfate ( $\text{CaSO}_4$ ; plaster of Paris) to the wine and is based on the relative solubilities of  $\text{CaSO}_4$  and calcium tartrate (CaT). CaT is less soluble in wine and so the process can be represented as:

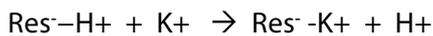


This releases  $2\text{H}^+$  ions per added  $\text{Ca}^{2+}$  and thus the pH is reduced.

In a trial on Palomino juice, Gómez et al. (2015) found that plastering reduced pH by 0.12 units, with minimal effect on TA and tartaric acid addition reduced pH by 0.17 units with close to doubling the TA. Unfortunately there was a significant increase in the sulfate concentration and many countries regulate the maximum sulfate level permitted (the Palomino trial came close to maximum). Additionally, the increase in calcium concentration enhances the opportunity for post-bottling CaT precipitation. Perhaps it is not surprising that plastering does not yet have full approval for use, except in the one specific wine style.

## Cation exchange resins

The use of cation exchange resins are now approved in many countries and this method is considered to be effective for reducing pH in juice and wine that is high in potassium. The process can be represented as:



where the resin (Res) in its  $\text{H}^+$  ion form removes potassium ions ( $\text{K}^+$ ) from the wine, releasing the  $\text{H}^+$  ions into the wine, thereby lowering the pH.

This process was previously considered to be appropriate for low-end wines, but is now applied to some premium wines. It is recommended to treat only about 20% of the wine to a low pH (about 2.7–2.8) and then mix this treated batch with the remaining wine. If the entire batch is treated, then some metallic flavours appear, leading to a reduction in quality. The perceived advantages of cation exchange include:

- it is more effective in correcting acidity and pH than adding tartaric acid
- it does not lead to tartrate instability
- it is relatively inexpensive compared to adding tartaric acid (provided the cost of the unit is not included)
- when performed correctly it does not negatively affect taste.

An industrial trial on 2012 Chardonnay from South Tyrol in Italy (Figure 9) compared cation exchange resin (CER) with tartaric acid addition (TAA) at juice level (Pixner 2014) and found that the reduction in cation concentration by CER was:

- potassium 24.7%
- calcium 21.7%
- magnesium 21.5%
- manganese 22.9%

Sensory profiling at 6 and 18 months (Figure 10) showed little difference in acidity perception between CER and TAA with similar scores also for cleanliness and fruitiness. However, 30 months after treatment, acidity perception was significantly lower for the CER treated wine (Figure 10), suggesting that acidity perception is more constant over time with TAA acid adjustment and less so with CER acid adjustment.

### Bipolar membrane electro dialysis

Bipolar membrane electro dialysis (BPED) is an extension of the more common electro dialysis used for tartrate stabilisation. In BPED techniques, the bipolar membrane consists of a cation-selective layer, an anion-selective layer and a contact region between the two layers (Figure 11). This technique has been claimed to adjust the pH to within 0.05 pH units, but it needs more detailed investigation including sensory impacts and comparison with nanofiltration for K<sup>+</sup> removal (see Colby (2007), [GWRDC report UA 05/07, April 2007](#)) followed by cation exchange for acidity increase.



Figure 9. Lowering wine pH with cation exchange resin technology in Italy.

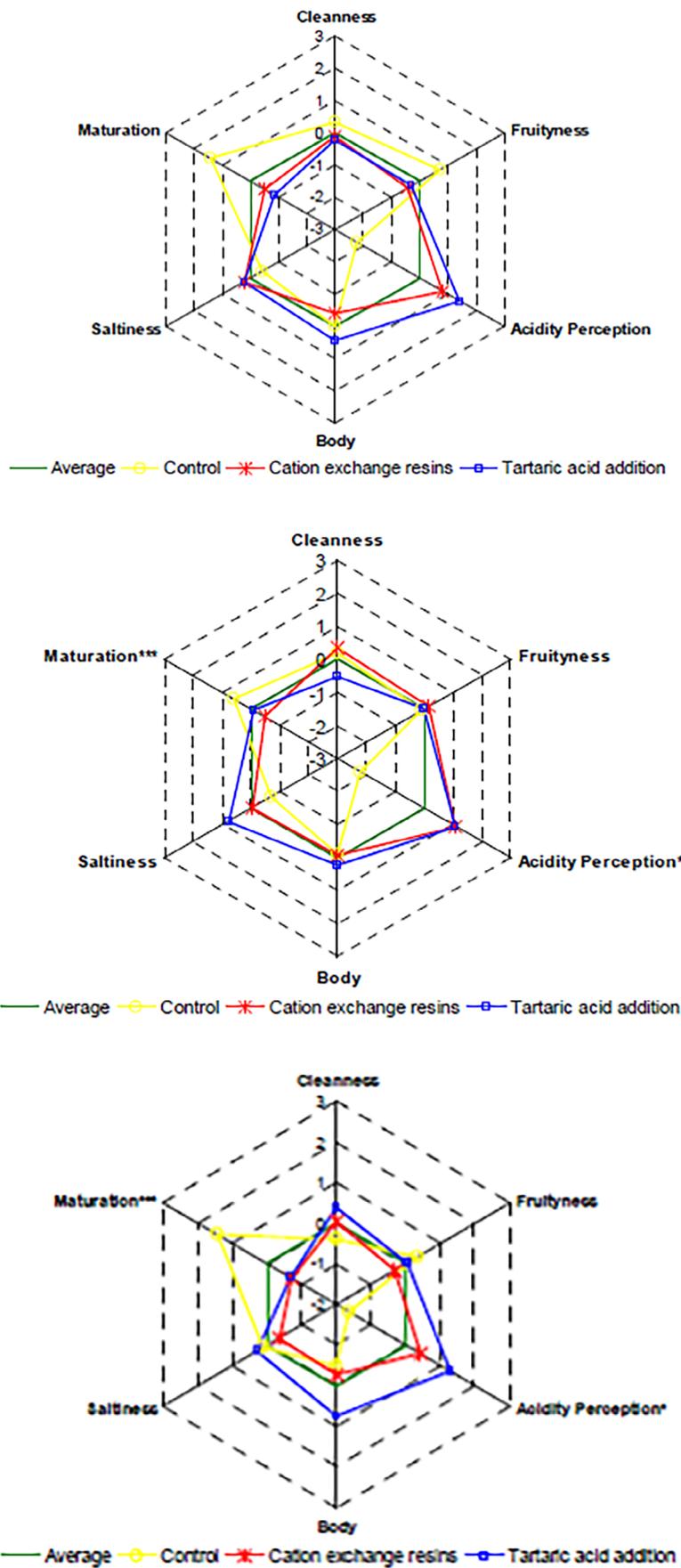


Figure 10. Sensory profiling of wines at 6 (top), 18 (middle) and 30 months (bottom) after bottling, comparing cation exchange resin (CER) and tartaric acid additions (TAA).

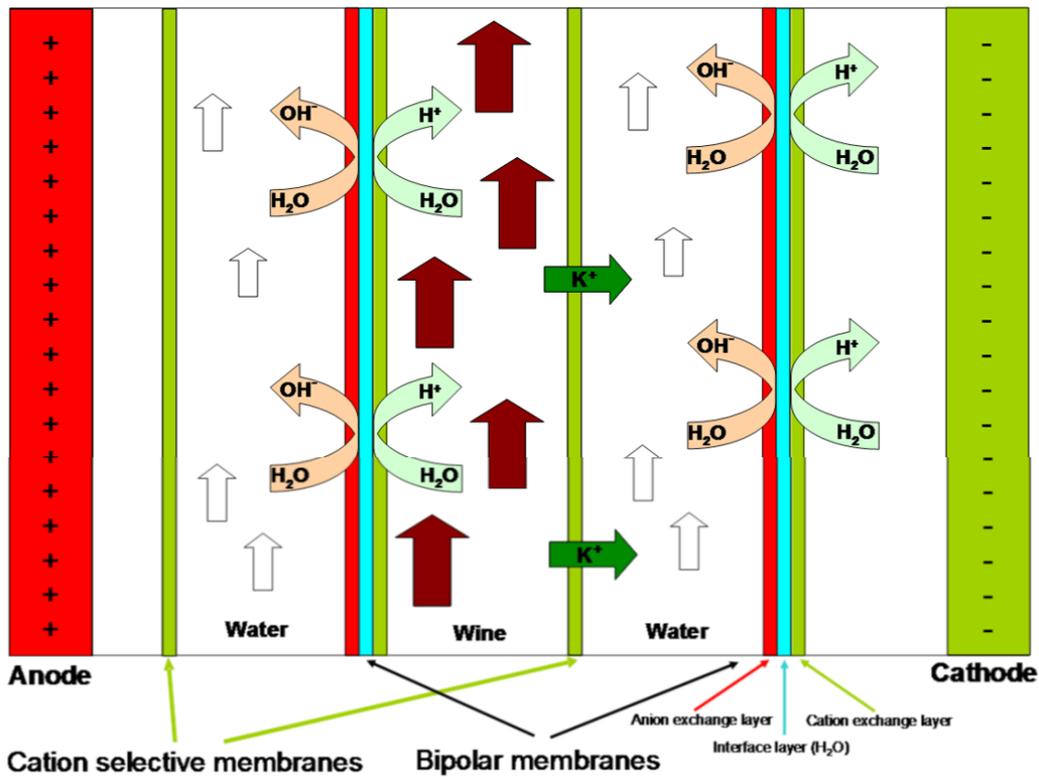


Figure 11. Bipolar membrane electro dialysis.

## Conclusions

Winemakers aim for the perfectly balanced wine and strive to achieve this through adjustments made in the winemaking process. There are many ways wineries can manipulate juice and wine to consistently produce quality wine for a particular market. However, in addition to manipulating wine, various vineyard management practices can be implemented during the growing cycle to ensure the desired fit-for-purpose wine quality outcomes can be achieved.



# Managing pH and titratable acidity in the vineyard

## Introduction

Consistently producing high quality grapes in changing climatic conditions continues to challenge viticulturists. Grape pH and titratable acidity (TA) influence the quality (Krstic et al. 2003) and ongoing vitality of wine. Various vineyard practices involving canopy, soil, irrigation and nutrition management, as well as temperature, can affect pH and TA.

## Canopy management

Shaded canopies cause higher grape juice pH and lower TA levels (Smart and Robinson 1991), therefore grape growers should aim to achieve an open canopy that is balanced between vine growth and fruit load. However, this needs to be justified against the benefits of shade protecting grapes from direct heat damage and the detrimental effects of high temperatures on grape composition (Hayman et al. 2012). The following basic principles apply to canopy management:

### Pruning

Severe pruning can cause excessive growth in the next growing season whereas minimal pruning controls excessive shoot vigour due to the retention of a higher amount of nodes and shoots per vine. Growers should aim to retain spur positions to lessen the amount of wood to be pruned or, where possible, train varieties to a cane (Dry 2020).

### Shoot positioning

Training shoots in a certain direction can either encourage (upwards) or retard growth (downward). Both can be achieved by using wires or specific trellis systems such as the Scott Henry trellis system (Smart and Robinson 1991).

### Shoot thinning

Thinning poorly positioned or short shoots assists in managing canopy density while improving exposure of the remaining shoots and bunches to light.

### Leaf removal

Removing leaves from the bunch zone exposes bunches to greater airflow and light penetration. Caution is required here as overexposure can lead to sunburn in warmer climates. The application of a sunscreen product might be required, but this will increase temperatures, resulting in decreased TA due to malic acid losses driven by temperature increased respiration (Kliwer 1964).

### Bunch thinning

Crop level can influence grape acidity. It is generally considered that a high crop load leads to high TA and a low crop load leads to low TA. For pH, the opposite is true; a high crop load leads to a low pH and low crop load leads to a high pH. Removing excess or crowded bunches will improve leaf area to fruit weight ratio, resulting in a higher level of quality within a given yield. Bunch thinning closer to véraison is considered less risky because it can cause increases in berry size of the remaining crop.

## **Irrigation**

Irrigation is an essential requirement for producing economic wine grape yields in the majority of Australian regions. Furthermore, the timing and extent of water additions can be used to manipulate fruit composition. Excessive irrigation can lead to increased potassium uptake and therefore higher juice and wine pH levels (Mpelasoka et al. 2003; Rogiers et al. 2016). Imposed water stress at late ripening will result in higher berry temperature and higher malate respiration, reducing TA (Edwards and Clingeleffer 2014).

Any form of mulch covering the soil surface under the vine row has the potential to limit evapotranspiration, thus retaining soil moisture and lowering soil temperature. Irrigation strategies need to consider this as feeder roots in this zone will readily transport potassium (K) into the vine. Recycled organic mulch based on wood waste products will significantly increase grape K and pH (Chan and Fahey 2011). Growers should aim for an irrigation strategy based on soil moisture monitoring equipment that suits the soil type, water availability, irrigation system, vineyard floor management, seasonal conditions, vine vigour and the desired fit-for-purpose wine style.

## **Nutrition**

Along with regular visual assessments of vine health and vigour, soil and plant nutrient status determined by soil testing and petiole analysis will ensure adequate plant nutrition can be provided throughout each vintage (Nicholas 2004). Excess potassium can lead to increased grape juice pH (Morris et al. 1983). Additionally, excess nitrogen results in greater shoot growth and shaded canopies if irrigation is applied.

## **Grape maturity**

Determining a harvest date that maintains the integrity of ripening berries to achieve a desired fit-for-purpose wine is usually decided upon between the grape grower and winemaker after assessing berry samples in the vineyard and the laboratory.

Ideally the wine pH should be below 3.6 and TA should be between 5–10 g/L. Cool nights with warm days will reduce pH while warm nights and warm days will increase pH at maturity (Gladstones 1992). Warm growing regions will usually have lower TA levels at the same sugar level compared to cool regions, because the respiration of malic acid in the berry is temperature driven (Sadras et al. 2013). Growers and winemakers will need to pay close attention to temperatures to achieve optimal harvest dates if temperatures continue to rise (Hall and Jones 2009).

One strategy to help overcome this could be to harvest small sections of the same block at different times and blend the parcels back together later in the winery to achieve a balanced wine. Likewise, blending a known low pH, high acid variety such as Furmint, could be used in low percentages to support a finished wine which has little acid and high pH.

## **Conclusions**

Now we know the effect these management practices can have on pH and TA, can we put a few of them to the test and find out what actually works in a couple of vineyards?



# The effect of foliar fertilisers, shoot thinning and composted mulch on berry pH and titratable acidity

## Background

NSW Department of Primary Industry Viticulture Development Officers were approached by local Mudgee winemaker Jacob Stein of Robert Stein Winery and viticulture consultant Paul Baguley of PB Ag Consulting Pty Ltd. They identified continued problems with the levels of pH and TA in the region's grapes which was affecting wine composition and quality, as well as the results of the region's wines at NSW and national shows. Accordingly, a trial was implemented to determine the effect of various treatments on berry pH and TA.

Foliar magnesium and potassium were chosen as treatments to see if their application could influence pH and TA changes in wine grapes. Composted mulch releases potassium in the first year of application to soils (Chan and Fahey 2011). Therefore, we were comparing if minerals added through foliar or soil applications would also make a difference to pH and TA in berries.

## Trial design

A fully randomised replicated complete block design trial was established in the Mudgee region (32.37° S, 149.37° E) before budburst in 2015 consisting of 5 treatments × 5 replicates × 2 sites (1 each of Shiraz and Merlot) with the following treatments:

1. Control (current practice = shoot thinning {ST})
2. Foliar magnesium (50% recommended rate + ST)
3. Foliar magnesium (100% recommended rate + ST)
4. Foliar potassium (100% recommended rate + ST)
5. Wood based mulch (7.5 cm deep x 60 cm wide + ST).

## Materials and methods

Soil sampling at both sites was undertaken with 5 replicate samples collected at 0–10 cm depth across each treatment before the application of any materials. Soils were analysed at the Sydney Environmental Soil Laboratory (SESL) for the following parameters:

- pH (1:5 H<sub>2</sub>O) 4A1, pH (1:5 CaCl<sub>2</sub>) 4B1, EC (1:5) 3A1, chloride 5A2 and nitrate 7B1 according to Rayment and Higginson (1992)
- Aluminium (SESL in-house method)
- PO<sub>4</sub>, K, SO<sub>4</sub>, Ca, Mg, Na, Fe, Mn, Zn, Cu and B according to Mehlich (1984)
- Buffer pH and hydrogen according to Adams and Evans (1962)
- Texture (Northcote 1971)
- Structure (Murphy and Allworth 1991)
- Colour (PM0003, Munsell 2000).

Shoot thinning was conducted at the start of flowering (EL 19) and the target, although random, was to remove 25% of all shoots. This was done at both sites and for all treatments.

Foliar Mg (Agrichem® Activist® Mag-Flo, 25% Mg, 1.7% N, 0.25% Ca, 0.21% Fe, 0.15% Mn and 0.15% Zn as trace elements) was applied to treatments 2 and 3 at the recommended label rates of 2.5–4 L/ha in a 1:70 dilution at 50% and 100% respectively for each treatment at pre-flowering (EL 12), during flowering (EL 19) and bunch closure (EL 32). This product was chosen over other Mg products as it had little nitrogen and trace elements as found in other available Mg foliar fertilisers.

Foliar K (Agrichem® Supa K 30, NPK: 0-0-30) was applied to treatment 4 at the recommended label rates of 2–4 L/ha in a 1:200 dilution at pre-flowering (EL 12), during flowering (EL 19) and bunch closure (EL 32). Again this product was chosen on the basis that it was high in K without other nutrients.

An 80/20 blend of Australian Native Landscapes (ANL) composted recycled organic mulch and compost was applied to treatment 5 at pre-flowering (EL 12) at 7.5 cm deep x 60 cm wide (= 153 m<sup>3</sup>/ha). This product was tested and passed the Australian Standard (AS4454-2012) for composts, soil conditioners and mulch. The main elements that were analysed are shown in Table 2.

Table 2. Analysis of 80/20 recycled organic composted mulch/compost blend.

Analysis	Unit	Result
Total N	% dry wt	0.71
Total P	% dry wt	0.20
Total K	% dry wt	0.23
Total Ca	% dry wt	1.16
Total Mg	% dry wt	0.16
Total Na	% dry wt	0.07
pH (1:5) water	pH units	6.10
EC (1:5)	dS/m	0.88
Total organic carbon	% dry wt	48.4
Carbon to nitrogen ratio	C:N	68.0
Nitrate N (NO <sub>3</sub> )	mg/kg	80.9

Petiole testing involved collecting 100 petioles from each treatment at both sites at flowering (EL 19) and véraison (EL 35). Testing and analysis were conducted at Sydney Environmental Soil Laboratory with values compared to petiole nutrient standards for grapevines in Australia (Reuter and Robinson 1986).

Sequential berry testing occurred from véraison (EL 35) until harvest (EL 38). Four bunches were randomly collected from each replicate and treatment at both sites. They were then stored in twin-sealed clip-lock bags on ice until

whole bunches were bag pressed, juice strained and cold settled in a refrigerator. The samples were then analysed in a benchtop OenoFoss® machine for pH, Brix, TA and other acids.

Harvest date and sampling were determined by the winery with 20 bunches randomly selected and weighed from each replicate and treatment across both sites. Five berries were taken from each bunch and weighed to make up a 100-berry sample from each replicate and treatment for testing at the National Wine Grape Industry Centre Experimental Winery using the following methods for juice analysis:

- Baumé using an Anton Paar DMA 35N portable density meter (LMWI 40-10)
- pH and titratable acidity (TA) using a Denver Instrument pH/mV meter or Metrohm Fully Automated 59 Place Titrand System (refer to LMLM 40-2, 40-3 and LMVI 40-15 (Iland 2004))
- Yeast assimilable nitrogen (YAN), ammonia, malic acid and acetaldehyde using a Thermofisher Konelab 20XT Auto analyser
- Anthocyanins and total phenolics via Shimadzu UV 1700 PharmaSpec (refer to LMLM 40-5, Iland 2004).

Minerals in the berries were assessed at the Environmental and Analytical Laboratories (EAL) at Charles Sturt University Wagga Wagga NSW, using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES).

## Results

In Merlot grapes, shoot thinning resulted in the highest TA levels, followed by low foliar Mg application and mulching, then high foliar Mg, while foliar K resulted in the lowest TA levels ( $P < 0.05$ ) (Figure 12). While reduced TA readings were recorded, they did not translate into berry K increases.

Grape pH was not influenced by any of the treatments (Figure 13). There were no treatment differences for either Baume or anthocyanin.

Berry calcium was highest in the control and low Mg groups compared with the other treatments (Figure 14).

As expected, several parameters measured in the petioles, including nitrogen and nitrate, changed between flowering and véraison (Table 3).

Applying mulch appeared to influence several soil parameters at both sites. However, the values need to be interpreted with caution as there were insufficient data for statistical analysis. Regardless, they provide some interesting insights.

Before mulch was applied, the soils at both the Merlot and Shiraz sites were slightly alkaline and both returned low effective cation exchange capacity for predominantly clay loam soils. After mulch was applied, the pH at both sites decreased, being closer to neutral (Table 4). Mulch also decreased salinity, but this effect was greater at the Shiraz site than the Merlot site.

Applying mulch increased calcium and decreased magnesium levels at both sites, decreased potassium levels at the Merlot site and decreased sodium levels at the Shiraz site (Table 4). Before mulch was applied, both sites were highly magnesian with Ca:Mg ratios below the optimum range of 4.1-6.0. After mulching, the Ca:Mg ratios of both sites improved, with the Shiraz site moving into the optimum range (Table 4).

Soil nutrient analysis (Table 5) shows that nitrate, magnesium and iron decreased at both sites while phosphate increased with mulching.

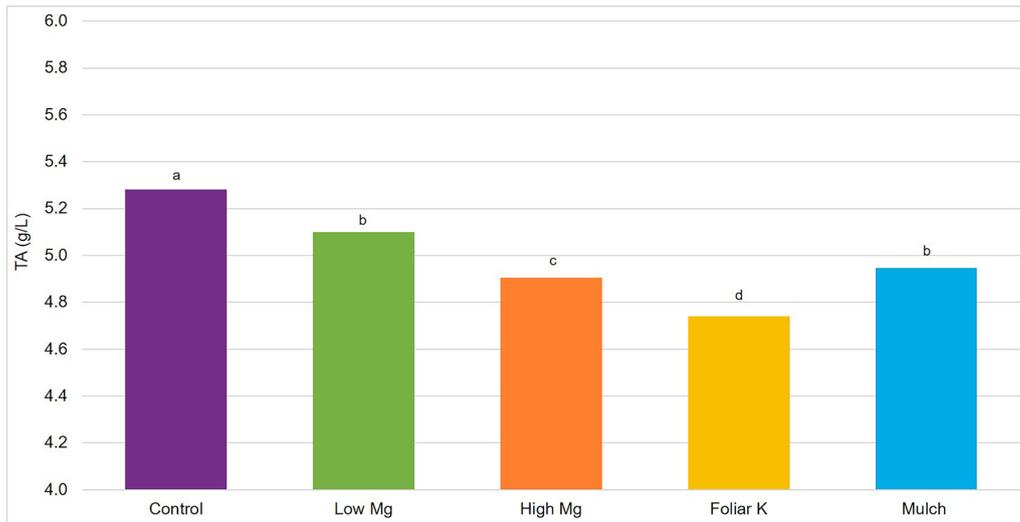


Figure 12. Titratable acidity differences between treatments at harvest (2016) in grams/Litre at the Merlot site. Different letters indicate significant differences at  $P < 0.05$ .  $LSD = 0.160$ .

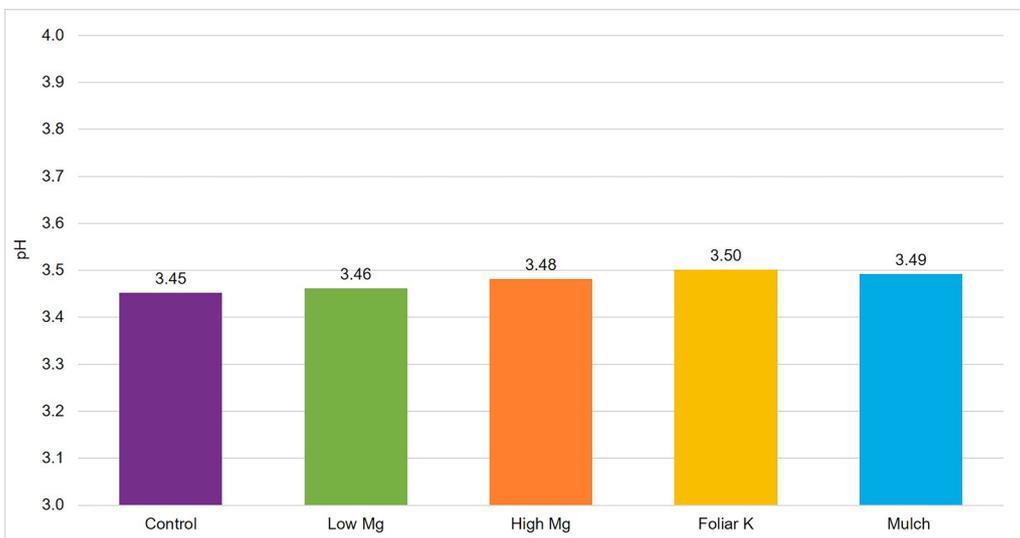


Figure 13. pH for each treatment at the Merlot site. There was no significant difference between treatments.

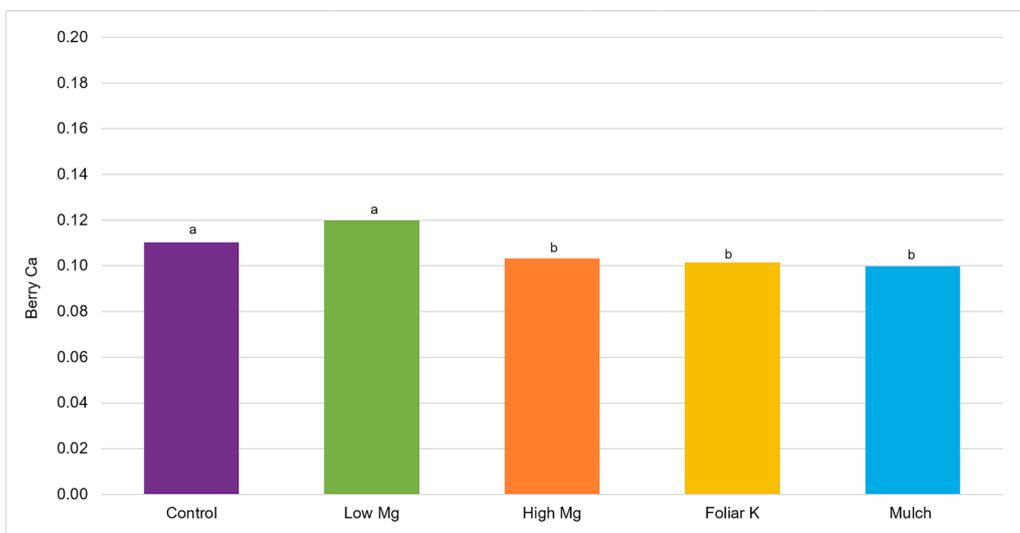


Figure 14. Berry calcium for each treatment at the Merlot site. Different letters indicate significant differences at  $P < 0.05$ .  $LSD = 0.0067$ .

Table 3. Petiole differences between treatments at the Merlot site.

	Control		Low Mg		High Mg		Foliar K		Mulch		Adequate range	
	Fl	V	Fl	V	Fl	V	Fl	V	Fl	V	Fl	V
N (%)	0.73	0.45	0.71	0.42	0.69	0.45	0.69	0.45	0.79	0.48	2.5-5.0	1.6-4.0
P (%)	0.66	0.59	0.64	0.48	0.66	0.47	0.65	0.49	0.74	0.63	0.16-0.40	0.12-0.30
K (%)	3.20	3.64	3.21	3.33	3.29	3.21	3.16	3.61	3.86	3.89	0.62-1.8	0.52-1.6
Ca (%)	2.60	3.13	2.57	3.25	2.56	2.96	2.62	3.01	3.21	3.23	1.2-2.8	1.8-3.2
Mg (%)	0.80	1.16	0.78	1.50	0.81	1.43	0.79	1.70	0.89	1.47	0.2-0.6	NA
NO <sub>3</sub> (mg/kg)	613	236	538	154	587	128	534	152	1120	265	340-1200	340-1200

Fl = flowering, V = véraison.

Table 4. Soil analysis from the Merlot and Shiraz sites before and after applying mulch.

Analysis	Merlot		Shiraz	
	Before mulch	After mulch	Before mulch	After mulch
pH in H <sub>2</sub> O	8.01	7.63	8.26	7.58
pH in CaCl <sub>2</sub>	7.59	6.93	7.92	6.86
Salinity (EC 1:5 dS/m)	0.09	0.07	0.23	0.08
eCEC 0-100	6.60	6.20	6.90	7.00
Calcium (%)	66.0	70.6	62.5	78.5
Magnesium (%)	29.5	22.7	24.2	16.2
Potassium (%)	3.30	5.20	6.80	3.60
Sodium (%)	1.20	1.50	6.50	1.70
Ca:Mg ratio	2.20	3.10	2.60	4.80

Table 5. Nutrient soil analysis from the Merlot and Shiraz sites before and after applying mulch.

Nutrient (mg/kg)	Merlot		Shiraz	
	Before mulch	After mulch	Before mulch	After mulch
Nitrate	17.3	1.44	7.29	2.49
Phosphate	28.4	37.1	54.0	64.9
Potassium	84.4	125.0	183.0	96.7
Sulfate	15.0	15.0	48.0	22.0
Calcium	874.0	876.0	866.0	1103.0
Magnesium	238.0	171.0	203.0	138.0
Iron	86.4	59.4	294.0	198.0
Manganese	174.0	143.0	53.0	66.0

## Discussion

This trial aimed to evaluate the effects of shoot thinning, foliar fertiliser use (magnesium and potassium) and composted mulch on pH and TA in wine grapes.

In Merlot grapes in Mudgee, shoot thinning resulted in the highest TA while applying foliar Mg resulted in the lowest TA levels. This is consistent with Reynolds et al. (2005) who reported early shoot thinning significantly increased TA in Pinot Noir berries and must. However, in Cabernet Franc must TA was decreased (Reynolds et al. 2005). It is likely that varietal and/or site differences influenced results in this trial. The pH of the Merlot fruit was not inversely related to TA, reinforcing the benefit of shoot thinning over other treatments.

While foliar K reduced TA readings, it did not translate into berry K increases. Potassium levels in grape berries are affected by numerous factors, including soil K level, antagonistic elements in the soil such as magnesium and calcium, grape variety and viticultural practices (Mpelasoka et al. 2003).

The decline in petiole nitrogen, nitrate and phosphorus and the increases in magnesium and calcium between flowering and véraison were also reported by Holzzapfel et al. (2019), who found that macronutrients such as nitrogen and phosphorus decline in annual parts of the vine up until véraison while magnesium and calcium increase until leaf-fall.

The low effective soil cation exchange capacity suggests that soils at both sites have low fertility, corresponding with sandy soil types. Interestingly, these are clay loam soils. Overall, antagonism exists at both sites with soil imbalances between Mg and Ca influencing nutrient availability when soil pH is high. In general terms, the soils at both sites are compacted and lack aeration.

Although treatment responses were expected from the foliar K and mulch applications, there was no statistical difference in Baume and anthocyanins between the treatments at either site. This result is perhaps not surprising given we also had no statistical differences in berry K and pH levels. Potassium is known to accumulate as do sugars in ripening winegrapes (Rogiers et al. 2017), and the influence of high pH is also known to reduce colour in winegrapes (Boulton et al. 1996).

Rain occurred on several days during mulch application, assisting the mobility of available K, nitrogen and nitrate for plant uptake. However, this did not translate into any significant differences in berry K or pH increases, whereas previous trials using the same 80/20 blend and mulch application rate showed significantly increased berry K and pH (Chan and Fahey 2011). Perhaps if background soil K levels were lower at both sites mulch application might have resulted in more robust findings. Soil tests conducted at the end of vintage on mulch treated soils showed increased soil calcium levels at both sites and a reduction in sodic conditions at the Shiraz site.

## Conclusions

Shoot thinning of Merlot vines significantly increased TA compared to the other treatments in this one-year trial. Early indications show foliar nutrient application can affect must TA, and berry Ca was increased by applying lower rates of Mg. Applying mulch increased petiole nutrient levels of nitrate and nitrogen at flowering in the Merlot site. However, these did not translate to increased YAN and berry K when analysed. Further evaluation of the benefits of shoot thinning and the other treatments should be undertaken over a longer duration to take varietal, site and seasonal differences into account.

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