Wine pH, copper and 'reductive' aromas in wines

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Managing wine pH is important for nearly all aspects of winemaking, including protection against microbial spoilage, colour stability, tartrate precipitation and wine aroma and flavour. Recent research at the AWRI has investigated the effects of wine pH and the interaction between wine pH and copper on the formation of 'reductive' aromas post-bottling in Chardonnay and Shiraz wines. Elevated residual copper concentrations were associated with increased hydrogen sulfide (H_2S), methanethiol (MeSH), and carbon disulfide (CS_2) concentrations; however, when the pH was lowered to 3.0, significantly less H_2S and MeSH were produced. Dimethyl sulfide (DMS) was not affected by copper additions; however, at lower pH up to 27% less DMS was produced in Shiraz wines after six months of storage.

INTRODUCTION

Certain volatile sulfur compounds (VSCs) normally found in wine are associated with 'reductive' aromas, often described as rotten egg, sewage, rubber, cooked vegetables and canned corn. The main compounds associated with these aromas are hydrogen sulfide (H_2S), methanethiol (MeSH) and dimethyl sulfide (DMS). Carbon disulfide (CS_2) may also have a negative impact on wine flavour, as it imparts rubbery and sulfidic aromas (Siebert *et al.* 2010).

Many factors affect the formation of VSCs in wines post-bottling, including early oxygen treatment during fermentation (Bekker *et al.* 2016a), the presence of the precursor compounds in wine, elevated copper concentrations post-bottling (Ugliano *et al.* 2011, Viviers *et al.* 2013) and anaerobic storage conditions (Ugliano *et al.* 2011). Wine pH also has the potential to influence the chemical reactions that are related to the formation or degradation and loss of flavour compounds. This can be through its effects on the precursor compounds or on catalytic compounds that facilitate the release of VSCs from their precursor compounds, or by influencing loss mechanisms.

Winemakers have the ability to instil their unique signature on wine composition through winemaking practices that include yeast selection, oxygen management during vinification and acid adjustments to manipulate juice, must, and wine to the desired pH. Although the role of copper in the formation of H_2S and MeSH has been established (Ugliano *et al.* 2011, Viviers *et al.* 2013), the ability of other winemaking variables, including pH, to modulate the effects of copper during the formation of VSCs had not been studied. As such, the aim of this study was to determine the effects of wine pH, and the effects of interaction between pH and copper, on the formation of VSCs associated with 'reductive' aromas in wines post-bottling.

AT A GLANCE

- The post-bottling formation of several 'reductive' aroma compounds in wine (hydrogen sulfide, methanethiol and carbon disulfide) was significantly affected by elevated copper concentrations.
- The effects of added copper on hydrogen sulfide and methanethiol formation were decreased when the wine pH was lowered.
- Significantly less dimethyl sulfide was produced in wines at a lower pH.
- There is potential to help minimise the risk of VSC formation in wines post-bottling through winemaking decisions that affect wine pH and copper concentration.

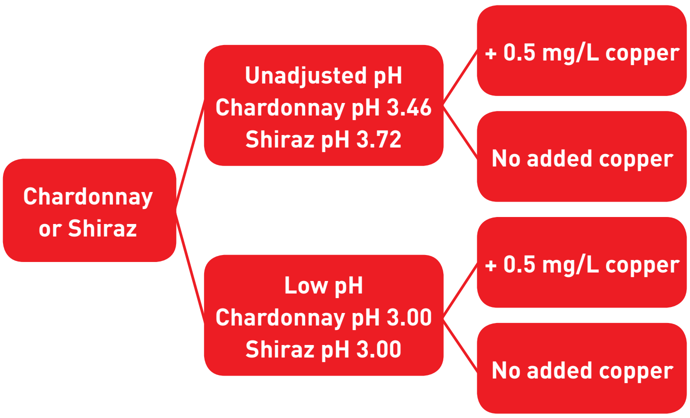

Figure 1. Experimental design and set-up used to study the effects of pH and the effects of the interaction between pH and copper on the formation of 'reductive' aromas in Chardonnay and Shiraz wines post-bottling.

EXPERIMENTAL DESIGN

A Chardonnay and a Shiraz wine (both with no residual copper) were selected and each was divided into two portions. The pH of one portion of wine was not adjusted (Chardonnay pH 3.46, Shiraz pH 3.72) and the pH of the second portion of the wine was adjusted using tartaric acid to pH 3.00 (Figure 1).

To investigate the interaction between residual copper and wine pH, the wines were again split into two portions and either treated with copper to give a final concentration of 0.5mg/L or left untreated (0mg/L residual copper) (Figure 1).

The VSC profiles of all wines were monitored over six months post-treatment. All experiments were conducted and all wines stored in an oxygen-free environment (Bekker *et al.* 2016b).

HOW DOES RESIDUAL COPPER AFFECT WINE?

All wines treated with copper displayed significantly increased H_2S concentrations (Figure 2a, 2b). This is in agreement with recent studies that have highlighted the effects of elevated residual copper concentrations on the formation of VSCs associated with 'reductive' aromas. Hydrogen sulfide concentrations were consistently significantly higher in wines with added copper than in wines without copper over the six months post-treatment.

Copper treatment was associated with a slight decrease in MeSH concentrations in the Chardonnay samples only at the six month time point (Figure 2c). This decrease in MeSH may be due to the quenching reaction between copper and MeSH to form a copper-thiol complex that decreased its concentration. In contrast, the Shiraz samples with added copper were associated with increased MeSH concentrations (Figure 2d). The different effects of copper on MeSH formation between red and white wine may be associated with the interaction of copper with wine compounds such as polyphenols and tannins, which are present in different concentrations in red and white wines. The loss of MeSH could also be through reactions with quinone compounds in white wines, or the formation of MeSH-adducts with red polyphenols.

Copper addition had no effect on DMS formation, and CS_2 formation was only significantly affected by increased copper concentrations in Chardonnay wines (Figure 2e). The reason for the variation in CS_2 concentrations in Chardonnay and Shiraz wines between analysis time points is not clear. However, the CS_2 concentrations measured in both Chardonnay and Shiraz wines were considerably lower than its odour threshold of 38µg/L and only slightly higher than the limit of quantitation for CS_2 analysis (0.5µg/L). As such it is likely that this low concentration of CS_2 did not have a meaningful effect on the aroma of the wine.

WINE PH AND 'REDUCTIVE' AROMAS

The effects of wine pH on H_2S and MeSH formation in Chardonnay and Shiraz wines were only observed in samples that were also treated with copper. In samples without added copper, pH had no effect on the amount of H_2S and MeSH produced in the Chardonnay or Shiraz wines post-bottling.

In samples with added copper, however, significantly less H_2S was produced in Chardonnay wines when the pH levels of the wines were adjusted to pH3.00 compared with Chardonnay samples with added copper at the unadjusted pH of 3.46 (Figure 2a). This shows that wine pH significantly affects H_2S formation when elevated residual copper concentrations are present. The effects of pH and copper interactions on H_2S formation in Shiraz wines were not as pronounced as in the Chardonnay wines, with significant decreasing effects of lower pH levels only measured directly after treatment and again after one month.

Methanethiol was not as strongly affected by lower pH conditions. Lower pH was only associated with significant effects on MeSH concentration at Day 0 in the Chardonnay samples. For Shiraz, decreasing the pH of the copper-treated Shiraz samples produced significantly less MeSH after one month and three months of storage but not after six months (Figure 3d). It is not clear why the interaction between pH and copper significantly affected MeSH formation only at certain stages of the experiment. It could be that the lower pH is affecting the reaction rate of the formation of MeSH. The differences may be a reflection of the

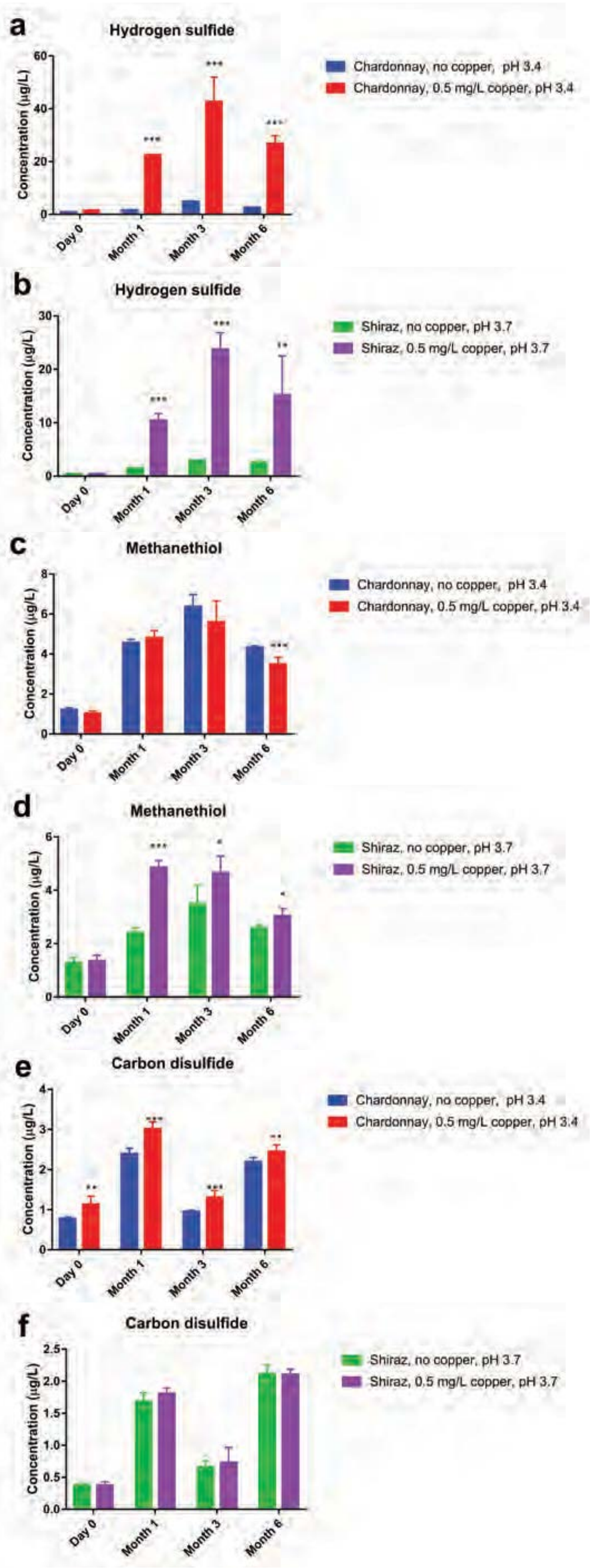

Figure 2. The effects of copper on the formation of hydrogen sulfide [(a), (b)], methanethiol [(c), (d)], and carbon disulfide [(e), (f)] in Chardonnay and Shiraz wines measured over the course of six months post-treatment. Significance of copper effect: P-value < 0.0001 (***), P-value < 0.001 (**); P-value < 0.01 (*).

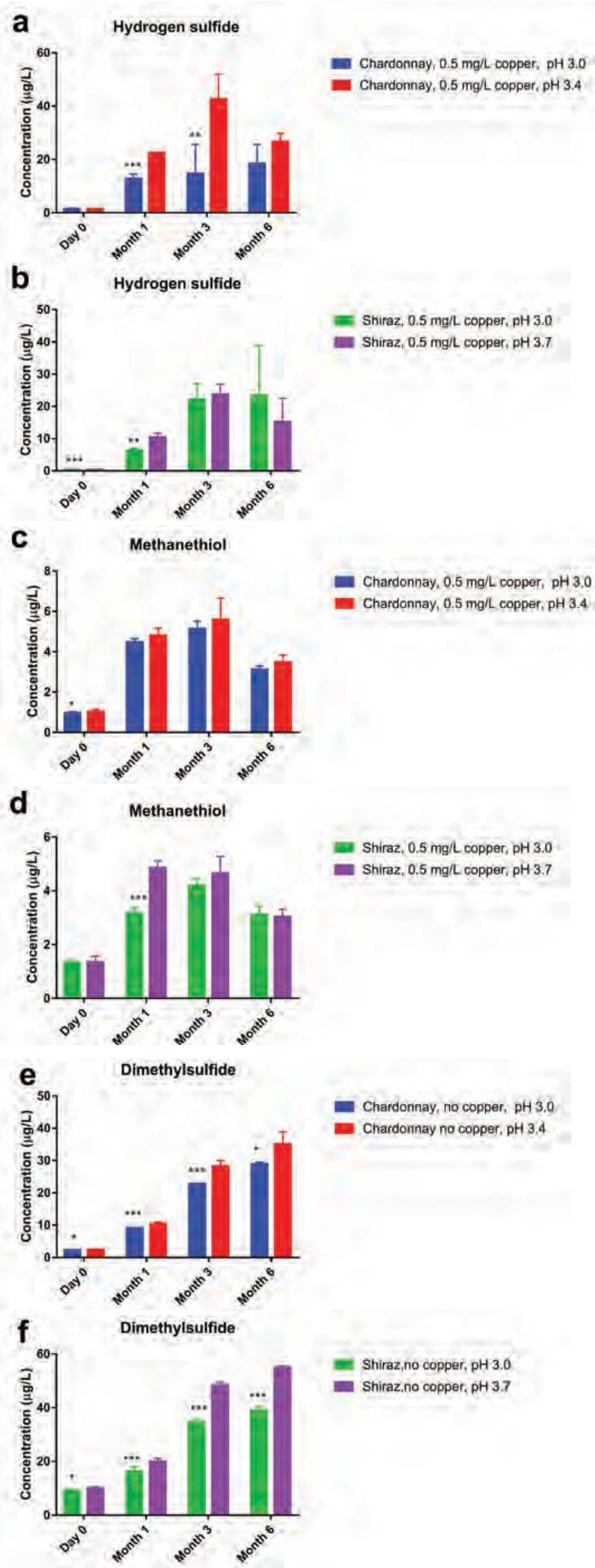

Figure 3. The effects of pH, and the interaction between pH and copper, on the formation of hydrogen sulfide [(a), (b)], methanethiol [(c), (d)], and dimethylsulfide [(e), (f)] in Chardonnay and Shiraz wines measured over the course of six months post-treatment. Significance of pH effect: P-value < 0.0001 (***), P-value < 0.001 (**); P-value < 0.01 (*).

time needed for the wines to reach the same end-point MeSH concentration.

Dimethyl sulfide was significantly affected by the pH of the wines, with lower concentrations of DMS measured in both Chardonnay and Shiraz samples throughout the course of the six-month experiment in wines with a lower pH (Figure 3e, 3f). Six months post-treatment there was 27% less DMS measured in Shiraz wines with a pH of 3.00 compared with Shiraz wines with a pH of 3.72. The effect of pH on DMS formation in wines post-bottling is remarkable given that DMS is a stable molecule that remains unaffected by oxygen treatment during fermentation (Bekker *et al.* 2016a) and is also unaffected by metals such as copper, iron or manganese (Viviers *et al.* 2013). The decreased DMS measured in this study is most likely due to the precursor compounds of DMS becoming less prone to release DMS at a lower pH level. It is known that one of the main precursors to DMS, S-methyl methionine (SMM), is stable in acid conditions but rapidly decomposes at pH greater than 7.00 (Cantoni 1960). The decrease in pH from 3.72 to 3.00 most likely prevented the formation of DMS from SMM by stabilising SMM.

CONCLUSIONS

This study demonstrated that the post-bottling formation of the 'reductive' aroma compounds H_2S, MeSH, DMS, and CS_2 was significantly affected by both copper additions and wine pH. For some of these compounds, the interaction between pH and copper treatment was an important factor in determining their final concentrations. Specifically, less H_2S and MeSH were produced through copper catalysed reactions in wines at a lower pH than in wines at a higher pH. Winemakers have some flexibility in managing both wine pH and residual copper and, therefore, there is potential to help minimise the risk of VSC formation in wines post-bottling through winemaking decisions.

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REFERENCES

Bekker, M.Z.; Day, M.P.; Holt, H.E.; Wilkes, E. and Smith, P.A. (2016a) Effects of oxygen exposure during fermentation on volatile sulfur compounds in Shiraz wine and a comparison of strategies for remediation of reductive character. Aust. J. Grape Wine Res. 22(1):24-35.

Bekker, M.Z.; Mierczynska-Vasileva, A.; Smith, P.A. and Wilkes, E.N. (2016b) The effects of pH and copper on the formation of volatile sulfur compounds in Chardonnay and Shiraz wines post-bottling. Food Chem. 207:148-156.

Cantoni, G.L. (1960) Onium compounds and their biological significance. Florkin, M., Mason, H.S. (eds.) Comparitive Biochemistry. A Comprehensive Treatise New York: Academic Press Inc.: 215.

Siebert, T.E.; Solomon, M.R.; Pollnitz, A.P. and Jeffery, D.W. (2010) Selective determination of volatile sulfur compounds in wine by gas chromatography with sulfur chemiluminescence detection. J. Agric. Food Chem. 58(17):9454–9462.

Ugliano, M.; Kwiatkowski, M.; Vidal, S.; Capone, D.; Siebert, T.; Dieval, J.-B. and Waters, E.J. (2011) Evolution of 3-mercaptohexanol, hydrogen sulfide, and methyl mercaptan during bottle storage of Sauvignon blanc wines. Effect of glutathione, copper, oxygen exposure, and closure-derived oxygen. J. Agric. Food Chem. 59(6):2564–2572.

Viviers, M.Z.; Smith, M.E.; Wilkes, E. and Smith, P.A. (2013) Effects of five metals on the evolution of hydrogen sulfide, methanethiol, and dimethyl sulfide during anaerobic storage of Chardonnay and Shiraz wines. J. Agric. Food Chem. 61(50):12385-12396. WVJ