EFFECTS OF SOIL CHARACTERISTICS ON MANGANESE TRANSFER FROM SOIL TO VINE AND WINE

Jean-Yves Cahurel[1], Pierre Martini[1]*, B. Chatelet[2], I. Letessier[3]

[1]Institut Français de la Vigne et du Vin, 210 boulevard Vermorel, CS 60320, 69661 Villefranche-sur-Saône, France
[2]Sicarex Beaujolais, 210 boulevard Vermorel, CS 60320, 69661 Villefranche-sur-Saône Cedex, France
[3]Sigales, 453 route de Chamrousse, 38410 S[t] Martin d'Uriage, France

*Corresponding author: pierre.martini@vignevin.com

Abstract

Aim: In recent times the export of Beaujolais wines has been jeopardised due to a limit of manganese content (Mn) in wine implemented by China (2 mg/L), related to suspicions of potassium permanganate fraud. Nevertheless, soil Mn content may be high in some soil types in Beaujolais. The aim of this study was to improve knowledge of manganese transfer from soil to vine and wine because data on this subject is scarce.

Methods and Results: Recent pedologic mapping of Beaujolais vineyards has enabled a Mn monitoring network to be set up in order to study Mn transfer from soil to vine and wine. Three soil types were considered. Two of the soils can be very high in EDTA Mn: soils from clays with cherts (soil type 7) and former piedmont deposits with leached soils (soil type 8). The third soil, though low in Mn, is the most important and symbolic of Beaujolais: granitic soil. Fifteen plots of Gamay were monitored during 3 years (2015-2017). Besides soil analysis made from pedologic pits, Mn content of petiole, must and wine (red standard wine-making of 40 kg grapes) were determined, as well as grape yield and biomass (pruning weight). Results show that Mn in petioles is better correlated with Mn in wine than Mn in must. Mn content of wine is little in relation with EDTA Mn in soil. It increases when soil pH or cation exchange capacity decreases.

Conclusions: This study has shown that Mn concentration in wine can be naturally very high (maximum of 14.6 g/L in this study). Soils with low cation exchange capacity and/or low pH, i.e. soil types 1 and 8, resulted in higher Mn content in wine. Low cation exchange capacity does not allow a great Mn fixation on clay-humic complex and low pH soil solubilizes metal generally and Mn in particular, so it can be taken up by the vine. Mn petiole content is a very good indicator of Mn content in wine. Maceration in red wine-making is also an element to take into consideration.

Significance and Impact of the Study: Mn content in Beaujolais wine can be very high because of soil type, rather than fraud. It is important to highlight this for wine exportations. Mn content in wine can be reduced by correcting the soil pH.

Keywords: Manganese, terroir, soil, Beaujolais, vine, wine

Introduction

In recent times the export of Beaujolais wines has been jeopardised due to a limit of manganese content (Mn) in wine implemented by China (2 mg/L). A better understanding of manganese transfer from soil to vine and wine could help to defend Beaujolais wine quality because high Mn content in wine could be due to natural phenomenon.

Currently, data on Mn transfer from soil to vine and wine are very scarce and it do not concern Beaujolais wine. They still show the importance of the soil type on the level of Mn in wine: soil pH that makes Mn more soluble and present in the soil solution seems to play a key role (Coga *et al.,* 2010; Delas, 1973; Kalanquin *et al.,* 2013), even if some authors highlight the manganese richness in the soil (Stobbaerts *et al.,* 1994). However, Blaize (2000) shows that the redox phenomenon also plays a key role on the solubility of Manganese: a reducing environment (compaction, congestion for example) will promote the solubilization of the manganese.

The amount of Mn in wine is variable, Cabrera-Vique *et al.* (2000) found wines from different French wine regions had manganese content ranging between 0.435 and 7.836 mg/l and between 1.336 and 4.984 mg/l in Beaujolais wines. Kalanquin *et al.* (2013) found manganese content ranged between 0.3 and 3.5 mg/l in Languedoc wines. They show, like other authors (Rivero Huguet, 2004), that Mn levels are higher in red wines than in white ones, due to maceration which extracts more Mn from grape skins and seeds. Seeds have the highest content of the berry followed by skins and finally pulp. Proportions may vary: for seeds it is between 44 and 69 %, for skins from 13 to 35 % and for pulp from 6 to 28% (Bertoli *et al.,* 2011; Esperaza *et al.,* 2011; Ramos *et al.,* 2016; Yang *et al.,* 2010).

The numerous data collected thanks to the work of pedologic mapping of Beaujolais vineyard has enabled a Mn monitoring network to be set up in order to study Mn transfer from soil to vine and wine depending on the type of soil, some soil characteristics (pH, organic matter levels which can hold the manganese and make it non-assimilable by the vine) and the vintage.

Materials and Methods

Mn content in soil was determined by the EDTA procedure (ISO 6233:1983). It corresponds to the Mn complexed with organic matter and with very poorly crystallized amorphous compounds which is relatively mobile. It is only a fraction of the manganese present in the soil. Other research on the other form of manganese in the soil could be useful (total, soluble, reducible, exchangeable).

On the vineyard map, the distribution of manganese is not random. Median Mn levels are very different (ranging from 1 to 10) depending on the classes of parent materials showing three peaks of which two are significant (Figure 1). The 7X which are soils from clays with cherts and the 8X which are former piedmont deposits with leached soils (the 3XB (Trias) is too small to be enhanced here). In detail in the 8X group we can observe significant differences according to the evolution and/or the dominant texture of the soil.

The study was based on these two groups:

- The 7X, large flats of residual clays. This soil is the most clayey on the surface with the higher amount of organic matter and the least acidic.
- The 8X, former piedmont deposits. This soil is leached so it has more clayey on surface than in depth, organic matter content depth depends on the texture of the surface (very low for sandy one, a bit more for the more clayey) with high pH (often adjusted in surface but mostly lower than 5.5 in depth).

To complete the study, the 1X (granite), which has low manganese content (as shown in Figure 1) was added because it is the most represented type of soil in Beaujolais. It is extremely sandy with very low organic matter content and is acidic (pH was often adjusted between 2011 and 2017). Manganese behavior can fluctuate in this type of soil because of its low complexation, therefore its low extraction using the EDTA method.

Fifteen plots were selected to have different Mn content, pH and organic matter level in each type of soil. The values indicated below correspond to the values collected at the opening of the pedological pits by Sigales company on each plot (Horizon 10-30 cm). The distribution of the plots depending on the soil type was as follows: 4 plots for type 1, 5 plots for type 7 and 6 plots for type 8. All the plots were monitored for three years (2015-2017). However, due to hail in 2016 and 2017, some measurements could not be done on certain plots, especially the Mn content in must and wine. When some figures are too complex to show all the vintage data, in order to be more readable, the vintage 2016 was selected as example because this is the only vintage that all the measurements were done on all the plots.

All the plots are planted with Gamay and on each of them an area was identified for monitoring, around the pedological pits. The annual measurements were:

- Petioles Mn content by sampling 50 petioles at the beginning of veraison.
- Biomass estimation by weighing prunings during dormancy
- Yield estimation by harvesting 45 kg of grapes
- Must Mn content by sampling 200 berries on harvested vines (extraction of must by centrifuge)
- Wine Mn content by standard vinification of harvested grapes (levuline killer yeast, 6 days maceration, same fermentation temperature, same wine equipment).

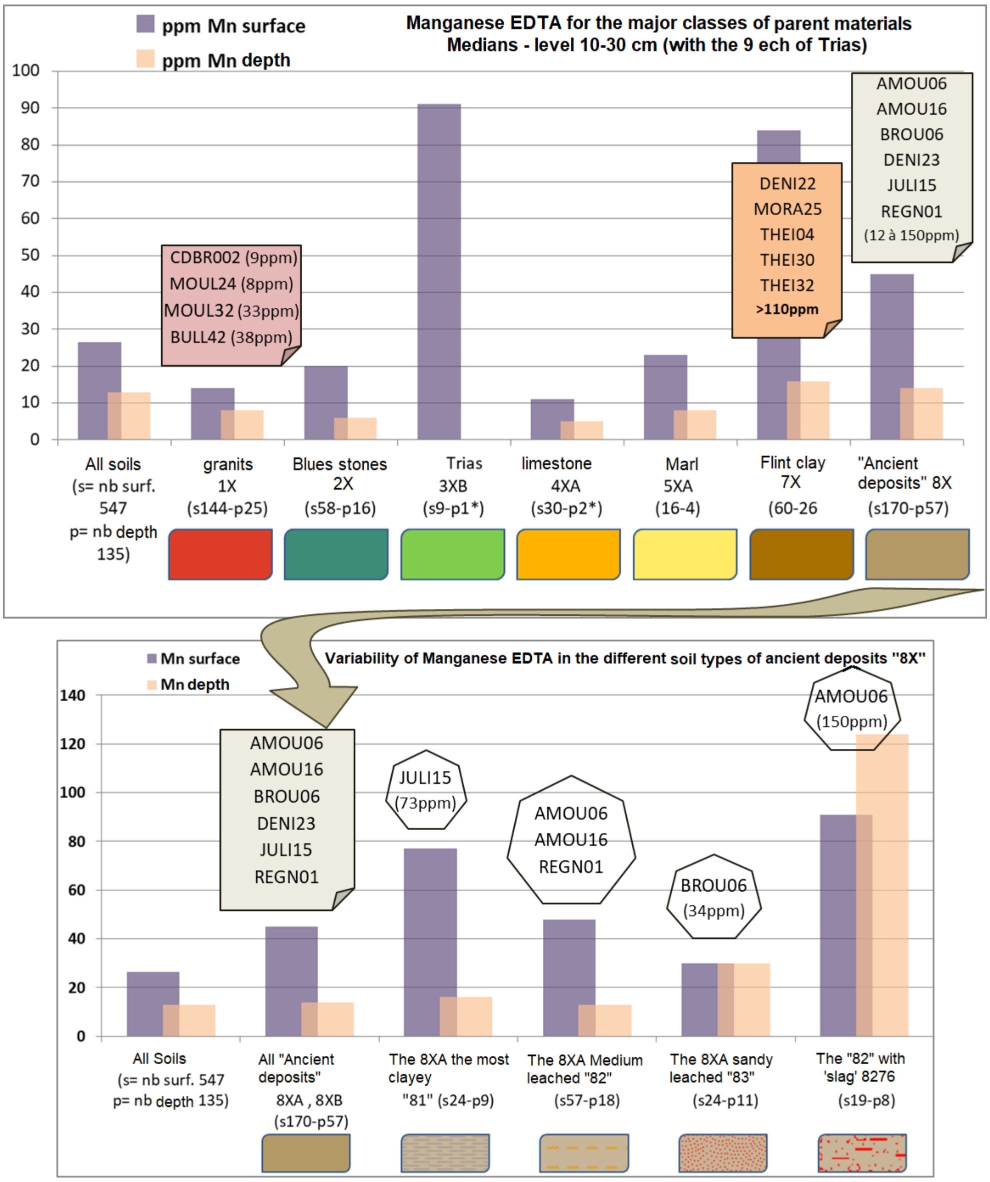

Figure 1: The 15 plots of the study in their parent materials or soils (median of the 547 Mn dosed profiles).

Results and Discussion

Whatever the vintage petioles, musts and wines from soil type 8 had the higher Mn content (Table 1). On the contrary, the one from soil type 7 had the lowest Mn content whereas those from soil type 1 had an average Mn content but with higher variability between plots.

Nearly 40% of the results on petioles are higher than the threshold of a manganese toxicity (0.5 g/kg) but no symptoms were identified during the three years. Values are between 0.041 and 1.58 g/kg. Interestingly, 68% of the Mn contents were higher than 2 mg/l in wines which represents 10 plots of the 15 monitored. Values were between 0.81 and 14.6 mg/l. It should be noted that the highest value finds in wine, according to literature (Gomez-Miguel *et al.,* 2014) were 10 mg/l.

Table 1 : Mean and standard deviation of different Mn content depending on the vintage and the soil type.

Type of soil	Vintage	Mn petiole mg/kg DM	Mn must mg/l	Mn wine mg/l
1	2015	**0.589** *(549)*	**2.0** *(1.3)*	**4.5** *(3.3)*
	2016	**0.450** *(443)*	**1.3** *(0.9)*	**2.0** *(0.5)*
	2017	**0.549** *(0)*	**2.1** *(1.2)*	**5.1** *(0)*
7	2015	**0.181** *(109)*	**0.7** *(0.2)*	**1.5** *(0.5)*
	2016	**0.163** *(75)*	**0.6** *(0.2)*	**1.2** *(0.6)*
	2017	**0.159** *(84)*	**0.8** *(0.4)*	**2.2** *(0.9)*
8	2015	**0.817** *(240)*	**3.3** *(1.9)*	**6.2** *(2.4)*
	2016	**0.698** *(334)*	**2.1** *(1.0)*	**5.3** *(2.5)*
	2017	**0.814** *(572)*	**1.7** *(0.9)*	**8.7** *(4.5)*

Comparison Between Vintages

Comparison between vintages shows that Mn content in petioles is well correlated to each other (except plot JULI15 in 2017). 2016 shows lower values than the two other vintages (Figure 2). It is the same for the correlations on Mn content in wine. 2017 is a little bit higher than excepted for two plots (JULI15 and BROU06). For the Mn content in must, if the correlation between 2015 and 2016 is really good (r^2=0.91), it is totally different for 2017 (r^2=0.61) where 4 plots do not follow the trend (including JULI15 and BROU06). Average values are similar between 2016 and 2017 and lower than the ones of 2015.

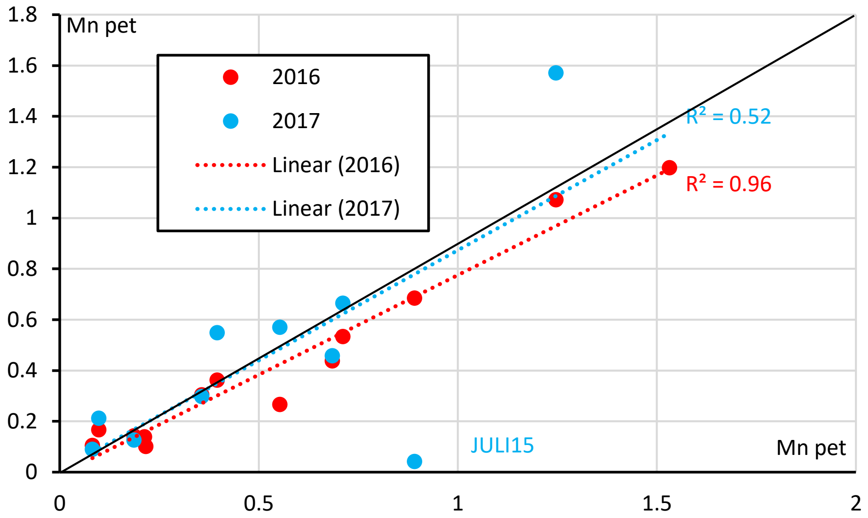

Figure 2: Relation between Mn contents in petioles of 2016 and 2017 vintages compared to 2015 vintage (g/kg DM).

The lower values identified in 2016 could be explained by the climatic conditions of the vintage. It was much wetter during spring and summer than the two other vintages (401 mm from April to September 2016 versus 163 mm in 2015 and 279 mm in 2017) which may have diluted the manganese levels in leaves and berries.

Relation Between Mn Levels in Petioles, Musts and Wines

The correlations per vintage between Mn levels in petioles, in musts and in wines are overall very good. They are slightly less between Mn levels in petioles and in musts, especially for 2015 vintage. Between 2015 and 2016, with the same Mn content in petioles, levels in must are divided by 1.5 and by 2 between 2015 and 2017 while Mn content in wine are identical between 2015 and 2016 and slightly higher in 2017 (Figure 3).

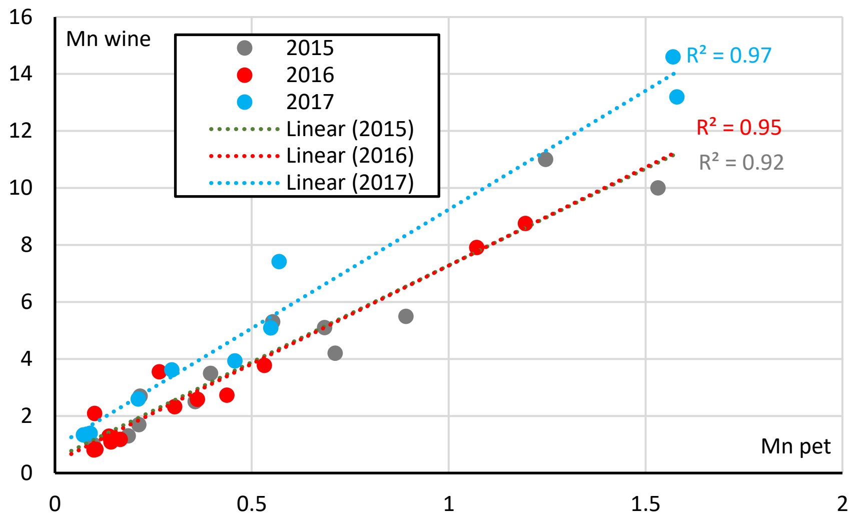

Figure 3: Relation between Mn content in petioles (g/kg DM) and in wine (mg/l).

Levels in wines are higher than the ones in musts (Figure 4) with an increasing difference between 2015 and 2017: factor of 1.7 for 2015, 2.7 for 2016 and 5 for 2017. It confirms that maceration makes it possible to extract manganese contained in seeds and skins and increase the Mn content in wine compared to the initial must content. These findings are independent of the type of soil.

A good correlation between Mn content in petioles and Mn content in wine and its low variation between vintage (r^2=0.90 for all vintage together versus 0.7 between petioles and musts and 0.64 between wines and musts) was observed. Thanks to this, in the remainder of the article, all the results will focus on Mn content in petioles, unfortunately, some data were missing (Mn content in petioles for MOUL24 and MOUL23 in 2017 and for MORA25 in 201). But these missing data have been calculated through the linear equations presented above (correlation with Mn content in must was used for MOUL24 and MOUL23 and correlation with Mn content in wine for MORA25).

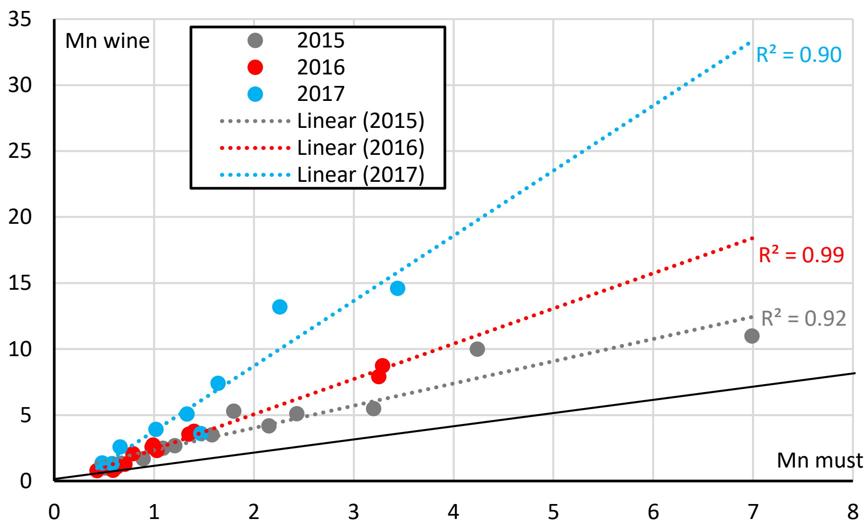

Figure 4: Relation between Mn levels in musts and in wines (mg/l).

Influence of the Soil Characteristics on the Mn Content in Petioles
There is not a real correlation between the Mn content in petioles and the richness in manganese of the soil regardless of year and type of soil.

Whatever the vintage a trend is emerging to have higher Mn content in petioles when the pH of the soil decreases, even if these two parameters are not well correlated (r^2=0.42, 0.44 and 0.36 for 2015, 2016 and 2017). For pH higher than 6.5, Mn content in petioles varies little and remains relatively low (under 0.57 g/kg DM).

When considering the soil type, correlations are a little bit improve (see example on Figure 5) but some plots are still not following the linear correlations found (the dot line): MOUL24 in 2015 and 2016 and JULI15 in 2017. For the three types of soil, trends found are independent of the vintage, so Figure 5 could be taken as an example. For soil type 1 and 8, when the soil pH decreases, there is a significant increase of Mn content in petioles while this increase is lower for soil type 7.

Out of correlation: MOUL24 in 2015 and 2016 and JULI15 in 2017. Trends for every type of soil are identical between vintages, so figure 5 could be taken as example. It shows a significant increase of Mn content in petioles when pH of soil decreases for soil type 1 and 8 and a much smaller increase for soil type 7.

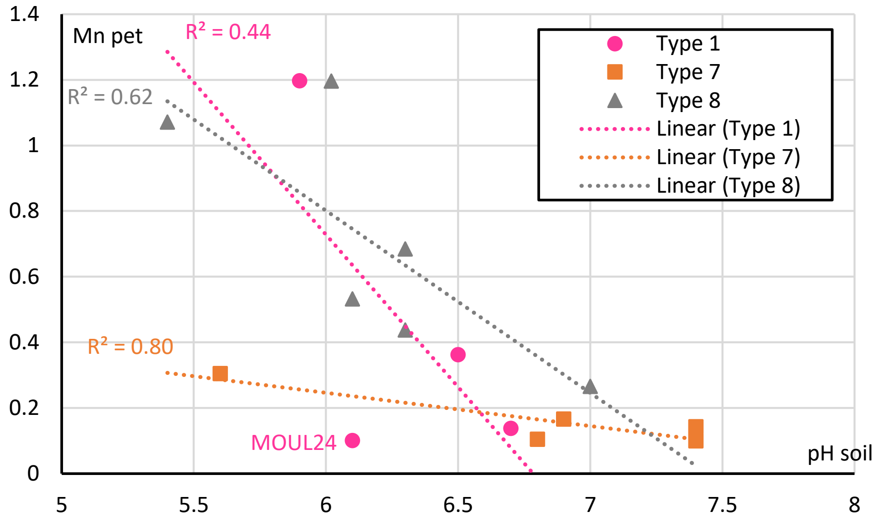

Figure 5: Relation between Mn content in petioles (g/kg DM) and pH of the soil for vintage 2016.

Whatever the vintage, there is no trend between Mn content in petioles and the level of organic matter of the soil. Consideration of soil type does not improve the result excepted for soil type 7 that levels in petioles increase with the decrease of organic matter levels (Figure 6).

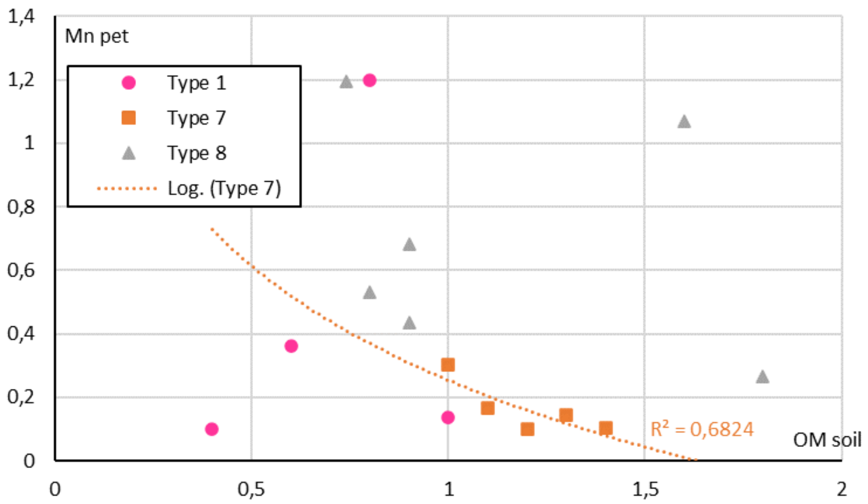

Figure 6: Relation between Mn content in petioles (g/kg DM) and organic matter level of the soil (%) for 2016 vintage.

Whatever the vintage a trend is emerging to have higher Mn content in petioles when the clay content of the soil decreases, like the pH. Similarly, these two parameters are not well correlated (r^2=0.40, 0.37 and 0.5 for 2015, 2016 and 2017 for linear relation; r^2=0.48, 0.43 and 0.62 for 2015, 2016 and 2017 for logarithmic relation). Some plots disrupt the correlation (BROU06 and MOUL24 for all the vintages and JULI15 for 2015 and 2016). By removing these plots, coefficients of determination increase significantly for the logarithmic relation: 0.8, 0.77 and 0.88 for 2015, 2016 and 2017.

Trends for every type of soil are identical between vintages, so Figure 7 could be taken as an example. It shows a significant increase in Mn content in petioles when clay content of soil decreases for soil type 1 and 8 and a much smaller increase for soil type 7 (which have generally higher clay content, higher than 20%).

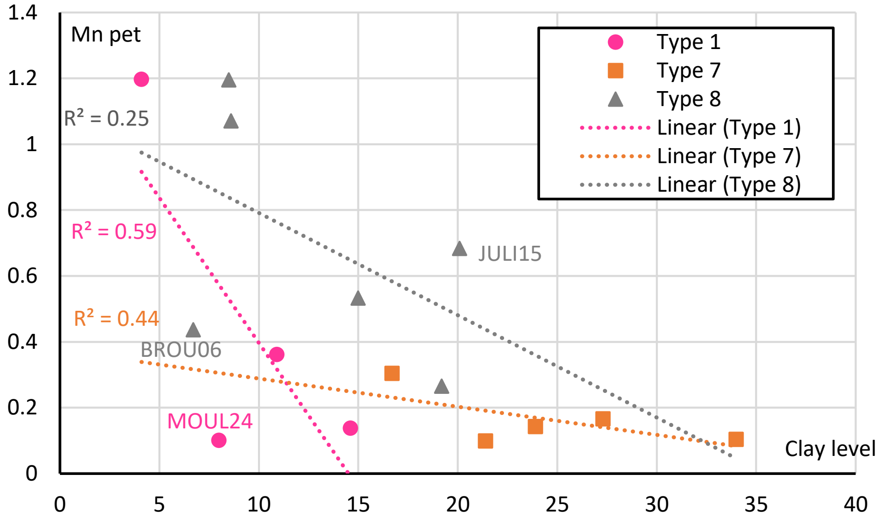

Figure 7: Relation between Mn content in petioles (g/kg DM) and clay level of the soil (%) for 2016 vintage.

Whatever the vintage a trend is emerging to have higher Mn content in petioles when the cation exchange capacity (CEC) of the soil decreases, like the pH and the clay level. Similarly, these two parameters are not well correlated (r^2=0.42, 0.45 and 0.47 for 2015, 2016 and 2017 for linear relation; r^2=0.44, 0.57 and 0.59 for 2015, 2016 and 2017 for power relation). Some plots disrupt the correlation (BROU06 for 2016 and 2017 and JULI15 for 2015 and 2016). By removing these two plots, coefficients of determination increase significantly: 0.64, 0.84 and 0.65 for 2015, 2016 and 2017.

Consideration of soil type significantly improves the relations for soil type 1 and 7. The absence of improvement for soil type 8 could be explain by the fact that this type of soil includes a larger diversity of soil type than the two others. Trends for every type of soil are identical between vintages (see Figure 8 as an example). It shows a significant increase of Mn content in petioles when CEC of soil decreases for soil type 1, the same trend for soil type 8 if we exclude these two plots and a much smaller increase for soil type 7.

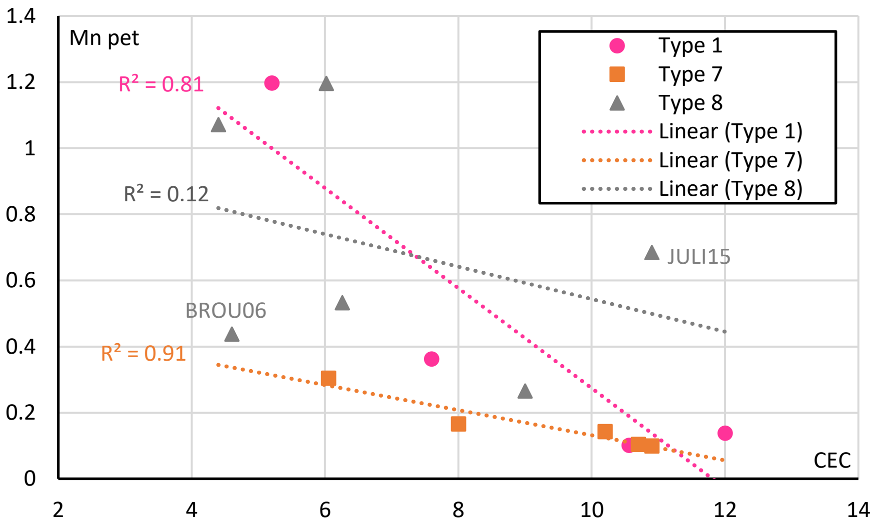

Figure 8: Relation between Mn content in petioles (g/kg DM) and CEC of the soil (cmol⁺/kg) for 2016 vintage.

The relations by soil type with Mn content in petioles are better with the CEC than with the other parameters of the soil previously shown except for type soil 8. For the two plots which not fit the relation with the CEC (BROU06 and JULI15), There is no problem with the relation with the pH of the soil. This might explain that the Mn content in petioles for these plots is due to the pH of the soil and not because of the CEC. Besides the good correlations obtained between the different Mn levels in the vine show that the values of Mn content in petioles and the Mn content in the musts and the wines, which exclude a sampling or an analysis problem.

Conclusion

This study has shown the importance of the soil type on the Mn content in the petioles and in the wines. On the contrary, the richness of EDTA-manganese in the soil do not seem to have significant effect. It is rather the cation exchange capacity and the pH which have the most significant impacts. The first in relation to the fixation of the Mn (cation) by the clay-humus complex and the second in relation to the solubilization of metals and acidity of the soil. These two parameters have a key role on the quantity of Mn available for the vine. The most suitable soils to give higher Mn content to the vine and the wine are the ones with low CEC (sandy soils particularly) and/or low pH (under 6). The soils from type 7 complex Mn related to their high contents of clay and organic matter which make manganese less available for the vine. The soil types 1 and 8 are leached thus with a lower clay content and complex less Mn. Soil type 8 also has a tendency towards reduction which promotes solubilization of the manganese.

The Mn content in the petioles is a great indicator of what we can finally find in the wine. This study has shown that we could find a wide range of Mn content in wine (0 to 14.6 mg/l) and this is due only to the type of soil on which the vine grows. In addition, the effect of the maceration was also shown and confirms data shown in the literature. Maceration length is not the same from one winemaker to another or from one appellation to another, this could also explain the wide range of Mn contents in wine. For example, during the study maceration length was only 6 days long and we can wonder if higher Mn levels in wines could have been obtained with longer maceration as it is usually done in the vineyard, especially in the Crus du Beaujolais.

References

Baize, D., 2000. *Guide des Analyses en Pédologie*, 2nd Edition. Editions INRA.

Bertoldi, D., Larcher, R., Bertamini, M., Otto, S., Concheri, G., Nicolini, G., 2011. Accumulation and distribution pattern of macro- and microelements and trace elements in *Vitis vinifera* L. cv. Chardonnay berries. Journal of Agricultural and Food Chemistry, 59: 7224-7236.

Cabrera-Vique, C., Teissedre, PL., Cabanis, MT., Cabanis, J-C., 2000. Manganese determination in grapes and wines from different regions of France. American Journal of Enology and Viticulture, 51(2): 103-107.

Coga, L., Slunjski, S., Herak Custic, M., Horvat, T., Petek, M., Gunjaca, J., 2010. Effect of soil pH reaction on manganese content and dynamics in grapevine (*Vitis vinifera* L.). Acta Horticulturae, 868: 203-208.

Delas, J., 1973. Effets des matières organiques sur les propriétés du milieu. Bulletin Technique d'Information, 46(285): 15.

Esparza, I., Santamaria, C., Fernandez, JM., 2011. Etude de l'association des métaux avec les composés majoritaires du vin. Revue des Œnologues, 38(141S): 56-58.

Kalanquin, D., Coste, M., Paricaud, T., Dubernet, M., Fil, J., Fourment, J-P., Prabonnaud, S., Thomas, G., 2013. Le manganèse dans les vins, origine et teneurs. Revue des Œnologues, 149: 33-35.

Ramos, MC., Romero, MP., 2016. Effects of soil characteristics and leaf thinning on micronutrient uptake and redistribution in 'Cabernet Sauvignon.' Vitis, 55(2): 113-120.

Rivero Huguet, ME., 2004. Monitoring of Cd, Cr, Cu, Fe, Mn, Pb and Zn in fine Uruguayan wines by atomic absorption spectroscopy. Atomic Spectroscopy, 25(4): 177-184**.**

Stobbaerts, R., Robberecht, H., Haesen, F., Deelstra, H., 1994. Manganese content of European wines. International Journal for Vitamin and Nutrition Research, 64(3): 233-236.

Yang, Y., Duan, C., Du, H., Tian, J., Pan, Q., 2010. Trace element and rare earth element profiles in berry tissues of three grape cultivars. American Journal of Enology and Viticulture, 61(3): 401-407.