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OIV COLLECTIVE EXPERTISE

MANGANESE IN VITIVINICULTURAL PRODUCTS: ORIGIN, INFLUENCE, TOXICITY

OIV
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This document, drafted and developed on the initiative of the OIV, is a collective expert report.

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SCOPE

The group of experts « Food safety » of the OIV has worked extensively on the safety assessment of different compounds found in vitivinicultural products.

This document aims to gather more specific information on manganese. This document has been prepared taking into consideration the information provide during the different sessions of the group of experts "Food safety" and information that provided by Member States in response to a circular letter.

Finally, this document, drafted and developed on the initiative of the OIV, is a collective expert report. This review is based on the help of scientific literature and technical works available until date of publishing.

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Where is the manganese in wine coming from?

The vineyard appears to be the major source of manganese in wines.

Sources of manganese in vineyards

■ Manganese is a naturally occurring element found in rock, soil and water. Combustion of gasoline containing the fuel additive methylcyclopentadienyl manganese tricarbonyl (MMT) releases manganese-containing emissions that also potentially contaminates soil, dust, and plants in vineyards near roadways (Lytle et al. 1995, Frumkin and Solomon 1997).

■ The main drivers of the concentration of manganese in grapevines (and grapes) appear to be soil bioavailability and local environmental conditions.

■ Manganese plays an important role in the synthesis of chlorophyll and nitrogen metabolism, and is present in soil as exchangeable manganese or manganese oxide. Manganese deficiency is expressed as yellowing of the interveinal area of older leaves and may be mistaken for zinc or iron deficiency. These symptoms may be found in vines on sandy, calcareous soils or in areas of high rainfall. Manganese toxicity is rare but can be seen as black spots on the leaves, shoots and bunch stems (Ashley 2009).

■ Manganese is present in soils, mainly as oxides, MnO_2 (pyrolusite) and MnO (OH) (manganite), but also $MnCO_3$ carbonates and silicates $MnSiO_3$, at levels ranging from 200 to 3,000 ppm (600 ppm on average).

Mn^{2+} ion may be released through weathering and chemical processes. A small portion of these ions remain free in the soil solution and this is the fraction assimilated by plants.
In acidic soils (pH value below 6), the free fraction (Mn^{2+}) is larger and vines will take up more. In basic, alkaline or well aerated soils, manganese availability decreases.

■ Vineyard management practices may modulate but not eliminate manganese levels and the vinification process does not usually add significantly to the levels already found in grapes, by affecting soil pH and influence the availability of Mn^{2+}, such as:

• Liming very acid soils decreases the Mn^{2+} in solution due to precipitation as MnO_2. Excessive liming of acid soils is a common cause of manganese deficiencies.

• Fertiliser, agrochemicals, irrigation water or other treatments containing manganese can increase levels in vines whereby inputs with acidifying properties can alter availability to the vine (La Pera et al. 2008).

• Cover crops by reducing the other nutrients as Fe, Cu or Zn.

Influences on vine manganese content

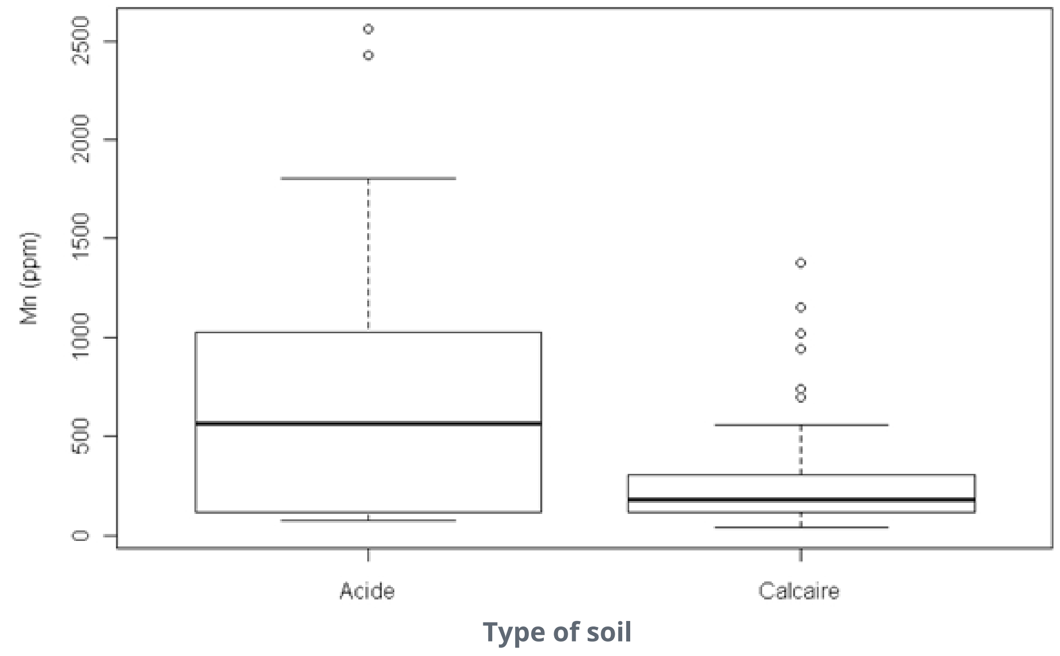
■ Manganese is a micronutrient of plants and its concentration is variable. An increase in the manganese content of petioles, particularly from fruit set has been observed.

■ It has been demonstrated that soil type is the most influential parameter on the manganese content of vines with soil pH being the main factor (Dubernet et al. 2014). High wine manganese concentrations consistently correspond with low soil pH values.

■ Vines grown on soils with high levels of compacted limestone, on waterlogged soils or on heavy clay soils can also have a high manganese content.

■ Although La Pera et al. (2008) identified manganese-containing fungicides as a possible primary source of manganese in grapes and wine, research at the AWRI found no clear link between the number of spray applications of one manganese-containing fungicide (mancozeb) and the final concentration of manganese in wine. Mancozeb sprays did not appear to be a primary source of manganese in grapes and wine (AWRI 2015).

■ Coetzee et al. (2005) and Van der Linde et al. (2010) showed that soil type is a major contributing factor to the element composition of a wine. Accordingly, it

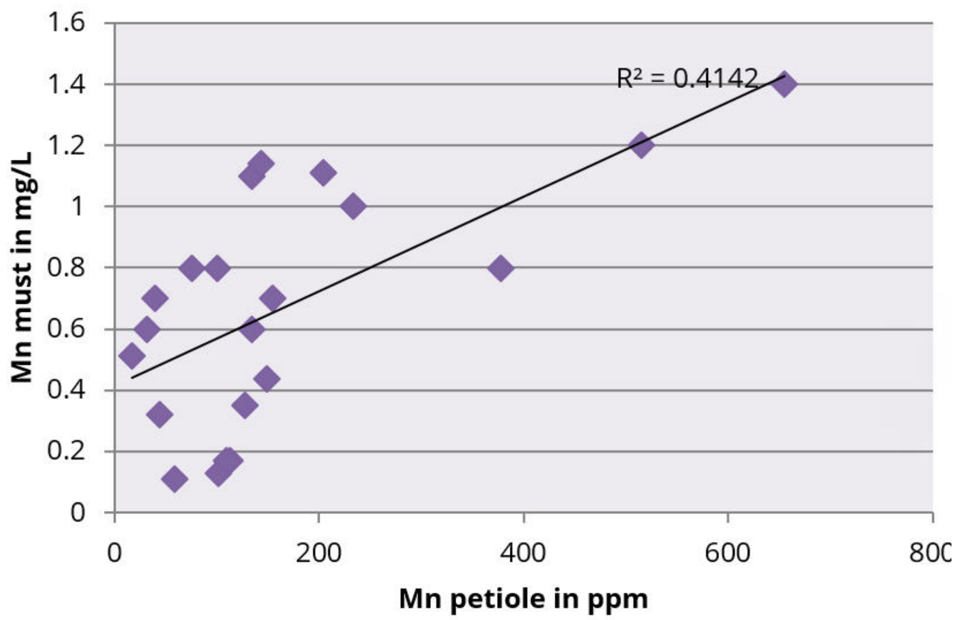


Influences on wine manganese content

is probable that the manganese concentration of wine is driven by the region of production, more specifically the soil properties where the grapes are grown.

■ A significant correlation in manganese levels was found between fruit/must and petioles.

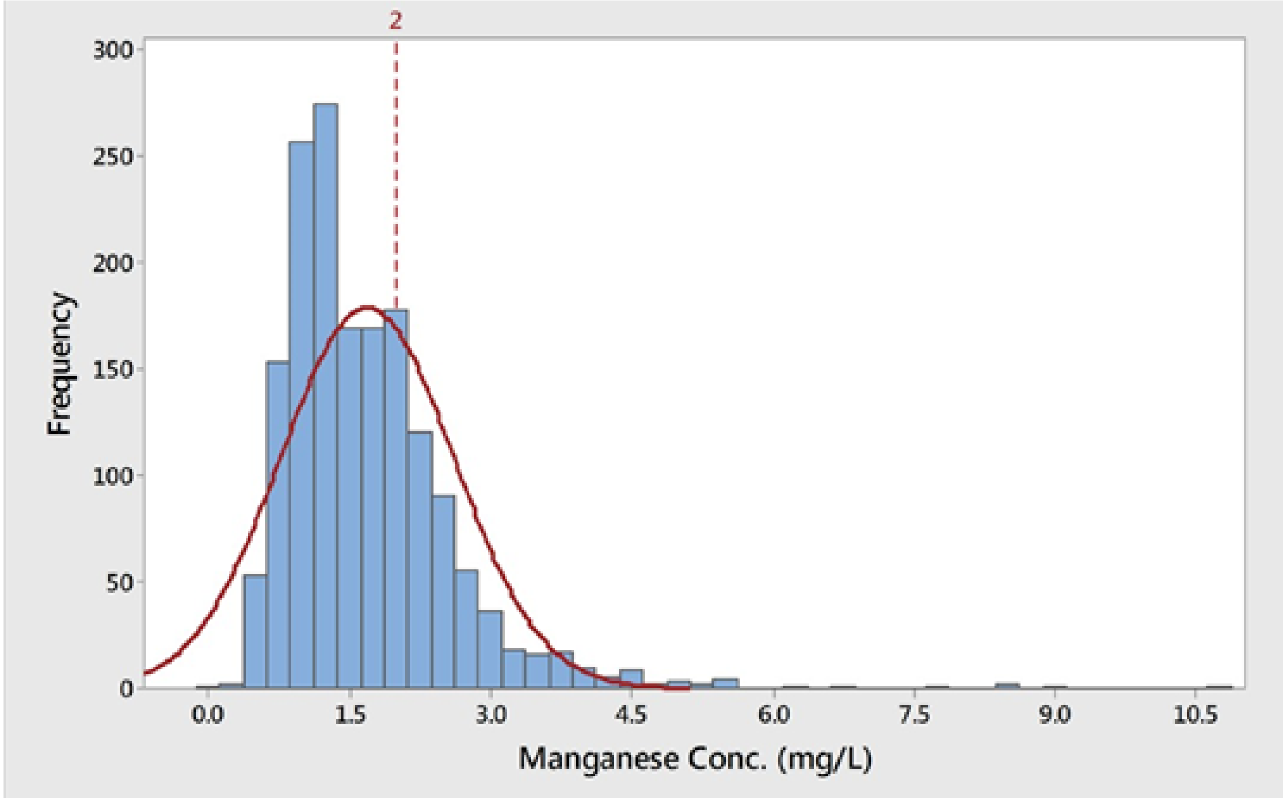
■ Bentonite has also been identified as a potential source of manganese in wine (Catarino et al. 2008).



Manganese content of wines

■ In South Africa, wine manganese concentrations ranged from 0.3 to 1.8 mg/L (average = 0.9 mg/L, n = 81). Red wines ranged from 0.3 to 2.9 mg/L (average = 1.3 mg/L, n = 104). A total of 15 red wines (14% of all red wines analyzed) exceeded the concentration of 2 mg/L.
A total of 10 sweet and fortified wines were analyzed and concentrations ranged from 0.9 to 3.6 mg/L (average of 2.0 mg/L). Five out of the 10 sweet and fortified wine samples analyzed exceeded the concentration of 2 mg/L (OIV 2014).

■ In Australia, manganese concentrations are higher for red wines than white wines; the median level for red wines was 1.7 mg/L with 28% exceeding 2 mg/L, and the median level for white wines was 1.1 mg/L with 16% exceeding 2 mg/L (AWRI 2015) as shown in the following figure.



■ In Brazil, the mean concentration of manganese in approximately 500 samples of Brazilian commercial wines was 2.09 mg/L with a SD of +/- 0.63 (OIV 2014).

■ In Argentina, the mean concentration of manganese in 156 samples commercial wines was 1.09 mg/L and ranged from 0.09 to 2.7 mg/L (OIV 2014).

■ In Chile, the mean concentration of manganese in 1022 red wine samples was 1.38 mg/L and ranged from 0.23 to 3.53 mg/L, and the mean concentration of manganese in 545 white wine samples was 1.19 mg/L and ranged from 0.25 to 4.63 mg/L (OIV 2018).

■ The manganese concentration of 80 wines from different French regions and vintages ranged from 0.436 to 7.836 mg/L (Cabrera-Vique et al. 2000). Similarly, from earlier surveys, the manganese concentration of French wines ranged from 1.2 to 3.3 mg/L (Latorre et al. 1992) and from 0.610 to 1.702 mg/L (Stroh et al. 1994), while the mean manganese concentration of 35 European wines from another survey was 2.7 mg/L and ranged from 0.5 to 7.3 mg/L (Stobbaerts et al. 1995).

■ Recently, the Spanish Ministry of Agriculture published a report on manganese levels in wines from different countries (Gómez-Miguel et al. 2014), which are summarised in the following table.

Countries / Nº Samples	Media	SD	Maximum	Minimum	(X-2SD)	(X+2SD)
Argentina (42)	0,590	0,160	1,070		0,270	0,910
Australia (126)	1,615	0,780	4,100	0,300	0,055	3,175
Brazil (267)	3,280	0,129	2,890	0,780	3,022	3,538
Bulgaria (2)	1,403	0,025	0,000	0,000	1,353	1,453
Canada (10)	0,470	0,344	1,502		0,000	1,158
Chile (7)	0,650	0,110	0,980		0,430	0,870
Croacia (67)	1,480	0,080	1,880	1,040	1,320	1,640
Czech Rep (2)	1,771	0,344	3,260	0,280	1,083	2,459
France (303)	1,287	0,465	7,836	0,100	0,357	2,217
Germany (1)	0,900	0,344	1,300	0,500	0,212	1,588
Greece (98)	1,302	0,055	10,000	0,720	1,193	1,412
Hungary (17)	1,430	0,003	5,000	0,100	1,424	1,436
Italy (101)	1,459	0,276	2,500	0,670	0,907	2,011
Moldavia (2)	0,825	0,015	0,000	0,000	0,796	0,854
Portugal (83)	1,156	0,276	1,500	0,200	0,605	1,708
Romania (60)	0,825	0,535	3,078	0,280	0,000	1,895
Serbia (8)	1,610	1,020	3,650	0,400	0,000	3,650
Slovenia (1)	1,190	0,344	1,780	0,600	0,502	1,878
South Africa (110)	1,150	0,499	2,647	0,000	0,152	2,148
Spain (1241)	1,237	0,294	9,500	0,100	0,648	1,826
Turkey (36)	0,458	0,024	1,822	0,021	0,411	0,506
Ukraine (2)	0,999	0,089	0,000	0,000	0,821	1,177
Uruguay (1)	1,470	0,344	2,200	0,740	0,782	2,158
Europe (35)	2,700	1,700	7,300	0,500	0,000	6,100
America (1)	2,445	0,344	4,080	0,810	1,757	3,133
15 countries (1)	1,678	0,344	3,020	0,335	0,990	2,366
World (2674)	1,361 (0,458-3,28)	0,344	10,000	0,000	0,673	2,049

■ The red winemaking process results in higher wine manganese concentrations, most likely due to the transfer of manganese during the extended grape skin (and seed) contact.

Manganese and Food safety

■ Manganese is a normal component of the human body and is considered to be an essential micronutrient being a co-factor of many enzymes (NRC 1989; Aschner and Aschner 2005). A deficiency can adversely affect body and brain function such as glucose metabolism and insulin secretion associated with type 2 diabetes and metabolic syndrome (Baly et al. 1984).

■ The general population is exposed to manganese through consumption of food and water, inhalation of air, and dermal contact with air, water, soil, and consumer products that contain manganese. The primary source of manganese intake is through diet.

■ Manganese levels in foodstuffs vary considerably, mostly below 5 mg/kg. Grain, rice, and nuts, however, may have manganese levels exceeding 10 mg/kg.

■ Average manganese intakes from adult Western and vegetarian diets in various surveys ranged from 0.7 to 10.9 mg/day, equating to 0.01–0.156 mg manganese/kg body weight/day, assuming a 70-kg body weight (Greger 1999; FNB 2001).

■ Manganese oral bioavailability varies with food type. Generally, it has low absorption in the gastrointestinal tract due to poor solubility in the food.

■ Manganese can accumulate in the brain, liver and pancreas although it is primarily excreted in the faeces.

■ Although low levels of manganese intake are necessary for human health (Keen et al. 1984), exposures to high manganese levels are neurotoxic and can cause adverse neurological effects, as well as adverse respiratory, reproductive, developmental effects and potentially adverse cardiovascular effects (Li and Yang 2018).

■ There is no clear understanding of the threshold for manganese deficiency/sufficiency or toxicity, and individual factors such as age, gender and ethnicity can influence an individual's susceptibility to manganese toxicity (O'Neal and Zheng 2015).

■ Experimental animal data are of limited value for assessing human risks because the physiological requirements for manganese vary among different species.

■ Current human data is also of limited value due to uncertainty regarding the exposure level and whether effects observed were solely attributable to manganese. Combined with the lack of NOAELs for critical endpoints from animal studies means that an upper level of exposure cannot be established as yet for human risk.

■ The margin between oral effect levels in experimental animals and humans, and the estimated intake of manganese from food is, however, very low. Given the potential higher susceptibility of some subgroups in the general population to the adverse effects of manganese, oral exposure to manganese beyond that normally present in food and beverages could represent a risk of adverse health effects without evidence of any health benefit.

■ A health advisory level (AL) for manganese of 0.3 mg/L has been established by the US Environmental Protection Agency (EPA 1995), while the World Health Organization (WHO) has established a manganese health guideline level of 0.4 mg/L.

■ Based on the upper range value of manganese intake of approximately 11 mg/day, identified using dietary surveys, at which there are no observed adverse effects (FNB/IOM, 2001), and using an uncertainty factor of 3 to take into consideration the possible increased bioavailability of manganese from water, a Tolerable Daily Intake (TDI) has been established at 0.06 mg/kg of body weight. 3.6 mg/day (WHO 1973, WHO 2011).

■ The guideline value of 0.4 mg/L is then derived from the TDI by assuming an allocation of 20% of the TDI to drinking-water and consumption of 2 liters of drinking-water per day by a 60-kg adult (WHO, 2008)

■ As there is insufficient evidence to derive an Average Requirement (AR) and thus a Population Reference Intake (PRI) for manganese, an Adequate Intake (AI) has been proposed by the European Food Safety Authority (EFSA 2013).

■ Observed average manganese intakes of adults in the EU are approximately 3 mg/day. In addition, null or positive balances have consistently been observed with manganese intakes above 2.5 mg/day.

■ An AI of 3 mg/day for adults has, therefore, been proposed for manganese in the EU. The adult AI also applies to pregnant and lactating women. For infants aged from 7 to 11 months, the range for the AI of 0.02–0.5 mg/day has been proposed while proposed AIs vary from 0.5 mg/day in young children aged 1–3 years to 3.0 mg/day in adolescent boys and girls. An AI for adults has similarly been proposed for manganese in the Australia, New Zealand and USA (FNB 2001, NHMRC 2006)[1].

■ For wine, an exposure scenario can be derived as follows:
- High wine consumption/day = 214 mL
- High content of manganese in wine = 1935.0 µg/L
- Resulting intake of manganese from wine (Percentage of TDI) = 414.7 µg/day (11.5 %).

■ **Therefore, it can be considered that the probability of an adverse health risk to wine consumers is very low (OIV 2013).**

[1] The AI in Australia and NZ is 5 mg/day for women and 5.5 mg/day for men, while in the USA the AI is 1.8 mg/day for women and 2.3 mg/day for men

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