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Manganese biofortification in grapevine by foliar spraying improves volatile profiles of Cabernet Sauvignon grapes and wine sensory traits

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ABSTRACT

Manganese (Mn) is involved in plant metabolism as an enzyme cofactor. However, the role of Mn in the formation of volatile compounds in grapes has rarely been studied. To address this gap, this study explored the effect of foliar Mn application on the aroma traits of grapes and wine. Mn nutrient solutions at different concentrations (0 (CK), 300, 1200, and 2400 mg/L) were sprayed on grapevines in 2017 and 2018 and the volatile compounds, odor activity, and sensory features of grapes and wine were investigated. The results showed that Mn application significantly increased Mn content in grape leaves and fruits at harvest. Compared with CK, the total volatile content of grapes was significantly increased by Mn treatment in both years because of the promotion of the accumulation of alcohols and esters. Particularly, 1200 mg/L Mn treatment resulted in a higher sensory score than CK, especially in terms of intensity, duration, and harmony. Multivariate analysis and odor activity values jointly identified eight volatile compounds (ethyl acetate, phenylethyl acetate, and phenylethyl alcohol, etc.) as key odorants that contribute to the floral and fruity flavors of Mn-treated wine. Overall, this study indicated that a moderate concentration of Mn is beneficial for improving the fragrance characteristics of grapes and wines. The results have implications for micronutrient management of grapevines to improve wine flavor quality.

Chemical compounds used in the study:

1-Hexanol	PubChem CID: 8103
Hexanal	PubChem CID: 6184
Ethyl acetate	PubChem CID: 8857
Isoamyl acetate	PubChem CID: 31276
Ethyl hexanoate	PubChem CID: 31265
Ethyl octanoate	PubChem CID: 7799
Phenylethyl acetate	PubChem CID: 7654
Phenylethyl alcohol	PubChem CID: 6054
Octanoic acid	PubChem CID: 379
β-Damascenone	PubChem CID: 5366074

1. Introduction

Volatile compounds are key olfactory components that impact grape and wine flavor and have been widely studied (Lin et al., 2019). Over 1000 compounds have been identified in grapes and wine using advanced instruments and analytical methods, which are mainly classified as alcohols, aldehydes, esters, terpenes, norisoprenoids, and benzenes (Tian et al., 2022). The varietal aroma from grapes significantly contributes to the overall wine aroma and determines the typical aromatic characteristics, such as the floral and fruity trait of Muscat varieties due to terpenes and norisoprenoids, herbaceous aroma of Cabernet Sauvignon and Merlot wines due to alcohols and aldehydes, and “foxy” aroma of *V. labrusca* and *M. rotundifolia* due 2-aminoacetophenone (Lin et al., 2019). Moreover, the enological technology during wine fermentation and aging via producing fermentation aroma and aging aromas such as esters and the sensory significance of monomer volatiles affect the overall aroma expression (Kong et al., 2021). Alem et al. (2018) found that environmental factors and vineyard viticultural management also affect the accumulation of grape aroma by regulating

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compound biosynthesis and concentration (due to fruit morphological changes), and thus wine quality. The availability of key nutrients in grapes at different growth stages significantly affects the accumulation of secondary metabolites (Topalovic et al., 2011). The nitrogen status of grapevines is associated with the biosynthesis of volatile compounds, such as alcohols and esters, and appropriate nitrogen fertilizer addition increases the concentration of 2-phenylethanol in Tempranillo (Garde-Cerdan et al., 2015; Gutiérrez-Gamboa et al., 2018). In addition, Lacroux et al. (2008) reported that the concentrations of berry thiols and wine aroma were enhanced by sulfur and nitrogen fertilizer application.

Manganese (Mn) is a crucial microelement in plant growth and fruit development (Ren et al., 2023). Mn has multiple functions that affect various aspects of the plant, such as directly affecting plant phenotype (height and biomass), participating in chemical reactions as an enzyme cofactor (photosynthetic pigment synthesis, antioxidant enzyme activity, and polyphenol metabolism), and regulating physiological processes (photosynthesis and stress resistance). Mn induces systemic acquired resistance to protect plants from pathogenic infections (Perfileva, 2024). However, Mn availability decreases under alkaline soil conditions, severely limiting plant root growth and crop productivity (Oliveira et al., 2023). Grapes are globally important fruit crops owing to their significant winemaking value; however, they are susceptible to Mn deficiency. The eastern foothills of Helan Mountain in Ningxia, located in northwest China, is a key wine-producing region in China owing to its unique geographical location and climatic conditions. However, Mn deficiency has been reported here due to the typical calcareous soil (Chen et al., 2020). Therefore, the adoption of appropriate nutritional management strategies is crucial for improving grape quality (Salifu et al., 2021).

Foliar Mn application is an effective method for alleviating Mn deficiency compared to soil Mn application because of its high absorption rate. In cereals, foliar $MnSO_4$ application to wheat enhances the Mn concentration in grains and wheat yield in Mn-deficient soils by improving Mn-use efficiency (Dhaliwal et al., 2023). Many researchers have extensively reported the impact of Mn application on fruit quality, including chemical components (total soluble solids, reducing sugars, and titratable acidity), physical morphology (fruit firmness, weight, and size), and post-harvest parameters (Anar et al., 2023; Ekinci, 2018). Recently, high concentrations of Mn were reported to increase the accumulation of individual phenols and modify the essential oil profiles of *Tanacetum parthenium* (Farzadfar et al., 2017). Our previous research found that foliar Mn application positively regulates polyphenol accumulation in grapes and wine, especially flavonoids (Chen et al., 2020). However, limited research has been devoted to the effect of Mn fertilizer on grape volatile profiles and wine flavor.

Therefore, this study aimed to explore the effects of Mn on the volatile components and aroma traits of grapes and wine. We applied inorganic Mn fertilizer to aboveground parts of grapevines grown in the Ningxia region with Mn deficiency. The volatile compounds of grapes and wine were analyzed. Partial Least Squares Discriminant Analysis (PLS-DA) was performed to screen for differential compounds between Mn applications and the control. Finally, the odor activity values and sensory features of wine were evaluated. The results of this study will be useful for the micronutrient management of grapevines to improve wine flavor quality.

2. Material and methods

2.1. Experimental design and sample collection

This study was carried out at the commercial vineyards of "Guanlan" Winery (38.43°N, 106.03°E), Yinchuan, Ningxia Hui Autonomous Region, China. Grapevines of self-rooted *Vitis vinifera* cv. Cabernet Sauvignon planted in 2014 was subjected to foliar Mn treatments in 2017 and 2018. The grapevines were sloping trunks with vertical shoot positioning systems, north–south oriented, spaced at 3.0 × 0.8 m, drip-irrigated, and managed based on the standard vinicultural methods. The meteorological data of the vineyards during the growing season were characterized in our previous study (Chen et al., 2020).

The Mn treatment design followed that described in our previous study (Chen et al., 2020). Three concentrations of $MnSO_4 \cdot H_2O$ (low (L): 300 mg/L; medium (M): 1200 mg/L; and high (H): 2400 mg/L) and deionized water (control, CK) were sprayed on grapevines on sunny afternoons (5–7 p.m.) without wind or rainfall in the next 24 h.

All treatments were carried out one week before and one week after first flowering, with three replicates per treatment and 24 grapevines per replicate at a random block layout design. Grapes were harvested when their soluble solids reached 23°Brix using a five-point sampling method. Subsequently, all grapes were transported to the laboratory on ice. Three hundred grapes per replicate were stored at −80 °C until analysis and the remaining grapes were used for wine making. Three replicates were performed for each sample.

2.2. Analysis of Mn elements in leaves and grapes, as well as soil composition

The vineyard soil was collected for component analysis before the experiment was conducted in 2017. Soil parameters included organic matter, pH, microelements (available N, P, K, Ca, and Mg), and microelements (available Cu, Zn, Fe, and Mn) (Shi et al., 2018). As Fig. S1 showing, the available nutrients in the 0–20 cm soil layer were higher than those in the 20–40 cm soil layer. However, the available soil P, Mn, Fe, and organic matter contents were below the standard values for those two soil layers, whereas those of pH, Ca, and Cu exceeded the standard values, and those of N, Mg, and Zn were within the normal ranges (Shi et al., 2018; Song et al., 2015). These results suggest that the vineyard has a highly calcareous, alkaline soil with low levels of available Mn element (Chen et al., 2020). In our previous study, the Mn level of grapevines was evaluated using petioles before treatment, with the results showing that the level was below the standard range (Chen et al., 2020).

Healthy leaves and grapes were collected during the grape harvest in 2018 to investigate the effect of Mn treatment on the Mn content in leaves and fruits. The results showed that Mn treatment significantly increased the Mn content in leaves and fruits compared to CK, and the M treatment had better effects than the other concentration treatments (Fig. S2).

2.3. Wine vinification

The winemaking experiment was conducted according to the method described by Song et al. (2016) with minor modifications. For each replicate, 20 kg of grapes were manually destemmed and crushed in two consecutive growing seasons of 2017 and 2018. Subsequently, the grape was transferred to a 20 L glass fermentation tank, and sulfur dioxide (60 mg/L) and pectinase (30 mg/L, Lallzyme Ex, Lallemand, France) were added. After 24 h, the commercial Lalvin RC 212 yeast strain (200 mg/L, Lallemand, France) was added to initiate fermentation. The alcoholic fermentation was carried at 20–25 °C. The wine cap was pressed three times a day and the temperature and specific gravity were recorded. When the specific gravity of the grape fell below 1, the pomace was separated from the wine and alcohol fermentation continued. When the specific gravity fell below 0.993 and the residual sugar below 4 g/L, sulfur dioxide (50 mg/L) was added to the wine to terminate fermentation. All wine samples were bottled and stored for two months at 10–15 °C in the cellar before analysis. Three replicates were performed for each sample.

2.4. Physicochemical indexes of grapes and wines

A total of 50 grapes were squeezed in each replicate, and the resulting juice was used to analyze the total soluble solids and titratable acids according to the method described by Shi et al. (2018). Maturity was defined as the ratio of total soluble solids to titratable acids. The enological parameters of the wine samples were determined based on a Compilation of International Wine Analysis Methods (OIV, 2022), including alcohol degree, residual sugar, titratable acids, and volatile acidity. Three replicates were performed for each sample.

2.5. Volatiles analysis of grapes and wines as well as odor activity value (OAV) calculation

Frozen grapes (50 g) were crushed, deseeded, and ground into a powder in liquid nitrogen with 2 g of polyvinylpolypyrrolidone and 0.5 g of D-gluconic acid lactone. The mixture was transferred to a 50 mL centrifuge tube, extracted at 4 °C for 4 h, and then centrifuged at 4 °C, 8000*g* for 10 min to obtain clear fruit juice. Finally, 5 mL of fruit juice or wine sample was poured into a headspace injection bottle with 1 g NaCl and 10 μL of internal standard (4-methyl-2-pentanol, Sigma Aldrich, MO, USA) for volatiles analysis.

Headspace Solid-Phase Micro-Extraction (HS-SPME; 80 μm/10 mm DVB/CWR/PDMS SPME fiber; Agilent, Santa Clara, CA, USA) was applied to concentrate aroma compounds, and Gas Chromatography-Mass Spectrometry (GC–MS; Agilent 7890-Agilent 5975C Inert MSD; Agilent, Santa Clara, CA, USA) was used to detect compounds by an HP-INNOWAX capillary column (60 m × 0.25 mm × 0.25 μm, J&W scientific, Folsom, CA, USA). Instrument detection conditions were determined based on Wen et al. (2015). An Automated Mass Spectral Deconvolution and Identification System was applied to identify the volatiles by matching the mass spectrum information in the NIST 11 library and the retention index of the reference standards. The volatile concentrations were quantified using internal standard and standard curve methods, while those of compounds without standard curves were calculated according to the standard curve of compounds with the same functional group and/or similar numbers of carbon atoms, expressed as μg/L fruit juice or wine. In addition, the odor activity value (OAV) of the wine volatiles was calculated according to the odor reference threshold described in previous studies (Kong et al., 2019; Lu et al., 2024; Wang et al., 2017; Yao, Jin, et al., 2021). Volatiles with OAV > 1 were considered to have made significant contributions to the typical aroma traits of the wine samples and are listed in Supplementary Table S1.

2.6. Sensory analysis of wines

The sensory tasting experiment was conducted according to the principles of the 1975 Declaration of Helsinki, and adequate countermeasures were taken to address the risks that might be encountered. The ethical approval for the sensory evaluation was obtained from the Academic Ethics Committee of Northwest A&F University. The sensory tasting panel consisted of 20 experts, including 10 males and 10 females aged 30–55 years from the College of Enology of Northwest Agriculture and Forestry University. All tasters voluntarily participate in the tasting test after being informed of the risks and obtaining their right to information and consent, and their privacy was adequately protected. They had over three years of experience in sensory tasting and professional sensory identification capabilities. The sensory characteristics of the wine samples were evaluated according to the method described by Song et al. (2016) with some modifications. The sensory characteristics test consisted of three parts: appearance (clarity and color), fragrance (elegance and refinement, harmony, intensity and duration, and development and complexity), and mouthfeel (balance, texture and structure, persistence and hierarchy, and retronasal fragrance and finish), which accounted for 20 %, 40 %, and 40 % of the 100-point scoring table, respectively. Each sub-index score ranges from 0 (worst) to 10 (best). All the wine samples were randomly numbered and tested using a blind taste system at room temperature.

2.7. Statistical analysis

Analysis of variance was conducted using SPSS 22.0 (IBM, Armonk, NY, USA; Tukey's test, $P < 0.05^*$, 0.01^{**}, 0.001^{***}) with three replicates for each sample. The figures were visualized using GraphPad Prism 8.0.2 (GraphPad Software, La Jolla, CA, USA). PLS-DA was performed to select biomarkers among the aroma compounds of grapes and wine using Simca 14.1 software (UMETRICS, Sweden). The PLS-DA model was established based on parameters with R2Y >0.8, Q2Y > 0.8, $P < 0.05$, and Q2 intercept <0 in 200 permutation tests. The associations between the concentration of wine volatiles with OVA >1 and wine sensory parameters were analyzed using Spearman's correlations in the psych package ($R^2 > 0.8$, $P < 0.05$). The results were visualized using the Cytoscape 3.10.0 software (https://cytoscape.org).

3. Results and discussion

3.1. Chemical parameters of grapes and wine

Grape maturity is an important factor that affects grape and wine quality. The maturity under all Mn treatments in 2017 and L treatment in 2018 exceeded than that of CK (Fig. S3), indicating that appropriate Mn application can promote grape ripening.

Mn-treated wines showed a higher alcohol content than CK wines, with a difference of 0.37 in 2017 and 0.35 in 2018 (Supplementary Table S2). This agrees with the findings of Bredun et al. (2022), who reported that boron application increases the alcohol content of wine. The increased alcohol content can be attributed to grape maturity and the accumulation of sugar in grapes. Titratable acids contents were averagely 7.60 g/L for Mn-treated wine and 8.18 g/L for CK wine in 2017 and averagely 5.33 g/L for Mn-treated wine and 5.29 g/L for CK wine in 2018. The residual sugar contents of all wine samples ranged from 1.8 to 2.3 g/L and the volatile acidity from 0.24 to 0.33 g/L, which was consistent with the results of previous studies and indicates that all wine samples met the quality requirements for subsequent analysis (Song et al., 2016; OIV, 2022).

3.2. HS-SPME/GC–MS analysis

3.2.1. Volatile profiles of grapes

The composition and content of volatiles in grapes from Mn treatments and CK at harvest in 2017 and 2018 are shown in Table 1, consistent with previous research results (Gao et al., 2019; Ju et al., 2017). A total of 76 free aromas were detected over the two years, including 7 terpenes, 5 norisoprenoids, 14 alcohols, 11 aldehydes, 3 ketones, 2 acids, 8 esters, 22 benzenes, and 4 others (Fig. 1A). In 2017, four, nine, and seven more volatiles were detected under L treatment than under M, H, and CK treatments, respectively, whereas, in 2018, all samples contained 76 different volatiles (Fig. 1B).

Aldehydes were the most abundant volatiles, contributing to 71–79 % and 59–66 % of the total aroma in 2017 and 2018, respectively. The total aldehyde content in Mn-treated grapes was significantly higher than that in CK, being 30 % higher on average in 2017. In 2018, the total aldehyde content in M- and H-treated grapes was 14 % and 2 % higher, respectively, than the CK. C6 aldehydes were the most abundant aldehydes, and hexanal and trans-2-hexenal were the two most abundant volatile compounds in both years. The hexanal and trans-2-hexenal contents in the Mn-treated grapes were significantly higher than those in the CK in 2017 and 2018. Alcohols constituted the most types of volatiles in grapes, indicating their contribution to the complexity of the grape aroma. The total amount of alcohol was higher in Mn-treated grapes than in CK over the two years, with an average increase of 27 % in 2017 and 40 % in 2018, which was mainly attributed to C6 alcohols, including (E)-2-Hexen-1-ol, (Z)-3-Hexen-1-ol, and 1-Hexanol. Esters significantly changed over the two years, with their total amount ranging from 2563.32 to 5979.86 μg/L in 2017 and 96.59–282.27 μg/L

Table 1
The contents (μg/L) of volatile compounds in grape berries at harvest in 2017 and 2018.

Number	Compounds	2017				2018				Y[c]	T	YxT
		L [a]	M	H	CK	L	M	H	CK			
Terpenes												
1	γ-Terpinene	3.35 ± 0.24 d[b]	14.36 ± 0.74 a	5.78 ± 0.13 c	8.74 ± 0.14 b	5.48 ± 1.75 a	3.32 ± 0.24 b	2.60 ± 0.18 d	2.97 ± 0.14 c	**[d]	**	**
2	Linalool	7.31 ± 0.04 d	15.76 ± 1.54 a	7.63 ± 0.65 c	10.99 ± 0.52 b	2.55 ± 0.26 b	2.70 ± 0.32 a	2.54 ± 0.07 b	2.53 ± 0.30 b	**	**	**
3	4-Terpinenol	1.11 ± 0.20 a	n	0.72 ± 0.08 b	n	0.62 ± 0.23 b	0.49 ± 0.06 c	1.42 ± 0.57 a	0.66 ± 0.17 b	***	***	***
4	Hotrienol	8.93 ± 0.17 b	4.30 ± 0.15 c	10.14 ± 0.38 a	2.51 ± 1.18 d	1.22 ± 0.16 b	1.25 ± 0.20 b	1.43 ± 0.56 a	0.95 ± 0.12 c	***	***	***
5	α-Terpineol	1.63 ± 0.26 b	2.67 ± 0.59 a	1.17 ± 0.30 c	0.93 ± 0.82 d	0.98 ± 0.31 b	0.76 ± 0.10 c	1.07 ± 0.41 a	0.79 ± 0.08 c	***	***	***
6	Citronellol	6.73 ± 1.43 b	7.92 ± 1.79 a	4.97 ± 0.22 c	3.24 ± 0.14 d	8.51 ± 1.87 d	12.10 ± 1.22 a	11.62 ± 0.84 b	10.59 ± 1.29 c	***	***	***
7	α-Calacorene	2.47 ± 0.55 b	4.32 ± 0.70 a	1.30 ± 0.11 d	1.76 ± 0.06 c	0.96 ± 0.24 b	1.19 ± 0.02 a	0.68 ± 0.33 c	0.92 ± 0.03 b	***	***	***
	Subtotal	31.53 ± 1.85 b	49.33 ± 11.50 a	31.71 ± 2.54 b	28.17 ± 0.98 c	20.32 ± 8.35 c	21.81 ± 2.40 a	21.36 ± 1.66 b	19.41 ± 2.01 d	***	***	***
	Proportion (%)	0.10 ± 0.002 c	0.18 ± 0.012 a	0.08 ± 0.006 c	0.12 ± 0.011 b	0.46 ± 0.204 a	0.41 ± 0.029 b	0.48 ± 0.090 a	0.46 ± 0.025 a			
Norisoprenoids												
8	3-methyl-6-(1-methylethylid)-Cyclohexene	2.58 ± 0.01 d	5.05 ± 0.80 a	4.42 ± 0.05 b	3.15 ± 0.14 c	2.00 ± 0.48 a	1.83 ± 0.08 b	1.56 ± 0.05 c	1.57 ± 0.06 c	**	**	**
9	6-methyl-5-Hepten-2-one	9.00 ± 0.64 b	3.45 ± 1.73 c	11.76 ± 0.60 a	2.76 ± 0.28 d	1.93 ± 0.74 c	3.01 ± 0.24 a	2.16 ± 0.21 b	1.96 ± 0.06 c	***	***	***
10	*β*-Damascenone	165.68 ± 38.72 c	496.73 ± 12.22 a	121.20 ± 8.29 d	256.13 ± 16.76 b	227.60 ± 44.51 d	302.84 ± 28.28 a	288.95 ± 21.12 b	286.93 ± 25.87 c	***	***	***
11	Geranylacetone	4.46 ± 0.89 a	n	2.89 ± 0.27 b	n	1.70 ± 0.05 d	8.19 ± 5.51 a	2.55 ± 0.05 b	2.10 ± 0.12 c	***	***	***
12	*β*-Ionone	2.50 ± 0.61 a	1.52 ± 0.05 c	2.18 ± 0.14 b	n	0.25 ± 0.02 c	0.51 ± 0.04 a	0.21 ± 0.21 d	0.36 ± 0.07 b	**	**	**
	Subtotal	184.22 ± 40.85 c	506.75 ± 9.64 a	142.45 ± 9.25 d	262.04 ± 16.34 b	233.48 ± 44.21 d	316.38 ± 34.16 a	295.43 ± 20.61 b	292.92 ± 26.08 c	***	***	***
	Proportion (%)	0.58 ± 0.11 c	1.88 ± 0.34 a	0.38 ± 0.02 d	1.15 ± 0.04 b	5.25 ± 1.13 d	5.94 ± 0.45 c	6.67 ± 1.07 b	6.89 ± 0.34 a			
Alcohols												
13	Isopentanol	153.71 ± 3.02 a	126.84 ± 15.92 c	145.78 ± 0.64 b	87.69 ± 1.73 d	22.49 ± 0.96 b	26.89 ± 0.12 a	22.60 ± 1.98 b	21.33 ± 0.55 c	***	***	***
14	2-Hexanol	27.75 ± 6.06 a	n	n	n	0.96 ± 0.06 d	1.00 ± 0.10 c	1.10 ± 0.20 a	1.05 ± 0.02 b	***	***	***
15	2-Heptanol	17.83 ± 6.61 c	26.25 ± 16.18 a	19.48 ± 1.17 b	17.35 ± 4.66 d	1.02 ± 0.11 d	1.10 ± 0.17 c	4.32 ± 3.06 b	5.34 ± 4.02 a	***	***	***
16	1-Hexanol	269.09 ± 49.65 c	291.34 ± 12.94 b	310.47 ± 4.12 a	216.24 ± 2.46 d	461.77 ± 14.10 b	488.82 ± 24.40 a	337.64 ± 0.06 c	326.85 ± 17.95 d	***	***	***
17	(E)-3-Hexen-1-ol	4.52 ± 0.89 b	4.27 ± 0.13 c	4.99 ± 0.63 a	3.08 ± 0.10 d	4.01 ± 0.13 b	4.06 ± 0.17 a	3.59 ± 0.19 c	3.42 ± 0.13 d	ns	*	*
18	(Z)-3-Hexen-1-ol	103.06 ± 7.24 b	116.71 ± 16.02 a	88.28 ± 0.73 c	41.40 ± 0.40 d	13.24 ± 0.50 a	8.92 ± 0.62 b	6.45 ± 0.20 c	5.33 ± 0.35 d	***	***	***
19	(E)-2-Hexen-1-ol	413.00 ± 6.04 a	269.60 ± 35.92 d	335.00 ± 44.60 c	363.98 ± 3.59 b	494.24 ± 19.21 b	537.31 ± 28.69 a	294.12 ± 8.38 c	281.39 ± 16.34 d	***	***	***
20	1-Octen-3-ol	35.23 ± 0.68 c	51.65 ± 4.05 a	40.02 ± 2.12 b	30.92 ± 0.62 d	7.38 ± 0.04 a	7.22 ± 0.58 c	7.30 ± 0.05 b	6.62 ± 0.29 d	**	**	**
21	1-Heptanol	11.59 ± 0.05 a	8.24 ± 1.26 c	10.35 ± 0.13 b	7.58 ± 0.03 d	1.34 ± 0.01 c	1.41 ± 0.09 a	1.41 ± 0.03 a	1.38 ± 0.08 b	***	***	***
22	2-ethyl-1-Hexanol	58.30 ± 2.42 b	49.75 ± 6.21 c	61.93 ± 4.02 a	39.12 ± 1.54 d	7.64 ± 0.13 c	9.23 ± 0.59 a	9.19 ± 0.49 a	8.41 ± 0.38 b	***	***	***
23	(*S*)-3-ethyl-4-methylpentanol	14.88 ± 0.99 a	7.58 ± 0.24 c	10.38 ± 0.82 b	5.64 ± 0.02 d	1.59 ± 0.05 d	2.08 ± 0.13 c	2.28 ± 0.08 b	2.67 ± 0.14 a	**	**	**
24	1-Octanol	12.74 ± 0.36 a	8.78 ± 0.35 c	11.78 ± 0.51 b	7.35 ± 0.18 d	2.23 ± 0.03 c	2.57 ± 0.06 a	2.49 ± 0.15 b	2.51 ± 0.06 b	**	**	**
25	(E)-2-Octen-1-ol	4.52 ± 0.07 b	2.99 ± 0.38 c	5.17 ± 0.17 a	2.21 ± 0.68 d	1.12 ± 0.001 d	1.19 ± 0.08 c	1.31 ± 0.06 a	1.25 ± 0.14 b	**	**	**
26	1-Dodecanol	n	n	n	n	0.57 ± 0.06 c	0.64 ± 0.02 b	1.66 ± 1.18 a	0.54 ± 0.04 c	***	***	***
	Subtotal	1126.22 ± 64.91 a	964.00 ± 108.15 c	1043.63 ± 29.54 b	822.56 ± 9.97 d	1019.60 ± 34.60 b	1092.44 ± 55.81 a	695.46 ± 10.06 c	668.09 ± 32.38 d	***	***	***
	Proportion (%)	3.55 ± 0.11 a	3.57 ± 0.16 a	2.77 ± 0.10 b	3.60 ± 0.07 a	22.94 ± 0.21 a	20.52 ± 0.39 b	15.70 ± 1.65 c	15.71 ± 0.15 c			
Number	**Compounds**	**2017**				**2018**				**Y**	**T**	**YxT**
		L	**M**	**H**	**CK**	**L**	**M**	**H**	**CK**			
Aldehydes												

(*continued on next page*)

Table 1 (*continued*)

Number	Compounds	2017				2018				Y[c]	T	YxT
		L[a]	M	H	CK	L	M	H	CK			
27	Hexanal	16,388.61 ± 427.61 b	13,319.41 ± 2417.47 c	19,965.86 ± 149.35 a	13,204.50 ± 516.81 d	1558.97 ± 105.88 d	1916.37 ± 15.77 a	1810.93 ± 277.71 b	1774.33 ± 37.00 c	***	***	***
28	Heptanal	33.27 ± 0.53 b	24.56 ± 0.31 c	40.62 ± 2.93 a	20.28 ± 3.35 d	3.38 ± 0.19 d	4.44 ± 0.19 a	3.67 ± 1.00 c	4.05 ± 0.18 b	**	**	**
29	(E)-2-Hexenal	7150.46 ± 129.58 a	6222.12 ± 815.78 c	6710.06 ± 41.75 b	4760.24 ± 57.27 d	1053.14 ± 27.65 b	1260.50 ± 33.88 a	1044.91 ± 105.43 c	1013.77 ± 31.25 d	***	***	***
30	Octanal	11.08 ± 0.003 b	8.49 ± 1.15 c	11.94 ± 0.15 a	7.82 ± 0.05 d	1.99 ± 0.05 b	1.93 ± 0.21 c	2.02 ± 0.31 b	2.32 ± 0.04 a	**	**	**
31	(Z)-2-Heptenal	3.78 ± 0.37 c	6.56 ± 0.08 a	6.00 ± 0.05 b	n	1.54 ± 0.14 a	1.57 ± 0.06 a	1.25 ± 0.04 c	1.33 ± 0.09 b	**	**	**
32	Nonanal	34.44 ± 1.67 c	163.97 ± 141.57 a	38.68 ± 1.59 b	22.39 ± 0.41 d	3.85 ± 0.001 b	4.49 ± 0.06 a	3.47 ± 1.08 c	3.80 ± 0.11 b	***	***	***
33	(E, E)-2,4-Hexadienal	118.96 ± 5.03 b	125.36 ± 15.85 a	114.94 ± 5.45 c	75.36 ± 6.18 d	12.14 ± 0.27 c	14.53 ± 0.30 a	12.40 ± 0.59 b	11.77 ± 0.48 d	***	***	***
34	(E)-2-Octenal	3.23 ± 0.09 b	4.97 ± 1.09 a	n	n	0.96 ± 0.02 c	1.12 ± 0.09 b	4.32 ± 3.06 a	4.32 ± 3.06 a	***	***	***
35	(E, E)-2,4-Heptadienal	16.56 ± 0.47 b	18.51 ± 0.71 a	18.30 ± 0.59 a	15.62 ± 0.16 c	3.33 ± 0.12 c	4.31 ± 0.31 a	3.68 ± 0.05 b	3.41 ± 0.02 c	***	***	***
36	(E)-2-Nonenal	4.53 ± 0.28 a	n	n	n	0.97 ± 0.01 d	1.37 ± 0.03 a	1.01 ± 0.15 c	1.10 ± 0.02 b	**	**	**
37	(E, Z)-2,6-Nonadienal	n	n	1.12 ± 1.12 a	n	1.49 ± 0.14 d	2.36 ± 0.05 a	2.00 ± 0.04 b	1.77 ± 0.14 c	**	**	**
	Subtotal	23,764.92 ± 560.67 b	19,893.95 ± 3391.97 c	26,907.52 ± 183.04 a	18,106.21 ± 579.87 d	2641.76 ± 133.79 d	3212.99 ± 50.30 a	2889.66 ± 386.31 b	2821.97 ± 68.96 c	***	***	***
	Proportion (%)	74.84 ± 0.27 b	73.73 ± 1.01 c	71.43 ± 0.02 d	79.32 ± 2.45 a	59.45 ± 1.55 d	60.36 ± 0.99 c	65.24 ± 2.92 b	66.37 ± 0.98 a			
Ketones												
38	2-Nonanone	35.20 ± 3.54 c	37.92 ± 0.26 b	43.10 ± 2.07 a	24.72 ± 1.45 d	10.94 ± 0.44 a	10.15 ± 0.21 b	7.25 ± 2.94 d	9.77 ± 0.09 c	**	**	**
39	Vinyl ethyl ketone	25.45 ± 4.66 b	14.16 ± 0.92 c	41.28 ± 2.20 a	10.25 ± 1.06 d	2.23 ± 0.10 c	3.53 ± 0.62 a	3.19 ± 0.29 b	1.55 ± 1.55 d	***	***	***
40	2,6-dimethyl-4-Heptanone	n	n	n	n	11.95 ± 0.43 b	12.60 ± 0.31 a	10.39 ± 2.94 d	11.09 ± 0.37 c	***	***	***
	Subtotal	60.65 ± 8.20 b	52.08 ± 0.66 c	84.38 ± 4.28 a	34.97 ± 3.00 d	25.12 ± 0.98 b	26.28 ± 0.52 a	20.83 ± 5.88 d	22.41 ± 0.46 c	***	***	***
	Proportion (%)	0.19 ± 0.02 a	0.19 ± 0.03 a	0.22 ± 0.01 a	0.15 ± 0.001 b	0.57 ± 0.04 a	0.49 ± 0.02 c	0.47 ± 0.10 c	0.53 ± 0.03 b			
Acids												
41	Acetic acid	41.50 ± 1.04 b	16.87 ± 10.08 c	57.79 ± 0.71 a	5.57 ± 0.38 d	9.65 ± 0.03 d	11.47 ± 0.64 c	18.21 ± 2.75 a	14.78 ± 1.83 b	***	***	***
42	Hexanoic acid	44.94 ± 8.80 a	37.16 ± 6.83 c	41.86 ± 0.18 b	10.52 ± 10.28 d	48.45 ± 3.88 d	81.91 ± 13.06 a	55.87 ± 5.00 c	71.30 ± 10.58 b	***	***	***
	Subtotal	86.44 ± 7.76 b	54.03 ± 3.26 c	99.65 ± 0.89 a	16.09 ± 9.90 d	58.10 ± 3.85 d	93.38 ± 13.70 a	74.08 ± 2.26 c	86.08 ± 12.41 b	***	***	***
	Proportion (%)	0.27 ± 0.02 a	0.20 ± 0.04 b	0.26 ± 0.001 a	0.07 ± 0.04 c	1.31 ± 0.05 d	1.75 ± 0.20 b	1.67 ± 0.20 c	2.02 ± 0.21 a			
Esters												
43	Ethyl acetate	486.28 ± 7.86 b	216.87 ± 21.71 d	604.68 ± 9.55 a	323.60 ± 26.37 c	214.60 ± 10.50 b	266.24 ± 10.71 a	191.72 ± 12.51 c	82.22 ± 3.73 d	***	***	***
44	Butyl acetate	3539.74 ± 119.10 b	2796.91 ± 565.63 c	5266.82 ± 22.67 a	2134.58 ± 80.97 d	3.52 ± 0.30 a	3.41 ± 0.11 b	2.36 ± 0.44 d	2.58 ± 0.02 c	***	***	***
45	Butyl acrylate	34.71 ± 4.22 c	26.00 ± 3.71 d	40.08 ± 1.30 a	35.10 ± 2.04 b	1.92 ± 0.13 b	2.03 ± 0.10 a	1.76 ± 0.39 d	1.83 ± 0.09 c	***	***	***
46	Hexyl acetate	17.56 ± 0.33 b	16.85 ± 1.11 c	23.24 ± 0.89 a	15.87 ± 0.24 d	1.11 ± 0.01 b	1.19 ± 0.10 a	0.91 ± 0.17 c	0.66 ± 0.11 d	***	***	***
47	Methyl (E)-2-hexenoate	19.35 ± 0.12 b	18.87 ± 3.40 c	29.14 ± 0.01 a	16.97 ± 3.29 d	3.64 ± 0.24 d	4.41 ± 0.39 b	4.24 ± 0.41 c	5.73 ± 0.20 a	**	**	**
48	(E)-3-Hexenyl acetate	n	5.41 ± 0.79 b	n	24.58 ± 4.80 a	1.21 ± 0.04 b	1.26 ± 0.21 b	1.35 ± 0.56 a	0.74 ± 0.01 c	***	***	***
49	Propanoic acid, 2-methyl-, 1-[(1,1-dimethylethyl) dioxy] ethyl ester	40.24 ± 23.85 b	42.56 ± 5.69 a	15.90 ± 1.73 c	12.62 ± 3.89 d	2.08 ± 0.12 c	3.08 ± 0.20 a	2.32 ± 0.19 b	2.29 ± 0.09 b	***	***	***
50	Methyl salicylate	n	n	n	n	0.79 ± 0.05 a	0.65 ± 0.07 b	0.66 ± 0.02 b	0.54 ± 0.02 c	***	***	***
	Subtotal	4137.88 ± 130.43 b	3123.47 ± 589.08 c	5979.86 ± 32.66 a	2563.32 ± 63.18 d	228.87 ± 10.53 b	282.27 ± 10.70 a	205.32 ± 13.67 c	96.59 ± 3.81 d	***	***	***
	Proportion (%)	13.03 ± 0.06 b	11.58 ± 0.37 c	15.87 ± 0.02 a	11.23 ± 0.27 d	5.15 ± 0.11 a	5.30 ± 0.03 a	4.64 ± 0.10 b	2.27 ± 0.004 c			
Benzenes												

(*continued on next page*)

Table 1 (*continued*)

Number	Compounds	2017				2018				Y[c]	T	YxT
		L [a]	M	H	CK	L	M	H	CK			
51	2-ethyl-Furan	42.70 ± 1.38 c	52.41 ± 1.15 b	74.61 ± 8.80 a	36.67 ± 5.22 d	3.28 ± 0.68 c	3.43 ± 0.01 b	3.11 ± 0.88 d	3.78 ± 0.05 a	***	***	***
Number	**Compounds**	**2017**				**2018**				**Y**	**T**	**YxT**
		L	**M**	**H**	**CK**	**L**	**M**	**H**	**CK**			
52	Toluene	70.34 ± 6.31 b	55.53 ± 7.46 c	104.90 ± 0.34 a	30.35 ± 1.72 d	21.44 ± 0.62 a	21.69 ± 0.56 a	15.93 ± 3.68 c	20.66 ± 0.46 b	***	***	***
53	p-Xylene	518.11 ± 3.27 b	387.70 ± 3.46 c	852.88 ± 13.38 a	149.60 ± 7.82 d	7.94 ± 0.15 b	8.44 ± 0.31 a	6.26 ± 1.30 c	7.82 ± 0.28 b	***	***	***
54	m-Xylene	633.44 ± 0.44 b	457.63 ± 16.82 c	982.53 ± 1.12 a	167.46 ± 9.84 d	12.65 ± 1.01 c	14.73 ± 0.83 a	11.36 ± 2.40 d	13.97 ± 0.17 b	***	***	***
55	o-Xylene	572.51 ± 0.67 b	519.81 ± 33.50 c	936.41 ± 12.24 a	181.14 ± 5.75 d	11.26 ± 0.09 c	13.01 ± 0.07 a	9.63 ± 1.87 d	11.64 ± 0.04 b	***	***	***
56	Styrene	24.41 ± 0.21 b	20.05 ± 1.67 c	35.31 ± 0.46 a	8.51 ± 0.81 d	6.96 ± 0.19 a	6.56 ± 0.14 b	4.86 ± 0.90 d	5.49 ± 0.16 c	**	**	**
57	p-Cymene	15.14 ± 0.26 d	43.65 ± 6.30 a	20.08 ± 0.89 c	23.03 ± 0.04 b	8.62 ± 3.51 a	4.94 ± 0.25 b	4.19 ± 0.27 d	4.61 ± 0.22 c	**	**	**
58	trans-2-(2-Pentenyl)-Furan	4.58 ± 0.07 b	3.95 ± 1.02 c	8.46 ± 0.10 a	2.40 ± 0.03 d	0.61 ± 0.02 c	0.78 ± 0.01 b	0.93 ± 0.23 a	0.75 ± 0.02 b	**	**	**
59	1-methyl-4-(1-methylethenyl)-Benzene	4.55 ± 0.19 c	7.66 ± 1.20 a	6.50 ± 0.26 b	3.59 ± 0.04 d	1.72 ± 0.35 a	1.65 ± 0.13 b	1.44 ± 0.05 c	1.33 ± 0.12 d	***	***	***
60	2,5-bis[(trimethylsilyl)oxy]-Benzaldehyde	59.25 ± 2.77 a	16.46 ± 4.01 c	37.87 ± 1.26 b	13.31 ± 0.98 d	2.51 ± 0.003 b	2.89 ± 0.13 a	2.17 ± 0.38 d	2.31 ± 0.03 c	***	***	***
61	Benzaldehyde	104.97 ± 1.45 c	228.38 ± 21.62 a	105.03 ± 2.26 c	126.04 ± 6.74 b	17.75 ± 6.89 a	14.29 ± 1.30 c	15.68 ± 0.78 b	14.28 ± 0.99 c	***	***	***
62	Benzeneacetaldehyde	0.55 ± 0.33 c	3.42 ± 0.69 b	4.90 ± 0.03 a	0.25 ± 0.25 d	0.47 ± 0.04 c	0.62 ± 0.05 a	0.54 ± 0.02 b	0.46 ± 0.02 c	*	*	*
63	Acetophenone	12.96 ± 0.40 c	13.93 ± 1.75 b	14.06 ± 0.34 a	5.09 ± 0.08 d	0.91 ± 0.002 b	1.02 ± 0.07 a	0.92 ± 0.05 b	0.77 ± 0.03 c	**	**	**
64	Naphthalene	74.21 ± 11.63 b	109.98 ± 19.75 a	57.78 ± 0.15 c	34.64 ± 0.15 d	12.59 ± 0.81 d	16.49 ± 1.21 a	13.23 ± 3.02 c	15.00 ± 1.28 b	***	***	***
65	3,4-dimethyl-Benzaldehyde	42.55 ± 9.24 b	67.64 ± 4.67 a	29.08 ± 1.67 c	26.52 ± 2.29 d	18.68 ± 3.43 a	15.78 ± 1.36 b	10.94 ± 0.45 c	10.21 ± 0.48 d	***	***	***
66	Benzyl alcohol	15.25 ± 1.19 c	20.41 ± 3.17 a	10.84 ± 0.80 d	16.34 ± 1.38 b	1.20 ± 0.06 d	1.29 ± 0.03 c	1.48 ± 0.06 b	1.57 ± 0.31 a	***	***	***
67	2-methyl-Naphthalene	8.96 ± 1.70 b	17.44 ± 2.25 a	8.00 ± 0.41 c	6.81 ± 1.20 d	1.00 ± 0.09 c	1.35 ± 0.10 a	1.13 ± 0.21 b	1.11 ± 0.08 b	***	***	***
68	Phenylethyl alcohol	23.40 ± 2.10 c	63.35 ± 9.85 b	18.10 ± 1.26 d	67.79 ± 8.13 a	2.07 ± 0.04 b	2.00 ± 0.05 c	2.33 ± 0.28 a	2.36 ± 0.42 a	***	***	***
69	Phenol	5.38 ± 0.57 a	1.46 ± 0.02 d	4.29 ± 0.08 b	2.11 ± 0.004 c	0.39 ± 0.01 b	0.44 ± 0.02 a	0.38 ± 0.01 b	0.39 ± 0.02 b	**	**	**
70	2-methoxy-4-vinylphenol	4.18 ± 0.59 a	3.68 ± 1.42 b	3.50 ± 0.12 c	0.47 ± 0.35 d	3.69 ± 0.14 d	5.60 ± 0.46 a	5.18 ± 0.19 b	4.61 ± 0.61 c	**	**	**
71	1,6-dimethyl-4-(1-methylethyl)-Naphthalene	0.20 ± 0.04 b	0.52 ± 0.20 a	n	n	0.35 ± 0.14 a	0.37 ± 0.02 a	0.22 ± 0.09 c	0.30 ± 0.03 b	***	***	***
72	2,5-bis(1,1-dimethylethyl)-Phenol	110.10 ± 17.02 b	189.85 ± 35.93 a	47.27 ± 3.28 c	46.43 ± 3.23 d	77.77 ± 9.15 d	137.66 ± 0.52 a	113.27 ± 9.04 c	118.20 ± 16.03 b	***	***	***
	Subtotal	2347.74 ± 46.65 b	2284.91 ± 149.35 c	3362.40 ± 42.90 a	948.55 ± 21.94 d	213.86 ± 19.57 d	275.03 ± 2.74 a	225.18 ± 23.68 c	241.62 ± 19.25 b	***	***	***
	Proportion (%)	7.39 ± 0.05 c	8.47 ± 0.77 b	8.93 ± 0.06 a	4.16 ± 0.03 d	4.81 ± 0.56 c	5.17 ± 0.11 b	5.08 ± 0.09 b	5.68 ± 0.23 a			
Others												
73	2,2,6-trimethyl-Cyclohexanone	4.33 ± 0.09 b	1.62 ± 0.06 d	4.63 ± 0.35 a	3.06 ± 0.32 c	1.18 ± 0.09 a	1.13 ± 0.06 b	1.02 ± 0.13 c	1.00 ± 0.02 c	**	**	**
74	Furfural	5.12 ± 0.07 d	51.81 ± 2.40 a	9.80 ± 0.58 c	41.54 ± 0.15 b	0.29 ± 0.05 a	0.31 ± 0.02 a	0.25 ± 0.001 b	0.25 ± 0.04 b	***	***	***
75	4-methyl-2-(2-methylprop-1-enyl)-3,6-dihydro-2H-pyran	0.51 ± 0.14 a	n	n	n	0.47 ± 0.16 a	0.34 ± 0.02 c	0.38 ± 0.07 b	0.32 ± 0.03 c	***	***	***
76	Ethanol, 2-(2-ethoxyethoxy)	3.83 ± 0.37 b	n	4.35 ± 0.40 a	n	0.68 ± 0.00 c	0.88 ± 0.05 b	0.64 ± 0.10 c	0.94 ± 0.23 a	***	***	***
	Subtotal	13.79 ± 0.49 d	53.43 ± 2.46 a	18.78 ± 0.62 c	44.60 ± 0.48 b	2.62 ± 0.29 a	2.66 ± 0.77 a	2.29 ± 0.45 c	2.51 ± 1.81 b	***	***	***
	Proportion (%)	0.04 ± 0.003 b	0.20 ± 0.023 a	0.05 ± 0.001 b	0.20 ± 0.004 a	0.06 ± 0.008 a	0.05 ± 0.011 a	0.05 ± 0.001 a	0.06 ± 0.039 a			
	Total	31,735.39 ± 860.84 b	26,981.95 ± 4238.96 c	37,670.38 ± 246.63 a	22,826.51 ± 707.70 d	4443.73 ± 109.38 b	5323.24 ± 170.06 a	4429.61 ± 395.40 c	4251.60 ± 166.25 d	***	***	***

[a] CK represents the control; L represents 300 mg/L Mn treatment; M represents 1200 mg/L Mn treatment; H represents 2400 mg/L Mn treatment.

[b] Different lowercase letters in the same line for each year indicate significant differences among different treatments (Tukey's test, $P < 0.05$).

[c] Y and T indicate year and treatment, respectively.

[d] ***, significant difference at $P < 0.001$; **, significant difference at $P < 0.01$; *, significant difference at $P < 0.05$; ns, no significant difference.

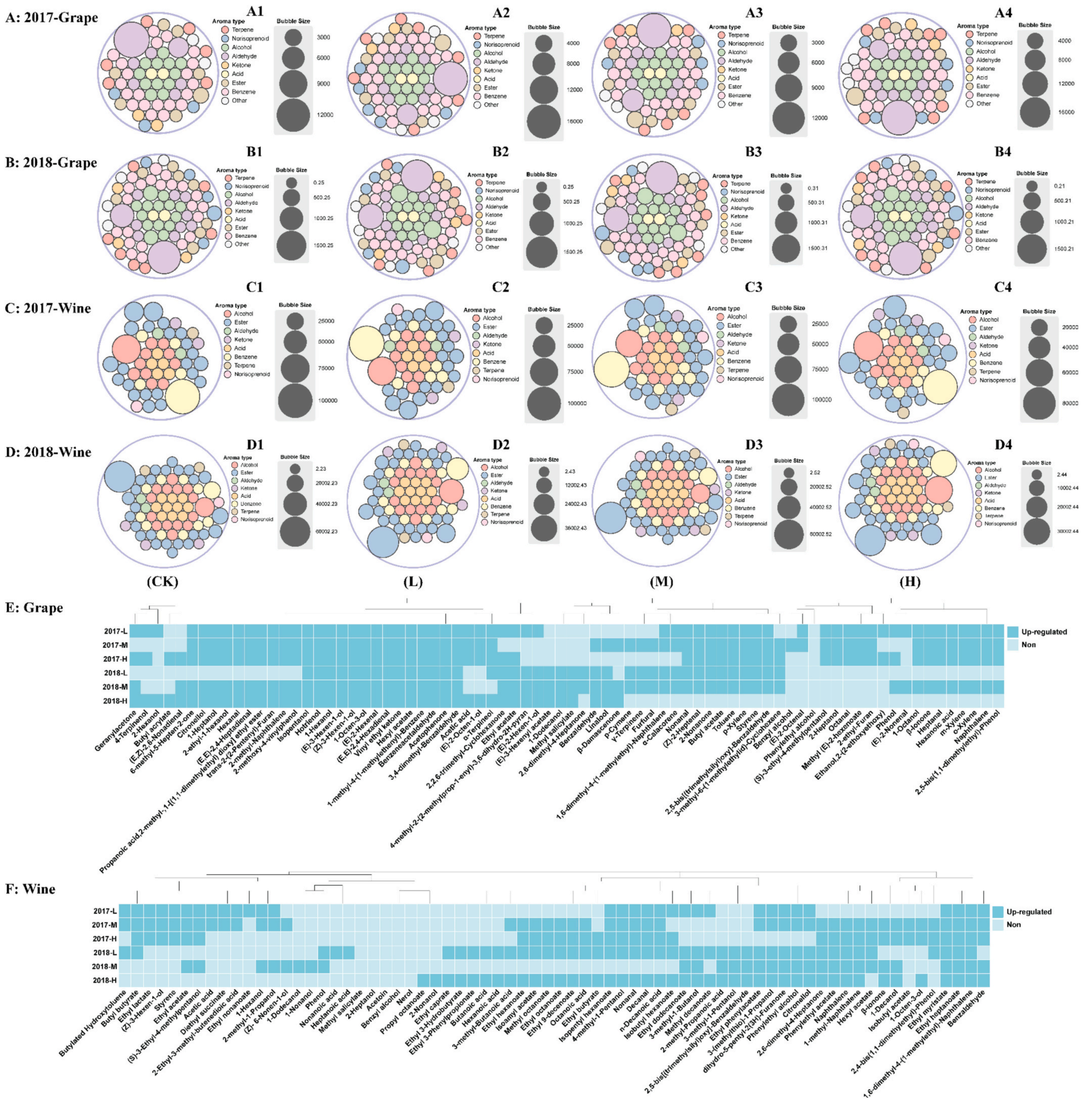

Fig. 1. Circle packing plots and differential binary heatmap of the volatile compounds in grape and wine from Mn-treated and control groups in 2017 and 2018. Circle packing plots represent the content of each monomer compounds in CK (A1, B1, C1, and D1), L treatment (A2, B2, C2, and D2), M treatment (A3, B3, C3, and D3), and H treatment (A4, B4, C4, and D4), and different colors represent types of volatile compounds. The binary heat map represents whether there is a difference in volatile compounds between the Mn treated and control groups in grape (E) and wine (F). CK represents the control; L represents 300 mg/L Mn treatment; M represents 1200 mg/L Mn treatment; H represents 2400 mg/L Mn treatment.

in 2018. Ethyl acetate remained at a relatively high level in both years, whereas butyl acetate was responsible for the main interannual differences in ester concentrations. Compared with the CK, Mn application significantly promoted the accumulation of grape esters, with an average increase of 72 % in 2017 and 1.5-fold in 2018. In addition, Mn treatment significantly increased the content of terpenes and norisoprene compared to CK over the two years, which may be because Mn acts as a major cofactor for terpene synthase (Farzadfar et al., 2017). The benzene content was equivalent to that of the esters and the top three compounds in terms of content were p-xylene, m-xylene, and o-xylene. Ketones and acids had the least diversity and content and contributed the least to the grape aroma. Compared to CK, the content of these compounds increased significantly in 2017.

The total grape volatile content significantly changed over the two years from 22,826.51–37,670.38 μg/L in 2017 and 42,451.60–5323.24 μg/L in 2018. Ju et al. (2017) and Tian et al. (2022) reported that grape volatiles are highly dependent on the inter-vintage climate. Therefore, the results of this study may have been caused by rainfall differences between 2017 and 2018, with more rainfall in the later stages of fruit ripening in 2018 leading to an increase in fruit moisture content, thus diluting the aroma to some extent (Chen et al., 2020). In 2017, the total volatile content in Mn-treated grapes was higher than that in CK grapes, mainly because of the high content and proportion of hexanal and butyl acetate. In 2018, treatment M significantly increased the content of alcohols and esters in grapes compared to CK (Fig. 1E), and thus resulted in a significantly higher total volatile content than CK, which provided a good material basis for brewing floral and fruity wines. Previous studies have shown that nutrient application is an effective way to improve crop productivity and secondary metabolism (Salifu et al., 2021). Chen et al. (2022) reported potassium fertilizer increases grape color and polyphenol content. Gutiérrez-Gamboa et al. (2018) found that the nitrogen content of vines affects the synthesis of grape volatiles, especially alcohols and esters. Overall, our results indicated that moderate Mn application can increase the intensity and complexity of grape aroma.

3.2.2. *Volatile profiles of wine*

The composition and content of volatiles in Mn-treated wines and CK wine over the two years are presented in Table 2, which generally aligns with the findings of previous studies (Gao et al., 2019; Song et al., 2016). In 2017, 52 volatile compounds were detected in all wine samples, consisting of 11 alcohols, 22 esters, 2 aldehydes, 2 ketones, 5 acids, 8 benzenes, 1 terpene, and 1 norisoprenoid (Fig. 1C). Three, three, and two more volatiles were detected under L, M, and H treatments than under CK, respectively. Compared to 2017, 18 unique compounds were detected in 2018, including 4 alcohols, 4 esters, 1 ketone, 5 acids, 3 benzenes, and 1 terpene (Fig. 1D). The total volatile contents in all wine samples in 2017 (302,570.3–337,597.67 μg/L) were significantly higher than those in 2018 (160,223.35–169,288.53 μg/L). These results indicate that wine aroma had higher intensity and lower complexity in 2017 than in 2018, which is in line with the grape aroma results described in Section 3.2.1. Remarkably, M-treated wine had the highest total aroma compared to the other treated wines and CK wine over the two years. These results are consistent with previous research reports that nutritional fortification can improve volatile flavor compounds in fermented food-related fields, such as the application of selenium nutrition in soy sauce (Gao et al., 2022; Gao et al., 2023).

There were also significant differences in the contents of various types of volatiles over the two years. In line with the results of Tian et al. (2022), alcohols and esters were the top two aromas in all wine samples and accounted for an average of 74 % of the total aroma content, bringing floral and fruity aroma characteristics to the wine. In 2017, alcohol had the highest content among different aroma types, ranging from 75,005.30–83,933.41 μg/L, accounting for 24–27 % of the total aroma, followed by esters (111,516.60–132,977.47 μg/L; 36–44 %). In contrast, esters were the most abundant volatiles in 2018 wines, ranging from 86,100.59–105,226.03 μg/L (54–63 %), which was consistent with the results of Cao et al. (2022), followed by alcohols (35,359.78–40,093.93 μg/L; 21–25 %). The ester content in M-treated wine was significantly higher than that in CK over the two years, with increases of 13 % in 2017 and 1 % in 2018 (Fig. 1F). These results are consistent with the findings of Song et al. (2016), who found that foliage-sprayed Zn fertilizer improved the abundance of esters in *Vitis vinifera* cv. Merlot. Additionally, more new esters were detected in wines than in grapes (Table 2). This may be because yeast convert sugars to produce esters via the action of esterases, hemiacetal dehydrogenases, and alcohol acetyl transferases during fermentation, resulting in a unique fermentation aroma (Gao et al., 2021; Kruis et al., 2017).

Terpenes and norisoprenoids typically impart strong floral and fruity aromas to wine because of their very low threshold, although their wine content is relatively low (Gonzalez-Barreiro et al., 2013; Styger et al., 2011). In 2017, only M treatment significantly increased the content of terpenes and norisoprenoids in wine, with increases of 42 % and 65 %, respectively, compared to CK. In 2018, compared to the CK, all Mn treatments promoted the accumulation of terpenes in wines, with an average increase of 10 %, whereas only M and H treatments significantly increased the norisoprenoid content, with an average increase of 7 %.

3.3. *Multivariate analysis of volatile components in grapes and wine*

PLS-DA was used to identify the differences in volatiles in grape and wine from Mn treatments and CK. In the score plot in Fig. 2 all grape and wine samples are separated, indicating that Mn application modified the aroma profiles of grapes and wine. We further evaluated the contribution of each compound to the different treatments based on the variable importance in the projection (VIP) in the model, where compounds with VIP > 1 were considered to significantly contribute to the differences. In 2017 grapes, 13 aroma compounds were selected as the candidate differential aromas, including one alcohol, three aldehydes, six benzenes, two esters, and one norisoprenoid (Fig. 2E). Compared to the 2017 grapes, fewer candidates were identified in the 2018 grapes, consisting of two alcohols, two aldehydes, two benzenes, one ester, one acid, and one norisoprenoid (Fig. 2F). However, only five candidate differential aroma were shared over the two years, including hexanal, (E)-2-Hexenal, ethyl acetate, *β*-Damascenone, and (E)-2-Hexen-1-ol. In both years, hexanal and (E)-2-Hexenal were the most distinct compounds between the Mn treatments and CK, with average VIP values of 3.68 in 2017 and 3.26 in 2018. Hexanal and (E)-2-Hexenal are the major C6 aldehydes in grapes, synthesized through the lipoxygenase-hydroperoxide lyase pathway by metabolizing fatty acids, and endow grape and wine with green, fresh, floral, and fruity aromatic characteristics (Yue et al., 2023). In addition, hexanal and (E)-2-Hexenal are the sources of green flavor in many red grape varieties, including Cabernet Sauvignon (Yue et al., 2023). Recently, hexanal content has been shown to change significantly in response to grapevine pruning systems and cluster shading, owing to differences in cluster-zone microclimates (Liu et al., 2024; Tian et al., 2022). In the present study, hexanal and (E)-2-Hexenal were more abundant in Mn-treated grapes than in the CK, indicating that Mn application can modify the metabolism of C6 volatiles in grapes. Ethyl acetate and *β*-Damascenone were also important candidates to separate different samples, which bring rich fruity and floral flavors to grapes. Ethyl acetate is generally considered the main contributor to the strawberry aroma in grapes (Wu et al., 2019; Yao, Chen, et al., 2021). *β*-Damascenone is abundant in grapes and has low thresholds especially in red wine to contribute to apple and floral aroma (Xia et al., 2024). Pineau et al. (2007) also reported that *β*-Damascenone contributes to the grape-derived fruity aroma of Cabernet Sauvignon wines. Notably, the contents of these two compounds were higher under Mn treatments than in CK, especially under M treatment, which implies that Mn treatment promotes the accumulation of mature grape aroma. Previous studies have shown that fruit ripening, accompanied by fruit senescence, increases the permeability of pulp cells and causes the accumulation of pyruvate, which is then converted into ethyl esters through a series of metabolic reactions (Yao, Jin, et al., 2021).

Ten candidate differential aromas were identified in 2017 wine, including one benzene, six esters, two alcohols, and one acid (Fig. 2G). Similarly, 14 candidates were identified in 2018 wine, including two benzenes, eight esters, two alcohols, one acid, and one ketone (Fig. 2H). Among these candidates, eight compounds were consistently identified over the two years, including six esters (ethyl acetate, isoamyl acetate, ethyl octanoate, phenylethyl acetate, ethyl caprate, and ethyl hexanoate), one benzene (phenylethyl alcohol), and one alcohol (3-methyl-1-Butanol). These results are consistent with those of Song et al. (2016), who identified ethyl hexanoate as the characteristic aroma of wines produced from zinc sulfate-treated grapes. To evaluate their contributions to the overall wine aroma, these candidates must be further validated.

3.4. *OAV analysis for wine volatiles*

To further clarify how Mn application affects the potential

Table 2
The content (μg/L) of free volatile compounds in wines made from Mn-treated and control grapes in 2017 and 2018.

Number	Compounds	2017				2018				Y[c]	T	YxT
		L [a]	M	H	CK	L	M	H	CK			
Alcohols												
1	2-methyl-1-Propanol	4544.24 ± 17.06 b[b]	4609.17 ± 12.88 a	4056.87 ± 60.79 d	4323.26 ± 72.64 c	4379.60 ± 53.18 b	4406.89 ± 7.14 a	3933.61 ± 33.28 c	4406.69 ± 246.16 a	***[d]	***	***
2	3-methyl-1-Butanol	75,822.26 ± 866.43 a	73,243.60 ± 1029.31 c	67,857.36 ± 459.39 d	74,407.57 ± 1197.49 b	32,314.79 ± 371.43 a	27,978.78 ± 398.18 c	32,036.15 ± 436.02 b	27,397.44 ± 1426.48 d	***	***	***
3	4-methyl-1-Pentanol	48.00 ± 1.08 b	59.51 ± 1.84 a	45.20 ± 0.91 c	41.72 ± 0.01 d	38.21 ± 0.20 a	27.28 ± 0.40 c	38.18 ± 0.25 a	27.57 ± 1.49 b	*	**	**
4	2-Heptanol	n	n	n	n	17.26 ± 2.34 b	16.35 ± 2.28 c	17.01 ± 4.14 b	18.63 ± 1.41 a	***	***	***
5	3-methyl-1-Pentanol	158.52 ± 2.78 c	166.01 ± 2.20 b	143.14 ± 1.99 d	177.45 ± 10.29 a	89.83 ± 0.16 b	63.04 ± 0.15 c	91.22 ± 1.18 a	60.26 ± 1.92 d	***	***	***
6	1-Hexanol	2783.67 ± 8.83 a	2676.46 ± 32.22 b	2451.73 ± 2.24 d	2517.78 ± 116.06 c	2821.66 ± 25.24 c	3091.00 ± 5.10 a	2713.25 ± 32.65 d	2972.58 ± 126.20 b	***	***	***
7	(*Z*)-3-Hexen-1-ol	32.41 ± 2.01 c	50.86 ± 0.34 a	35.19 ± 1.26 b	27.17 ± 9.71 d	20.99 ± 0.71 b	21.09 ± 0.19 b	16.75 ± 0.17 c	21.93 ± 1.14 a	**	**	**
8	(*S*)-3-Ethyl-4-methylpentanol	95.01 ± 5.74 a	67.57 ± 9.97 b	37.03 ± 2.01 c	28.67 ± 0.63 d	72.07 ± 0.79 c	78.84 ± 0.41 a	72.24 ± 0.99 c	77.86 ± 3.06 b	**	**	**
9	2-Nonanol	n	n	n	n	41.48 ± 3.25 c	37.04 ± 0.09 d	61.67 ± 1.64 a	50.55 ± 2.22 b	***	***	***
10	1-Octen-3-ol	64.74 ± 0.21 d	122.11 ± 6.21 a	95.57 ± 1.27 b	68.93 ± 1.84 c	60.98 ± 1.10 d	75.51 ± 0.09 c	90.64 ± 1.76 a	76.77 ± 1.99 b	**	**	**
11	1-Nonanol	n	n	n	n	88.85 ± 1.42 d	154.36 ± 1.10 a	106.15 ± 4.35 c	116.06 ± 4.44 b	***	***	***
12	(Z)- 6-Nonen-1-ol	13.44 ± 13.44 d	20.90 ± 2.45 a	16.24 ± 2.29 c	19.47 ± 2.86 b	23.14 ± 0.05 d	42.33 ± 1.53 a	29.63 ± 1.21 c	30.86 ± 1.31 b	**	**	**
13	3-(methylthio)-1-Propanol	350.91 ± 0.99 a	337.08 ± 8.83 b	231.28 ± 53.37 d	279.39 ± 6.46 c	92.42 ± 0.04 b	76.28 ± 0.40 c	100.65 ± 24.06 a	67.85 ± 5.22 d	***	***	***
14	1-Decanol	20.21 ± 0.07 d	39.90 ± 1.47 a	35.69 ± 1.23 b	22.48 ± 0.69 c	23.27 ± 0.16 d	28.75 ± 0.25 a	26.65 ± 0.54 b	26.19 ± 1.46 c	ns	**	**
15	1-Dodecanol	n	n	n	n	8.38 ± 1.66 c	8.73 ± 0.01 a	7.94 ± 2.29 d	8.54 ± 0.87 b	***	***	***
	Subtotal	83,933.41 ± 34.37 a	81,393.17 ± 6016.65 c	75,005.30 ± 19,316.46 d	81,913.89 ± 5796.88 b	40,092.93 ± 639.23 a	36,106.27 ± 539.04 c	39,341.74 ± 1786.48 b	35,359.78 ± 3341.06 d	***	***	***
	Proportion (%)	27.43 ± 0.20 a	24.11 ± 1.05 d	24.79 ± 2.99 c	26.87 ± 0.57 b	23.90 ± 0.34 b	21.33 ± 0.09 c	24.55 ± 1.53 a	21.32 ± 0.31 c			
Esters												
16	Ethyl acetate	17,057.76 ± 21.36 b	16,703.35 ± 559.88 c	17,605.24 ± 90.98 a	16,294.99 ± 89.43 d	47,794.07 ± 933.04 c	66,121.74 ± 1004.44 a	37,354.82 ± 595.60 d	62,419.02 ± 3993.24 b	***	***	***
17	Isobutyl acetate	423.89 ± 9.61 d	549.58 ± 24.03 b	614.33 ± 9.46 a	460.53 ± 3.67 c	429.70 ± 11.36 c	446.82 ± 7.32 b	371.27 ± 1.80 d	507.52 ± 24.79 a	**	**	**
18	Isoamyl acetate	30,425.18 ± 721.97 d	39,465.51 ± 1605.14 b	42,881.59 ± 658.90 a	34,059.38 ± 53.68 c	10,779.62 ± 203.41 a	7857.91 ± 46.77 d	9568.25 ± 207.00 b	8308.28 ± 493.20 c	***	***	***
19	Ethyl hexanoate	11,440.89 ± 221.08 d	14,568.41 ± 596.92 a	13,818.68 ± 184.07 b	11,792.45 ± 81.57 c	7193.68 ± 180.86 a	5597.88 ± 78.04 d	7139.12 ± 257.19 b	5813.72 ± 407.36 c	***	***	***
20	Hexyl acetate	818.87 ± 10.89 d	1040.85 ± 36.89 b	1324.97 ± 24.72 a	992.59 ± 2.73 c	534.08 ± 11.37 a	502.02 ± 4.69 b	389.87 ± 12.69 d	422.64 ± 27.89 c	***	***	***
21	Ethyl heptanoate	126.64 ± 0.05 a	124.06 ± 2.35 b	112.62 ± 2.10 c	104.69 ± 0.38 d	160.07 ± 6.12 a	138.05 ± 3.52 c	145.80 ± 8.74 b	137.41 ± 12.69 d	*	**	**
22	Ethyl lactate	172.29 ± 3.86 b	205.99 ± 9.76 a	108.17 ± 10.16 c	82.78 ± 82.78 d	146.41 ± 1.91 d	202.21 ± 10.11 c	247.58 ± 2.92 b	414.74 ± 31.64 a	***	***	***
23	Methyl octanoate	145.25 ± 0.99 d	196.48 ± 0.69 a	183.79 ± 2.04 b	167.05 ± 0.33 c	120.20 ± 4.75 a	97.34 ± 2.02 d	115.03 ± 6.79 b	107.45 ± 11.62 c	**	**	**
24	Ethyl octanoate	31,632.79 ± 359.88 d	38,990.13 ± 99.11 a	35,576.42 ± 19.36 b	32,902.34 ± 120.34 c	18,539.73 ± 751.47 b	15,194.32 ± 414.32 d	19,032.67 ± 1310.93 a	17,142.27 ± 1828.35 c	***	***	***
25	Ethyl 3-Hydrobutyrate	n	n	n	n	8.05 ± 1.25 b	6.29 ± 0.99 d	9.61 ± 0.31 a	6.91 ± 0.57 c	**	**	**
26	Ethyl nonanoate	156.85 ± 0.04 a	101.27 ± 0.48 d	116.38 ± 0.47 c	119.77 ± 5.68 b	294.84 ± 9.09 d	343.72 ± 11.42 b	297.83 ± 19.68 c	473.50 ± 29.29 a	***	***	***
27	Ethyl caprate	10,682.09 ± 166.38 c	10,192.26 ± 83.21 d	11,003.00 ± 122.75 b	11,216.26 ± 91.16 a	7114.25 ± 167.94 b	6533.32 ± 56.40 d	8807.89 ± 889.70 a	6655.42 ± 798.98 c	***	***	***
28	Diethyl succinate	413.30 ± 12.75 b	629.99 ± 49.18 a	385.75 ± 68.79 d	392.82 ± 32.40 c	142.79 ± 1.13 c	134.13 ± 2.30 d	159.59 ± 4.49 b	440.12 ± 31.13 a	***	***	***
29	Ethyl 9-decenoate	475.51 ± 21.19 d	808.69 ± 12.70 b	839.49 ± 0.73 a	592.39 ± 1.42 c	365.12 ± 8.93 b	313.48 ± 3.27 d	429.49 ± 34.86 a	335.30 ± 35.90 c	***	***	***
30	Methyl salicylate	n	n	n	n	3.79 ± 1.08 b	2.52 ± 0.08 d	2.88 ± 0.02 c	3.85 ± 0.09 a	**	**	**
Number	**Compounds**	**2017** **L**	**M**	**H**	**CK**	**2018** **L**	**M**	**H**	**CK**	**Y**	**T**	**YxT**
31	Ethyl phenylacetate	115.94 ± 2.54 b	121.11 ± 9.49 a	84.11 ± 6.11 d	98.56 ± 3.87 c	41.52 ± 1.95 b	31.45 ± 0.44 c	43.06 ± 2.05 a	27.94 ± 0.78 d	***	***	***
32	Ethyl dodecanoate	1458.63 ± 109.84 a	777.06 ± 16.42 d	1213.93 ± 1.40 c	1313.63 ± 20.36 b	356.16 ± 17.33 a	271.37 ± 8.69 c	340.59 ± 37.91 b	214.87 ± 25.29 d	***	***	***
33	Ethyl 3-Phenylpropionate	n	n	n	n	5.94 ± 0.15 b	4.39 ± 0.04 d	7.55 ± 0.56 a	5.19 ± 0.14 c	**	**	**

(*continued on next page*)

Table 2 (*continued*)

Number	Compounds	2017				2018				Y[c]	T	YxT
		L [a]	M	H	CK	L	M	H	CK			
34	Butyl butyrate	74.49 ± 1.17 a	33.55 ± 1.32 c	36.94 ± 4.84 b	20.43 ± 7.53 d	18.16 ± 0.66 a	16.67 ± 0.03 c	15.60 ± 0.60 d	17.70 ± 0.15 b	***	***	***
35	Ethyl butyrate	880.60 ± 16.92 d	940.58 ± 43.49 c	1073.03 ± 18.60 a	957.15 ± 3.36 b	366.95 ± 7.60 a	304.40 ± 4.54 d	361.06 ± 7.72 b	332.53 ± 18.88 c	***	***	***
36	Isobutyl hexanoate	140.32 ± 3.17 a	113.04 ± 3.32 d	128.54 ± 4.02 b	121.61 ± 3.15 c	21.87 ± 1.32 a	16.80 ± 0.52 c	19.53 ± 1.74 b	19.49 ± 2.50 b	***	***	***
37	Isopentyl hexanoate	209.49 ± 4.83 b	250.56 ± 7.30 a	210.14 ± 6.30 b	203.83 ± 4.76 c	154.83 ± 9.51 b	101.08 ± 3.19 d	157.13 ± 17.22 a	126.37 ± 16.86 c	***	***	***
38	Propyl octanoate	n	n	n	n	2.98 ± 0.13 c	2.77 ± 0.07 d	4.06 ± 0.54 a	3.88 ± 0.49 b	**	**	**
39	Methyl decanoate	39.09 ± 0.12 a	33.01 ± 1.71 c	37.54 ± 1.24 b	37.82 ± 1.00 b	31.66 ± 1.16 b	29.68 ± 0.22 c	37.02 ± 3.59 a	31.24 ± 4.23 b	ns	*	*
40	Phenylethyl acetate	4594.07 ± 32.18 d	6220.10 ± 468.20 a	5581.05 ± 297.16 b	5348.34 ± 458.31 c	1185.68 ± 13.19 a	939.19 ± 21.62 c	1021.25 ± 54.77 b	665.45 ± 29.58 d	***	***	***
41	Ethyl myristate	32.65 ± 0.08 c	33.18 ± 3.53 b	41.76 ± 1.02 a	32.45 ± 1.66 c	23.73 ± 0.74 a	16.48 ± 0.001 c	22.04 ± 2.74 b	12.32 ± 0.72 d	**	**	**
	Subtotal	111,516.60 ± 908.79 d	132,098.76 ± 2466.13 b	132,977.47 ± 710.50 a	117,311.86 ± 514.37 c	95,835.88 ± 2344.84 c	105,226.03 ± 1663.12 a	86,100.59 ± 3476.75 d	104,645.13 ± 7831.10 b	***	***	***
	Proportion (%)	36.44 ± 0.17 d	39.13 ± 1.22 b	43.95 ± 3.03 a	38.48 ± 0.69 c	57.13 ± 0.36 d	62.16 ± 0.26 b	53.74 ± 1.65 c	63.11 ± 0.38 a			
Aldehydes												
42	Nonanal	47.86 ± 2.86 c	59.51 ± 9.47 a	50.23 ± 13.06 b	17.30 ± 5.84 d	14.75 ± 1.14 a	10.88 ± 1.27 d	13.54 ± 0.19 b	12.10 ± 0.75 c	***	**	**
43	Decanal	23.70 ± 0.61 a	16.49 ± 0.96 b	11.15 ± 6.20 c	8.65 ± 5.21 d	6.71 ± 1.29 a	4.35 ± 0.70 d	5.42 ± 1.07 b	4.59 ± 0.13 c	**	**	**
	Subtotal	71.56 ± 3.95 b	76 ± 5.46 a	61.38 ± 13.99 c	25.95 ± 3.82 d	21.46 ± 4.10 a	15.23 ± 14.98 d	18.96 ± 14.32 b	16.69 ± 38.20 c	***	***	***
	Proportion (%)	0.02 ± 0.0002 a	0.02 ± 0.0006 a	0.02 ± 0.0001 a	0.01 ± 0.0005 a	0.01 ± 0.001 a	0.01 ± 0.01 a	0.01 ± 0.01 a	0.01 ± 0.01 a			
Ketones												
44	2,6-dimethyl-4-Heptanone	69.03 ± 1.07 c	77.13 ± 1.35 a	71.35 ± 2.12 b	69.20 ± 2.02 c	20.43 ± 0.66 a	17.60 ± 0.22 c	19.85 ± 0.20 b	17.12 ± 0.35 d	***	**	**
45	Acetoin	n	n	n	n	42.76 ± 1.61 d	89.90 ± 13.04 c	160.12 ± 13.08 b	286.39 ± 35.66 a	***	***	***
46	Dihydro-5-pentyl-2(3H)-Furanone	27.91 ± 0.45 b	30.91 ± 4.29 a	16.90 ± 7.65 d	27.13 ± 3.77 c	23.87 ± 0.12 b	23.57 ± 0.18 c	29.29 ± 1.67 a	18.89 ± 1.07 d	ns	*	*
	Subtotal	96.94 ± 0.15 b	108.04 ± 5.25 a	88.25 ± 1.45 c	96.33 ± 1.44 b	87.06 ± 0.29 d	131.07 ± 0.51 c	209.26 ± 0.43 b	322.40 ± 1.00 a	***	***	***
	Proportion (%)	0.03 ± 0.00001 a	0.03 ± 0.001 a	0.03 ± 0.0001 a	0.03 ± 0.0007 a	0.05 ± 0.0002 d	0.08 ± 0.0001 c	0.13 ± 0.0005 b	0.19 ± 0.0006 a			
Acids												
47	Acetic acid	949.62 ± 97.79 b	958.93 ± 82.03 a	678.21 ± 86.21 d	735.03 ± 36.85 c	590.44 ± 6.45 c	767.24 ± 115.44 b	567.82 ± 40.03 d	1075.63 ± 126.77 a	***	***	***
48	2-methyl-Propanoic acid	n	n	n	n	84.82 ± 3.28 a	77.10 ± 5.98 c	80.50 ± 2.12 b	74.80 ± 4.85 d	***	**	**
49	Butanoic acid	n	n	n	n	41.82 ± 0.81 b	34.09 ± 1.50 d	43.26 ± 1.95 a	39.20 ± 2.97 c	***	**	**
50	3-methyl-Butanoic acid	63.01 ± 5.01 d	94.78 ± 6.67 a	65.11 ± 11.68 c	67.74 ± 1.25 b	172.65 ± 3.28 b	112.86 ± 6.14 d	187.93 ± 3.71 a	116.80 ± 6.09 c	***	**	**
51	Hexanoic acid	n	n	n	n	680.37 ± 37.26 b	480.24 ± 7.89 d	722.39 ± 50.07 a	564.96 ± 6.99 c	***	***	***
52	Heptanoic acid	n	n	n	n	6.67 ± 0.67 a	5.60 ± 0.27 c	6.29 ± 0.46 b	6.32 ± 0.53 b	**	**	**
53	Octanoic acid	1140.86 ± 34.96 d	3260.87 ± 424.97 a	1754.80 ± 355.04 b	1486.74 ± 193.12 c	1116.60 ± 9.41 b	838.36 ± 30.10 d	1345.68 ± 74.07 a	1004.84 ± 50.12 c	***	***	***
54	Nonanoic acid	n	n	n	n	17.27 ± 0.13 a	11.00 ± 0.27 d	12.22 ± 1.61 c	15.56 ± 0.43 b	**	**	**
55	n-Decanoic acid	331.72 ± 3.39 c	668.12 ± 71.22 a	479.92 ± 68.79 b	259.17 ± 222.42 d	275.93 ± 8.60 a	167.40 ± 8.89 d	266.64 ± 16.87 b	184.97 ± 2.48 c	***	***	***
56	2-Ethyl-3-methyl-butenedioic acid	35.41 ± 4.60 b	62.15 ± 8.81 a	31.05 ± 5.22 d	32.97 ± 3.46 c	21.01 ± 0.12 c	19.06 ± 0.34 d	25.98 ± 1.04 b	78.85 ± 4.75 a	**	**	**
	Subtotal	2520.62 ± 134.37 c	5044.85 ± 578.23 a	3009.09 ± 510.03 d	2581.65 ± 452.40 b	3007.58 ± 46.14 c	2512.95 ± 176.47 d	3258.71 ± 182.54 a	3161.93 ± 200.36 b	***	***	***
	Proportion (%)	0.82 ± 0.05 c	1.49 ± 0.15 a	0.99 ± 0.11 b	0.85 ± 0.13 c	1.79 ± 0.005 c	1.48 ± 0.12 d	2.03 ± 0.13 a	1.91 ± 0.01 b			
Benzenes												
57	Styrene	70.69 ± 0.63 c	88.00 ± 4.45 a	78.41 ± 0.27 b	59.56 ± 0.42 d	143.34 ± 7.14 c	139.30 ± 5.98 d	144.63 ± 8.13 b	145.50 ± 16.48 a	**	**	**
58	Naphthalene	171.69 ± 16.85 d	202.27 ± 11.70 b	293.96 ± 7.38 a	199.70 ± 5.45 c	139.88 ± 13.35 b	211.75 ± 23.26 a	134.29 ± 5.06 c	94.31 ± 0.26 d	**	***	***
59	1-methyl-Naphthalene	190.98 ± 28.93 d	246.65 ± 17.62 b	279.48 ± 5.02 a	213.58 ± 7.25 c	18.23 ± 2.08 b	25.19 ± 2.40 a	16.96 ± 0.58 c	12.66 ± 0.005d	***	***	***
60	1,6-dimethyl-4-(1-methylethyl)-Naphthalene	5.66 ± 0.42 b	10.10 ± 0.44 a	1.69 ± 0.09 c	n	2.43 ± 0.30 b	2.73 ± 0.11 a	2.44 ± 0.09 b	2.23 ± 0.11 c	*	*	*
61	Benzyl alcohol	n	n	n	n	73.70 ± 0.74 d	97.10 ± 0.85 c	99.90 ± 6.77 b	115.11 ± 9.10 a	**	**	**

(*continued on next page*)

Table 2 (*continued*)

Number	Compounds	2017				2018				Y[c]	T	YxT
		L [a]	M	H	CK	L	M	H	CK			
62	2,5-bis[(trimethylsilyl)oxy]-Benzaldehyde	n	n	n	n	33.90 ± 0.78 b	33.77 ± 1.81 b	35.62 ± 1.72 a	31.48 ± 2.93 c	**	**	**
63	Benzaldehyde	7.65 ± 0.01 a	5.80 ± 2.66 b	1.19 ± 1.19 c	n	18.68 ± 0.08 d	24.36 ± 1.36 b	25.60 ± 0.08 a	20.15 ± 0.01 c	***	***	***
64	Butylated Hydroxytoluene	14.45 ± 0.85 a	8.04 ± 0.61 b	n	n	24.29 ± 2.07 a	17.83 ± 1.09 c	16.96 ± 2.47 d	22.65 ± 2.18 b	**	**	**
65	Phenol	n	n	n	n	4.38 ± 0.55 b	4.54 ± 0.01 a	3.36 ± 1.61 d	4.02 ± 0.71 c	**	**	**
66	2,4-bis(1,1-dimethylethyl)-Phenol	1777.00 ± 151.94 d	2391.41 ± 76.88 b	3093.28 ± 56.92 a	2098.00 ± 22.12 c	1095.17 ± 8.73 a	938.34 ± 32.38 d	1019.18 ± 40.20 c	1026.65 ± 30.71 b	***	***	***
67	Phenylethyl alcohol	105,516.72 ± 805.06 b	115,738.47 ± 7086.46 a	87,559.75 ± 18,741.08 d	100,244.66 ± 4392.53 c	26,956.18 ± 180.99 b	23,589.37 ± 153.76 c	29,584.80 ± 2282.56 a	20,648.73 ± 1515.70 d	***	***	***
	Subtotal	107,754.84 ± 44.74 b	118,690.74 ± 34.21 a	91,307.76 ± 10.44 d	102,815.50 ± 12.28 c	28,510.18 ± 7.85 b	25,084.28 ± 18.95 c	31,083.74 ± 7.08 a	22,123.49 ± 25.42 d	***	***	***
	Proportion (%)	35.21 ± 0.01 a	35.16 ± 0.01 a	30.18 ± 0.02 c	33.73 ± 0.001 b	17.00 ± 0.01 b	14.82 ± 0.01 c	19.40 ± 0.002 a	13.34 ± 0.00002 d			
Terpenes												
68	Citronellol	29.08 ± 0.26 b	34.00 ± 2.86 a	20.43 ± 5.08 d	24.01 ± 3.19 c	45.67 ± 0.02 b	41.41 ± 0.11 c	49.66 ± 0.54 a	40.87 ± 1.06 c	**	**	**
69	Nerol	n	n	n	n	6.32 ± 0.12 d	7.03 ± 0.2441.7 c	7.16 ± 0.39 b	7.49 ± 0.43 a	**	**	**
	Subtotal	29.08 ± 0.26 b	34.00 ± 2.86 a	20.43 ± 5.08 d	24.01 ± 3.19 c	51.99 ± 0.10 b	48.44 ± 0.13 c	56.82 ± 0.93 a	48.36 ± 1.50 c	**	**	**
	Proportion (%)	0.01 ± 0.01 a	0.01 ± 0.02 a	0.01 ± 0.01 a	0.01 ± 0.005 a	0.03 ± 0.0005 a	0.03 ± 0.0002 a	0.04 ± 0.0003 a	0.03 ± 0.001 a			
Norisoprenoids												
70	β-ionone	92.16 ± 0.92 c	152.11 ± 9.19 a	100.62 ± 2.51 b	92.38 ± 4.99 c	145.36 ± 0.27 d	164.26 ± 1.47 a	153.53 ± 5.33 b	149.20 ± 2.00 c	***	***	***
	Subtotal	92.16 ± 0.92 c	152.11 ± 9.19 a	100.62 ± 2.51 b	92.38 ± 4.99 c	145.36 ± 0.27 d	164.26 ± 1.47 a	153.53 ± 5.33 b	149.20 ± 2.00 c	***	***	***
	Proportion (%)	0.03 ± 0.0002 b	0.05 ± 0.002 a	0.03 ± 0.001 b	0.03 ± 0.001 b	0.09 ± 0.001 a	0.10 ± 0.001 a	0.10 ± 0.002 a	0.09 ± 0.005 a			
	Total	306,015.20 ± 1030.23 b	337,597.67 ± 4248.56 a	302,570.30 ± 19,183.68 d	304,861.57 ± 6790.38 c	167,752.44 ± 3039.66 b	169,288.53 ± 1961.39 a	160,223.35 ± 1547.37 d	165,826.98 ± 11,412.81 c	***	***	***

[a] CK represents the control; L represents 300 mg/L Mn treatment; M represents 1200 mg/L Mn treatment; H represents 2400 mg/L Mn treatment.

[b] Different lowercase letters in the same line for each year indicate significant differences among different treatments (Tukey's test, $P < 0.05$).

[c] Y and T indicate year and treatment, respectively.

[d] ***, significant difference at $P < 0.001$; **, significant difference at $P < 0.01$; *, significant difference at $P < 0.05$; ns, no significant difference.

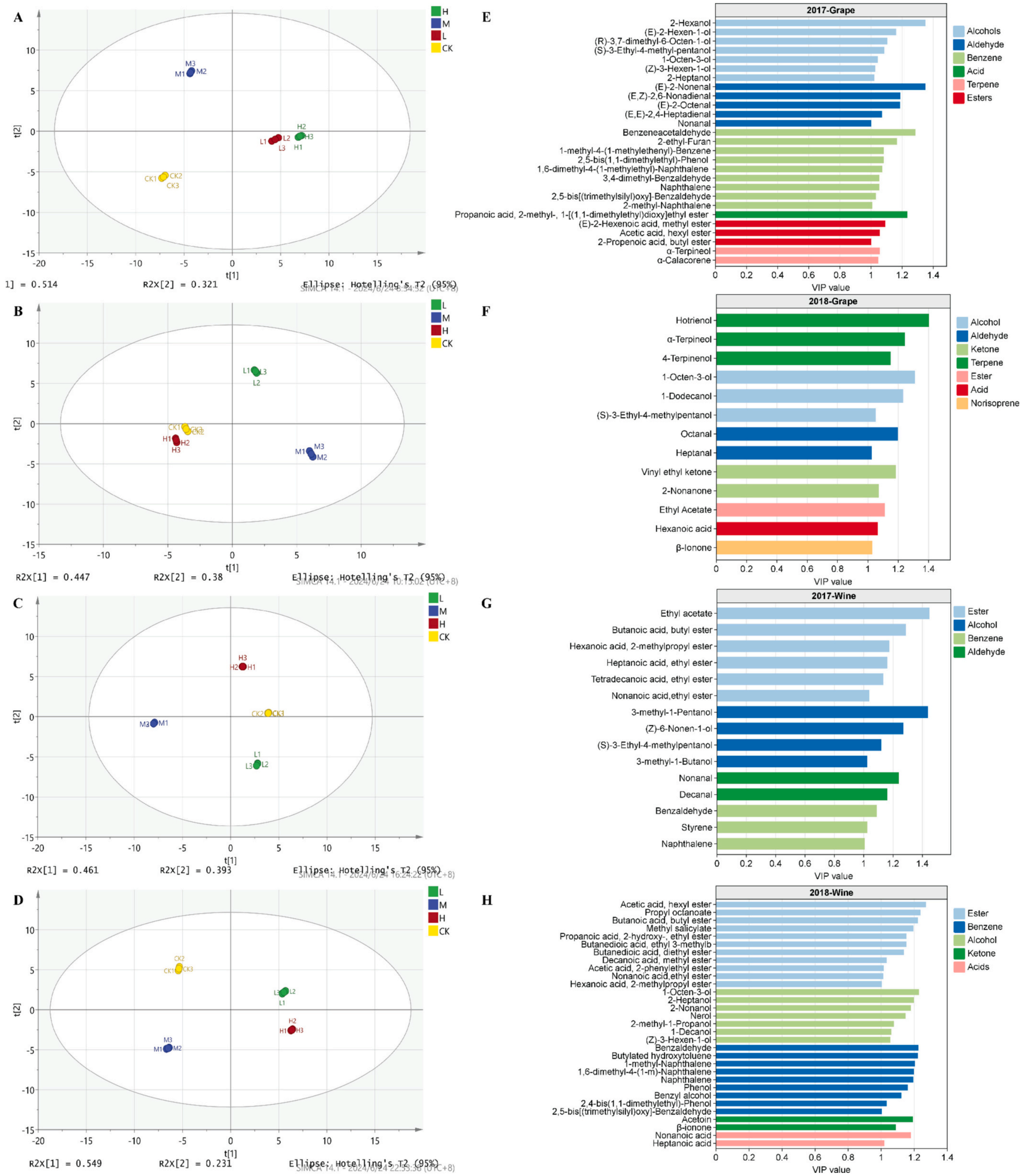

Fig. 2. PLS-DA analysis of grape and wine volatile compounds from Mn-treated and control groups in 2017 and 2018. The PLS-DA score plots of grape volatile compounds in 2017 (A) and 2018 (B) and wine volatile compounds in 2017 (C) and 2018 (D). The VIP values of PLS–DA models for the candidate differential volatile compounds in 2017 grape (E) and wine (G), and 2018 grape (F) and wine (H). CK represents the control; L represents 300 mg/L Mn treatment; M represents 1200 mg/L Mn treatment; H represents 2400 mg/L Mn treatment.

contribution of aroma compounds to wine aroma, we calculated the OVA of individual compounds in wine based on the reference threshold (Supplementary Table S1; Fig. 3A). According to the criterion of OVA >1, 21 volatile compounds were identified in the 2017 and 2018 wine samples, including three alcohols, 11 esters, two aldehydes, two acids, one benzene, one terpene, and one norisoprenoid. Among these compounds, isoamyl acetate (261.93–1429.39), ethyl hexanoate (1119.58–2913.68), ethyl octanoate (3038.86–7798.03), and β-ionone (1024.00–1615.11) showed the highest OAVs both in 2017 and 2018 wine samples, which gives wine a floral and fruity-like odor (Kong et al., 2019; Li, Liu, et al., 2022; Wang et al., 2017). However, 1-Dodecanol and hexanoic acid were only active in the 2018 wine samples and contributed to the violet and fatty-like aroma (Li, Wang, et al., 2022; Yao, Jin, et al., 2021). In 2017 and 2018, respectively, 13 volatiles out of 21 and 6 volatiles out of 21 exhibited higher OVA under M and H treatments compared to the CK, mainly including ethyl acetate, isoamyl

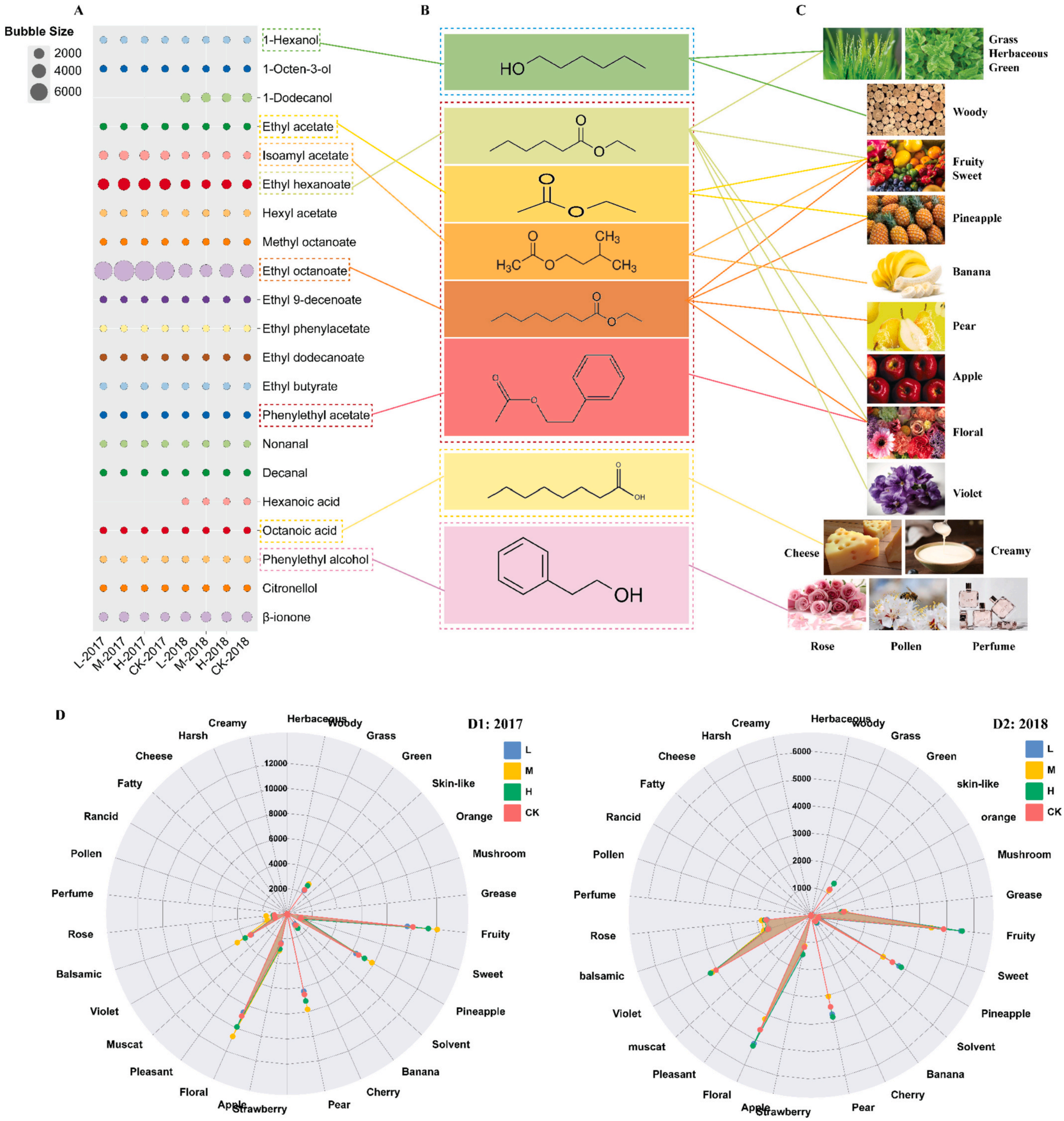

Fig. 3. The aroma series of volatile compounds, and the relationships among aroma activity values, key odorants, and its odor description. OAVs of volatile compounds (showing volatile compounds with OVA >1, A), chemical structural formula of key odorants (B), and aroma description of key odorants (C). Volatiles aroma series in 2017 (D1) and 2018 (D2). CK represents the control; L represents 300 mg/L Mn treatment; M represents 1200 mg/L Mn treatment; H represents 2400 mg/L Mn treatment.

acetate, ethyl hexanoate, ethyl octanoate, phenylethyl acetate, octanoic acid, phenylethyl alcohol, and *β*-ionone (Supplementary Table S1). In general, these 21 volatiles were considered to be odor-active in the wine samples in this study. Lu et al. (2023) selected 23 key volatile compounds with OAV $>$ 1 by determining the aroma profiles of Cabernet Sauvignon wine resulting from different vineyards and harvest ripens. These volatiles included ethyl hexanoate, ethyl acetate, isoamyl acetate, and phenylethyl alcohol, which is consistent with our findings.

In addition, we classified 30 aroma series according to the aroma descriptors of the volatiles with an OAV $>$ 1. Among these series, green, fruity, sweet, pineapple, banana, pear, apple, floral, violet, balsamic, and rose showed high intensities in the 2017 and 2018 wine samples, which significantly separated the Mn-treated and CK wines (Fig. 3D). Green, fruity, pineapple, pear, floral, violet, and rose showed higher intensities in wines resulting from M and H treatments in 2017 (Fig. 3D1) and H treatment in 2018 (Fig. 3D2) compared to CK, which was due to the contributions of ethyl acetate, ethyl hexanoate, ethyl octanoate, ethyl 9-decenoate, ethyl dodecanoate, ethyl phenylacetate, isoamyl acetate, hexyl acetate, methyl octanoate, phenylethyl acetate, phenylethyl alcohol, 1-Dodecanol, nonanal, *β*-ionone, and citronellol.

Esters mainly contribute fruity and floral aromas to wine and most exhibit high OVA in wine, such as isoamyl acetate, isobutyl acetate, ethyl hexanoate, ethyl octanoate, and 2-phenylethyl acetate (Kong et al., 2021). Song et al. (2016) showed that ethyl hexanoate, ethyl octanoate, ethyl butyrate, and ethyl acetate are critical odorants associated with fruity and floral aromas in Merlot wines and that ethyl hexanoate is an important contributor to the aroma traits of Zn-treated wines. In addition, phenylethyl alcohol is an important odorant and exhibits high concentrations in Chinese Cabernet Sauvignon wine, which imparts a typical rose aroma to wine (Lu et al., 2024). Overall, this study indicates that foliar Mn treatments enhance the fruity and floral aromas of wine because of the high concentration of esters in wine, which is beneficial for improving the aroma quality of wine.

3.5. Identification of key odorants influencing aroma variations in Mn-treated wine

The key odorants influencing aroma variation in Mn-treated and CK wines were identified by further analyzing the OAV and odor description of each candidate differential aroma screened based on VIP $>$ 1 in the PLS-DA models of the wine samples.

As shown in Fig. 3, eight candidate differential aromas identified in 2017 and 2018 using PLS-DA were selected as key odorants in the wine samples, including 1-Hexanol, ethyl acetate, isoamyl acetate, ethyl hexanoate, ethyl octanoate, phenylethyl acetate, phenylethyl alcohol, and octanoic acid. Among these, 1-Hexanol, ethyl acetate, phenylethyl acetate, and phenylethyl alcohol were significantly more abundant in M-treated wine than those in CK wine in 2017 and 2018, with differences of 4–11 %, 3–6 %, 16–41 %, and 14–16 %, respectively. Similarly, the contents of isoamyl acetate, ethyl hexanoate, ethyl octanoate, and octanoic acid were 15–26 %, 17–23 %, 8–11 %, and 18–34 % higher in H-treated wine than in CK wine in both years. As discussed in Section 3.4, these key volatiles are important fruit and floral odorants, such as the odor descriptions of pineapple from ethyl acetate and ethyl octanoate, banana from isoamyl acetate, pear from ethyl octanoate, violet from ethyl hexanoate, and rose from phenylethyl alcohol (Fig. 3A–3C). N. Li et al. (2024) reported that esters and phenylethyl alcohol are the key odorants in Cabernet Sauvignon wine, consistent with the typical fruity flavor of Bordeaux wine. Esters in wine have a wide range of sources, among which fermentation is an important pathway for producing esters in addition to those inherent in grape varieties themselves (He et al., 2022). During alcohol fermentation, esters are produced by the yeast metabolism of fatty acids and higher alcohols and contribute to the desired fruity flavor. Yao, Chen, et al. (2021) found that isoamyl lactate, octanoic acid, and phenethyl acetate are responsible for the high fermentation aroma of Cabernet Sauvignon wine from the Xinjiang region. These results were further supported by the results of this study because the key odorants that contribute to wine aroma differences mostly exist only in wine samples rather than grapes. Additionally, four key esters other than phenylethyl acetate were beneficial for the sweet aroma of wine samples in this study, and their interaction with other odorants may enhance the sweet aroma flavor of wine (Ma et al., 2021).

3.6. Sensory evaluation of wine and its correlation with wine volatiles

Scoring wine sensory parameters through sensory evaluation by tasters is important as a supplementary strategy for evaluating wine quality when qualitatively and quantitatively analyzing grape flavor compounds using instruments (Song et al., 2016). In this study, we first conducted sensory triangle tests on wine samples to determine whether there were differences between Mn-treated wines and the CK wine and whether they improved or reduced wine sensory quality (Ruiz-Garcia et al., 2012). As shown in Supplementary Table S3, all Mn-treated wines were separated from CK wine and the average discrimination accuracy between Mn-treated wines and CK wine in 2017 (80 %) was higher than that in 2018 (58.3 %). Mn-treated wines had the highest discrimination accuracy in both years, with 90 % in 2017 and 65 % in 2018. Tasters showed a higher preference for Mn-treated wines than for CK wine, with M-treated wine having the highest preference ratio over the two years, with 72 % in 2017 and 85 % in 2018. Therefore, we performed a detailed sensory evaluation of M-treated and CK wines and compared their differences.

The sensory analysis results of the wines under M treatment and CK in 2017 and 2018 are shown in Fig. 4A. Among all sensory parameters, color significantly ($P < 0.05$) changed in M-treated and CK wines over the two years and showed higher values in M-treated wine, while there was no significant difference in clarity. In terms of aroma, M-treated wine exhibited a higher score in intensity and duration in 2017 and development and complexity in 2018 than CK wines, which was consistent with the results in Sections 3.2 and 3.4, with M-treated wine exhibiting high total aroma and OVA (Table 2 and Supplementary Table S1). In addition, M-treated wine showed higher sensory scores for mouthfeel than CK wine, with a significant difference ($P < 0.05$) in balance and harmony in 2018. Ultimately, the highest total score was observed in M-treated wine compared to CK wine over the two years and reached a significant level in 2018, indicating the potential of foliar Mn application for improving the sensory traits of wine. In line with our results, Song et al. (2016) reported that appropriate supplementation of leaves with zinc fertilizer could improve the aroma and taste characteristics of wine. However, the interannual differences in sensory traits in this study may be explained by the distinct content and composition of volatiles in grape and wine, as grape and wine had higher total volatile amounts in 2017 but more volatile types were observed in 2018 owing to climatic factors during these two years (Chen et al., 2020).

The sensory characteristics of wine are influenced by aroma compounds, such as specific combinations of aroma compounds that contribute to the aroma characteristics of wine (Kong et al., 2019). Therefore, a correlation network was constructed to reveal the association between sensory parameters and volatiles (OAV $>$ 1), based on the condition that $R^2 > 0.8$ and $P < 0.05$ (Fig. 4B). All compounds other than *β*-ionone exhibited high connectivity with other nodes, implying they were the core volatiles in the network. Among these compounds, phenylethyl alcohol, phenylethyl acetate, hexyl acetate, and ethyl phenylacetate were positively correlated with wine appearance (color), fragrance (intensity and duration), and mouthfeel (retronasal fragrance and finish), whereas ethyl octanoate, isoamyl acetate, ethyl hexanoate, ethyl 9-decenoate, methyl octanoate, ethyl phenylacetate, octanoic acid, nonanal, and decanal were all positively correlated with color, intensity, and duration. These results indicate that esters contribute to the sensory presentation of wine, which is consistent with the results of Section 3.5, with esters being the key odorants in wine samples. Esters typically bring floral and fruity flavors to wine, such as pineapple, banana, and

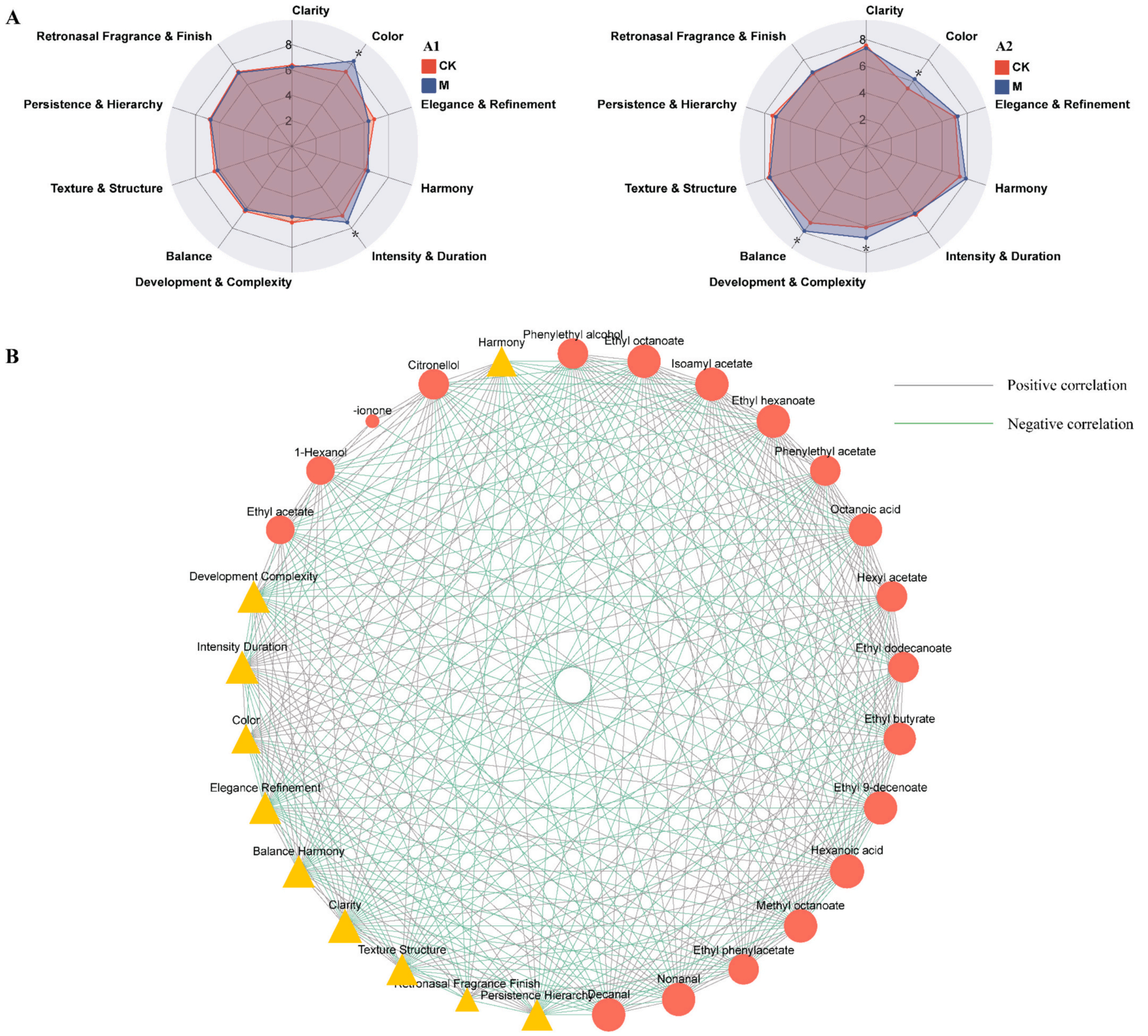

Fig. 4. Wine sensory characteristics, as well as the correlation network between the concentration of wine volatiles with OVA >1 and wine sensory parameters. Sensory characteristics of Mn-treated and control wines in 2017 (A1) and 2018 (A2), and analysis of variance was conducted by Tukey's test with * representing a significant difference at the $P < 0.05$ level. The correlation network (B) was constructed based on Spearman's correlation analysis, with $R^2 > 0.8$, $P < 0.05$. The edge color represents positive (grey) and negative (green) correlation, and edge thickness represents the correlation coefficient. The node shapes mean different types of parameters, with triangle representing sensory parameters and circular representing wine volatiles with OVA >1. The size of each node is proportional to the number of connections (i.e. degree). For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article. CK represents the control; M represents 1200 mg/L Mn treatment. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

rose; thus, a high content of esters may be beneficial for enhancing the aroma intensity and duration of wine, and their interaction with other compounds has positive effects on other sensory aspects of wine (Lu et al., 2023; N. Li et al., 2024).

4. Conclusion

Foliar Mn application increased Mn content in leaves and fruits, positively regulated the accumulation of alcohols and esters in grapes, and modified the volatile components and sensory characteristics of wine. Particularly, 1200 mg/L Mn treatment resulted in wine with a higher content of esters, total volatiles, and sensory score, especially in intensity, duration, and harmony, than CK. Ethyl acetate, phenylethyl acetate, and phenylethyl alcohol were the key odorants that contributed to the floral and fruity flavors in Mn-treated wine compared to CK. In conclusion, the results suggest that suitable Mn applications to grapevines can alleviate Mn deficiency and improve the aroma quality of grape and wine.

CRediT authorship contribution statement

Ruihua Ren: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Conceptualization. **Miaomiao Wang:** Visualization. **Lijian Zhang:** Investigation. **Fuxian**

Ren: Investigation. **Bowei Yang:** Resources. **Huangzhao Chen:** Data curation. **Zhenwen Zhang:** Funding acquisition, Conceptualization. **Qingqing Zeng:** Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fochx.2024.102150.

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