SUPPLEMENTARY DATA

On terroir – The choice of model emphasises different measured attributes in data sets

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Analytical Methods

Glutathione analysis

Glutathione analysis was modified from published methods (Adams & Liyange, 1991); 2 mL of 5 % 5-sulfosalicylic acid (SSA) was added to 250 mg of frozen ground grape in a 5 mL tube, left at room temperature for 5 min with vortex mixing twice, centrifuged at 3,200 × g for 10 min at room temperature and the supernatant transferred to a 1.5 mL Eppendorf tube containing 30 mg PVPP. The supernatant was left at room temperature for 5 min and then spun at 20,000 × g for 5 min. A 10 µL aliquot of the supernatant was added to 150 µL of assay buffer (100 mM potassium phosphate pH 7, 1 mM EDTA, 40 µg/mL 5,5'-dithio-bis(2-nitrobenzoic acid), 0.15 units/mL glutathione reductase) in a Corning polystyrene flat bottom 9 well plate and left at room temperature for 5 min. The reaction was initiated by the addition of 50 µL of NADPH (0.16 mg/mL) and absorbance was measured at 412 nm every min for 5 min. A calibration curve from 25–200 µM of glutathione with duplicate data points was used for quantification.

Vitamin B5 and B6 analysis

Vitamins B5 (pantothenic acid) and B6 (pyridoxine) were quantified from 1 g frozen berry tissue with d2-pyridoxine internal standard by adding 2 mL of 50 mM ammonium formate and 100 µL of 5 ng/µL d2-pyridoxine internal standard. The samples were incubated overnight at 37 °C before centrifugation at 4,000 × g for 10 min, the supernatant collected, and 1 mL transferred to a glass vial for injection onto the LC-MS. Separation and detection were carried out using a 1200 series HPLC coupled to a 6410 triple quad mass spectrometer (Agilent, Santa Clara, CA). The injected samples (4 µL) were separated on a 2.1 x 100 mm x 2.7 µm InfinityLab Poroshell 120 SB-AQ column (Agilent) maintained at 25 °C during the analysis. Two eluents were used (A: water +0.1 % formic acid and B: acetonitrile + 0.1 % formic acid) with a flow rate of 0.25 mL/min with a gradient of: 0–3 min 100 % A; 3–8.5 min 80 % A and 20 % B; 8.5–10 min: 5 % A and 95 % B; 10–15 min 100 % B 15–30 min 100 % A to equilibrate column. The effluent was introduced into the ESI ion source with a desolvation gas temperature of 350 °C, the nebulizer pressure at 40 psi, a gas flow rate of 8.0 L/min and a capillary voltage of 1.0 kV. Detection was performed by multiple reaction monitoring in positive ion mode. Optimization of fragmentation was done with commercially obtained d2-pyridoxine (CDN isotopes) and pyridoxine and calcium pantothenate standards using the Agilent MassHunter Optimizer software. The collision energy ranged between 12 and 21 eV. The following transitions were used for quantification; d2-pyridoxine *m/z* 172.0–154, pyridoxine *m/z* 170.1–152, pantothenic acid *m/z* 220.2–90.0.

Fatty Acids

Fatty acids were extracted from 1 g ground, de-seeded berry samples using published methods (Han & Yuan, 2009) and quantified using an internal standard (50 µl of 1.2 mM d33-heptadecanoic acid (C/D/N Isotopes Inc.)). One mL of chloroform and 2 mL of methanol were added to the sample and mixed for 1 h on a flatbed stirrer. Separation of the fatty acids and their methylation products was by modifying existing methods (Yunoki *et al.*, 2004). First, to partition the phases, 1 mL of both chloroform and water were added, the solutions mixed and then centrifuged at 200 × g for 2 min. The lower chloroform layer was collected, re-extracted with 3 mL of chloroform:methanol:water (3:48:47) twice then concentrated under N_2. Methylation of the fatty acids was done by adding 2 ml methanol in 5 % HCl to the samples and incubating for 2 h at 95 °C. The samples were cooled to room temperature and 1 mL water and 2 mL n-hexane added. After shaking the upper layer was collected and the bottom layer extracted twice more with 2 mL n-hexane. The combined n-hexane extracts were concentrated under N2. The extract was resuspended in 100 µL dichloromethane for injection onto the GCMS. A 1:10 dilution was also made for quantification of the more abundant fatty acids.

Separation of the fatty acids was conducted with an Agilent 6890 gas chromatograph and 5973 mass spectrometer. The inlet was in split mode (10:1) at a temperature of 230 °C, and 1 µL of each sample (undiluted and diluted) was injected onto a ZB-5 column (length 30 m, 0.25 mm i.d., film thickness 0.25 µm; Phenomenex). Helium carrier gas was maintained at a constant flow of 1.5 mL/min. The oven temperature program was: initial 40 °C for 1 min, then ramped at 12 °C/min to 200 °C, then ramped at 0.5 °C/min to 230 °C, followed by a ramp of 3 °C/min until a final temperature of 250 °C and held for 15 min. The mass spectrometer was set with a transfer line temperature of 250 °C, source temperature of 240 °C, quadrupole temperature of 150 °C and ionising potential at 70 eV. Positive-ion electron impact spectra (70 eV) were recorded in scan mode (range: *m/z* 40–500, scan rate: 3.15 scans/s). Extracted ions used to quantify the fatty acid methyl esters relative to the internal standard (methyl ester of D33-heptadecanoic acid) are listed in Table S1. The identities of the fatty acid methyl esters were determined by comparing mass spectra with those of authentic standards and spectral libraries.

Table S1. List of methyl esters quantified in the grape fatty acid extracts, retention indices and the ions used for quantification.

Compound	Retention indices[1]	Quantification ion (*m/z*)
Methyl dodecanoate (12:0)	1810	66
Methyl tridecanoate (13:0)	1927	74
Methyl tetradecanoate (14:0)	2034	74
Methyl pentadecanoate (15:0)	2114	74
Methyl (*Z*)-9-hexadecenoate (16:1 n-7)	2230	55
Methyl heptadecanoate (17:0)	2303	74
Methyl (*Z*)-10-heptadecenoate (17:1 n-7)	2345	55
Methyl nonadecanoate (19:0)	2523	74
Methyl 2-hydroxyhexadecanoate (16:0 OH)	2611	97
Methyl eicosanoate (20:0)	2634	74
Methyl (*Z*)-13-eicosanoate (20:1 n-7)	2661	55
Methyl heneicosanoate (21:0)	2726	74
Methyl (*Z*,*Z*,*Z*)-11,14,17-eicosatrienoate (20:3 n-3)	2752	79
Methyl docosanoate (22:0)	2834	74
Methyl (*Z*)-13-docosenoate (22:1 n-9)	2850	55
Methyl tricosanoate (23:0)	2926	74
Methyl tetracosanoate (24:0)	3000+	74
Methyl pentacosanoate (25:0)	3000+	74
Methyl hexacosanoate (26:0)	3000+	74
Methyl heptacosanoate (27:0)	3000+	74
Methyl octacosanoate (28:0)	3000+	74

Compound	Retention indices[1]	Quantification ion (*m/z*)
Methyl 2-hydroxy-tetracosanoate (24:0 OH)	3000+	97
Methyl tricontanoate (30:0)	3000+	74
Quantified in 1:10 dilution		
Methyl hexadecanoate (16:0)	2239	74
Methyl octadecanoate (18:0)	2434	74
Methyl oleate (18:1 n-9)	2478	55
Methyl elaidate (tr18:1 n-9)	2486	264
Methyl linoleate (18:2 n-6)	2493	67
Methyl linolenate (18:3 n-3)	2594	79

[1] *RI calculated from retention relative to the retention of a series of n-alkanes (C_8-C_{30}).*

Grape carotenoids

Grape carotenoids were analysed using adapted methods (Lashbrooke *et al.*, 2010). Briefly a 500 mg sample of seedless ground grapes was transferred into a 2 mL amber microcentrifuge tube and placed on ice before the addition of 1 mL cold acetone, 0.1 % N-ethyldiisopropylamine and 10 µL of 1 mg/mL β-apo-carotenal in chloroform. The mixture was then vortexed for 10 s and sonicated for 30 min on ice. Following centrifugation at 21,000 × g at 4 °C for 5 min, 600 µL of the supernatant was added to 1 mL of cold extraction buffer (50 mM Tris-HCl (pH 7.5), 1 M NaCl) on ice. After the addition of 200 µL cold ethyl acetate, the mixture was vortexed briefly and sonicated for 5 min on ice. After a 5 min centrifugation at 21,000 × g at 4 °C, 50 µL of the upper ethyl acetate phase was sampled in low light conditions and placed in an amber high-recovery HPLC vial containing 200 µL of cold methanol and 0.125 % *w/v* butylhydroxytoluene.

Samples were run (20 µl injection) on an Agilent 1200 series HPLC fitted with an Acclaim C30 column (3 µm, 2.1 mm × 250 mm) and an Acclaim C30 guard column (5 µm, 2.1 mm × 10 mm) held at 25 °C. The column flow rate was 250 µL/min using two solvents: A, methanol, 3 % *v/v* water, 0.2 % *w/v* ammonium acetate, 0.05 % triethylamine; B, Tert-butylmethylether, 0.05 % triethylamine. The solvent gradient used was: 0–17 min 100 % A; 17–29 ramp to 32 % A and 68 % B; 29–34 hold at 32 % A and 68 % B; 34–36 min ramp to 100 % A; 36–55 hold at 100 % A to equilibrate the column. Diode array detector signals were captured at 420 nm, 450 nm, and 470 nm

at bandwidths of 16 nm, 4 nm, and 4 nm respectively with the reference being 800 nm for each signal with a bandwidth of 100 nm. Spectra were also collected for each sample ranging from 250–850 nm with a 1 nm step.

Bound Grape Volatile Compounds

The extraction of "bound" volatiles from the grape samples from 2 g of powdered grape material was adapted from published methods (Martin *et al.*, 2012) with hydrolysis of bound volatiles conducted using citric acid and heat, and released compounds extracted using diethyl ether and hexane (1:1) as outlined (Kotseridis *et al.*, 1999). Briefly, 2 g of powdered grape was mixed with 8 mL of water, mixed every 2 min for 10 min and centrifuged at 3,500 × g for 15 min at 4 °C. The supernatant was passed through a Strata-X SPE column (60 mg/3 ml, Phenomenex) conditioned previously with 3 ml methanol and 3 ml water. The column was washed with 6 ml water and 6 ml pentane before the "bound" volatiles were eluted with 6 ml methanol. The extracts were then dried using a vacuum evaporator without heat (Savant SpeedVac, ThermoFisher, MA, USA). Hydrolysis of the "bound" volatiles was conducted using citric acid and heat, and compounds released were extracted using diethyl ether and hexane (1:1), as outlined (Kotseridis *et al.*, 1999). A 10 µl aliquot of 45 mg/L ethyl-4-acetyl benzoate in 50 % ethanol was added as an internal standard. Extracted volatile compounds were analysed using a GCMS (Agilent 6890N gas chromatograph and 5973 mass spectrometer) by injection of 1 µL aliquot of each hydrolysate into an inlet in pulsed splitless mode at a temperature of 220 °C and separated on a ZB-Wax column (length 30 m, 0.25 mm i.d., film thickness 0.25 µm; Phenomenex). The pressure pulse was 25.0 psi for 0.6 min at which time purging at 30 ml/min began. Helium was used as the carrier gas at a constant flow of 1.2 ml/min. The temperature program of the oven was as follows: 40 °C, held for 1 min; ramped at 10 °C/min up to 90 °C; ramped at 4 °C/min to 190 °C; ramped at 10 °C/min to 240 °C and held for 10 min. Positive-ion electron impact spectra (70 eV) were recorded in scan mode (range: *m/z* 35–350, scan rate: 4.45 scans/s). A laboratory generated library (377 compounds) as well as the US National Institute of Standards and Technology-11 (NIST-11) and the Wiley Registry 9th Edition mass spectral libraries was used to identity volatile compounds. Compound identification, retention indices and quantification ions and level are listed in Table S4.

The analysis of grape volatile compounds was conducted using the method of Kalua & Boss (2009) with internal standards and ions as outlined in Tables S2 and S3.

Table S2. List of internal standards used for quantification of grape volatile compounds by GCMS.

Internal standard	Retention indices[1]	Concentration in vial (µg/L)	Quant. ion (*m/z*)
d8-Ethyl acetate	870	1.97	66
d16-Octanal	1241	1.64	96
2-n-Hexyl furan	1295	0.27	152
d17-2-Ethyl-1-Hexanol	1433	1.33	94
(*Z*)-3-Hepten-1-ol	1443	34	81
d11-Hexanoic acid	1799	37.2	63
d7-Benzyl alcohol	1822	10.4	115

[1] *RI calculated from retention relative to the retention of a series of n-alkanes (C8-C26).*

Table S3. Compounds for which relative quantities were obtained in the headspace of crushed grape samples.

COMPOUND	RETENTION INDICES[1]	ID. CRITERIA[2]	QUANT. ION (*M/Z*)	INTERNAL STANDARD[3]
ETHYL ACETATE	875	A	61	d8-EA
2-BUTANONE	895	B	72	d17-EH
2-METHYL BUTANAL	906	B	57	d16-Oct
3-METHYL BUTANAL	909	A	58	d16-Oct
1-METHOXY-HEXANE	938	B	56	d17-EH
2-ETHYL-FURAN	943	B	81	2-HF
2-METHYL-3,4-DIHYDRO-2H-PYRAN	945	C	98	d17-EH
2,5-DIMETHYLOCTANE	953	B	57	d17-EH
2,6-DIMETHYLOCTANE	964	B	57	d17-EH
PENTANAL	969	A	58	d16-Oct
METHYL BUTANOATE	976	B	74	d8-EA
METHYL GLYCOLATE	984	C	90	d8-EA
DECANE	999	A	57	d17-EH
1-METHOXYCYCLOHEXENE	1001	B	114	d17-EH
A-PINENE	1009	A	93	d17-EH
1-PENTEN-3-ONE	1012	A	55	d17-EH
4-HEPTANONE	1019	B	114	d17-EH
METHYLBENZENE	1027	A	91	d7-BA
2-BUTENAL	1029	B	70	d16-Oct
HEXANAL	1075	A	56	d16-Oct

COMPOUND	RETENTION INDICES[1]	ID. CRITERIA[2]	QUANT. ION (*M/Z*)	INTERNAL STANDARD[3]
ETHYLBENZENE	1107	A	91	d7-BA
(*E*)-2-PENTENAL	1114	A	83	d16-Oct
2-N-BUTYL FURAN	1115	B	81	2-HF
***P*-XYLENE**	1121	B	91	d7-BA
(*E*)-3-HEXENAL	1123	B	69	d16-Oct
1-BUTANOL	1129	A	56	d17-EH
1-PENTEN-3-OL	1144	A	57	Z3H
1,1-DIMETHOXYHEXANE	1151	A	75	d17-EH
3-ETHYLTHIOPHENE	1153	B	112	d17-EH
HEPTANAL	1169	B	70	d16-Oct
METHYL HEXANOATE	1172	B	74	d8-EA
LIMONENE	1176	A	93	d17-EH
CYCLOHEXENE OXIDE	1183	A	83	d17-EH
EUCALYPTOL	1189	A	108	d17-EH
ISOAMYL ALCOHOL	1191	A	70	d17-EH
(*E*)-2-HEXENAL	1207	A	83	d16-Oct
2-PENTYL-FURAN	1215	A	81	2-HF
1-PENTANOL	1229	A	55	d17-EH
3-OCTANONE	1236	A	99	d17-EH
STYRENE	1238	A	104	d7-BA
HEXYL ACETATE	1254	A	56	d8-EA
2-OCTANONE	1265	A	58	d17-EH

COMPOUND	RETENTION INDICES[1]	ID. CRITERIA[2]	QUANT. ION (*M/Z*)	INTERNAL STANDARD[3]
3-HYDROXY-2-BUTANONE	1266	A	88	d17-EH
OCTANAL	1270	A	84	d16-Oct
1-OCTEN-3-ONE	1281	A	70	d17-EH
2,2,6-TRIMETHYL-CYCLOHEXANONE	1293	B	82	d17-EH
(*Z*)-3-HEXENYL ACETATE	1297	A	82	d8-EA
(*Z*)-2-PENTEN-1-OL	1298	B	57	Z3H
(*E*)-2-HEPTENAL	1302	A	83	d16-Oct
VINYL CAPROATE	1305	C	99	d8-EA
3-ETHOXYPENTANE	1307	C	87	d17-EH
6-METHYL-5-HEPTEN-2-ONE	1316	A	108	d17-EH
1-HEXANOL	1331	A	56	d17-EH
(*E*)-3-HEXEN-1-OL	1340	A	67	Z3H
(*Z*)-3-HEXEN-1-OL	1361	A	67	Z3H
NONANAL	1374	A	98	d16-Oct
2,4-HEXADIENAL	1381	A	81	d16-Oct
(*E*)-2-HEXEN-1-OL	1383	A	57	Z3H
(Z)-2-HEXEN-1-OL	1392	A	67	Z3H
2,2,6-TRIMETHYL-4-METHYLENE-2H-PYRAN	1403	C	123	d17-EH
(*E*)-2-OCTENAL	1406	A	70	d16-Oct
ETHYL OCTANOATE	1416	A	88	d8-EA
(*E*)-LINALOOL OXIDE	1420	A	111	d17-EH

COMPOUND	RETENTION INDICES[1]	ID. CRITERIA[2]	QUANT. ION (*M/Z*)	INTERNAL STANDARD[3]
1-OCTEN-3-OL	1429	A	57	Z3H
1-HEPTANOL	1432	A	55	d17-EH
(*E,Z*)-2,4-HEPTADIENAL	1443	A	81	d16-Oct
FURFURAL	1444	A	95	2-HF
ACETIC ACID	1449	A	60	d11-HA
2-ETHYL-1-HEXANOL	1468	A	83	d17-EH
(*E,E*)-2,4-HEPTADIENAL	1471	A	81	d16-Oct
DECANAL	1480	A	112	d16-Oct
THEASPIRANE A	1480	B	138	d17-EH
BENZALDEHYDE	1501	A	106	d16-Oct
(*E*)-2-NONENAL	1513	A	70	d16-Oct
THEASPIRANE B	1518	B	138	d17-EH
2,5-DIHYDRO-THIOPHENE	1522	C	85	d17-EH
LINALOOL	1527	A	93	d17-EH
1-OCTANOL	1535	A	83	d17-EH
5-METHYL-2-FURFURAL	1552	B	110	2-HF
5,6-DIHYDRO-2H-PYRAN-2-CARBOXALDEHYDE	1577	C	83	d17-EH
(*E*)-2-OCTEN-1-OL	1593	A	57	Z3H
B-CYCLOCITRAL	1597	B	152	d17-EH
Γ-BUTYROLACTONE	1608	A	86	d17-EH
PHENYLACETALDEHYDE	1623	A	91	d16-Oct

COMPOUND	RETENTION INDICES[1]	ID. CRITERIA[2]	QUANT. ION (*M/Z*)	INTERNAL STANDARD[3]
1-HEPTEN-3-ONE	1633	C	55	d17-EH
2-FURANMETHANOL	1638	A	98	2-HF
HUMULENE	1649	A	93	d17-EH
DIETHYL SUCCINATE	1655	A	129	d8-EA
Γ-TERPINEOL	1678	A	121	d17-EH
(*E,E*)-2,4-NONADIENAL	1680	A	81	d17-EH
DODECANE-6,7-DIONE	1700	B	99	d17-EH
PENTANOIC ACID	1731	A	60	d11-HA
B-CADINENE	1736	B	161	d17-EH
5-ETHYL-2(5H)-FURANONE	1738	B	83	d17-EH
2-PHENYLETHYL ACETATE	1794	A	104	d8-EA
B-DAMASCENONE	1799	A	121	d17-EH
HEXANOIC ACID	1836	A	60	d11-HA
BENZYL ALCOHOL	1855	A	108	d7-BA
PHENYLETHYL ALCOHOL	1889	A	91	d7-BA
METHYL 2-OXO-HEXANOATE	1945	C	85	d17-EH
PHENOL	1988	A	94	d7-BA

[1] RI calculated from retention relative to the retention of a series of n-alkanes (C_8-C_{26}). [2] A, identity confirmed by matching mass spectra and RI with that of authentic standards; B, tentative assignment based upon comparison with mass spectral libraries and published RI; C, compound not identified or named based on mass spectral match only. [3] d8-EA = d8-ethyl acetate, d16-Oct = d16-octanal, 2-HF = 2-n-hexyl furan, d17-EH = d17-2-ethyl-1-hexanol, Z3H = (Z)-3-hepten-1-ol, d11-HA = d11-hexanoic acid, d7-BA = d7-benzyl alcohol.

Table S4. Compounds for which relative quantities were obtained in the bound volatile fractions of the grape samples.

Compound	Retention indices[1]	Quant. Ion (*m/z*)
2-Ethenyltetrahydro-2,6,6-trimethyl-2H-pyran	1110	139
***m*-Xylene**	1134	91
***o*-Xylene**	1161	91
3-Hexanone	1165	57
3-Hexanol	1182	55
2-Hexanol	1201	45
(*E*)-2-Hexenal	1205	83
2-Pentyl furan	1231	81
cis-Rose oxide	1234	139
Styrene	1279	104
1,3-Dimethyl-1-cyclohexene	1289	95
4-Methoxy-1,3-benzenediamine	1397	123
(*Z*)-Linalool oxide	1425	94
α-Ionene	1431	159
3,4,5-Trimethylpyrazole	1444	109
(*E*)-Linalool oxide	1451	94
Benzaldehyde	1506	105
1-(2,4-Dimethyl-3-furyl)ethanone	1547	123
2-Methyl-2-butanol	1567	59
4-Methyl-2-pentanol	1591	69
Ocimenol	1638	93

Compound	Retention indices[1]	Quant. Ion (*m/z*)
α-Fenchene	1667	93
4-Oxoisophorone	1673	96
1,1,4,6,7-Pentamethyl-2,3-dihydroindene	1715	173
1,2-Dihydro-1,1,6-trimethylnaphthalene (TDN)	1722	157
β-Damascenone	1801	121
1(2,3,6-Trimethylphenyl)but-1,3-diene (TPB)	1807	157
Guaiacol	1835	124
Benzyl Alcohol	1864	108
1,1,6,8-Tetramethyl-1,2-dihydro-naphthalene	1890	171
α-Calacorene	1891	157
1-[4-(1-Hydroxy-1-methylethyl)phenyl]-ethanone	1910	163
3-(2,6,6-Triimethyl-1-cyclohexen-1-yl)-2-propenal	1921	163
2,2-Dimethyl-3,3-(1'2'-ethylidene)-5-methyl-1,2-dihydrobenzofuran	1943	173
1,2-Dihydro-2,5,8-trimethyl-naphthalene	1971	157
4-(2,6,6-Trimethylcyclohexa-1,3-dienyl)but-3-en-2-one	1985	175
Unknown 1	2003	163
1,2-Dihydro-1,4,6-trimethyl-naphthalene	2011	157
2-Methylenebornane	2031	107
1,2-Dihydro-3,5,8-trimethyl-naphthalene	2039	157
1-(2,3,6-Trimethylphenyl)-3-buten-2-one	2095	173
1,2-Dihydro-4,6,8-trimethyl-naphthalene	2187	157

Compound	Retention indices[1]	Quant. Ion (*m/z*)
2-Hydroxy-5-methylacetophenone	2191	135
4-(2,6,6-Trimethyl-2-cyclohexen-1-yl)-3-buten-2-ol	2201	95
1-(2,3,6-Trimethylphenyl)-2-butanone	2219	132
Megastigmatrienone	2285	175
2,3-Dihydro-3,3,4,5-tetramethyl-1H-Inden-1-one	2296	173
2,3-Dimethyl-4-amino-1,4-benzoquinone	2305	151
2,4-bis(1,1-Dimethylethyl)-phenol	2320	191
4-(2,4,6-Trimethylphenyl)-butan-2-ol(1)	2370	192
4-(2,3,6-Trimethylphenyl)-2-butanone	2377	157
4-Vinylphenol	2408	120
(Z)-5-Methyl-4-phenyl-3-hexen-2-ol	2443	157
2,3-Dihydro-2,4,7-trimethyl-1H-indene-2-methanol	2506	157
3-Hydroxy-β-damascone	2528	193
3-Oxo-α-ionol	2600+	108
Eucalyptol	1184	85
1-Hexanol	1334	56
(E)-3-Hexen-1-ol	1357	67
Cyclohexanol	1382	82
Vitispirane	1507	192
3-Methyl-4-heptanone	1552	100
2-Hexanone	1579	58
Unk monoterpene 1	1598	93

Compound	Retention indices[1]	Quant. Ion (*m/z*)
4-Methyl-benzaldehyde	1626	120
8-Methyl-tricyclo[3.3.0.0(2,8)]octan-3-one	1666	94
α -Terpineol	1677	93
Methyl salicylate	1757	120
Unknown 3	1790	190
Octa-2,4,6-triene	1811	108
2,5-Hexanediol	1830	85
p-Cymen-8-ol	1832	135
Hexanoic acid	1845	60
Unknown 4	1859	173
Unknown 5	1893	85
Benzothiazole	1934	135
2-Ethylhexanoic acid	1944	88
Heptanoic acid	1952	60
1-Nonadecene	2034	83
Octahydro-1,1-dimethyl-7H-benzocyclohepten-7-one	2067	177
Octanoic acid	2072	60
7-Methyl-1-naphthol	2103	177
Nonanoic acid	2161	60
Unknown 7	2244	193
1-Docosene	2250	83
Decanoic acid	2274	60

Compound	Retention indices[1]	Quant. Ion (*m/z*)
4-(2,4,6-Trimethylphenyl)-butan-2-ol(2)	2364	192
Dodecanoic acid	2430	60
Benzoic acid	2471	105
Methyl vanillate	2584	151
7,9-di-tert-butyl-1-oxaspiro[4,5]deca-6,9-diene-2,8-dione	2600+	205
Methyl 2-hydroxy-4-methylbenzoate	2600+	134
Vanillyl acetone	2600+	194
2,4-Hexanedione	1284	114
1,3-Dihydro-5-propyl-isobenzofuran	1781	162
4-Ethyl-benzaldehyde	1796	134
8-Hydroxycoumarin	1834	162
2-Isopentyl-1,3,5-trimethylbenzene	1927	190
Ethyl 4-ethoxybenzoate	2150	121
2-Methyl-2-decanol	2159	59
2-Methyl-2-dodecanol	2401	59
Butyl benzoate	2600+	105
Methyl syringate	2600+	212

[1] RI calculated from retention relative to the retention of a series of n-alkanes (C_8-C_{26}).

Table S5. Attributes and reference standards used for panel training for sensory descriptive analysis of fine Australian Shiraz wines.

Attribute	Definition (reference standard, in 25 ml base wine)
Aroma and flavour	
Alcohol	The smell of ethanol 0.75 ml Ethanol (Tarac Technologies, Australia)
Dark fruits	Any combination of dark fruit (2 frozen blueberries (Woolworths Frozen Mixed Berries, Australia) and 1 frozen blackberry (Woolworths Frozen Mixed Berries, Australia), both cut in half
Red fruits	Any combination of red fruit *e.g.* Strawberry, raspberry, red cherry (half frozen strawberry (Woolworths Frozen Mixed Berries, Australia) and 2 frozen raspberries (Woolworths Frozen Mixed Berries, Australia)
Dried fruits	Prune, fig, raisin (half-dried prune (Sunsweet Prunes Pitted, Grocery Corporation Pty. Ltd, Australia)), 3 raisins (Macro, Australia)
Confectionery	Candy, lolly, fruit drops (quarter raspberry drop (Allen's Ripe Raspberries Lollies, Australia))
Jammy	Fruit jam, stewed fruits (1 tsp Fruit of the Forest Jam (Cottee's, Australia) and Plum jam (Cottee's, Australia))
Green	Leafy, herbaceous, green capsicum (5 cm of fresh cut grass and 1 × 1 cm fresh green capsicum)
Chemical/medicinal	Band-aid, medicinal, barnyard (1 cm piece of band-aid (Leukoplast GMBH, Hamburg, Germany))
Mint/eucalypt	Mint (1 × 1 cm of fresh mint leaf and 1 × 1 cm fresh eucalyptus leaf)
Earthy	Earthy, mushrooms, forest floor (1 slice of fresh mushroom, pinch of potting soil)
Savoury	Savoury, meaty, soy sauce (0.2 g of beef stock powder (Continental, Unilever, Australia)), and a pinch of Vegemite (Vegemite, Australia)
Pepper	Pepper (a pinch of freshly ground black (G-Fresh, Australia)) and white pepper (McKenzie's, Australia)

Floral	Perfume, violet, rose (0.03 ml Natural Rosewater (Queen, Australia))
Smoky/toasty	Bushfire, charred wood (charred wood toothpick)
Spice	Sweet spice, allspice, liquorice (pinch fresh cinnamon (MasterFoods, Mars Food Australia)), and pinch allspice (Select, Woolworths Australia)
Cooked vegetables	1 tablespoon of canned sliced green bean juice plus 1 tablespoon of canned mixed vegetables (peas and carrots) (both Woolworths, Australia)
Wood	Raw wood, pencil shaving (a pinch of un-toasted oak chips)
Taste	
Bitter	Basewine 10 %, Base wine plus 0.8 g/L caffeine (Sigma-Aldrich, China) 60 %
Sweet	Basewine 20 %, 10 g/L Sucrose (Woolworths Homebrand, Australia) 90 %
Sour	1 g/L Tartaric acid (Merc, Australia) 10 %, 2 g/L Tartaric acid 90 %,
Overall fruit	No reference standard
Mouthfeel	
Astringency	10 % 0.3 g/L grape seed extract (Tarac Technologies, Australia)+0.5 g/L tartaric acid, 90 % 1.0 g/L grape seed extract+0.5 g/L tartaric acid
Body	Base wine 20 %, Base wine plus 0.1 g/L Xanthan gum (The Melbourne Food Ingredient Depot, Australia) 80 %
Tanning quality	Smooth to rough
Heat	10 % Base wine 13.5 %, 90 % Base wine plus 3 % EtOH (16.5 % in total)
Aftertaste	
Fruity aftertaste	Duration of any fruit aftertaste
Non-fruit	Duration of any non-fruit aftertaste (excluding astringency and basic tastes)

Table S6. Data block variables used in the vintage and four vintage supervised and non-supervised discriminant analysis and clustering models.

				Use in AMOPLS, *k*-means and machine learning models				
	Data block description	Variable number	Attribute	2018	2019	2020	2021	All Vintages
	1. Vine performance	1	Pruning shoot number	X	X	X	X	X
		2	Pruning weight m/kg	X	X	X	X	X
		3	Yield m/kg	X	X	X	X	X
		4	Bunch number	X	X	X	X	X
		5	Average bunch weight g	X	X	X	X	X
		6	Porosity	X	X	X	X	X
		7	Plant area index	X	X	X	X	X
	2. Crop maturation	8	Tannin	X	X			
		9	Tannin Mg/L epicatechin Eq	X	X		X	
		10	Tannin homogenate	X	X		X	
		11	Phenolics Mg/berry	X	X	X	X	X
		12	Phenolics Mg/g	X	X	X	X	X
		13	Anthocyanin Mg/berry	X	X	X	X	X
		14	Anthocyanin Mg/g	X	X	X	X	X
		15	Berry Wgt g	X	X	X	X	X
		16	pH (grape)	X	X	X	X	X
		17	Titratable acidity (grape)	X	X	X	X	X
		18	Brix	X	X	X	X	X
		19	Baume					
	3. Grape amino acids	20	Hydroxyproline	X	X	X	X	X
		21	Aspartic acid	X	X	X	X	X
		22	Asparagine	X	X	X	X	X
		23	Serine	X	X	X	X	X
		24	Glutamic acid	X	X	X	X	X
		25	Histidine	X	X	X	X	X
		26	Glutamine	X	X	X	X	X
		27	Glycine	X	X	X	X	X
		28	Arginine	X	X	X	X	X
		29	Threonine	X	X	X	X	X
		30	Beta-Alanine	X	X	X	X	X
		31	Alanine	X	X	X	X	X
		32	Proline	X	X	X	X	X
		33	gamma-Aminobutyric acid	X	X	X	X	X
		34	Cysteine					
		35	Tyrosine	X	X	X	X	X
		36	Valine	X	X	X	X	X
		37	Methionine	X	X	X	X	X
		38	Lysine	X	X	X	X	X
		39	Isoleucine	X	X	X	X	X
		40	Leucine	X	X	X	X	X

				Use in AMOPLS, *k*-means and machine learning models				
	Data block description	Variable number	Attribute	2018	2019	2020	2021	All Vintages
		41	Phenylalanine	X	X	X	X	X
	4. Grape bound volatiles	42	2-Ethenyltetrahydro-2,6,6-trimethyl-2H-pyran	X	X	X	X	X
		43	p-Xylene (gbv)	X				
		44	4-Methyl-3-penten-2-one	X				
		45	m-Xylene (gbv)	X				
		46	o-Xylene (gbv)	X				
		47	3-Hexanone (gbv)	X	X	X	X	X
		48	3-Hexanol	X	X	X		
		49	Eucalyptol (gbv)	X	X	X		
		50	2-Hexanol	X	X	X	X	X
		51	(E)-2-Hexenal (gbv)	X	X	X	X	X
		52	2-Pentyl furan	X	X	X	X	X
		53	cis-Rose oxide	X	X	X	X	X
		54	Ethenyl benzene	X	X			
		55	2,4-Hexanedione		X	X		
		56	1,3-Dimethyl-1-cyclohexene	X	X	X	X	X
		57	1-Hexanol (gbv)	X	X	X	X	X
		58	(E)-3-Hexen-1-ol (gbv)		X	X	X	
		59	Cyclohexanol		X	X	X	
		60	4-Methoxy-1,3-benzenediamine	X				
		61	Linalool oxide 1	X	X	X	X	X
		62	Alpha-Ionene	X	X	X	X	X
		63	3,4,5-Trimethylpyrazole	X				
		64	Linalool oxide 2	X	X	X	X	X
		65	Benzaldehyde (gbv)	X	X	X	X	X
		66	Vitispirane	X	X	X	X	X
		67	1-(2,4-Dimethyl-3-furyl)ethanone	X	X			
		68	3-Methyl-4-heptanone (gbv)		X			
		69	2-Methyl-2-butanol (gbv)	X	X			
		70	2-Hexanone		X			
		71	4-Methyl-2-pentanol	X	X			
		72	Unk monoterpene 1		X	X	X	
		73	4-Methyl-benzaldehyde	X	X	X	X	X
		74	Ocimenol	X	X	X	X	X
		75	alpha-Fenchene	X	X	X	X	X
		76	8-Methyl-tricyclo[3.3.0.0(2,8)]octan-3-one		X	X	X	
		77	4-Oxoisophorone	X	X	X	X	X
		78	Alpha-Terpineol	X	X	X	X	X
		79	1,1,4,6,7-Pentamethyl-2,3-dihydroindene	X	X	X	X	X
		80	1,2-Dihydro-1,1,6-trimethyl-naphthalene	X	X	X	X	X
		81	Methyl salicylate		X	X	X	

Data block description	Variable number	Attribute	Use in AMOPLS, *k*-means and machine learning models				
			2018	2019	2020	2021	All Vintages
	82	1,3-Dihydro-5-propyl-isobenzofuran	X	X	X	X	X
	83	Unknown 3 (gbv)		X	X	X	
	84	4-Ethyl-benzaldehyde	X	X	X	X	X
	85	Damascenone	X	X	X	X	X
	86	1-(2,4,6-Trimethylphenyl)buta-1,3-diene	X	X	X	X	X
	87	Octa-2,4,6-triene		X	X	X	
	88	2,5-Hexanediol		X	X	X	
	89	Para-cymen-8-ol		X	X	X	
	90	8-Hydroxycoumarin	X	X	X	X	X
	91	Guaiacol	X	X	X	X	X
	92	Hexanoic Acid (gbv)		X	X	X	
	93	Benzyl alcohol (gbv)	X	X	X	X	X
	94	1,1,6,8-Tetramethyl-1,2-dihydro-naphthalene	X	X			
	95	Unknown 4 (gbv)		X			
	96	alpha-Calacorene	X	X	X	X	X
	97	Unknown 5 (gbv)		X	X		
	98	1-[4-(1-Hydroxy-1-methylethyl)phenyl]-ethanone	X	X	X	X	X
	99	3-(2,6,6-Triimethyl-1-cyclohexen-1-yl)-2-propenal	X	X	X	X	X
	100	2-Isopentyl-1,3,5-trimethylbenzene	X	X	X	X	X
	101	Benzothiazole		X	X	X	
	102	2,2-Dimethyl-3,3-(1'2'-ethylidene)-5-methyl-1,2-dihydrobenzofuran	X	X	X	X	X
	103	2-Ethylhexanoic acid		X	X	X	
	104	Heptanoic acid		X	X	X	
	105	1,2-Dihydro-2,5,8-trimethyl-naphthalene	X	X	X	X	X
	106	Unknown 6 (gbv)		X			
	107	4-(2,6,6-Trimethylcyclohexa-1,3-dienyl)but-3-en-2-one	X	X	X	X	X
	108	Unknown 1 (gbv)	X	X	X	X	X
	109	1,2-Dihydro-1,4,6-trimethyl-naphthalene	X	X	X	X	X
	110	2-Methylenebornane	X	X	X	X	X
	111	1,2-Dihydro-3,5,8-trimethyl-naphthalene,	X	X	X	X	X
	112	1-Nonadecene		X	X		
	113	Octahydro-1,1-dimethyl-7H-benzocyclohepten-7-one		X	X	X	
	114	Octanoic acid		X	X	X	
	115	1-(2,3,6-Trimethylphenyl)-3-buten-2-one	X	X	X	X	X
	116	7-Methyl-1-naphthol	X	X	X	X	X
	117	Ethyl 4-ethoxybenzoate	X	X	X	X	X
	118	2-Methyl-2-decanol	X	X	X	X	X
	119	Nonanoic acid		X	X	X	

	Data block description	Variable number	Attribute	Use in AMOPLS, *k*-means and machine learning models: 2018	2019	2020	2021	All Vintages
		120	1,2-Dihydro-4,6,8-trimethyl-naphthalene,	X	X			
		121	2-Hydroxy-5-methylacetophenone	X	X		X	
		122	4-(2,6,6-Trimethyl-2-cyclohexen-1-yl)-3-buten-2-ol	X	X	X	X	X
		123	1-(2,3,6-Trimethylphenyl)-2-butanone	X	X	X	X	X
		124	Unknown 7 (gbv)		X	X	X	
		125	1-Docosene		X	X	X	
		126	Megastigmatrienone	X	X	X	X	X
		127	2,3-Dihydro-3,3,4,5-tetramethyl-1H-Inden-1-one	X	X	X	X	X
		128	Decanoic acid (gbv)		X	X	X	
		129	2,3-Dimethyl-4-amino-1,4-benzoquinone	X	X	X	X	X
		130	2,4-bis(1,1-Dimethylethyl)-phenol	X	X	X	X	X
		131	4-(2,4,6-Trimethylphenyl)-butan-2-ol(1)	X	X	X	X	X
		132	4-(2,3,6-Trimethylphenyl)-2--butanone	X	X	X	X	X
		133	2-Methyl-2-dodecanol		X	X	X	
		134	4-Vinylphenol	X	X	X	X	X
		135	4-(2,4,6-Trimethylphenyl)-butan-2-ol(2)		X	X	X	
		136	(Z)-5-Methyl-4-phenyl-3-hexen-2-ol	X	X	X	X	X
		137	Dodecanoic acid		X	X	X	
		138	2,3-Dihydro-2,4,7-trimethyl-1H-indene-2-methanol	X	X	X	X	X
		139	Benzoic acid		X		X	
		140	3-Hydroxy-beta-damascone	X	X		X	
		141	Methyl vanillate	X	X	X	X	X
		142	3-Oxo-alpha-ionol	X	X	X	X	X
		143	Butyl benzoate	X	X	X	X	X
		144	7,9-di-tert-butyl-1-oxaspiro[4,5]deca-6,9-diene-2,8-dione		X			
		145	Methyl 2-hydroxy-4-methylbenzoate	X	X	X	X	X
		146	Vanillyl acetone		X	X		
		147	Methyl syringate	X	X	X	X	X
	5. Grape carotenoids	148	Neoxanthin	X	X	X	X	X
		149	Lutein	X	X	X	X	X
		150	Zeaxanthin	X	X	X	X	X
		151	Chlorophyll B	X	X	X	X	X
		152	Chlorophyll A	X	X	X	X	X
		153	Beta-Carotene	X	X	X	X	X
		154	Unknown 1 (gc)	X	X	X	X	X
		155	Unknown 2 (gc)	X	X	X	X	X
		156	Pheophytin B	X	X	X	X	X

				Use in AMOPLS, *k*-means and machine learning models				
	Data block description	Variable number	Attribute	2018	2019	2020	2021	All Vintages
		157	Pheophytin A	X	X	X	X	X
		158	Total carotenoids	X	X	X	X	X
		159	Glutathione ug g	X	X	X	X	X
		160	Pantothenate ng g	X	X	X	X	X
		161	Pyridoxine ng g	X	X	X	X	X
	6. Grape fatty acids	162	Methyl dodecanoate	X	X	X	X	X
		163	Methyl tridecanoate	X	X	X	X	X
		164	Methyl tetradecanoate	X	X	X	X	X
		165	Methyl pentadecanoate	X	X	X	X	X
		166	Methyl (*Z*)-9-hexadecenoate	X	X	X	X	X
		167	Methyl heptadecanoate	X	X	X	X	X
		168	Methyl (Z)-10-heptadecenoate	X	X	X	X	X
		169	Methyl nonadecanoate	X	X	X	X	X
		170	Methyl 2-hydroxyhexadecanoate	X	X	X	X	X
		171	Methyl eicosanoate	X	X	X	X	X
		172	Methyl (*Z*)-13-eicosanoate	X	X	X	X	X
		173	Methyl heneicosanoate	X	X	X	X	X
		174	Methyl (*Z*,*Z*,*Z*)-11,14,17-eicosatrienoate	X	X	X	X	X
		175	Methyl docosanoate	X	X	X	X	X
		176	Methyl (Z)-13-docosenoate	X	X	X	X	X
		177	Methyl tricosanoate	X	X	X	X	X
		178	Methyl tetracosanoate	X	X	X	X	X
		179	Methyl pentacosanoate	X	X	X	X	X
		180	Methyl hexacosanoate	X	X	X	X	X
		181	Methyl heptacosanoate	X	X	X	X	X
		182	Methyl octacosanoate	X	X	X	X	X
		183	Methyl 2-hydroxy-tetracosanoate	X	X	X	X	X
		184	Methyl triacontanoate	X	X	X	X	X
		185	Methyl hexadecanoate	X	X	X	X	X
		186	Methyl octadecanoate	X	X	X	X	X
		187	Methyl (Z)-9-octadecenoate	X	X	X	X	X
		188	Methyl (E)-9-octadecenoate	X	X	X	X	X
		189	Methyl (Z,Z)-9,12-octadecenoate	X	X	X	X	X
		190	Methyl (Z,Z,Z)-9,12,15-octadecenoate	X	X	X	X	X
	7. Grape volatiles	191	Ethyl acetate (grape vol.)	X	X	X	X	X
		192	2-Butanone	X	X	X	X	X
		193	2-Methyl butanal	X	X	X	X	X
		194	3-Methyl butanal	X	X	X	X	X
		195	1-Methoxy-hexane	X	X	X	X	X
		196	2-Ethyl-furan	X	X	X	X	X
		197	2-Methyl-3,4-dihydro-2H-pyran	X	X	X	X	X
		198	2,5-Dimethyloctane	X	X		X	

Data block description	Variable number	Attribute	Use in AMOPLS, *k*-means and machine learning models				
			2018	2019	2020	2021	All Vintages
	199	2,6-Dimethyloctane	X	X	X	X	X
	200	Pentanal	X	X	X	X	X
	201	Methyl butanoate	X	X	X	X	X
	202	Methyl glycolate	X	X	X	X	X
	203	Decane	X	X	X	X	X
	204	1-Methoxycyclohexane	X	X	X	X	X
	205	alpha-Pinene	X	X	X	X	X
	206	1-Penten-3-one	X	X	X	X	X
	207	4-Heptanone	X	X	X	X	X
	208	Methylbenzene	X	X	X	X	X
	209	2-Butenal	X	X	X	X	X
	210	Hexanal	X	X	X	X	X
	211	Ethylbenzene	X	X	X	X	X
	212	2-Pentenal	X	X	X	X	X
	213	2-n-Butyl furan	X	X	X	X	X
	214	p-Xylene (grape vol.)	X	X	X	X	X
	215	3-Hexenal	X	X	X	X	X
	216	1-Butanol	X	X	X	X	X
	217	1-Penten-3-ol	X	X	X	X	X
	218	Dimethoxyhexane	X	X			
	219	3-Ethylthiophene	X	X	X	X	X
	220	Heptanal	X	X	X	X	X
	221	Methyl hexanoate	X	X	X	X	X
	222	Limonene (grape vol.)	X	X	X	X	X
	223	Cyclohexene oxide	X	X	X	X	X
	224	Eucalyptol (grape vol.)	X	X	X	X	X
	225	IsoamylAlcohol	X	X	X		
	226	(E)-2-Hexenal (grape vol.)	X	X	X	X	X
	227	Pentylfuran	X	X	X	X	X
	228	1-Pentanol	X	X	X	X	X
	229	3-Octanone	X	X	X	X	X
	230	Styrene	X	X	X	X	X
	231	Hexyl acetate (grape vol.)	X	X	X	X	X
	232	1-Octen-3-one	X	X			
	233	Hydroxy2butanone	X	X			
	234	Octanal	X	X	X	X	X
	235	Octen3one	X	X	X	X	X
	236	2,2,6-Trimethyl-cyclohexanone	X	X	X	X	X
	237	(Z)-Hexenyl acetate	X	X	X	X	X
	238	(Z)-2-Penten-1-ol	X	X		X	
	239	(E)-2-Heptenal	X	X	X	X	X
	240	Vinyl caproate	X	X	X	X	X
	241	3-Ethoxypentane	X	X	X	X	X
	242	6-Methyl-5-hepten-2-one	X	X	X	X	X
	243	1-Hexanol (grape vol.)	X	X	X	X	X

Data block description	Variable number	Attribute	Use in AMOPLS, *k*-means and machine learning models				
			2018	2019	2020	2021	All Vintages
	244	(E)-3-Hexen-1-ol (grape vol.)	X	X	X	X	X
	245	(Z)-3-Hexen-1-ol	X	X	X	X	X
	246	Nonanal	X	X	X	X	X
	247	2,4-Hexadienal	X	X	X	X	X
	248	(E)-2-Hexen-1-ol	X	X	X	X	X
	249	(Z)-2-Hexen-1-ol	X	X	X	X	X
	250	2,2,6-Trimethyl-4-methylene-2H-pyran	X	X	X	X	X
	251	(E)-2-Octenal	X	X	X	X	X
	252	Ethyl octanoate (grape vol.)	X	X	X	X	X
	253	(E)-Linalool oxide	X	X	X	X	X
	254	1-Octen-3-ol	X	X	X	X	X
	255	1-Heptanol	X	X	X	X	X
	256	(E,Z)-2,4-Heptadienal	X	X	X	X	X
	257	Furfural (grape vol.)	X		X	X	
	258	Acetic acid (grape vol.)	X	X	X	X	X
	259	2-Ethyl-1-hexanol	X	X	X	X	X
	260	(E,E)-2,4-Heptadienal	X	X	X	X	X
	261	Decanal	X	X	X	X	X
	262	Theaspirane A	X	X	X	X	X
	263	Benzaldehyde (grape vol.)	X	X	X	X	X
	264	(E)-2-Nonenal	X	X	X	X	X
	265	Theaspirane B	X	X	X	X	X
	266	2,5-Dihydro-thiophene	X	X	X	X	X
	267	Linalool (grape vol.)	X	X	X	X	X
	268	1-Octanol	X	X	X	X	X
	269	5-Methyl-2-furfural	X	X	X	X	X
	270	5,6-Dihydro-2H-pyran-2-carboxaldehyde	X	X	X	X	X
	271	(E)-2-Octen-1-ol	X	X	X	X	X
	272	beta-Cyclocitral	X	X	X	X	X
	273	gamma-Butyrolactone	X	X	X	X	X
	274	Phenylacetaldehyde (grape vol.)	X	X	X	X	X
	275	1-Hepten-3-one	X	X	X	X	X
	276	2-Furanmethanol	X		X	X	
	277	Humulene	X	X	X	X	X
	278	Diethyl succinate	X	X	X	X	X
	279	gamma-Terpineol	X	X	X	X	X
	280	(E,E)-2,4-Nonadienal	X	X	X	X	X
	281	Dodecane-6,7-dione	X	X	X	X	X
	282	Pentanoic Acid	X		X		
	283	beta-Cadinene	X	X	X	X	X
	284	5-Ethyl-2(5H)-furanone	X	X	X	X	X
	285	2-Phenylethyl acetate (grape vol.)	X		X	X	
	286	beta-Damascenone	X	X	X	X	X
	287	Hexanoic acid (grape vol.)	X	X	X	X	X

				Use in AMOPLS, *k*-means and machine learning models				
	Data block description	Variable number	Attribute	2018	2019	2020	2021	All Vintages
		288	Benzyl alcohol (grape vol.)	X	X	X	X	X
		289	Phenylethyl alcohol	X	X	X	X	X
		290	Methyl 2-oxo-hexanoate	X	X	X	X	X
		291	Phenol	X	X	X	X	X
	8. Grape phenolics	292	Delphinidin-3-glucoside (grape)	X	X	X	X	X
		293	Cyanidin-3-glucoside (grape)	X	X	X	X	X
		294	Petunidin-3-glucoside (grape)	X	X	X	X	X
		295	Peonidin-3-glucoside (grape)	X	X	X	X	X
		296	Malvidin-3-glucoside (grape)	X	X	X	X	X
		297	Delphinidin-3-acetyl-glucoside (grape)	X	X	X	X	X
		298	Cyanidin-3-acetyl-glucoside (grape)	X	X	X	X	X
		299	Petunidin-3-acetyl-glucoside (grape)	X	X	X	X	X
		300	Peonidin-3-acetyl-glucoside (grape)	X	X	X	X	X
		301	Malvidin-3-acetyl-glucoside (grape)	X	X	X	X	X
		302	Delphinidin-3-coumaroyl-glucoside (grape)	X	X	X	X	X
		303	Petunidin-3-caffeoyl-glucoside (grape)	X	X	X	X	X
		304	Cyanidin-3-coumaroyl-glucoside + malvidin-3-caffeoyl-glucoside (grape)	X	X	X	X	X
		305	Petunidin-3-coumaroyl-glucoside (grape)	X	X	X	X	X
		306	Peonidin-3-coumaroyl-glucoside (grape)	X	X	X	X	X
		307	Malvidin-3-coumaroyl-glucoside (grape)	X	X	X	X	X
		308	Total anthocyanin (by HPLC (grape))	X	X	X	X	X
		309	Extractable tannin (as mg/g berry weight (grape))	X	X	X	X	X
		310	Extractable anthocyanin (as mg/g berry weight (grape))	X	X	X	X	X
	9. Grape tannin	311	Epigallocatechin extension	X	X	X	X	X
		312	Catechin extension	X	X	X	X	X
		313	Epicatechin extension	X	X	X	X	X
		314	Epicatechin gallate extension	X	X	X	X	X
		315	Catechin terminal	X	X	X	X	X
		316	Epicatechin terminal	X	X	X	X	X
		317	Epicatechin gallate terminal	X	X	X	X	X
		318	Total tannins mg	X	X	X	X	X
		319	Degree of polymerisation	X	X	X	X	X
		320	Epigallocatechin extension %	X	X	X	X	X
		321	Catechin extension %	X	X	X	X	X
		322	Epicatechin extension %	X	X	X	X	X
		323	Epicatechin gallate extension %	X	X	X	X	X
		324	Catechin terminal %	X	X	X	X	X

				Use in AMOPLS, *k*-means and machine learning models				
	Data block description	Variable number	Attribute	2018	2019	2020	2021	All Vintages
		325	Epicatechin terminal %	X	X	X	X	X
		326	Epicatechin gallate terminal %	X	X	X	X	X
	10. Wine basic chemistry	327	Alcohol	X	X	X	X	X
		328	Glucose+Fructose	X	X	X	X	X
		329	Specific gravity	X	X	X	X	X
		330	pH (wine)	X	X	X	X	X
		331	Titratable acidity (pH8.2)	X	X	X	X	X
		332	Volatile acidity	X	X	X	X	X
		333	Free sulfur dioxide	X	X	X	X	X
		334	Total sulfur dioxide	X	X	X	X	X
		335	Titratable acidity (pH7.0)		X	X	X	
		336	Malic Acid		X	X	X	
	11. Wine metals	337	Calcium	X	X	X	X	X
		338	Chromium	X	X	X	X	X
		339	Cobalt	X	X	X	X	X
		340	Copper	X				
		341	Iron	X	X	X	X	X
		342	Lead	X	X	X	X	X
		343	Lithium	X	X	X	X	X
		344	Magnesium	X	X	X	X	X
		345	Manganese	X	X	X	X	X
		346	Nickel	X	X	X	X	X
		347	Potassium	X	X	X	X	X
		348	Sodium	X	X	X	X	X
		349	Strontium	X	X	X	X	X
		350	Zinc	X	X	X	X	X
		351	Selenium				X	
	12. Wine phenolics & colour	352	Delphinidin-3-glucoside (wine)	X	X	X	X	X
		353	Cyanidin-3-glucoside (wine)	X	X			
		354	Petunidin-3-glucoside (wine)	X	X	X	X	X
		355	Peonidin-3-glucoside (wine)	X	X	X	X	X
		356	Malvidin-3-glucoside (wine)	X	X	X	X	X
		357	Vitisin A	X	X		X	
		358	Delphinidin-3-acetyl-glucoside (wine)	X	X	X	X	X
		359	Cyanidin-3-acetyl-glucoside (wine)	X	X			
		360	Petunidin-3-acetyl-glucoside (wine)	X	X	X	X	X
		361	Peonidin-3-acetyl-glucoside (wine)	X	X	X	X	X
		362	Malvidin-3-acetyl-glucoside (wine)	X	X	X	X	X
		363	Delphinidin-3-coumaroyl-glucoside (wine)	X		X	X	
		364	Peounidin-3-caffeoyl-glucoside (wine)	X	X			

Data block description	Variable number	Attribute	Use in AMOPLS, *k*-means and machine learning models				
			2018	2019	2020	2021	All Vintages
	365	Cyanidin-3-coumaroyl-glucoside+malvidin-3-caffeoyl-glucoside (wine)	X	X	X	X	X
	366	Petunidin-3-coumaroyl-glucoside (wine)	X	X	X	X	X
	367	Peonidin-3-coumaroyl-glucoside (wine)	X	X	X	X	X
	368	Malvidin-3-coumaroyl-glucoside (wine)	X	X	X	X	X
	369	Polymeric pigments	X	X	X	X	X
	370	Total anthocyanins (wine)	X	X	X	X	X
	371	Quercetin-3-glucuronide	X	X	X	X	X
	372	Syringetin-3-glucoside	X	X	X	X	X
	373	Myricetin	X	X	X	X	X
	374	Quercetin	X		X	X	
	375	Laricitrin	X	X			
	376	Kaempferol	X	X	X	X	X
	377	Isorhamnetin	X	X	X	X	X
	378	Chemical age-1	X	X	X	X	X
	379	Chemical age-2	X	X	X	X	X
	380	Wine colour density	X	X	X	X	X
	381	Wine colour density – sulfur dioxide corrected	X	X	X	X	X
	382	Hue – wine colour hue	X	X	X	X	X
	383	Ion % – anthocyanins in ionised form %	X	X	X	X	X
	384	Total phenolics	X	X	X	X	X
	385	Non-bleachable pigments	X	X	X	X	X
	386	Total tannin	X	X	X	X	X
	387	Tannin molecular mass by subunit composition	X	X	X	X	X
	388	Mean degree of polymerisation	X	X	X	X	X
	389	Trihydroxylation %	X	X	X	X	X
	390	Galloylation %	X	X	X	X	X
	391	Mass conversion %	X	X	X	X	X
	392	Epigallocatechin-phloroglucinol %	X	X	X	X	X
	393	Catechin-phloroglucinol %	X	X	X	X	X
	394	Epicatechin-phloroglucinol %	X	X	X	X	X
	395	Catechin %	X	X	X	X	X
	396	Epicatechin gallate – phloroglucinol %	X	X	X	X	X
	397	Epicatechin %	X	X	X	X	X
	398	Epicatechin gallate %	X	X	X	X	X
	399	Tannin molecular mass (50 % elution)	X		X	X	
	400	CIELab – L*	X	X	X	X	X
	401	CIELab – a*	X	X	X	X	X
	402	CIELab – b*	X	X	X	X	X

				Use in AMOPLS, *k*-means and machine learning models				
	Data block description	Variable number	Attribute	2018	2019	2020	2021	All Vintages
	13. Wine polysaccharides	403	Mannose	X	X	X	X	X
		404	Rhamnose	X	X	X	X	X
		405	Glucuronic acid	X	X	X	X	X
		406	Galacturonic acid	X	X	X	X	X
		407	Glucose	X	X	X	X	X
		408	Galactose	X	X	X	X	X
		409	Xylose	X	X	X	X	X
		410	Arabinose	X	X	X	X	X
		411	Fucose	X	X	X	X	X
		412	Total polysaccharides	X	X	X	X	X
		413	Proline mg L	X		X	X	
	14. Wine volatiles	414	2-methyl propyl acetate	X	X	X	X	X
		415	2-methyl butyl acetate	X	X	X	X	X
		416	3-methyl butyl acetate	X	X	X	X	X
		417	Hexyl acetate (wine vol.)	X	X	X	X	X
		418	2-methyl propanol	X	X	X	X	X
		419	Butanol	X	X	X	X	X
		420	2-methyl butanol	X	X	X	X	X
		421	3-methyl butanol	X	X	X	X	X
		422	Ethyl acetate (wine vol.)	X	X	X	X	X
		423	Ethyl propanoate	X	X	X	X	X
		424	Ethyl-2-methyl propanoate	X	X	X	X	X
		425	Ethyl butanoate	X	X	X	X	X
		426	Ethyl-2-methyl butanoate	X	X	X	X	X
		427	Ethyl-3-methyl butanoate	X	X	X	X	X
		428	Ethyl hexanoate	X	X	X	X	X
		429	Ethyl octanoate (wine vol.)	X	X	X	X	X
		430	Ethyl decanoate	X	X	X	X	X
		431	2-phenylethyl acetate (wine vol.)	X	X	X	X	X
		432	2-phenylethanol	X	X	X	X	X
		433	Propanoic acid	X		X	X	
		434	2-methyl propanoic acid	X		X	X	
		435	Butanoic acid	X	X	X	X	X
		436	2-methyl butanoic acid	X	X	X	X	X
		437	3-methyl butanoic acid	X	X	X	X	X
		438	Hexanoic acid (wine vol.)	X	X	X	X	X
		439	Octanoic acid (wine vol.)	X	X	X	X	X
		440	Decanoic acid (wine vol.)	X	X	X	X	X
		441	E2-Hexenol	X	X	X	X	X
		442	Z3-Hexenol	X	X	X	X	X
		443	Limonene (wine vol.)	X				
		444	1,8-Cineole	X	X	X	X	X
		445	Linalool (wine vol.)	X		X	X	

				Use in AMOPLS, *k*-means and machine learning models				
	Data block description	Variable number	Attribute	2018	2019	2020	2021	All Vintages
		446	(-)-cis-Rose oxide	X	X	X	X	X
		447	(-)-trans-Rose oxide	X	X		X	
		448	α-Terpineol	X	X	X	X	X
		449	β-Citronellol	X	X	X	X	X
		450	Nerol	X				
		451	Geraniol	X		X	X	
		452	β-Damascenone	X	X	X	X	X
		453	β-Ionone	X	X	X	X	X
		454	Carbon disulfide	X	X	X	X	X
		455	Dimethyl sulfide	X	X	X	X	X
		456	Hydrogen sulfide	X			X	
		457	Methanethiol	X	X	X	X	X
		458	Methyl thioacetate	X	X	X	X	X
		459	4-methyl-4-mercaptopentan-2-one	X				
		460	3-Mercaptohexan-1-ol	X	X	X	X	X
		461	3-mercaptohexylacetate	X	X	X	X	X
		462	2-Methylpropanal	X	X		X	
		463	3-Methylbutanal	X	X			
		464	E-2-Hexenal	X	X	X	X	X
		465	Methional	X	X		X	
		466	Phenylacetaldehyde (wine vol.)	X	X		X	
		467	E-2-Nonenal	X				
		468	Maltol	X	X	X		
		469	Eugenol	X		X	X	
		470	Benzaldehyde (wine vol.)	X	X	X	X	X
		471	Acetic Acid (wine vol.)		X	X	X	
		472	Hexanol		X	X	X	
		473	Unknown (wine vol.)		X	X	X	
		474	1,1,6,-trimethyl-1,2-dihydronapthalene		X	X	X	
		475	Furfural thiol		X			
		476	Furfural (wine vol.)		X	X	X	
	15. Wine sensory	477	LV1	X	X	X	X	X
		478	LV2	X	X	X	X	X
		479	LV3	X	X	X	X	X
		480	LV4	X	X	X	X	X
		481	LV5	X	X	X	X	X
			n =	438	453	433	438	383

Table S7. Subregion site replicate selection for models for each vintage. Shaded cells indicate a complete set of data in all data tables for that sample enabling selection for modelling for single and combined vintage models. Numbers in each cell indicate a unique sample index for each site and vintage combination for the duration of the investigation. The total number of *Subregion* site replicates modelled each year appear in the bottom row.

Region	Site	2018			2019			2020			2021		
		R1	R2	R3	R1	R2	R3	R1	R2	R3	R1	R2	R3
Northern grounds	SR1	1	2	3	76	77	78	151	152	153	226	227	228
Northern grounds	SR2	4	5	6	79	80	81	154	155	156	229	230	231
Northern grounds	SR3	7	8	9	82	83	84	157	158	159	232	233	234
Northern grounds	SR4	10	11	12	85	86	87	160	161	162	235	236	237
Central grounds	SR5	13	14	15	88	89	90	163	164	165	238	239	240
Central grounds	SR6	16	17	18	91	92	93	166	167	168	241	242	243
Central grounds	SR7	19	20	21	94	95	96	169	170	171	244	245	246
Central grounds	SR8	22	23	24	97	98	99	172	173	174	247	248	249
Eastern edge	SR9	25	26	27	100	101	102	175	176	177	250	251	252
Eastern edge	SR10	28	29	30	103	104	105	178	179	180	253	254	255
Eastern edge	SR11	31	32	33	106	107	108	181	182	183	256	257	258
Eastern edge	SR12	34	35	36	109	110	111	184	185	186	259	260	261
Southern grounds	SR13	37	38	39	112	113	114	187	188	189	262	263	264
Southern grounds	SR14	40	41	42	115	116	117	190	191	192	265	266	267
Southern grounds	SR15	43	44	45	118	119	120	193	194	195	268	269	270
Southern grounds	SR16	46	47	48	121	122	123	196	197	198	271	272	273
Western ridge	SR17	49	50	51	124	125	126	199	200	201	274	275	276

	Western ridge	SR18	52	53	54	127	128	129	202	203	204	277	278	279
	Western ridge	SR19	55	56	57	130	131	132	205	206	207	280	281	282
	Western ridge	SR20	58	59	60	133	134	135	208	209	210	283	284	285
	Eden valley	SR21	61	62	63	136	137	138	211	212	213	286	287	288
	Eden valley	SR22	64	65	66	139	140	141	214	215	216	289	290	291
	Eden valley	SR23	67	68	69	142	143	144	217	218	219	292	293	294
	Eden valley	SR24	70	71	72	145	146	147	220	221	222	295	296	297
	Eastern edge	SR25	73	74	75	148	149	150	223	224	225	298	299	300
		n =	61			65			56			58		

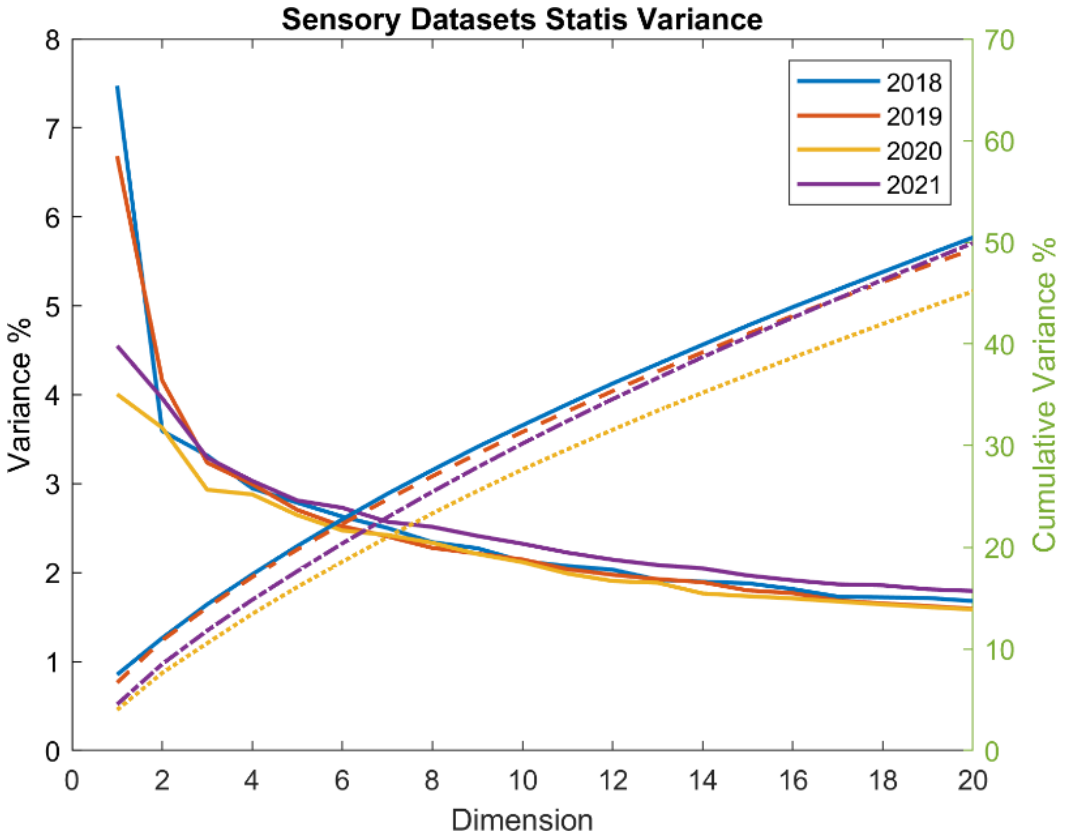


Figure S1. Variance and cumulative variance for each dimension for sensory data sets for vintages 2018 to 2021. Five latent variables were chosen to represent the consensus space for each vintage.

Table S8. AMOPLS model relative sums of squares for explanatory factors, Residual Structure Ratio indices and *p*-values for each effect.

Model	Explanatory Factor (EF)	EF *p*-value	Relative Sum of Squares	RSR
All Vintages 2018-2021	Vintage	$p = 0.0001$	0.4051	2.7047
	Subregion	$p = 0.0001$	0.0640	1.1620
	Residuals		0.5309	1.0000
2018	Subregion	$p = 0.0001$	0.2115	1.7863
	Site	$p = 0.0001$	0.4199	2.1125
	Residuals		0.3686	1.0000
2019	Subregion	$p = 0.0001$	0.2504	2.2019
	Site	$p = 0.0001$	0.4269	2.3458
	Residuals		0.3226	1.0000
2020	Subregion	$p = 0.0001$	0.2045	2.0829
	Site	$p = 0.0001$	0.4353	2.4831
	Residuals		0.3197	1.0000
2021	Subregion	$p = 0.0001$	0.2636	2.0829
	Site	$p = 0.0001$	0.4253	2.3292
	Residuals		0.3111	1.0000

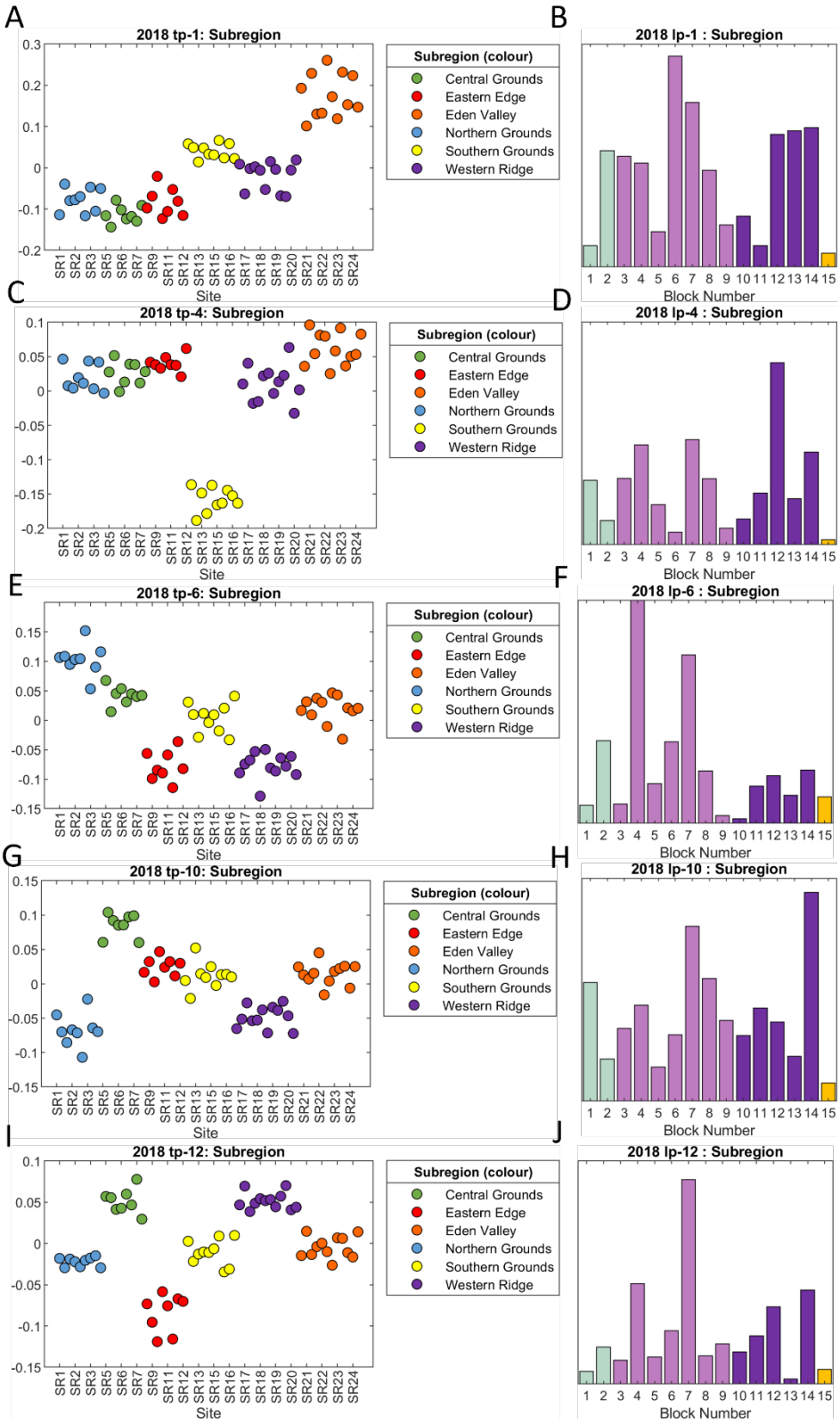


Figure S2. Subregion predictive scores (tp) from the AMOPLS model of 2018 data for Eden valley (A: tp–1), Southern grounds (C; tp–4); Northern grounds (E: tp–6); Central grounds (G: tp–10), and Eastern edge (I: tp–12). Data block contributions to each predictive score associated with identified subregions are shown on the right in panels B, D, F, H, & J. Data block numbers correspond to Table 1 of the manuscript.

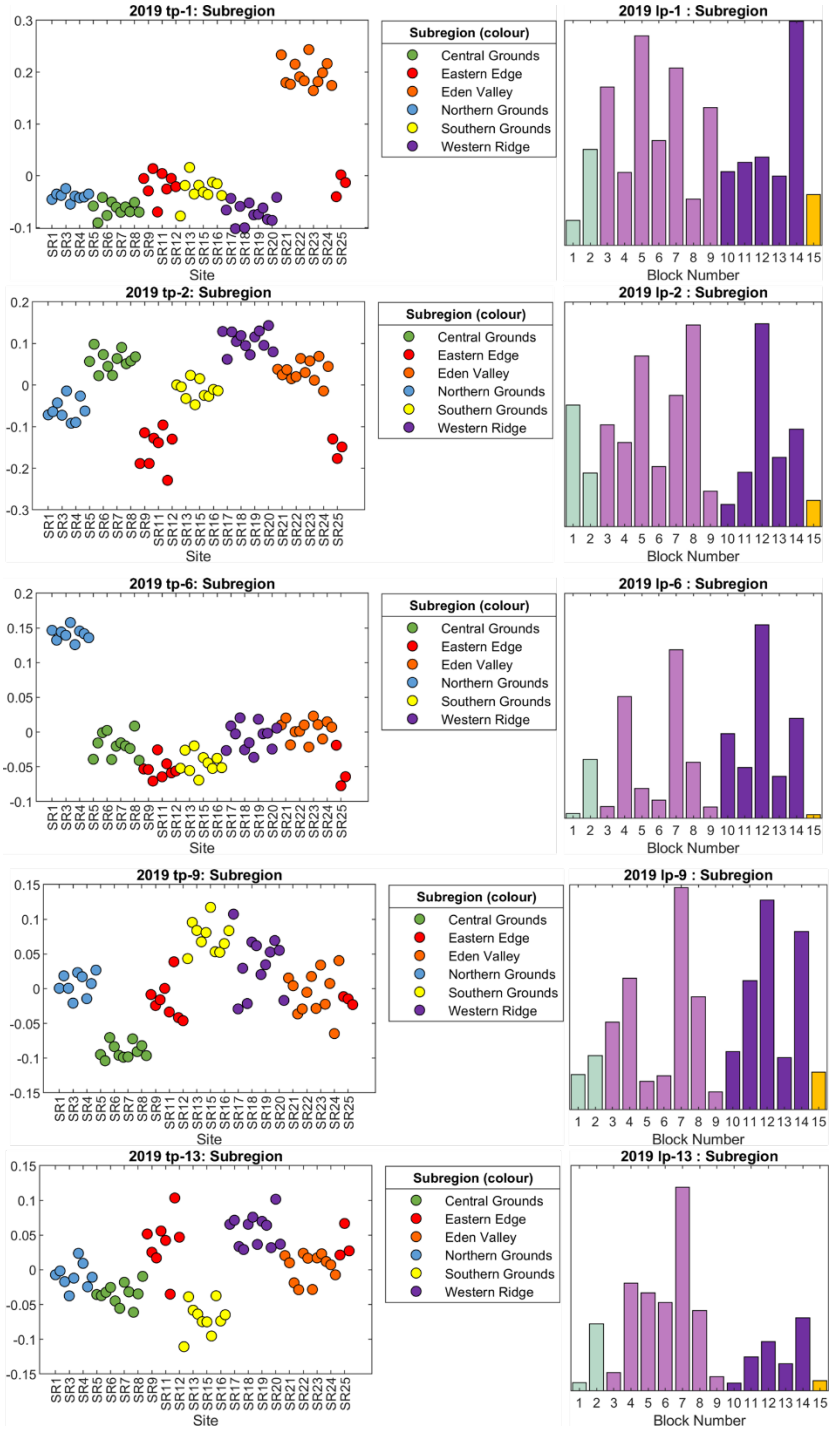


Figure S3. Subregion predictive scores (tp) from the AMOPLS model of 2019 data for Eden valley (tp–1); Eastern edge (tp–2); Northern grounds (tp–6); Central grounds (tp–9) and Southern grounds (tp–13). Data block contributions to each predictive score associated with identified subregions are shown on the right. Data block numbers correspond to Table 1 of the manuscript.

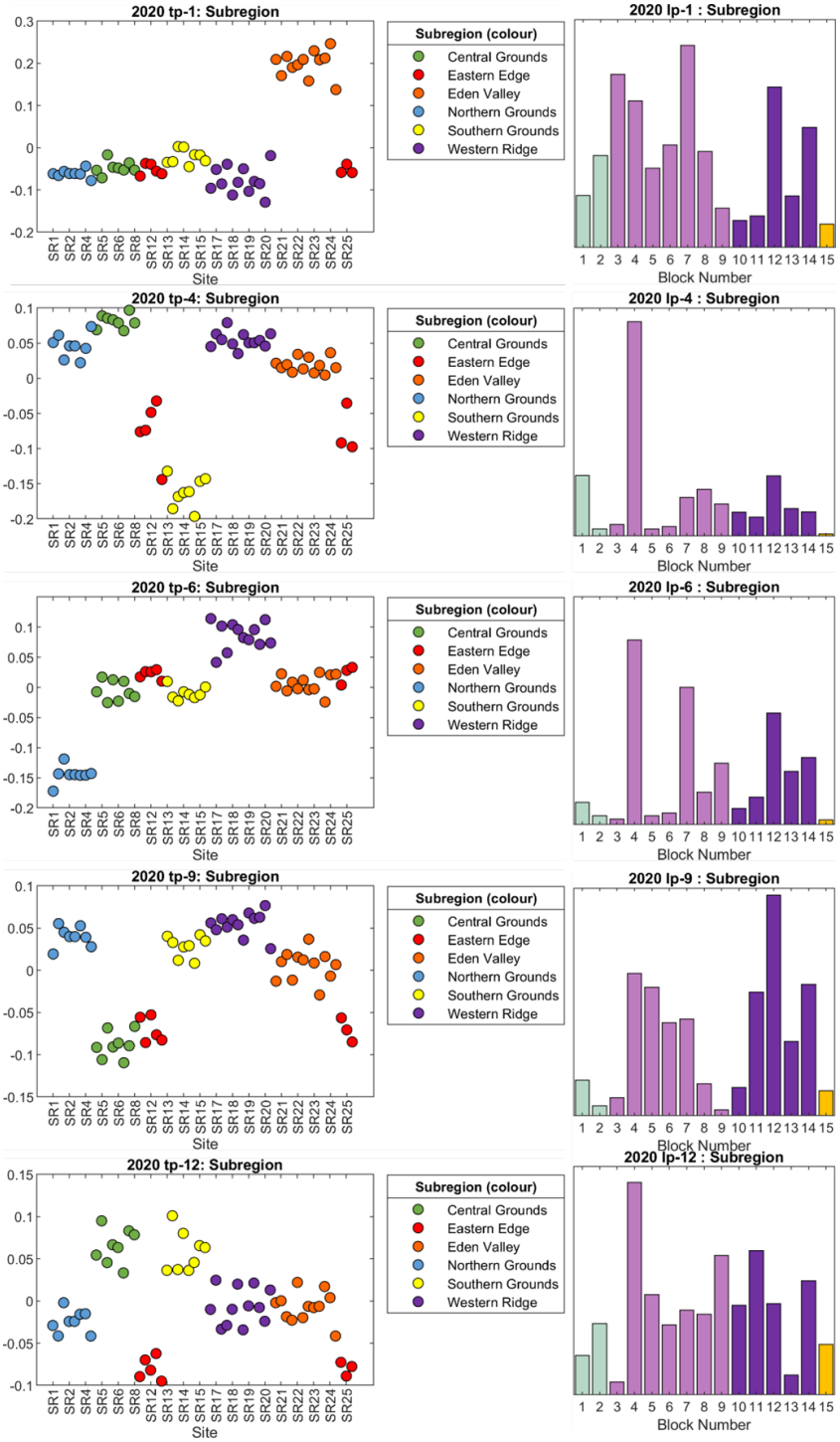


Figure S4. Subregion predictive scores (tp) from the AMOPLS model of 2020 data for Eden valley (tp–1); Southern grounds (tp–4); Northern grounds (tp–6); combined Central grounds and Eastern edge (tp–9) and Eastern edge (tp–12). Data block contributions to each predictive score associated with identified subregions are shown on the right. Data block numbers correspond to Table 1 of the manuscript.

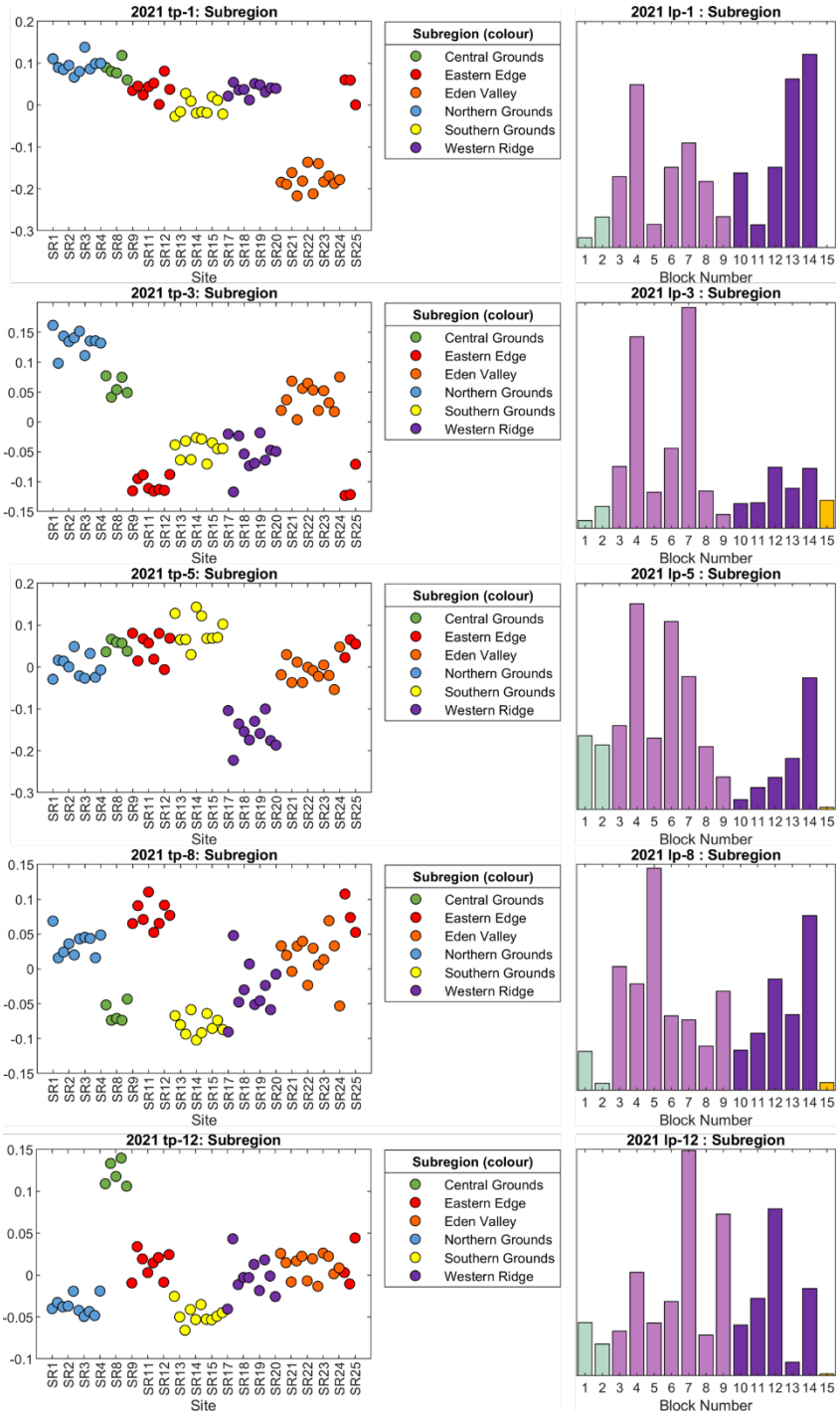


Figure S5. Subregion predictive scores (tp) from the AMOPLS model of 2021 data for Eden valley (tp–1), Northern grounds (tp–3); Western ridge (tp–5); Eastern edge (tp–8), and Central grounds (tp–12). Data block contributions to each predictive score associated with identified subregions are shown on the right. Data block numbers correspond to Table 1 of the manuscript.

Table S9. Mean growing degree days for sites in Barossa Grounds subregions for each vintage of the investigation.

Region	2018	2019	2020	2021
Central grounds	2169	2140	1916	1871
Eastern edge	2056	2033	1799	1754
Eden valley	1973	1946	1711	1662
Northern grounds	2128	2109	1878	1829
Southern grounds	2200	2167	1946	1896
Western ridge	2161	2137	1909	1863

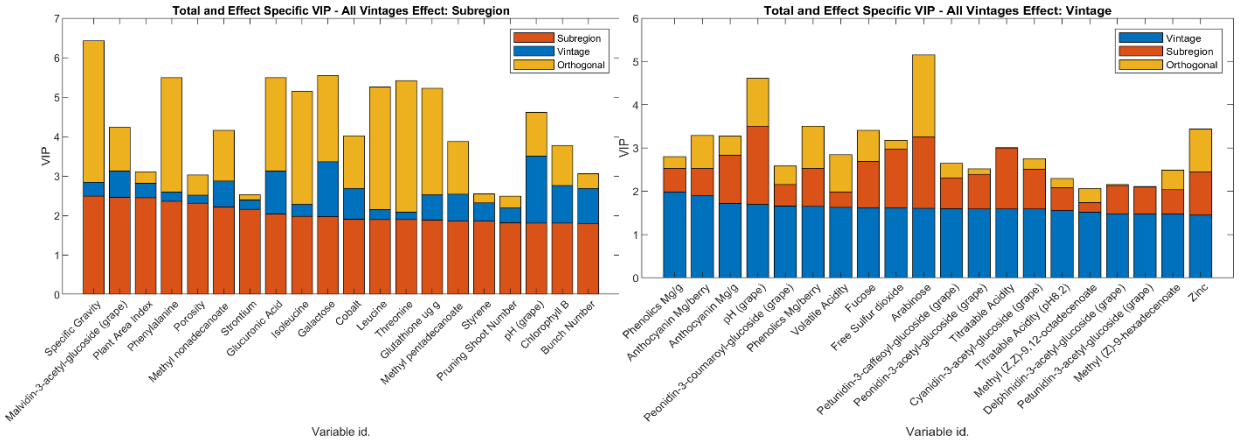


Figure S6. Variable importance to projection (VIP) scores for explanatory factors '*Vintage*' (left) and '*Subregion*' (right) for the four vintage AMOPLS model. Contributions of each variable to either 'Vintage', 'Region' or the extracted orthogonal components are illustrated. Influential variables typically have VIP scores greater than one for any EF.

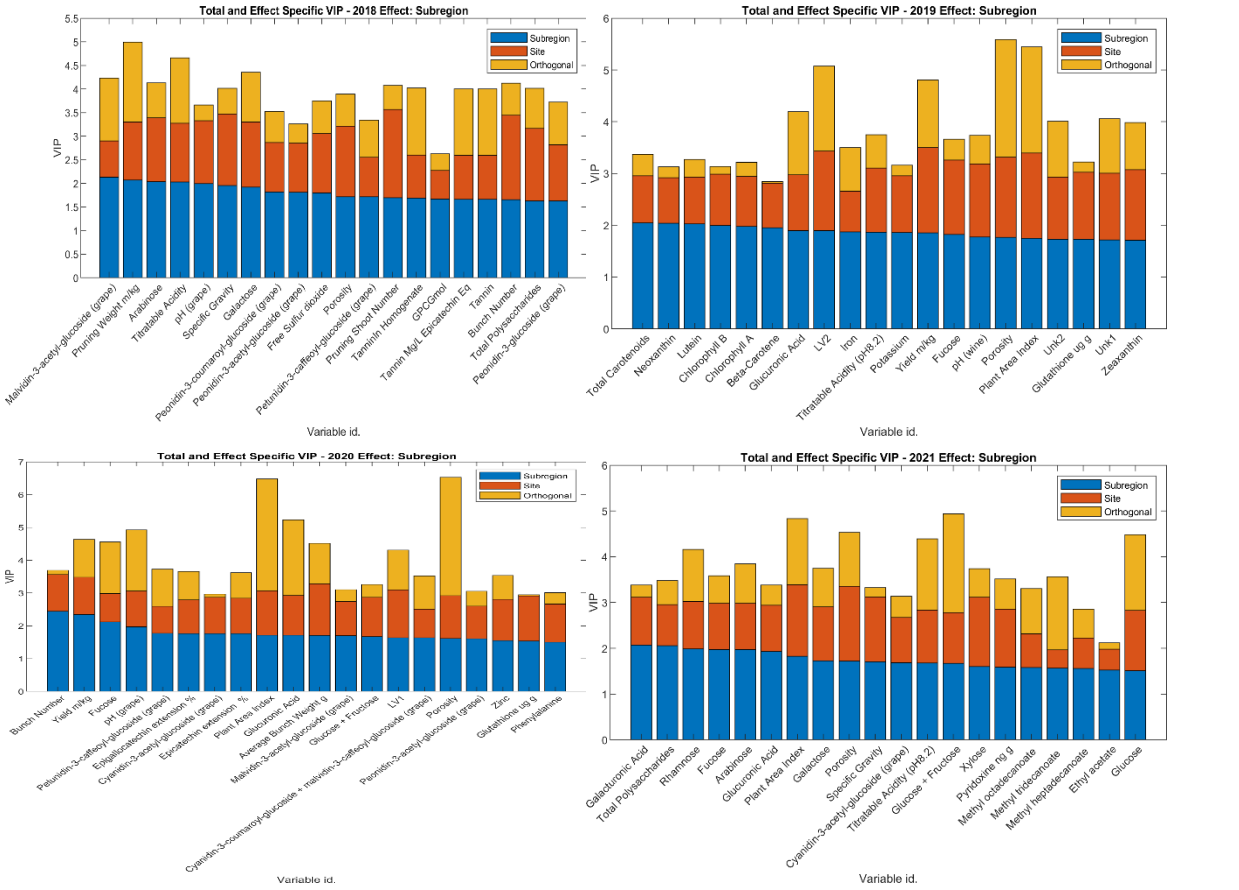
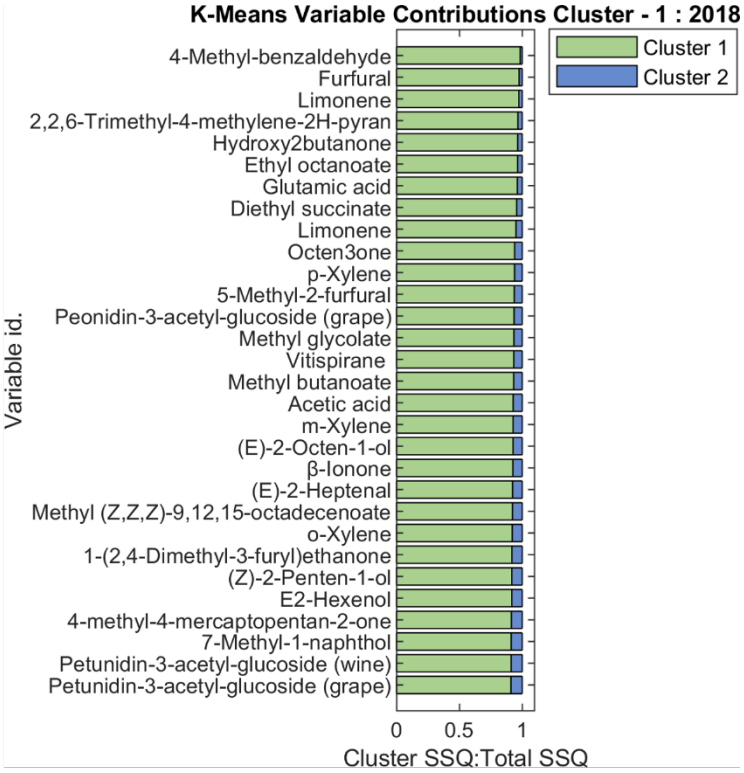


Figure S7. Variable importance to projection (VIP) scores for the explanatory factors '*Subregion*' for the 2018–2021 vintage AMOPLS model. Contributions of each variable to either 'Region', 'Site' or the extracted orthogonal components are illustrated. Influential variables typically have VIP scores greater than one for any EF.



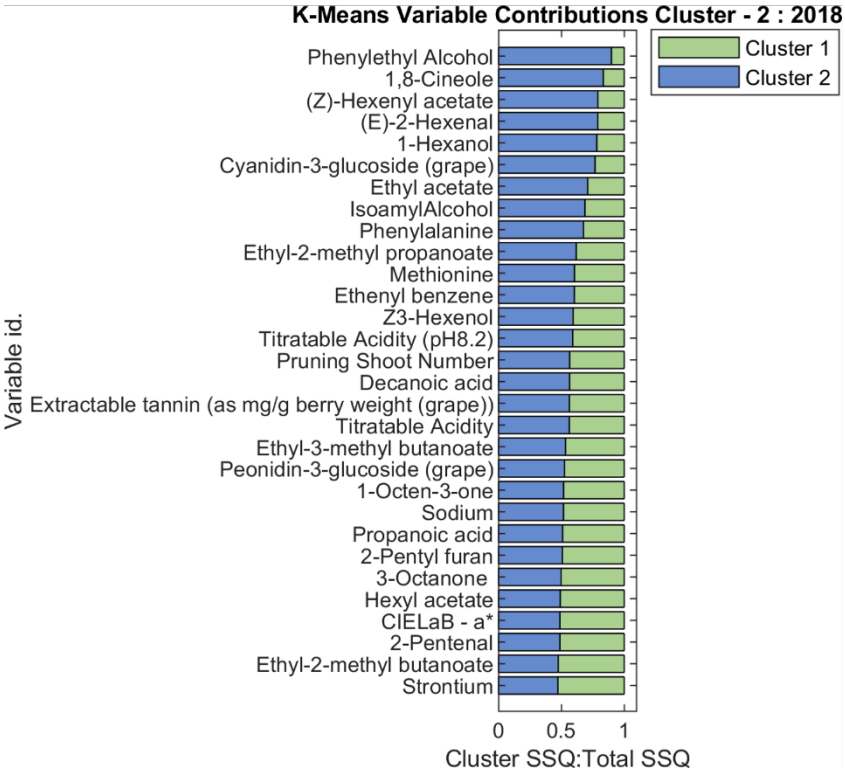


Figure S8. Variable importance of the thirty most influential attributes for *k*-means clusters for vintage 2018. Variable importance to a specific is shown as a ratio of the sum of squares for samples in each cluster to the sum of squares of all samples for the measured attribute.

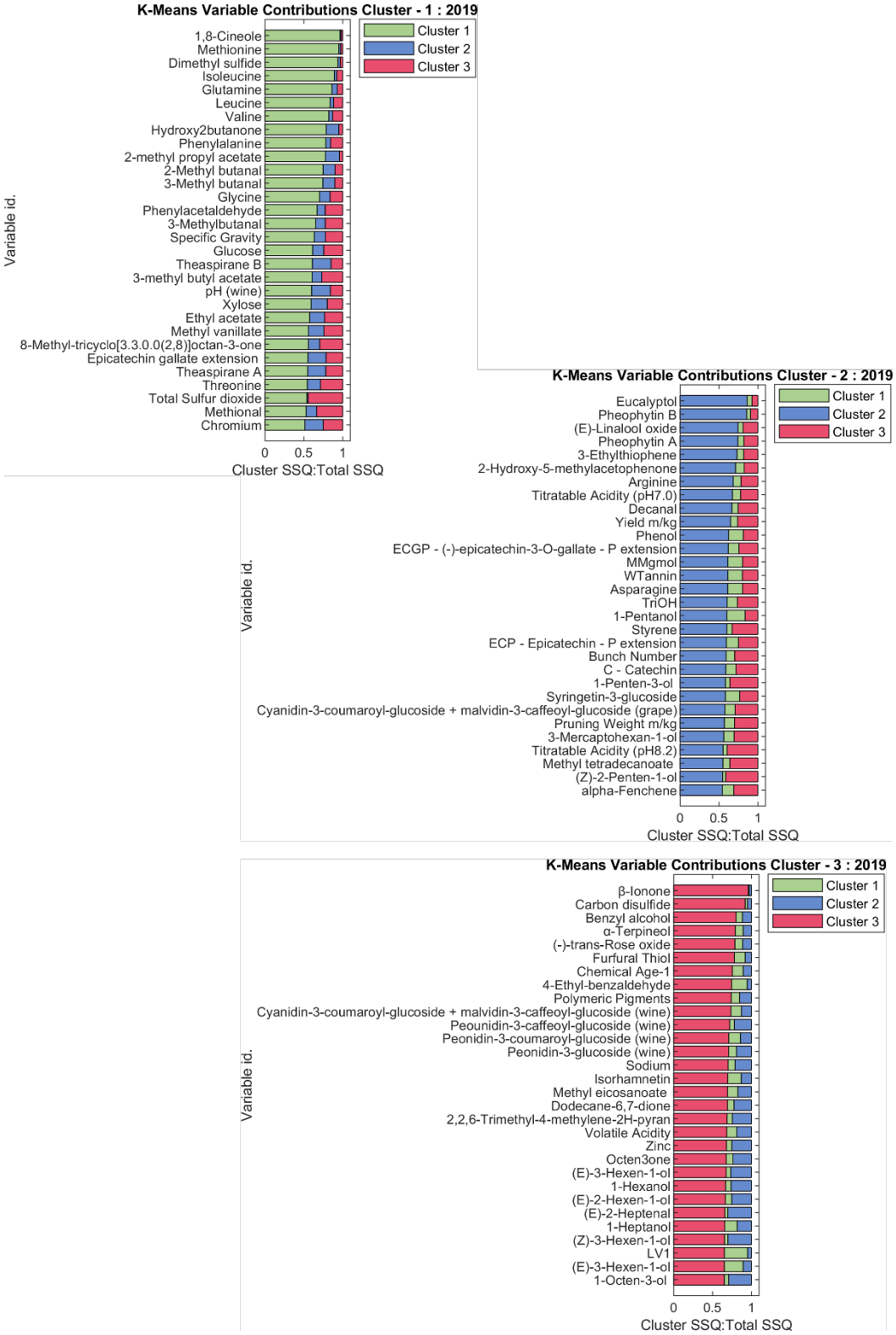


Figure S9. Variable importance of the thirty most influential attributes for *k*-means clusters for vintage 2019. Variable importance to a specific is shown as a ratio of the sum of squares for samples in each cluster to the sum of squares of all samples for the measured attribute.



Figure S10. Variable importance of the thirty most influential attributes for *k*-means clusters for vintage 2020. Variable importance to a specific is shown as a ratio of the sum of squares for samples in each cluster to the sum of squares of all samples for the measured attribute.

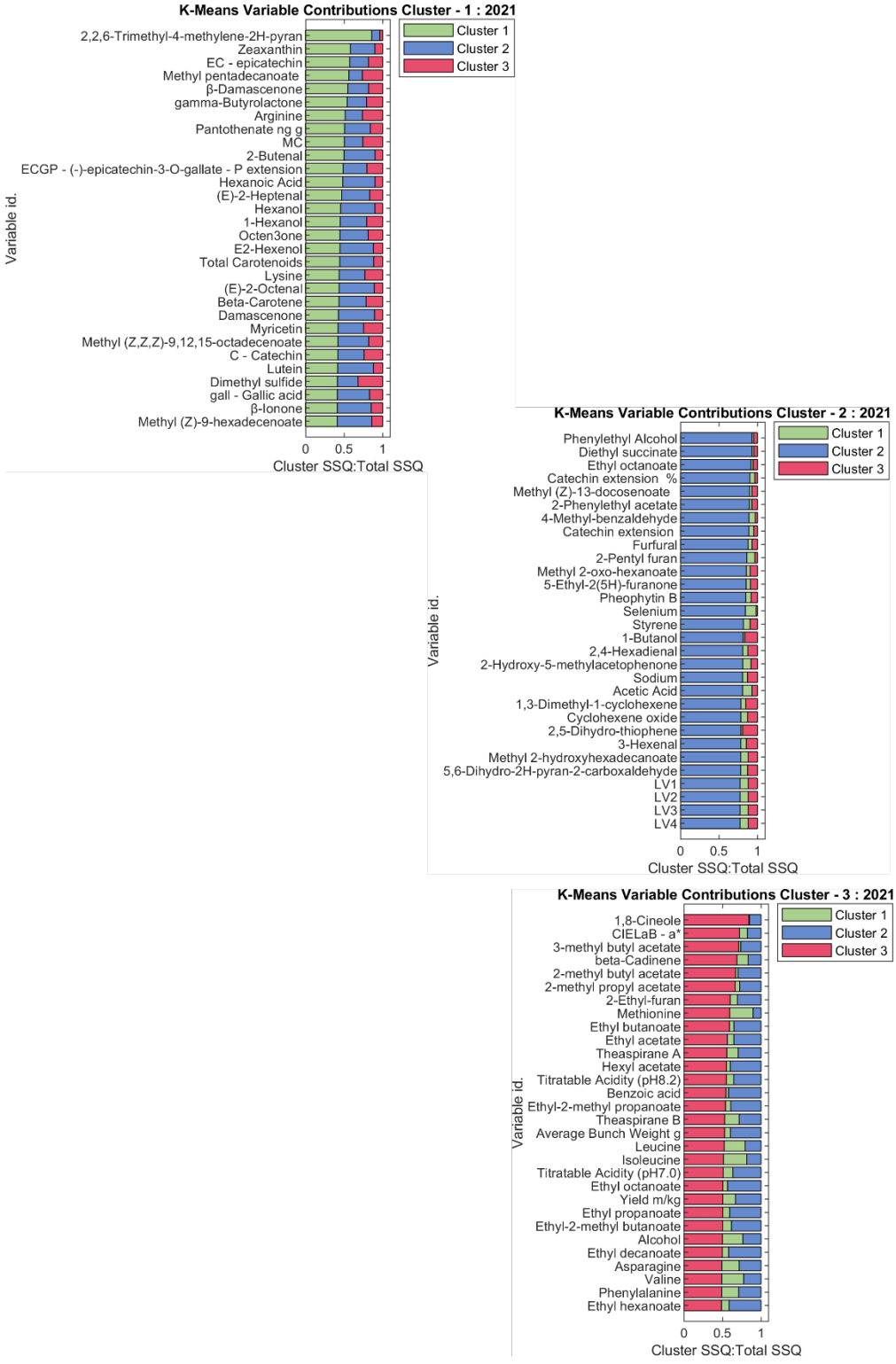


Figure S11. Variable importance of the thirty most influential attributes for *k*-means clusters for vintage 2018. Variable importance to a specific is shown as a ratio of the sum of squares for samples in each cluster to the sum of squares of all samples for the measured attribute.

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