Investigations Into Impacts of MOG on Aroma Compounds of Red Wine Cultivars

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Materials Other Than Grapes (MOG)

- Has always been an issue since the advent of mechanical harvesting
- Continual improvements in harvester technology has reduced the problem significantly
- However—regions with cold winters that grow late-season red varieties (e.g. Cabernet Sauvignon) have, due to climate change, been harvesting fruit much later in the season than traditional late October
- The consequence has been mid-November harvests after hard frosts, and the incorporation of MOG into loads at very high levels
- This “frozen MOG” has led to issues of anomalous aromas--“floral taint” in late-season red wines

Possible Contributions From MOG
Initial Hypotheses

- Terpenes and other odorants
- Bitter taste compounds
- Malic acid increase from leaves and petioles
- Metal content (Na, K, Mg, Fe)
- Decreased anthocyanins and color intensity

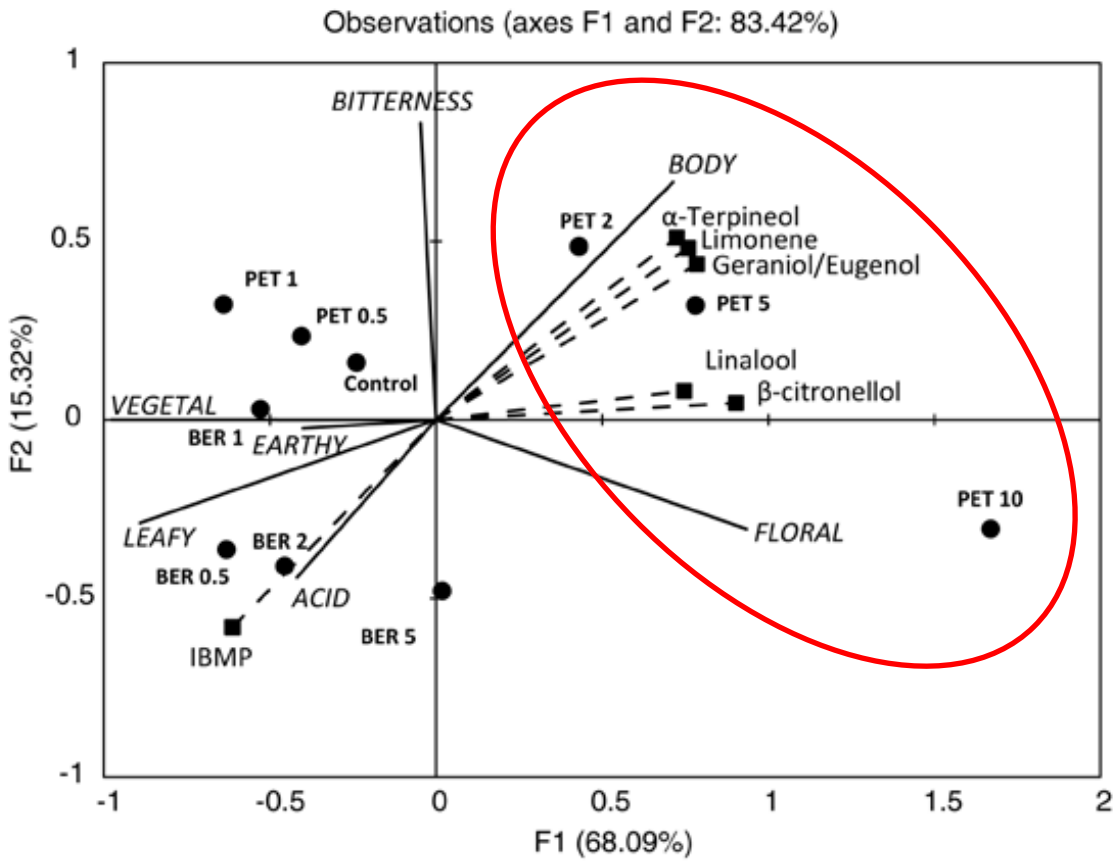
Other Contributions from MOG and Freezing of Grapes

Ongoing 2018-2019

- Reduced methoxypyrazines due to light freezing of grapes.

- Breakdown of glycosides in leaves, petioles, and fruit—and subsequent release of terpene and norisoprenoid aglycones—we are working on this.

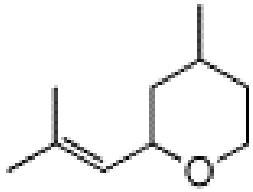
Previous Literature With Petioles in Cabernet Sauvignon (Australia)



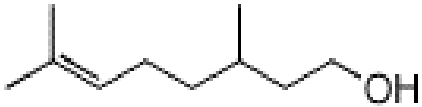
BER, PET = Unripe berries of petioles added to fermentations (% wt./volume)

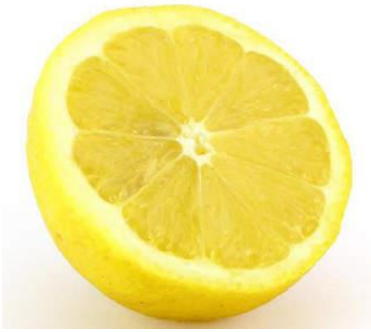
Ward et al. *Am J. Enol. Vitic.* **2015**, 66(4) 435-443.

Cis-Rose Oxide

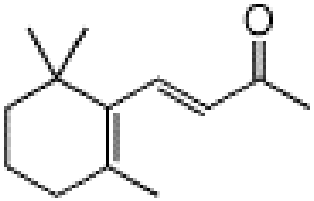


Citronellol





β - Ionone



Geraniol

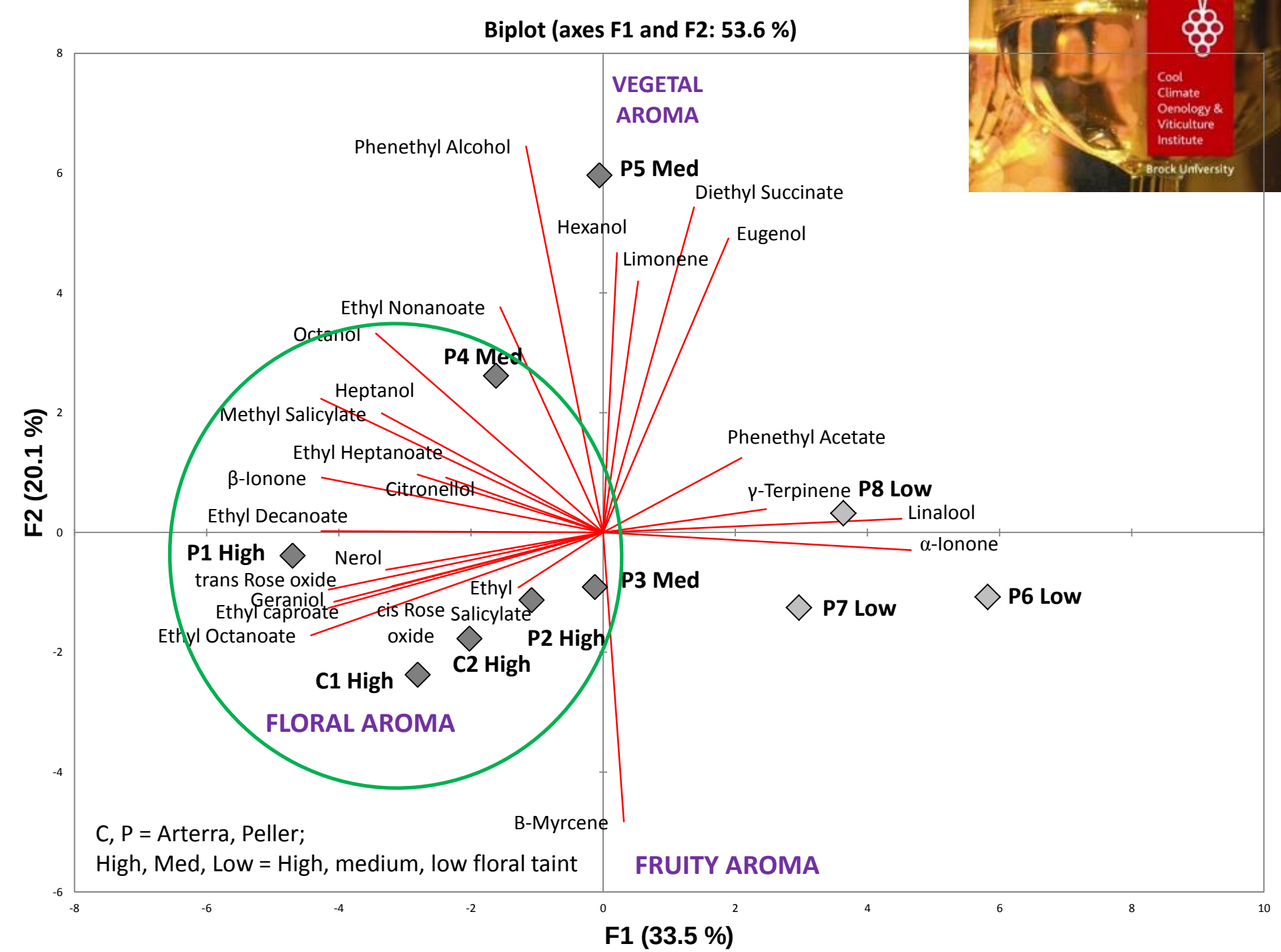
Linalool

I. Analysis of Commercial Wines

- Tanks of several Cabernet franc and Cabernet Sauvignon wines previously identified by the winemakers as having “floral taint” were sampled (3 x 500 mL) from Andrew Peller Ltd. (APL) and Arterra wineries
- Several APL commercial wines both displaying/ not displaying floral taint were likewise sampled
- All with extracted using the Gerstel stir bar technology and subjected to GC-MS

I. Analysis of Commercial Wines contd.

- Sensory analysis of 2015 commercial wines was carried out by ≈20 panelists using multidimensional sorting


Biplot (axes F1 and F2: 53.6 %)
VEGETAL AROMA
Phenethyl Alcohol
P5 Med
Diethyl Succinate
Hexanol
Eugenol
Limonene
Ethyl Nonanoate
Octanol
P4 Med
Heptanol
Methyl Salicylate
Phenethyl Acetate
Ethyl Heptanoate
β-Ionone
Citronellol
γ-Terpinene
P8 Low
Linalool
Ethyl Decanoate
α-Ionone
P1 High
Nerol
trans Rose oxide
P3 Med
Ethyl Salicylate
Geraniol
Ethyl caproate
cis Rose oxide
P7 Low
P6 Low
Ethyl Octanoate
P2 High
C2 High
C1 High
FLORAL AROMA
B-Myrcene
FRUITY AROMA
C, P = Arterra, Peller;
High, Med, Low = High, medium, low floral taint
F2 (20.1 %)
F1 (33.5 %)
8
6
4
2
0
-2
-4
-6
-8
-6
-4
-2
0
2
4
6
8
10
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Aroma compounds in commercial Ontario red wines, 2015 vintage

(yellow-highlighted columns are likely above threshold; green rows = low floral taint samples)

Sample	β-Ionone	α-Ionone	β-Damascenone	Citronellol	Geraniol	cis Rose oxide	trans Rose oxide	γ-Terpinene	Limonene
P6 Low	0.153±0.039	1.929±0.233	2.66±0.04	1.313±0.074	7.347±4.078	0.021±0.009	0.014±0.003	0.044±0.005	0.222±0.032
P7 Low	0.224±0.024	2.322±0.238	2.06±0.67	0.921±0.143	5.979±0.650	0.016±0.005	0.010±0.002	0.059±0.009	0.182±0.003
P8 Low	0.160±0.001	2.536±0.108	2.83±0.14	1.413±0.093	3.893±0.241	0.036±0.006	0.000±0.002	0.056±0.020	0.175±0.014
P9 Low	0.152±0.001	3.226±0.120	2.20±0.07	0.920±0.040	4.091±0.250	0.019±0.002	0.005±0.004	0.137±0.002	0.145±0.038
P10 Low	0.188±0.000	4.859±0.133	2.61±0.03	0.849±0.024	4.371±0.143	0.045±0.009	0.008±0.003	0.206±0.068	0.202±0.040
P3 Med	0.259±0.002	1.869±0.005	4.03±0.23	0.940±0.102	4.708±0.284	0.084±0.000	0.040±0.001	0.134±0.017	0.152±0.017
P4 Med	0.238±0.026	1.675±0.182	3.39±0.06	0.922±0.015	4.976±0.271	0.034±0.005	0.016±0.001	0.087±0.007	0.176±0.028
P5 Med	0.259±0.006	1.792±0.164	4.38±0.07	1.361±0.027	6.347±0.312	0.022±0.000	0.007±0.006	0.104±0.013	0.137±0.011
C1 High	0.232±0.021	0.884±0.014	2.42±0.09	1.209±0.212	7.716±1.487	0.049±0.005	0.027±0.001	0.072±0.000	0.215±0.053
C2 High	0.244±0.042	0.662±0.084	2.18±0.31	0.928±0.141	6.870±0.566	0.058±0.020	0.033±0.012	0.065±0.058	0.183±0.040
P1 High	0.291±0.007	1.423±0.030	5.17±1.07	2.088±0.090	7.486±1.217	0.217±0.035	0.068±0.007	0.138±0.015	0.143±0.013
P2 High	0.274±0.039	1.504±0.318	2.46±0.03	0.957±0.114	5.033±0.350	0.111±0.025	0.026±0.003	0.080±0.009	0.115±0.014
Threshold	0.09	2.6	0.05	100	30	0.2	450	---	15
Mean Low	0.175	2.95	2.47	1.08	5.14	0.027	0.007	0.100	0.185
Mean Med-High	0.257*	1.40	3.43*	1.20*	6.16*	0.082*	0.031*	0.097	0.160
OAV	**2.86**	**0.538**	**68.6**	**0.012**	**0.205**	**0.410**	**0.155**	**---**	**0.011**

C, P = Arterra and Peller, respectively

All concentrations are in µg/L

OAV = Odor activity value

Aroma compounds in commercial Ontario red wines, 2015 vintage

(yellow-highlighted columns are above threshold; green rows = low floral taint samples)

Sample	Ethyl hexanoate	Ethyl heptanoate	Ethyl octanoate	Ethyl nonanoate	Ethyl decanoate	Heptanol	Octanol	Phenethyl acetate	Phenethyl alcohol
P6 Low	204.0±25.5	1.07±0.06	158.4±12.1	0.394±0.009	21.8±1.6	33.6±2.6	15.85±1.58	30.4±0.96	43039±1222
P7 Low	147.1±7.6	1.08±0.05	112.9±11.3	0.505±0.033	21.5±2.2	35.7±2.4	13.96±1.14	33.9±3.03	47142±7851
P8 Low	201.0±47.0	1.13±0.13	270.7±62.5	0.423±0.056	69.9±14.0	29.7±3.5	13.24±2.49	25.6±5.33	40914±4456
P9 Low	201.0±9.6	1.32±0.03	284.8±17.0	0.523±0.023	69.8±3.9	35.7±1.1	12.14±0.44	52.4±1.43	46305±2684
P10 Low	130.8±45.2	1.27±0.16	187.5±4.1	0.770±0.002	52.4±2.4	31.1±5.4	12.62±4.00	53.7±2.66	34148±1032
P3 Med	203.6±15.4	1.79±0.21	288.1±34.5	0.638±0.025	75.2±2.9	38.0±4.9	16.64±3.56	47.3±6.29	42635±1036
P4 Med	237.4±27.7	1.44±0.06	342.4±36.4	1.842±0.083	107.4±10.1	43.1±5.5	19.09±2.33	43.1±9.41	60569±1118
P5 Med	245.3±6.3	1.65±0.01	227.4±3.0	0.934±0.014	60.6±0.4	39.2±0.2	14.25±0.49	55.7±2.02	51031±1192
C1 High	222.6±33.8	1.63±0.13	399.3±29.3	0.857±0.025	143.0±6.0	40.4±0.1	13.98±1.48	47.2±3.21	40500±2510
C2 High	210.1±19.4	1.62±0.13	390.4±44.7	0.912±0.092	123.1±13.0	37.9±3.6	15.36±3.32	27.3±1.90	38734±6476
P1 High	251.4±22.5	1.41±0.10	352.6±34.9	0.649±0.050	113.9±11.1	44.0±2.4	17.65±0.02	37.7±3.70	46739±1406
P2 High	238.9±20.0	1.70±0.04	327.4±6.1	0.661±0.061	80.0±1.7	35.5±1.4	13.31±1.91	33.2±5.25	41107±6179
Threshold	5	2.2	5	---	200	3	110	250	10000
Mean Low	176.8	1.17	202.8	0.52	47.1	33.2	13.56	39.2	42310
Mean Med-High	229.9*	1.61*	332.5*	0.93*	100.5*	39.7*	15.75*	41.6*	45902*
OAV	45.98	0.73	66.5	---	0.5	13.2	0.143	0.167	4.59

C, P = Constellation (now Arterra) and Peller, respectively

All concentrations are in µg/L

OAV = Odor activity value

II. Analysis of Controlled Fermentations

- Controlled fermentations with Cabernet franc and Cabernet Sauvignon took place in November 2016 to 2018 involving several levels of frozen leaves and petioles
- The 2016 and 2017 wines were subjected to GC-MS analysis
- The 2018 wines will be likewise analyzed


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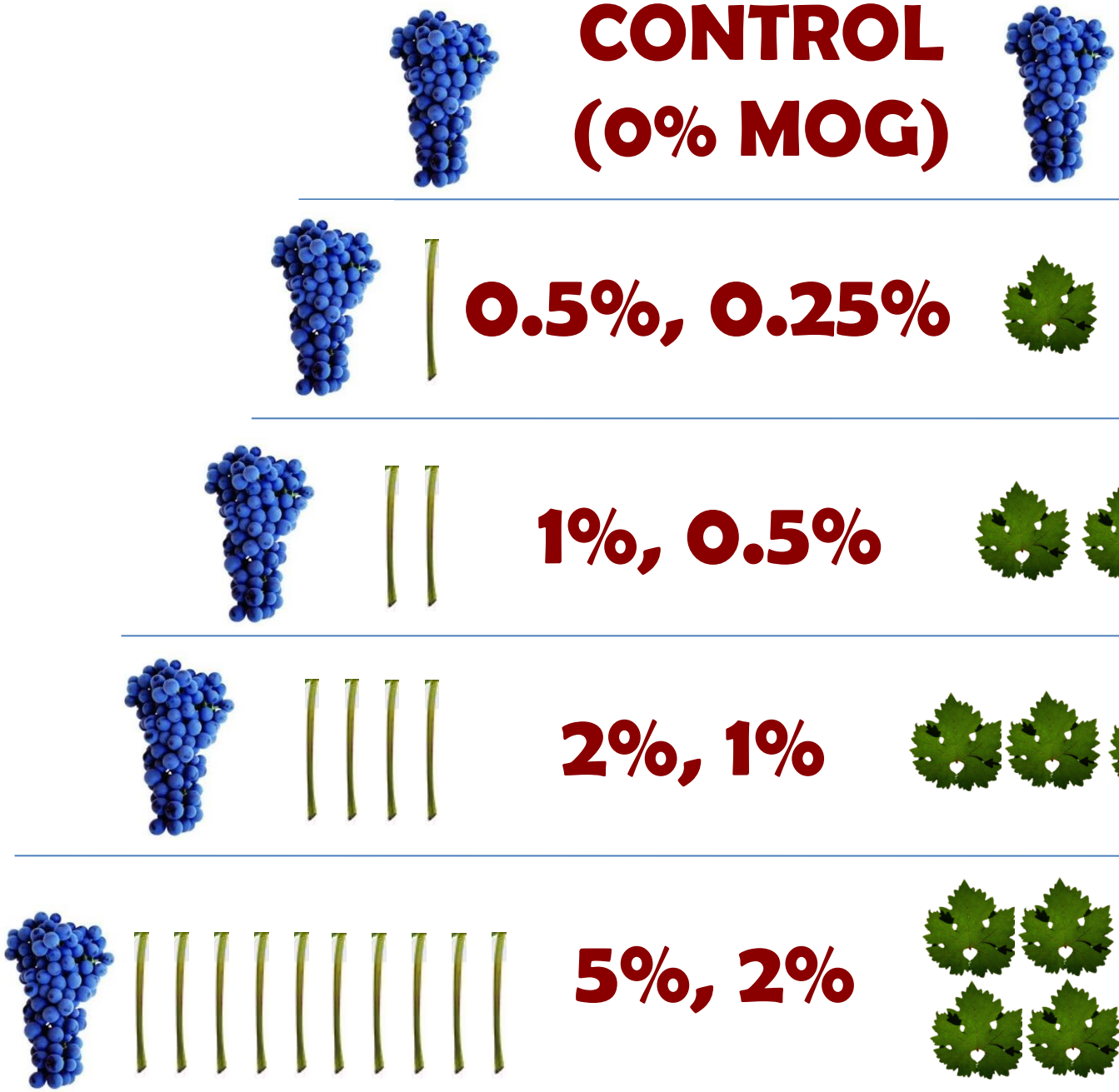
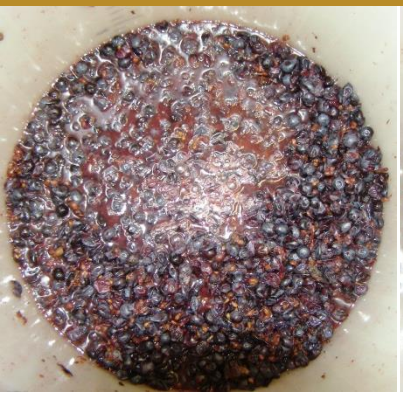

CONTROL
(0% MOG)
0.5%, 0.25%
1%, 0.5%
2%, 1%
5%, 2%

Controlled Fermentations 2016-2018
(pictured: Dr. Jiaming Wang with 2017 fermentations)

2016 to 2018 controlled fermentations



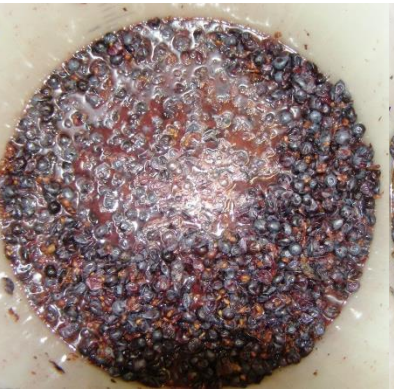
control

0.25 % leaves

0.5 % leaves

1 % leaves

2 % leaves



control

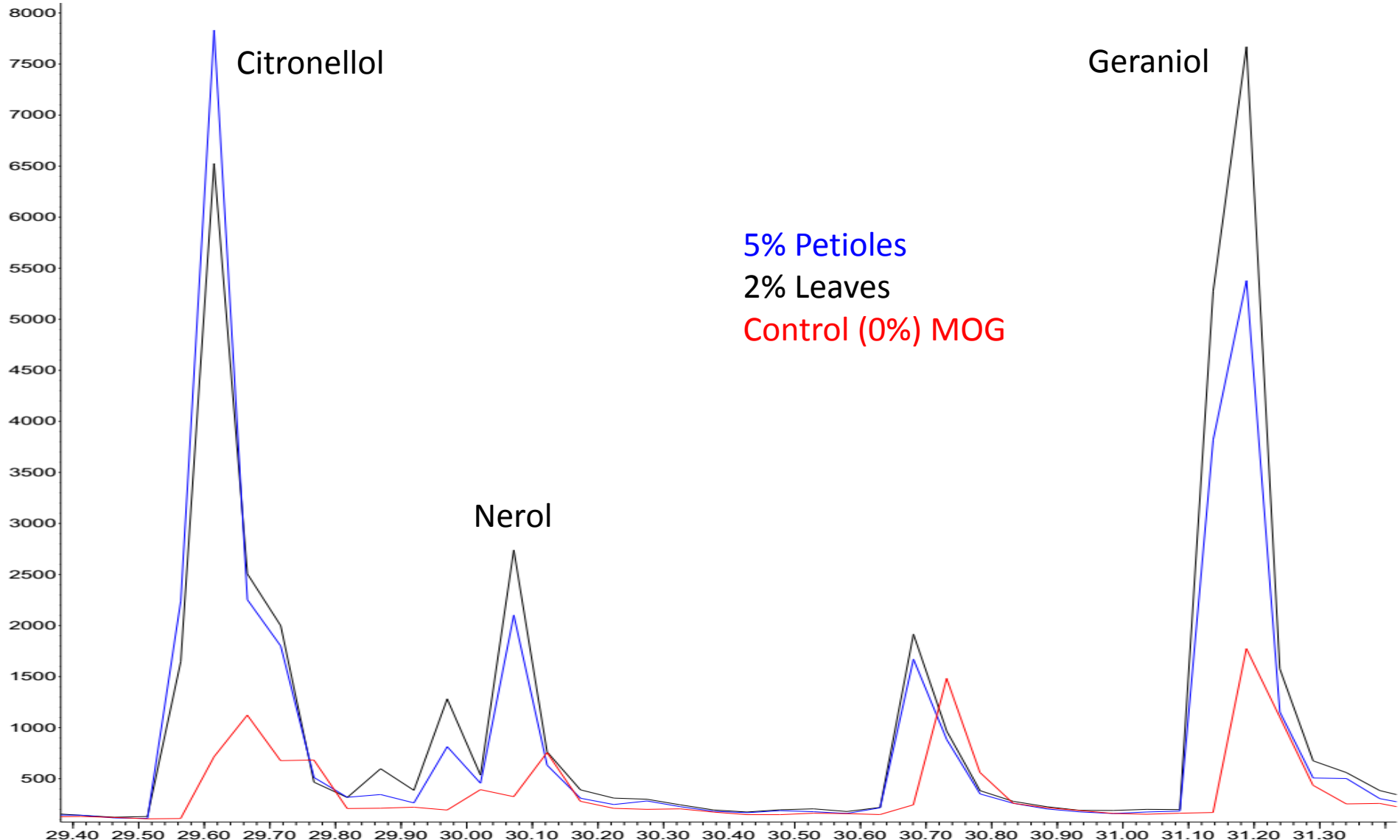
0.5 % petioles

1 % petioles

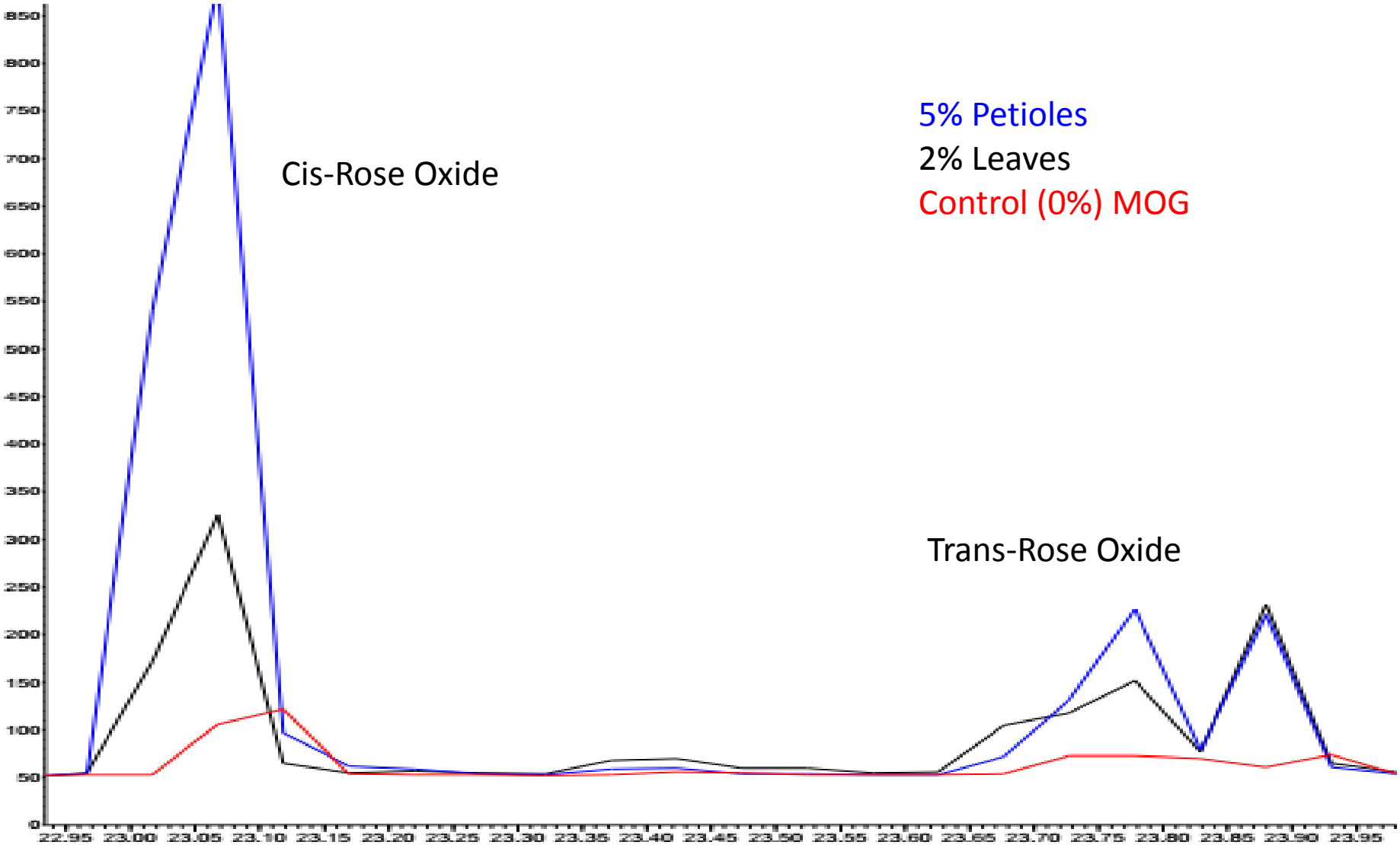
2 % petioles

5 % petioles

GC-MS Terpenes



GC-MS Rose Oxides



The "Smoking Guns" (and those loaded with blanks). Cabernet franc.

Compound	Important?		Compound	Important?		Compound	Important?	
	2016	2017		2016	2017		2016	2017
Isobutanol	---	X	γ-Terpinene	√	√	β-Damascenone	√	√ P
Isoamyl alcohol	---	√ P	Terpinolene	√	√	α-Ionone	√	√
Phenethyl alcohol	X	√ P	Nerolidol	√	√	β-Ionone	√	√
Hexanol	√	√	trans-Rose oxide	√	√	Methyl salicylate	√	√
Heptanol	√	√ P	Limonene	√	√	Ethyl salicylate	√	√
Octanol	√	√	Myrcene	√	√			
Ethyl isobutyrate	---	X	Nerol oxide	---	√			
Isoamyl acetate	---	X	α-Citral	√	√			
Ethyl caproate	X	√ P	β-Citral	X	√ P			
Ethyl octanoate	X	X	cis-Rose oxide	√	√			
Ethyl decanoate	X	√ P	Linalool	√	√			
Diethyl succinate	√	√ P	Geraniol	√	√			
Isobutyl acetate	---	X	Citronellol	√	√			
Ethyl nonoate	X	√	Nerol	√	√			
Phenethyl acetate	X	√	α-Terpineol	√	√			
Hexyl acetate	---	√	cis-Linalool oxide	√	√			
Ethyl heptanoate	√	√ P	trans-Linalool oxide	---	√ P			
Isoamyl caproate	√	√	Eugenol	√	√			

LEGEND

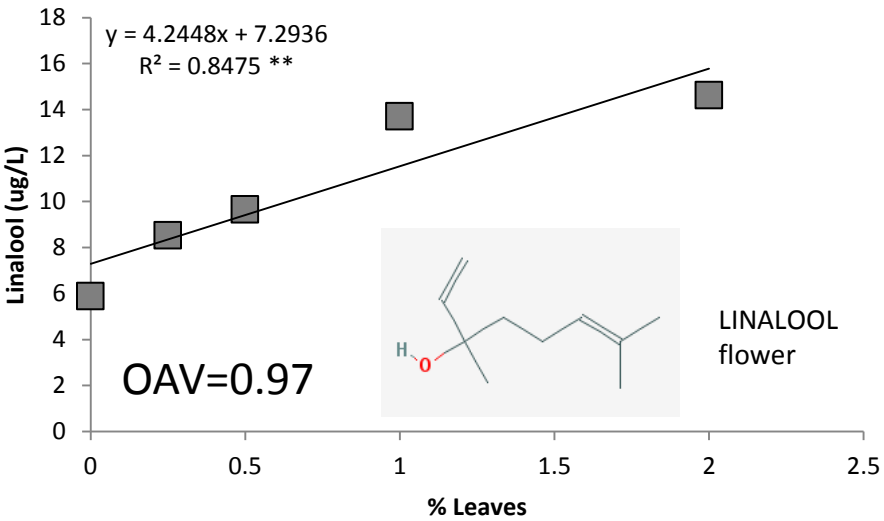
Green = above threshold with increasing relationship with increased leaves or petioles

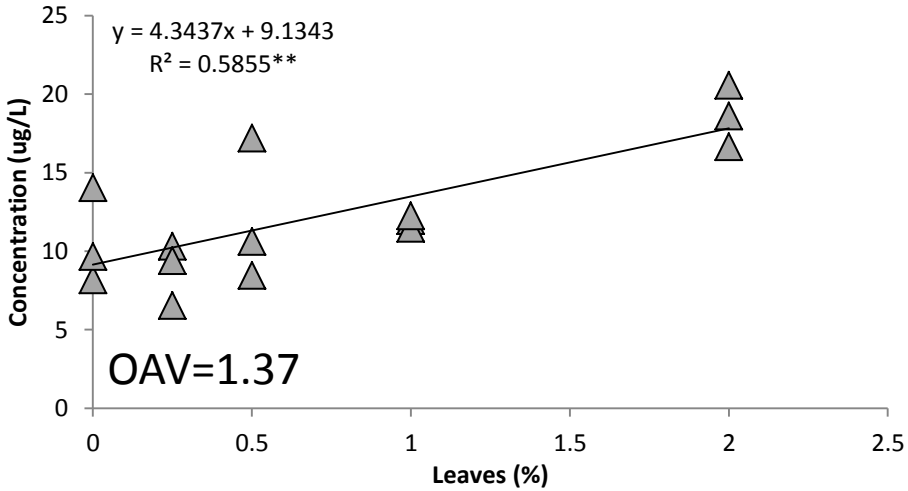
Orange = above threshold; no strong relationship with MOG levels

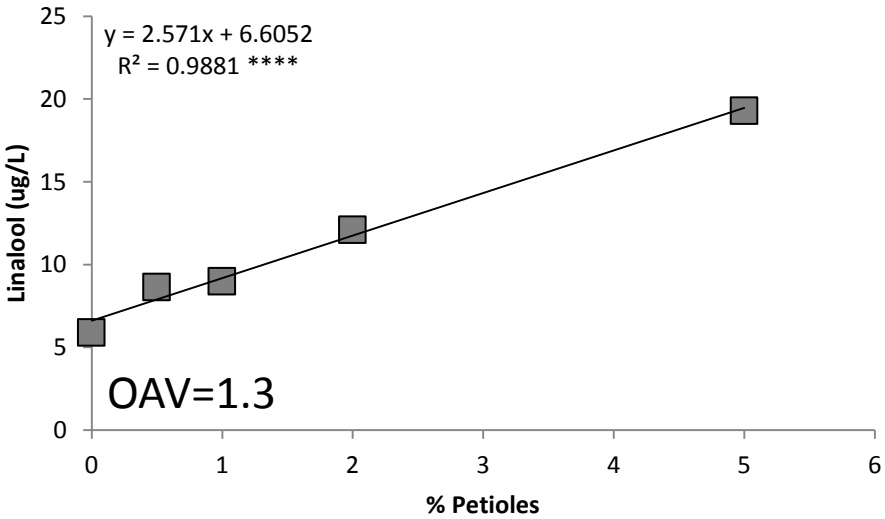
Non-shaded = below threshold at all MOG levels, or thresholds not published

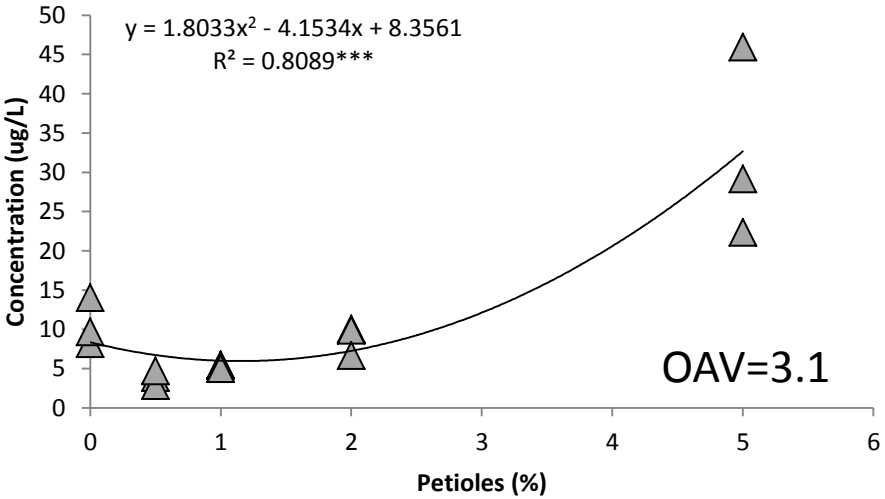
Aroma compounds in Ontario Cabernet franc wines 2016 and 2017. Terpenes--Linalool.

Percent values are weights per volume leaves and petioles.

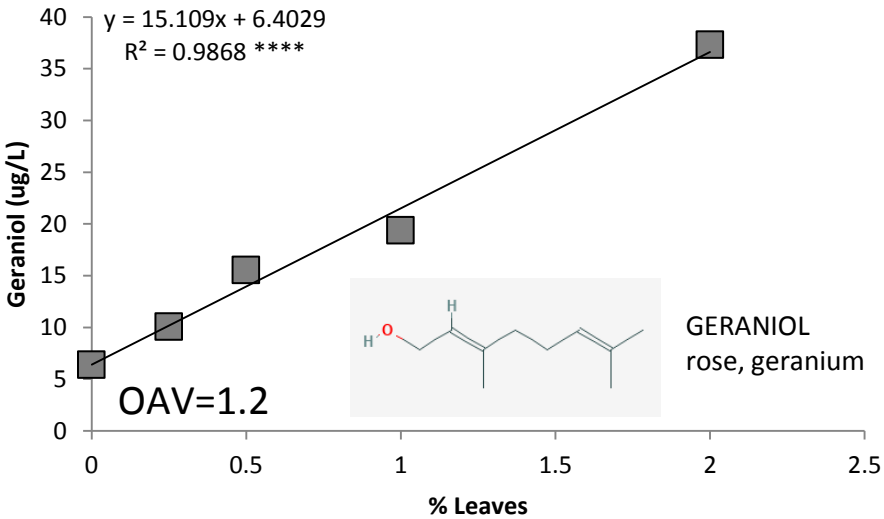


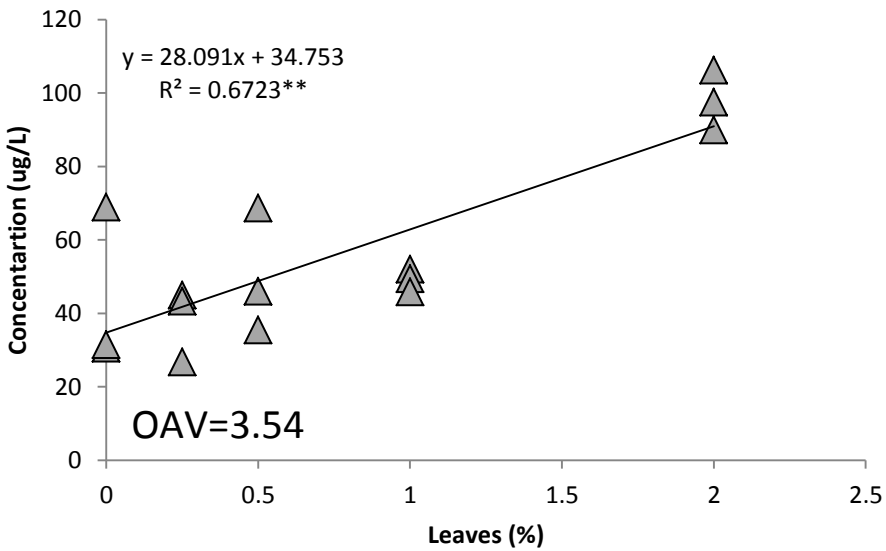


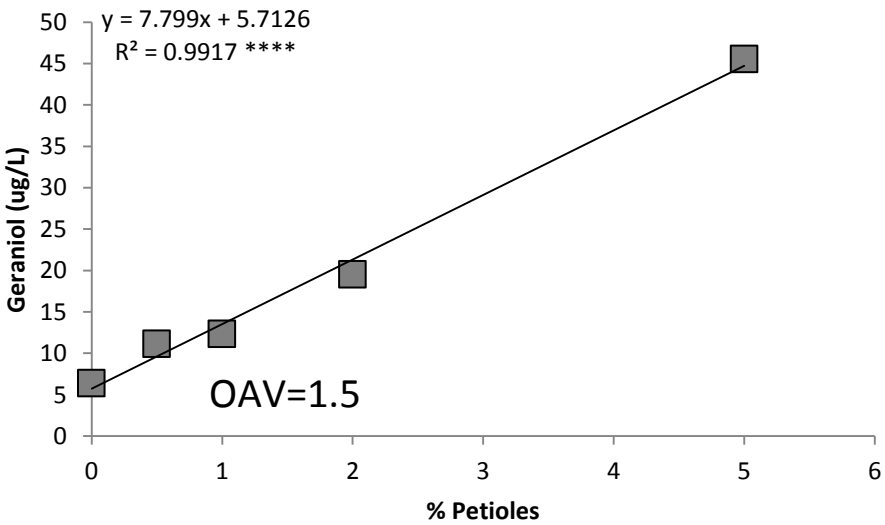


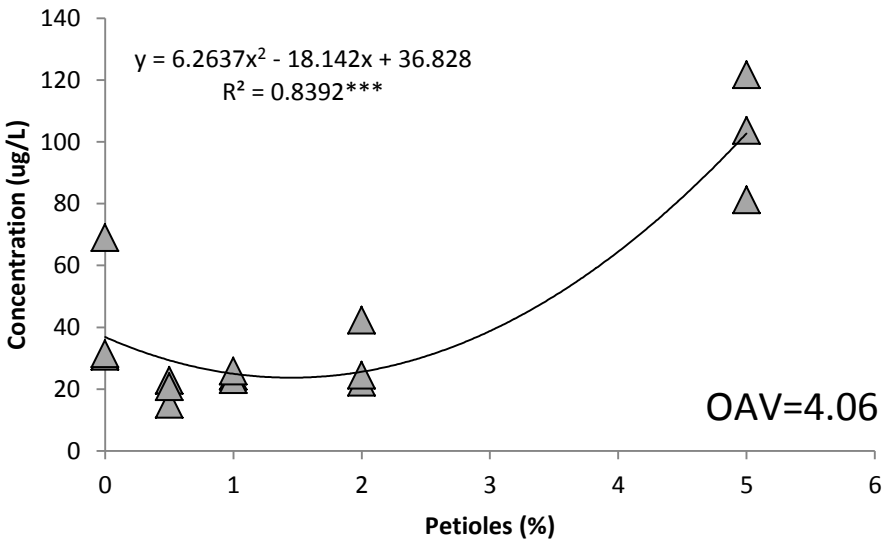


Aroma compounds in Ontario Cabernet franc wines 2016 and 2017. Terpenes--Geraniol.



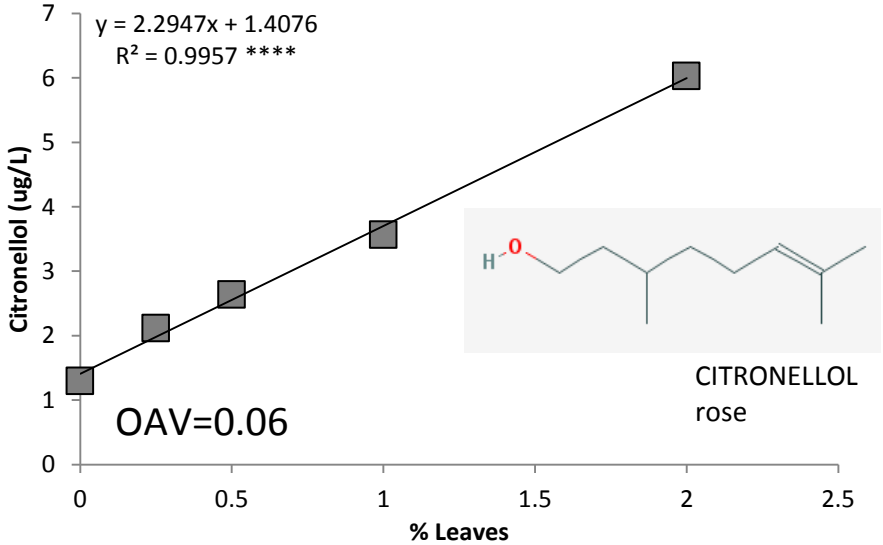


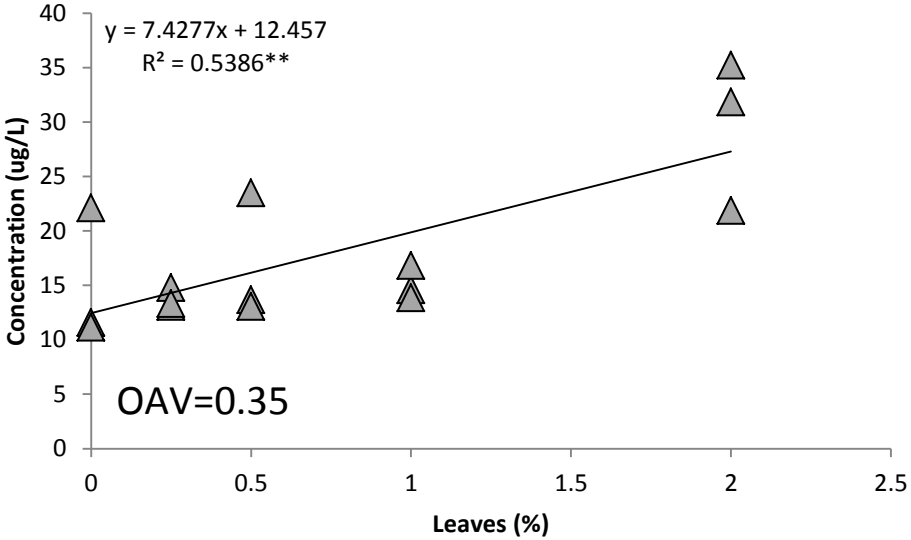


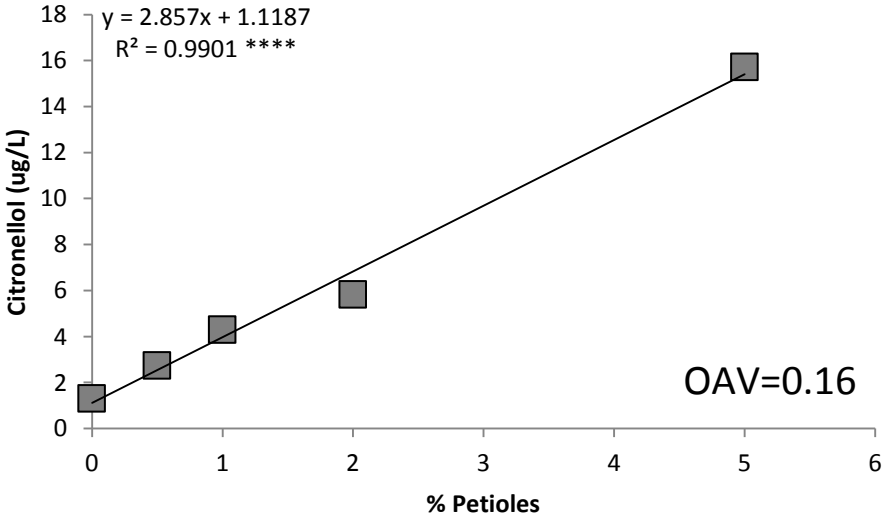


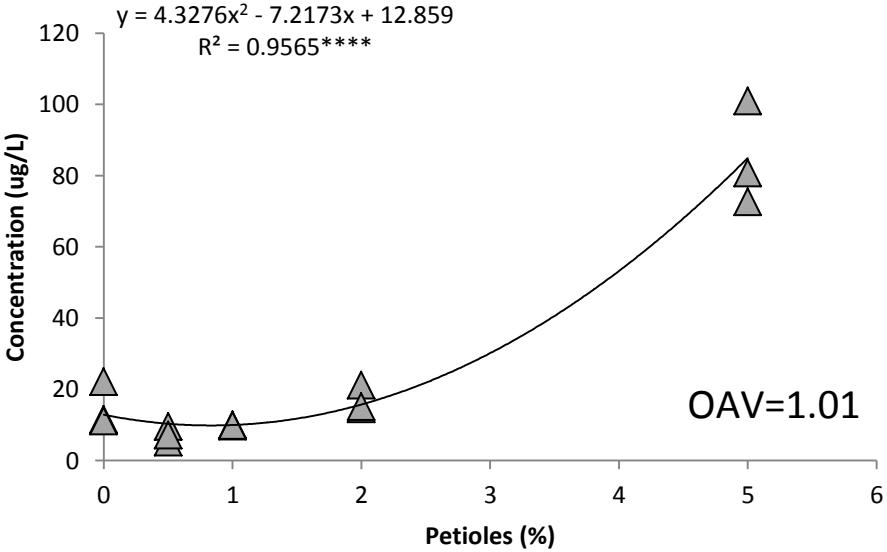
Aroma compounds in Ontario Cabernet franc wines 2016 and 2017. More terpenes--Citronellol.

[Nerol (sweet), α-Citral (lemon), α-Terpineol (pine), and other terpenes responded similarly but had OAV < 1]

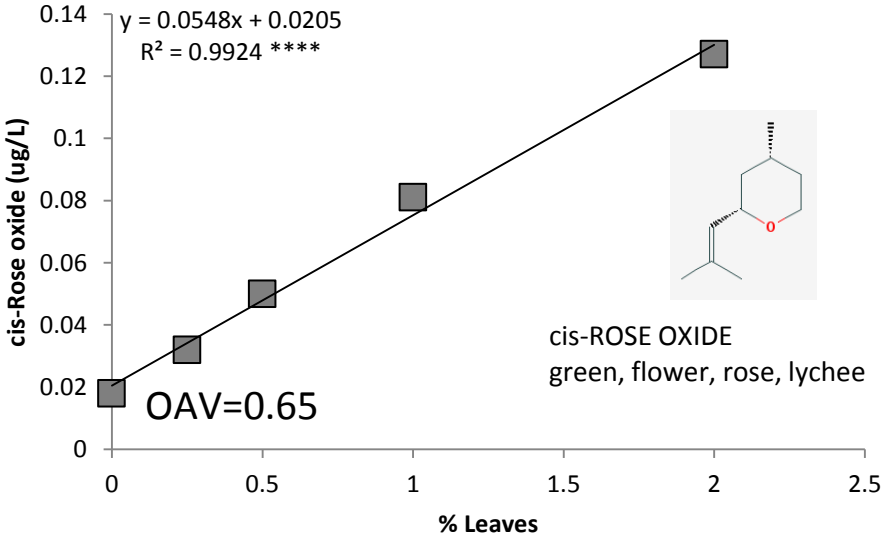


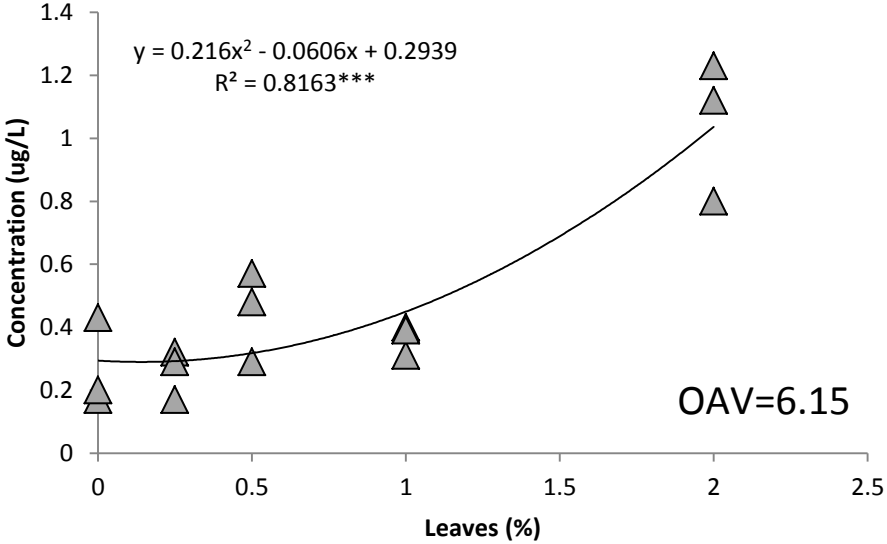


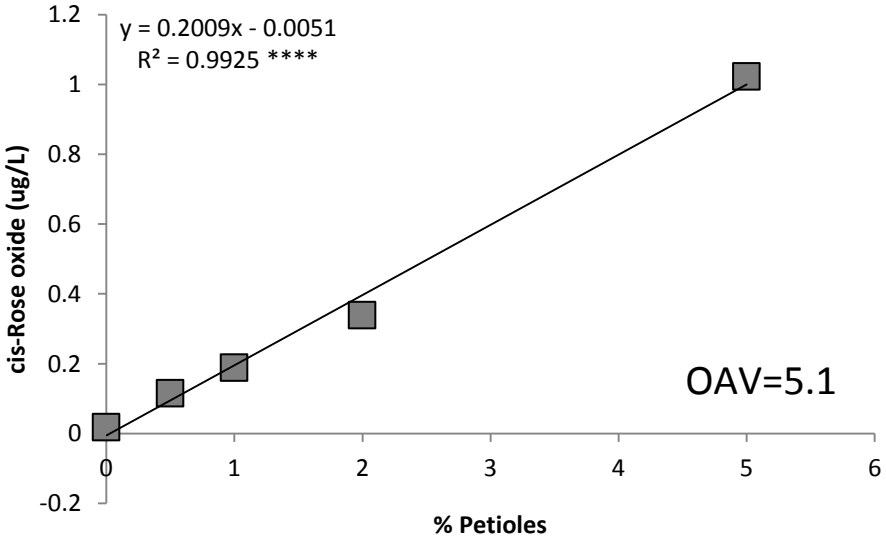


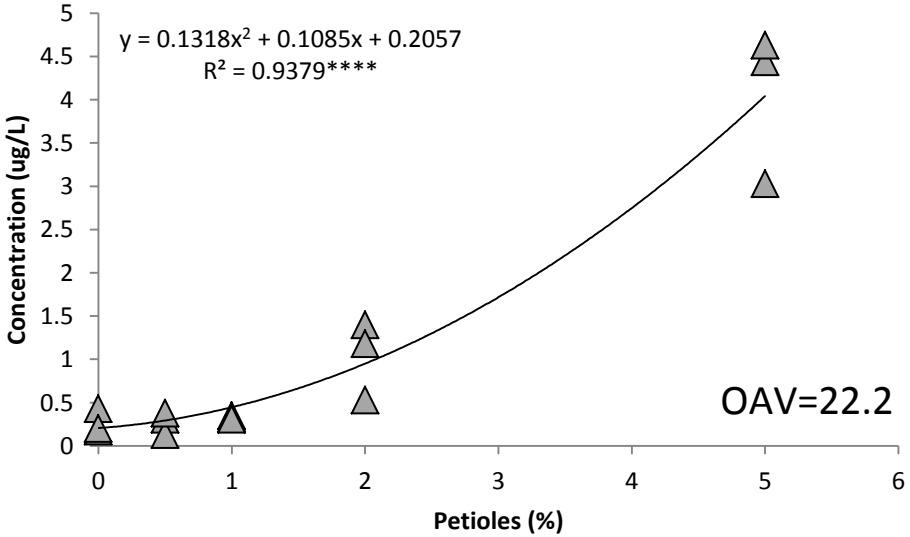


Aroma compounds in Ontario Cabernet franc wines 2016 and 2017. Still more terpenes—cis-Rose oxide.

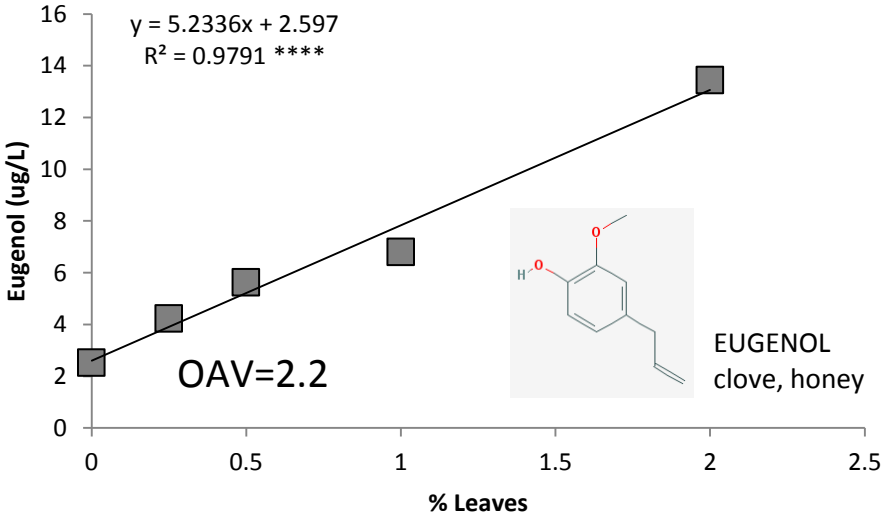


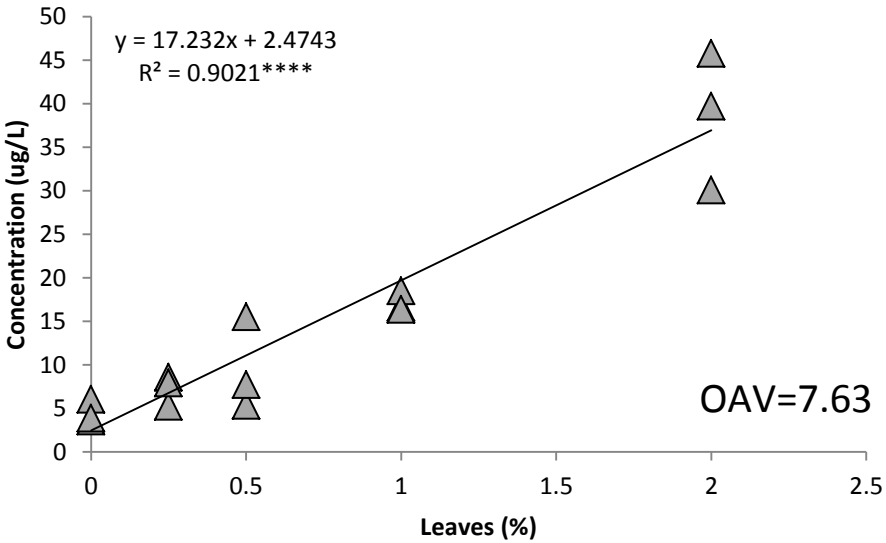


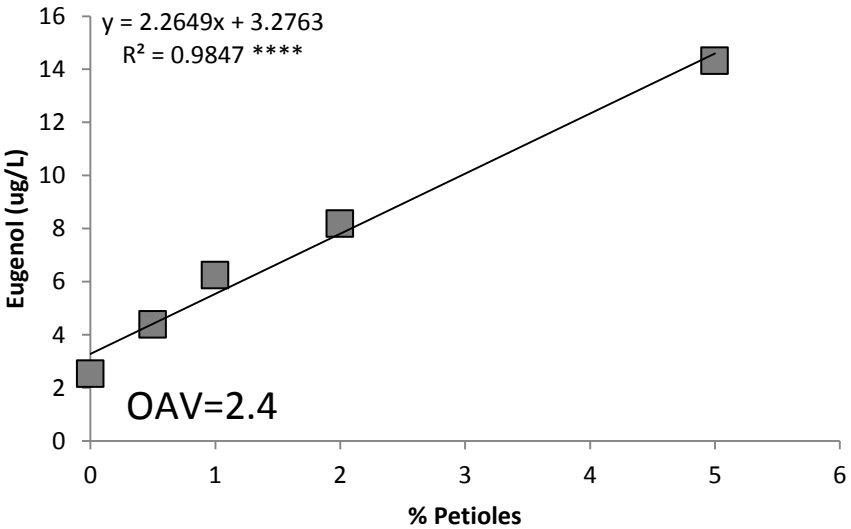


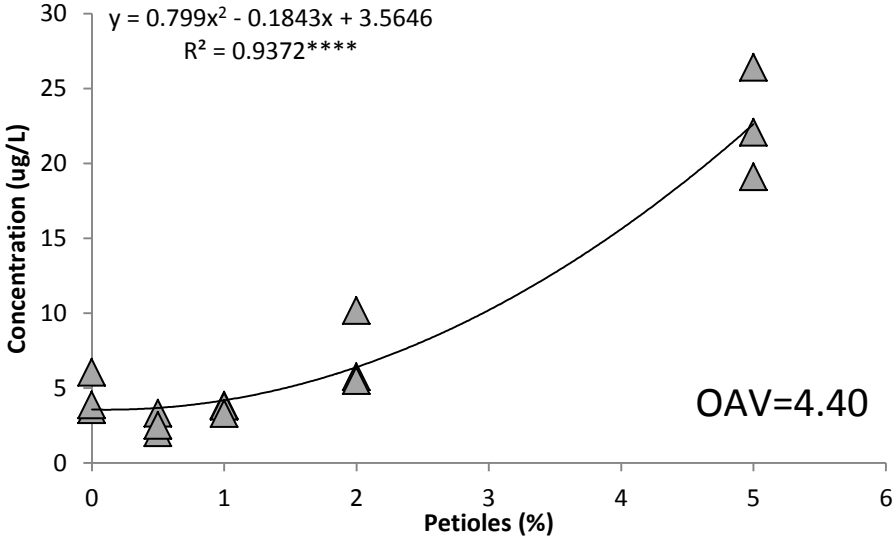


Aroma compounds in Ontario Cabernet franc wines 2016 and 2017. Terpene alcohols--Eugenol.

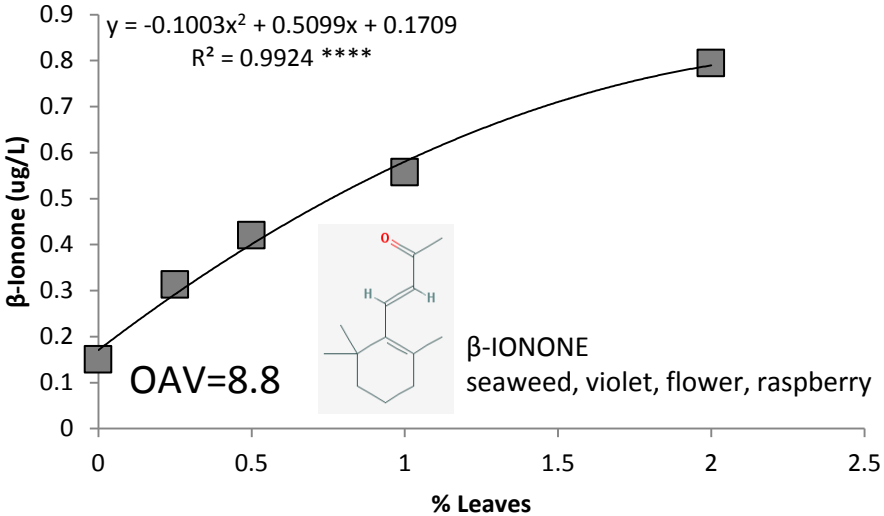


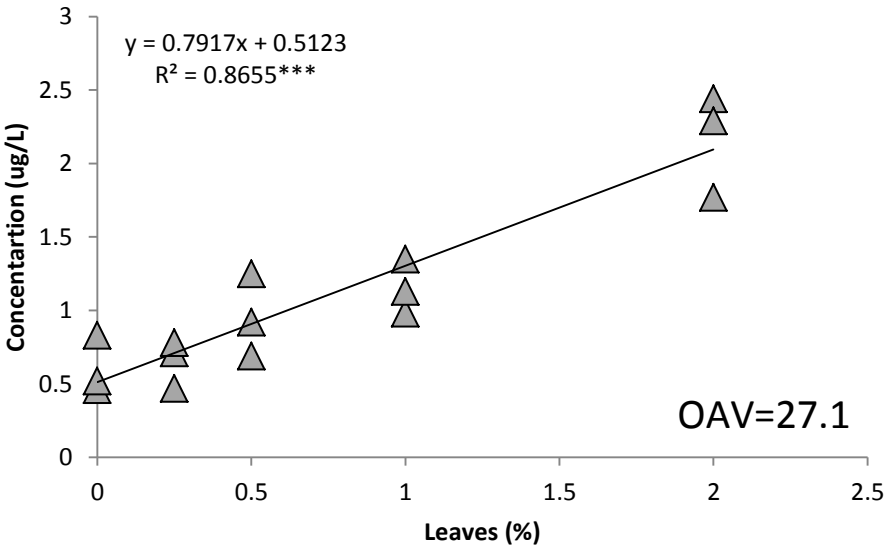


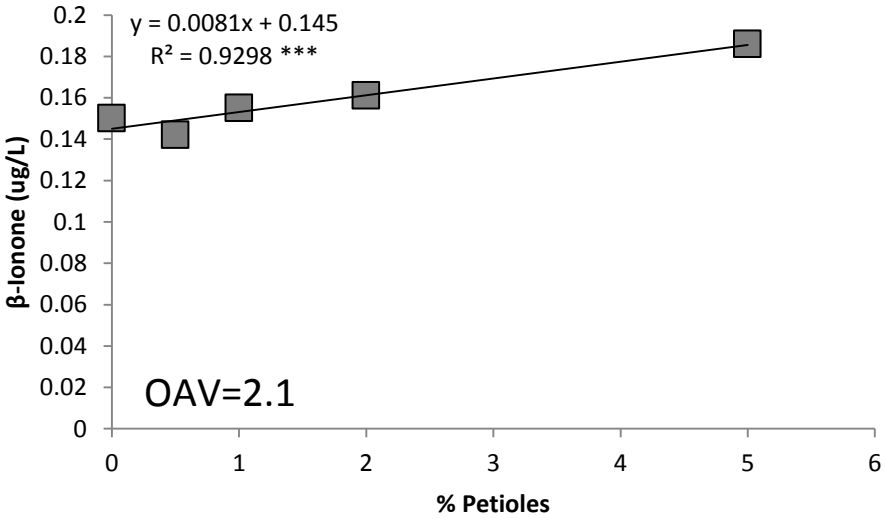


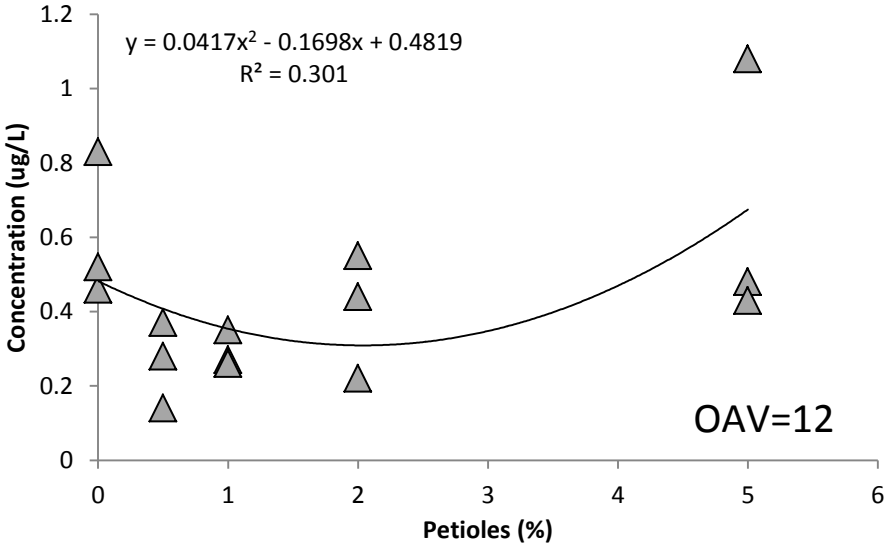


Aroma compounds in Ontario Cabernet franc wines 2016 and 2017. Isoprenoids—ß-Ionone.



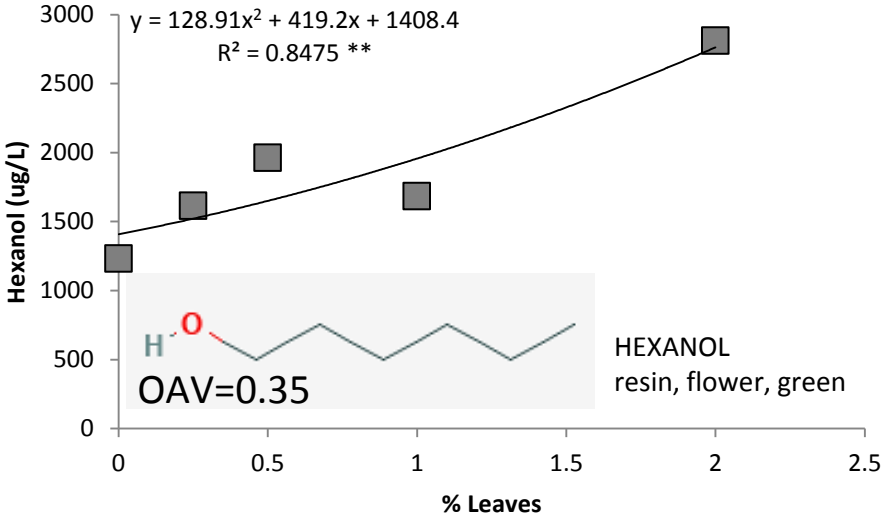


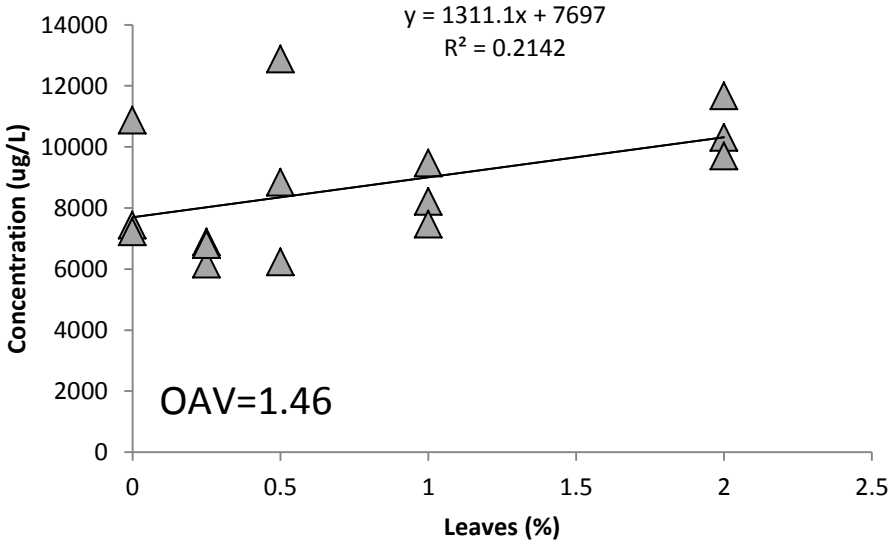


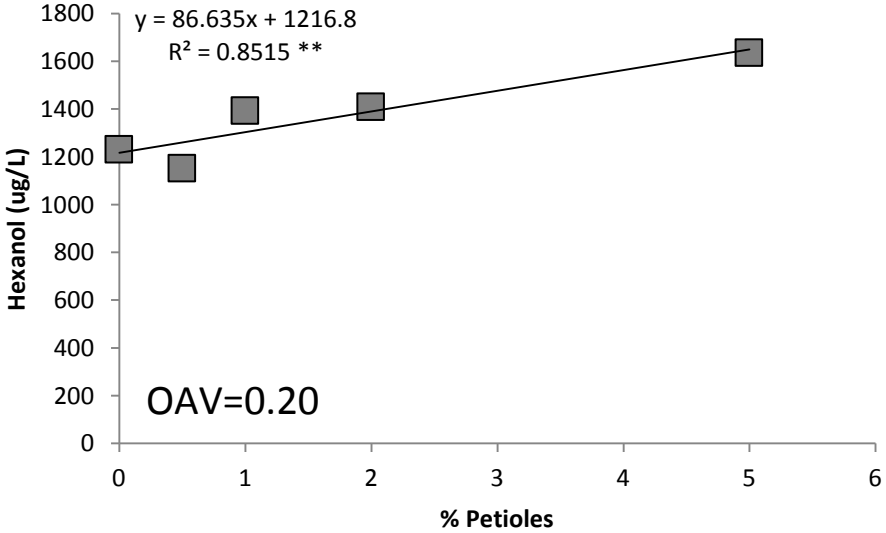


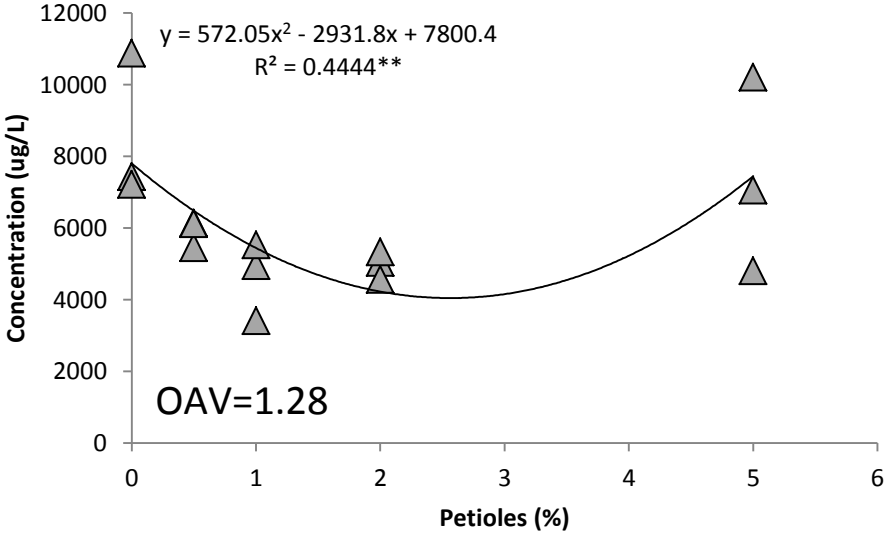
Aroma compounds in Ontario Cabernet franc wines 2016 and 2017. Higher alcohols--Hexanol.

[Octonol (moss, nut, mushroom) responed similarly but OAV < 1]



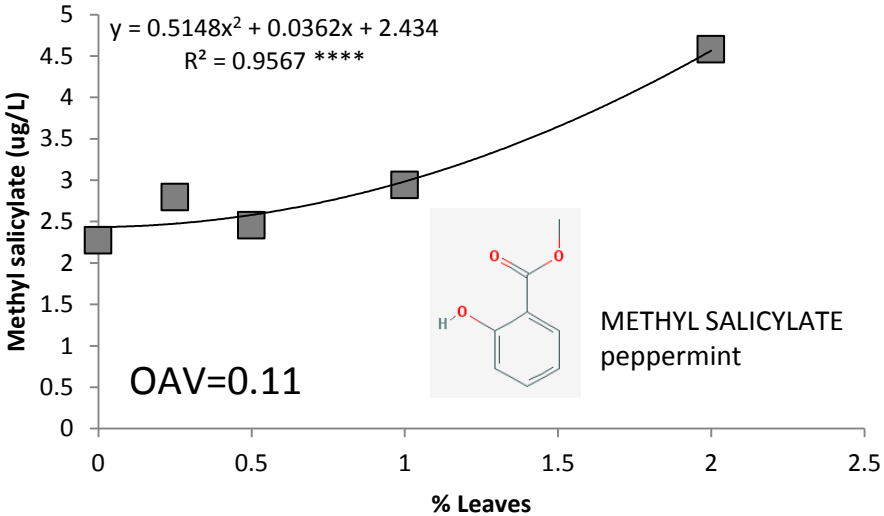


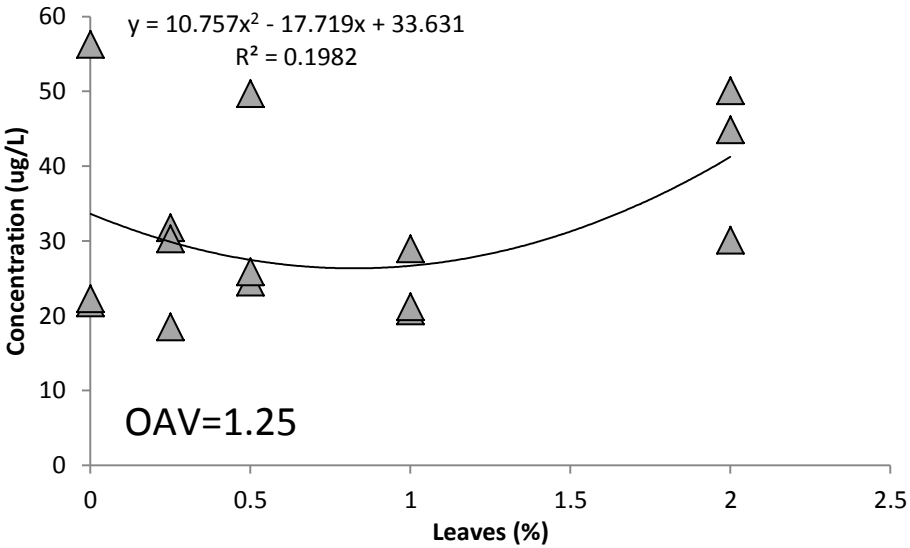


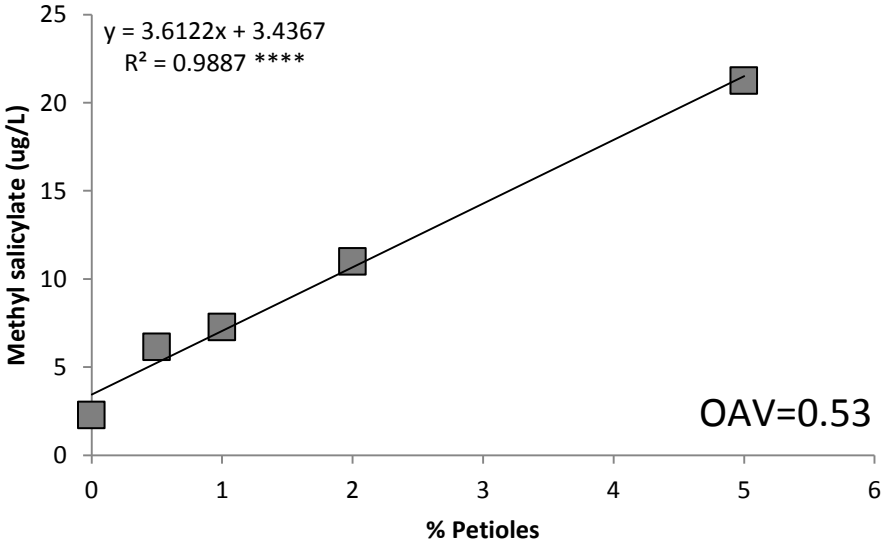


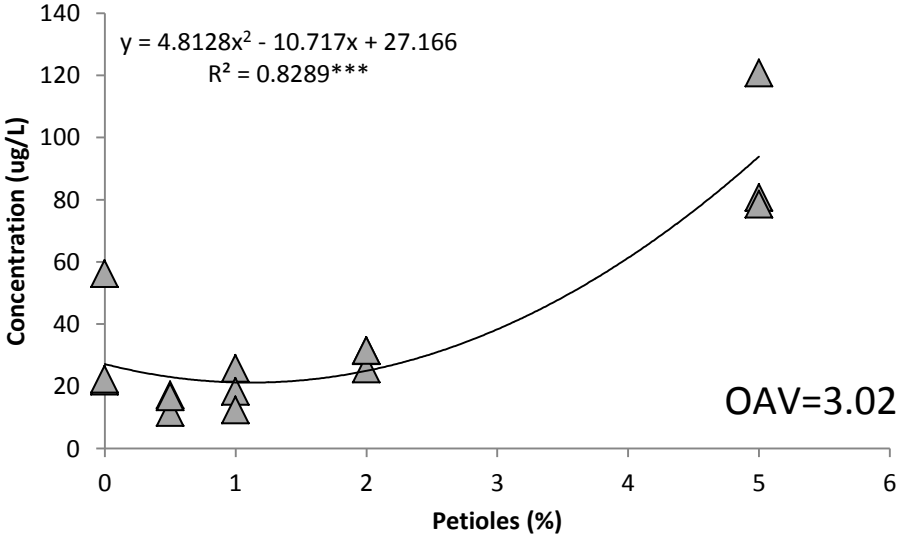
Aroma compounds in Ontario Cabernet franc wines 2016 and 2017. Salicylates—Methyl salicylate.

[Ethyl Salicylate (wintergreen, mint) responded similarly]

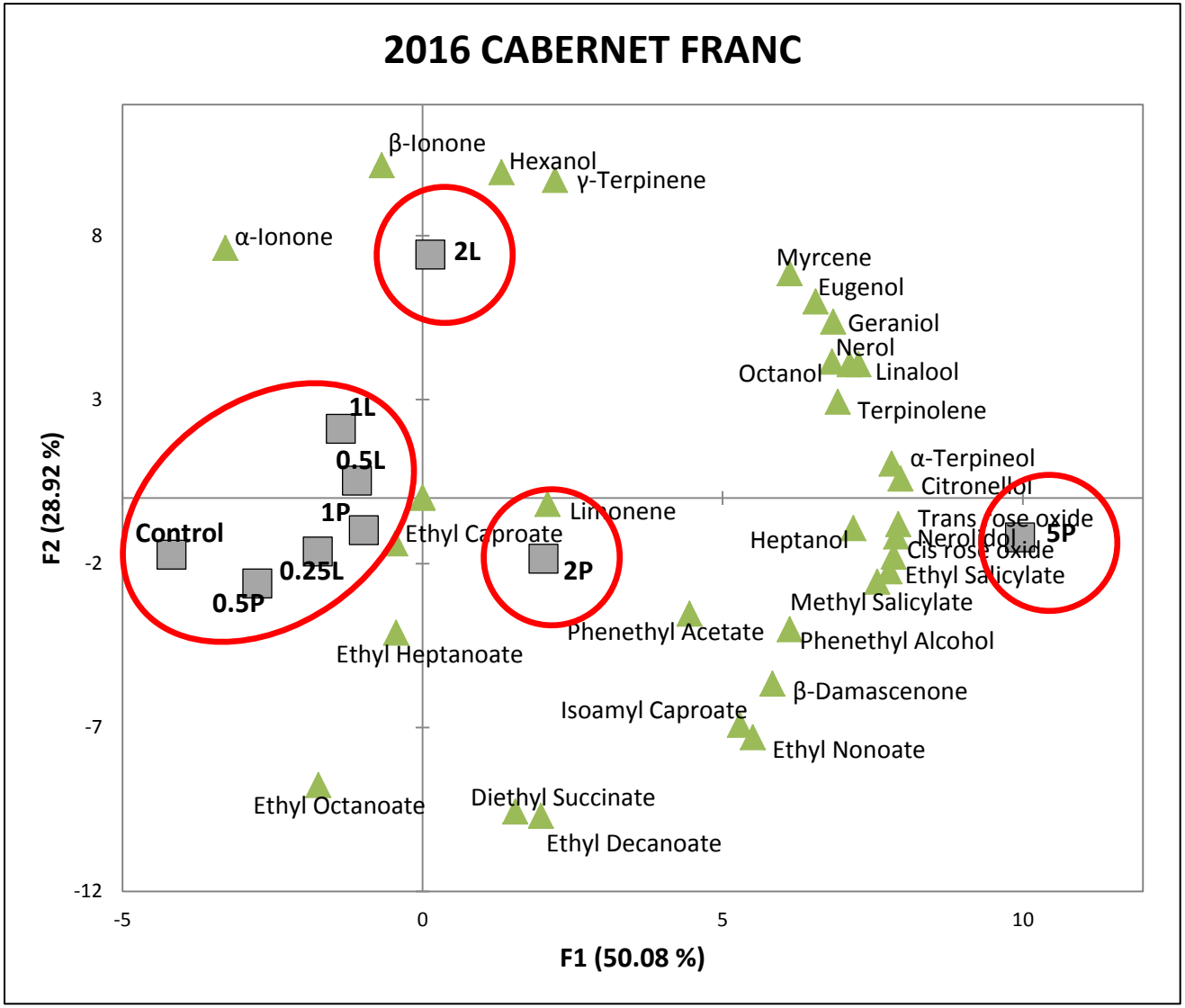




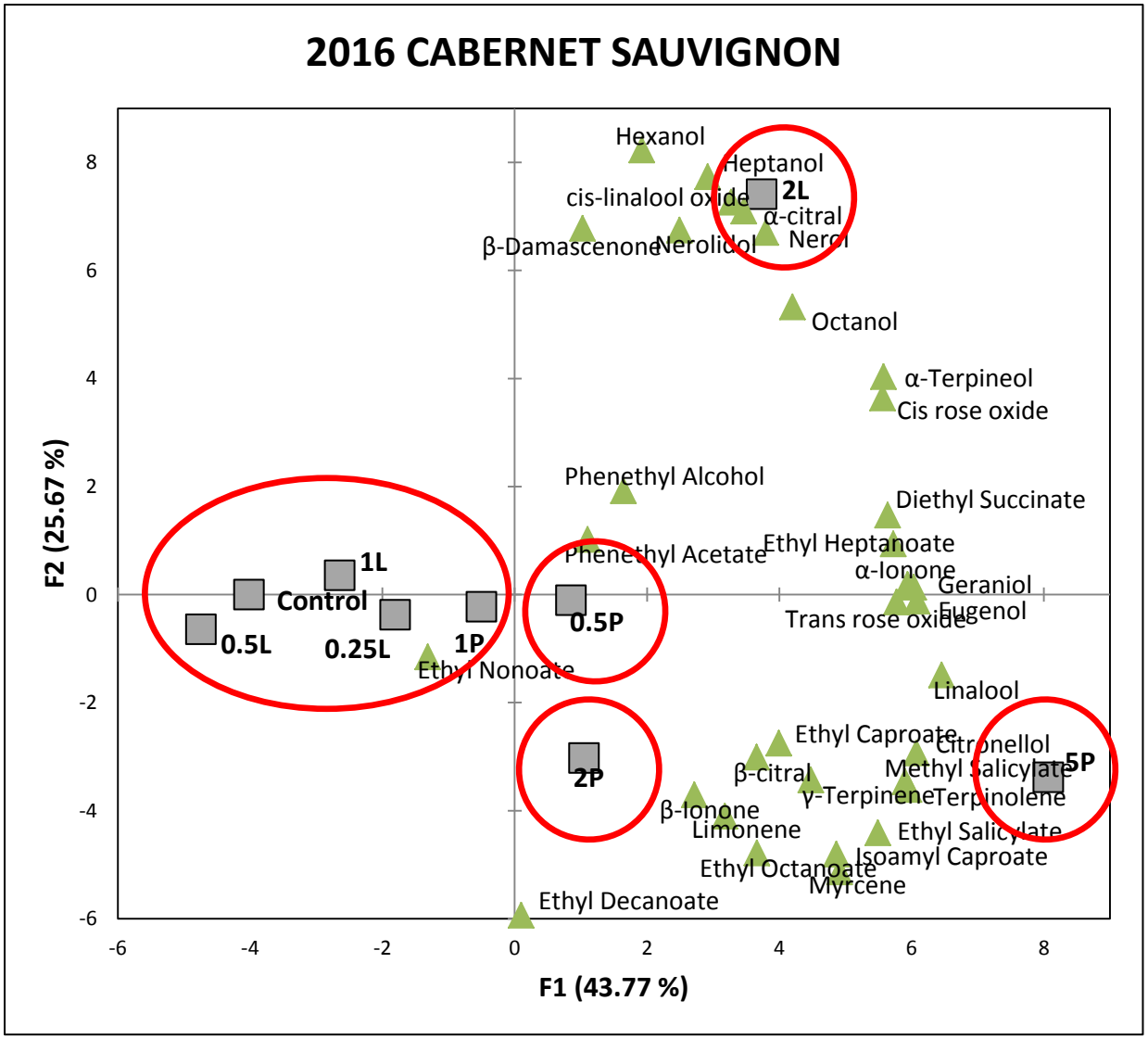




2016 PCA Cabernet franc



2016 PCA Cabernet Sauvignon



Continuing Activities- 2016 to 2018 Wines

- GC-MS and chemical analysis of 2018 Cabernet Franc and Cabernet Sauvignon wines (ongoing under supervision of Dr. Lan)

- Sensory analysis for both varieties (descriptive analysis) for 2016 and 2017. The 2016 wines are undergoing descriptive sensory analysis.

- Conventional wine composition

2017 to 2019 Seasons

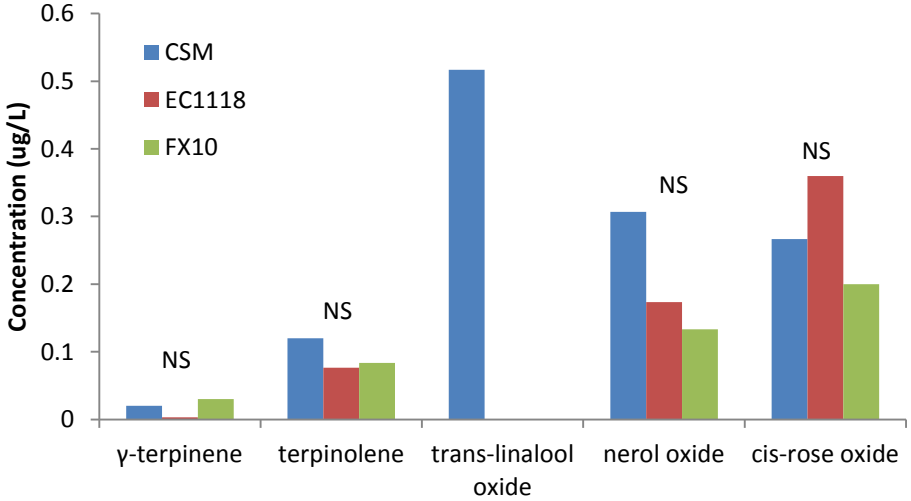
Still lots of work to do…

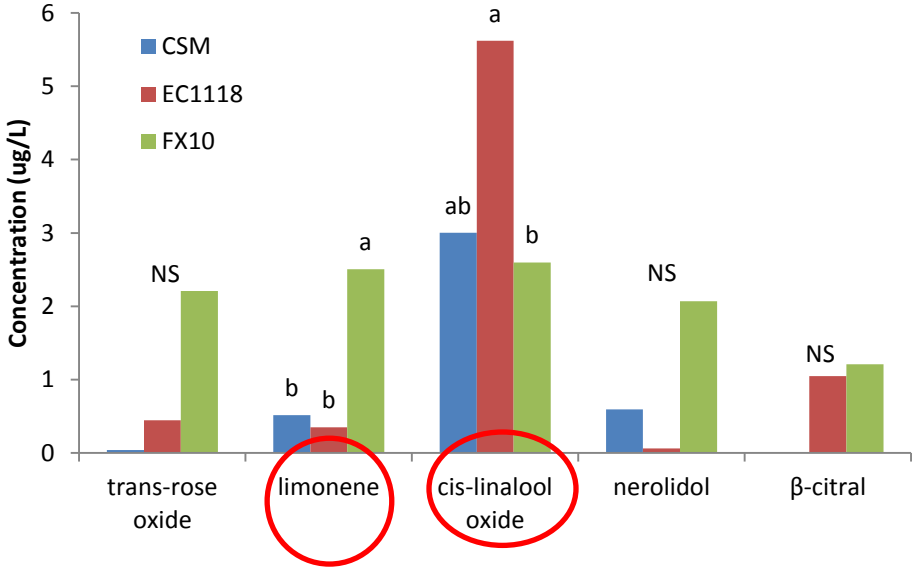
- **Combined leaf and petiole treatments with different yeast strains (CSM, EC1118, FX10)**
- **Field trials involving different harvest treatments**
  - Hand Harvest
  - Machine Harvest
  - Leaf removal prior to harvest (mechanical)
  - Machine Harvest with Opti-Sorting
  - Machine Harvest using Gregoire GR8 (2018 only)
  - Machine Harvest followed by optical sorting table (2017 only)
- **Need to perform: GC-MS on all 2018 wines (115 fermentations), basic analyses, and sensory analysis**

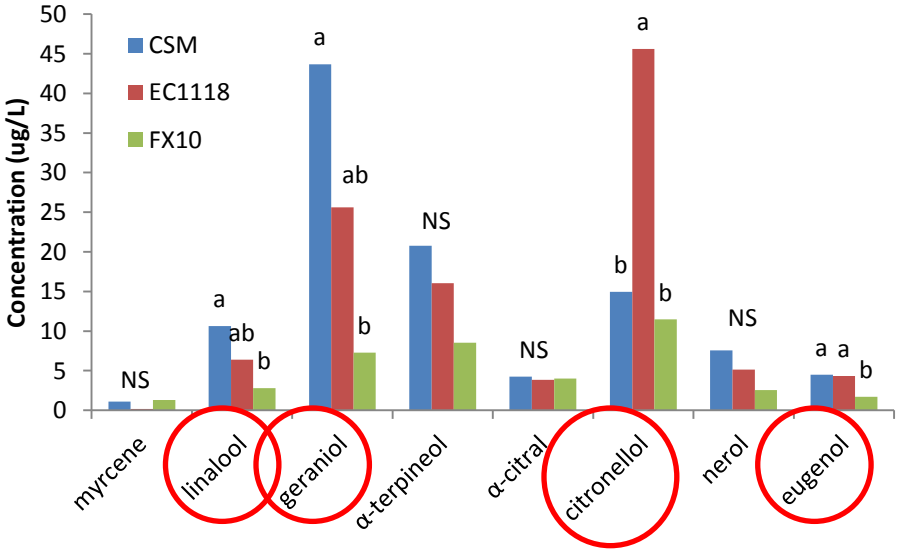
2017 Fermentation setup

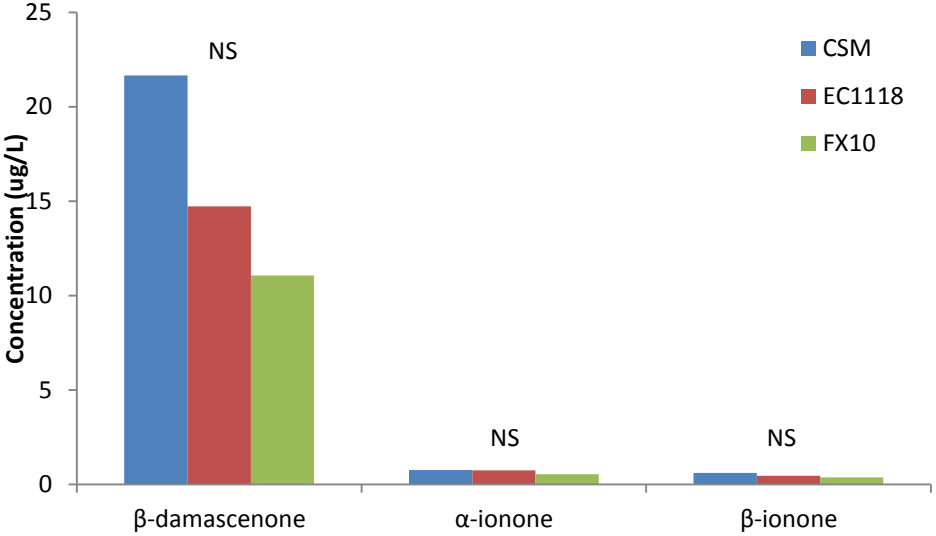
Impact of Yeast Strains 2017

Control



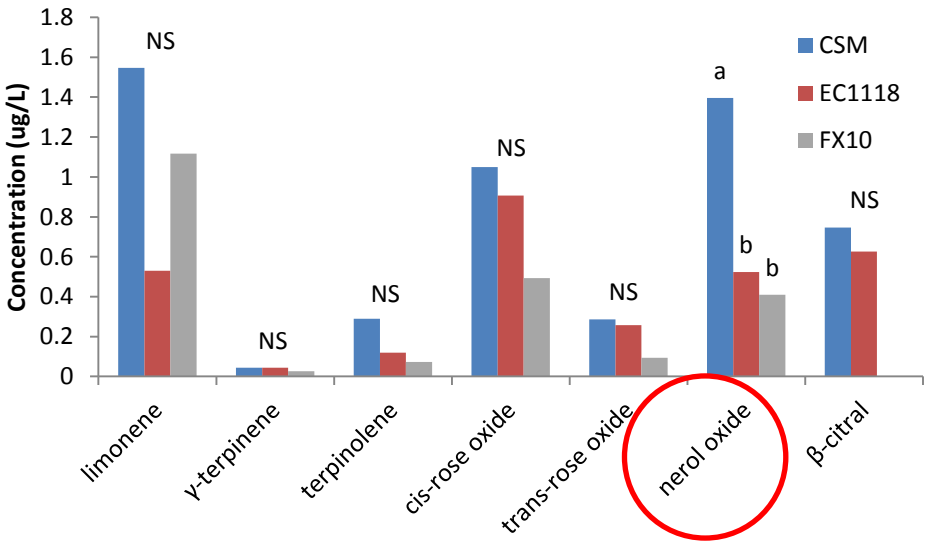


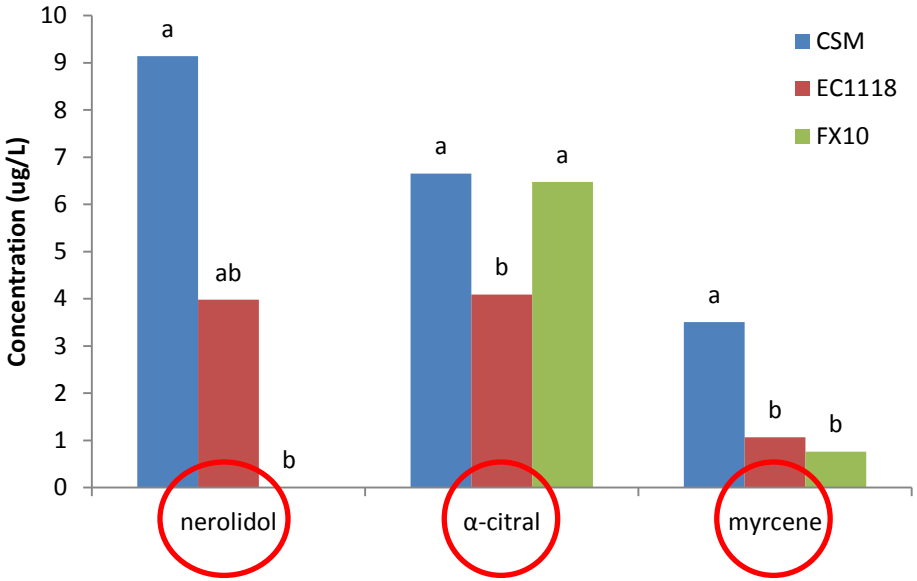


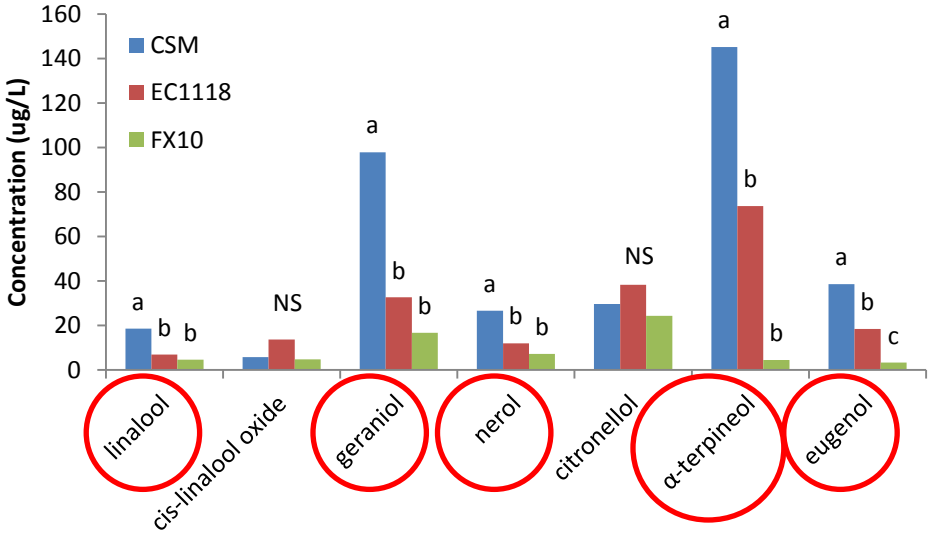


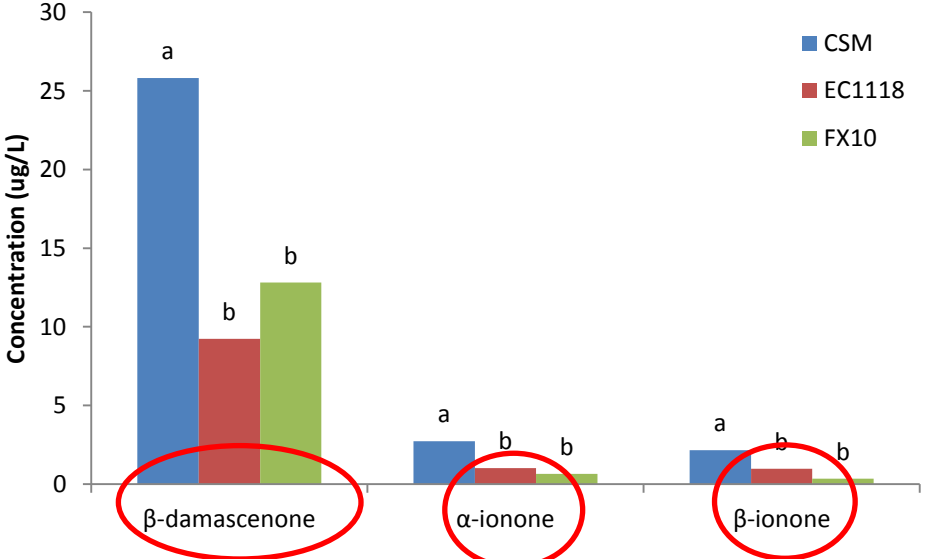
Impact of Yeast Strains 2017

2% Leaves



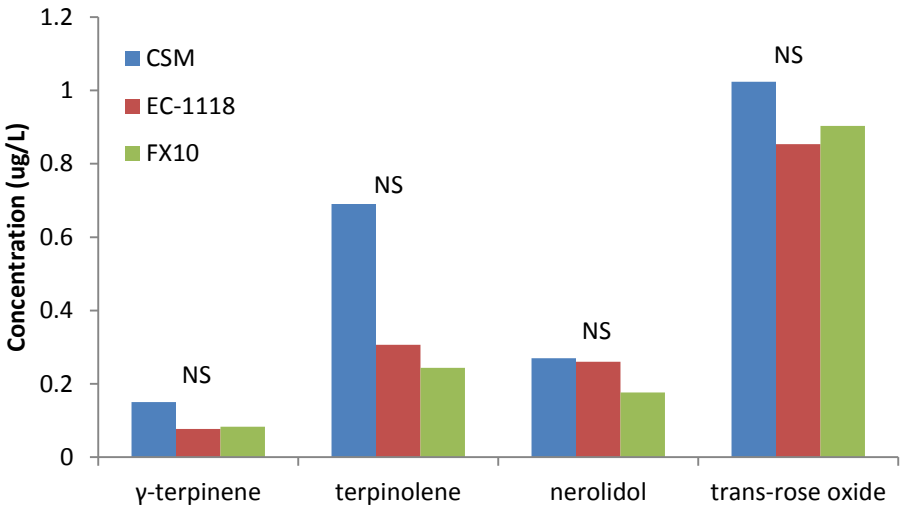


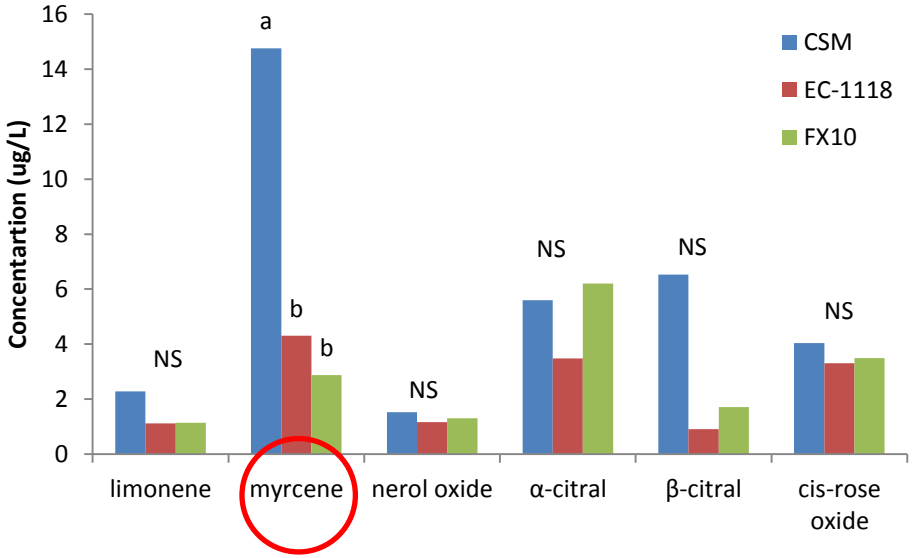


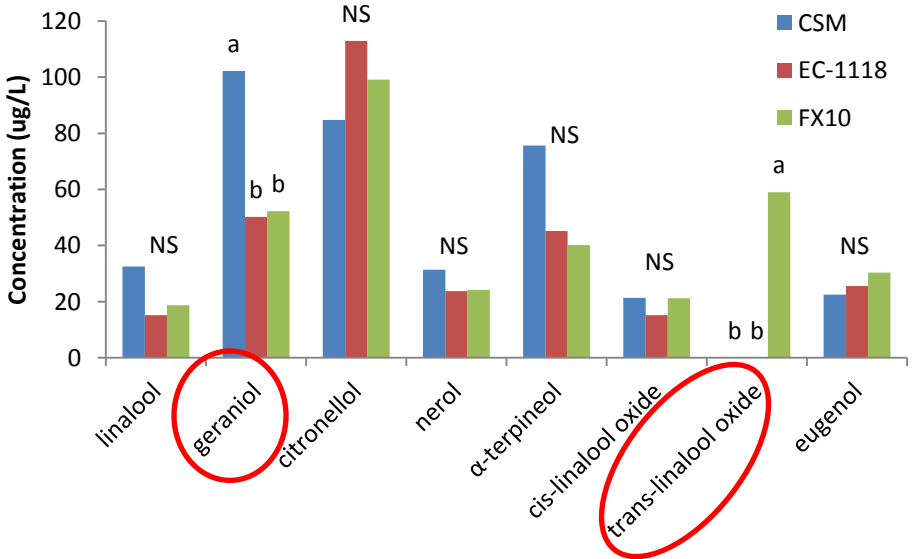


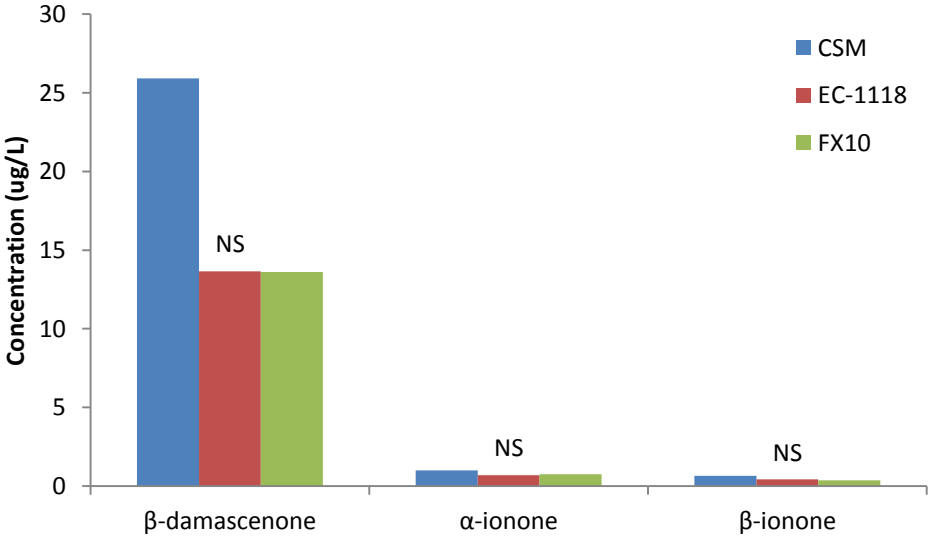
Impact of Yeast Strains 2017

5% Petioles









Yeast Effects Summary

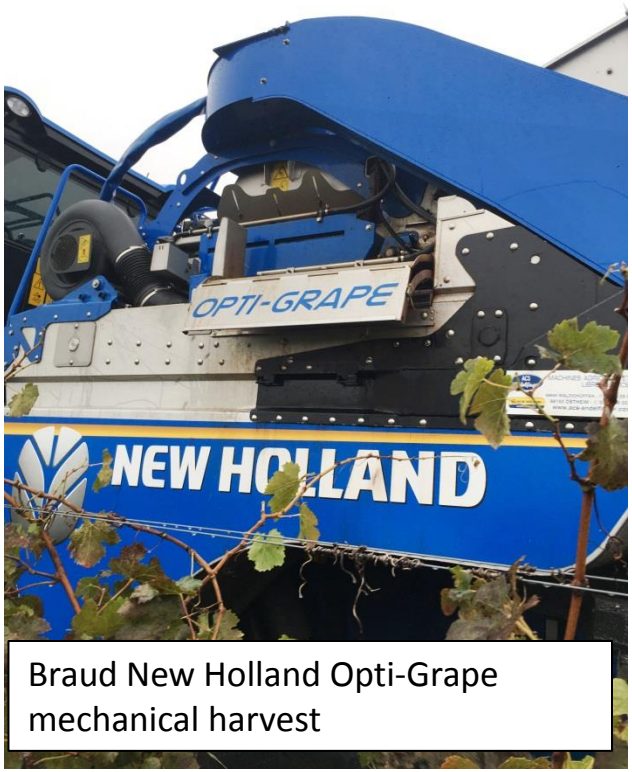
Blue= Control; Green= 2% leaves; Red = 5% Petioles

Compound	CSM	1118	FX-10	Compound	CSM	1118	FX-10
γ-Terpinene	---	---	---	Myrcene	↑ ↑	↓ ↓	↓ ↓
Terpinolene	---	---	---	Linalool	↑ ↑	↔ ↓	↓ ↓
trans-Linalool oxide	↓	↓	↑	Geraniol	↑ ↑ ↑	↔ ↓ ↓	↓ ↓ ↓
Nerol oxide	↑	↓	↓	α-Terpineol	↑	↓	↓
cis-Rose oxide	---	---	---	α-Citral	↑	↓	↑
trans-Rose oxide	---	---	---	Citronellol	↓	↑	↓
Limonene	↓	↓	↑	Nerol	↑	↓	↑
cis-Linalool oxide	↔	↑	↓	Eugenol	↑ ↑	↑ ↓	↓ ↓↓
Nerolidol	↑	↔	↓	β-Damascenone	↑	↓	↓
β-Citral	---	---	---	α-Ionone	↑	↓	↓
				β-Ionone	↑	↓	↓

Harvest Treatments

Conventional mechanical harvest

Conventional mechanical harvest with leaf removal prior

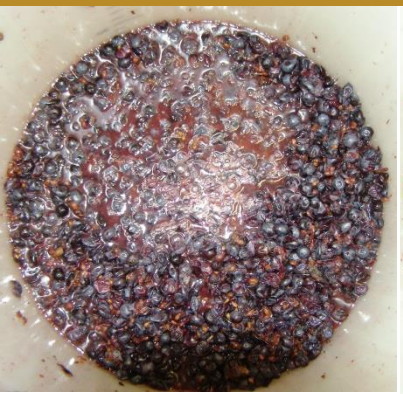


Braud New Holland Opti-Grape mechanical harvest

<u>Not shown</u>

- **Hand harvest**
- **Gregoire G8 mechanical harvester (2018 only)**
- **Optical sorter (2017 only)**

2017 Fermentations and materials removed per load at de-stemming

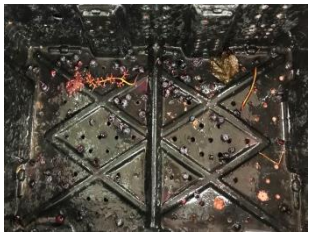


HAND HARVEST

MECHANICAL HARVEST

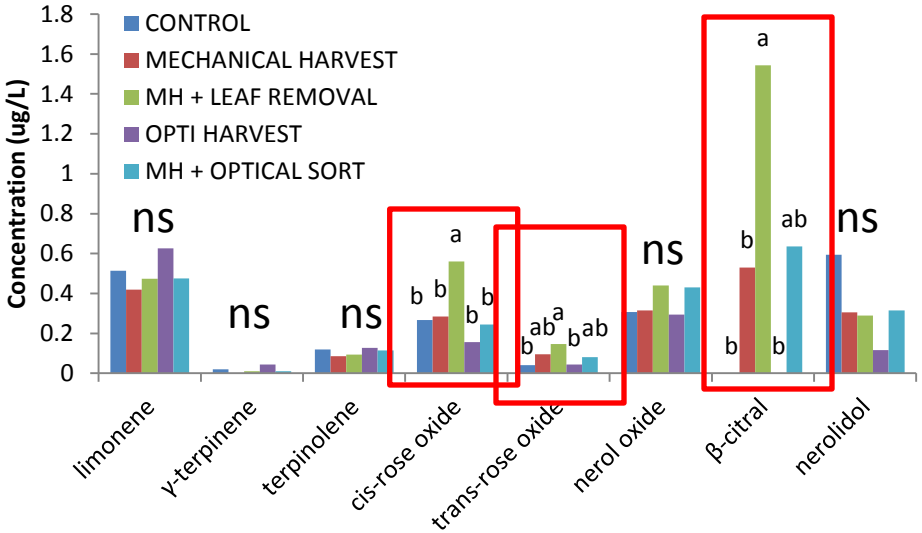
MECHANICAL HARVEST PRECEDED BY LEAF REMOVAL

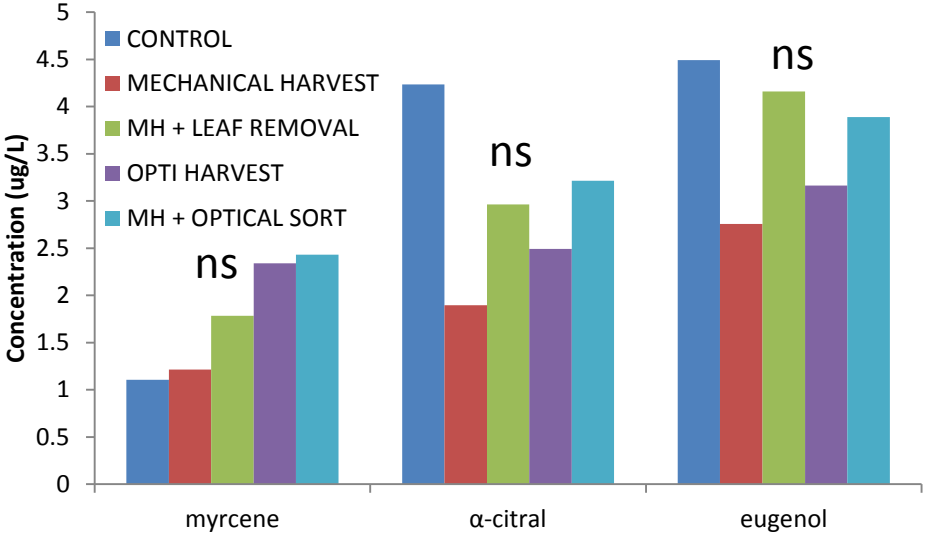
MECHANICAL HARVEST "OPTI"

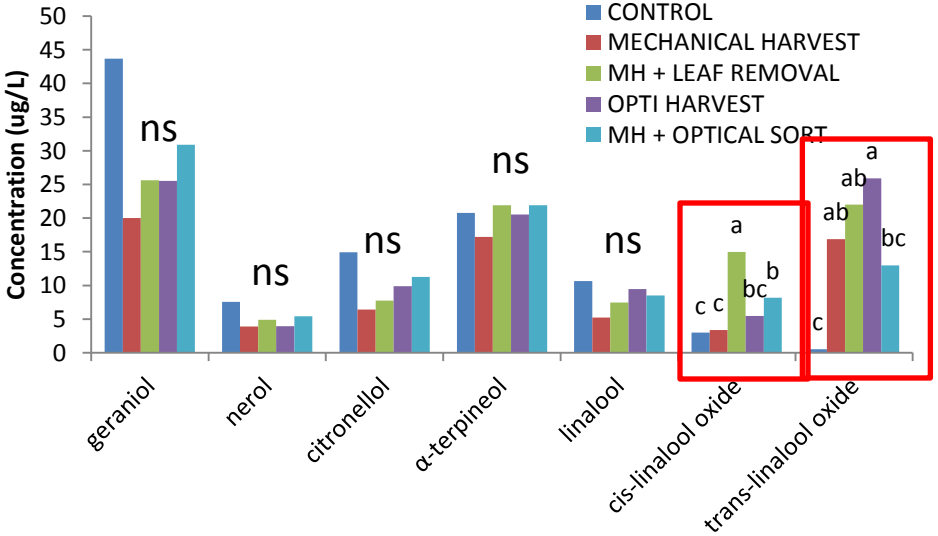


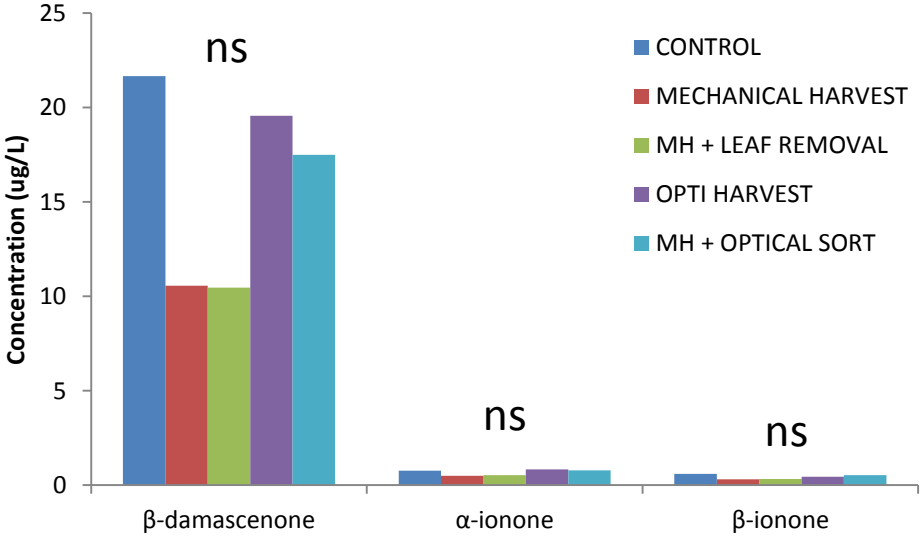
MECHANICAL HARVEST + OPTICAL SORTING

Impact of Harvest Strategies 2017- Terpenes and Norisoprenoids

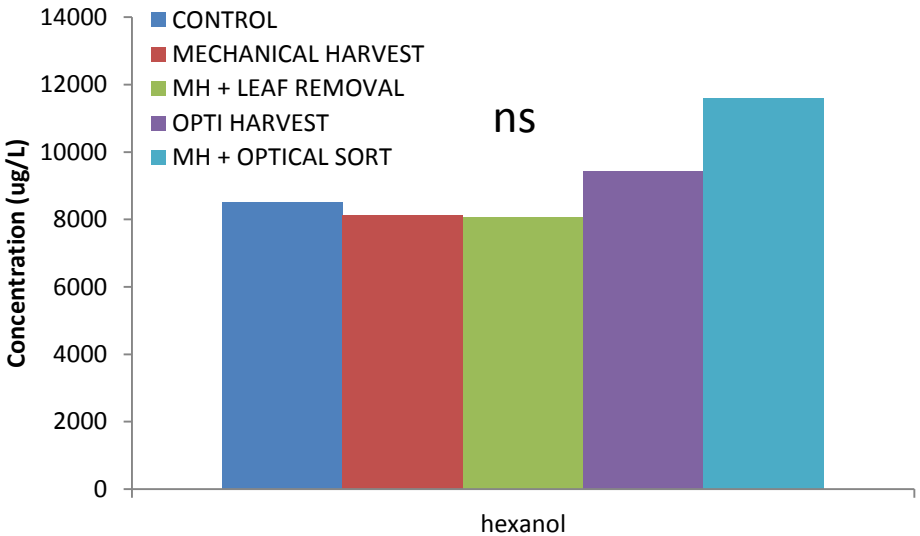


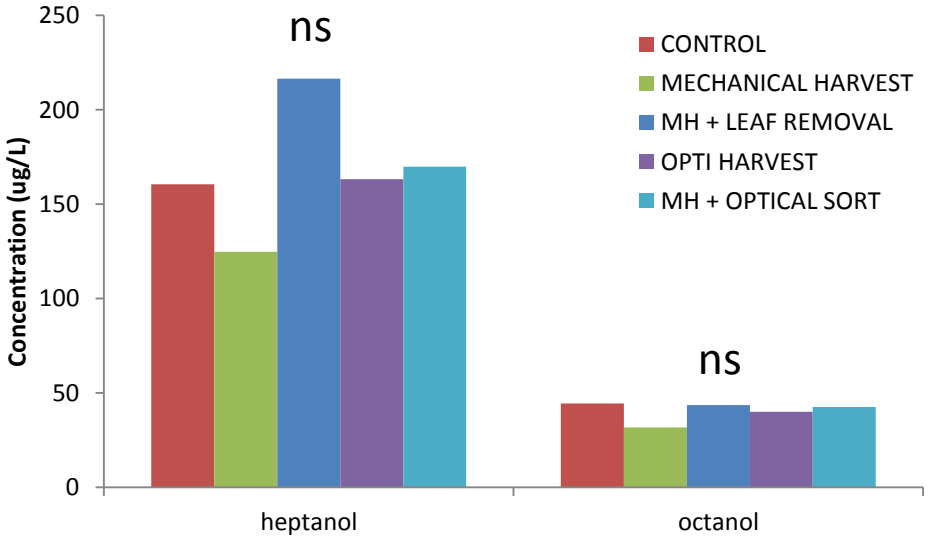


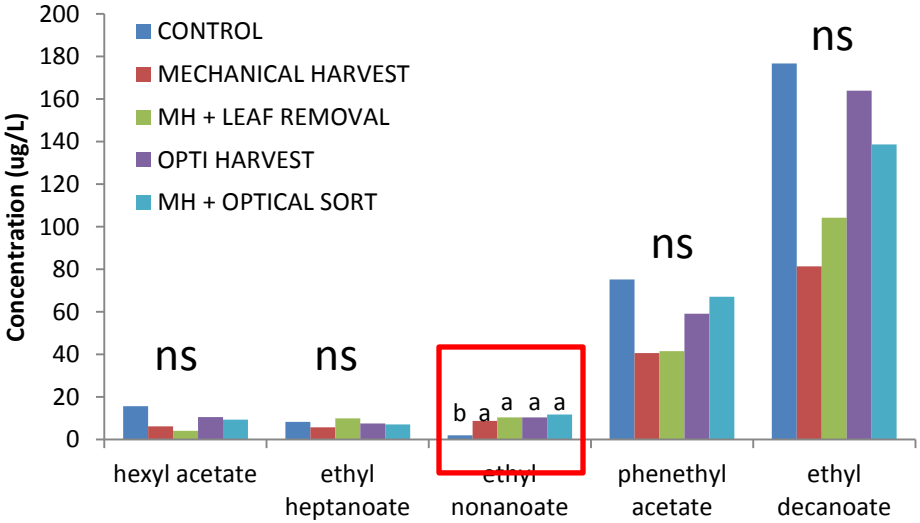


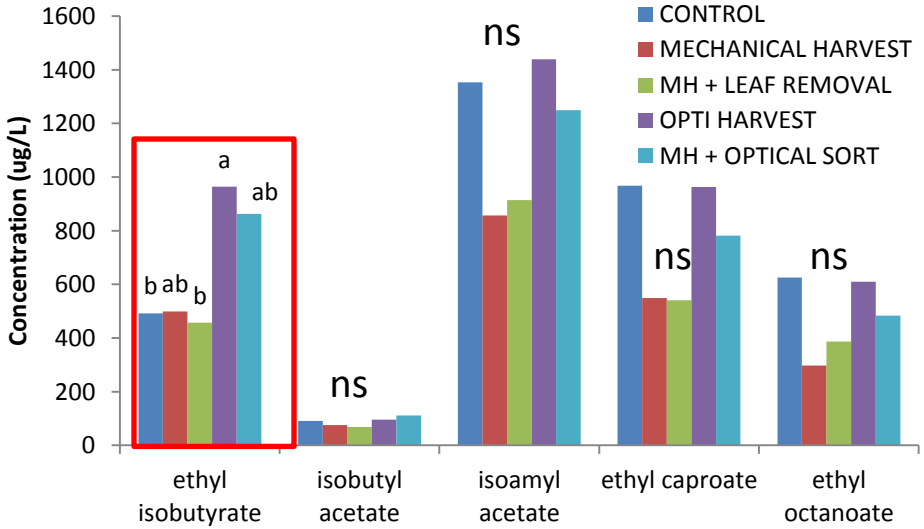


Impact of Harvest Strategies 2017-Alcohols and esters









Possible Contributions From MOG

- Terpenes and other odorants √
  - Confirmed by GC-MS
- Bitter taste compounds √
  - Bitterness was partly used in multidimensional sorting to distinguish the wines
- Malic acid increase from leaves and petioles √
  - Acidity was likewise used by tasters to distinguish wines
- Metal content (Na, K, Mg, Fe) ?
  - Under investigation (Barry Cameron, Univ. of Wisconsin, Milwaukee)
- Decrease in anthocyanins and color intensity √
  - Preliminary lab data (e.g. OD 520, total anthocyanins) clearly show this

Tentative Conclusions

- "Floral taint" associated with frozen MOG is due primarily to several terpenes (linalool, geraniol, *cis*- and *trans*-rose oxide, citronellol, nerol), methyl and ethyl salicylate, and ß-ionone
- Several esters and other aliphatic compounds also appear to be related—including phenethyl alcohol; ethyl heptanoate, octanoate, nonoate and decanoate; hexanol, octanol
- However—some of these, although very responsive, may be below threshold. But, (a) Most thresholds have been measured in water and are much lower in alcohol, and (b) There are lots of interactions between chemicals that we don't fully understand.

Thanks!

Ontario GRAPE & WINE RESEARCH Incorporated

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Custom Farming · Custom Harvesting · GPS Planting

LAKEVIEW VINEYARD EQUIPMENT INC.

ANDREW PELLER LIMITED

ARTERRA WINES CANADA

VINELAND ESTATES WINERY

DIAM

More Thanks

Thanks to our interns Chao Wang (l) and Yuan Zhang (r) during 2017 vintage