MPs and TDN* – achieving control of acronyms in the vineyard and winery

* and other C_{13} norisoprenoids

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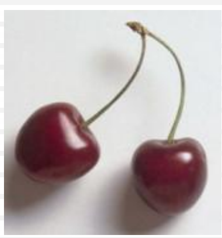
Masking and wine

Fundamental Theorem of Calculus

$$\int_a^b f(x)dx = F(b) - F(a)$$

Fundamental Theorem of Wine Aroma (FTWA)

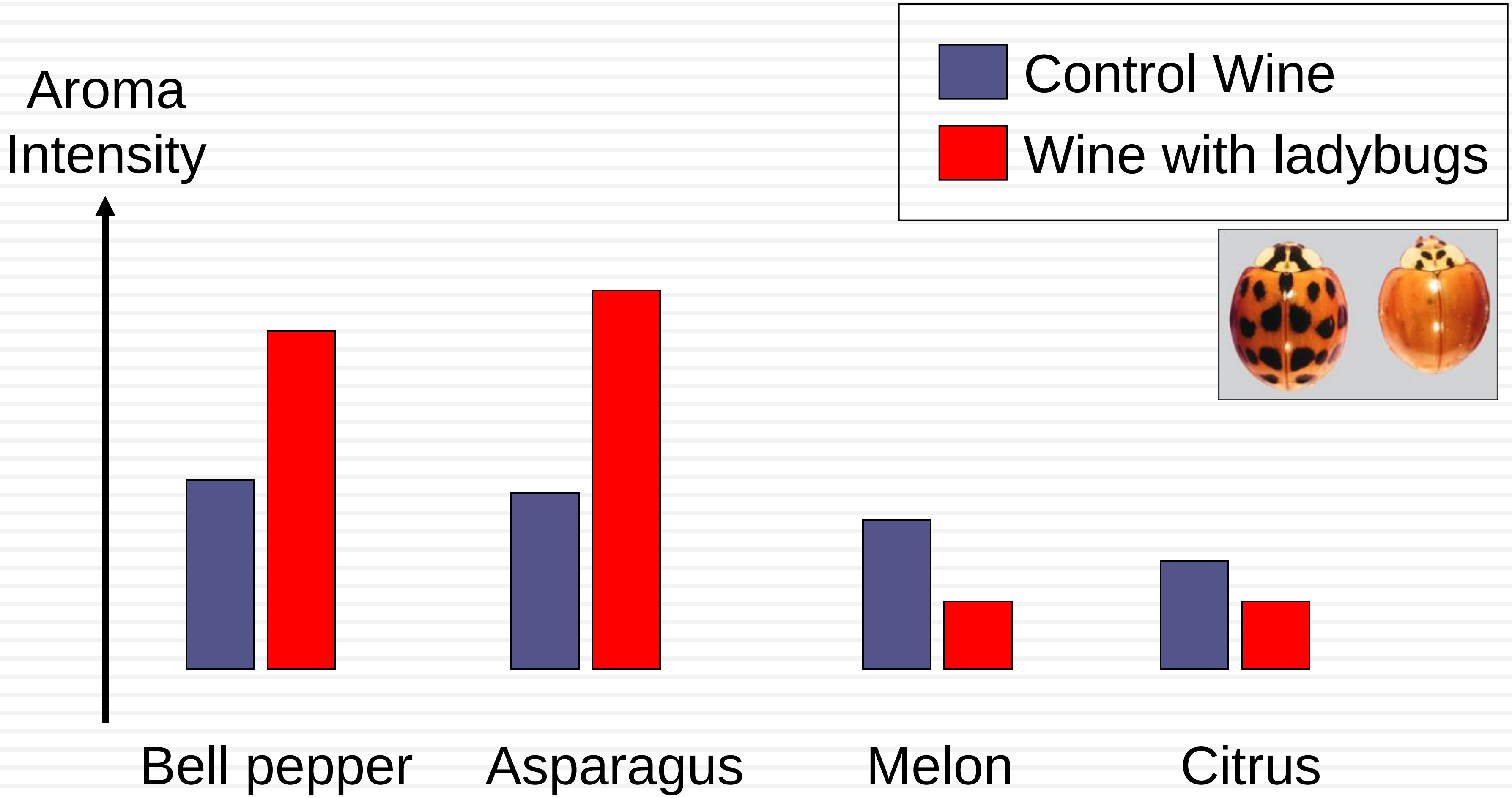


"Vegetal", "Musty", "Rubber"

"Fruity", "Sweet"

Not-so-ripe and ripe aromas mask each other

Masking: 10 MALB (multi-colored Asian ladybeetles) added to 1L of juice



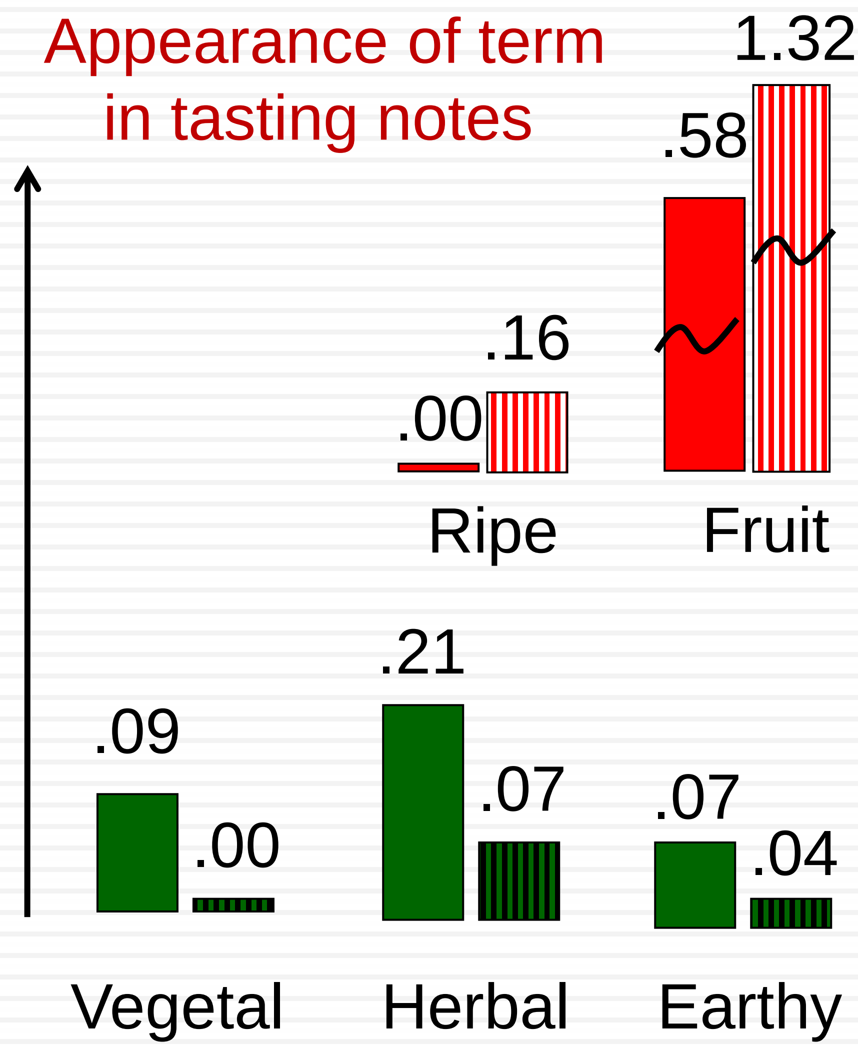
Data adapted from Pickering, et.al. (AJEV, 2004)

Vegetal aromas: often treated as a scourge in red wines

Wine Spectator scores & tasting notes for Long Island, NY reds

Solid green / solid red	75-85 points (182 wines)
Striped green / striped red	85-90 points (85 wines)

Low scoring wines more likely to have vegetal descriptors, less likely to have fruit descriptor



Adapted from data compiled by Larry Perrine at Channing Daughters Winery (NY)

But, "vegetal" doesn't always mean "unacceptable"

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Food Quality and Preference 18 (2007) 849–861

Food Quality and Preference

www.elsevier.com/locate/foodqual

The distinctive flavour of New Zealand Sauvignon blanc: Sensory characterisation by wine professionals

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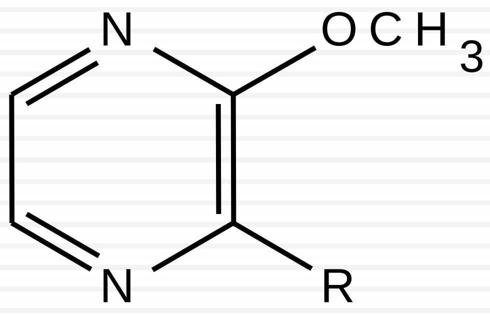
[b] *University of Otago, Dunedin, New Zealand*
[c] *Food and Wine Group, Agriculture and Life Sciences, Lincoln University, P.O. Box 84, L.U., Canterbury, New Zealand*

"Specific flavour characteristics (e.g., green capsicum; boxwood) were predictive of high typicality ratings for a wine, whilst others (e.g., mineral) were predictive of low typicality ratings. The chemical concentrations of IBMP and IPMP correlated positively with perceived green flavours, and inversely with perceived ripe and fruity flavours"

The most notorious contributors to "veggie" 3-Alkyl-2-methoxypyrazines (MPs)



R = *alkyl group*

Detection threshold in wine
IBMP: 5-15 ppt (ng/L)
IPMP: 0.5-2 ppt

IBMP range of 5-20 ng/L (up to 50) typically reported for "Bordeaux" grapes: Cabernet, Merlot, Sauv blanc

R	Abbr	Typical conc. in CS or CF (ppt)	Aroma	
isobutyl	IBMP	5-20	Capsicum, vegetal	*Predominant MP in grapes*
sec-butyl	sBMP	n.d. - 1	Peas, potatoes	*Usually not detectable*
isopropyl	IPMP	n.d. – 2	Asparagus, earth, peas	*Predominant MP in Asian lady beetle*

MP distribution and extraction during winemaking

Within berry

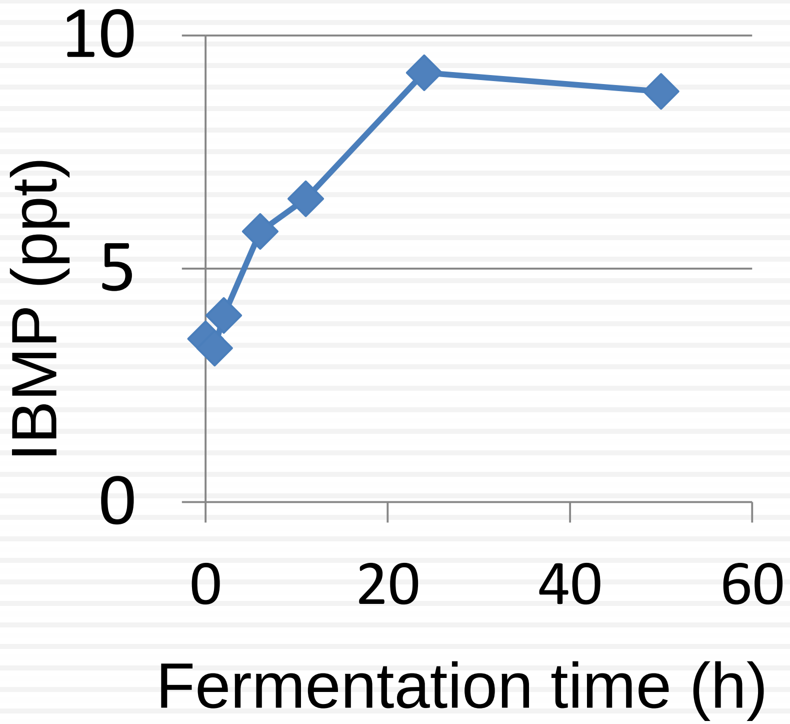
Skin: 95%

Seeds: 4%

Pulp: <1%

Within cluster, rachis accounts for ~50% of MP

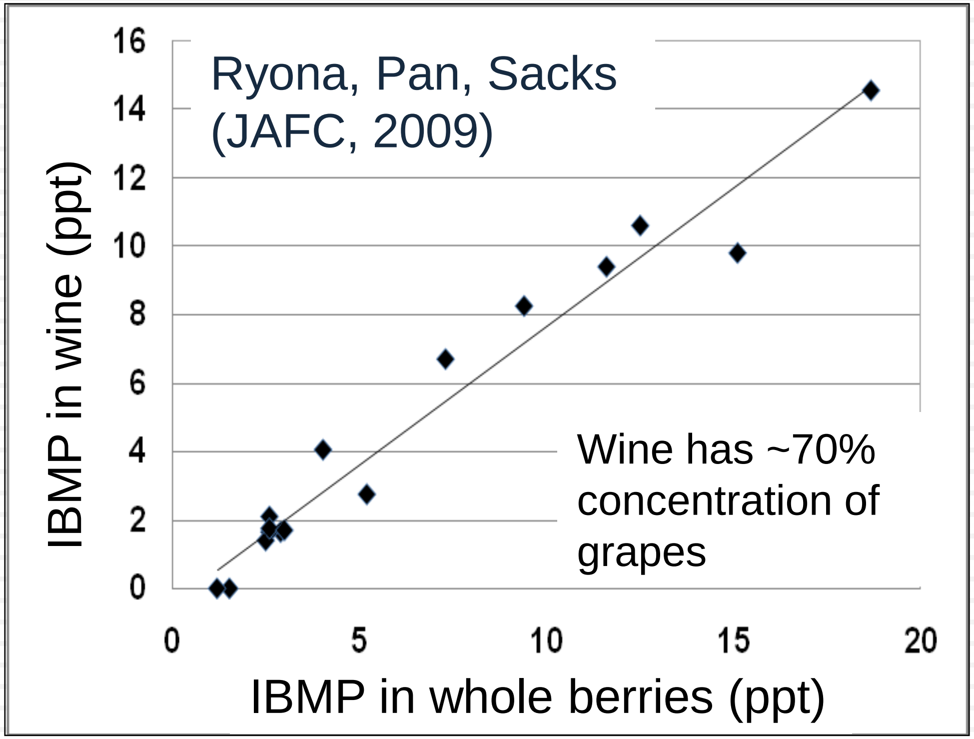
Extraction kinetics comparable to or slightly faster than anthocyanins



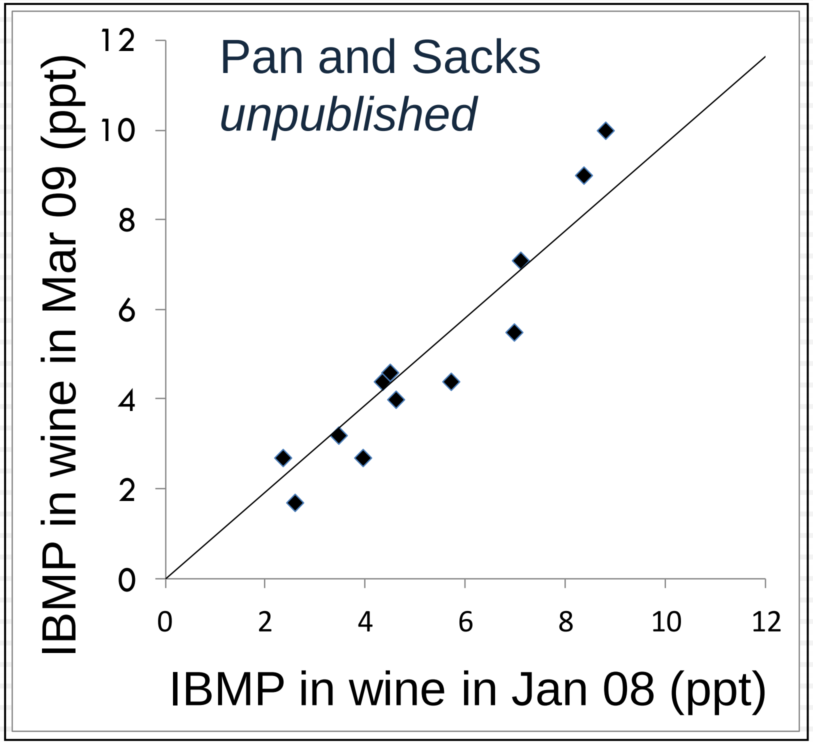
Adapted from Roujou de Boubee 2001 thesis

IBMP in wine correlates with MP in grapes, and its stable in bottle

IBMP in wines vs. grapes for 16 small lot Cabernet franc fermentations



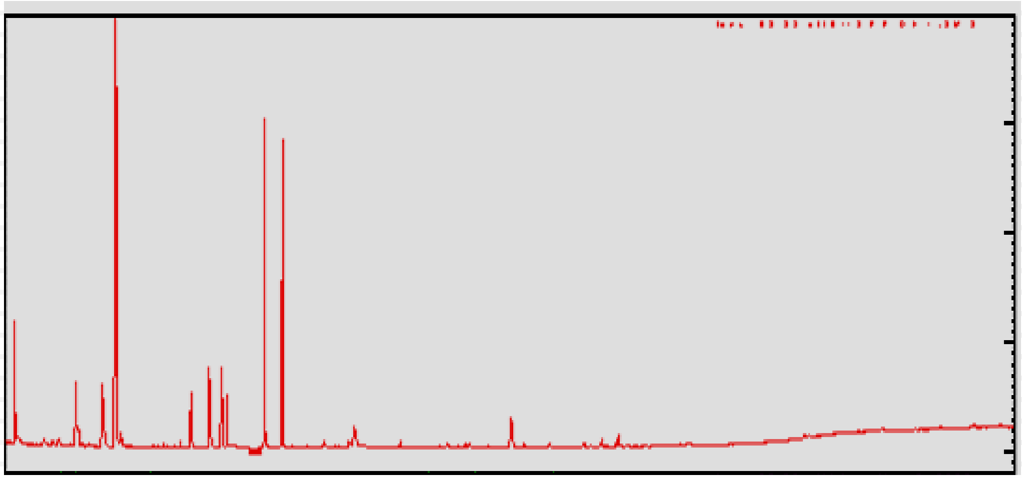
IBMP in wine vs. IBMP in same wine 14 months later



Post-harvest practices: Challenging to **selectively** remove MPs without changing other volatiles

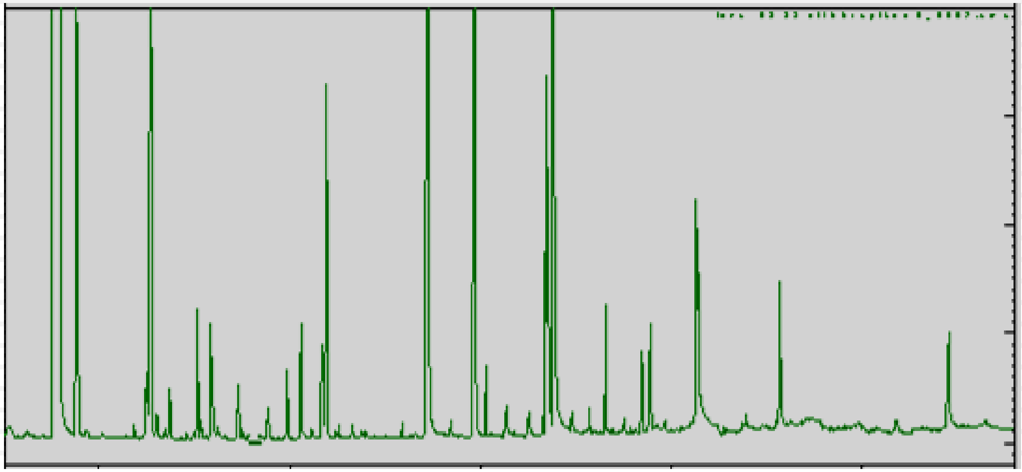
Timing	Treatment	Notes
Pre-fermentation	Thermovinification, flash détente Destemming Polymeric fining	Possibility for MP volatilization, but will cause other changes to wine 50% of MP in Cab Sauv cluster is in rachis (Roujou de Boubee) See next slide
Fermentation	Yeast strain Microx, temp, etc	No evidence of yeast degradation (SA Harris thesis), some non-selective binding to lees; masking possible No evidence of direct effect, but will change other volatiles (masking)
Post-fermentation	Standard fining: carbon, bentonite etc Odorant binding protein?	Poor selectivity or ineffective. (Pickering et al, 2005) Patented by Brock U., still waiting on publications regarding selectivity

Idea we've explored: add non-polar sorbent before fermentation, MPs removed before other volatiles appear



Grape Juice by GC-MS

(MPs are present, but not most wine volatiles)



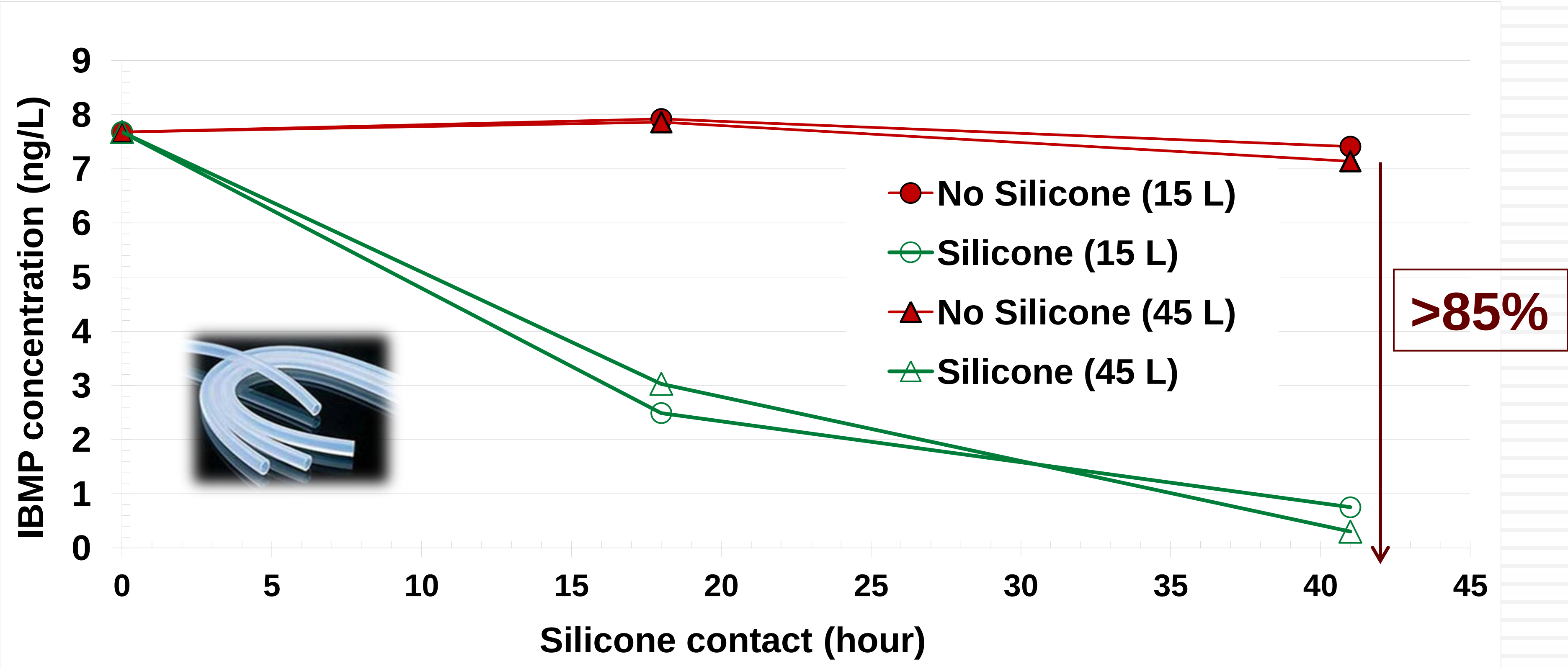
Wine by GC-MS

(majority of volatiles appear)

Example results: 40 g/L chopped silicone tubing

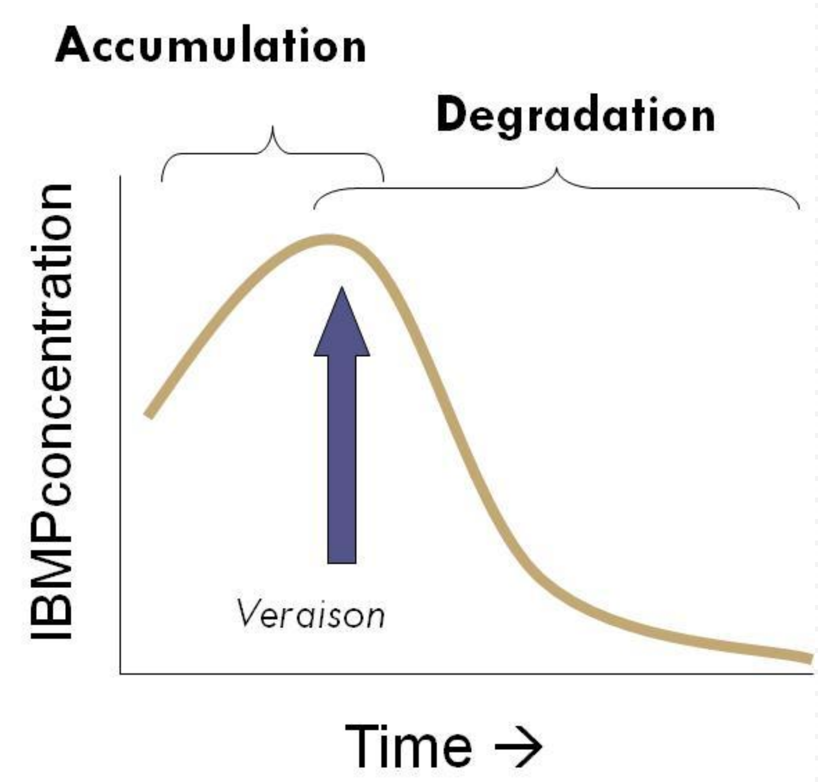
(Ryona, Reinhardt, and Sacks, Food Res Int, 2012)

2007 Cabernet Franc Rose



Generally, 50-90% reduction in MPs; no significant reduction of other wine volatiles (esters, fusel alcohols, most terpenoids, etc)

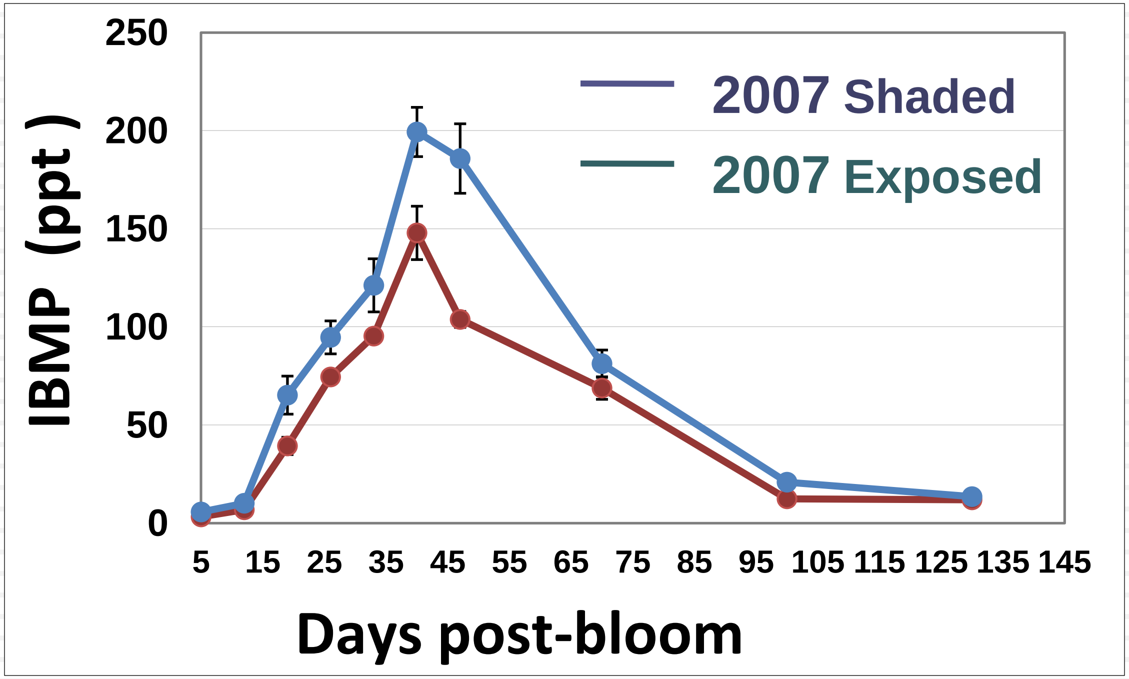
Before the winery: What controls MPs in the vineyard?



IBMP accumulates pre-veraison, degrades post-veraison

Factors classically associated with lower MPs at harvest
- Better cluster exposure
- Warmer growing regions
- Less vine vigor

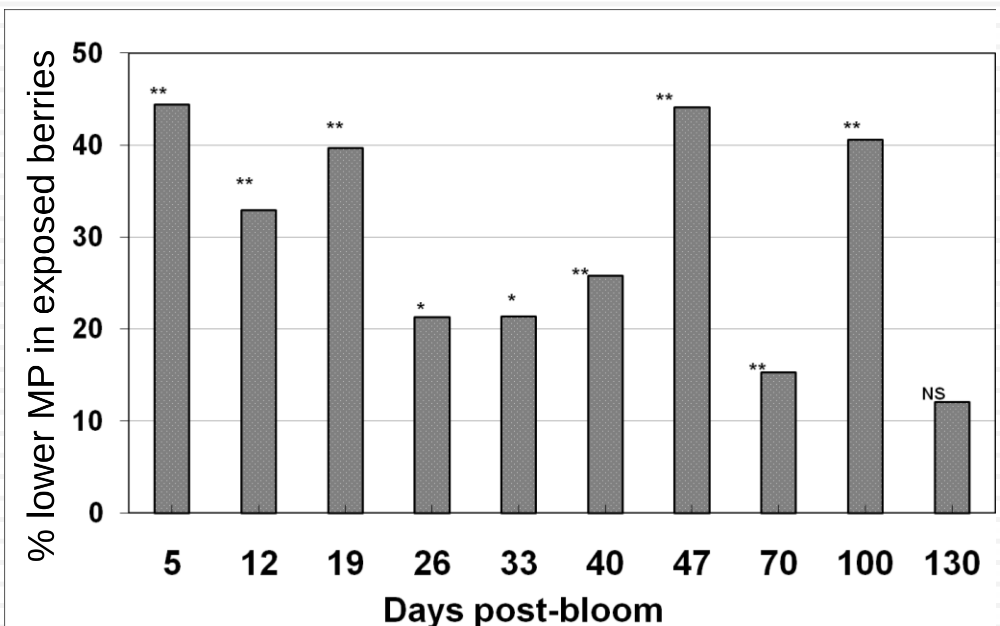
Do these factors effect accumulation or degradation?



Ryona, et.al. *J. Ag Food Chem*, **2008**

(left) Example data: Exposed and shaded Cabernet franc, same vine

(right) Exposed fruit accumulates less IBMP, degradation rate not affected.
MPs don't "burn off"

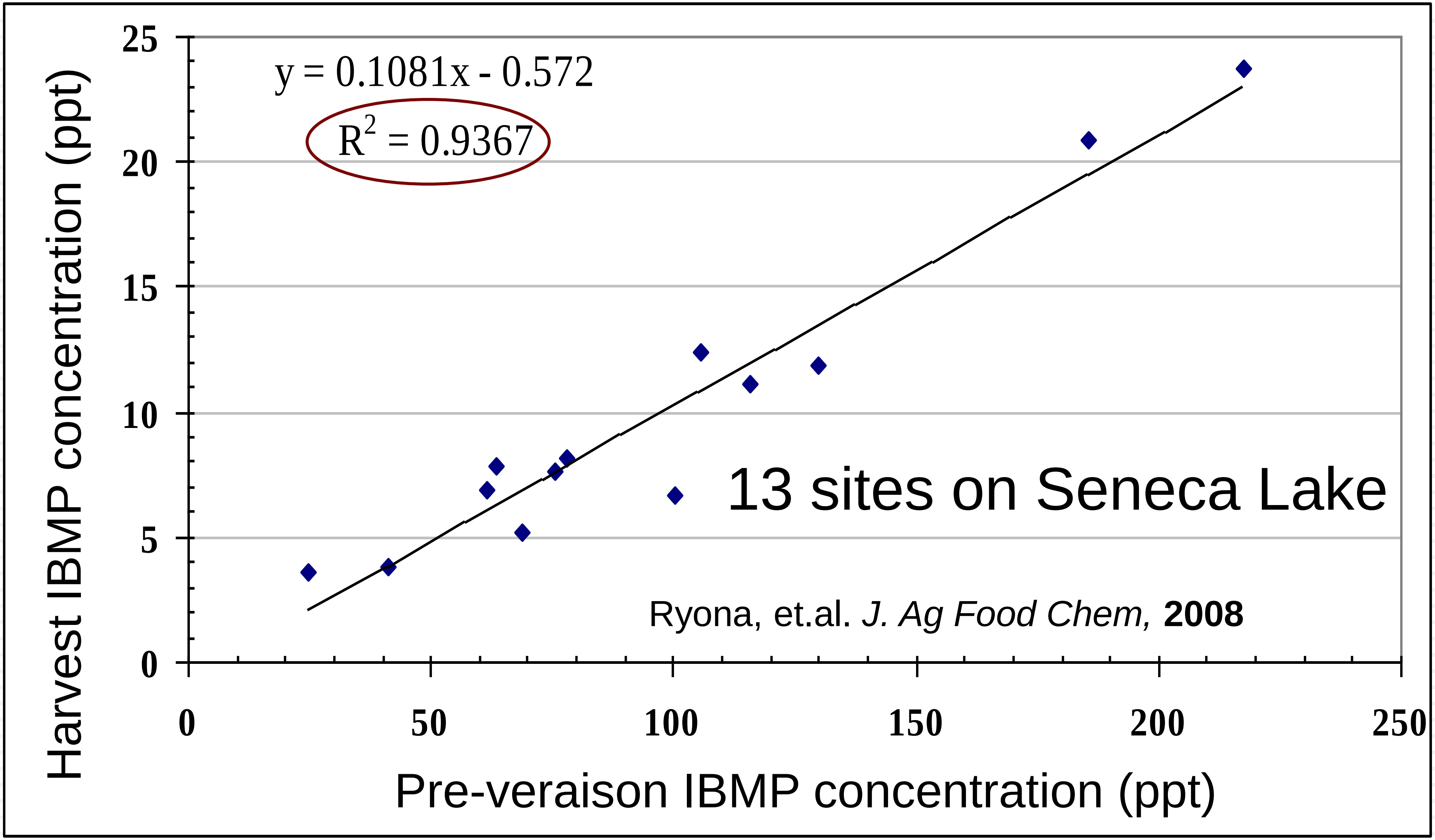


Similar results:

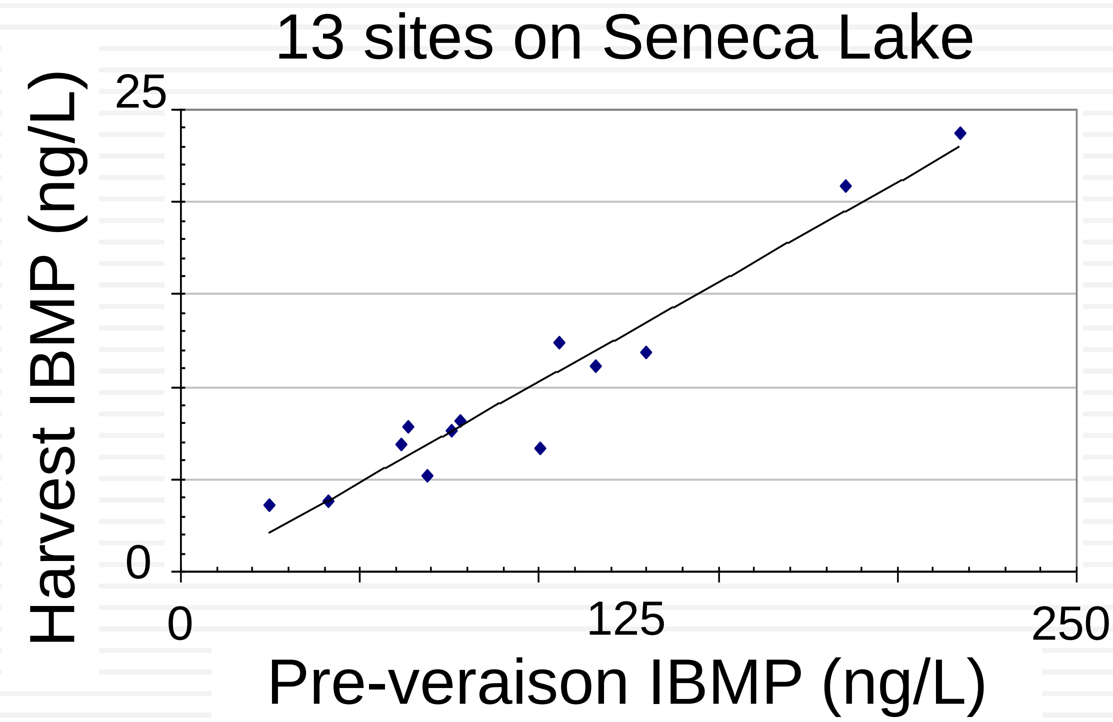
Lakso and Sacks; *Kliewer Symposium* (2009)

Koch, et al; *Physiol. Planta* (2012)

The importance of *accumulation*: all things being equal, MP at harvest reflects MP at veraison



Can cluster shading be "The Lone Gunman" to explain differences in MPs?



Within a site, cluster shading results in MPs differences of factor of 2

But, within a region, we see nearly an order of magnitude of range in pre-veraison and harvest IBMP!

Multivariate Field Study
"What variables really matter?"

- 10 sites in NYS
  - 2 Long Island
  - 2 Lake Erie
  - 6 Finger Lakes
- 10 vines at each site
  - 2 x 5 vine panels

Along with:
Justine Vanden Heuvel
Justin Scheiner

Summary of Multivariate Studies

IBMP **accumulation** pre-veraison independently and significantly associated with

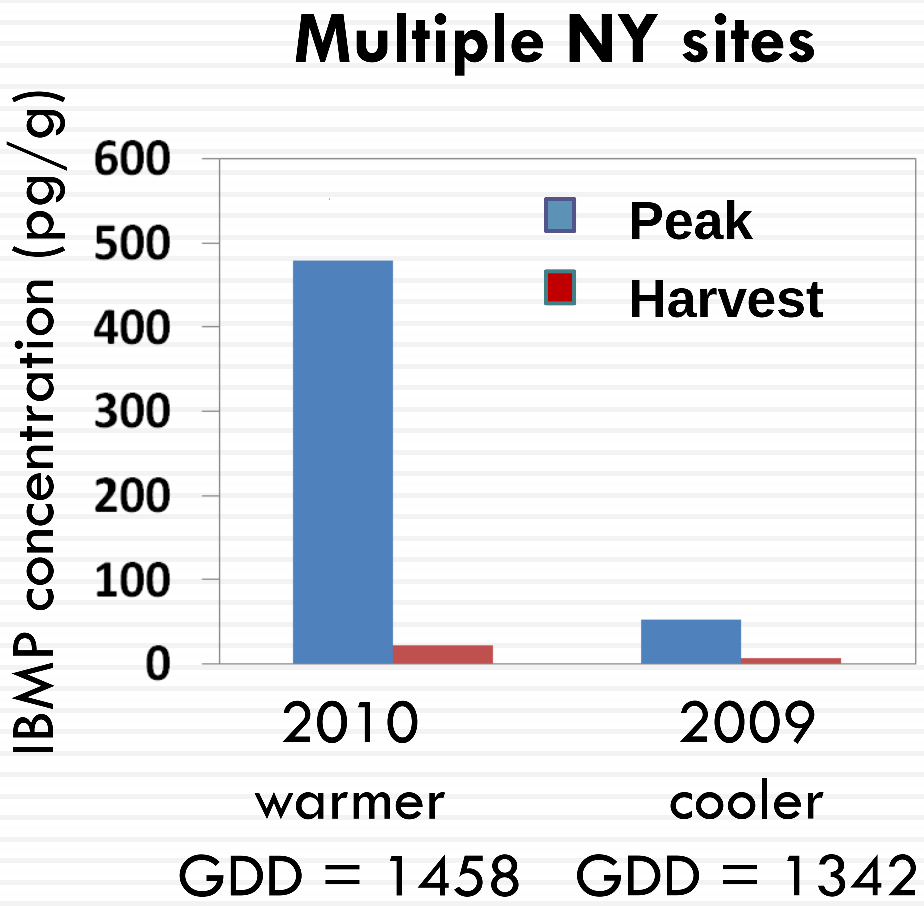
- **higher temperature(!)**
- **greater water availability and vine growth**
- and within some sites, **cluster shading**

IBMP **degradation** post-veraison correlates with

- maturity indices (sugar accumulation, etc)
- and not much else

Scheiner, Vanden Heuvel, Pan, and Sacks. *AJEV* **2012**

Surprise: **warmer seasons = more IBMP accumulation,** although faster degradation



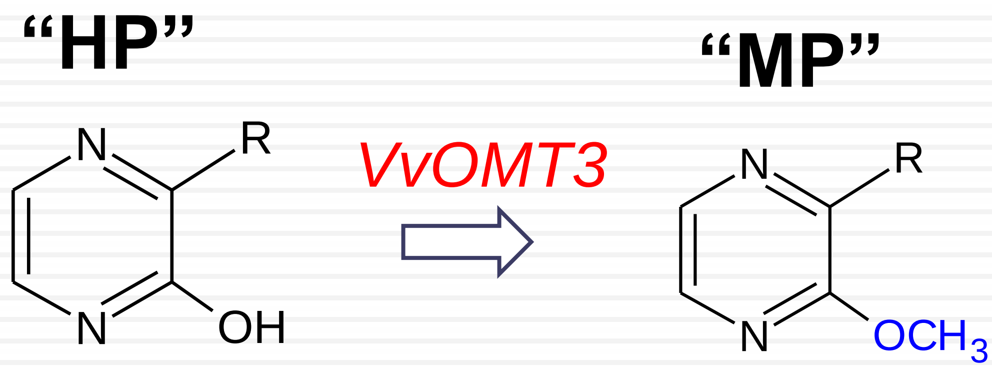
Earlier work by Allen and colleagues: warmer sites have less MP ***at harvest****.*

Harvest date, water status, etc. will matter too.

Note: highest pre-veraison IBMP our lab has ever seen was 800 pg/g from Central Valley (California) Merlot.

- *Lots of irrigation, N, heat.*

Newly emerging: Molecular biology understanding of what affects MPs



OMT3 = *O-methyl transferase 3*

Partially explaining differences
* among cultivars
* resulting from treatments

J. Dunlevy thesis
Dunlevy, et al *Plant Journal* (2013)
Guillaumie, et al *Plant Phys* (2013)

Summary of factors affecting MPs

If you want lower MPs in your wine, start with low MPs in your grapes

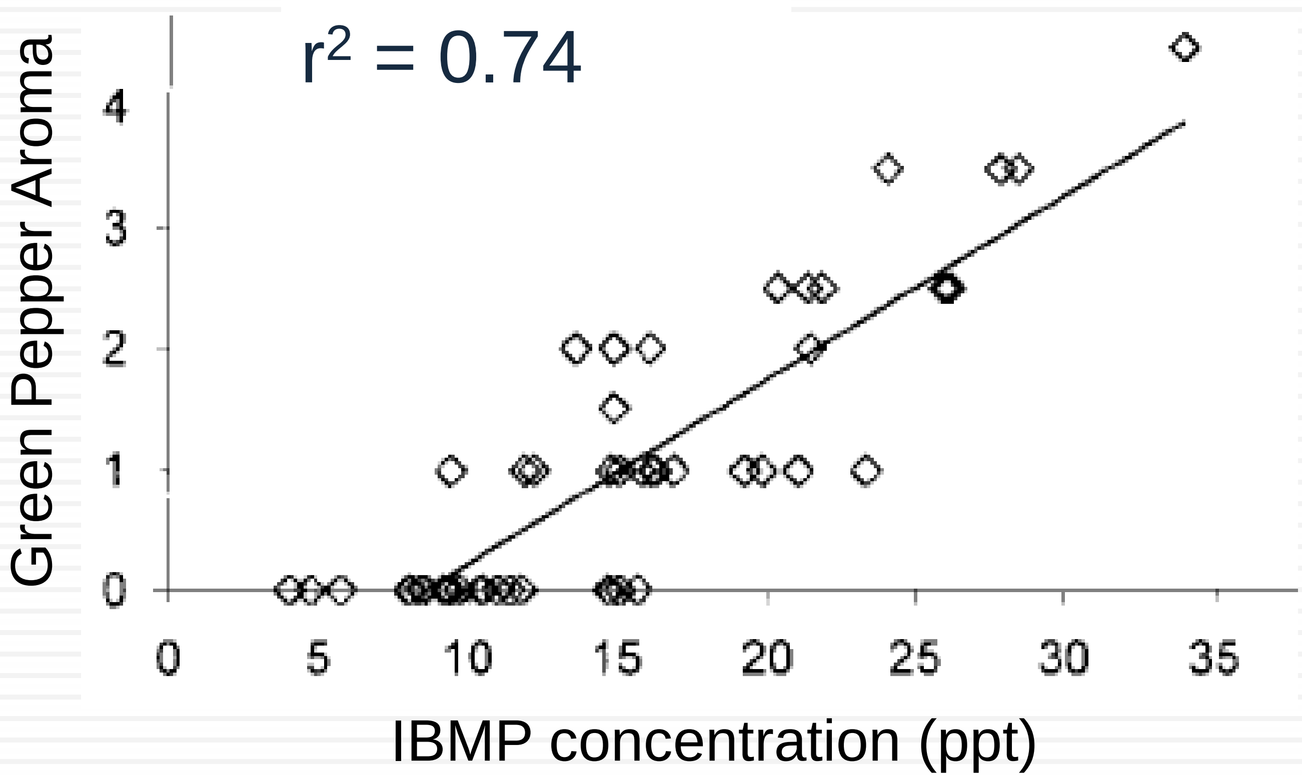
- Variety. Do you have to plant Cabernet Sauvignon?
- Accumulation:
    * vigor related factors: lower water status, etc;
    * increase cluster exposure (but, not as important as previous point)
- Degradation
    * Harvest timing

Note: if you want more MPs, do the opposite!

Selectivity hard to achieve in winery

- Good destemming, sorting will reduce
- Fruit masks veggie, and vice versa. For example, avoid reduction (a little Cu may make a difference)
- Alternate approaches: rose production, thermovin, polymer fining, etc
- Are you sure the issue is MPs? May want to measure.

The last issue: how good a predictor of "capsicum/bell pepper aroma" are MPs in wine?

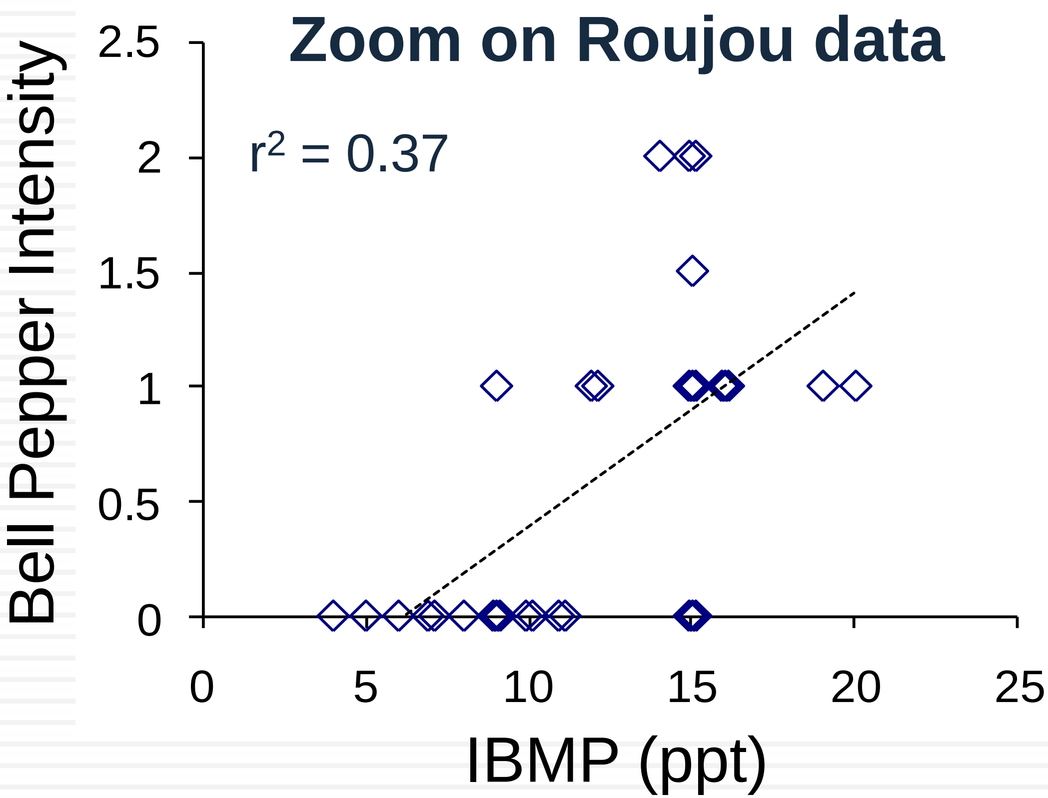


Fifty Bordeaux and Loire reds, judged by expert panel

Exceptional correlation between IBMP and "green pepper"

Roujou de Boubee, et.al. (JAFC 2000)

Correlation of MPs and “bell pepper” more modest around typical concentrations (5-20 ppt)



Modest or poor correlations observed in other reports

Chapman, et al (JAFC, 2004)
Falcao, et al (JAFC, 2007)
Preston, et al (AJEV 2008)
Scheiner, et.al. (AJEV, 2012)

Take home message

Presence or absence of other compounds important, either due to masking or because there are other herbaceous odorants

Should this be a surprise? Its not like IBMP is the only odor-active compound in capsicum

Identification and Synthesis of 2-Heptanethiol, a New Flavor Compound Found in Bell Peppers‡

HERVÉ SIMIAN,† FABIEN ROBERT, AND IMRE BLANK*

Nestlé Research Center, P.O. Box 44, 1000 Lausanne 26, Switzerland

2-Heptanethiol was identified for the first time as a constituent of red and green bell pepper extracts. The chemical structure of this new aroma compound was proposed on the basis of mass spectra and retention indices and confirmed by chemical synthesis and nuclear magnetic resonance spectroscopy measurements. Its aroma properties were described as sulfury, onion-like, and vegetable-like, reminiscent of bell pepper at lower concentrations, with an orthonasal detection threshold of 10 μg/L of water. No differences in odor note and threshold value were observed for the

Also important to capsicum: thiols, C6 aldehydes and alcohols

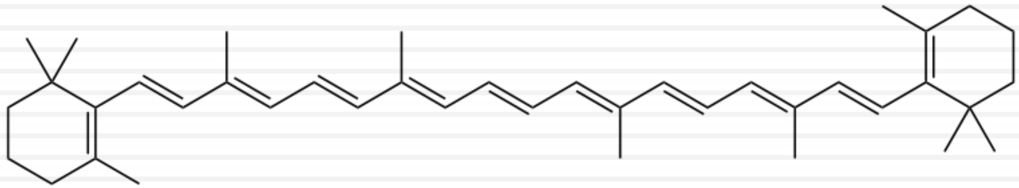
Capsicum samples

Subject change: C_{13}-norisoprenoids particularly TDN and damascenone

Q: What's a **norisoprenoid** (better name: an **apocarotenoid**)?
A: A compound derived by degradation of carotenoids
→ C_{13} = 13 carbons

Q: What's a carotenoid?

A: 40 carbon compounds, yellow-orange-red colors
In green tissue (e.g. unripe grape berries, roles in photosynthesis)



Beta-carotene (example of carotenoid)

Lots of steps ⇒

C_{13}-norisoprenoids in wine

TDN and damascenone are (nearly) undetectable in fresh grapes; precursors formed post-veraison

Carotenoids

↓ *Enzymatic (and non-enzymatic?) degradation around veraison*

C_{13}-norisoprenoid precursors in grapes

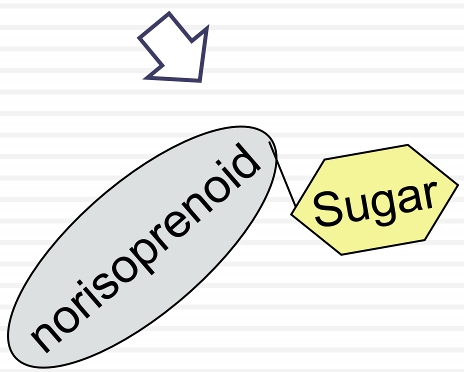
↓ *Glycosylation in the 1-4 weeks after veraison*

Odorless glycosylated C_{13}-norisoprenoid precursors in grapes

↓ *1) Enzymatic and/or acid hydrolysis during fermentation and storage*

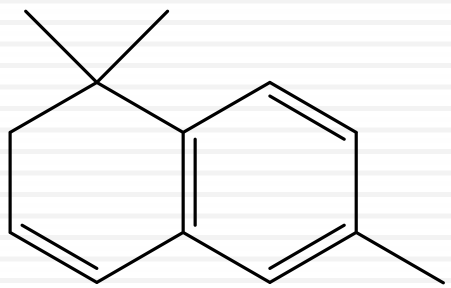
2) Acid catalyzed rearrangements

TDN and damascenone in wines



A key contributor to “kerosene” aromas: TDN

1,1,6-trimethyldihydronaphthalene (TDN)



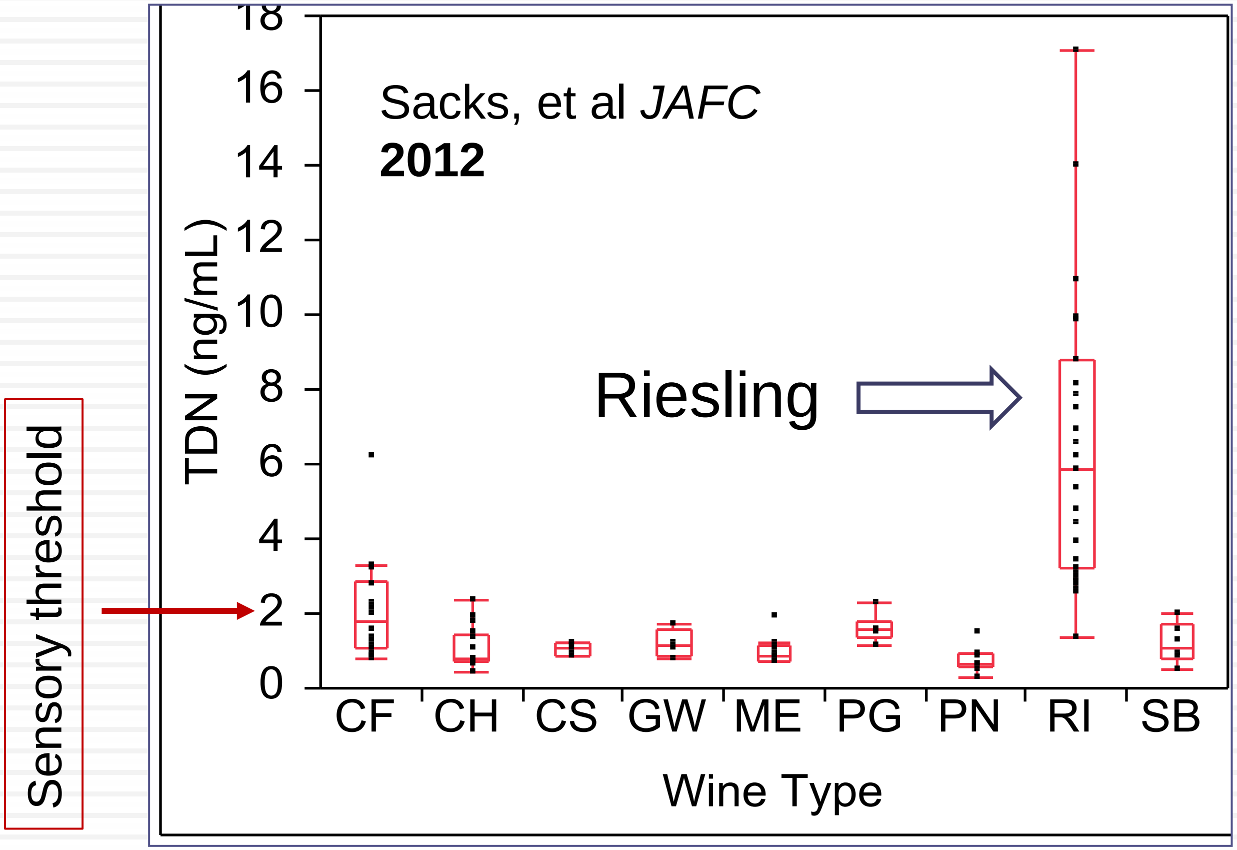
“petrol”, “kerosene”, “rubber”

Detection threshold = 2 ppb (2 ng/mL)
Recognition threshold = ??

At peri-threshold concentrations, probably part of the varietal character of young Riesling.

At higher, recognizable concentrations: a good way to start an argument at a wine tasting about quality

TDN in wines by variety

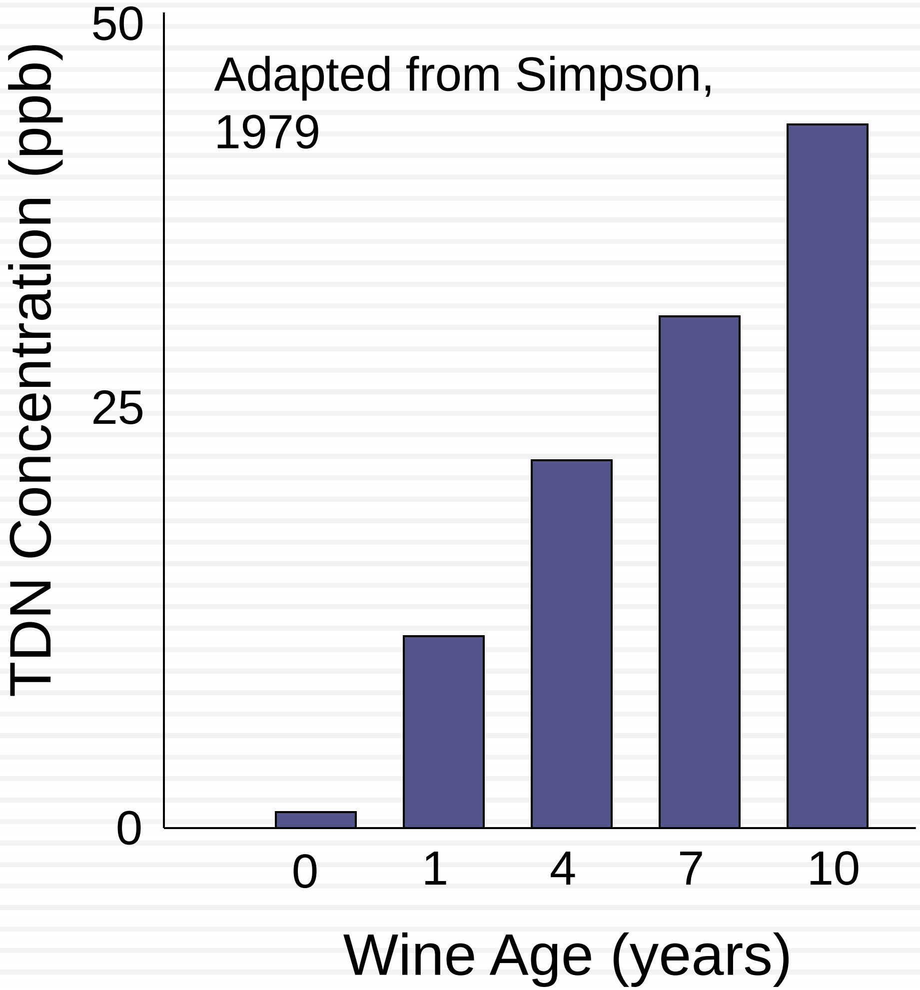


As usual: genetics trumps viticulture

Riesling wines are uniquely high in TDN

TDN concentrations in 1-2 year old varietal wines from New York State.

TDN can continue to increase in bottle



TDN precursors will slowly **hydrolyze** and rearrange under acid conditions to form TDN during storage

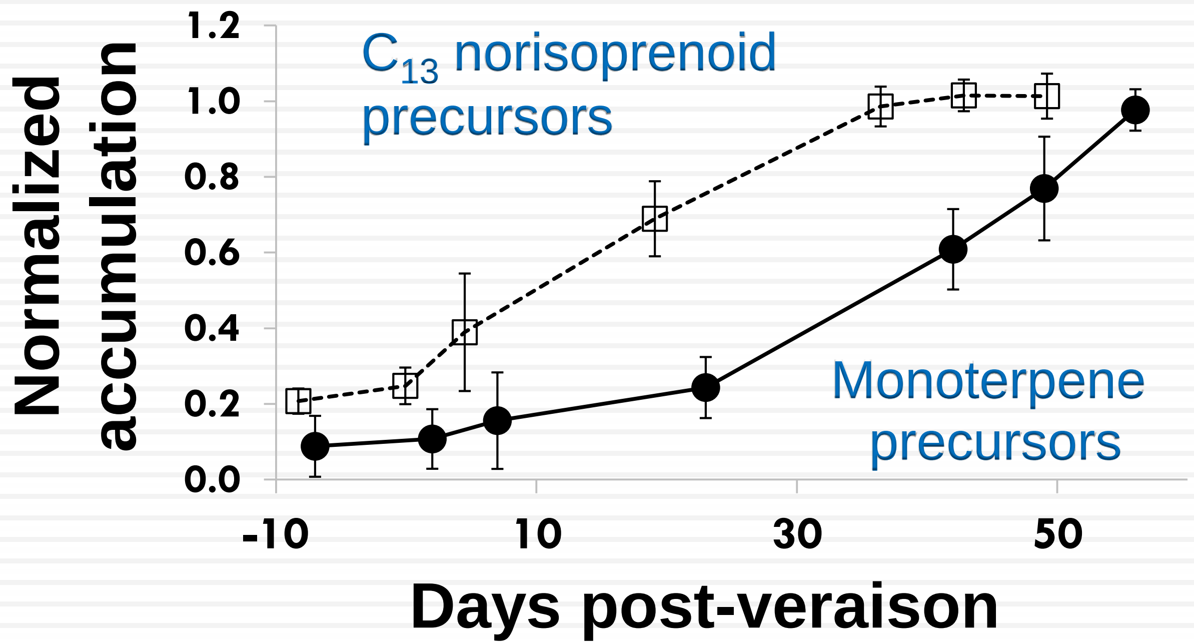
Levels increase during storage, in aged wines can eventually exceed 50 ppb

Summary of winemaking effects on TDN

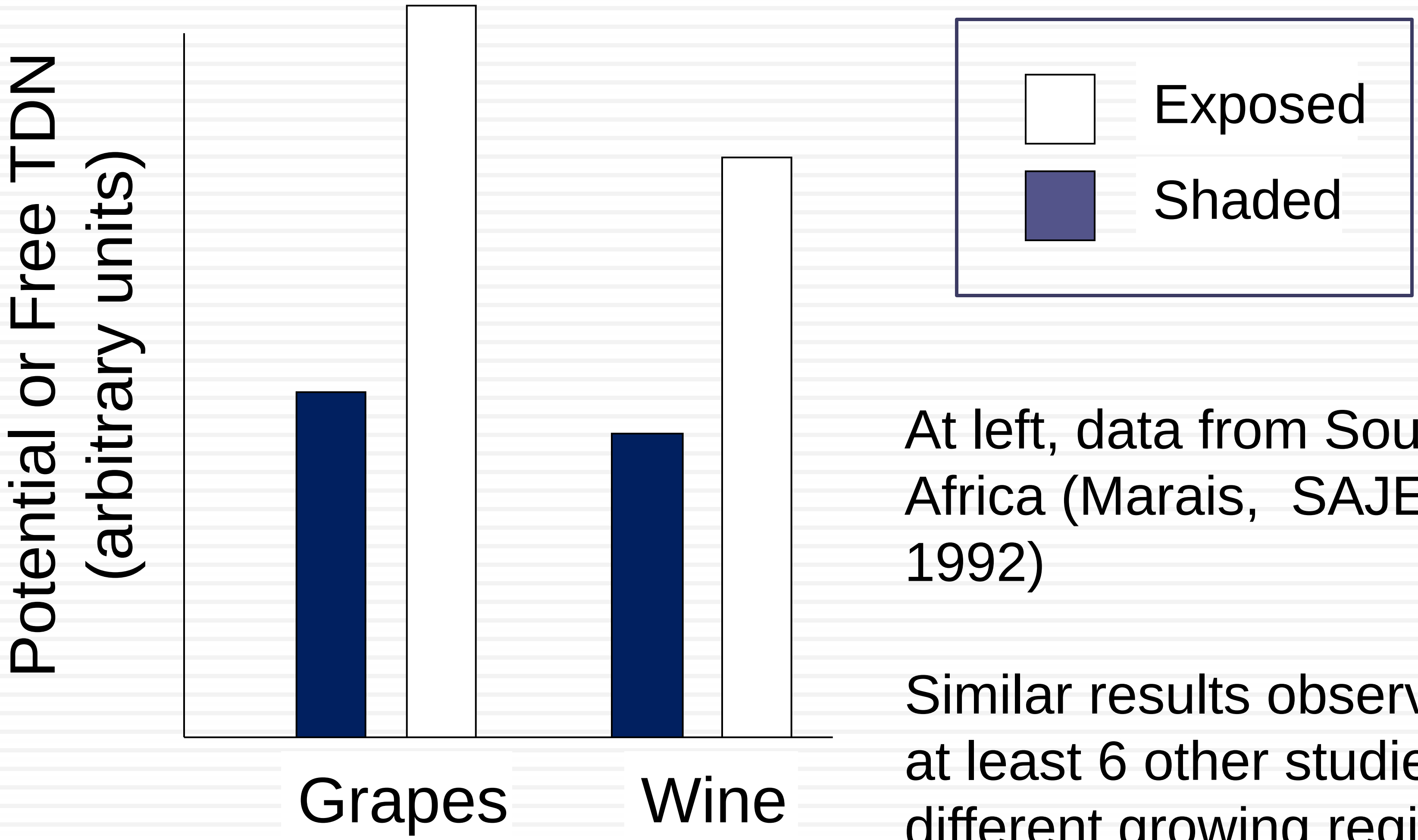
- Variable release of precursors by yeast?
  - May be less important because of hydrolysis during storage
- Post-fermentation, precursors can be hydrolyzed under acidic conditions
  - Lower pH = faster formation
  - Higher storage temps = faster formation
- Not sensitive to oxidation
- Highly non-polar
  - Absorption (“scalping”) by synthetic closures

And, in the vineyard: TDN precursors accumulate soon after veraison

Harvest timing probably not a good way to modify TDN (or other C_{13}-norisoprenoids), although will affect other masking compounds



TDN and cluster exposure: best established odorant correlation in viticulture?



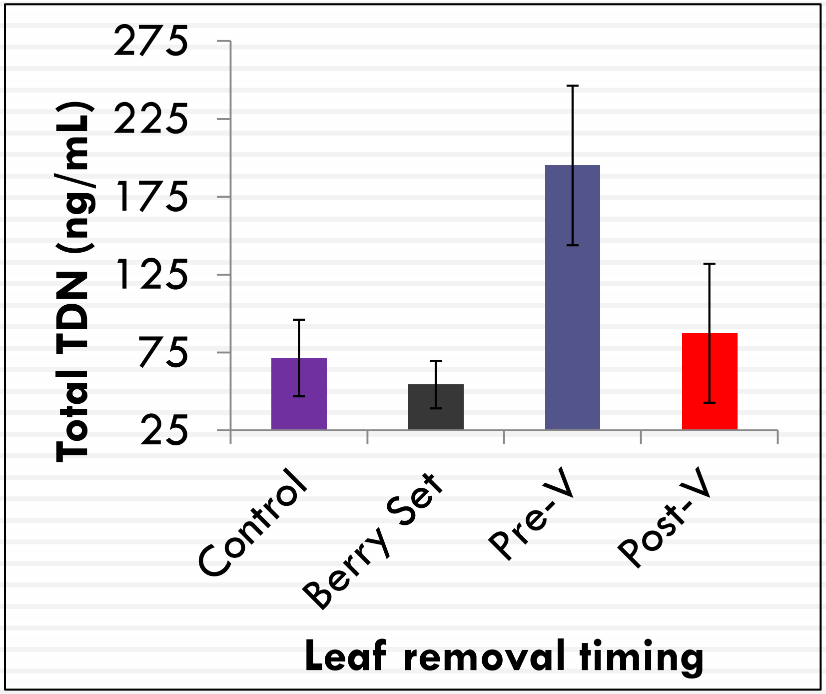
At left, data from South Africa (Marais, SAJEV, 1992)

Similar results observed in at least 6 other studies in different growing regions

Summary of viticultural effects on TDN

Greater exposure of clusters to sunlight, e.g. through leaf removal or artificial shading

- Marais 1992 and at least 6 other studies
- Critical timing: just prior to veraison (Kwasniewski, et al 2010)



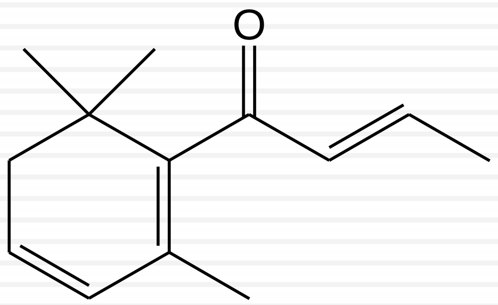
Also warmer climate, less nitrogen fertilization, less irrigation increase

- Possibly confounded with sunlight effect

Harvest timing less important

Last up: β-damascenone

Descriptors: Cooked apple, honey



Threshold in water: 2 ppt
Threshold in 10% EtOH: 50 ppt

Typical concentration in red wines: 1-5 ppb

Damascenone reported to be at very high factor (50-100 fold) above 10% EtOH detection threshold

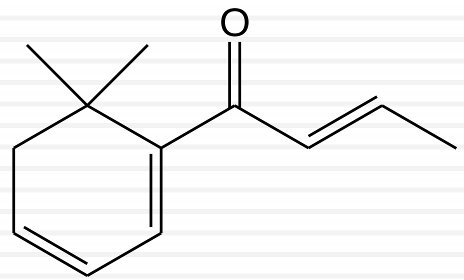
If MPs or TDN are at 50-fold concentration above detection threshold, then the wine would be redolent of capsicum or petrol.
But most wines don't smell like applesauce

β-damascenone at high concentrations relative to threshold in many other foodstuffs . . . Most which don't smell like cooked apples, either!

- Tomato (especially cooked tomatoes)
- Berry fruits (especially jams)
- Tobacco
- Coffee, Tea
- Stonefruits
- Apples
- Kiwifruit
- and on . . .

β-Damascenone: detection threshold highly matrix dependent

Concentration added to create detectable difference by triangle test



(Pineau, et.al JAFC, 2007)

Matrix	Water	10% EtOH	Dearomatized red wine	Red wine
Difference threshold (ppt)	2	50	850-2100	7000

Damascenone: an “enhancer” or ”modifier”, not an “impact odorant”

Sample	Sensory descriptor
10% EtOH Ethyl Esters	Fruity, apple
10% EtOH Ethyl Esters Damascenone/ionone	Berry
10% EtOH Ethyl Esters Damascenone/ionone	Raisin, Dried plum

Adapted from Ferreira, JAFC, 2007

Damascenone: Vineyard and winery effects Rather messy

- No obvious varietal dependence
- Inconsistent results of viticultural treatments (e.g. light exposure)

- Differences in enzymatic release during fermentation
- Heat treatment can result in large increases
- Variable response during storage
  - Occasionally, increases reported, likely because of acid-catalyzed precursor degradation
  - May be cancelled by formation of adducts with SO2

Tasting comments