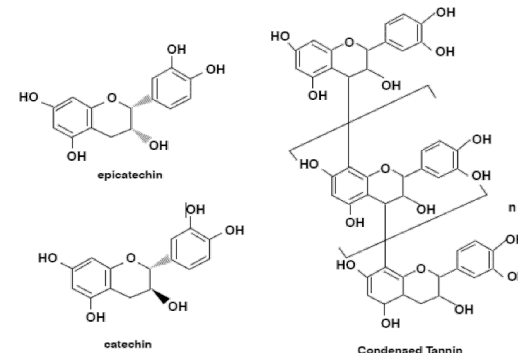
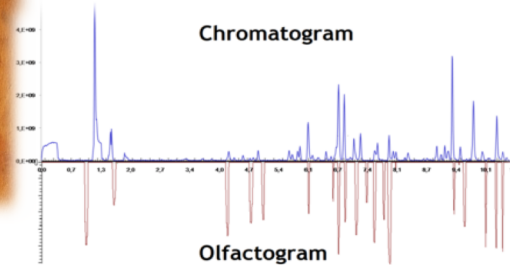


Unraveling wine chemical fingerprints in relationship to varietal and geographical diversity

Prof. Maurizio Ugliano
Dept. of Biotechnology
University of Verona



Wine identity, typicality, quality, value...



State of the Wine Industry 2018

Written by Rob McMillan, EVP and Founder
Silicon Valley Bank Wine Division

$$\text{value} = \frac{\text{quality} + \text{experience}}{\text{price}}$$

Aroma, mouthfeel, color,
lack of defects

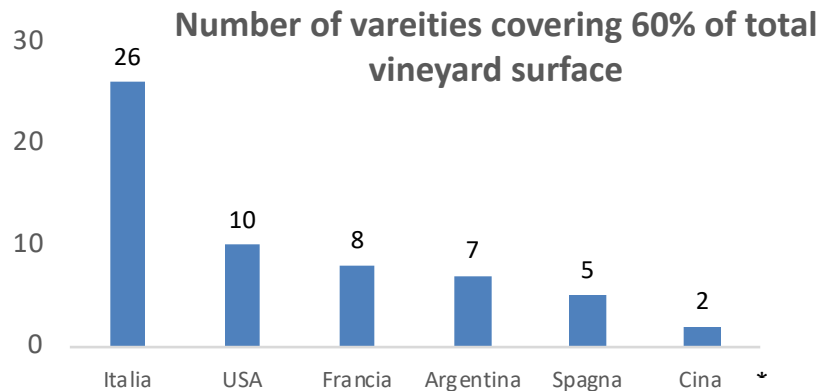
- Identity
- Variety
- Origin
- Typicality

Diversity

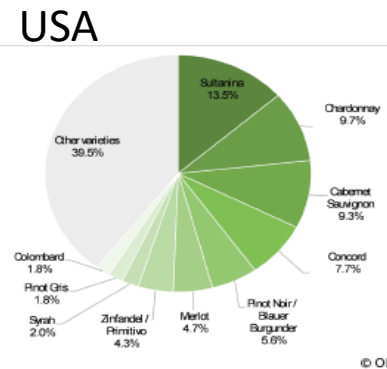
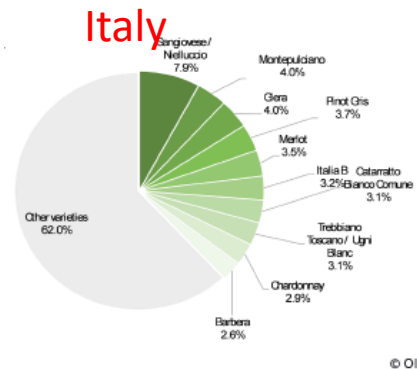
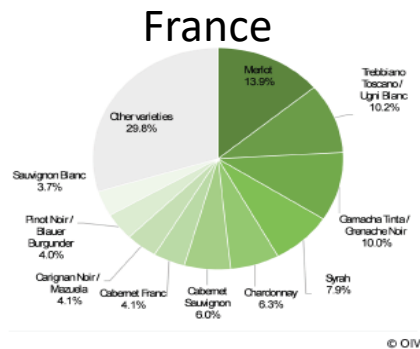
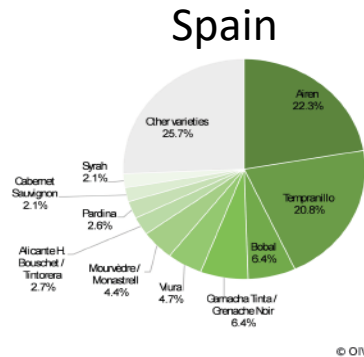
Sustainable practices

To retain value at higher prices we need
to increase *quality e experience*

Diversity within individual countries



Source: OIV 2017 "Distribution of the world's grapevine varieties"



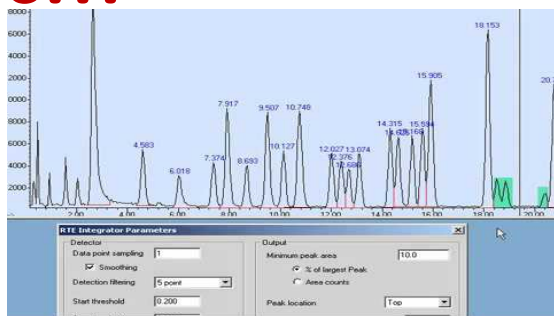
How much do we know?

- Grape chemical fingerprints are not always wine chemical fingerprints
- Grape aroma varietal and geographical identity is not easy to assess
 - More clear with wine
 - Sauvignon blanc a classic example
- Vinification practices can 'disguise' identity, or sometimes create/reveal new identities
- Could aging (cellar/bottle) be a driver of more defined chemical fingerprints?
 - Analytically it seems easier to define relevant chemical fingerprints (eg geographical typicality) in aged wines rather than in young wines or grapes
- Riesling a classic example with TDN, but recent data also on Grenache (DMS), Pinot noir, Chardonnay, Corvina wines
- Aging can also lead to less defined chemical boundaries
 - Oxidative aromas developing over time
 - Other taints developing over time (*Brett*, VA, etc)
- What about geographical identities?

Where should we start?

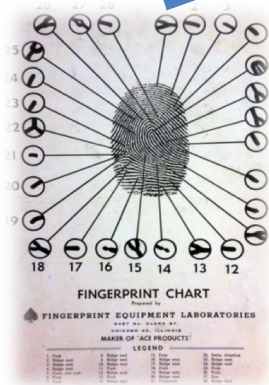


Don't panic!!!



Advanced analytical approaches (eg chromatography)

First: chose how to approach the problem

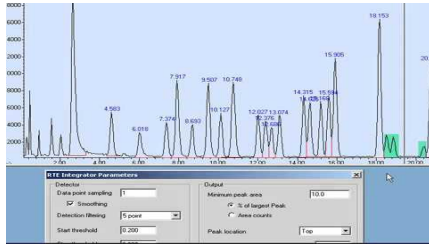


Profiling/fingerprinting



Rationalizing behaviors

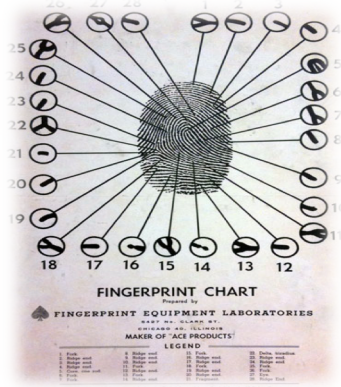
Where should we start?



Pros: Identification and quantification of key metabolites, discovering new metabolites or reactions (untargeted approaches)

Cons: expensive lab equipment, skilled operators, time consuming data processing

Advanced analytical approaches (eg chromatography)



Pros: Rapid analyses, relatively inexpensive equipment

Cons: sometimes difficult to associate fingerprinting features to chemical compounds

Data interpretation sometimes difficult (aka all samples look the same!!)

Profiling/fingerprinting



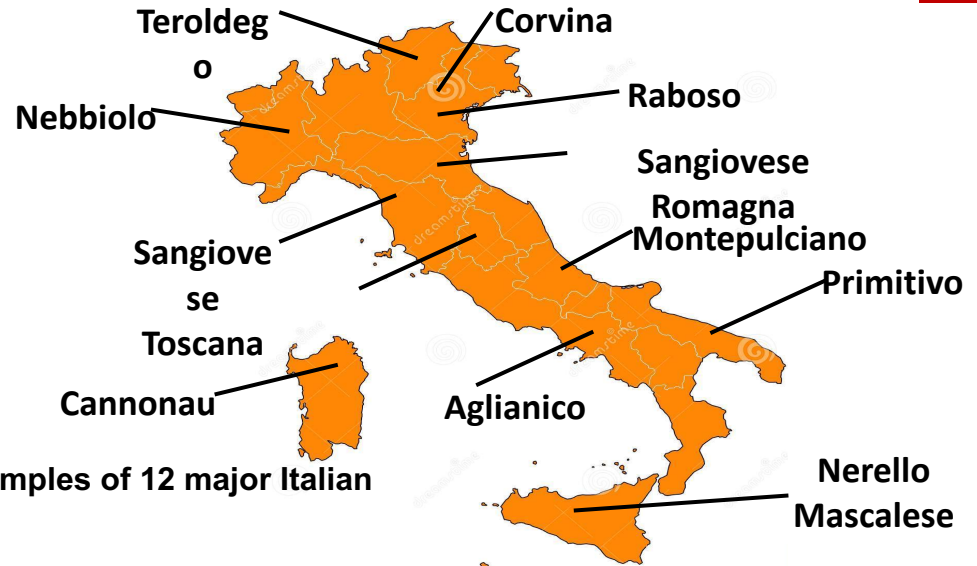
Rationalizing behaviors



Chemical fingerprints and varietal diversity

Phenolics

The diversity of tannins in Italian red wines

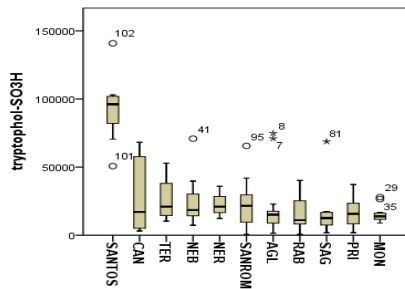
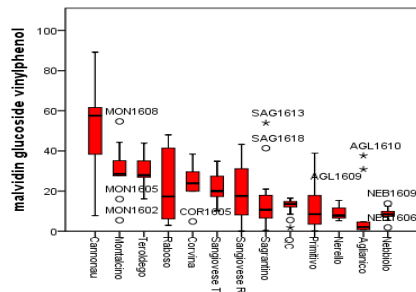
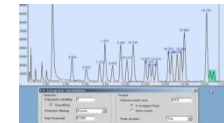


- ✓ 109 red wine samples of 12 major Italian appellations
- ✓ Vintage 2016
- ✓ Samples straight out of tank, no contact with oak, no tannin addition
- ✓ Free SO₂ adjusted to 50mg/L
- ✓ Bottled using synthetic closures with defined OTR

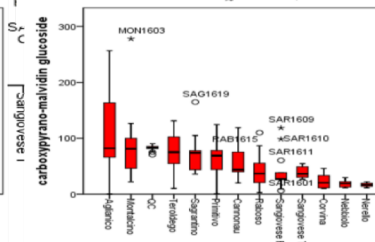
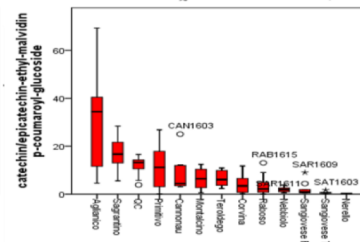
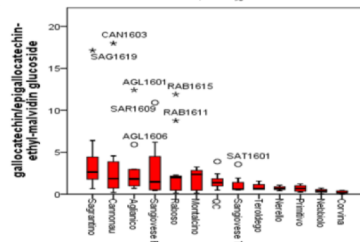
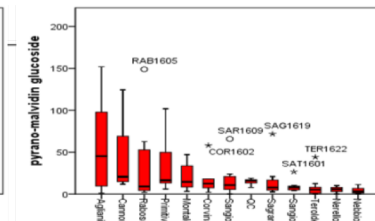
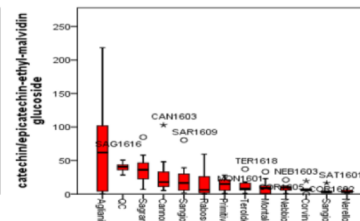
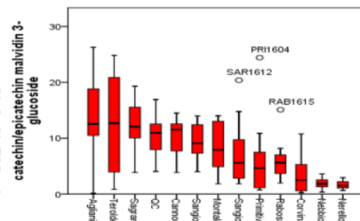
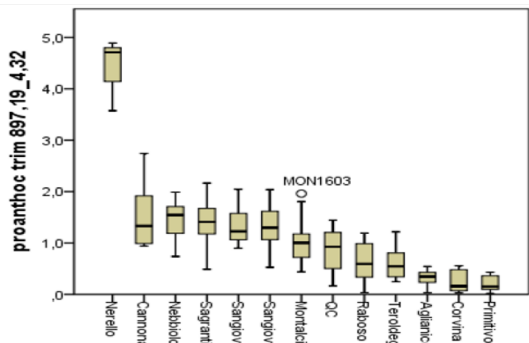
Chemical fingerprints and varietal diversity

Phenolics

Untargeted LC-MS
(data from Panagiotis Arapitsas and Fulvio Mattivi at FEM)



We started with the idea of learning about tannin composition....
.... We ended up learning things we didn't even think we should worry about!!

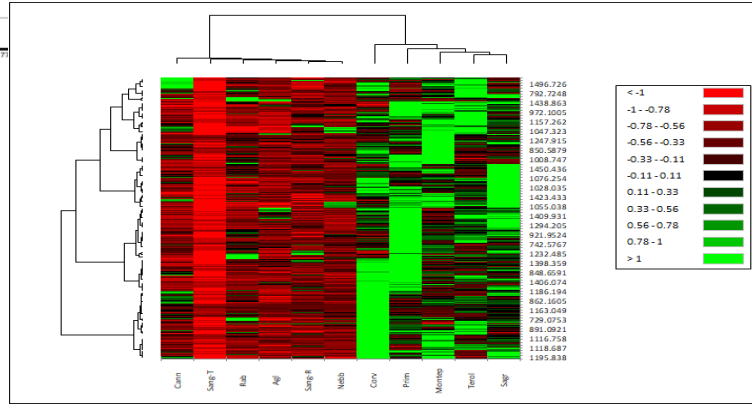
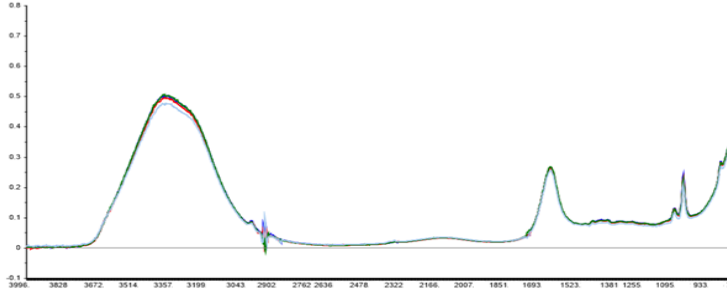
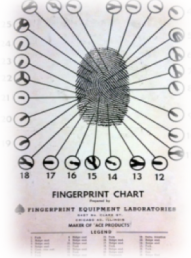


Chemical fingerprints and varietal diversity

Phenolics

MIR

(data from Andrea Versari and his team at UniBO)

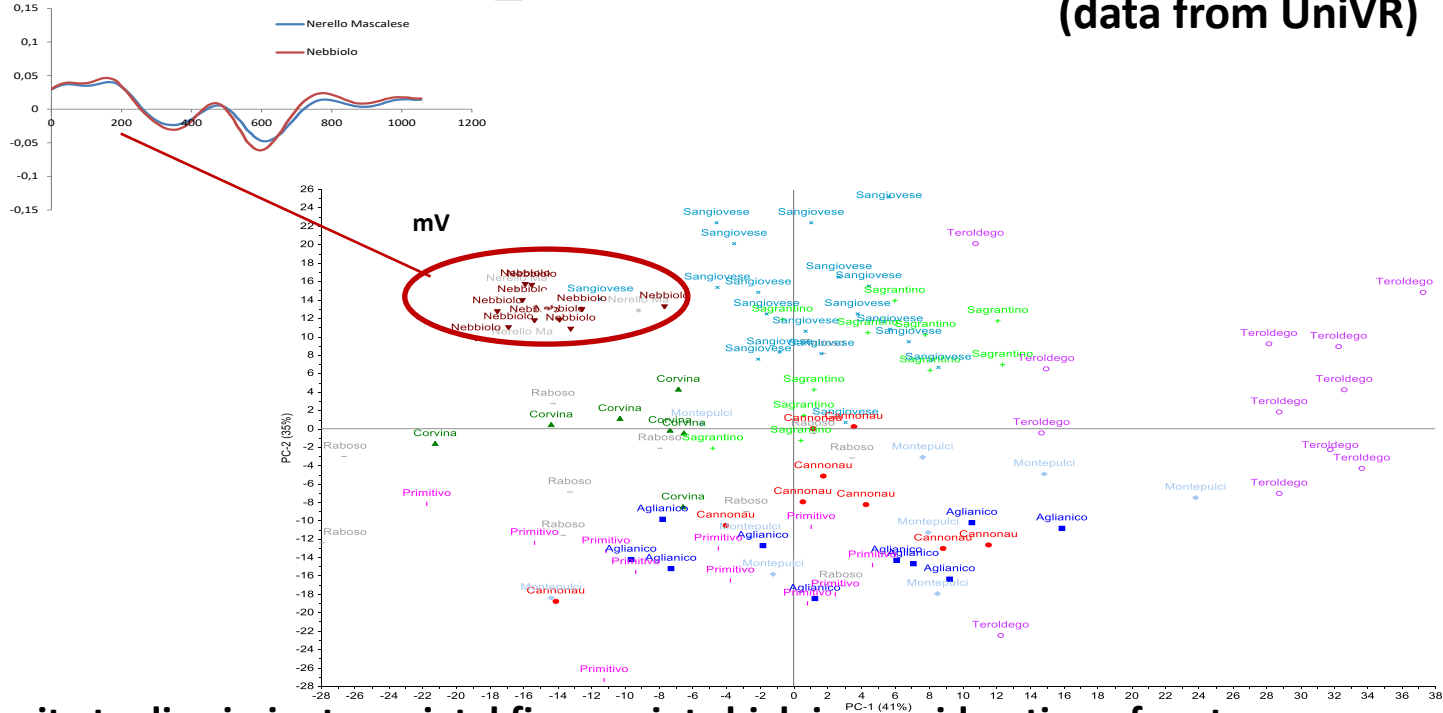
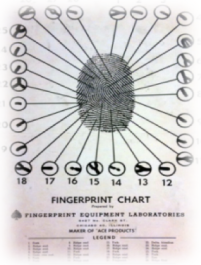


Pretty good capacity for classification of wines

Chemical fingerprints and varietal diversity

Linear sweep voltammetry
(data from UniVR)

Phenolics



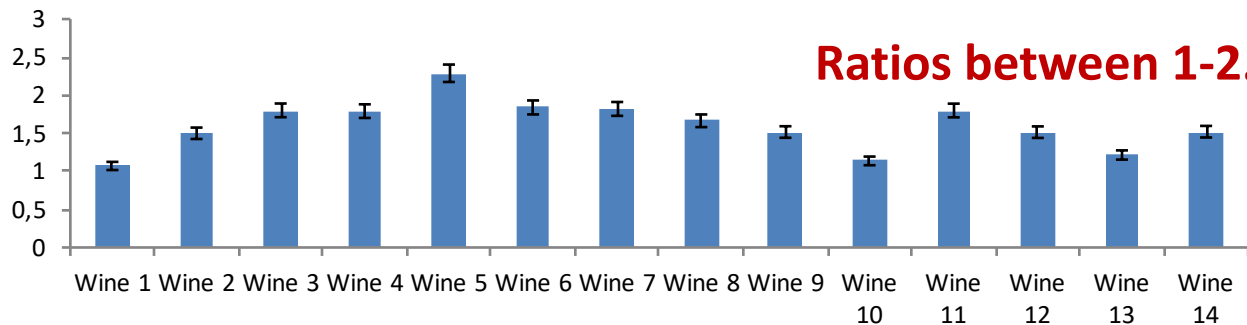
Capacity to discriminate varietal fingerprints high in consideration of cost and ease of use
Difficult to associate with chemical composition

Chemical fingerprints and varietal diversity

Rationalizing behaviors



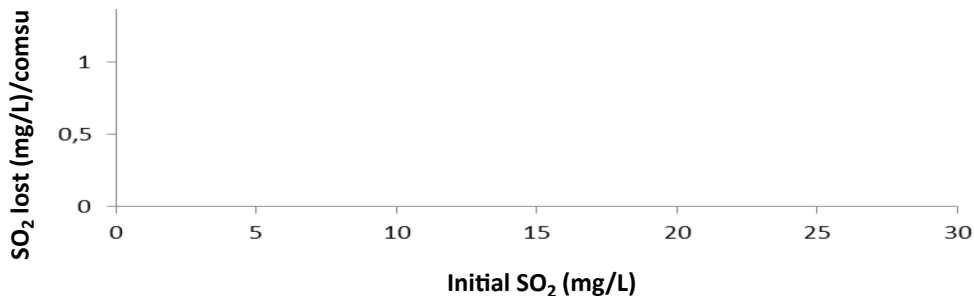
SO_2/O_2 ratio of 14 commercial white wines having consumed 5 mg/L of O_2



Can we identify chemical fingerprints for this diversity of behaviors?

Untargeted voltammetric approaches for characterization of oxidation patterns in white wines

Asael Gonzalez, Stephane Vidal, Maurizio Ugliano*

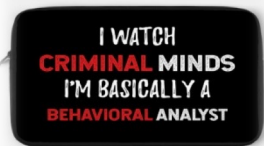


The more Free SO₂ is present, the higher the SO₂/O₂ ratio and the more SO₂ is lost for a given amount of oxygen consumed...

...but not for all wines

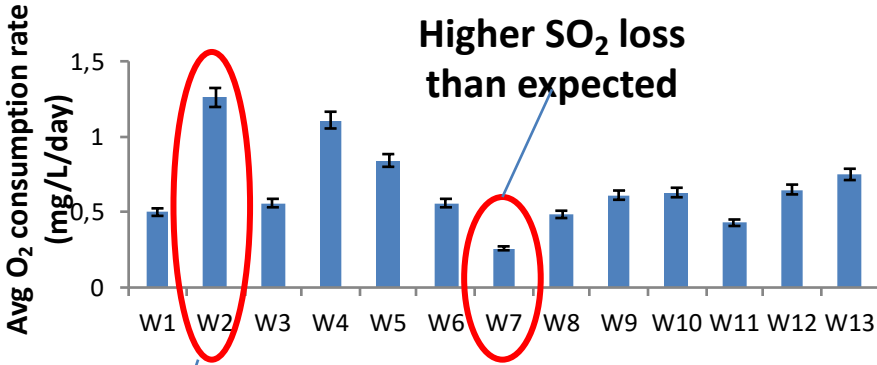
Chemical fingerprints and varietal diversity

Rationalizing behaviors - SO₂ antioxidant efficacy



Chemical fingerprints and varietal diversity

Rationalizing behaviors - SO₂ antioxidant efficacy



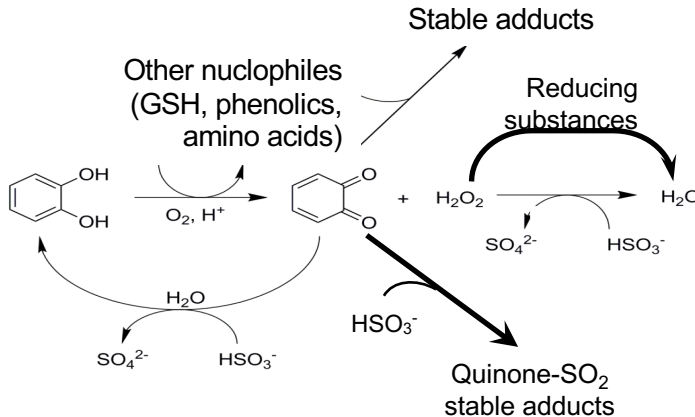
Higher SO₂ loss than expected

Lower SO₂ loss than expected

Questions

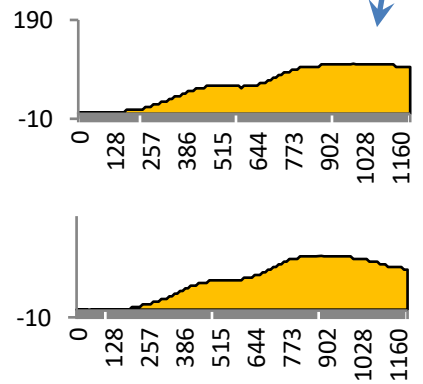
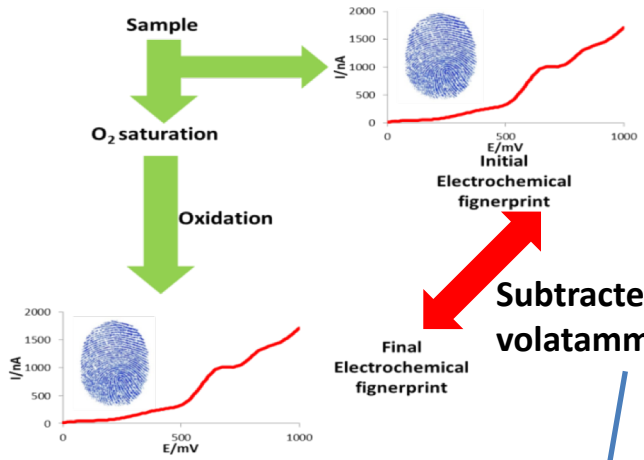
Is the behavior of W7 and W2 due to their content in quinones trapping and/or H₂O₂ reducing agents?

Are there fingerprint features that are characteristic of W7 and W2?

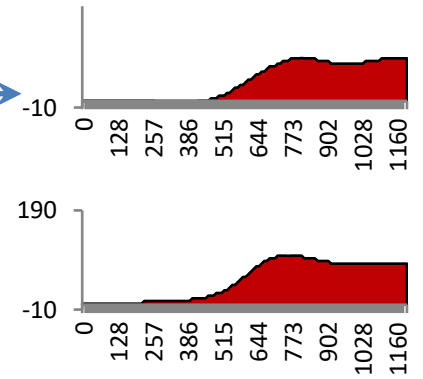


Chemical fingerprints and varietal diversity

Rationalizing behaviors - SO₂ antioxidant efficacy



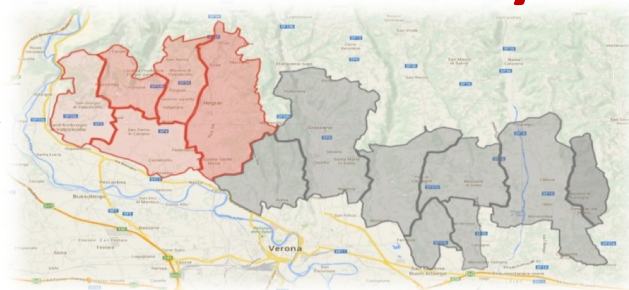
Examples of profiles corresponding to higher SO₂ efficacy



Examples of profiles corresponding to lower SO₂ efficacy

Chemical fingerprints and geographical diversity

A case study on Valpolicella wines



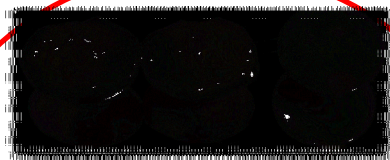
Province of Verona
Valpolicella wine region



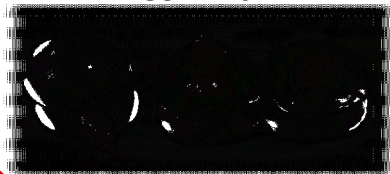
Grape submitted to post-harvest withering for production of **Amarone**



Robert Parker



Corvina



Corvinone

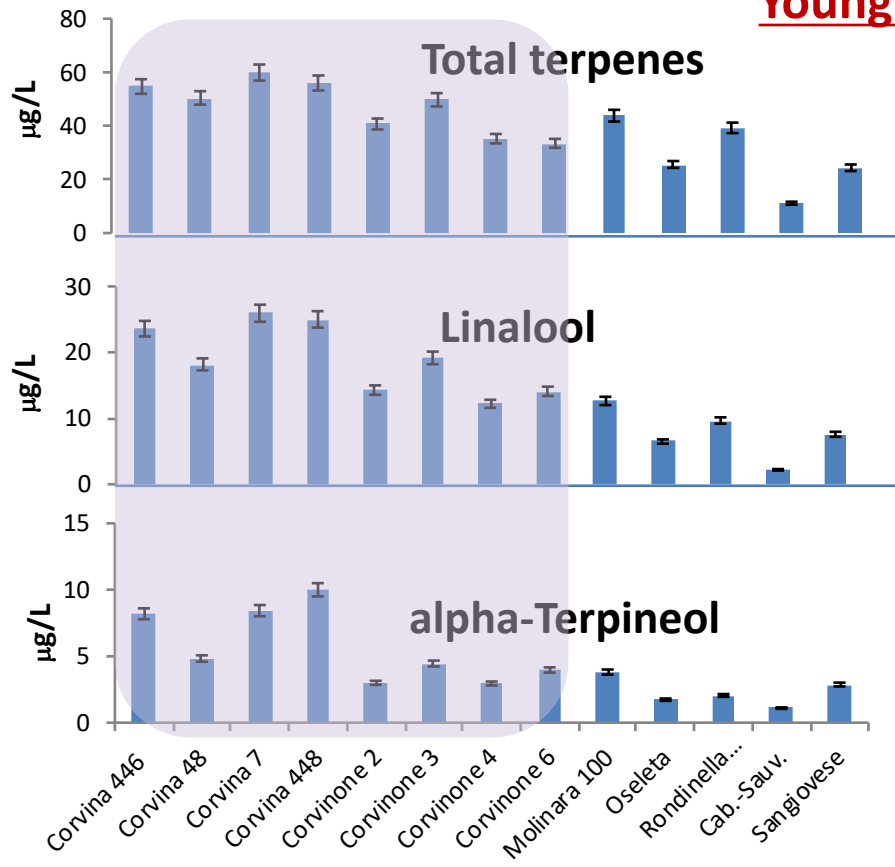


No post-harvest withering for production of **Valpolicella classico**

Chemical fingerprints and geographical diversity

A case study on Valpolicella wines

Young wines



Corvina relatively high content of total terpenes and linalool compared to wines from other red varieties.

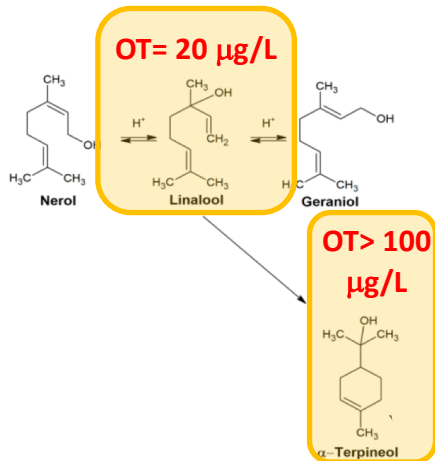
Could explain flora attributes of young wines

No other specific marker of tobacco or minty/balsamic aroma compounds

Chemical fingerprints and geographical diversity

A case study on Valpolicella wines

a)

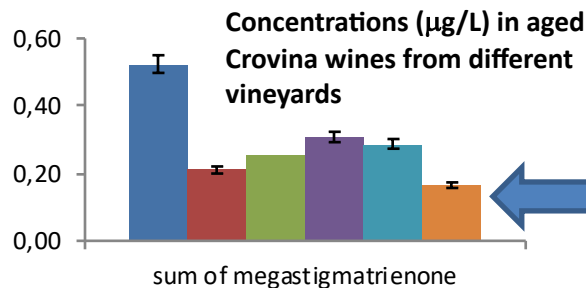
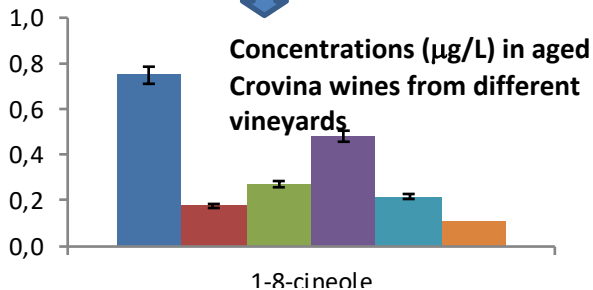


Aging...



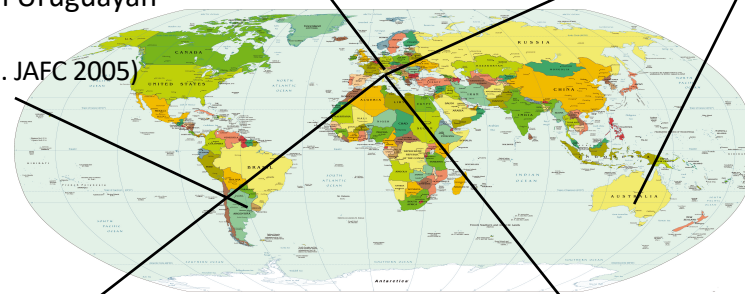
Chemical fingerprints and geographical diversity

A case study on Valpolicella wines



Cineoles in aged Valpolicella reds from terpenols rearrangements
(Slaghenaufi e Ugliano, *Frontiers in Chemistry* 2018)

Cineoles in Uruguayan Tannat
(Farina et al. *JAF* 2005)



Cineoles in Bordeaux reds from vineyards with *Artemisia verlotiorum*
(Poitou et al *JAF* 2017)

Cineoles in Australian Cabernet from vineyards close to eucalypt trees
(Capone et al. *JAF* 2012, Antalick et al. *JAF* 2015)

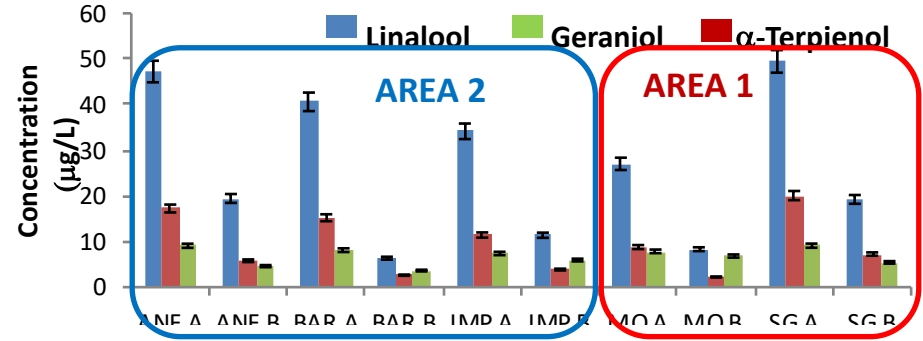
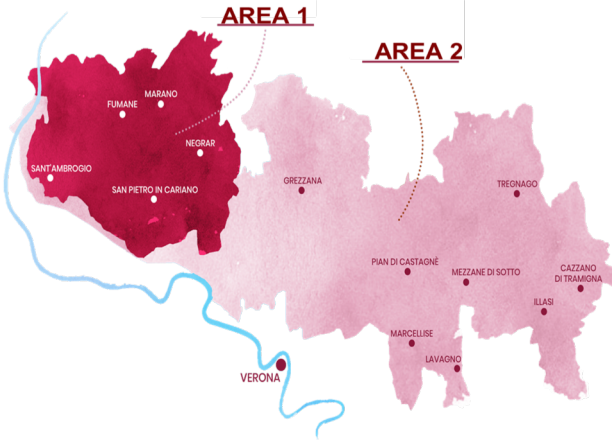
Tabanones in aged Valpolicella reds without oak contact
(Slaghenaufi e Ugliano, *Frontiers in Chemistry* 2018)

Tabanones in aged Bordeaux wines and spirits due to oak contact
(Slaghenaufi et al)

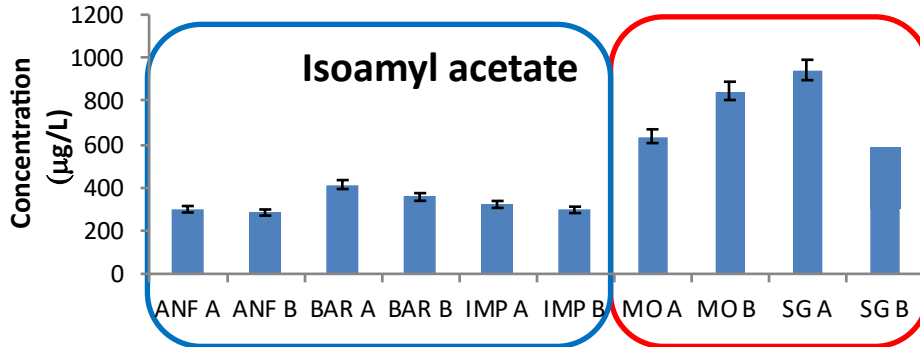
Cineoles and tabanones potentially able to discriminate geographical identity at the level of single vineyard wines.
Trends consistent across 3 consecutive vintages.

Chemical fingerprints and geographical diversity

A case study on Valpolicella wines



Differences exist but they don't discriminate according to geographical location

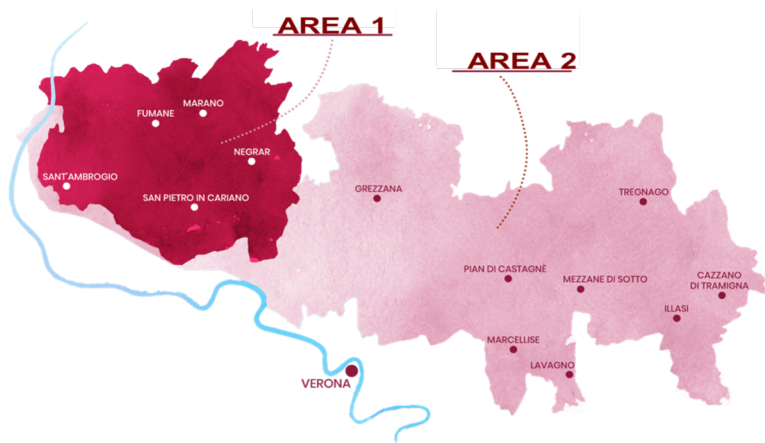


Fermentation esters better discriminating capacity!!!

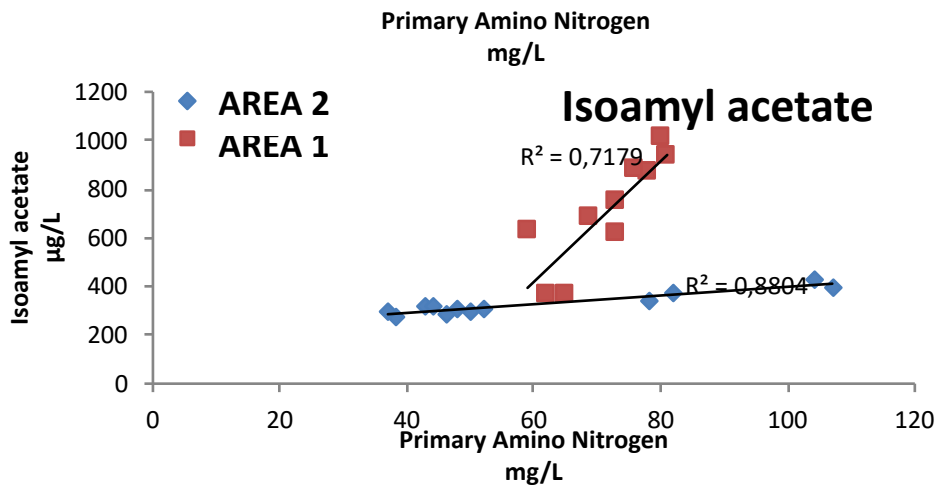
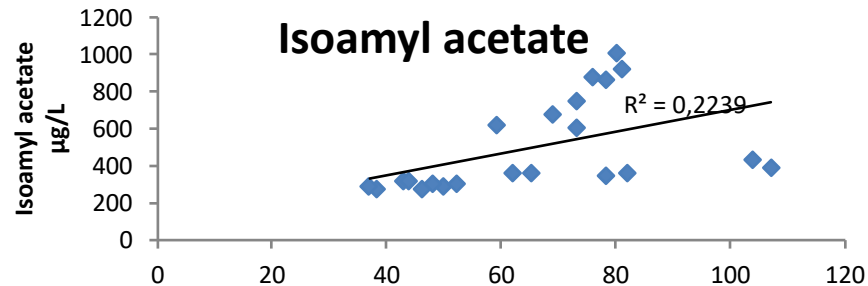


Chemical fingerprints and geographical diversity

A case study on Valpolicella wines



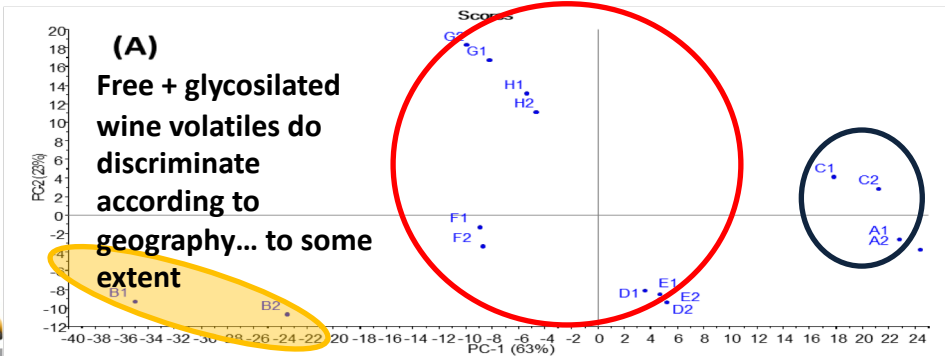
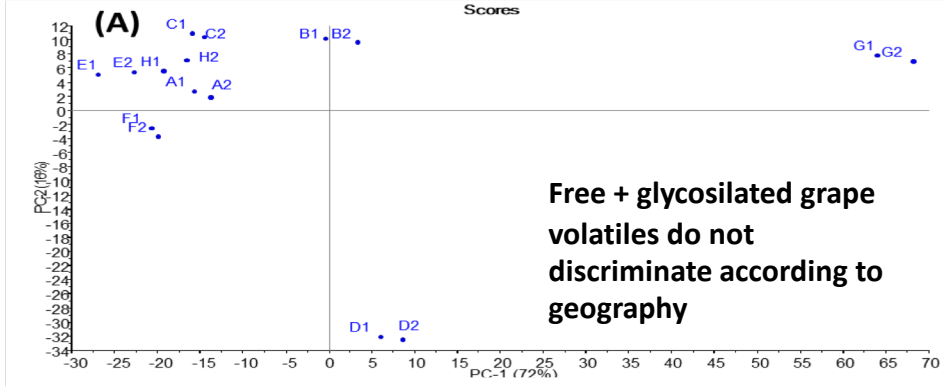
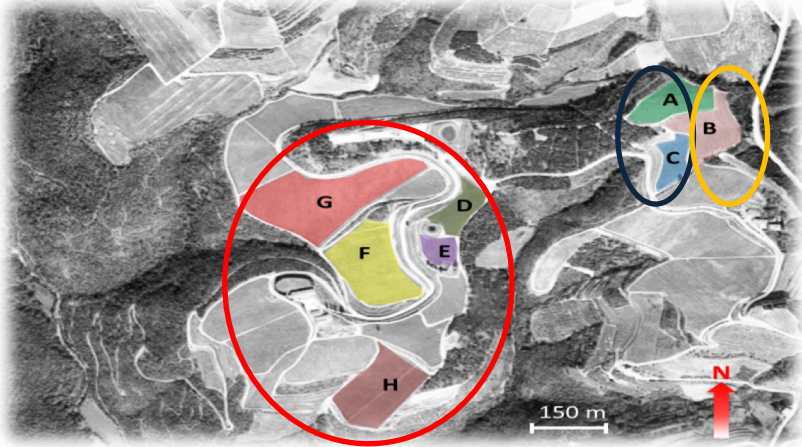
Grape YAN, in particular FAN, seems to be one important point of connection between grape composition and wine chemical fingerprint in relation to grape origin



Chemical fingerprints and geographical diversity

A case study on Valpolicella wines

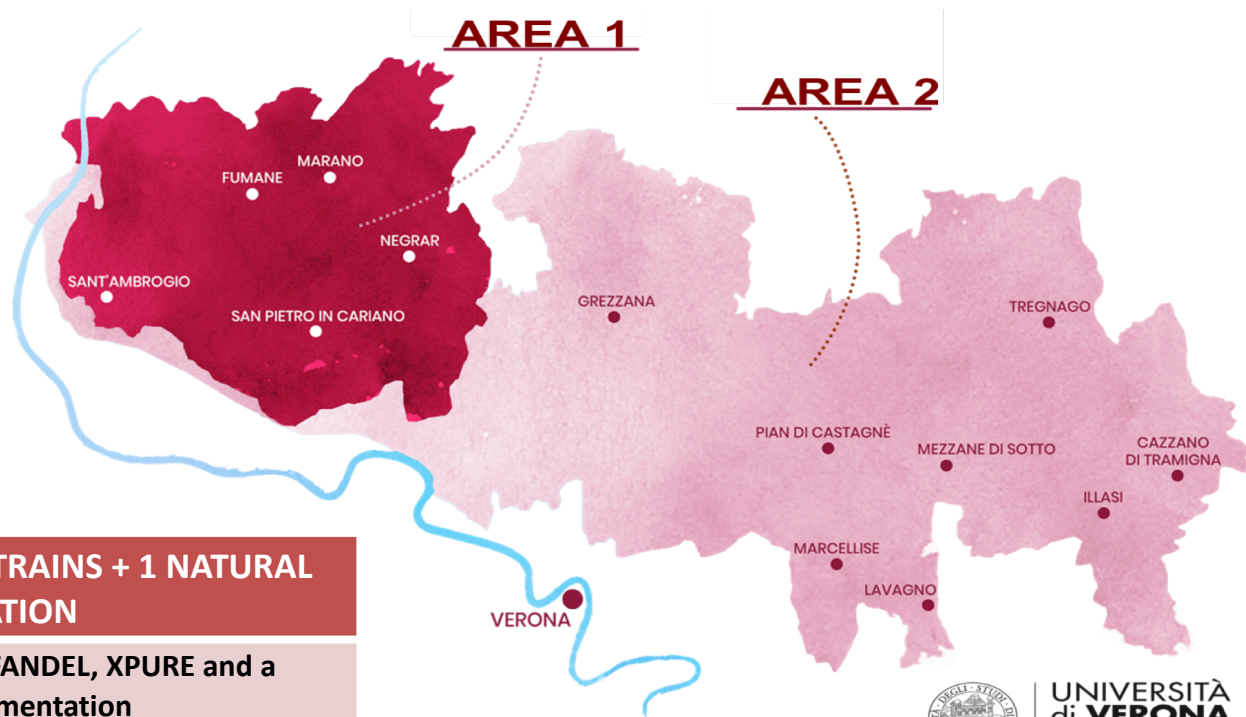
2. Different vineyards within a 20 ha estate



Chemical fingerprints and geographical diversity

A case study on Valpolicella wines

Can yeast strain reveal or hide aroma signature of wine geographical identity?



CORVINONE GRAPES
2 AREAS GRAPE ORIGIN

Area 1 and Area 2
within Valpolicella

4 COMMERCIAL YEAST STRAINS + 1 NATURAL
FERMENTATION

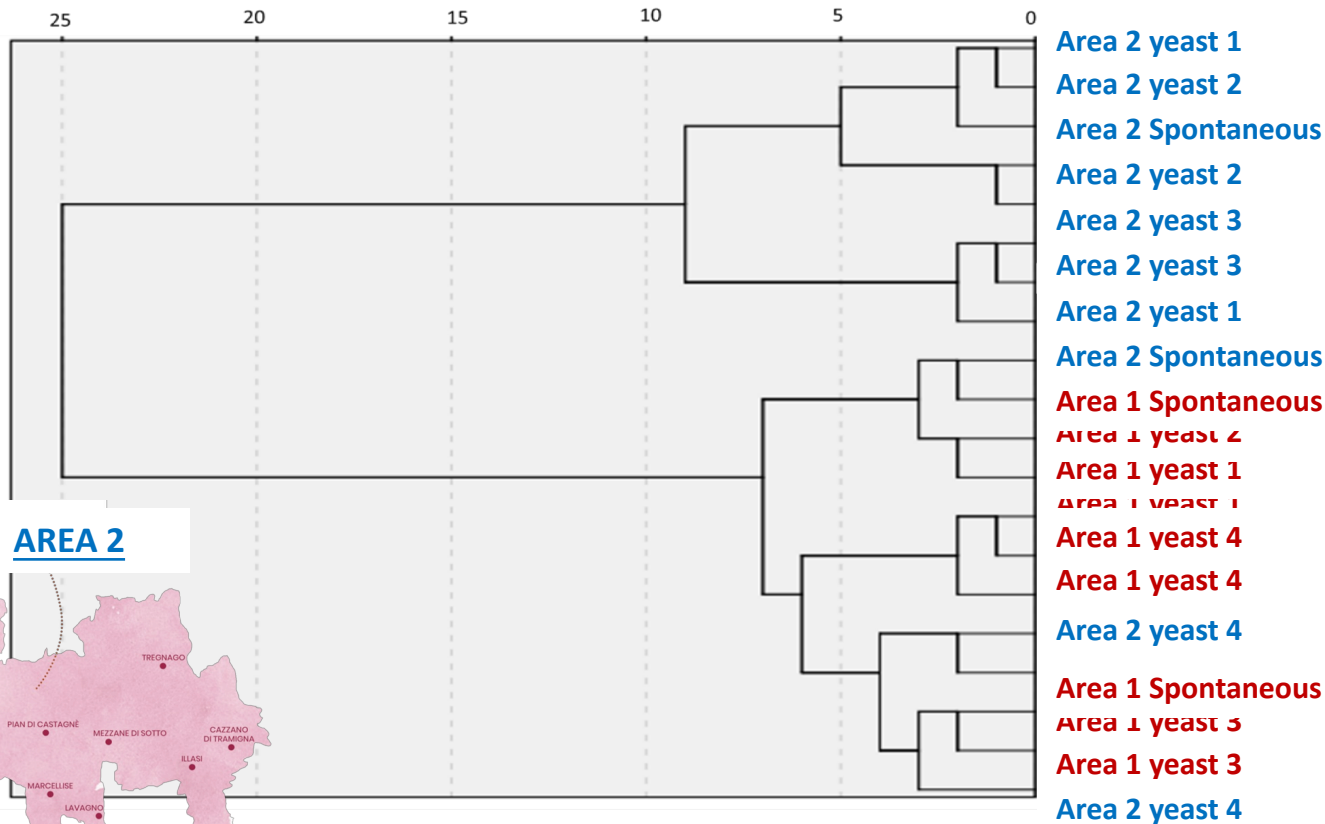
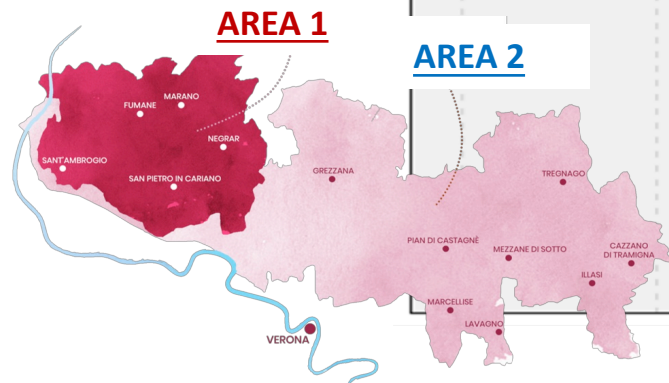
AWRI 796, AWRI 1503, ZINFANDEL, XPURE and a
spontaneous fermentation

Chemical fingerprints and geographical diversity

A case study on Valpolicella wines

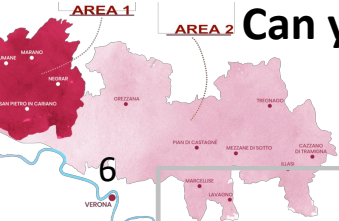
Can yeast strain reveal or hide aroma signature of wine geographical identity?

Two main groups largely based on grape origin. Sense of place still clearly detected by tasters. What is the chemical basis?



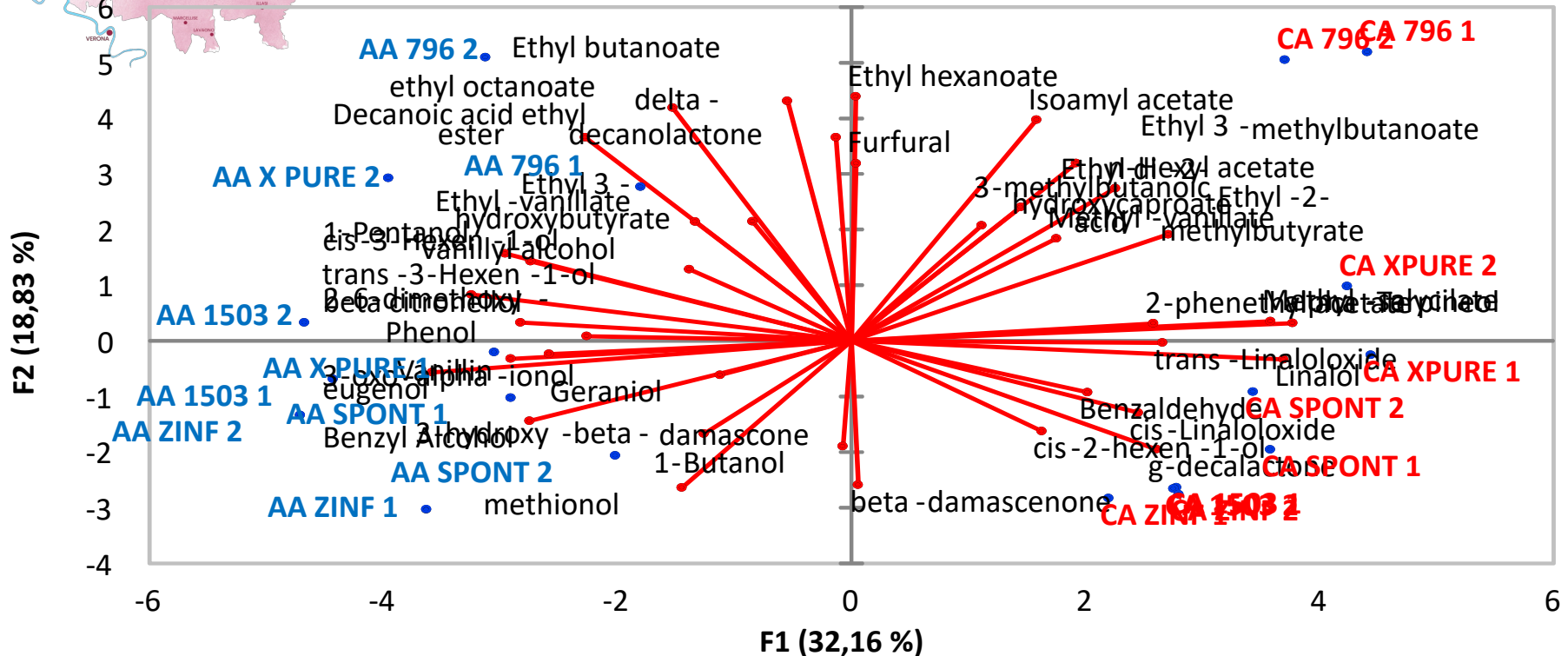
Chemical fingerprints and geographical diversity

A case study on Valpolicella wines



Can yeast strain reveal or hide aroma signature of wine geographical identity?

Biplot (axes F1 and F2: 50,98 %)





Verona, 22nd - 24th June
Camera di Commercio di Verona



**Deadline for proposals
February 14th**

HURRY UP!!!

- Diversity of wine types is one of the most fascinating aspects of wine culture as well as winemaking
- Chemical fingerprints exist that can allow to characterize, investigate and classify such diversity
- Analytically there are different approaches to different aspects of diversity
- Ultimately we need to build workflows integrating sensory/behavior classification of diversity and analytical approaches to explain it
- Chemical markers of geographical diversity include not only grape-derived compounds (eg terpenoids) but also fermentation-derived esters. The latter



Thank you!!