Impacts of Regulated Deficit Irrigation on Cabernet Sauvignon Grapes and Wine

Jim Harbertson, Richard Larsen, Federico Casassa, Markus Keller

Washington State University

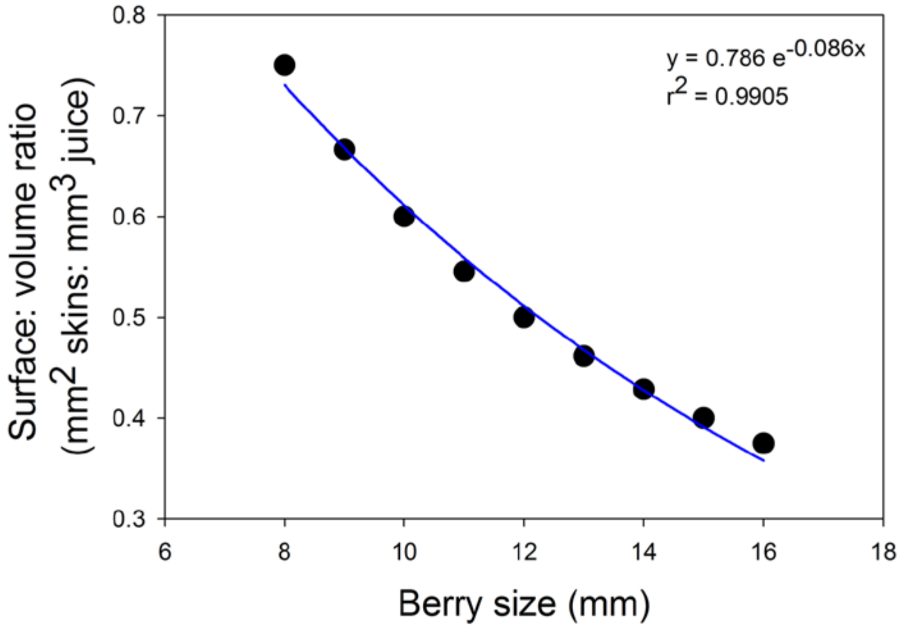
Viticulture & Enology Program

RDI

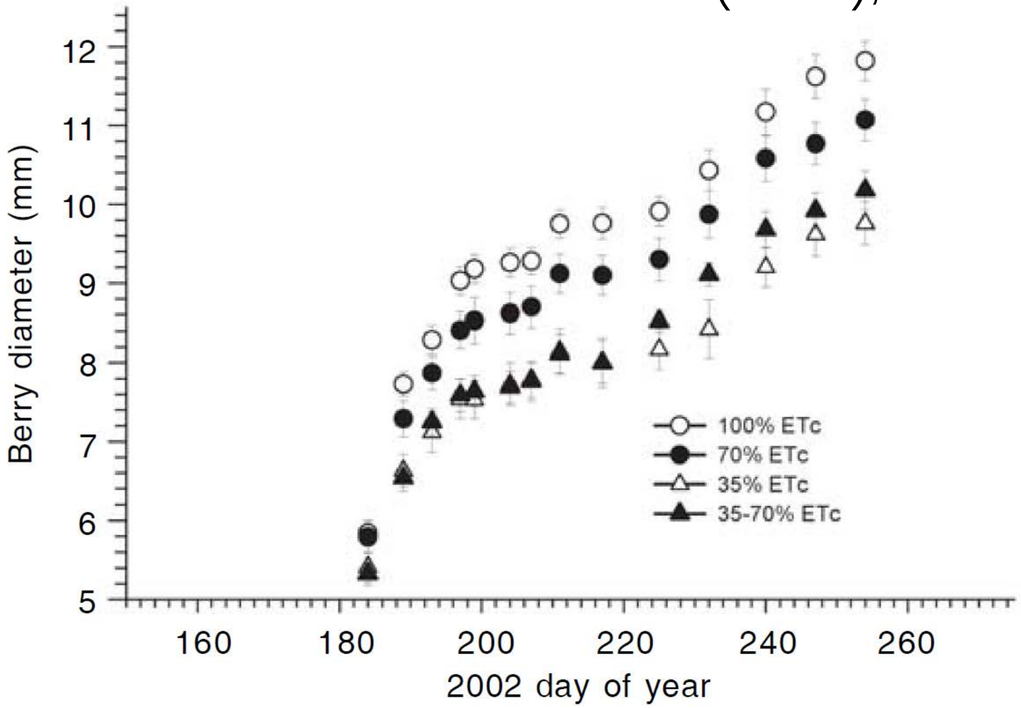
- Provide less than full evapotranspiration demand (Keller, 2005)
  - – More uniform ripening
  - – Reduce water usage
  - – Reduce vigor
  - – Control berry size

Berry size

- Winemakers want small berries
- Berries do not grow like balloons



Shellie (2004), cv. Merlot



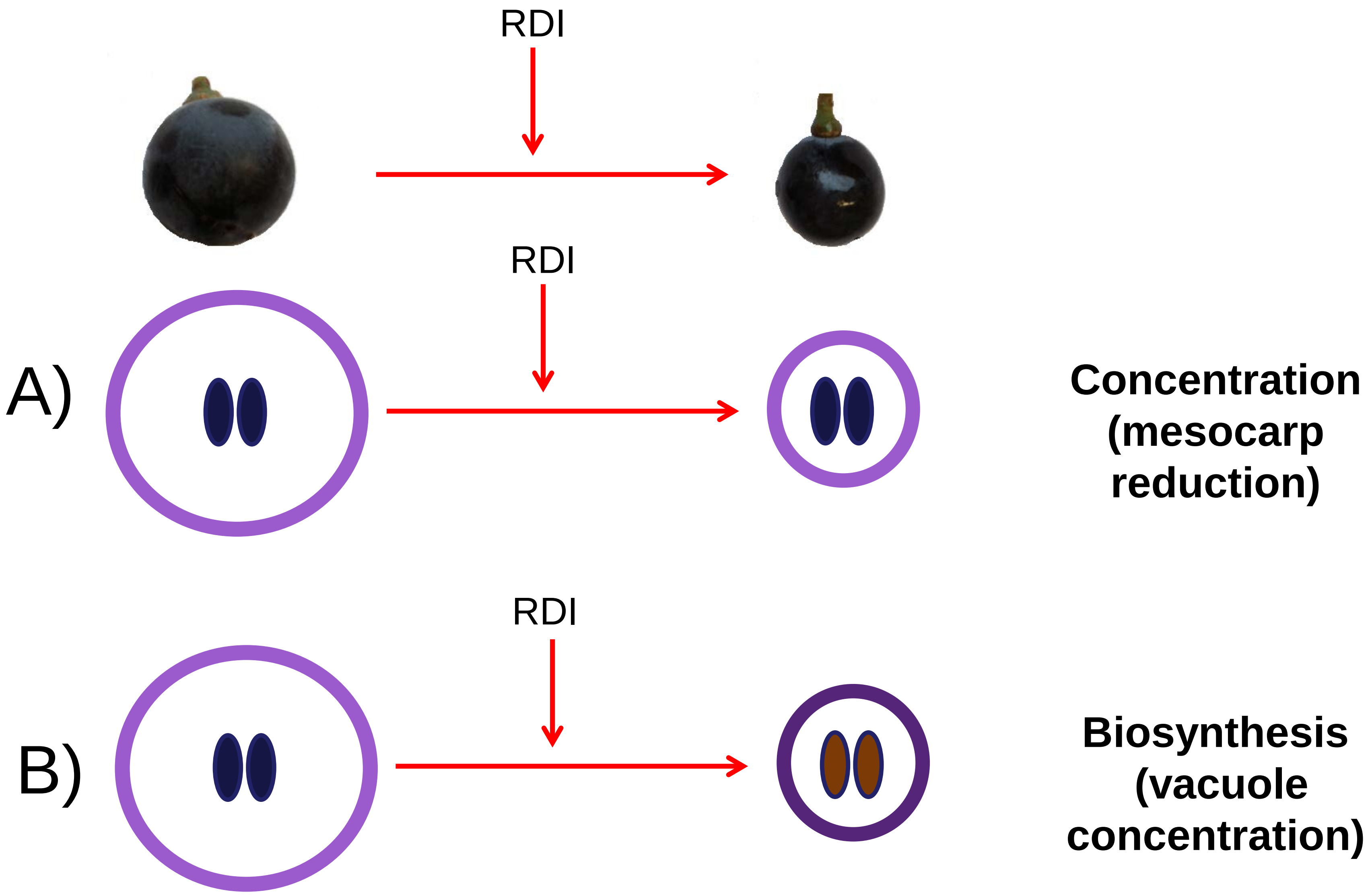
Winemakers Like Phenolics

- Grape and wine pigments: Anthocyanins
- Astringency of Red Wine:
  - Tannins are heterogeneous class of molecules
  - Interaction with salivary proteins
- Long Term Color:
  - Polymeric Pigments known as stable Color
  - Anthocyanins react with tannins and other phenolics
- Antioxidant
  - Role of SO_2, Fe, Cu

Where do they come from and why does that matter?

- Skins contain anthocyanins and large MW tannins
  - Large MW Tannins are effective protein ppt
- Seeds contain low molecular weight tannins
  - Small MW tannins are more less effective protein ppt
  - Tend to be more bitter than astringent
- When you pick fruit and how you make wine influences types of tannins and amount of pigments you extract

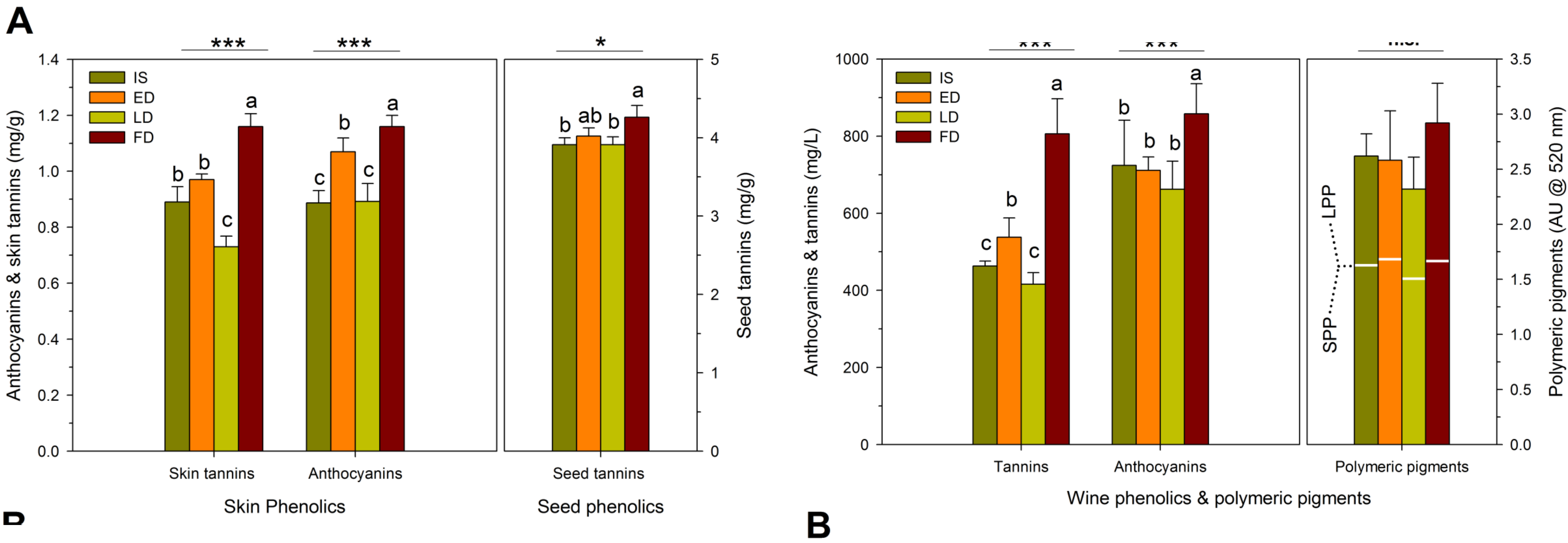
Back to RDI & berry size



Two Sets of Experiments

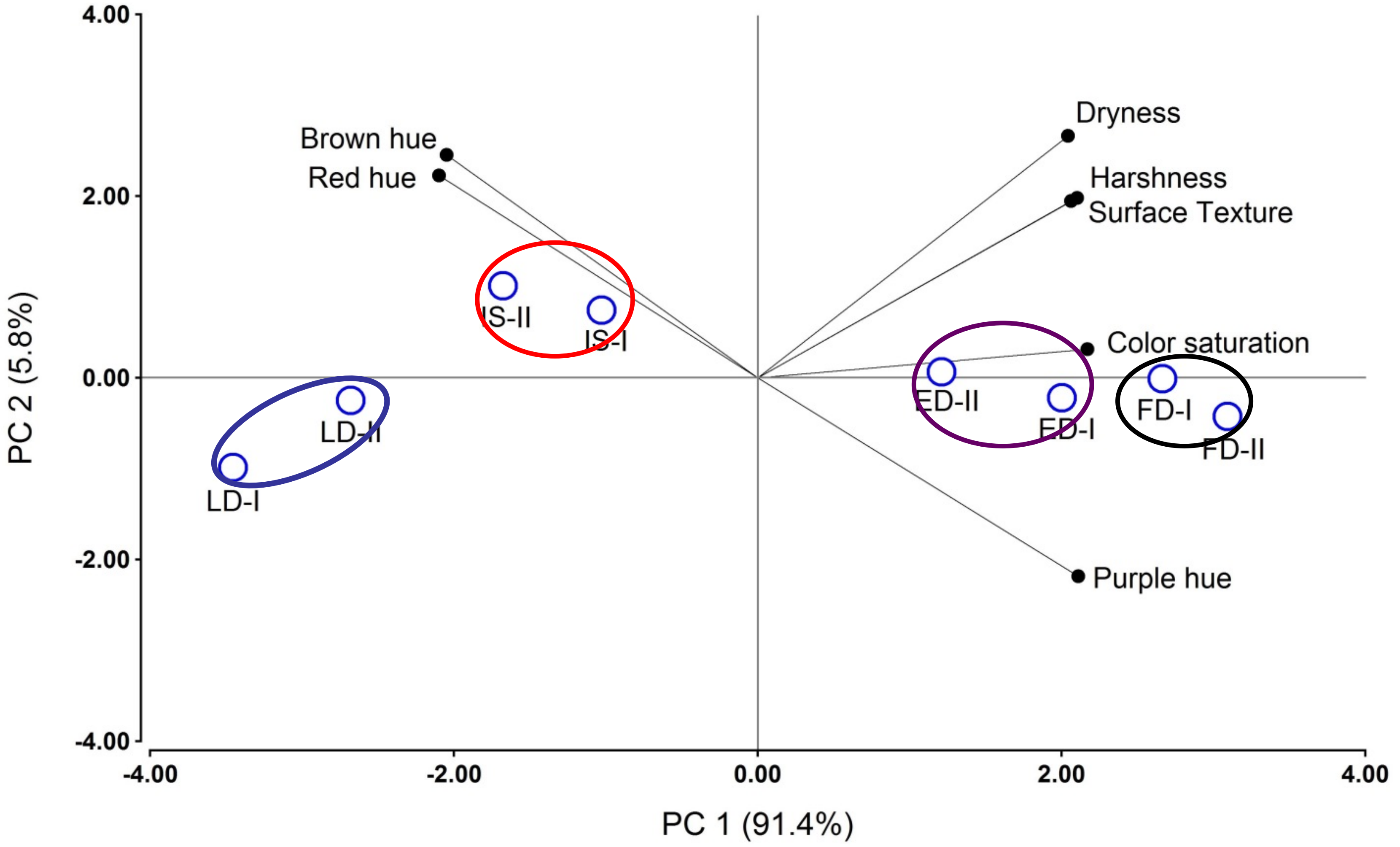
- Dr. Keller, Dr. Smithyman, Dr. Riley Dr. Larsen & now Dr. Casassa
- Cold Creek Vineyard: Cabernet Sauvignon
- 1st Exp. When should deficit be applied? <u>Early</u>, Late, or *Full*?
- 2nd Exp. Full season deficit severity and compensation

Fruit & Wine Chemistry



Industry Standard (IS) fruit & Late Deficit fruit and wine have low phenolics

Early and Full Deficit fruit and wines have high phenolics



Late Deficit and Industry Standard Wines driven by Red and Brown hue

Early and Full Deficit Wines driven by Astringency, Color

So who would win a fight between…

- T-Rex and Great White Shark?
- Lion and Tiger?
- Snake and Mongoose?
- Great White Shark and Orca?
- Answer: Clearly it depends.
- Land vs. Water; Future vs. Past

- We pit vineyard vs. winery in these experiments
- Which one controls phenolic content of wine?
- Deficit Irrigation in the Vineyard vs….Extended Maceration & Saignée
- Not really.
- But it makes it more exciting.

Berry weight and yield

(2011, 2012, 2013)

Berry weight, irrigation percent reduction and yields over 3 consecutive seasons (2011-2013) in Cabernet Sauvignon grapes of the different RDI treatments.

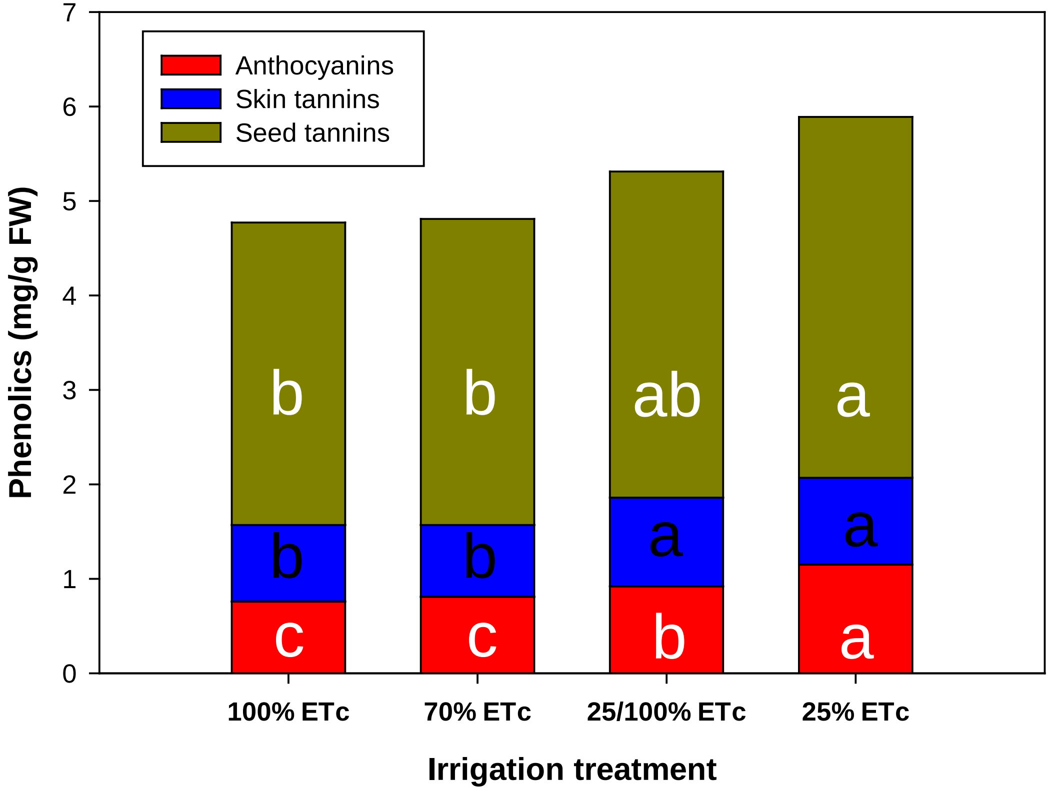
Treatments	Entire season Ψs (MPa)	Berry weight		Irrigation		Yield	
		Berry weight (g)	% reduction	Applied (mm)	% reduction	Kg/ vine	% reduction
Full irrigation: 100% ET_c	-0.83 a	1.15 a	-----	315 a	-----	6.53 a	-----
Industry Std: 70% ET_c	-1.03 b	1.11 a	**3 %**	228 b	**28 %**	4.91 b	**27 %**
Late irrigation: 25/100% ET_c	-1.03 b	0.99 b	**14 %**	180 c	**43 %**	5.68 b	**15 %**
Full deficit: 25% ET_c	-1.22 c	0.87 c	**35 %**	77 d	**76 %**	2.76 c	**60 %**

Different letters within values in the same column indicate significant differences for Fisher's LSD test and $p < 0.05$.

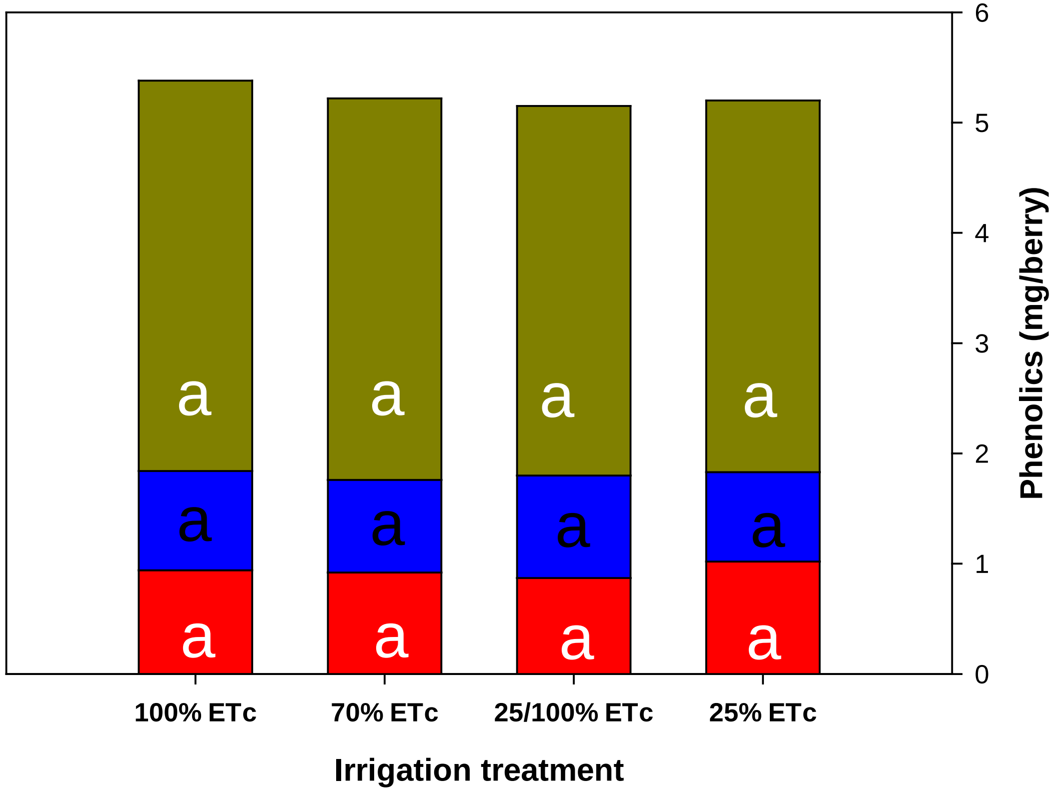
Fruit phenolics

(2011, 2012, 2013)

Phenolics FW basis



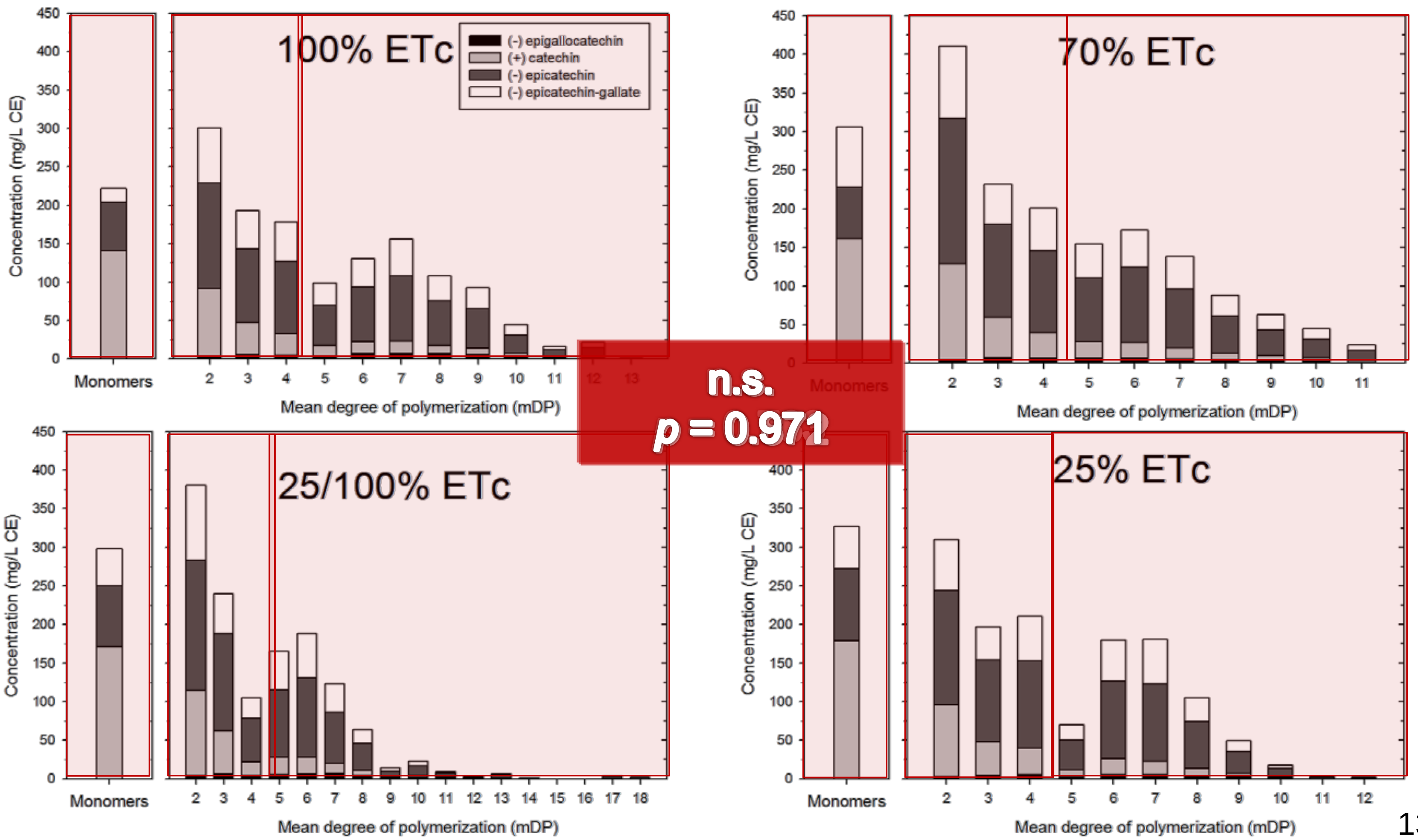
Phenolics *per berry* basis



Casassa, Keller, Harbertson, unpublished

YEAR : Tannin Structure

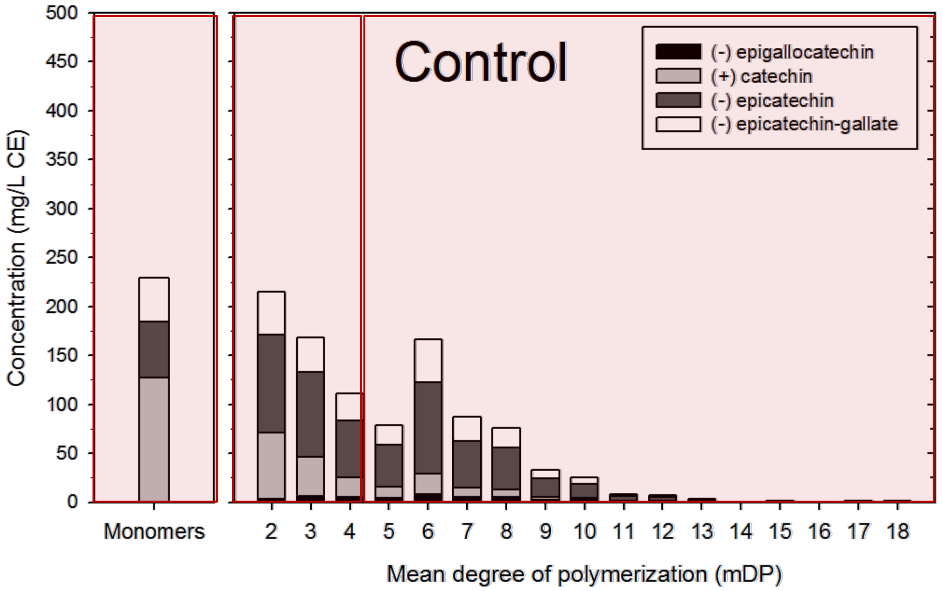
Tannin distribution by concentration: RDI

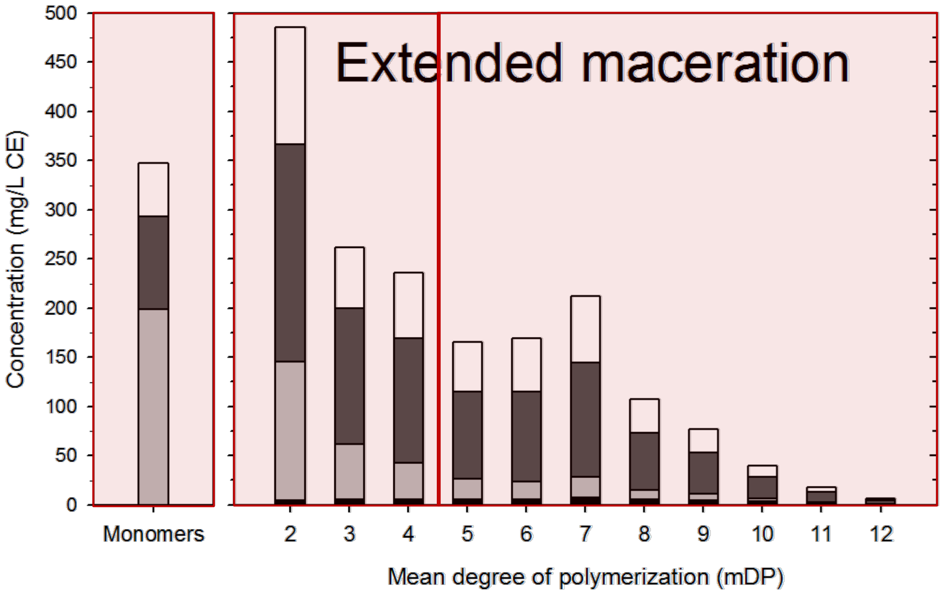


Casassa, F., R. Larsen, C.W. Beaver., M.S. Mireles, M. Keller, W. Riley, R. Smithyman and J.F. Harbertson. Journal of Agricultural and Food Chemistry.

Effect of EM and RDI

Tannin distribution

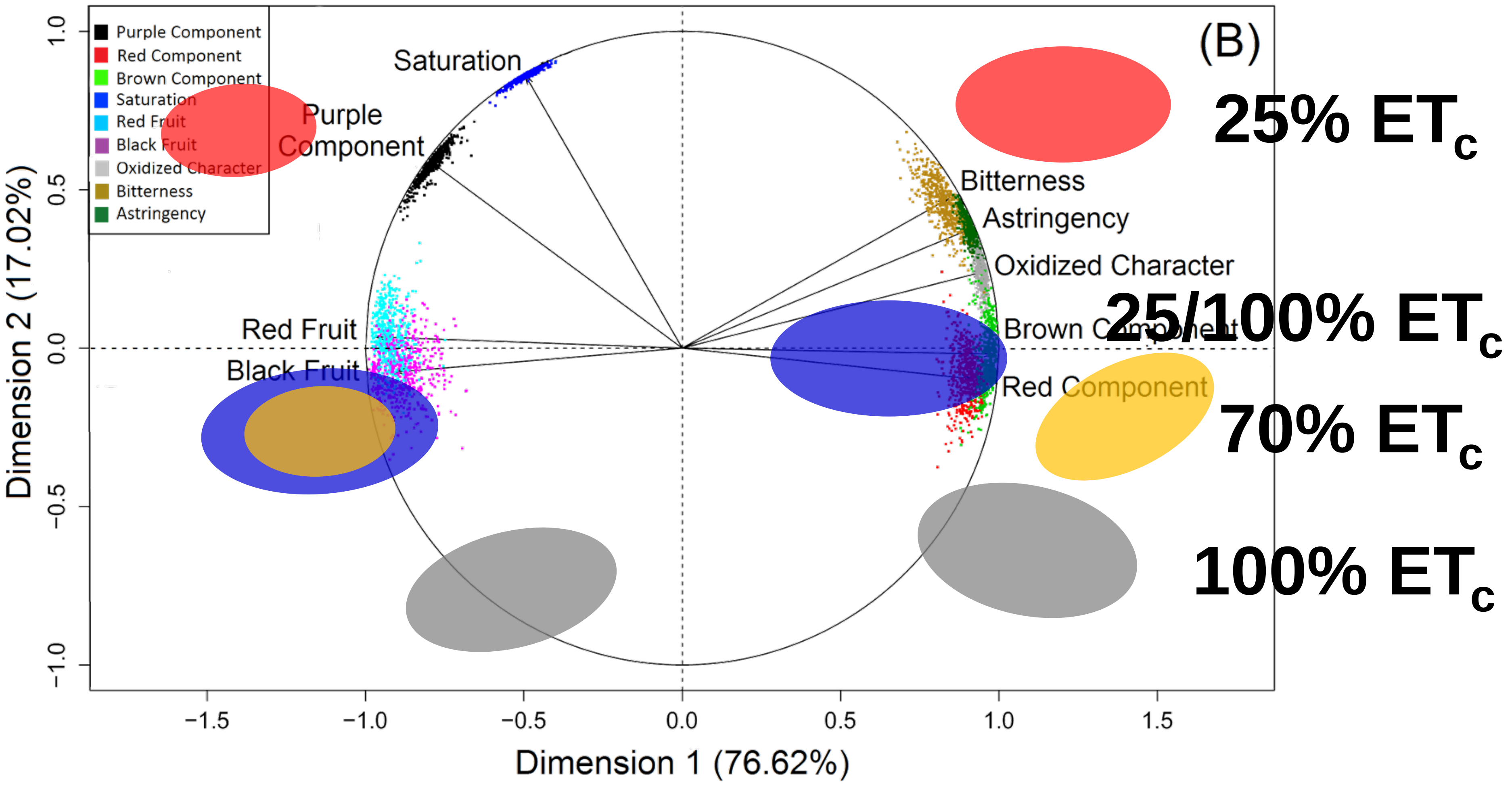




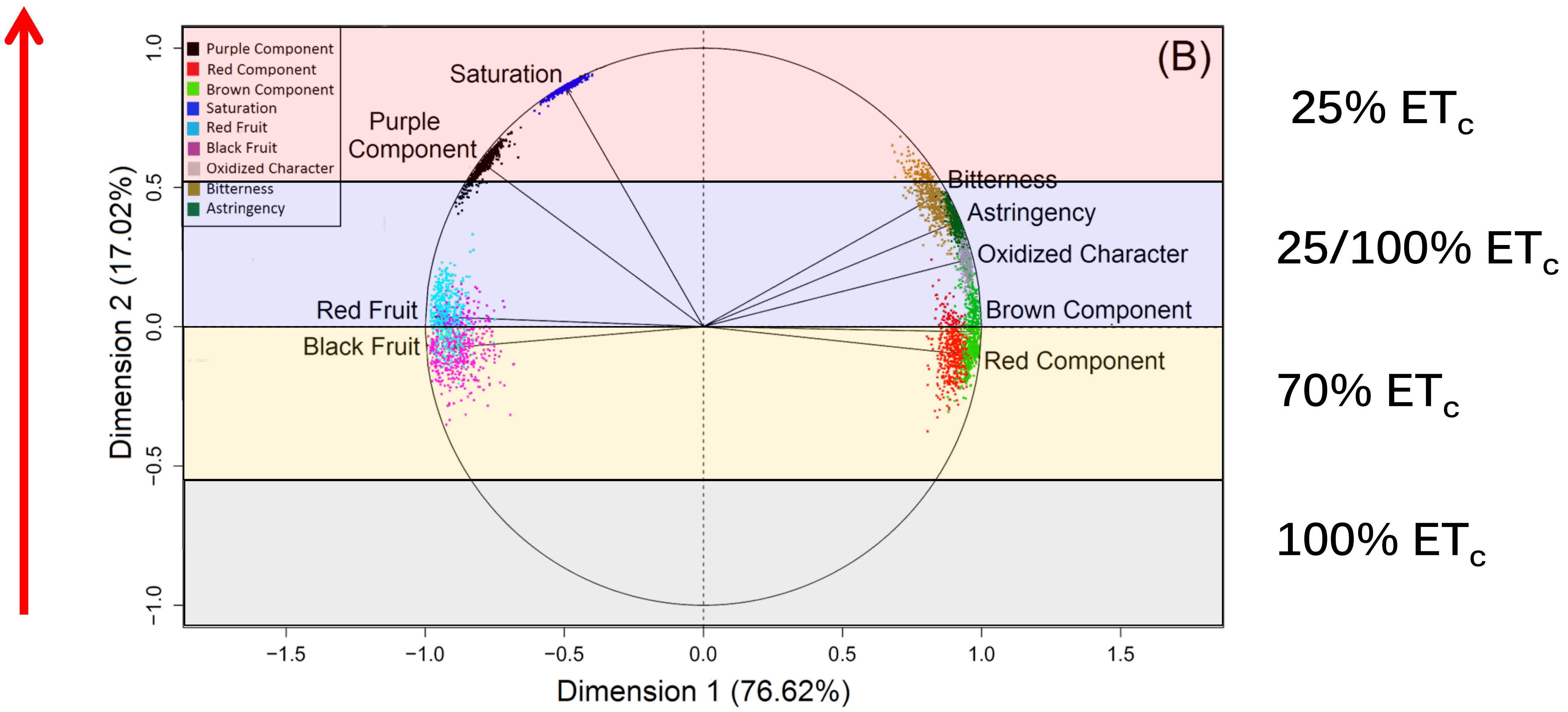
$p < 0.0109$

Effect of EM and RDI

Quantitative Descriptive Analysis 2011

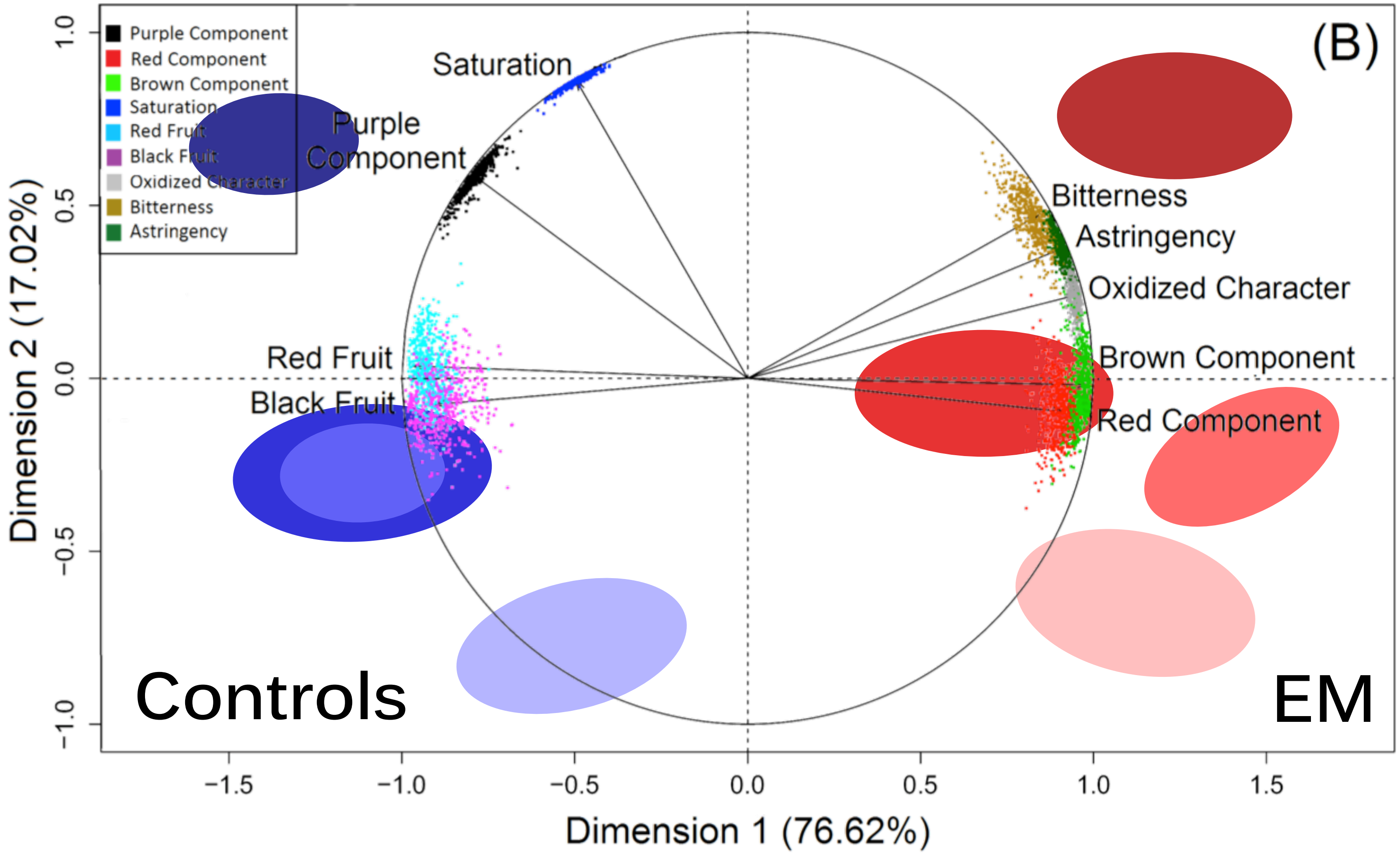


Descriptive analysis (2011)



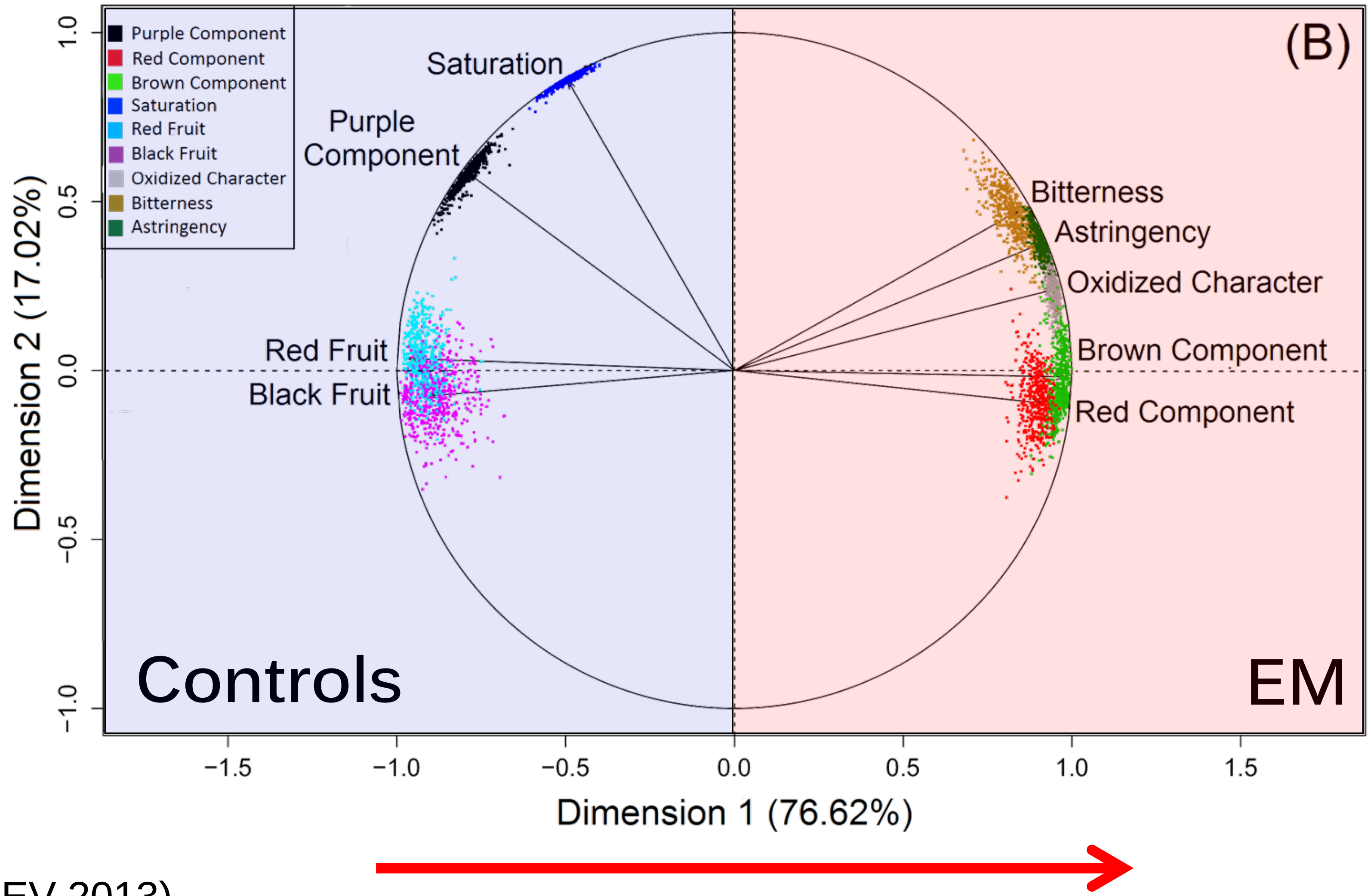
Casassa et al. (AJEV 2013)

Descriptive analysis (2011)



Casassa et al. (AJEV 2013)

Descriptive analysis (2011)



Casassa et al. (AJEV 2013)

Conclusions

- Winemaking Techniques vs. Vineyard Techniques: Draw!
  - Extended Maceration has impact on tannin structure and perception of astringency whereas RDI did not
  - Extended Maceration impacted tannins, wine color and had more evident impact than vineyard treatments
  - Flavor profile changes evident from sensory showing RDI has impact too
- Vineyard Treatments Reduce Yield too much
  - 25% ET_c reduced yield by 66% but differential gain in phenolics and color did not outweigh crop reduction
  - 25/100 % ET_c was best choice for maintaining yield and some phenolic improvements

Acknowledgements

Viticulture & Enology Program
WASHINGTON STATE UNIVERSITY

- Washington Wine Commission
- Chateau Ste. Michelle Wine Estates
  - Dr. Russell Smithyman, Dr. Bill Riley, Joe Cotta, & Juan Uribe
- My coauthors and collaborators:
  - Viticulture: M. Keller, L. Mills
  - Enology: F. Casassa, R. Larsen, M. Mireles, C. Beaver
- *Sensory Impact of Extended Maceration and Regulated Deficit Irrigation on Washington State Cabernet Sauvignon Wines.* L. F. Casassa, R.C. Larsen, C.W. Beaver, M.S. Mireles, M. Keller, W.R. Riley, R. Smithyman, J.F. Harbertson. American Journal of Enology and Viticulture 2013, 64 (4) 505-514.
- *Effects of Vineyard and Winemaking Practices Impacting Berry Size on Evolution of Phenolics during Winemaking.* L.F. Casassa, R.C. Larsen, J.F. Harbertson. American Journal of Enology and Viticulture 2016, 67:257-268
- ASEV.org (ASEV Best Paper Award Winners: 2014 & 2017)

Sensory Impact of Extended Maceration and Regulated Deficit Irrigation on Washington State Cabernet Sauvignon Wines

L. Federico Casassa,[1,2] Richard C. Larsen,[3] Christopher W. Beaver,[1] Maria S. Mireles,[1] Markus Keller,[4] William R. Riley,[5] Russell Smithyman,[5] and James F. Harbertson[1]*

Abstract: Irrigation practices such as regulated deficit irrigation (RDI) and winemaking practices such as extended maceration have been experimentally evaluated from a chemical perspective but their impacts on sensory composition and interactive effects merit scientific attention. This study evaluated the sensory impact of extended maceration applied to Cabernet Sauvignon grapes sourced from a vineyard subjected to four RDI treatments: replenishment of 100%, 70%, and 25% of full-vine crop evapotranspiration (ET_c) from fruit set until veraison followed by 100% ET_c until harvest (labeled 100% ET_c, 70% ET_c, and 25% ET_c, respectively) and 25% ET_c from fruit set to veraison followed by 100% ET_c from veraison to harvest (labeled 25/100% ET_c). Each RDI treatment was replicated four times (n = 4) and made into wine, with two replicates designated as controls (10 day skin contact) and two as extended maceration (30 day skin contact). Wines were evaluated by descriptive analysis with a trained panel (n = 15) and chemical and sensory data were correlated using canonical correlation analysis. Wine-perceived saturation and purple component ratings were highest in 25% ET_c wines and were highly correlated with the concentration of flavonols, malvidin- and delphinidin-derivatives, and small polymeric pigments. Fruit-based aroma descriptors were highest in the 25/100% ET_c and 70% ET_c wines. Extended maceration increased perceived astringency and bitterness, which were in turn correlated with the concentration of flavan-3-ol and oligomeric proanthocyanidins. These results suggest that moderate RDI protocols such as 70% ET_c and 25/100% ET_c impact positively the fruity aroma component (black and red fruit), whereas extended maceration lowered fruity aromas, possibly due to the masking effect of the oxidized character perceived in these wines.

Key words: extended maceration, regulated deficit irrigation, wine aroma, oxidation, astringency, bitterness

In wines, observed variations in sensory attributes such as color (hue and saturation) and taste and mouthfeel properties (such as bitterness and astringency) are primarily the result of the composition and concentration of two phenolic classes, anthocyanins and proanthocyanidins (Lesschaeve and Noble 2005, Preys et al. 2006). Anthocyanins are pigments that modulate wine color directly due to their spectral properties and indirectly by participating in reactions such as copigmentation resulting in the typical hyperchromic shift (more color) and bathochromic shift (more purple color) observed in young red wines (Boulton 2001). Isolated anthocyanins are tasteless or indistinctly flavored (Vidal et al. 2004). However, when anthocyanins react with proanthocyanidins during winemaking, polymeric pigments are formed and these in turn can modulate astringency (Weber et al. 2013).

Proanthocyanidins (also referred to as tannins) and, to a lesser extent, monomeric flavan-3-ols, display high affinity for proline-rich proteins found in the saliva of humans and other mammals (Mehansho et al. 1987, Poncet-Legrand et al. 2007). The tactile sensation of astringency arises from the formation of proanthocyanidin-protein complexes upon contact of the wine proanthocyanidins with the oral epithelium in a reaction driven by both hydrophobic interactions and hydrogen bonding (Baxter et al. 1997, Simon et al. 2003). Epicatechin-3-*O*-gallate and catechin can precipitate proline-rich proteins when the molar ratio of flavan-3-ols to protein exceeds 27 (Poncet-Legrand et al. 2006), which highlights the potential cooperative role of flavan-3-ols in astringency perception in red wine.

Management of the maceration period during red wine production is arguably the most common practice to achieve the selective diffusion of phenolics, aroma precursors, and free aroma compounds from the skins, seeds, and stems (when present). Extended maceration (EM) is a widely used winemaking technique based on extending the contact of the fermentation solids with the wine after fermentation is

[1]School of Food Science, Washington State University, Irrigated Agriculture Research and Extension Center, 24106 N. Bunn Rd., Prosser, WA 99350; [2]Wine Research Center, Estación Experimental Agropecuaria Mendoza, Instituto Nacional de Tecnología Agropecuaria, Luján de Cuyo, Mendoza, Argentina; [3]Viticulture and Enology Program, and [4]Department of Horticulture, Washington State University, IAREC, 24106 N. Bunn Rd., Prosser, WA 99350; and [5]Ste. Michelle Wine Estates, 660 Frontier Rd., Prosser, WA 99350.

*Corresponding author (email: jfharbertson@wsu.edu; tel: 509 786-9296; fax: 509 786-9370)

Acknowledgments: The authors are grateful to the panelist members from the WSU–Prosser community and to Snoqualmie, Canoe Ridge, and Columbia Crest wineries for their commitment to this study.

Manuscript submitted May 2013, revised Aug 2013, accepted Aug 2013

Copyright © 2013 by the American Society for Enology and Viticulture. All rights reserved.

doi: 10.5344/ajev.2013.13068

JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Article

pubs.acs.org/JAFC

Impact of Extended Maceration and Regulated Deficit Irrigation (RDI) in Cabernet Sauvignon Wines: Characterization of Proanthocyanidin Distribution, Anthocyanin Extraction, and Chromatic Properties

L. Federico Casassa,† Richard C. Larsen,‡ Christopher W. Beaver,† Maria S. Mireles,† Markus Keller,§ William R. Riley,∥ Russell Smithyman,∥ and James F. Harbertson*,†

†School of Food Science, Washington State University (WSU), Irrigated Agriculture Research and Extension Center, 24106 North Bunn Road, Prosser, Washington 99350-8694, United States

‡Viticulture and Enology Program, Washington State University, Irrigated Agriculture Research and Extension Center, 24106 North Bunn Road, Prosser, Washington 99350-8694, United States

§Department of Horticulture, Washington State University, Irrigated Agriculture Research and Extension Center, 24106 North Bunn Road, Prosser, Washington 99350-8694, United States

∥Ste. Michelle Wine Estates, Prosser, Washington 99350-8694, United States

Supporting Information

ABSTRACT: The impact of extended maceration (EM) was studied in Cabernet Sauvignon grapes sourced from a vineyard subjected to four regulated deficit irrigation (RDI) treatments: (I) 100% replenishment of crop evapotranspiration (100% ET_c), (II) 70% ET_c, (III) 25% ET_c until véraison, followed by 100% ET_c until harvest, and IV) 25% ET_c. Each vineyard replicate was made into wine with two replicates designated as controls (10-day skin contact) and two as extended maceration (EM, 30-day skin contact). The mean degree of polymerization (mDP), size distribution, concentration, and composition of wine proanthocyanidins (PAs) and monomeric flavan-3-ols of 90 fractions were characterized by preparative and analytical HPLC techniques. The maceration length imparted a larger effect on most chemical parameters. The RDI treatment had no effect on the extraction patterns of anthocyanins, PAs, and/or on the origin of the PAs extracted into the wines. Conversely, EM led to anthocyanin losses and increased PA extraction during maceration, with ~73% of seed-derived PAs. Accordingly, the concentration of monomeric flavan-3-ols, oligomeric ($2 \leq mDP < 5$) and polymeric PAs ($mDP \geq 5$) was higher in EM wines. The size distribution of the wines' PAs revealed two major peaks as a function of concentration at mDP 2 (22–27% of total PAs mass) and at mDP 6–7 (12–17% of total PAs mass) and was found to follow a non-normal Rayleigh-type distribution.

KEYWORDS: *extended maceration, regulated deficit irrigation, anthocyanin extraction, proanthocyanidin distribution*

INTRODUCTION

Phenolic compounds are ubiquitous in plant-derived food and beverage products. These are functional biomolecules possessing a specific three-aromatic ring system defined by a C6–C3–C6 structure bearing diverse hydroxyl and nonhydroxyl substitutions.[1] In *Vitis vinifera* L., phenolics are synthesized via the phenyl-propanoid biosynthetic pathway, which is modulated by both biotic and abiotic factors, with irrigation practices being among them.[2,3] From a chemical and sensory standpoint, the two most relevant phenolic classes in grapes and wines are anthocyanins and proanthocyanidins. Anthocyanins occur as vacuolar components in the skin tissue (and in the mesocarp of the *teinturier* varieties) and are present as monomers of six glycosylated forms, including malvidin, cyanidin, petunidin, peonidin, delphinidin, and pelargonidin.[4,5] Glycosylation typically occurs at the C3 position and renders the molecule water-soluble, thus facilitating their early extraction during maceration.[4,6]

Proanthocyanidins (PAs) are present in seeds, skins, and stem/rachis as oligomers and polymers of four flavan-3-ol subunits: (+)-catechin, (−)-epicatechin, (−)-epigallocatechin, and (−)-epicatechin-3-*O*-gallate.[7,8] The average number of constitutive flavan-3-ol monomers in the PA structure, which are linked by covalent C4→C8 (or less commonly C4→C6) interflavanic bonds, is referred to as mean degree of polymerization (mDP). In wines of five *V. vinifera* cultivars, the polymeric ($mDP \geq 5$) PA fraction accounted for 77–95% of the total PA distribution.[9] However, in the previous study fractionation was performed in C18 Sep-Pak cartridges and quantification was achieved by the vanillin essay, which lacks specificity in wine extracts.[10,11] In a separate study, the polymeric fraction represented 77–84% of the total PA distribution and showed a mDP variable from 6.3 to 13, but the presence of oligomers, particularly B-type dimers, was also observed.[12] Wines also contain a non-negligible amount of monomeric flavan-3-ols, with their content varying from 29 to 41 mg/L up to 189 mg/L, of which catechin alone represents 60–73% of the total flavan-3-ol content.[12,13]

Received: February 15, 2013
Revised: May 29, 2013
Accepted: May 29, 2013
Published: May 29, 2013

Effects of Vineyard and Winemaking Practices Impacting Berry Size on Evolution of Phenolics during Winemaking

L. Federico Casassa,[1] Richard C. Larsen,[2] and James F. Harbertson[2]*

Abstract: Four methods of regulated deficit irrigation (RDI), an irrigation technique whereby water is supplied at rates at or below the full evapotranspiration (ET_c), were applied to Cabernet Sauvignon grapes. The grapes were thereafter processed with three winemaking techniques: control (10-day maceration), extended maceration (EM; 30-day maceration), and saignee (removal of 16% of must by volume at crushing). The 25% ET_c treatment had higher concentrations (fresh weight basis) of skin anthocyanins and seed tannins. Overall, skin tannins showed increased biosynthesis in 100% ET_c and 25/100% ET_c, whereas seed tannins were mostly (positively) affected due to a reduction of fresh weight in 25% ET_c. Extraction of anthocyanins and tannins during winemaking ranged from 40 to 73% and from 17 to 26%, respectively. During maceration, the extraction curves for both anthocyanins and tannins were unaffected by the RDI treatments; quantitative differences were caused primarily by the winemaking treatments and secondarily by the RDI treatments. Consistent with a higher content of anthocyanins, 25% ET_c wines had higher concentrations of polymeric pigments and greater color saturation and a* (red color component) both at day 30 and after 120 days post-crushing. EM enhanced seed tannin extraction, which resulted in a 50% increase in wine tannins relative to control and saignee wines, but it lowered anthocyanins and color saturation. Saignee increased anthocyanins at day 5 by 22% and tannins by 24% (relative to control wines), resulting in higher concentrations of polymeric pigments after 120 days. Both saignee and control wines had a roughly equivalent proportion of seed- and skin-derived tannins, whereas EM wines had 73% seed-derived tannins.

Key words: anthocyanins, extended maceration, regulated deficit irrigation, saignée, tannins, wine color

Anthocyanins and tannins are phenolic compounds bearing a three-aromatic ring system defined by a C6–C3–C6 structure that possess specific hydroxyl and nonhydroxyl substitutions. Anthocyanins and tannins are responsible for the sensory features that distinguish red wines from other beverages (Cheynier 2006), including taste sensations such as bitterness (Robichaud and Noble 1990), tactile sensations such as astringency (Arnold et al. 1980), and visual sensations such as color saturation and hue (Somers 1978). Anthocyanins and tannins cannot elicit aromatic sensations due to restrictions imposed by their molecular weights, which are higher than the 300 Da limit for volatility (Rowan 2011). Nevertheless, they may affect the partitioning of aromatic compounds between vapor and liquid phases, ultimately modulating both ortho- and retronasal perceived aroma (Muñoz-González et al. 2014). Therefore, anthocyanins and tannins can modulate the whole sensory spectrum of red wines.

Anthocyanins are responsible for wine color and occur as vacuolar inclusions in grape skins (and in the mesocarp of the teinturier cultivars) as glycosylated monomers of malvidin, cyanidin, petunidin, peonidin, delphinidin, and pelargonidin (Cheynier 2006). Anthocyanins are highly reactive within the wine matrix and can undergo both nucleophilic and electrophilic substitutions (He et al. 2012). Anthocyanins can react with tannins during winemaking to form polymeric pigments, which can modulate astringency (Wollmann and Hofmann 2013).

Proanthocyanidins, also referred to as tannins, occur in seeds, skins, and stem/rachis as oligomers and polymers of four flavan-3-ol subunits: (+)-catechin, (-)-epicatechin, (-)-epigallocatechin, and (-)-epicatechin-3-*O*-gallate (Prieur et al. 1994, Souquet et al. 1996). Seed- and skin-derived tannins differ in their chemical compositions, which affect their sensory properties. Seed tannins have lower molecular weights than skin tannins and are composed of (+)-catechin, (-)-epicatechin, and epicatechin-3-*O*-gallate, with monomeric flavan-3-ols, dimers and trimers being the predominant species. Seeds are predominantly bitter because of their high content of monomeric flavan-3-ols (Thorngate and Noble 1995) and proanthocyanidin dimers and trimers, which tend to be more bitter than astringent. Moreover, as the percentage of galloylation of seed tannins increases (or in the wine made from them), it enhances their ability to precipitate with proline-rich-proteins (PRPs) found in human saliva, thus increasing

[1]Wine and Viticulture Department, California Polytechnic State University, San Luis Obispo, CA 93407; and [2]Viticulture and Enology Program, Washington State University, Wine Science Center, 2710 Crimson Way, Richland, WA 99354.

*Corresponding author (jfharbertson@wsu.edu; tel: 509 372-7506)

Acknowledgments: The authors are grateful to Ste. Michelle Wine Estates (SMWS) and particularly to Russ Smithyman and Bill Riley for the generous donation of fruit and labor for this project. The authors also extend their gratitude to Markus Keller, Pascual Romero, Alan Kawakami, and Lynn Mills for collecting weather data, yield components, and pruning weights and helping with the analysis of fruit data. Christopher Beaver and Maria Mireles are thanked for assistance with the collection of wine phenolic data. LFC is thankful to the Fulbright Commission and the Walter Clore scholarship for financial support. The Wine Advisory Committee, the Washington Wine Commission, the Washington Grape and Wine Research Program, and the WSU Agricultural Research Center are thanked for funding this research.

Supplemental data is freely available with the online version of this article at www.ajevonline.org.

Manuscript submitted Nov 2015, revised Mar 2016, accepted Mar 2016

Copyright © 2016 by the American Society for Enology and Viticulture. All rights reserved.

doi: 10.5344/ajev.2016.15105