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The Fate of Hop Volatiles During Dry-Hopping

Dean Hauser & Scott Lafontaine
Shellhammer Laboratory
Department of Food Science and Technology



Oregon State
University

BACKGROUND & MOTIVATION



Oregon State
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Background & Motivation

Dry Hopping

- Hugely popular for achieving intense hop aroma in beer
- Low-temperature (relative to hot-side), aqueous extraction
- Some dosage rates up to 5lb/bbl (2kg/hL)

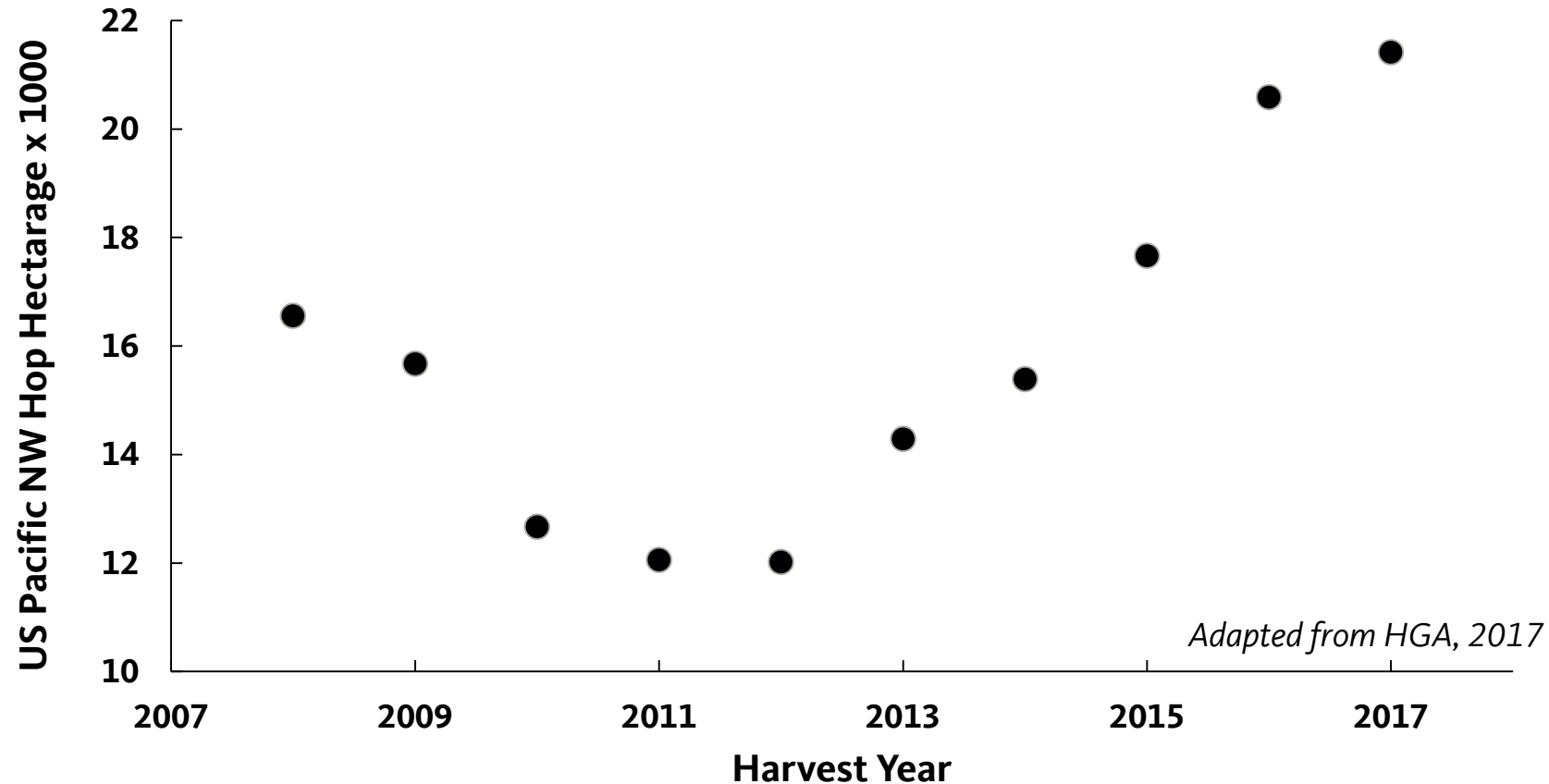
Waste

- Significant product loss
- “Spent” dry-hop waste



<https://mtlehmanbrewery.wordpress.com/page/2/>

Background & Motivation: Trends in Hop Growing & Usage



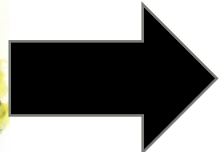
- **Shift from 50/50 to 80/20 Aroma/Dual Purpose hops (2012-2017)(HGA)**
- **7.9% Increase in Hop Dosage in Craft (2015-2016, 5.37 to 5.79 g/L) (BA)**

Mass Balance of Dry-Hopping



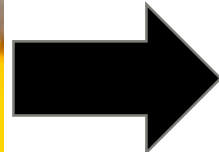
HOPS

- Alpha Acids
- Beta Acids
- Volatile Oils
- Soluble Solids

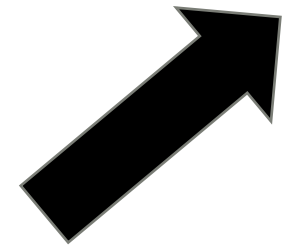


BEER

- Iso-Alpha Acids
- Volatile Oils

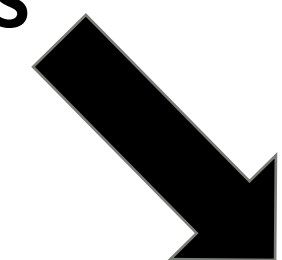


**PROCESS
LOSS**



Dry-Hopped Beer

- Iso-Alpha Acids
- Volatile Oils
- Hops Solids
- Alpha Acids

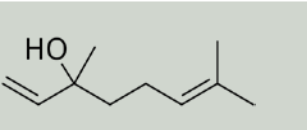
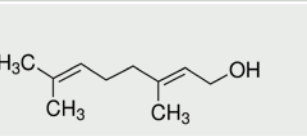
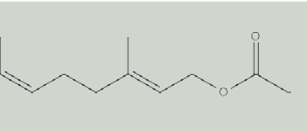
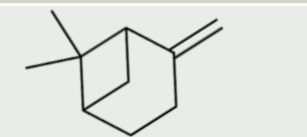
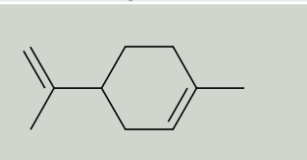
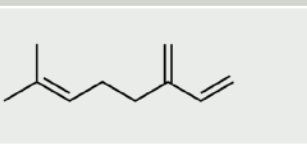
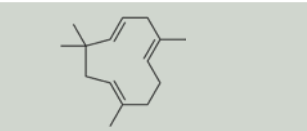


“Spent Hops”

Composition of Hop Essential Oil - Overview

Major Grouping	Hydrocarbons	Oxygenated Compounds	Sulfur Compounds
Typical Proportion of Hop Essential Oil	~64%	~35%	~1%
Examples	Monoterpenes (Myrcene) Sesquiterpenes (Humulene, Caryophyllene) Aliphatic hydrocarbons	Terpenes (linalool, geraniol) Sesquiterpene alcohols & other alcohols Epoxides, Ketones, Esters	Thioesters Sulfides Other sulfur compounds
Flavor Threshold in Beer	mg/L to ug/L		ng/L

Aroma Quality and Physical Properties of Selected Hop Volatiles

Compound	Structure	Aroma Descriptors	Log(K _{ow}) (25°C)	Aqueous Solubility (ppm, 25°C)
Linalool		Floral, citrus	3.5 ¹ , 3.4 ²	1542 ⁵
Geraniol		Floral, rose-like, fruity	3.6 ¹ , 3.5 ²	404 ⁴ , 877 ⁵
Geranyl Acetate		Floral, rose-like	4.0 ¹	18 ⁴
Beta Pinene		Spicy, piney	4.2 ¹ , 4.4 ³	32 ⁴ , 13 ⁶
Limonene		Citrus, orange	4.4 ¹ , 4.5 ³	13 ⁴ , 12 ⁶
Myrcene		Resinous, pine, herbal	4.9 ² , 4.3 ³	<10 ⁴
Alpha Humulene		Woody, pine	7.0 ²	N/A

1. Griffin et al. 1999; 2. Kishimoto 2008; 3. Copolovici and Niinemets 2005; 4. Weidenhamer et al. 1993; 5. Martins et al. 2017; 6. Tamura and Li 2005

Objectives

- 1) What quantity of hop essential oil is left behind in spent dry-hops?
- 2) What compositional changes occur within the volatile fraction?
- 3) What factors effect the retention or extraction of these components?
 - **Cultivar, initial concentration**, agitation, residence time, temperature, beer composition

MATERIALS & METHODS



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Materials: The Hops & The Beer

Hop Varieties:

Amarillo

- 12 reps, 10 different kilning conditions

Cascade

- 8 reps, 2 farms, 7 harvest maturities

Centennial

- 8 reps, 2 farms, 7 harvest maturities



“Unhopped” Beer Specifications:

Grist

- 85% Pale 2-row
- 13.5% Carmel 10L
- 0.5% Carmel 120L

Original Gravity – 10.6 P

Real extract – 3.16 P

BU = 20 mg/L (iso-extract)

ABV = 4.8%



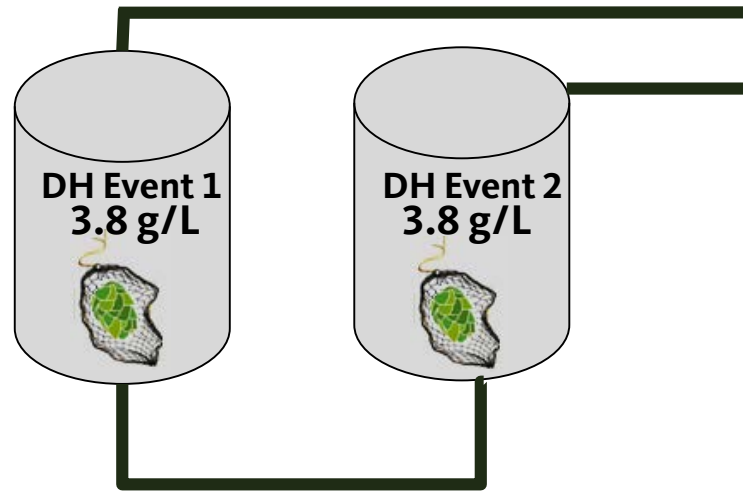
Methods: Dry-Hopping



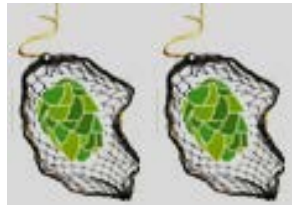
1. Hops are ground



2. Dry Hopped in 40L Beer at 3.8 g/L (1lb/bbl) for 24 hrs, 15.6 °C, 10psi



3. Filtration



4. Spent Hops are Collected and Blended

Methods: Analytical Workup



HOPS



SPENT HOPS



FINISHED BEER

Target	Method
Total Oil	Steam Distillation (ASBC Hops 13)
Moisture	Oven Drying (ASBC Hops 4)**
Oil Constituents in Hops and Spent Hops	Direct Injection GC-MS (Modified ASBC Hops 17)
Oil Constituents in Beer	HS-SPME-GC-MS (Sharp et al 2017)

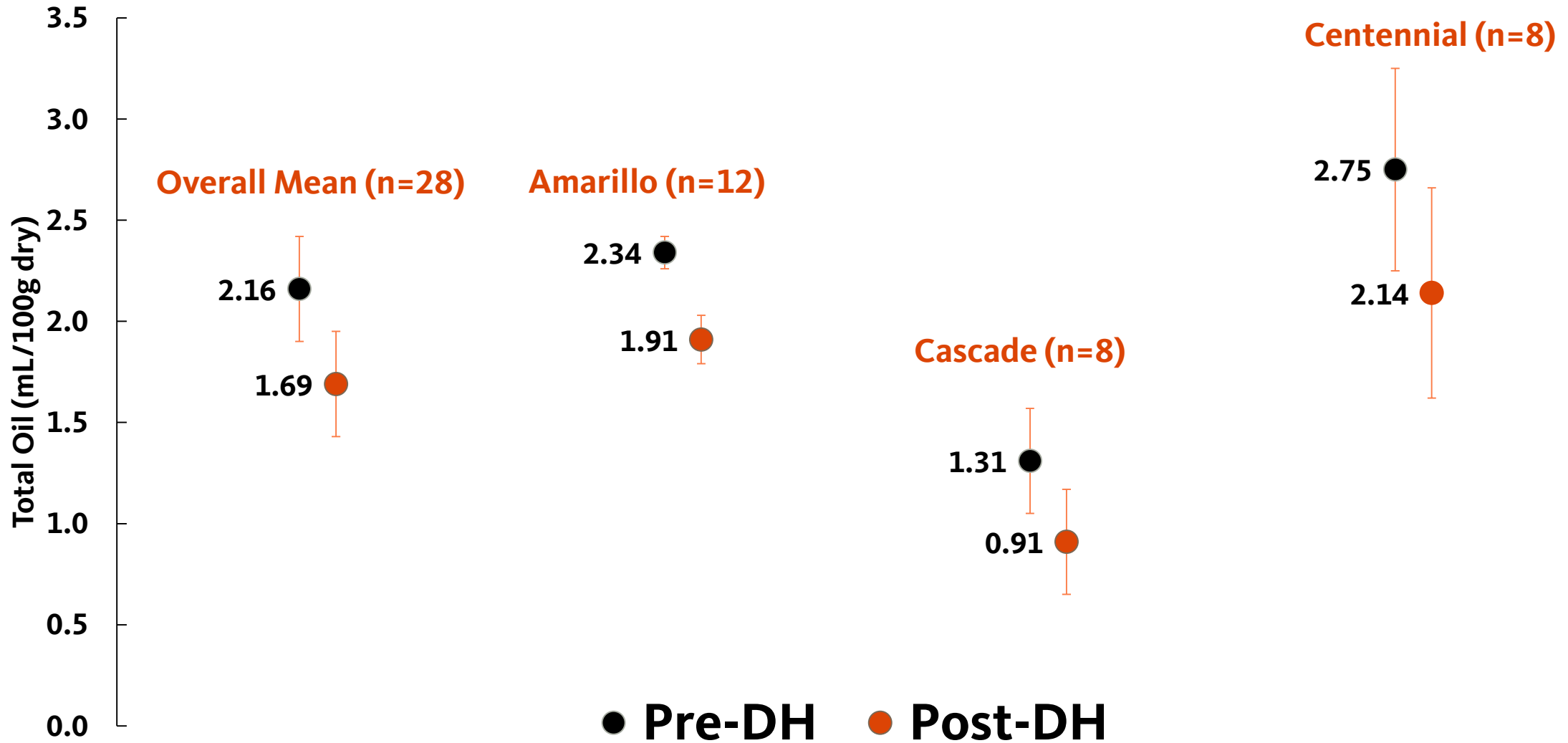
RESULTS:

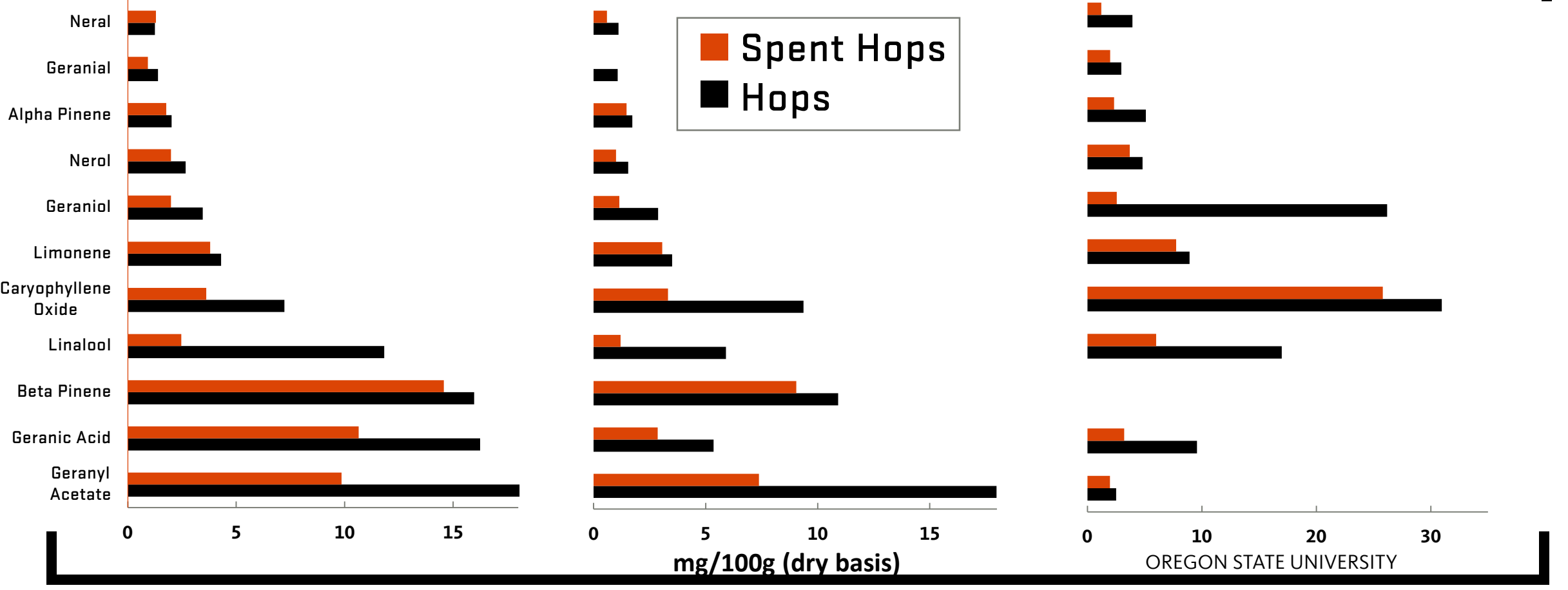
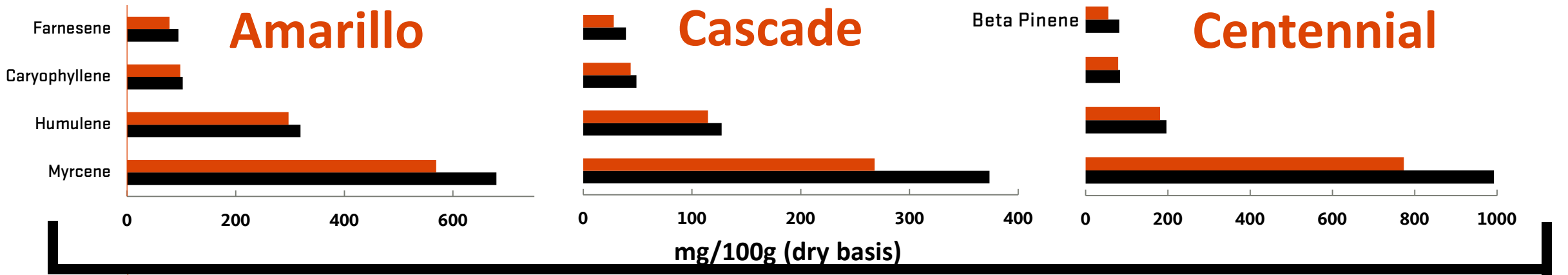
WHAT'S IN A "SPENT" HOP



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Before and After: Total Oil (as is)



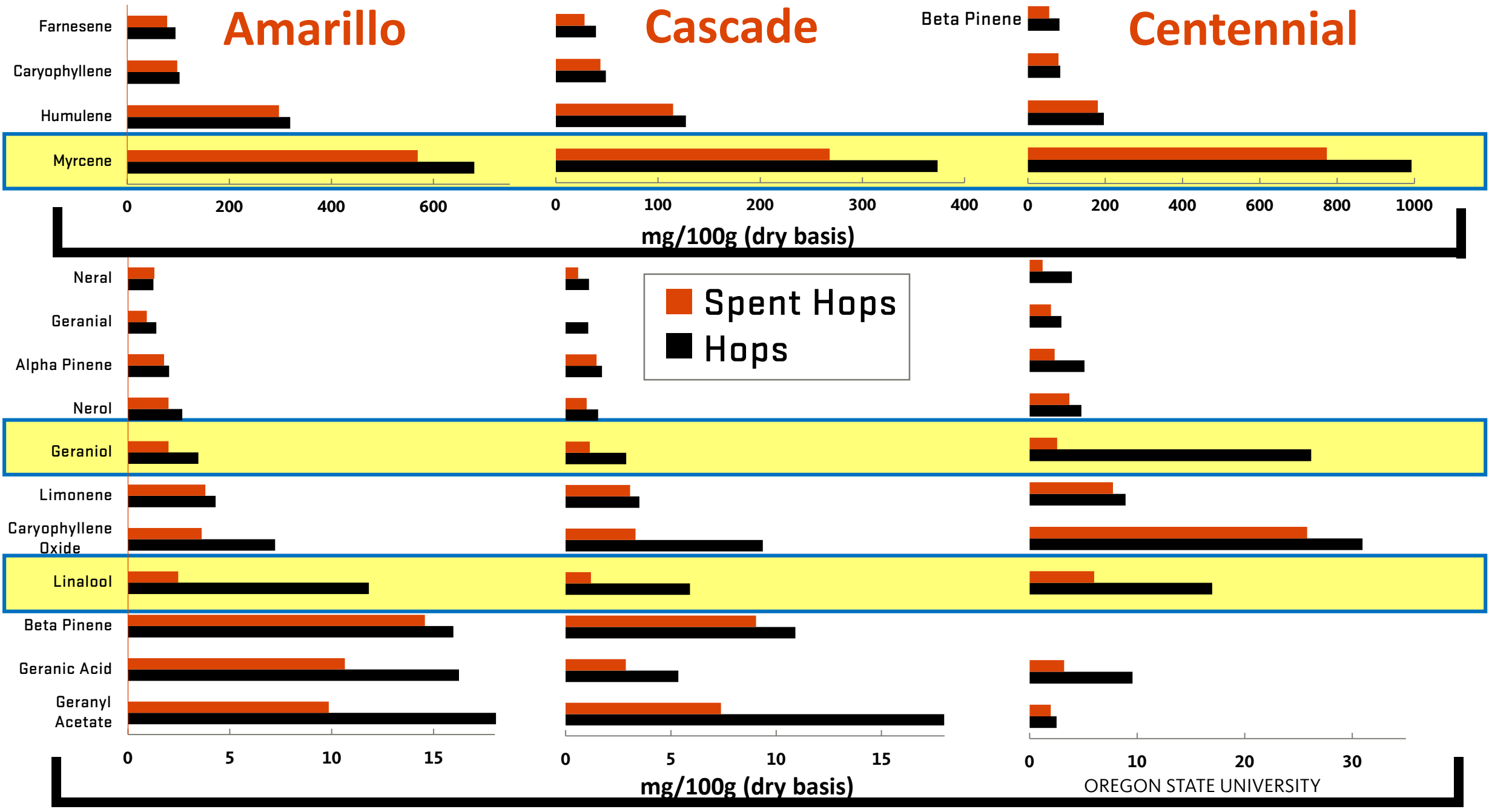


Amarillo

Cascade

Beta Pinene

Centennial



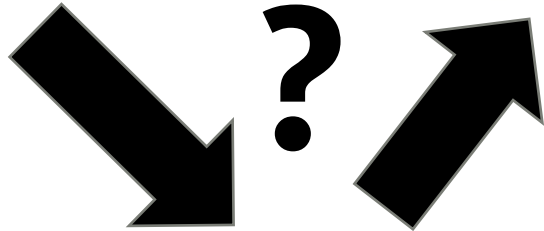
Accounting for the Concentration Effect

**After Adjusting to Dry Basis,
More Alpha Post-DH than Pre**

9.47% Alpha



10.18% Alpha



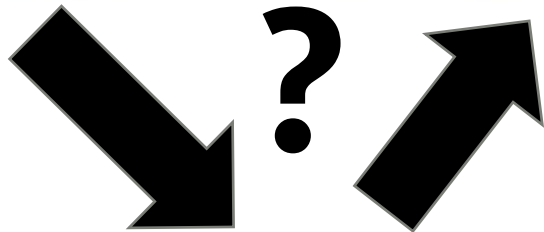
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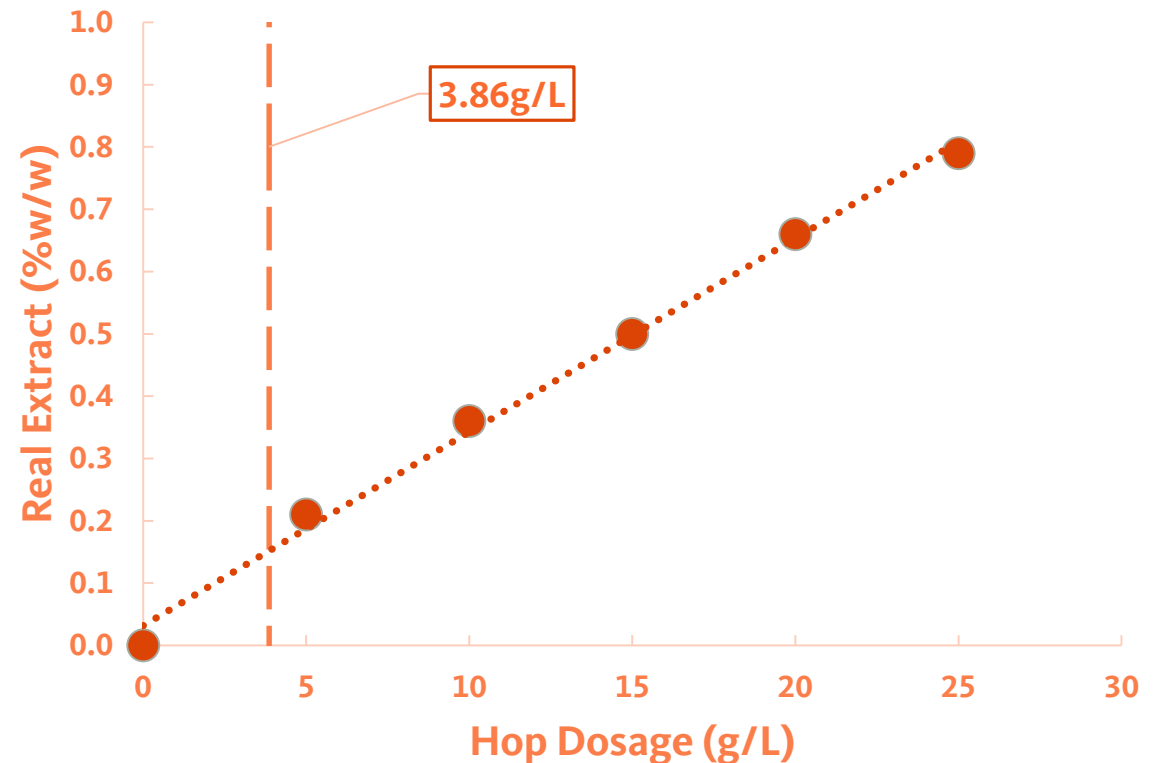
9.47% Alpha



10.18% Alpha



**Real extract vs Dry-Hop Dosage in
Buffered 5% Ethanol (%v/v)**



Adapted from Kirkpatrick 2018

Accounting for the Concentration Effect

Methods to Account for Solids Loss

1. Change in Real Extract of Experimental Beer from Dry-Hopping (Beer Alcolyzer)
2. Acetate buffered pH 4.3, 5% Ethanol Extraction + Change in Real Extract (Beer Alcolyzer)

9.47% Alpha



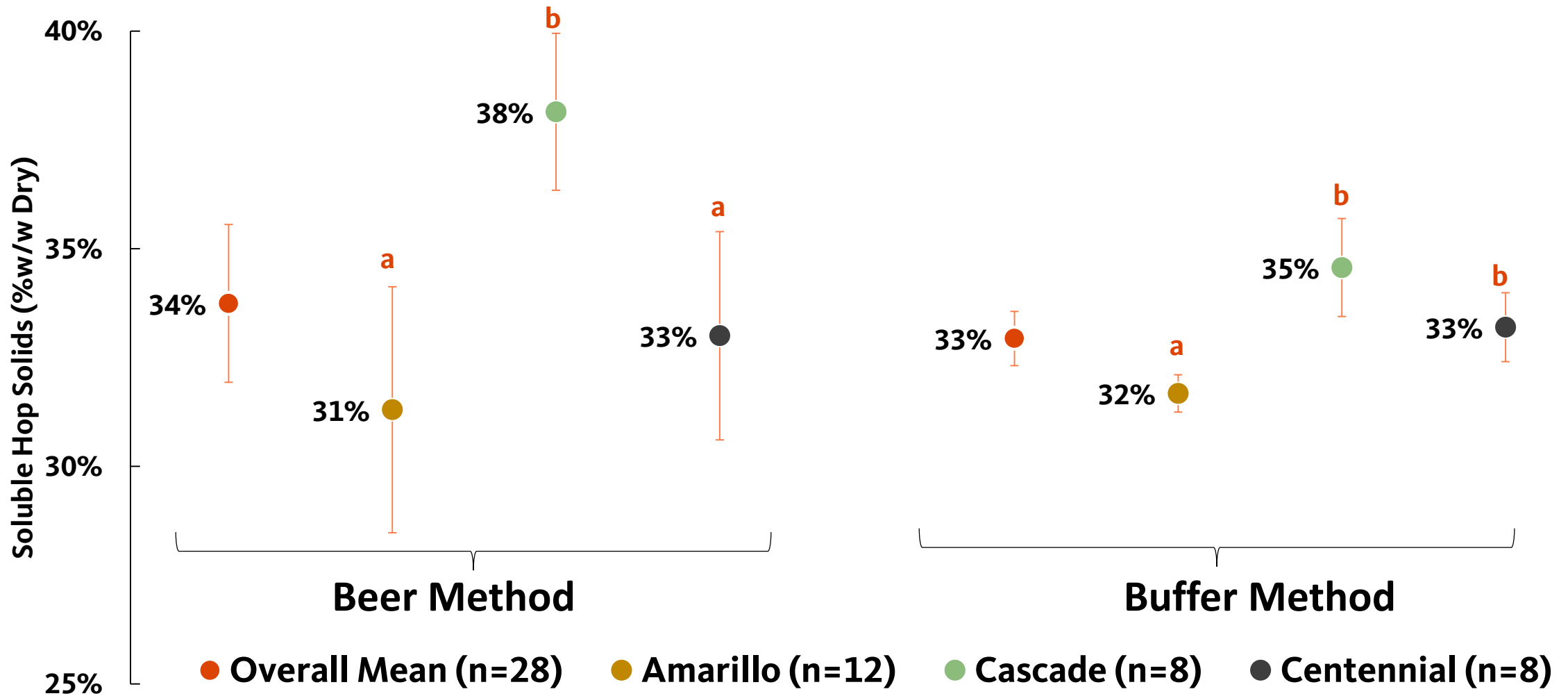
?

10.18% Alpha



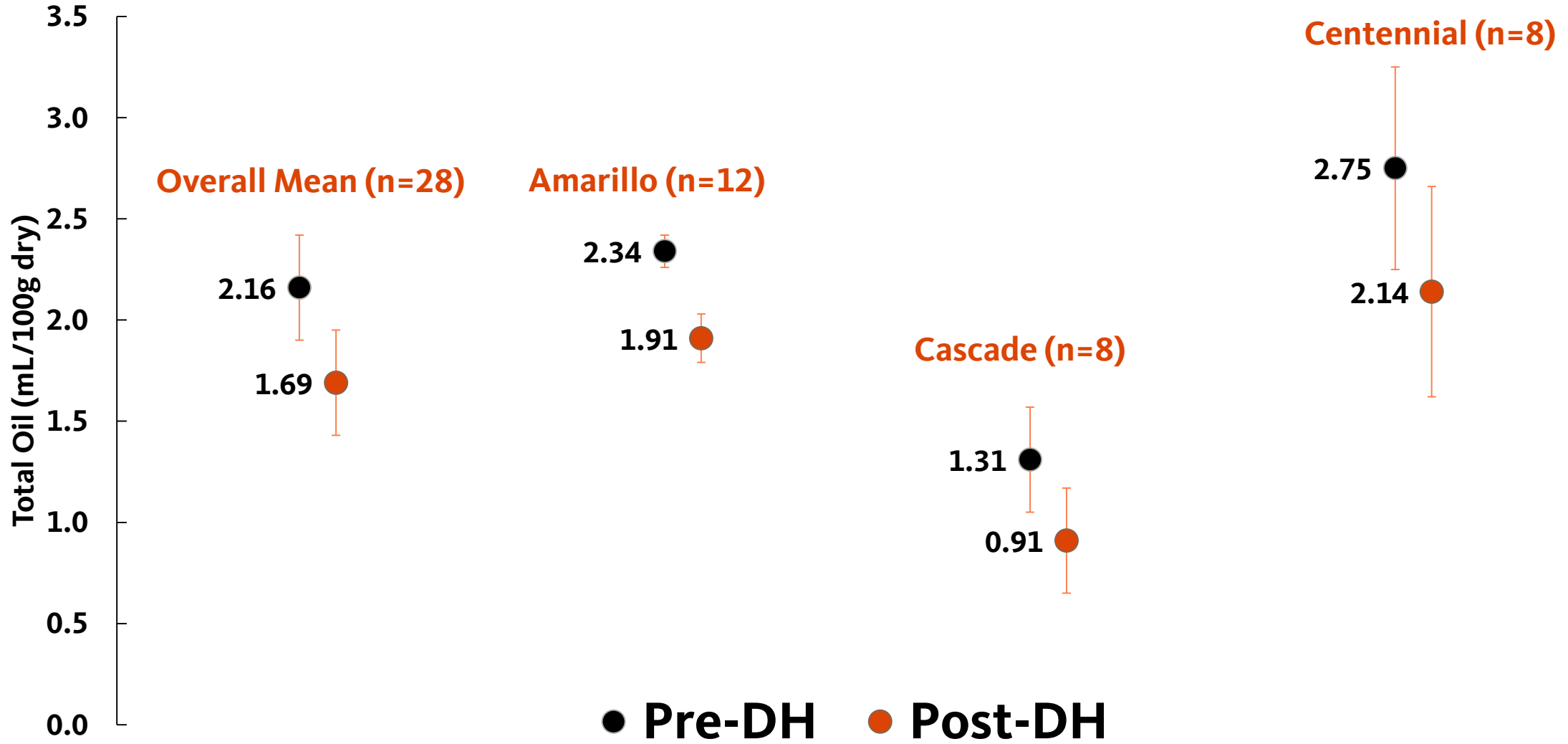
Soluble Hop Solids

Solids Loss During Dry-Hopping

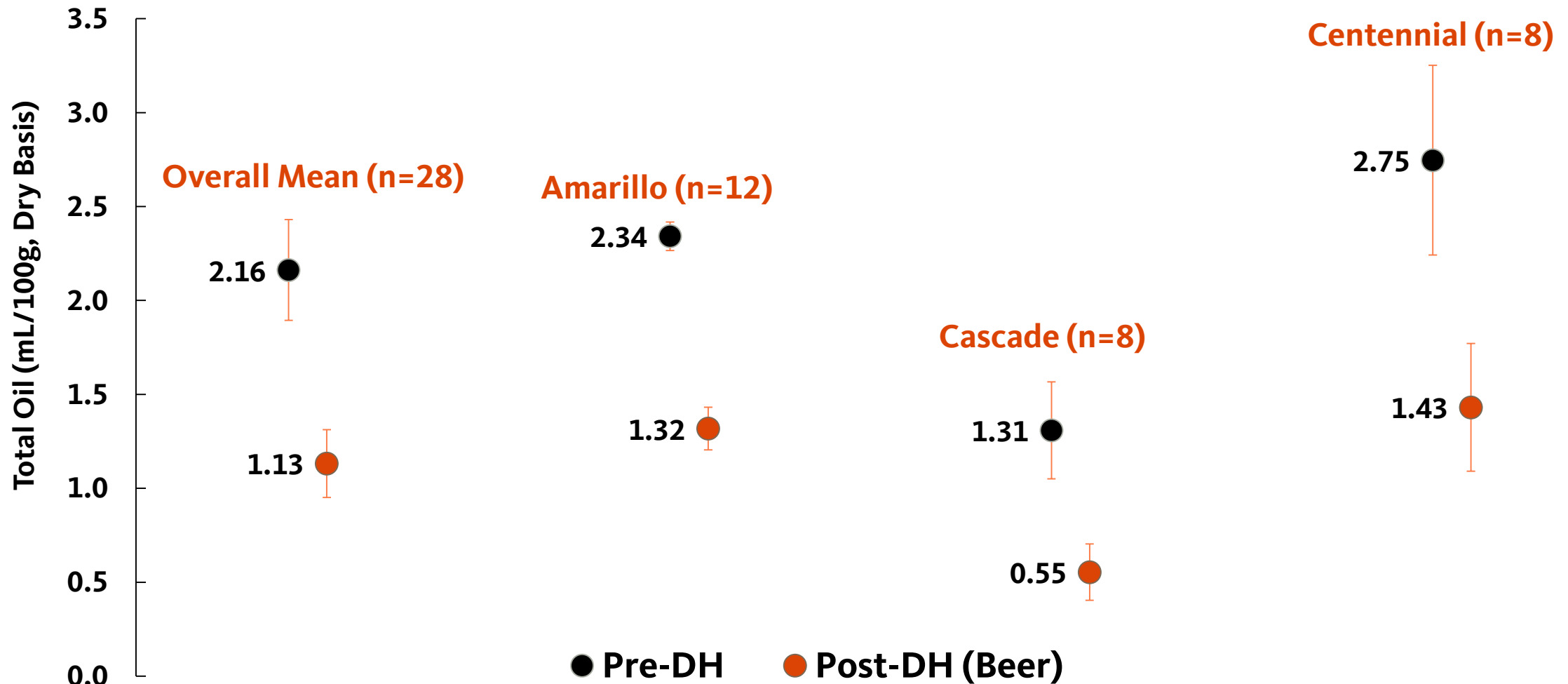


*Letters indicate Tukey HSD Groupings, alpha = 0.05

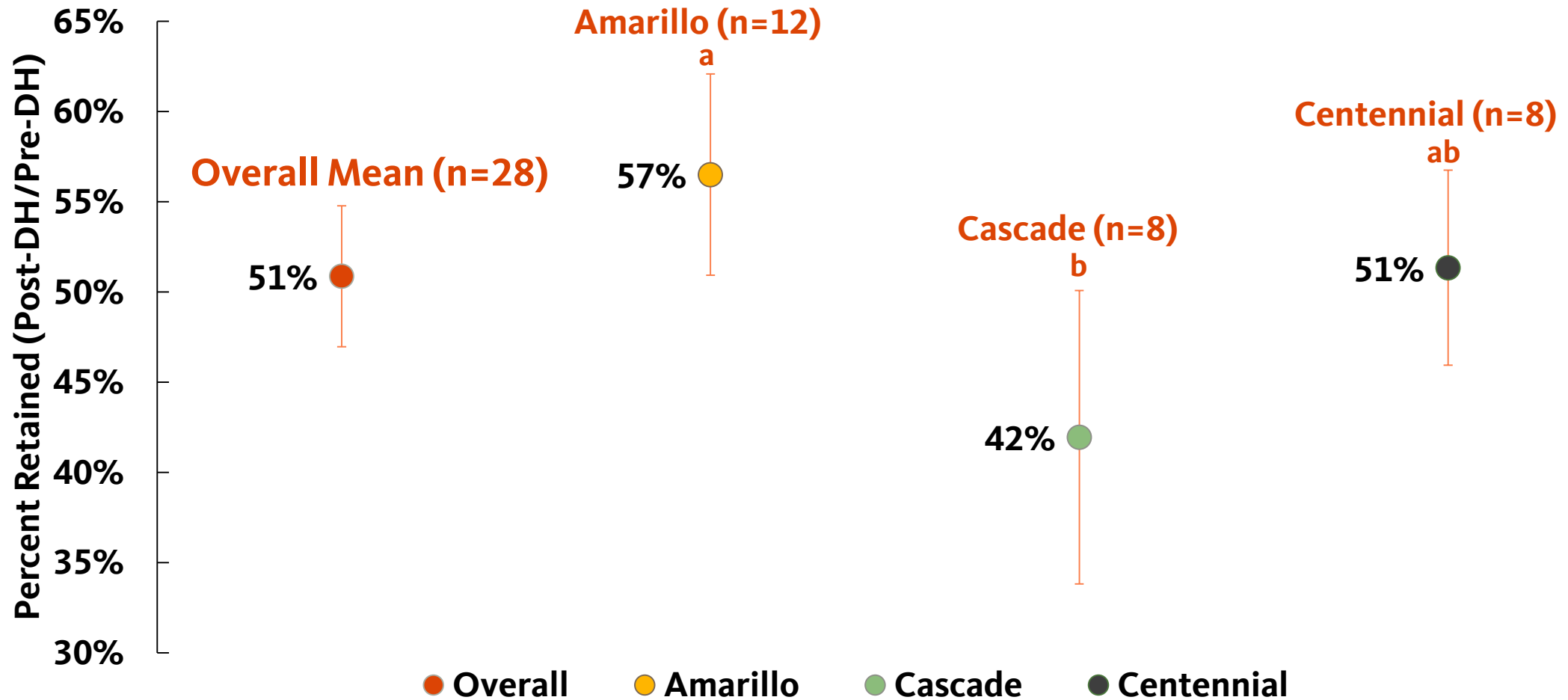
Before and After: Total Oil (as is)



Before and After: Total Oil

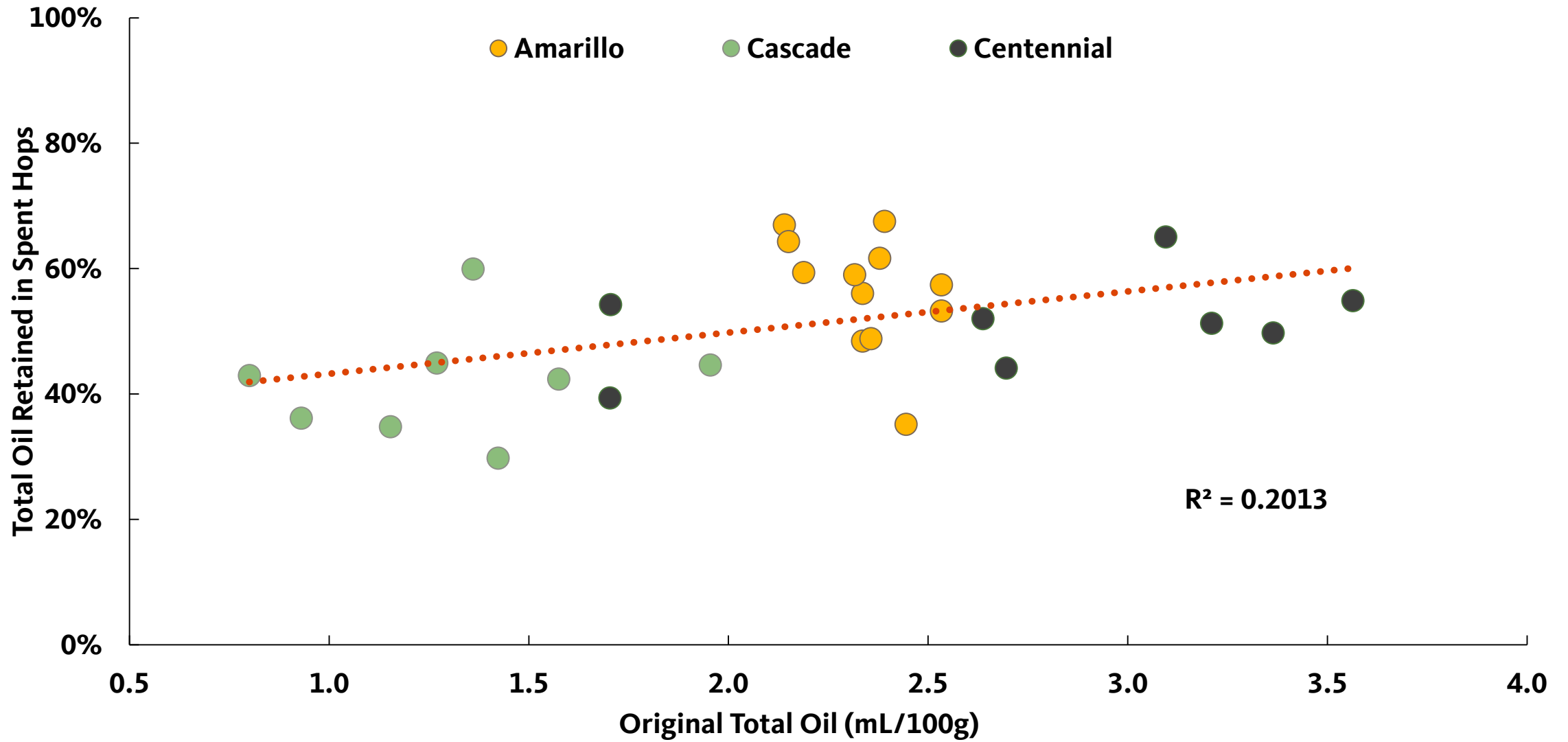


Retention in Spent Hops: Total Oil

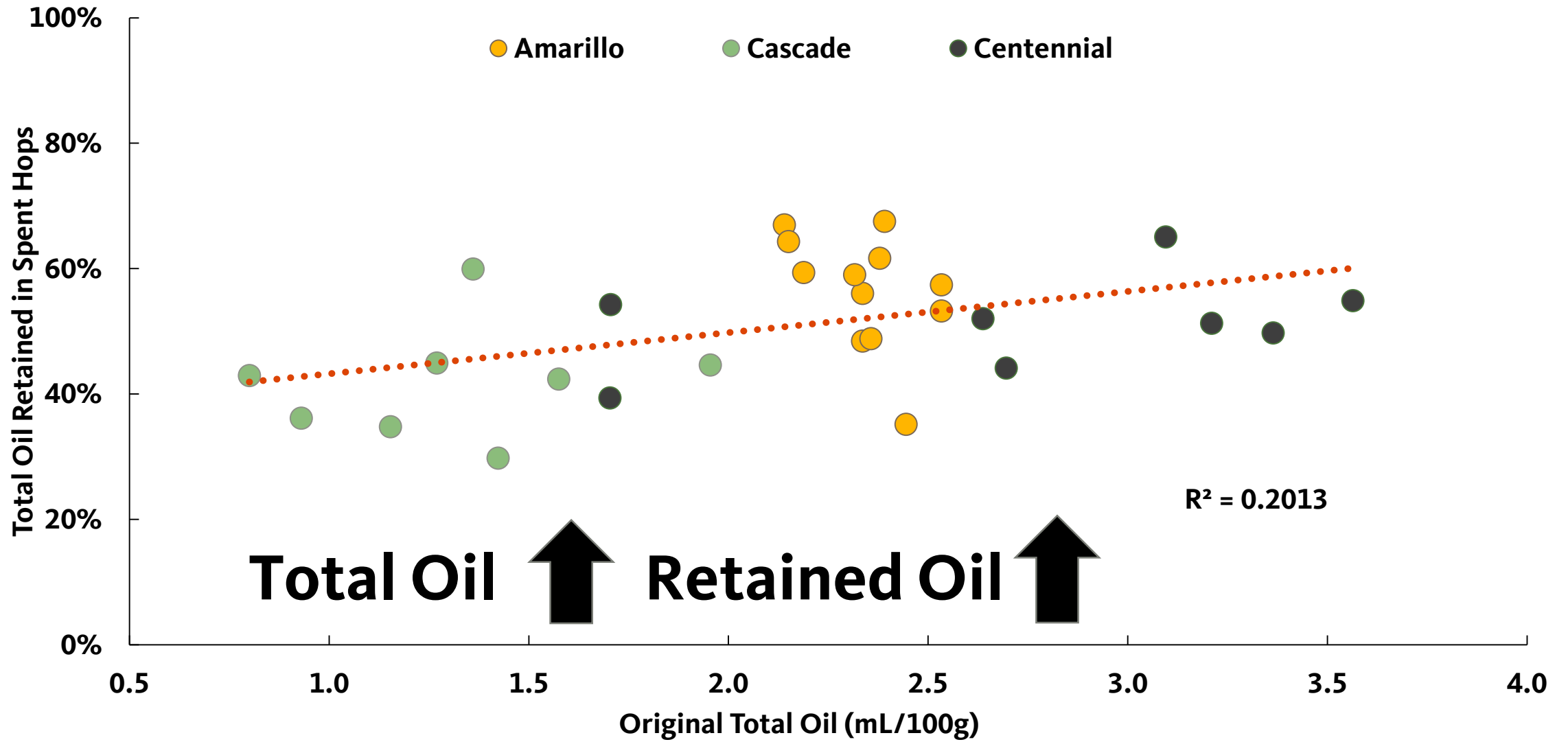


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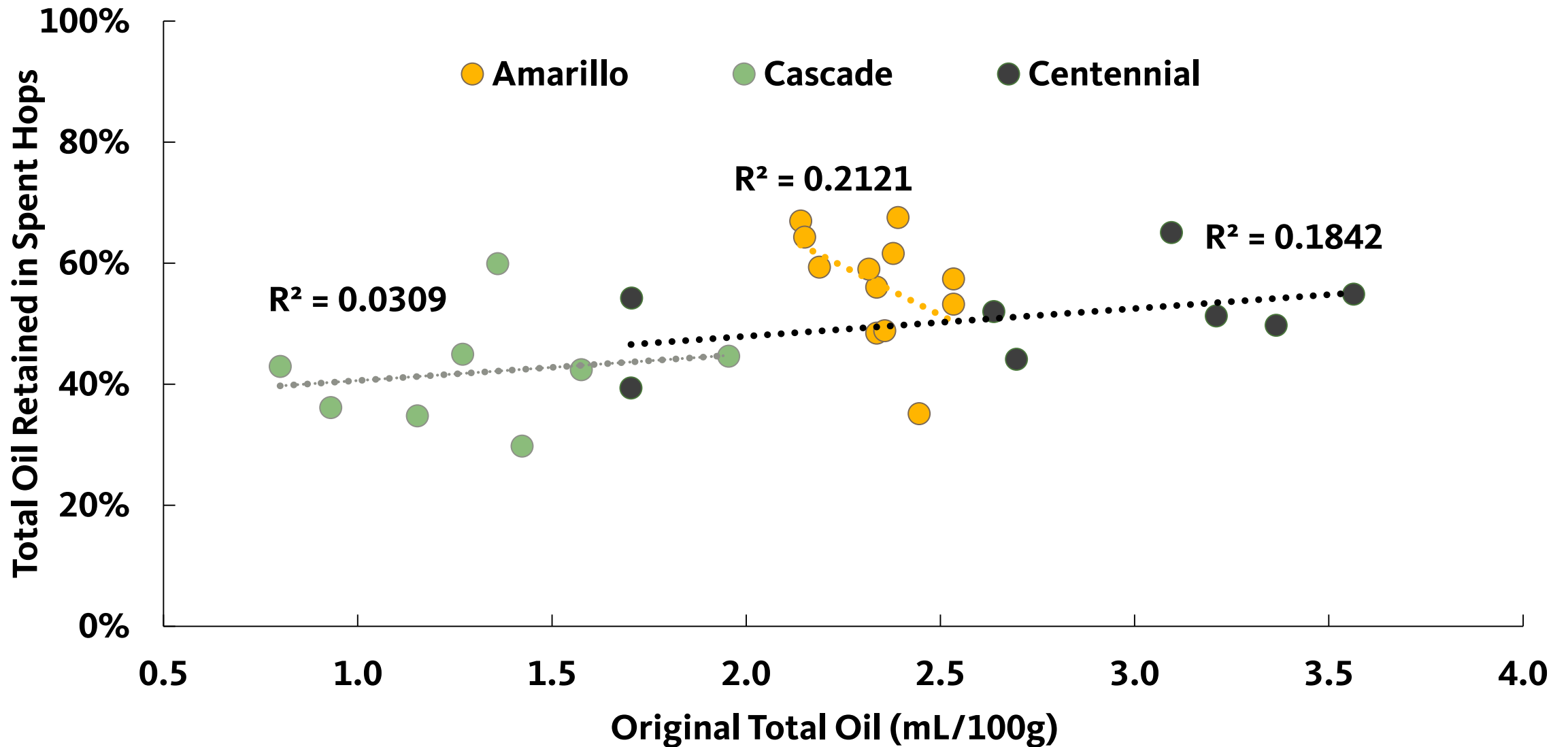
Retention in Spent Hops as a Function of Initial Oil



Retention in Spent Hops as a Function of Initial Oil



Retention in Spent Hops as a Function of Initial Oil

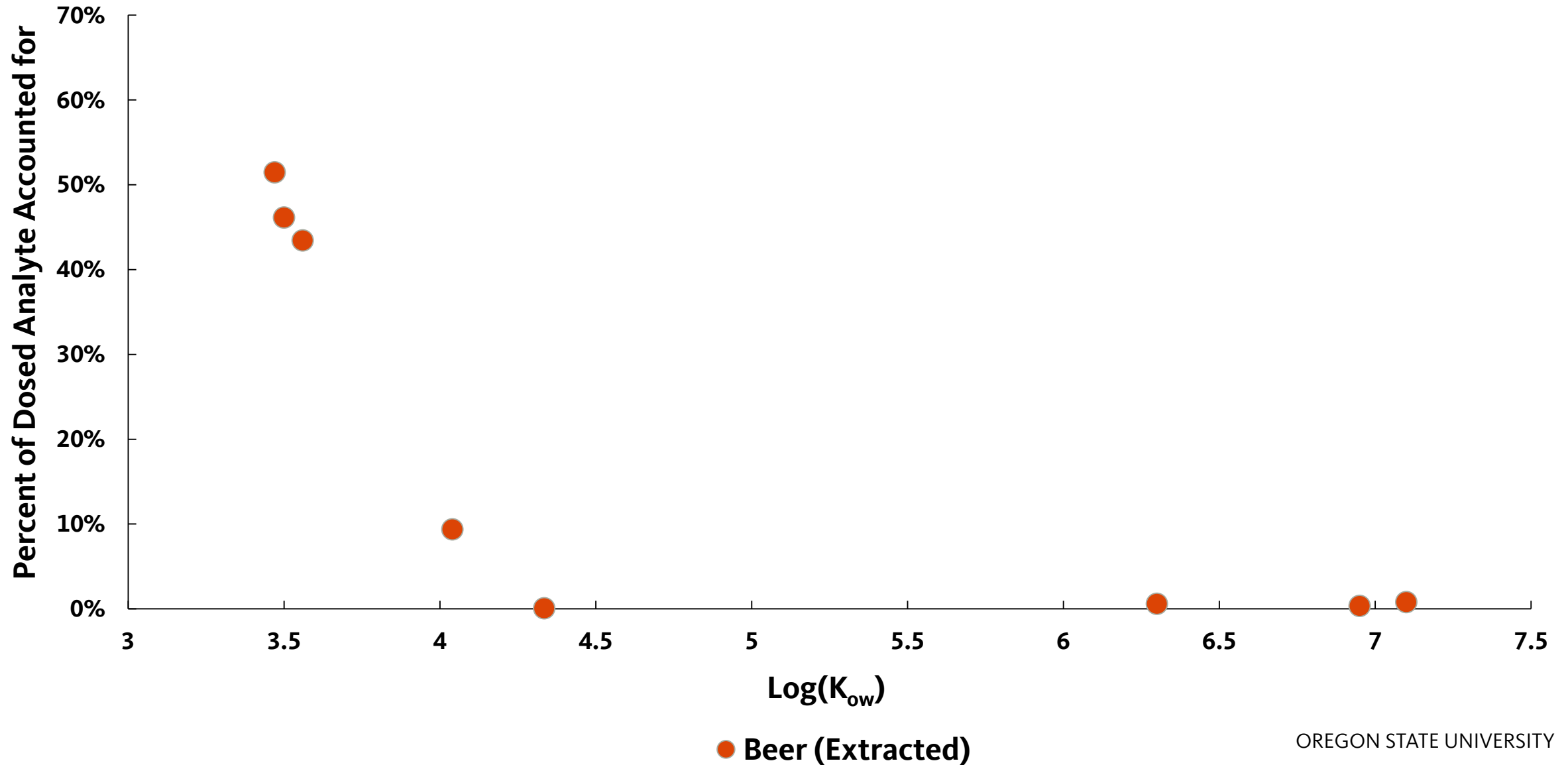


ANALYTE SPECIFIC EXTRACTION & RETENTION

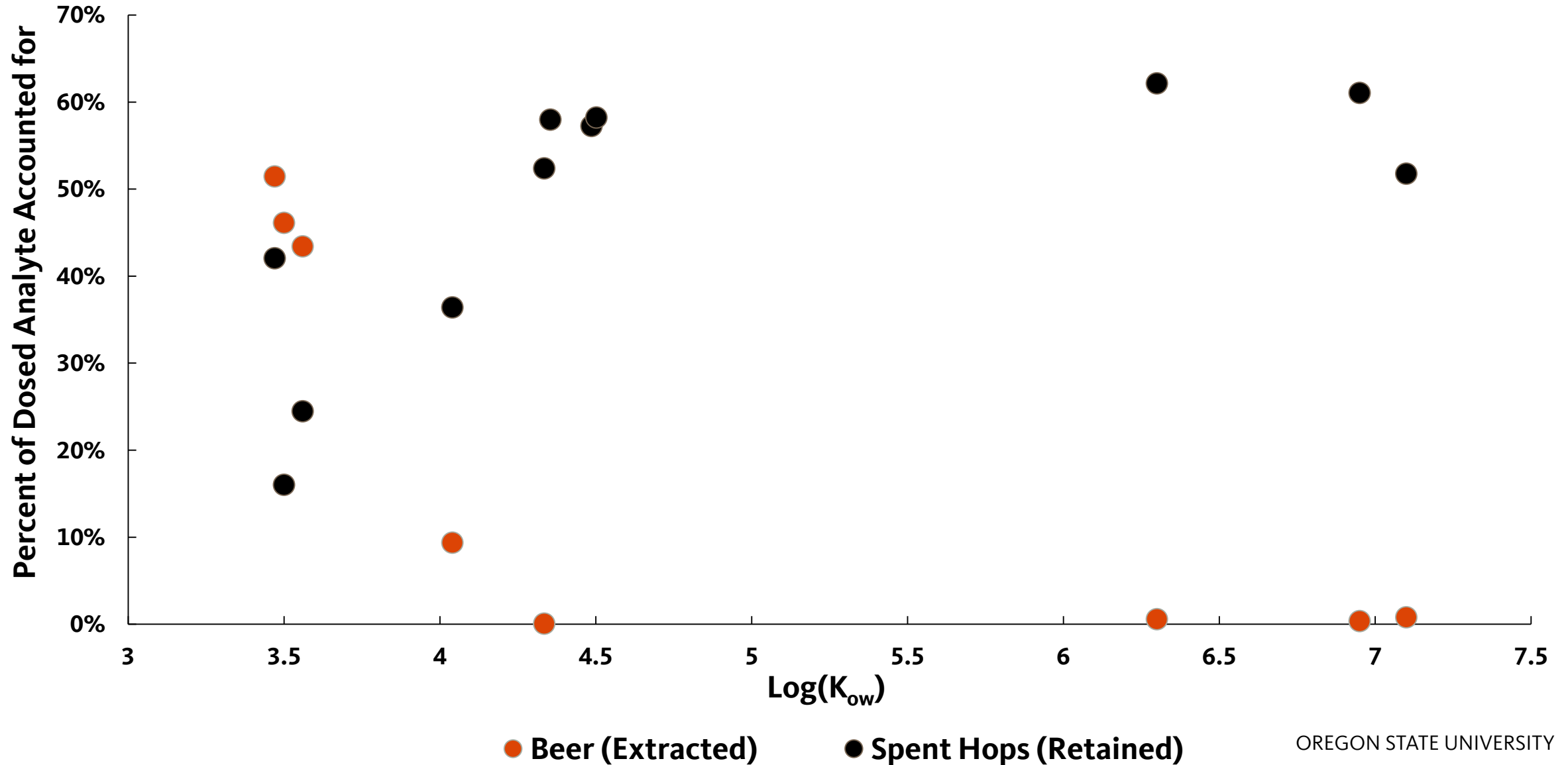


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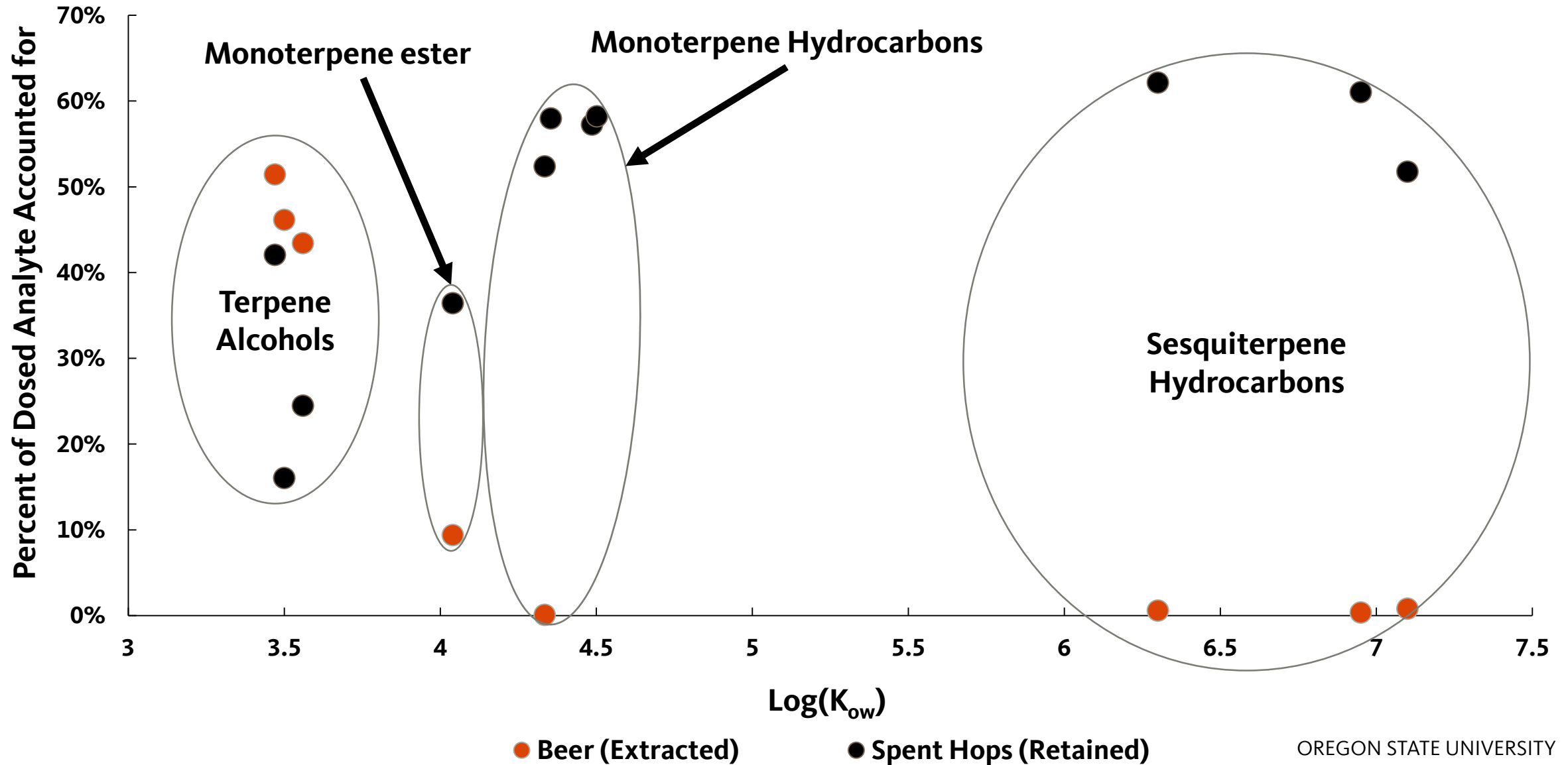
Extraction Rates by Octanol-Water Partition Coefficient



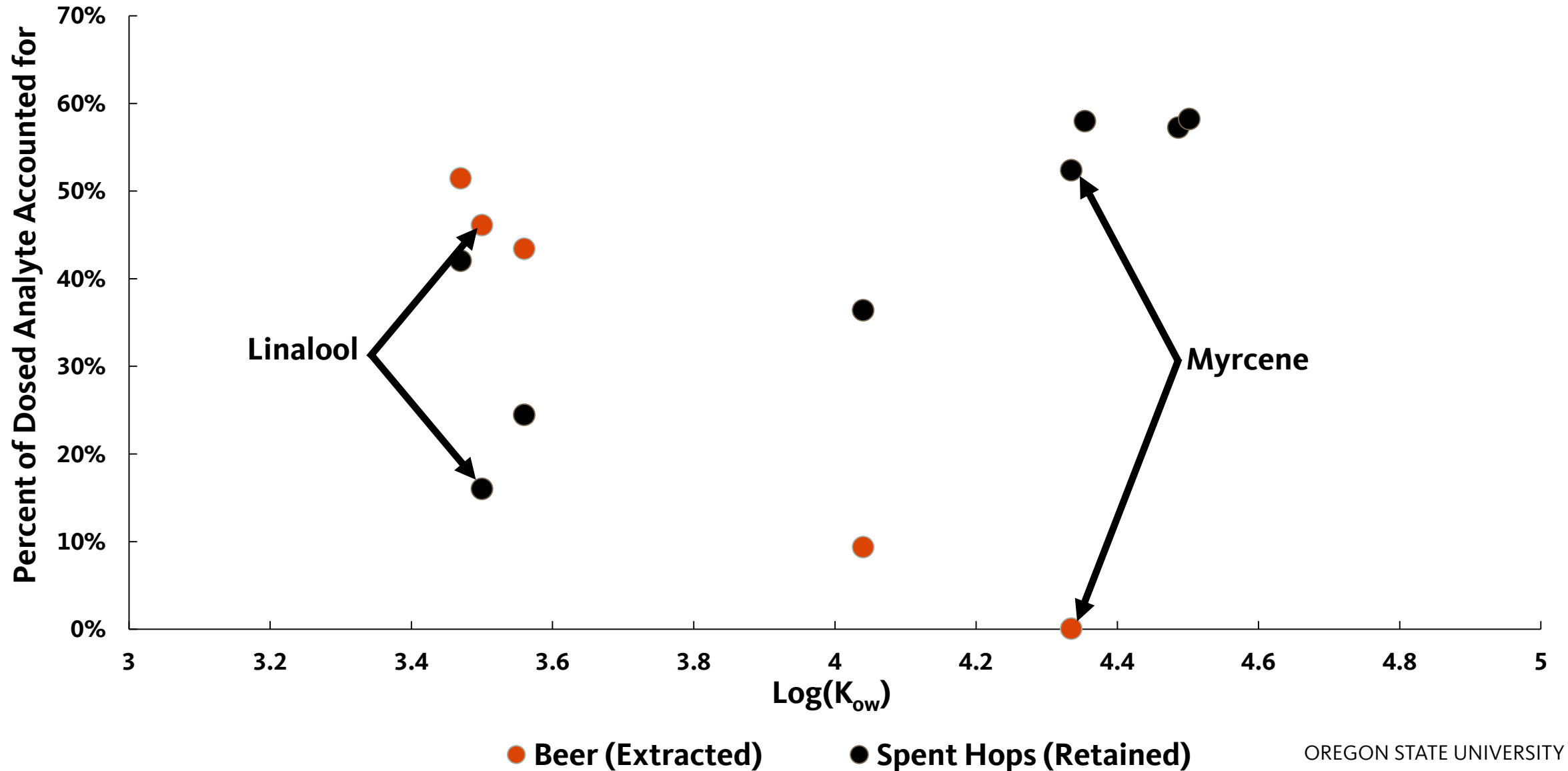
Extraction and Retention Rates by Octanol-Water Partition Coefficient



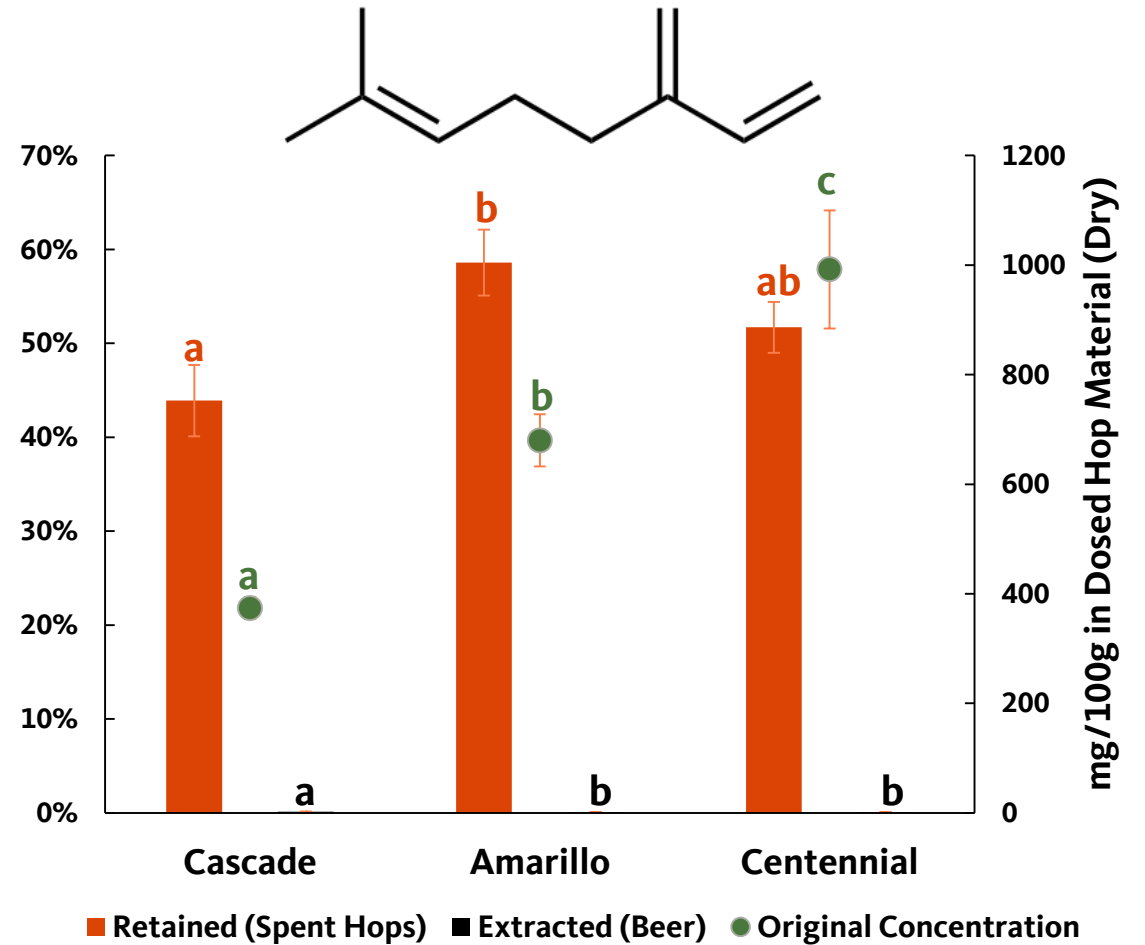
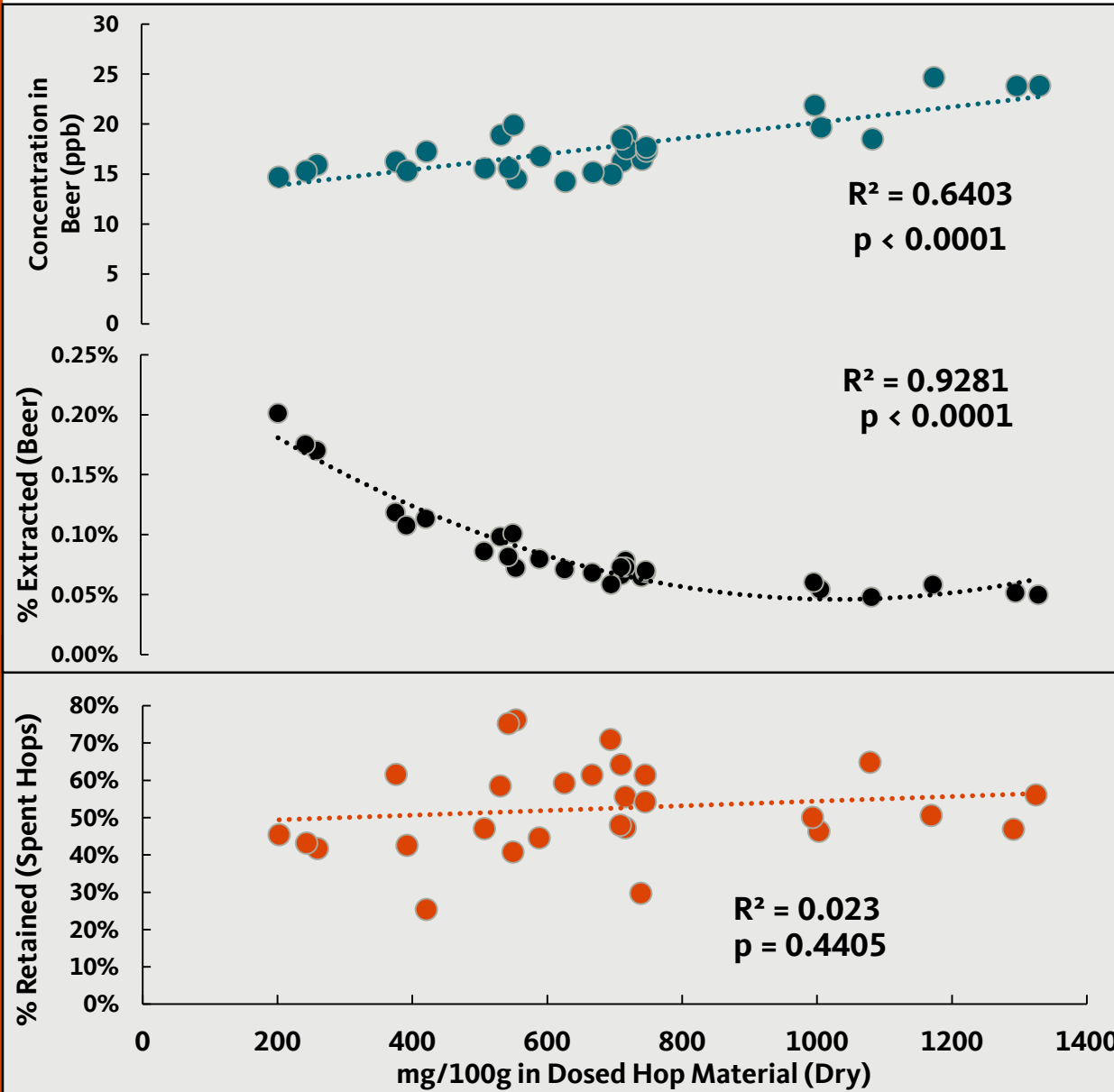
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Extraction and Retention Rates by Octanol-Water Partition Coefficient

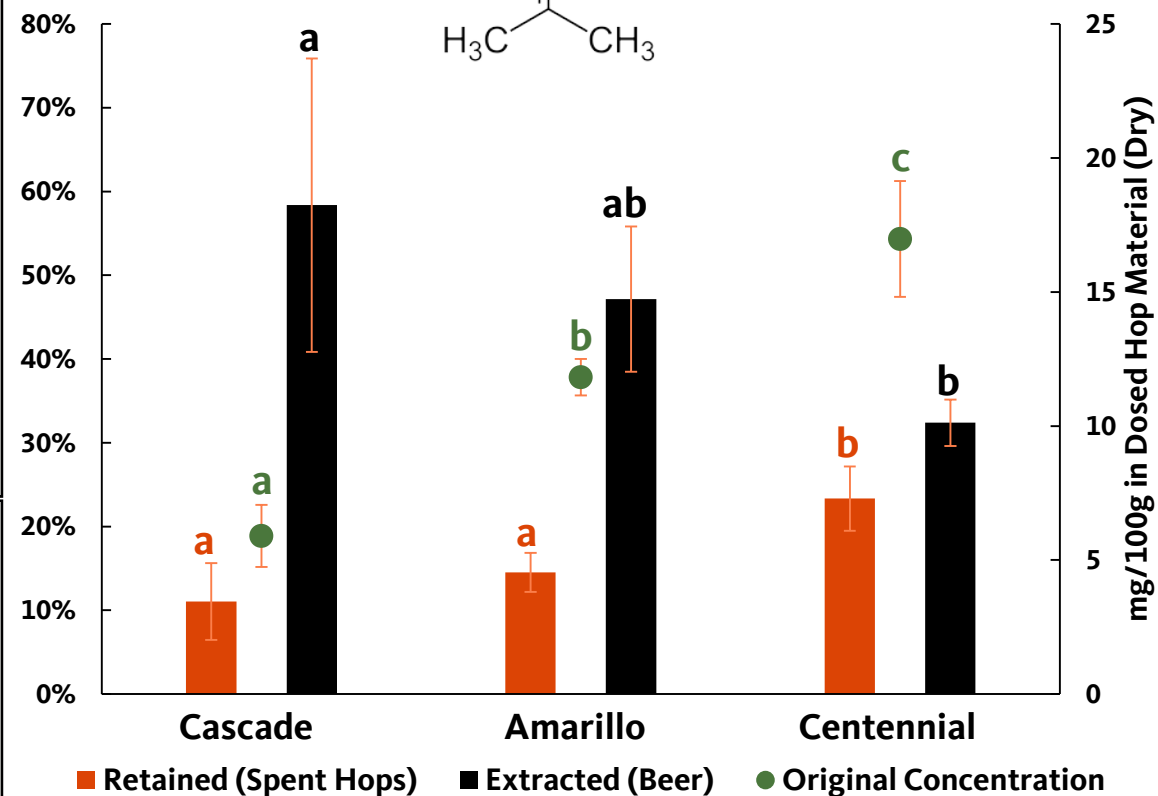
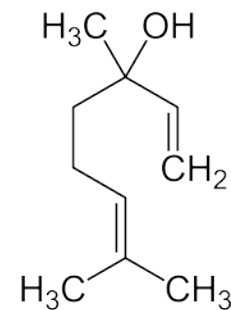
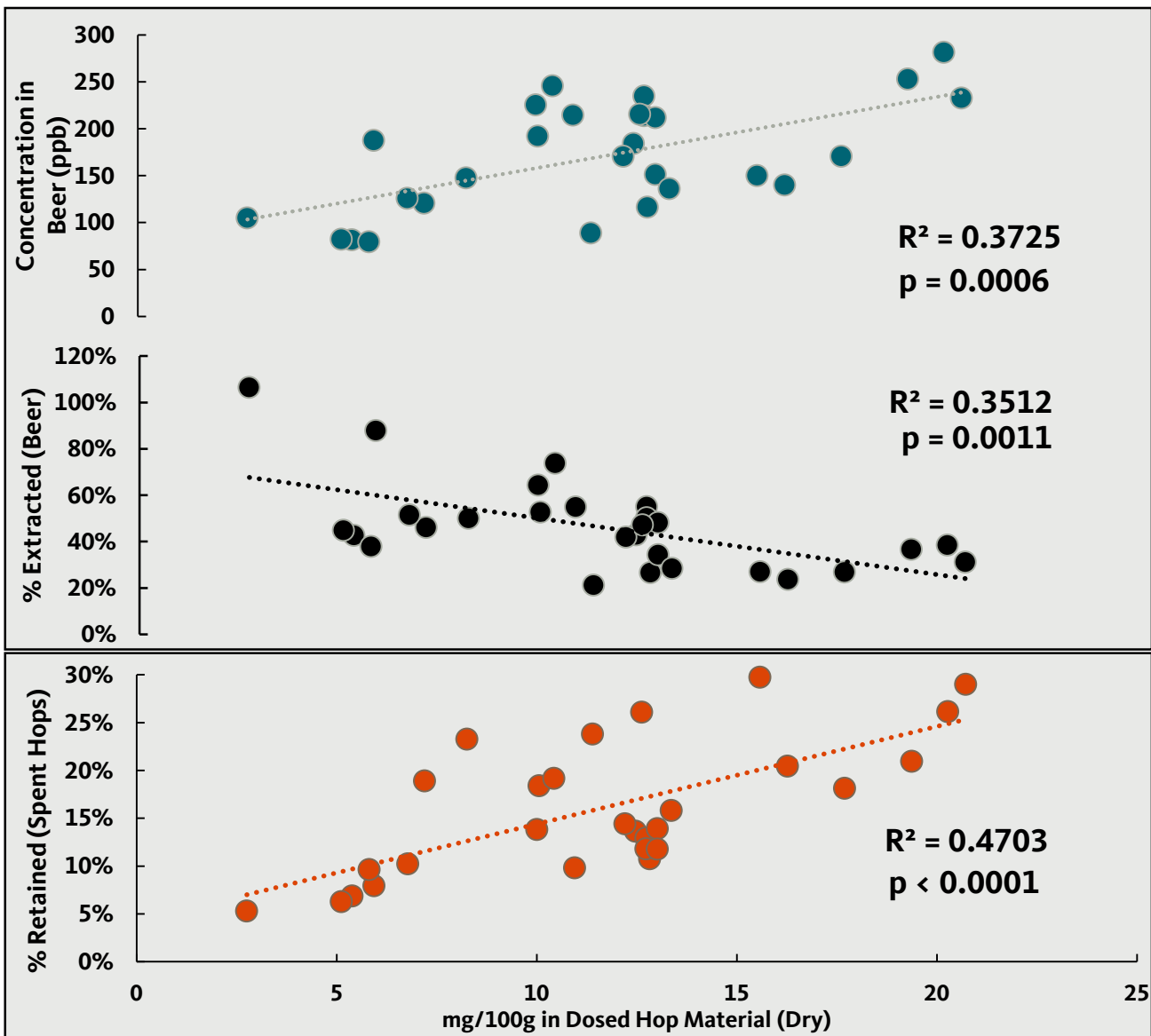


Beta Myrcene: $\log(K_{ow})=4.33$, Flavor Threshold in Beer : ~ 10-1000 ppb



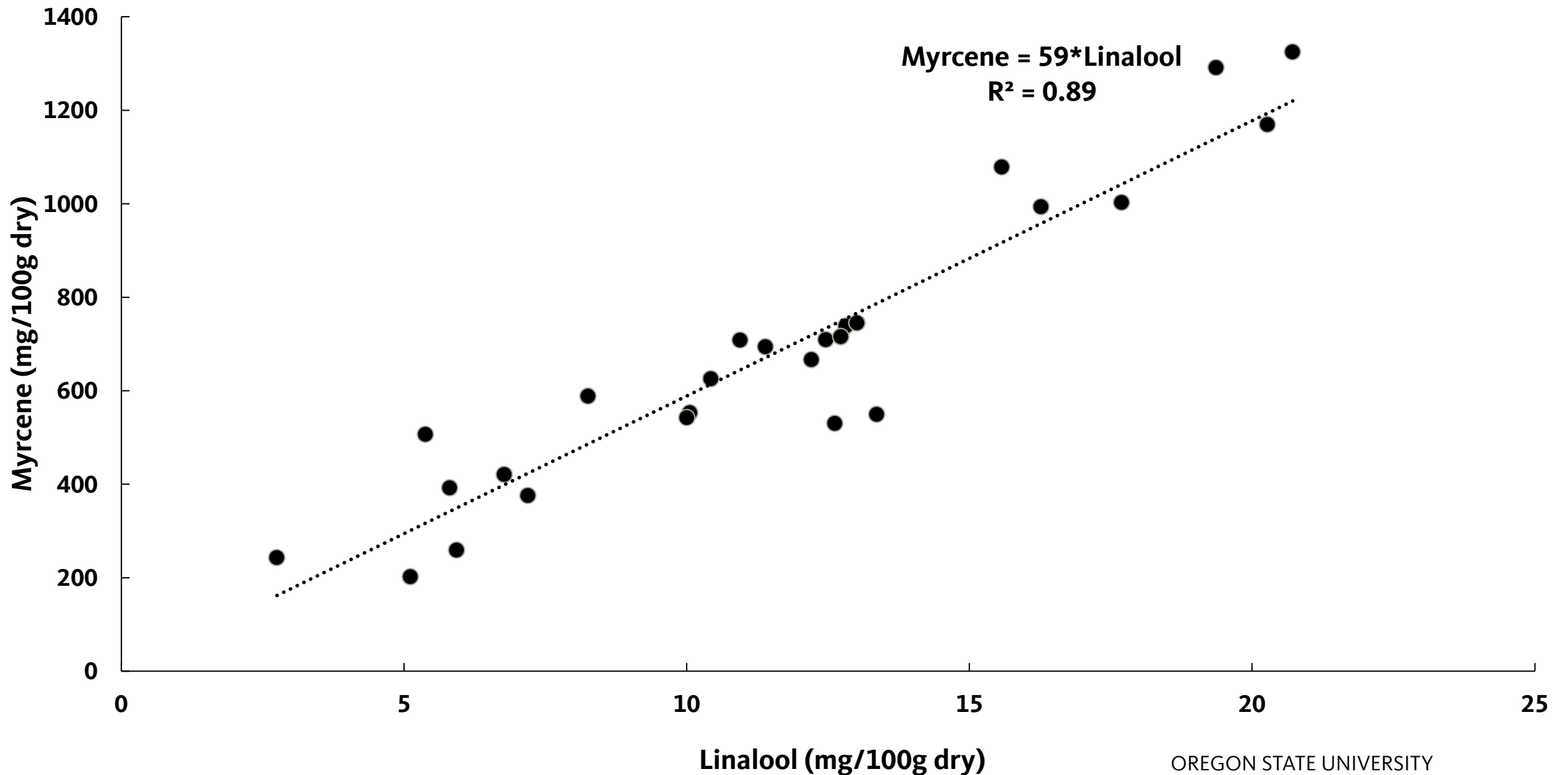
*Letters indicate Tukey HSD Groupings, alpha = 0.05

Linalool: $\log(K_{ow})=3.50$, Flavor Threshold in Beer : ~0.14-100 ppb

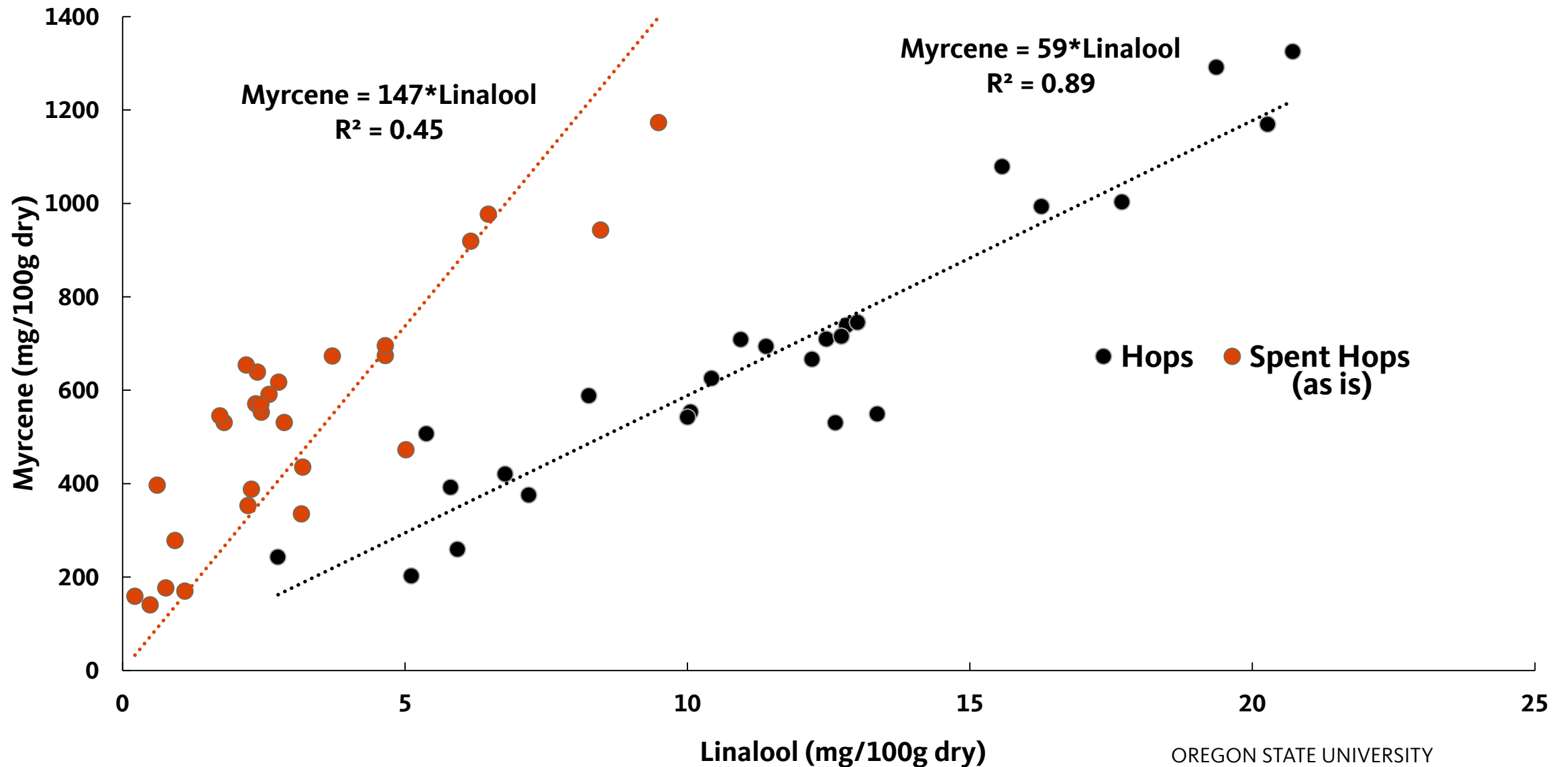


*Letters indicate Tukey HSD Groupings, alpha = 0.05

Relative Changes in Oil Composition: Myrcene/Linalool Ratio



Relative Changes in Oil Composition: Myrcene/Linalool Ratio



CONCLUSIONS & IMPLICATIONS



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Conclusions

Total Oil

- Overall average retained was ~51% (77% as is)

Octanol-Water Partition Coefficients

- Good proxy for polarity, model for extraction/retention rates

Oil Constituents (relative changes)

- [Hydrocarbons]  [Oxygenated Compounds] 

Dose Dependence of Extraction & Retention (In Linalool & Myrcene)

- Increasing dose leads to
 1. **Higher** Concentration in Beer,
 2. **Lower** Extraction Rates,
 3. **Higher** Retention Rates (depending on nature of compound)

Acknowledgements

- **Hop Research Council**
- **Dr. Tom Shellhammer** – MS Advisor
- **Jeff Clawson** – Pilot Brewery Manager
- Shellhammer Lab
 - **Scott Lafontaine, Kaylyn Kirkpatrick**
- OSU Undergraduates
 - **Lorena Ramos, Nick Spatafora**
- Hopsteiner
 - **Dr. Paul Matthews**
- BridgePort Brewing Company
 - **Jeff Edgerton and Christian Engstrom**
- Virgil Gamache Farms
 - **Darren Gamache, Ryan Foster**



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Thank You for Your Attention

QUESTIONS?



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