S. R. Lafontaine, C. B. Pereira, D. M. Vollmer and T. H. Shellhammer

The Effectiveness of Hop Volatile Markers for Forecasting Dry-hop Aroma Intensity and Quality of Cascade and Centennial Hops

Eighty-four individual hop samples were gathered over three harvest years to determine chemical factors in hops that serve as indicators of a hop's aroma potential during dry-hopping. Two public American hop varieties that are important to U.S. hop farmers and used by craft brewers globally, Cascade (n = 51) and Centennial (n = 33), were evaluated. Using a constant dry-hopping rate (3.8 g/L), significantly different aroma intensities and qualities were observed across the various samples of hops within each cultivar. Multiple linear regression analysis based on the concentrations of 16 hop oil analytes identified geraniol to be more effective than total oil content in predicting Cascade aroma quality and intensity in dry-hopped beer. Centennial hops differed from Cascade in that β-pinene was identified as being a more improved indicator of dry-hop aroma as compared to total oil content. In each hop variety, the single hop volatiles explained approximately 50 % of the variation in the sensory qualities of the dry-hopped beer, while total hop oil content explained less than 30 % of the same variation. These results suggest that the dry-hop aroma potential of different hop varieties is predicted by different hop volatiles and that total oil content is not the best indicator of a hop's dry-hop aroma intensity or quality.

Descriptors: *humulus lupulus*, beer, hop quality, sensory, dry-hopping

1 Introduction

The demand for aroma hops has drastically changed over the last decade [3]. Craft brewers, and now large brewing operations, are purchasing greater quantities of hops to support brewing hop-forward and "craft" style brands. Since 2007, the top two public American hop varieties grown in the U.S. and used by brewers have been Cascade and Centennial [3]. Currently, the pricing model for these hops is based to some extent on visual and aromatic quality (appearance, rub & sniff evaluations), but principally upon on a weight basis.

Dry-hopping is a brewing practice generally recognized as a cold extraction of hops in fermented or partially fermented beer [42]. The main objective of late/whirlpool-hopping and dry-hopping is to add intense hop aroma to beer with minimal bitterness [10]. Currently, the main analytical indicator that the brewing industry relies on to gauge the aroma intensity and quality of hops is total oil content. However, *Vollmer* et al. [55] recently observed that total oil content is not a great indicator of hop aroma potential during dry-hopping and suggested that the composition of hop essential oil might be more important. While a number of hop distributors report concentrations of select volatiles in hydrodistilled oil as metrics of aroma hop quality, it still remains unclear which of these volatiles actually serve as indicators of a hop aroma intensity and quality in dry-hopped beer. If the function of adding hops to beer is primarily to impart aroma during dry-hopping (as opposed to bitterness), then pricing based on different indicator(s) in hops for hop aroma intensity and quality performance in dry-hopped beer could be useful. Furthermore, these indicators may be hop variety-dependent due to the complexity of hop aroma.

Hop oil consists of hundreds of unique compounds [17, 45]. While a number of studies have investigated the key volatiles that define the aroma of hops and hop essential oil [9, 46, 52], the complexity of the brewing process and hop oil has made it challenging to establish a list of volatiles that can serve as indicators or predictors of hoppy aroma in beer [39]. The perception of hop aroma can be influenced by synergistic or masking effects that occur in mixtures of hop volatiles and within the beer itself [11, 48]. The aroma intensity and quality that hops attribute to beer depends on both the timing of hop additions throughout the brewing process as well as the influence of individual hop varieties. This is because chemical profiles between varieties are unique and hop volatiles experience differences in extraction rates, removal processes and reactions when they are added during the kettle boil, whirlpool, and/or during fermentation or post-fermentation (i.e. dry-hopping) [6, 17, 21, 23, 28, 36, 37, 43, 49-51, 53]. Therefore, defining indicators of hop

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Authors

Scott R. Lafontaine, Daniel M. Vollmer, Thomas H. Shellhammer, Department of Food Science & Technology, Oregon State University, Corvallis, United States; Cliff B. Pereira, Department of Statistics, Oregon State University, Corvallis, United States; corresponding author: Scott.Lafontaine@oregonstate.edu

aroma quality depends on how the brewer plans to use hops. Hops intended for dry-hopping might have different quality specifications than hops used in kettle/ whirlpool additions.

Past research has been heavily focused on the aroma impact of hop volatiles that are transferred during kettle or late hop additions [17, 23, 36, 50, 51]. The aroma imparted to beer as a result of kettle additions has been described as "noble", "floral", and "spicy" [39] because the hop volatiles that remain at levels above their detection thresholds are the oxygenated terpene [35] and sesquiterpenoid [37] fractions along with some other chemical classes [17, 23, 51]. Nevertheless, a main function of kettle hopping is to add bitterness to beer. As a result humulone concentrations, which are the precursors of iso-humulones (the main drivers of hop derived beer bitterness), serve as the main quality index for hops intended for kettle additions.

For late and whirlpool hop additions, the contact time with hot wort is much shorter and the amounts of hops used are considerably higher. Due to the shorter contact time and reduced temperatures, there is less potential for humulones to isomerize to bitter-tasting iso-humulones [18]. Thus, brewers use whirlpool hopping as a way to impart hop aroma while reducing the hop's bitter contribution. Therefore, concentrations of hop volatiles and aroma precursors, such as thiol precursors [40] and geraniol precursors [47] are important to consider. Particularly, if aroma precursors are added prior to primary fermentation, the bound volatile can be liberated by yeast enzymatic activity during fermentation and lead to increases in beer aroma perception [43].

However, by adding hops to fermenting or fermented beer (i.e. dry-hopping), brewers can further increase hop aroma intensity without adding any iso-humulone bitterness. While studies have shown that there may be overlap in the volatiles that are important for both late- and dry- hop additions [28, 43, 50], attempts to define harvest indicators of hop aroma potential for hops intended for dry-hop additions have been inconclusive. This is because there are a number of different dry-hopping techniques and parameters that influence the extraction rate of hop volatiles such as varietal differences [50], temperature [34], static vs dynamic extraction systems [56], scale [41], contact time [4], and yeast interactions/ biotransformations [49]. The aroma quality that dry-hopping imparts to beer is different than late- and whirlpool- hopping and has been described as "citrusy", "piney" and "resinous" suggesting the importance of other aroma compounds [39].

Nickerson et al. [32] and *Engel* et al. [53] developed the hop aroma component profile (HACP) specifically for late- and dry-hopped beers. The HACP was comprised of 22 analytes found in hydrodistilled hop oil that were thought to be important for hoppy beer flavor. The HACP was developed to adjust late- or dry- hopping rates based on volatile concentrations in hydrodistilled hop oil at harvest or during storage to achieve a greater level of consistency of hop aroma in beer. While their approach was unique, the low sample size (n = 3) made it difficult to identify the individual components' significance in impacting hop aroma perception in beer or address the amount of variation that existed within single cultivars of hops. There is also the potential that different markers of hop oil composition can be responsible for the hop aroma imparted to beer

Table 1 Overview of select harvest data for the 2014, 2015 and 2016 Cascade hops.

Sample ID	Farm State	Farm (coded)	Harvest Date	Harvest Year	Total Oil[#] (ml/100g)
CAS_06_14	WA	1	9/1	14	1.00
CAS_07_14	WA	1	9/1	14	1.70
CAS_10_14	WA	1	9/2	14	1.50
CAS_11_14	WA	1	9/2	14	0.90
CAS_13_14	WA	1	9/9	14	1.70
CAS_15_14	WA	1	9/10	14	1.70
CAS_16_14	WA	1	9/11	14	1.70
CAS_17_14	WA	1	9/13	14	1.90
CAS_18_14	WA	2	8/14	14	0.70
CAS_20_14	WA	2	8/21	14	1.00
CAS_21_14	WA	2	8/27	14	1.20
CAS_22_14	WA	2	9/12	14	2.00
CAS_24_14	WA	2	9/22	14	1.75
CAS_01_14	WA	3	8/20	14	0.60
CAS_14_14	WA	3	9/9	14	1.20
CAS_02_14	OR	4	8/23	14	0.70
CAS_04_14	OR	4	8/28	14	1.70
CAS_12_14	OR	4	9/2	14	1.00
CAS_03_14	OR	6	8/26	14	1.40
CAS_05_14	OR	6	9/1	14	1.10
CAS_08_14	OR	6	9/2	14	1.80
CAS_09_14	OR	6	9/2	14	1.30
CAS_28_15	WA	1	9/7	15	1.37
CAS_27_15	WA	1	9/5	15	0.60
CAS_12_15	WA	2	8/11	15	0.47
CAS_11_15	WA	2	8/18	15	1.03
CAS_10_15	WA	2	8/25	15	1.53
CAS_13_15	WA	2	9/2	15	1.48
CAS_14_15	WA	2	9/9	15	2.59
CAS_01_15	OR	4	9/6	15	1.69
CAS_02_15	OR	4	8/25	15	1.43
CAS_03_15	OR	4	.	15	1.19
CAS_05_15	WA	5	9/8	15	1.02
CAS_04_15	WA	5	9/8	15	0.81
CAS_07_15	ID	7	8/30	15	0.70
CAS_06_15	ID	7	9/8	15	0.91
CAS_08_15	OR	8	9/4	15	1.48
CAS_24_15	WA	9	9/1	15	0.65
CAS_21_15	ID	10	8/29	15	0.61
CAS_29_15	WA	11	.	15	1.42
CAS_26_15	WA	12	9/2	15	0.90
CAS_25_15	OR	13	8/22	15	0.82
CAS_09_15	ID	14	.	15	0.77
CAS_16_15	WA	15	9/3	15	1.08
CAS_15_15	WA	16	.	15	1.19
CAS_17_15	OR	17	.	15	1.15
CAS_18_15	WA	18	.	15	1.71
CAS_20_15	WA	19	.	15	1.27
CAS_19_15	WA	20	8/28	15	0.79
CAS_23_15	WA	21	9/1	15	1.20
CAS_22_15	ID	24	8/31	15	0.62

[#]Total oil at the time of dry-hopping. Colored by farm

Table 2 Overview of select harvest data for the 2015 and 2016 Centennial hops

Sample ID	Farm State	Farm (coded)	Harvest Date	Harvest Year	Total Oil[#] (ml/100g)
Cent_09_15	WA	1	8/31	15	1.97
Cent_05_15	OR	4	8/22	15	1.78
Cent_06_15	OR	4	8/26	15	1.98
Cent_07_15	OR	4	8/20	15	1.75
Cent_08_15	OR	4	.	15	1.40
Cent_10_15	WA	5	8/30	15	1.05
Cent_11_15	WA	5	9/6	15	2.06
Cent_02_15	WA	21	8/23	15	1.77
Cent_04_15	OR	22	8/20	15	1.97
Cent_12_15	ID	30	.	15	1.94
Cent_01_15	WA	38	8/21	15	1.22
Cent_03_15	OR	39	8/18	15	1.89
Cent_04_16	WA	5	9/3	16	1.62
Cent_05_16	WA	5	9/4	16	2.15
Cent_08_16	WA	5	9/2	16	1.35
Cent_02_16	WA	11	8/29	16	1.81
Cent_10_16	WA	11	9/1	16	1.66
Cent_21_16	WA	12	8/31	16	1.95
Cent_13_16	ID	14	9/11	16	2.29
Cent_17_16	ID	14	9/10	16	2.00
Cent_01_16	WA	21	8/24	16	1.50
Cent_09_16	WA	29	9/8	16	2.19
Cent_07_16	OR	31	8/26	16	1.05
Cent_15_16	WA	32	9/1	16	1.44
Cent_03_16	WA	35	8/24	16	1.29
Cent_16_16	WA	36	9/6	16	2.12
Cent_19_16	WA	37	8/24	16	1.61
Cent_11_16	WA	38	8/25	16	1.39
Cent_18_16	OR	39	8/24	16	1.36
Cent_12_16	OR	40	8/31	16	1.74
Cent_06_16	WA	41	9/13	16	2.27
Cent_14_16	WA	41	9/20	16	2.51
Cent_20_16	WA	41	9/6	16	2.16

[#]Total oil at the time of dry-hopping

for different varieties of hops. Although considerable research has been performed on investigating extraction rates of hop volatiles into beer under different parameters [6, 43, 50], few studies [7, 54] have considered the amount of chemical variation that exists within single hop varieties and none have considered the variation in the aroma intensity and quality attributed to beer during dry-hopping for a given hop variety, which prevents these studies have making conclusive predictions about which oil constituents in hops determine dry-hop aroma performance of these varieties in beer.

There is a potentially tremendous benefit to brewers, hop growers, and breeders in identifying chemical (and other) indicators that are indicative of high or low overall hop aroma intensity and quality in finished dry-hopped beer. A number of harvest and post-harvest factors have been shown to change the composition of hop oil such as nutrient or growing conditions [7, 54], hop cone ripening time [2, 25, 29, 44], kilning conditions [24], and storage conditions [52]. Therefore, identifying indicators of aroma quality could help farmers adjust growing practices to promote and/or retain important hop volatile development and aid brewers in modifying or developing brewing strategies to best utilize their aroma hops.

For that reason, a reproducible and static pilot scale dry-hopping approach [55] was used to evaluate a large sample size of Cascade and Centennial samples over multiple harvest years. The primary objective of this project was to determine whether the total oil content of hops or an individual/combination of 16 hop oil volatiles could be used as indicators of hop aroma intensity and quality in dry-hopped beer. The goals of this study were to identify indicators of dry-hop aroma quality for Cascade and Centennial and to evaluate the variation in hop chemistry and dry-hop aroma that exists within these important varieties across multiple harvest years.

2 Materials and Methods

2.1 Experimental design

Over the 2014, 2015, and 2016 harvest years 84 hop samples were obtained via donations from farmers and hop dealers encompassing two American varieties that are widely used by craft brewers for dry-hopping [3]; Cascade (n = 51) and Centennial (n = 33) (Tables 1, 2 and S1, S1 see p. 128). Whole cone hops were received in the form of brewer's cuts (a 500–700 g compressed portion of a large (100 kg) hop bale) or bale cores directly from the farmer. Cascade hops were obtained following the harvest in 2014 and 2015, while Centennial hops were obtained after the 2015 and 2016 harvests. The samples were collected from different farms throughout the Pacific Northwest (in WA, OR, and ID). Upon arrival at Oregon State University, hops were placed in high barrier flexible pouches, flushed with nitrogen, sealed, and stored frozen (–20 °C) for up to 5 months until they were used for dry-hopping on a pilot 40 L scale and chemically analyzed.

Sensory descriptive analysis performed by a trained panel was used to evaluate the hop aroma intensity and quality of these dry-hopped beers. Panel performance was evaluated using two-way analysis of variance with a mixed model (including the factors panelist, sample, and replication as well as corresponding two-way interactions). Internal process replicates were performed by dry-hopping randomly selected hop lots twice. These internal process replicates were evaluated using discrimination tests (triangle tests) to ensure that the differences observed among the treatments was not due to the dry-hopping process but rather to the differences in dry-hopped treatments.

Hydrodistillation was used to collect total oil contents on the day each dry-hopping event occurred. GC-FID and GC-MS were used to characterize 16 target hop volatiles that comprised the hydrodistilled oil. Multiple linear regression was used to identify salient aroma hop chemistry indicators (total oil and 16 selected hop volatile concentrations) that could predict hop aroma intensity and quality in beer. Additional statistical analysis approaches were

used to group the dry-hopping treatments based on their sensorial or chemical similarities.

2.2 Unhopped beer production

To evaluate the dry-hop aroma of the different hop samples, an unhopped beer was prepared by commercial breweries in Portland: Craft Brew Alliance for the 2014 Cascade harvest samples and Bridgeport Brewing for the 2015 Cascade harvest samples. The unhopped wort was prepared with 86 % pale two row, 13.5 % Caramel 10 °L, and 0.5 % Caramel 120 °L malt (Great Western, Vancouver, WA). The starting extract concentrations to evaluate the 2014 and 2015 Cascade harvest samples were 10.9°P and 11.3°P, respectively. Fermentation was carried out with Wyeast 1056 ale yeast at 18–19 °C for the 2014 Cascade harvest samples and Wyeast 1728 at 19–20 °C was used for the 2015 Cascade harvest samples. Following fermentation and post clarification, iso-humulones (IsoHop, John I Haas, Yakima, WA) were added at a target concentration of 18 mg/L. This resulted in ~ 40 hL of a 15.0 BU, 4.5 % ABV unhopped base beer for the 2014 Cascade harvest samples and ~ 55 hL of a 20.0 BU, 4.8 % ABV unhopped base beer for the 2015 Cascade harvest samples.

The starting extract concentrations for the 2015 and 2016 Centennial harvest samples were 10.7 °P and 11.1°P, respectively. For these dry-hopping treatments fermentation was carried out with BridgePort Brewing Company's house yeast strain at 19–20 °C. Following fermentation and post clarification, iso-humulones (IsoHop, John I Haas, Yakima, WA) were added at a target concentration of 18 mg/L. This resulted in ~ 46 hL of a 19.7 BU, 4.4 % ABV unhopped base beer to evaluate the 2015 Centennial harvest samples and ~ 52 hL of a 19.0 BU, 4.4 % ABV unhopped base beer to evaluate the 2016 Centennial harvest samples. Beer was carbonated and packaged into 60 L stainless steel kegs, shipped to Oregon State University, and held at 4 °C until dry-hopping.

2.3 Dry-hopping protocol and hop preparation

The dry-hopping process established by *Vollmer* et al. [55] has been shown to be reproducible on a pilot scale. In brief, 24 hours prior to hop addition, the unhopped beer was removed from the cooler at 4 °C and allowed to warm for approximately 24 hours to 15 °C. For each treatment, 40 L of warmed beer was transferred into each of two modified 60 L stainless kegs with a 10.2 cm stainless steel opening fitted with a standard Sankey D-system coupler and modified spear (Sabco, Toledo, OH, U.S.A.). A dry hopping rate of 386 g hop /hL of beer was used for each of the treatments. The whole cone hops were coarsely ground into a hop grist which was divided up by mass into two mesh bags (EcoBag, Ossining, NY). These bags were stored inside high barrier pouches flushed with N_2 until the dry-hopping event. For each dry-hop treatment, the two kegs filled with 40 L beer were temporarily de-pressurized and opened under a stream of low pressure CO_2. Simultaneously, the high barrier pouch bag was opened and the mesh bag containing ground hop grist was added to the beer. After the addition, the headspace was flushed with CO_2 and purged. After purging, the kegs were inverted three times to ensure proper mixing.

After 24 hours of dry-hopping, the beer was filtered to stop the dry-hopping process. The average temperature of the dry-hopping events ranged from 13.3–15 °C. Dry-hopping was stopped after 24 hr because prior work by *Wolfe* et al. [57] showed that the extraction of key hop volatiles occurred within 24 hr during dry-hopping. During filtration the two kegs were blended via a three-way fitting prior to entering a plate and frame filter using diatomaceous earth impregnated cellulose pads (HS2000, Pall Corporation, Port Washington, NY, U.S.A.) [55]. Dissolved oxygen (DO) was monitored during filtration using an Orbisphere 3100 Portable Oxygen Analyzer (Hach, Loveland, CO). Bright beer was not collected until DO was below 110 µg/L. After DO was within specification, bright, filtered beer was collected in a closed 19.6 L stainless steel keg with sufficient backpressure to reduce foaming. Between each filter run, filter pads were exchanged to prevent carry-over of beer from one treatment to the next. Filtered beer was stored at 2 °C and under CO_2 overpressure (83 kPa) until sensory evaluation.

2.4 Sensory: Discrimination testing of internal process replicates

Discrimination testing was performed on the internal process replicates to examine dry-hopping process variation within treatments. The replicates were evaluated by panels of self-identified craft beer drinkers (Table S2, see p. 129). Panelists were presented with four triangle tests, the first of which was a warm up. Within each triangle test there were three samples; two of the samples were the same and one of the samples was different. Based only on the orthonasal aroma of the sample, the panelists were instructed to select the odd sample for each of the four triangle tests. For each of the 3 sets of duplicates, the design of the triangle test ensured an equal frequency of appearance of each duplicate as the "odd" sample. The serving order within each triangle tests was also randomized. The dry-hopped beer was dispensed from the keg into a pitcher, which was used to pour ~ 60 mL of beer into 300 mL sample glasses coded with randomized 3-digit numbers, which were covered with plastic lids. The beer was allowed to warm to room temperature before sensory analysis. Each station was used ~ 2 times over the course of 2 hrs.

2.5 Sensory: Descriptive analysis

To evaluate the sensory qualities of the 2014, 2015, and 2016 harvest samples, 4 descriptive analysis panels were used to quantify perceived hop intensity and quality of the dry-hopped beers. The general approach used trained panelists to scale only the orthonasal aroma of the beer treatments. Panelists were selected based on previous experience with evaluating hoppy beer flavor.

Intensive training sessions using commercial beer and a random set of blind coded dry-hop treatments were completed in advance of data collection to develop a relevant lexicon of sensory attributes, establish a scale that best explained the differences in the samples, and to train panelists to use external reference samples as anchors for these most salient attributes. During each session, the panelists had access to external reference samples that had sensory descriptors with intensity scores assigned by consensus during training, and their purpose was to serve as anchors for the 0–15 point intensity scale. The external references and descriptive

attributes used to evaluate the different harvest samples are outlined in Table S3 (see p. 129) and included the following descriptors: Overall Hop Aroma Intensity (OHAI), Citrus, and Herbal/Tea for both cultivars and additionally just for Centennial, Tropical/Catty, Tropical/Fruity, and Pine/Resinous/Dank. These sensory descriptors were not meant to encompass the entire sensory impression of the beer but just the aromatic impact of each hop to the base beer. Due to the seasonal nature of commercial beer production and panel feedback, the same commercial beers and rankings were unable to be used throughout the entire three years of the study. This change in references could have impacted how the panelists were assessing the beers on a year to year basis but is not expected to have had a major impact on the trends observed in the results. More in-depth details of each descriptive analysis panel, including the differences in how the descriptive analysis panels were carried over the different harvest years, can be found in the supporting information.

2.6 Hop chemical analysis

Concurrent with the hop sampling for the dry-hopping, approximately 150 g of the homogenized hop grist was taken for chemical analysis.

2.7 Hop essential oil analysis – reagents and standards

β-Myrcene, β-pinene, linalool, geraniol, citral, limonene, geranyl acetate, α-pinene, nerol, isobutyl isobutyrate, methyl heptanoate, β-caryophyllene, α-humulene, β-farnesene, and caryophyllene oxide were obtained from Sigma-Aldrich (St. Louis, MO). 2-Octanol was obtained through Alfa Asear (Haverhill, MA). Hexanes purchased from J.T. Baker (Center Valley, PA) were redistilled to remove impurities before analysis. Sodium chloride was purchased from EMD Millipore (Billerisa, MA).

2.8 Hop essential oil analysis

At the time of dry-hopping, hydrodistillation was performed to determine the total oil content of the homogenized hop grist using ASBC Hops-13 [1]. Post-distillation, hop oil was collected in 2.5 mL amber vials with foil-lined closures. After filling with oil the amber vials were flushed with nitrogen. Hop oil was stored at –20 °C until subsequent compositional analysis.

In 2014, hop oil compositional analysis was performed under modified conditions from ASBC Hops-17 [1]. In 2015 and 2016, hop oil compositional analysis was performed using previously published methodology [27] using a HP 6890 gas chromatograph with an Agilent 5972a mass spectrometer (GC-MS) under modified conditions from ASBC Hops-17. In brief, a 1 % 2-octanol (8190 ppm) solution was prepared in reagent grade hexane. Hop oils were diluted to 10 % with the 1 % 2-octanol/hexane solution in crimped glass vials. 1 µL of the diluted hop oil was directly injected into the injection port held at 200 °C and operating in split mode (1:20) using the septum purge option. The analytical column was a 30m x 250 µm x 0.25 µm Zebron ZB- 1 MS (Phenomenex, Torrance, CA) and ultra-pure helium was used as the carrier gas (a constant flow rate, 1.4 ml/min). The following temperature program was used: 50 °C hold for 1 min, 50–180 °C (2 °C/min) hold for 10 minutes, 180–200 °C (3 °C/min) and 250 °C hold for 5 minutes. The auxiliary line and mass spectrometer were operated at 280 and ~ 180 °C respectively. The mass spectrometer was operated using electron-impact mode at 70 eV and set up to detect ions with a mass-to-charge ratio (m/z) of 30–350. 4-point calibration curves (50, 100, 400, and 800 ppm) were created for all target analytes. For high concentration target analytes (β-myrcene, α-humulene, β-caryophyllene, and β-farnesene) three additional calibration points were added (1000, 5000, and 9000 ppm). Target analytes were quantified using the following ions for each analyte: m/z 41 (geranial), m/z 45 (2-octanol), m/z 69 (β-farnesene, geraniol, nerol, neral, and geranyl acetate), m/z 71 (isobutyl isobutyrate and linalool), m/z 74 (methyl heptanoate), m/z 79 (caryophyllene oxide), and m/z 93 (α-pinene, β-pinene, β-Myrcene, β-caryophyllene, and α-humulene). The target analyte concentrations in hop oil were then standardized on a per-mass basis using the total oil content determined during hydrodistillation.

2.9 Statistical analysis

Two-way analysis of variance with a mixed model (including the factors panelist, sample, and replication as well as corresponding two-way interactions), multiple comparison analysis (Fisher's LSD), and graphical construction were carried out using XLSTAT 2017 (Addinsoft, New York, NY). Two tailed t-tests using $\alpha = 0.05$ were carried out using JMP Pro 12 (Buckinghamshire, England). These tests and graphical outputs were used to gauge the panel and panelist effectiveness in generating descriptive data, evaluate the significant differences in aroma quality and intensity among the dry-hopping treatments, and assess the associations between the chemical and sensory data collected.

Multiple linear regression was performed on the chemical and sensory data to identify chemical predictors of sensory intensity and quality. Model selection was conducted using the GLMSELECT procedure in SAS version 9.4 (TS1M3). Stepwise forward selection was used with sixteen hop volatiles and total oil as factors of interest in the context of a 2nd-order response surface type model (linear and quadratic in each factor as well as linear-by-linear interaction). Because of the small sample size relative to the potential number of predictors, three strategies were employed to prevent overfitting of the data. First, a model hierarchy requirement was included (quadratic terms could only enter the model when the linear term was already present in the model and a linear-by-linear interaction term could enter the model only when the two individual linear terms were already present). Second, multiple methods of selection were used (SBC, AICC and Press) to look for predictors selected by all 3 methods. Third, bootstrap resampling followed by model selection with SBC was conducted ($n \geq 100$ resamples) to verify that predictors were selected in a large proportion of the varying bootstrap samples.

3 Results and Discussion

3.1 Discrimination testing: Evaluating internal process replicates

Discrimination testing on the internal process replicates found no difference between the internal process replicates (Table S2, see

p. 129), confirming that the pilot dry-hopping process was reproducible and had a negligible impact on the dry-hop aroma within the same treatments. For descriptive analysis testing one of the internal replicates was randomly selected as the observation for that hop treatment.

3.2 Descriptive analysis: Assessing the dry-hop aroma intensities and qualities of beer dry-hopped with Cascade and Centennial

The impact of the hop treatments on the sensory intensity and quality of the dry-hopped beer was evaluated via two-way ANOVAs with mixed models (Table S4 and S5, see pp. 131-132). This outcome demonstrated the broad and significant range of aromatic intensities and qualities that can occur within a single cultivar of hops depending on where the hop was grown, how it was grown, and when and how it was picked and dried. Significant panelist × sample effects were observed for some of the attributes and this interaction indicates that there were slight differences in the way the panelists scaled these attributes [31]. Significant panelist × rep interactions were also observed for some of the hop aroma quality attributes (mainly Herbal/Tea) and this interaction indicates that from one session to another, panelist(s) scores were not consistent for all the products. This interaction mainly occurred because panelist(s) misidentified the unhopped beer (control) during at least one session. The F-values for all significant interactions were substantially lower than those for the sample and panelist effects and, with these few exceptions, the panelists could effectively replicate their attribute scaling for the samples across all replications thereby demonstrating generalized consistency throughout each of the descriptive analysis panels.

The least squared means and results from Fisher's LSD ($p < 0.05$) multiple comparisons for the sensory attributes from the descriptive analysis panels were summarized (Table S6 and S7, see pp. 133-134). Fisher's LSD tests were chosen as the mean comparison technique instead of a more conservative method, such as Tukey's HSD tests, to highlight the potential differences that exist between the dry-hop aroma profiles of the treatments. Over the four panels, although the unhopped base was identified by panelists to have some aroma, it was not grouped with any of the dry-hopped treatments for any of the aroma attributes.

For Cascade, Overall Hop Aroma Intensity (OHAI) was significantly correlated with citrus quality for the 2015 samples but not for the 2014 samples (Tables S8 and S9, see pp. 135-136). An early harvest sample in 2014 (CAS_01_14, 8/20/14) attributed a high aroma intensity to beer that was mainly Herbal in quality, and this single point disrupted the OHAI-Citrus correlation for 2014. Therefore, differences in citrus quality, as opposed to OHAI, were used to compare the Cascade dry-hop treatments over the two harvest years. The average Citrus scores for the highest LSD groupings were 1.7 x and 1.3 x higher over the 2014 and 2015 harvest years respectively when compared to the lowest Citrus LSD groupings (Table S6, see p. 133). Although there was no significant difference (two-tailed t-test, p-value = 0.94) in the OHAI ratings between the two harvest years. The dry-hop treatments in 2015 were rated significantly higher in both Herbal and Citrus (two-tailed t-test, p-value < 0.001) than the dry-hop treatments from 2014. As stated previously, this could be due to changes in hop chemistry as a function of harvest year or changes in the descriptive analysis panels. Previous research has also shown that Cascade dry-hop quality can change between harvest years [7].

For Centennial, OHAI was significantly correlated with both Citrus and Tropical/Catty over the two harvest years (Table S10, see p. 137). With the exception of Tropical/Catty, which was scored higher in the 2015 samples (two-tailed t-test, p-value = 0.01), there were no significant differences (two-tailed t-test, p-value = 0.14) observed over the two harvest years between the sensory ratings. When compared to the lowest OHAI LSD groupings, the average OHAI scores for the highest LSD groupings were 1.4 x and 1.8 x higher in OHAI for the 2015 and 2016 harvest years respectively (Table S7, see p. 134).

These results highlight that at the same static dry-hopping rate of 3.86 g/L there are significant and measurable differences in the aroma intensities and qualities attributed to beer from different commercially available Cascade and Centennial samples procured from within the same harvest year. Understanding what drives these differences will help create strategies to produce higher quality aroma hops and more consistent dry-hopped beer.

3.3 Chemical analyses: Comparing hop variety and harvest year

The samples of Cascade and Centennial hops used in this study represented a wide range of total oil contents (Table 1 and 2) as well as concentrations of the 16 hop volatiles (Tables S11–S13, see pp. 138-140), and the variation was visible both within and between the different harvest years. When comparing the entire data sets between the two varieties the Centennial samples had significantly higher total oil contents as well as concentrations of many of the hop volatiles (two-tailed t-test, p-value < 0.05). This was expected, and in fact Centennial is sometimes anecdotally referred to as "super Cascade" within the brewing industry. Nonetheless, Cascade had the highest concentrations of geranyl acetate and β-farnesene (two-tailed t-test, p-value < 0.0001). β-Farnesene has been shown to be a marker compound of Cascade and was not detected in Centennial [19, 44]. Both α-pinene and β-myrcene concentrations were similar in Cascade and Centennial (two-tailed t-test, p-value = 0.30 and 0.46, respectively). Other studies have also shown that hop essential oil composition is varietal specific [17, 19, 44].

When comparing the total oil content and the concentrations of the 16 hop volatiles in each variety between the two harvest years, significantly higher total oils and concentrations of β-myrcene, linalool, nerol, neral, geraniol, geranial, β-caryophyllene, α-humulene, β-farnesene, and caryophyllene oxide were observed in the 2014 Cascade samples as compared to 2015 (two-tailed t-test, p-value < 0.03). While, significantly higher concentrations of geranyl acetate, limonene, methyl heptanoate, α-pinene and isobutyl isobutyrate were observed in the 2015 Cascade harvest samples (two-tailed t-test, p-value < 0.002) and concentrations of β-pinene were not different between the harvest years (two-tailed t-test, p-value = 0.16). For Centennial there was no difference observed in total oil, α-humulene, nerol, neral, β-caryophyllene, and linalool between

the harvest years (two-tailed t-test, p-value = 0.17). However, concentrations of β-myrcene, methyl heptanoate, geraniol, limonene, α-pinene, β-pinene, and isobutyl isobutyrate were higher in the 2015 samples (two-tailed t-test, p-value < 0.03). Concentrations of geranyl acetate, geranial, and caryophyllene oxide were higher in the 2016 samples as compared to 2015 (two-tailed t-test, p-value < 0.0001). These observations are in agreement with *Forster* et al. [7] who also showed that oil composition can vary within single varieties between harvest years.

Notable, while many of the hop volatiles were positively correlated with one another (Tables S8-S10, see pp. 119-121), caryophyllene oxide was often negatively correlated with most of the hop volatiles regardless of the cultivar. These trends are in agreement with *Nielsen* et al. [33] who hypothesized caryophyllene oxide to be a marker of hop oxidation during post-harvest processing.

It is clear that harvest year had a very pronounced impact on the dry-hop aroma quality/intensity and chemical characteristics of the hop lots, especially for the Cascade. The climate in the Pacific Northwest over these harvest years might explain this observation since 2015 was unusually dry and hot compared to 2014 and 2016 [13-15]. In addition, prior research has identified trends between growing regions and hop chemistry [22, 54]. In this study and in agreement with Forster et al. [7], growing regions/ terroir did not seem to explain the observed differences in hop lot chemistry or dry-hop aroma sensory (data not shown). However, there were some significant correlations observed between harvest date and the volatile concentrations in hop oil, total oil contents, and dry-hop aroma potential [25]. This indicates that harvest maturity may have more of an influence on dry-hop aroma quality and intensity as well as chemistry than growing region. These observations are indirectly supported by a number of published studies [12, 16, 29, 38, 44].

3.4 Multiple linear regression modeling - identifying indicators of hop aroma intensity and quality in Cascade hops

Model selection was performed in SAS GLMSELECT using total oil content and the concentrations of the 16 hop volatiles (including linear, quadratic, and linear-by-linear interactions). The data for the Cascade samples were modeled on a harvest year basis due to the significant year effects in both the chemistry and sensory results and the sample sizes for the two harvest years of Cascade (n = 22 for 2014 and n = 29 for 2015). A key assumption of model selection via multiple linear regression is that the data are treated as independent observations. This was considered a possible issue for the samples from the 2014 harvest because multiple samples were obtained from the same farms and fewer farms were represented in the sample set as compared to the 2015 data set. Therefore, multiple linear model selection of the Cascade hops began with the 2015 harvest year because it encompassed the most extensive and diverse samples originating from 20 unique farms throughout Washington, Oregon, and Idaho (Tables 1 and S1; S1 see p. 128).

Multiple linear regression modeling was applied to the 2015 harvest data multiple times using the different selection criteria (SBC, AICC and Press) to predict OHAI. The most important (and in nearly all cases the sole) predictor of OHAI was geraniol. This single-component model fit OHAI relatively well (R^2 = 0.56) for the 2015 harvest samples and was selected over 15 x more than the next most frequently selected model identified via resampling. However, when using the 2014 harvest data no predictors entered the model for OHAI. As mentioned previously, this result is likely due to the early harvest sample (Cas_01_14) which had a very high OHAI impression but was dominated by Herbal/Tea aroma as opposed to Citrus. The dry-hop aroma quality of Cascade has recently been shown to vary from Herbal to Citrus during ripening [25], indicating that citrus quality may serve as an indicator of dry-hop aroma development for Cascade.

Therefore, dry-hop citrus quality was modeled using the same approach on the 2015 samples. Again, the only predictor that was selected with all 3 selection criteria was linear in geraniol. This simple linear model described Citrus relatively well (R^2 = 0.50). When using SBC for selection, linear in geraniol came into 69 % of the models (it was the predictor with the highest frequency). For comparison linear in total oil content was selected in only 5 % of the models. Geranial was identified as a candidate for future investigation because it entered at least one selection method, but not all. Interestingly, total oil content did not enter any of the models as a predictor. Comparing the linear model in geraniol (R^2 = 0.50) to the linear model in total oil content (R^2 = 0.24), it is evident that geraniol describes more of the variation for dry-hop citrus quality (Figure 1, C and D). Furthermore, an outlier sample with a very high total oil content (total oil = 2.59) was very influential in the relationship between total oil content and citrus quality (Figure 1 D). If this sample were removed from the dataset the slope and R^2 between total oil and citrus quality would decrease considerably. Using multiple regression with both geraniol and total oil in the model shows there is still strong evidence for a linear in geraniol effect even after total oil is already in the model (p = 0.0011), but there is no evidence of any predictive ability for total oil with geraniol already in the model (p =0.56) (Table 3).

Similar to 2015, performing model selection for the 2014 Cascade harvest found that linear in geraniol was the only predictor selected by all 3 selection methods. Linear in geraniol described citrus quality (R^2 = 0.44) much better than total oil (R^2 = 0.07) (Figure 1, A and B). Using SBC for selection linear in Geraniol came into the model for 91 % of the samples (the highest). No other predictor came into > 60 % of the samples. Again, for comparison linear in total oil content was selected in only 15 % of the samples.

Table 3 **Multiple regression parameter results for the 2015 Cascade hops highlighting the importance of Geraniol concentration in hydrodistilled hop oil (mg/100g) compared to total oil content (mL/100g) as an indicator of Citrus dry-hop aroma quality**

Parameter Estimates

Variable	DF	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	1	4.073	0.281	14.49	<.0001
Geraniol	1	0.499	0.136	3.68	0.0011
Total Oil	1	0.163	0.280	0.58	0.5658

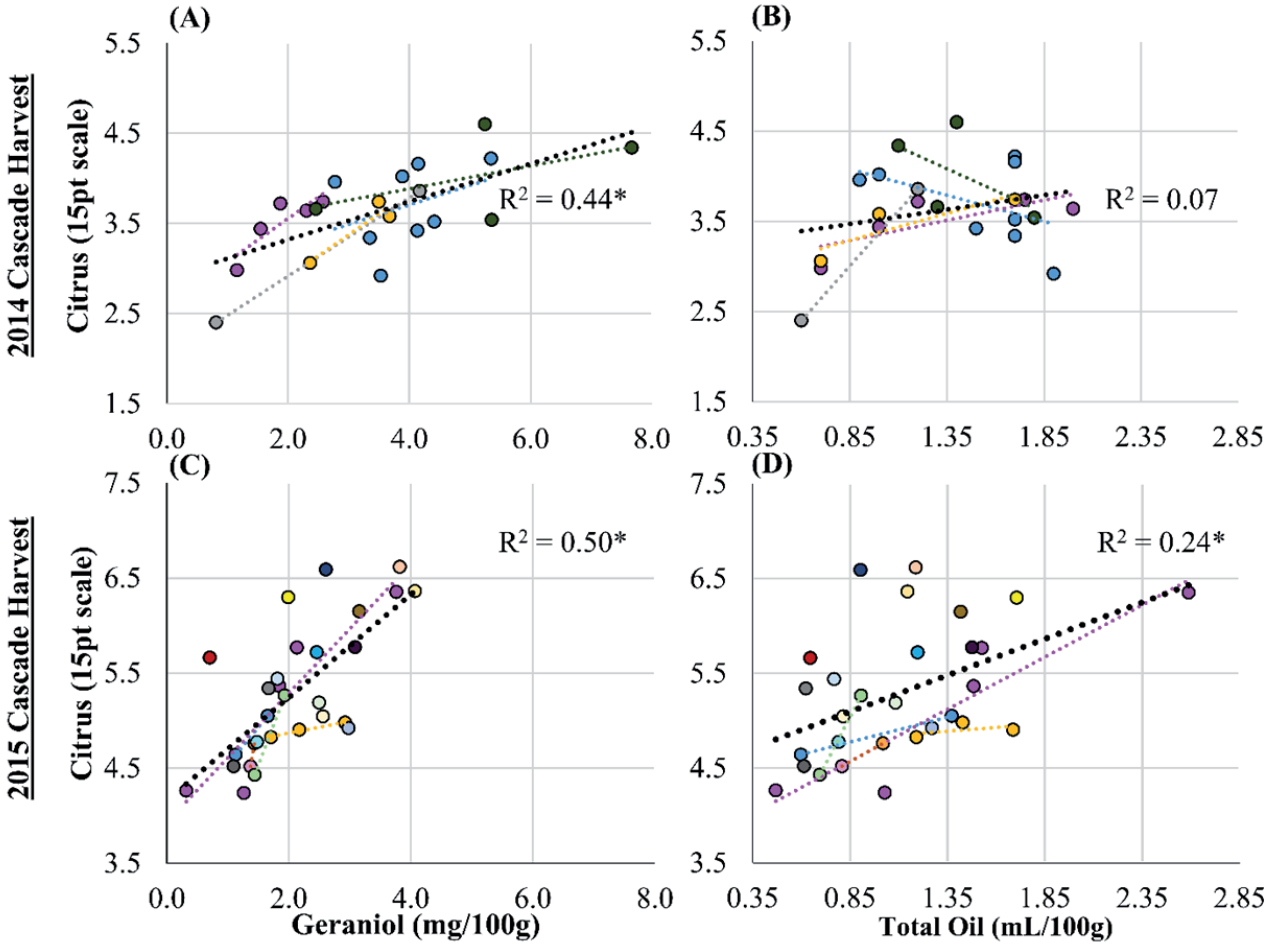

Fig. 1 **Comparing the relationships between dry-hop citrus quality and hop quality factors (Geraniol concentration in hydrodistilled hop oil (mg/100g) (A and C) and total oil content (mL/100g) (B and D)) for the 2014 and 2015 Cascade hops**

It is evident (Figure 1, A and C, see next page) that slopes between geraniol and Citrus were different between these two harvest years, indicating a significant year effect. Thus, despite having similar geraniol concentrations over the two years, the hops produced different citrus intensities. This could be a function of hop chemistry or differences in how the panel scaled citrus quality over the two harvest years. This makes it challenging to assign hard boundaries around what makes an optimal Cascade for dry-hopping based on geraniol concentrations. However, the geraniol concentrations (mg/100g) for the four lowest citrus samples in both the 2014 and 2015 harvests ranged from 0.8–3.5 and 0.3–1.4, respectively. While the geraniol concentrations (mg/100g) for the four highest scored citrus samples in both 2014 and 2015 harvests ranged from 4.2–7.7 and 2.6–4.1, respectively. Despite being broad, these ranges may serve as a good starting place to guide organoleptic evaluations of Cascade hops on a year-to-year basis.

When considering Pearson correlations between citrus quality and the 16 hop volatiles over the two harvest years (Tables S8 and S9, see pp. 135-136), geraniol had the highest correlations with citrus quality over the two harvest years. Notably, other hop volatiles often associated with dry-hop flavor, such as β-myrcene (which often comprises ~ 50 % of Cascade hop oil), were not highly correlated with Cascade dry-hop aroma quality. This observation is in agreement with other studies [26] and it is hypothesized that the physical-chemical properties of these analytes make them insoluble in beer and therefore they are not extracted to an appreciable degree during dry-hopping in clarified beer. However, recently concentrations of these volatiles have been shown to be elevated in hazy hop forward beers [30].

The significance of geraniol as an indicator of Cascade aroma in beer is supported by work of *Peacock* et al. [35] which highlighted the importance of geraniol in describing the specific “kettle-hop” and floral hop aroma of Cascade as compared to European hop varieties. However, as stated previously kettle hopping presents an entirely different set of extraction conditions/kinetics as well as oxidation/biotransformation reactions for hop volatiles as compared to dry-hopping. Recently *Takoi* et al. [47] identified Cascade as a ‘geraniol rich hop’ indicating that Cascade has high levels of free geraniol and Vollmer et al. [28] identified geraniol as a charter impact compound for dry-hop beer flavor. One should also keep in mind that in the presence of yeast geraniol may be transformed to other compounds such as citronellol [20]. In the present study dry-hopping was performed in the absence of yeast. While it is evident geraniol is not the only driver of Cascade aroma quality, these results offer evidence that geraniol is a better than total oil at gauging the aromatic intensity of Cascade hops used for dry-hopping.

3.5 Multiple linear regression modeling – Identifying indicators of hop aroma quality in Centennial hops

When performing model selection on Centennial, the data were combined for 2015 and 2016 due to the smaller sample sizes (N = 12 and N = 21 respectively). To incorporate possible differences

Table 4 **Multiple regression parameter results for the 2015 and 2016 Centennial hops highlighting the importance of β-pinene concentration in hydrodistilled hop oil (mg/100g) compared to total oil content (mL/100g) as an indicator of citrus dry-hop aroma quality**

Parameter Estimates					
Variable	**DF**	**Parameter Estimate**	**Standard Error**	**t Value**	**Pr > |t|**
Intercept	1	1.993	0.618	3.22	0.0030
β-pinene	1	0.118	0.039	3.05	0.0047
Total Oil	1	0.219	0.511	0.43	0.6711

between years, harvest year was included in the model selection process as a classification variable to allow there to be both additive year effects and year-by-predictor interactions.

For citrus quality, the only predictor that came into the model for every model selection method was linear in β-pinene (R^2 = 0.45). Caryophyllene oxide was identified as a candidate for future investigation because it entered at least one selection method, but not all. When resampling with SBC for model selection, linear in β-pinene came into the model for 81 % of the samples (the highest percentage of any predictor). By comparison, total oil content was selected for the model in only 24 % of the samples. Comparing linear in β-pinene (R^2 = 0.46) to linear in total oil content (R^2 = 0.29), it is evident that β-pinene describes more of the variation for dry-hop citrus quality in the Centennial hop data (Figure 2). Multiple regression with both β-pinene and total oil in the model shows that once β-pinene is in the model, there is no evidence of any predictive ability for total oil (p = 0.67). Conversely with total oil in the model, there is still strong evidence for a linear in β-pinene effect (p = 0.0047) (Table 4).

The β-pinene concentrations (mg/100g) for the four lowest citrus samples over the 2015 and 2016 harvests ranged from 6.2–12.5, while the four highest ranged from 19.9–23.6. This shows that the highest rated citrus samples had approximately twice as much β-pinene as the lowest citrus samples. These ranges, while not absolute, provide an initial guide to the relative magnitude of β-pinene on the organoleptic evaluations of Centennial hops.

Recently, Takoi et al. showed that β-pinene was found in relatively high concentrations in Centennial and Citra hops, but was not found to be transferred into beer during dry-hopping at high rates [5]. This is evidence that β-pinene might not be the compound that is directly responsible for the hop aroma impression of dry-hopped beer. In the present study we do not attempt to characterize citrus quality by measuring the hop volatiles in beer. Rather, the goal was to examine the composition of hops and hop oil and identify a marker or markers useful to brewers for estimating their aroma performance in beer. While there was a significant correlation between total oil and OHAI, total oil did not enter any of the statistical models as a predictor for any of the sensory descriptors. Furthermore, total oil was less effective than β-pinene for describing Centennial dry-hop citrus quality (Figure 2).

4 Conclusions/Industrial Considerations

The objectives of this study were to examine the composition of hops and hop oil with the goal of identifying a marker or markers in hops that are useful to breeders, growers, and brewers for estimating dry-hop aroma performance in beer. From the results, it is clear that a significant amount of variation in both hop chemistry and dry-hop aroma potential exists within Cascade and Centennial hops within a single harvest year and across multiple harvest years. When comparing the results of multiple linear regression modeling over the three harvest years, total oil was never selected as a predictor of hop aroma intensity for either Cascade or Centennial. These results support those of Vollmer et al. [55] and suggest that a hop's total hop oil content may not serve as the best indicator of its dry-hop aroma potential. Specific hop volatile components, namely geraniol for Cascade and β-pinene for Centennial, were identified as statistically relevant for forecasting dry-hop aroma quality. These results suggest that the markers of dry-hop aroma

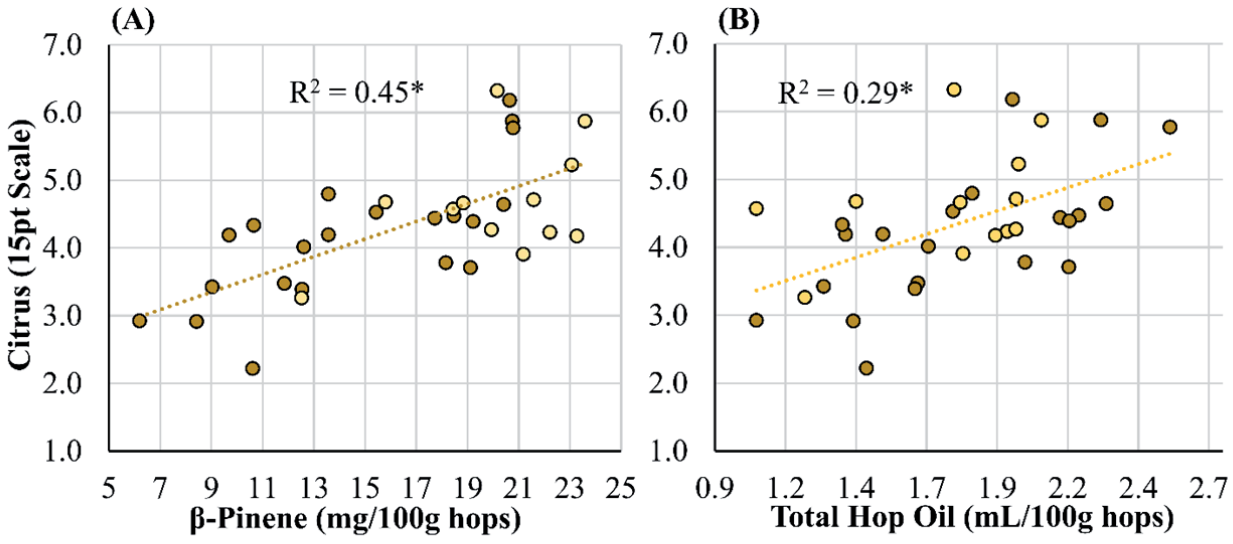

Fig. 2 **Comparing the relationships between dry-hop citrus quality with A. β-pinene concentrations in hydrodistilled hop oil (mg/100g) and B. Total oil content (mL/100g) for the 2015 (light yellow) and 2016 (dark yellow) Centennial hops**

are varietal-dependent. Although these single volatiles only describe approximately 50 % of variation in the dry-hop citrus quality these varieties display in beer, they offer improvement over total oil content which explains less than 30 % of the variation. It is important to point that in the present study dry-hopping was performed in the absence of yeast. In the case of dry-hopping in the presence of yeast, biotransformation reactions should be considered as they have the potential to modify the aromatic quality and intensity contributions of hop volatiles [49].

It is clear there are other hop volatiles that may add additional ability to forecast a hop's aroma potential during dry-hopping. For instance, there is increasing evidence that polyfunctional thiols, which were not considered in this study, are important for dry-hop beer flavor [8, 22, 40, 46, 48]. Future studies should investigate the variation of these volatiles within single varieties at harvest and evaluate if they play a role in predicting that dry-hop aroma of hops in beer. Looking beyond just hop aroma, recent studies have shown that humulinones (as a result of hop acid oxidation) can contribute significantly to beer bitterness in hop forward beers [10]. Therefore, concentrations of humulinones should also be considered as a quality metric for hops destined for dry-hopping as they directly impact beer flavor.

Interestingly, total oil content did not serve as a good predictor of hop aroma intensity in dry-hopped beer. And in some instance, there existed a negative correlation between total oil content and overall hop aroma intensity (Figure 1). By comparison, these negative correlations were not observed between geraniol and overall hop aroma intensity. One possible explanation for this observation is that post-harvest processing factors (kilning, baling, etc.) have a greater impact on total oil content than geraniol. Given that a majority of hop oil (>50 %) is made up of hydrocarbons, such as β-myrcene, β-caryophyllene, and α-humulene, which are less aromatically important than the terpene alcohols and esters for dry-hop aroma, their loss during post-harvest processing and kilning may have less of an impact on dry-hop aroma potential than losses in geraniol. Future work should investigate the impact of post-harvest processing, such as kilning on hop chemistry and dry-hop aroma potential in beer.

Results from this study offer brewers and growers insight on how best to use analytical information that is already being collected on hops. Hop companies routinely measure geraniol and β-pinene, along with other hop volatiles, in addition to total oil. These results suggest that a hop's total oil content is a poor indicator for forecasting a hop's aroma potential for dry-hopping and that these hop volatiles (geraniol for Cascade and β-pinene for Centennial) may be more important to consider. When examined from the brewer's or hop grower's quality control perspective, the concentrations of geraniol for Cascade and β-pinene for Centennial could be used to guide organoleptic evaluations (color, rub-and-sniff, etc.) when assessing hop aroma quality on a year-to-year basis and as a way to generate unbiased data for selecting hops destined for dry-hopping. For instance, high geraniol Cascade or high β-pinene Centennial hops might be better suited for dry hopping, while those containing lower amounts of these volatiles might be better suited for kettle or whirlpool hopping. Concentrations of these hop volatiles might also serve as potential targets for hop breeders who are trying to develop higher yielding and more disease resistant replacements with similar aroma profiles to these popular American varieties. Finally, this information is also relevant to growers who can fine-tune harvest timing or post-harvest processing parameters to promote the production of these hop volatiles [25].

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Conflict of interest

None.

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Supporting Information

Table S1 **Overview of the Cascade and Centennial hop samples procured from hop distributors following the 2014, 2015 and 2016 harvests**

Cultivar		Cascade		Centennial	
Harvest Year		14	15	15	16
Region	Farm	(n)	(n)	(n)	(n)
WA	1	8	2	1	.
	2	5	5	.	.
	3	2	.	.	.
	5	.	2	2	3
	9	.	1	.	.
	11	.	1	.	2
	12	.	1	.	1
	15	.	1	.	.
	16	.	1	.	.
	18	.	1	.	.
	19	.	1	.	.
	20	.	1	.	.
	21	.	1	1	1
	29	.	.	.	1
	32	.	.	.	1
	35	.	.	.	1
	36	.	.	.	1
	37	.	.	.	1
	38	.	.	1	1
	41	.	.	.	3
Total		15	18	5	16
OR	4	3	3	4	.
	6	4	.	.	.
	8	.	1	.	.
	13	.	1	.	.
	17	.	1	.	.
	22	.	.	1	.
	31	.	.	.	1
	39	.	.	1	1
	40	.	.	.	1
Total		7	6	6	3
ID	7	.	2	.	.
	10	.	1	.	.
	14	.	1	.	2
	24	.	1	.	.
	30	.	.	1	.
Total		.	5	1	2
Overall Total		22	29	12	21

Table S2 Discrimination (Triangle) test results of internal dry-hopping process replicates

Triangle Tests	Number of hoppy beer consumers	Number of females	Age range	Number of correct responses	Z-value	p-value
2015 Cascade internal dry-hopping process replicates						
Cas_11_15_1 vs Cas_11_15_2	54	20	23–66	19	0.14	0.44
Cas_10_15_1 vs Cas_10_15_2	54	20	23–66	15	– 0.99	0.16
Cas_13_15_1 vs Cas_13_15_2	54	20	23–66	24	1.56	0.06
Cas_14_15_1 vs Cas_14_15_2	54	20	23–66	21	0.71	0.24
2015 Centennial internal dry-hopping process replicates						
Cent_12_15_1 vs Cent_12_15_2	40	17	21–66	13	– 0.28	0.39
2016 Centennial internal dry-hopping process replicates						
Cent_7_16_1 vs Cent_7_16_2	43	17	21–66	14	– 0.12	0.45

Table S3 Sensory reference standards with intensity scores used in descriptive analysis panels over the different harvest years

	Pilot beers%						Commercial beer						
Attributes	**Unhopped Control**	**386 g/hL**	**1600 g/hL**	**100% Chinook**	**100% Centennial**	**100% Cascade**	**Hop Valley Sir Orange-A-Lot**	**Ballast Point Grapefruit Sculpin**	**Hop Valley Citrus Mistress**	**Sierra Nevada Pale Ale**	**Ballast Point Pineapple Sculpin**	**10-Barrel Joe IPA**	**Founders All Day IPA**
Cascade 2014 Harvest Descriptive Analysis Anchors													
OHAI*	.	.	.	.	.	.	8	15	.	.	.	.	.
Cascade 2015 Harvest Descriptive Analysis Anchors													
OHAI*	0	8–9	14–15	.	.	.	.	14–15	7–8	.	.	.	.
Citrus	0	7–8	5–6	.	.	.	.	13–14	6–7	.	.	.	.
Herbal/Tea	0	5–6	12–13	.	.	.	.	1–2	6–7	.	.	.	.
Centennial 2015 Harvest Descriptive Analysis Anchors													
OHAI*	0	.	.	6	9	8	.	.	.	7	10–11	14–15	.
Citrus	0	.	.	2	7	8	.	.	.	6	6	5–6	.
Herbal/Tea	0	.	.	3	4–5	6	.	.	.	5	2	1	.
Tropical/Catty	0	.	.	4–5	2–3	3	.	.	.	3	4	9–10	.
Tropical/ Fruity	0–1	.	.	2-3	5-6	3	.	.	.	4	7–8	4–5	.
Pine/ Resinous/ Dank	0	.	.	1	2	2	.	.	.	2	4	4	.
Centennial 2016 Harvest Descriptive Analysis Anchors													
OHAI*	0	.	.	.	.	.	.	†	.	5–6	.	†	12
Citrus	0	.	.	.	.	.	.	11	.	3	.	5–6	6–7
Herbal/Tea	0	.	.	.	.	.	.	.	.	4	.	1	5
Tropical/Catty	0	.	.	.	.	.	.	.	.	1	.	9–10	3–4
Tropical/ Fruity	0–1	.	.	.	.	.	.	7–8	.	1	.	4–5	2–3
Pine/ Resinous/ Dank	0	.	.	.	.	.	.	.	.	2	.	4	7–8

*OHAI = Overall Hop Aroma Intensity (.) did not measure

†Did not scale OHAI for this external reference standard

%These pilot beers were made in the Oregon State University pilot brewery. They served as external references alongside the commercial beers so that the panelists could anchor their attribute scaling during the descriptive analysis panels. The scores for these beers were defined by the panelists during the training sessions

Sensory analyses protocols and panel/panelist validation

Panelists were given ~60 mL of dry-hopped beer in a 300 mL glass covered with a plastic lid. For the 2014 Cascade harvest samples beer was packaged and served from bottles that had been warmed to room temperature for 35-45 min. For the rest of the study beer was served from two 8-head draft systems operating at at ~1°C and at 82.7 kPa (Micro Matic, Northridge, CA). Beer was poured into sample glasses ~1 hour before the start of testing, capped with a plastic lid, and allowed to warm to room temperature. For the 2014 Cascade harvest samples panelist responses were collected on paper ballots. For the rest of the study panelist responses were collected on Chromebook tablets using Qualtrics (Provo, UT). For each of these sessions, Qualtrics was also used to randomly assign the serving order of samples for each panelist.

Descriptive Analysis – Cascade 2014 Harvest

23 dry-hopped beers (22 different hop lots (dry-hopped at 3.8 g/L) and one unhopped control) were evaluated by a trained panel experienced with assessing hop forward beer aroma. The panel was comprised of 11 trained panelists (9 males and 2 females; 25-65 yrs. old). Three intensive training sessions were completed in advance of data collection. Based on discussion from these training sessions the final ballot included the attributes: Overall Hop Aroma Intensity (OHAI), Citrus, Herbal, Resinous/hop oil, Tropical Fruit to be evaluated on a 0-15 point scale. Over the course of 15 sessions, the panelists evaluated all of the samples five times in a randomized fashion. 10 samples were evaluated per session and the presentation order was blocked by replication and randomized for each panelist.

Descriptive Analysis – Cascade 2015 Harvest

30 dry-hopped beers (29 different hop lots (dry-hopped at 3.8 g/L) and one unhopped control) were evaluated by a trained panel experienced with assessing hop forward beer aroma. The panel was comprised of 13 trained panelists (11 males and 2 females; 25–66 yrs. old). Four intensive training sessions were completed in advance of data collection. Based on discussion from these training sessions and the results from the 2014 Cascade harvest panel, the final ballot included the attributes: Overall Hop Aroma Intensity (OHAI), Citrus, and Herbal/Tea to be evaluated on a 0–15 point scale. An efficient resolvable incomplete block design was used to create a presentation order for the samples across four replications (SAS, Cary, NC). Over the course of 20 sessions, the 13 panelists evaluated all the samples five times in a randomized fashion. The first replication (i.e. sensory block) was used to familiarize the panelists with the samples and the testing environment. Because of the large number of treatments, it took the panelists four sessions (3 sessions of 8 samples and 1 session of 9 samples) to evaluate all the hopped samples per replication.

Descriptive Analysis – Centennial 2015 Harvest

13 dry-hopped beers (12 different hop lots and one unhopped control) were evaluated by 15 trained panelists experienced in evaluating hop forward beer aroma (11 males and 4 females; 25–66 yrs old). Four intensive training sessions were completed in advance of data collection. Based on discussion from these training sessions the final ballot included the attributes: OHAI, Citrus, Herbal/Tea, Pine/Resinous/Dank, Tropical/Fruity, and Tropical/Catty to be evaluated on a on a 0–15 point scale. An efficient resolvable incomplete block design was used to create a presentation order for the samples across four replications (SAS, Cary, NC). Unlike the 2014 and 2015 Cascade harvest descriptive analysis panels the unhopped control was nested into each session. Over the course of 10 sessions, the 15 panelists evaluated all the samples five times in a randomized fashion. The first replication was used to familiarize the panelists with the samples and the testing environment. It took the panelists 2 sessions, of 7 samples, to experience all the hopped samples per replication

Descriptive Analysis – Centennial 2016 Harvest

12 trained panelists (9 males and 3 females; 21–55 yrs old) were used to evaluate the 2016 Centennial harvest samples. 22 dry-hopped beers (21 different hop lots and 1 unhopped control) were evaluated. Four intensive training sessions were completed in advance of data collection. Based on discussion from these training sessions the final ballot included the attributes: OHAI, Citrus, Herbal/Tea, Pine/Resinous/Dank, Tropical/Fruity, and Tropical/Catty to be evaluated on a on a 0–15 point scale. To evaluate the Centennial samples an efficient resolvable incomplete block design was used to create a presentation order for the samples across four replications (SAS, Cary, NC). The unhopped control was nested into each session. It took 3 sessions of 8 samples to experience all the treatments per replication. Over the course of 15 sessions, the 15 panelists evaluated all the Centennial samples five times in a randomized fashion. The first 2 replications were used to familiarize the panelists with the samples.

Descriptive Analysis – Panelist/panel evaluation

Following each descriptive analysis panel, every panelist was evaluated on their performance based upon their ability to discriminate differences among the dry-hop treatments on at least one of the sensory attributes, replicate among all sessions, and their lack of interactions. Any panelists that failed these three criteria were removed from further analyses.

For the 2014 Cascade harvest samples 1 panelist of the original 11 panelists was removed from the data set resulting in 50 observations per attribute, per sample. For the 2015 Cascade harvest samples, 3 panelists of the original 13 panelists were removed from the data set resulting in 40 observations per attribute, per sample. For the 2015 Centennial harvest samples, 5 panelists of the original 15 panelists were removed from the data sets resulting 40 observations per attribute, per sample. For the 2016 Centennial harvest samples 5 panelists of the original 12 panelists were removed from the data sets resulting in 21 observations per attribute, per sample.

Table S4 Mixed model analysis of variance of the sensory attributes for the descriptive analysis panels over the harvest years for Cascade treatments

2014 Cascade Mixed Model ANOVA

			OHAI		Citrus		Herbal/Tea	
Source	**Type**	**DF**	**F**	**P-value**	**F**	**P-value**	**F**	**P-value**
Sample	Fixed	22	8.7	**< 0.0001**	3.6	**< 0.0001**	8.9	**< 0.0001**
Panelist	Random	9	22.6	**< 0.0001**	29.0	**< 0.0001**	10.8	**< 0.0001**
Rep	Fixed	4	1.3	0.289	0.9	0.496	1.1	0.375
Sample*Panelist	Random	198	2.3	**< 0.0001**	1.9	**< 0.0001**	2.1	**< 0.0001**
Sample*Rep	Fixed	88	1.2	0.146	1.0	0.431	1.1	0.213
Panelist*Rep	Random	36	0.8	0.819	1.6	**0.016**	1.7	**0.009**
Error		792						

2015 Cascade Mixed Model ANOVA

			OHAI		Citrus		Herbal/Tea	
Source	**Type**	**DF**	**F**	**P-value**	**F**	**P-value**	**F**	**P-value**
Sample	Fixed	29	6.8	**< 0.0001**	4.4	**< 0.0001**	3.9	**< 0.0001**
Panelist	Random	9	24.6	**< 0.0001**	20.9	**< 0.0001**	28.3	**< 0.0001**
Rep	Fixed	3	0.2	0.874	0.5	0.659	0.2	0.903
Sample*Panelist	Random	261	1.5	**< 0.0001**	1.5	**< 0.0001**	1.3	**0.007**
Sample*Rep	Fixed	87	1.0	0.451	0.8	0.903	1.3	**0.032**
Panelist*Rep	Random	27	1.3	0.134	1.1	0.328	1.5	**0.041**
Error		783						

Values in **bold** indicate p-value < 0.05

Table S5 Mixed model analysis of variance of the sensory attributes for the descriptive analysis panels over the harvest years for Centennial treatments

2015 Centennial Mixed Model ANOVA

			OHAI		Citrus		Tropical/ Catty		Tropical/ Fruity		Pine/Resinous/ Dank		Herbal/ Tea	
Source	**Type**	**DF**	**F**	**P-value**	**F**	**P-value**	**F**	**P-value**	**F**	**P-value**	**F**	**P-value**	**F**	**P-value**
Sample	Fixed	12	41.1	**< 0.0001**	27.6	**< 0.0001**	11.5	**< 0.0001**	8.2	**< 0.0001**	13.0	**< 0.0001**	16.9	**< 0.0001**
Panelist	Random	9	1.5	0.201	4.8	**0.001**	4.5	**0.001**	7.0	**< 0.0001**	10.9	**< 0.0001**	9.4	**< 0.0001**
Rep	Fixed	3	1.0	0.419	0.8	0.504	0.6	0.598	0.9	0.458	0.5	0.671	0.7	0.579
Sample*Panelist	Random	108	1.4	**0.026**	1.3	0.056	1.4	**0.013**	1.9	**< 0.0001**	1.4	**0.008**	2.1	**< 0.0001**
Sample*Rep	Fixed	36	0.9	0.611	1.3	0.134	1.2	0.226	1.1	0.350	0.9	0.647	1.2	0.255
Panelist*Rep	Random	27	1.3	0.176	1.9	**0.005**	0.6	0.913	1.6	**0.038**	2.5	**< 0.0001**	1.4	0.113
Error		364												

2016 Centennial Mixed Model ANOVA

Source	**Type**	**DF**	**F**	**P-value**	**F**	**P-value**	**F**	**P-value**	**F**	**P-value**	**F**	**P-value**	**F**	**P-value**
Sample	Fixed	21	18.6	**< 0.0001**	11.8	**< 0.0001**	9.0	**< 0.0001**	6.3	**< 0.0001**	9.9	**< 0.0001**	7.3	**< 0.0001**
Panelist	Random	6	9.8	**< 0.0001**	21.7	**< 0.0001**	15.9	**< 0.0001**	18.9	**< 0.0001**	29.0	**< 0.0001**	6.2	**0.000**
Rep	Fixed	2	1.3	0.308	1.6	0.243	0.6	0.547	2.8	0.100	1.2	0.319	0.03	0.974
Sample*Panelist	Random	126	2.4	**< 0.0001**	2.8	**< 0.0001**	2.2	**< 0.0001**	1.8	**< 0.0001**	2.4	**< 0.0001**	2.9	**< 0.0001**
Sample*Rep	Fixed	42	1.5	**0.024**	1.7	**0.007**	1.9	**0.002**	1.2	0.187	1.4	**0.046**	1.0	0.515
Panelist*Rep	Random	12	1.1	0.363	2.2	**0.010**	1.8	**0.047**	1.1	0.338	1.3	0.243	2.9	**0.001**
Error		294												

Values in **bold** indicate p-value < 0.05

Table S6 Sensory attributes of the Cascade 2014 and 2015 dry-hop treatments sorted by increasing Citrus quality

Sample ID	OHAI	Citrus	Herbal	Sample ID	OHAI	Citrus	Herbal/Tea
„Unhopped“ base	2.8 [m]	1.2 [h]	1.4 [h]	„Unhopped“ base	3.0 [h]	1.9 [i]	2.5 [h]
CAS_01_14	9.0 [abc]	2.4 [g]	7.2 [a]	CAS_11_15	7.2 [efg]	4.2 [h]	5.3 [cdefg]
CAS_02_14	6.1 [l]	2.9 [fg]	2.4 [g]	CAS_12_15	6.7 [g]	4.3 [h]	5.0 [efg]
CAS_03_14	7.5 [efghi]	3.0 [fg]	3.6 [bcd]	CAS_07_15	6.7 [g]	4.4 [gh]	4.7 [fg]
CAS_04_14	6.6 [ijkl]	3.1 [efg]	2.9 [defg]	CAS_21_15	7.0 [fg]	4.5 [gh]	5.1 [defg]
CAS_05_14	6.5 [jkl]	3.3 [def]	2.9 [defg]	CAS_04_15	7.3 [efg]	4.5 [gh]	5.4 [cdefg]
CAS_08_14	6.2 [kl]	3.4 [cdef]	2.4 [g]	CAS_27_15	6.6 [g]	4.6 [fgh]	4.5 [g]
CAS_07_14	7.9 [defgh]	3.4 [cdef]	3.6 [bcde]	CAS_19_15	6.7 [g]	4.8 [efgh]	4.9 [efg]
CAS_06_14	7.1 [hijk]	3.5 [bcdef]	2.9 [defg]	CAS_03_15	7.6 [cdefg]	4.8 [efgh]	5.5 [cdefg]
CAS_09_14	6.2 [kl]	3.5 [bcdef]	2.3 [g]	CAS_05_15	7.0 [fg]	4.8 [efgh]	4.8 [efg]
CAS_10_14	7.3 [fghij]	3.6 [bcdef]	2.8 [efg]	CAS_01_15	7.0 [g]	4.9 [efgh]	5.2 [defg]
CAS_11_14	8.7 [abcd]	3.6 [bcdef]	4.1 [bc]	CAS_20_15	7.4 [defg]	4.9 [efgh]	5.1 [defg]
CAS_12_14	7.3 [fghij]	3.7 [bcdef]	2.8 [fg]	CAS_25_15	7.6 [cdefg]	5.0 [efgh]	5.6 [cdefg]
CAS_13_14	8.1 [bcdef]	3.7 [bcdef]	3.4 [cdef]	CAS_02_15	7.3 [defg]	5.0 [efgh]	5.2 [defg]
CAS_14_14	8.1 [cdefg]	3.7 [bcdef]	2.8 [efg]	CAS_28_15	7.3 [defg]	5.1 [efgh]	5.1 [defg]
CAS_15_14	8.9 [abc]	3.7 [bcdef]	4.4 [b]	CAS_16_15	7.3 [efg]	5.2 [defgh]	4.7 [efg]
CAS_16_14	6.9 [hijkl]	3.9 [abcde]	3.1 [defg]	CAS_06_15	7.5 [defg]	5.3 [cdefgh]	5.5 [cdefg]
CAS_17_14	7.1 [ghijk]	4.0 [abcd]	2.4 [g]	CAS_22_15	7.4 [defg]	5.3 [bcdefg]	5.1 [defg]
CAS_18_14	7.3 [fghij]	4.0 [abcd]	2.5 [g]	CAS_09_15	7.4 [defg]	5.4 [bcdefg]	4.7 [efg]
CAS_20_14	9.0 [ab]	4.2 [abc]	3.1 [defg]	CAS_13_15	7.6 [cdefg]	5.4 [bcdefg]	5.1 [defg]
CAS_21_14	8.5 [bcde]	4.2 [abcd]	3.0 [defg]	CAS_23_15	8.0 [bcdef]	5.7 [abcde]	5.4 [cdefg]
CAS_22_14	8.1 [bcdef]	4.3 [ab]	3.1 [defg]	CAS_24_15	7.4 [defg]	5.7 [abcdef]	5.4 [cdefg]
CAS_24_14	9.5 [a]	4.6 [a]	4.0 [bc]	CAS_10_15	8.5 [abc]	5.8 [abcde]	6.0 [cde]
				CAS_08_15	8.1 [bcde]	5.8 [abcde]	5.7 [cdef]
				CAS_29_15	8.8 [ab]	6.2 [abcd]	6.3 [abc]
				CAS_18_15	8.1 [bcde]	6.3 [abc]	5.3 [cdefg]
				CAS_17_15	9.0 [ab]	6.4 [ab]	7.1 [a]
				CAS_14_15	8.3 [abcd]	6.4 [ab]	5.6 [cdef]
				CAS_26_15	9.2 [a]	6.6 [a]	6.9 [ab]
				CAS_15_15	9.0 [ab]	6.6 [a]	5.5 [cdefg]

Mean scores.
Letters in brackets indicate statistically significant groupings within each descriptor (Fisher's LSD tests, p-value < 0.05).
OHAI = overall hop aroma intensity

Table S7 Sensory attributes of the Centennial 2015 and 2016 dry-hop treatments sorted by increasing overall hop aroma intensity (OHAI)

Sample ID	OHAI	Citrus	Herbal/Tea	Tropical/Catty	Tropical/Fruity	Pine/Resinous/ Dank
"Unhopped" base	1.3 [h]	0.6 [f]	0.5 [e]	0.5 [d]	0.8 [e]	0.2 [e]
Cent_01_15	5.4 [g]	3.5 [e]	2.9 [d]	2.0 [c]	2.5 [d]	1.2 [d]
Cent_05_15	6.3 [fg]	3.9 [de]	3.2 [cd]	2.9 [b]	2.9 [cd]	1.9 [bc]
Cent_08_15	6.6 [ef]	4.3 [cd]	3.7 [bc]	2.5 [bc]	3.2 [bcd]	1.8 [c]
Cent_04_15	6.8 [def]	4.5 [bcd]	3.5 [bcd]	2.7 [bc]	2.9 [cd]	2.4 [ab]
Cent_10_15	7.0 [cdef]	4.5 [bcd]	3.6 [bc]	2.6 [bc]	3.0 [cd]	1.9 [bc]
Cent_02_15	7.0 [cdef]	4.5 [bcd]	3.4 [cd]	2.7 [bc]	3.0 [cd]	2.2 [abc]
Cent_12_15	7.2 [bcde]	5.0 [abc]	3.8 [bc]	2.7 [bc]	3.4 [abc]	2.2 [abc]
Cent_03_15	7.4 [bcde]	4.5 [bcd]	3.5 [bc]	3.0 [b]	3.4 [abc]	1.9 [bc]
Cent_06_15	7.7 [bcd]	5.1 [ab]	3.8 [bc]	2.9 [b]	3.9 [ab]	2.4 [ab]
Cent_07_15	7.9 [abc]	5.4 [a]	3.7 [bc]	2.8 [b]	4.2 [a]	2.2 [abc]
Cent_09_15	8.1 [ab]	5.1 [abc]	4.1 [ab]	3.7 [a]	3.6 [abc]	2.5 [ab]
Cent_11_15	8.8 [a]	5.2 [ab]	4.8 [a]	3.9 [a]	3.5 [abc]	2.6 [a]
"Unhopped" base	0.6 [j]	0.1 [j]	0.5 [j]	0.4 [h]	0.6 [h]	0.1 [j]
Cent_15_16	4.4 [i]	2.2 [i]	2.8 [i]	1.6 [g]	1.8 [g]	2.1 [i]
Cent_11_16	5.3 [hi]	2.9 [hi]	3.1 [ghi]	1.7 [fg]	2.2 [efg]	2.3 [hi]
Cent_7_16	5.4 [hi]	2.9 [hi]	3.5 [defghi]	1.6 [g]	2.3 [efg]	2.6 [ghi]
Cent_3_16	5.8 [gh]	3.4 [fgh]	3.4 [efghi]	1.9 [efg]	2.1 [fg]	3.0 [efghi]
Cent_17_16	5.9 [fgh]	3.8 [cdefgh]	3.1 [hi]	2.1 [cdedfg]	2.9 [ef]	2.8 [fghi]
Cent_4_16	6.0 [efgh]	3.5 [efgh]	3.2 [fghi]	2.0 [defg]	2.4 [efg]	3.1 [efgh]
Cent_5_16	6.0 [efgh]	3.7 [defgh]	3.2 [fghi]	2.0 [defg]	2.6 [efg]	2.8 [fghi]
Cent_10_16	6.1 [defgh]	4.0 [cdefg]	3.3 [fghi]	2.2 [cdedfg]	2.9 [ef]	3.5 [defg]
Cent_19_16	6.1 [defgh]	3.4 [gh]	3.8 [cdefgh]	2.4 [bcde]	2.2 [efg]	2.8 [fghi]
Cent_20_16	6.6 [cdefg]	4.4 [cdefg]	3.7 [cdefghi]	2.2 [cdedfg]	3.0 [cdef]	3.3 [efg]
Cent_16_16	6.7 [cdefg]	4.4 [cdef]	4.0 [bcdefgh]	2.6 [bcd]	3.1 [bcde]	3.6 [def]
Cent_18_16	6.7 [cdefg]	4.2 [cdefg]	3.7 [cdefghi]	2.4 [bcde]	3.0 [bcdef]	3.0 [efghi]
Cent_1_16	6.8 [cdefg]	4.2 [cdefg]	4.3 [abcde]	2.4 [bcde]	2.9 [def]	3.6 [def]
Cent_12_16	6.9 [cdefg]	4.5 [cd]	3.7 [cdefghi]	2.3 [cde]	3.0 [bcdef]	3.9 [cde]
Cent_8_16	7.0 [cdef]	4.3 [cdefg]	4.5 [abcd]	2.3 [cdef]	2.9 [ef]	3.6 [defg]
Cent_9_16	7.2 [cde]	4.5 [cde]	4.0 [bcdefg]	2.1 [defg]	3.0 [bcdef]	3.5 [defg]
Cent_13_16	7.3 [bcd]	4.6 [cd]	3.8 [cdefgh]	2.8 [bc]	4.1 [a]	3.3 [efg]
Cent_2_16	7.6 [bc]	4.8 [bc]	4.1 [bcdef]	2.6 [bcd]	3.0 [bcdef]	4.5 [bcd]
Cent_6_16	8.5 [ab]	5.9 [a]	4.5 [abc]	3.0 [b]	3.8 [abcd]	5.4 [ab]
Cent_14_16	9.3 [a]	5.8 [ab]	5.1 [a]	3.8 [a]	3.9 [abc]	4.8 [abc]
Cent_21_16	9.3 [a]	6.2 [a]	4.9 [ab]	3.7 [a]	4.0 [ab]	5.6 [a]

Mean scores.
Letters in brackets indicate statistically significant groupings within each descriptor (Fisher's LSD tests, p-value < 0.05).
OHA I= overall hop aroma intensity

Table S8 Pearson Correlation Coefficients for 2014 harvest Cascade (n = 22)

Variables	OHAI	Citrus	Herbal	Total Oil	Isobutyl Isobutyrate	α-Pinene	β-Pinene	β-myrcene	Methyl Heptanoate	Limonene	Linalool	Nerol	Neral	Geraniol	Geranial	Geranyl acetate	β-caryophyllene	α-humulene	β-farnesene	Caryophyllene Oxide
OHAI	**1.00**																			
Citrus	0.37	**1.00**																		
Herbal	**0.65**	-0.37	**1.00**																	
Total Oil	–0.03	0.27	–0.28	**1.00**																
Isobutyl Isobutyrate	–0.02	0.27	–0.24	**0.88**	**1.00**															
α-Pinene	0.04	0.24	–0.22	**0.96**	**0.91**	**1.00**														
β-Pinene	0.06	0.25	–0.19	**0.97**	**0.90**	**0.99**	**1.00**													
β-myrcene	0.05	0.25	–0.20	**0.97**	**0.89**	**0.98**	**1.00**	**1.00**												
Methyl Heptanoate	–0.03	0.24	–0.27	**0.89**	**0.91**	**0.93**	**0.91**	**0.89**	**1.00**											
Limonene	–0.02	0.20	–0.20	**0.91**	**0.86**	**0.95**	**0.94**	**0.93**	**0.92**	**1.00**										
Linalool	–0.14	0.40	**–0.43**	**0.81**	**0.90**	**0.82**	**0.78**	**0.77**	**0.89**	**0.79**	**1.00**									
Nerol	–0.13	**0.50**	**–0.52**	**0.72**	**0.69**	**0.68**	**0.67**	**0.68**	**0.75**	**0.66**	**0.84**	**1.00**								
Neral	0.06	0.18	–0.14	**0.92**	**0.94**	**0.93**	**0.93**	**0.93**	**0.90**	**0.88**	**0.80**	**0.56**	**1.00**							
Geraniol	–0.05	**0.66**	–0.42	0.37	**0.44**	0.30	0.29	0.30	0.38	0.24	**0.66**	**0.68**	0.27	**1.00**						
Geranial	–0.29	0.15	–0.30	0.12	0.02	0.08	0.07	0.06	0.26	0.18	0.32	**0.59**	–0.07	0.40	**1.00**					
Geranyl acetate	–0.23	0.00	–0.31	**0.77**	**0.83**	**0.84**	**0.80**	**0.79**	**0.79**	**0.75**	**0.76**	**0.52**	**0.80**	0.25	0.05	**1.00**				
β-caryophyllene	–0.17	**0.44**	**–0.49**	**0.74**	**0.68**	**0.71**	**0.71**	**0.72**	**0.77**	**0.73**	**0.81**	**0.97**	**0.59**	**0.60**	**0.61**	**0.54**	**1.00**			
α-humulene	–0.18	0.41	**–0.48**	**0.71**	**0.65**	**0.69**	**0.69**	**0.70**	**0.75**	**0.70**	**0.78**	**0.96**	**0.54**	**0.58**	**0.65**	**0.52**	**0.99**	**1.00**		
β-farnesene	–0.32	**0.55**	**–0.67**	**0.55**	**0.51**	**0.46**	**0.46**	**0.48**	**0.53**	**0.47**	**0.71**	**0.91**	0.37	**0.75**	**0.59**	0.36	**0.88**	**0.85**	**1.00**	
Caryophyllene Oxide	0.08	0.08	–0.21	–0.15	–0.13	–0.10	–0.14	–0.17	–0.03	–0.16	–0.11	–0.11	–0.14	0.04	–0.17	–0.13	–0.20	–0.18	–0.17	**1.00**

Values in **bold** are different from 0 with a significance level alpha = 0.05

Table S9 Pearson Correlation Coefficients for 2015 harvest Cascade (n = 29)

Variables	OHAI	Citrus	Herbal	Total Oil	Isobutyl Isobutyrate	α-Pinene	β-Pinene	β-myrcene	Methyl Heptanoate	Limonene	Linalool	Nerol	Neral	Geraniol	Geranial	Geranyl acetate	β-caryophyllene	α-humulene	β-farnesene	Caryophyllene Oxide
OHAI	**1.00**																			
Citrus	**0.90**	**1.00**																		
Herbal	**0.85**	**0.67**	**1.00**																	
Total Oil	**0.45**	**0.49**	0.27	**1.00**																
Isobutyl Isobutyrate	**0.45**	**0.53**	0.22	**0.97**	**1.00**															
α-Pinene	**0.43**	**0.48**	0.25	**1.00**	**0.98**	**1.00**														
β-Pinene	**0.46**	**0.50**	0.28	**0.99**	**0.97**	**0.99**	**1.00**													
β-myrcene	**0.40**	**0.46**	0.21	**0.98**	**0.97**	**0.99**	**0.99**	**1.00**												
Methyl Heptanoate	**0.43**	**0.49**	0.25	**0.99**	**0.98**	**0.99**	**0.98**	**0.99**	**1.00**											
Limonene	**0.46**	**0.50**	0.28	**1.00**	**0.98**	**1.00**	**0.99**	**0.99**	**0.99**	**1.00**										
Linalool	**0.55**	**0.60**	0.35	**0.91**	**0.90**	**0.91**	**0.91**	**0.88**	**0.90**	**0.91**	**1.00**									
Nerol	0.35	**0.45**	0.19	**0.81**	**0.85**	**0.83**	**0.81**	**0.85**	**0.87**	**0.82**	**0.76**	**1.00**								
Neral	0.04	0.10	–0.07	**0.45**	**0.47**	**0.45**	**0.40**	**0.44**	**0.49**	**0.44**	**0.46**	**0.57**	**1.00**							
Geraniol	**0.75**	**0.71**	**0.57**	**0.62**	**0.61**	**0.60**	**0.62**	**0.56**	**0.60**	**0.62**	**0.80**	**0.54**	0.28	**1.00**						
Geranial	**0.62**	**0.62**	**0.61**	**0.60**	**0.56**	**0.60**	**0.62**	**0.56**	**0.60**	**0.61**	**0.67**	**0.48**	0.33	**0.62**	**1.00**					
Geranyl acetate	**0.52**	**0.57**	0.34	**0.78**	**0.78**	**0.76**	**0.73**	**0.71**	**0.77**	**0.76**	**0.80**	**0.72**	**0.52**	**0.75**	**0.58**	**1.00**				
β-caryophyllene	**0.41**	**0.42**	0.31	**0.86**	**0.76**	**0.85**	**0.83**	**0.80**	**0.84**	**0.84**	**0.81**	**0.70**	**0.44**	**0.59**	**0.63**	**0.78**	**1.00**			
α-humulene	0.33	0.34	0.27	**0.66**	**0.57**	**0.66**	**0.63**	**0.62**	**0.67**	**0.65**	**0.60**	**0.62**	**0.37**	**0.46**	**0.53**	**0.66**	**0.93**	**1.00**		
β-farnesene	0.11	0.17	0.02	**0.63**	**0.56**	**0.62**	**0.56**	**0.59**	**0.64**	**0.60**	**0.54**	**0.63**	**0.45**	0.33	**0.43**	**0.73**	**0.80**	**0.85**	**1.00**	
Caryophyllene Oxide	0.13	0.12	0.13	–0.26	–0.29	–0.28	–0.30	–0.33	–0.26	–0.27	–0.23	–0.18	–0.23	0.04	–0.08	0.03	0.01	0.24	0.19	**1.00**

Values in **bold** are different from 0 with a significance level alpha = 0.05

Table S10 Combined 2015 and 2016 Centennial Harvest Pearson Correlation Coefficients (n = 33).

Variables	OHAI	Citrus	Herbal	T/Catty	T/ Fruity	P/ R/D	Total Oil	Isobutyl Isobutyrate	α-Pinene	β-Pinene	β-myrcene	Methyl Heptanoate	Limonene	Linalool	Nerol	Neral	Geraniol	Geranial	Geranyl acetate	β-caryophyllene	α-humulene	Caryophyllene Oxide
OHAI	**1.00**																					
Citrus	**0.95**	**1.00**																				
Herbal	**0.83**	**0.72**	**1.00**																			
T/Catty	**0.84**	**0.78**	**0.56**	**1.00**																		
T/ Fruity	**0.86**	**0.87**	**0.71**	**0.67**	**1.00**																	
P/ R/D	**0.54**	**0.48**	**0.65**	0.22	**0.36**	**1.00**																
Total Oil	**0.55**	**0.54**	0.31	**0.58**	**0.46**	**0.44**	**1.00**															
Isobutyl Isobutyrate	**0.46**	**0.53**	0.13	**0.69**	**0.53**	**–0.35**	**0.35**	**1.00**														
α-Pinene	0.30	**0.35**	0.01	**0.59**	0.31	**–0.55**	0.10	**0.92**	**1.00**													
β-Pinene	**0.63**	**0.67**	0.32	**0.75**	**0.61**	0.04	**0.74**	**0.83**	**0.67**	**1.00**												
β-myrcene	**0.54**	**0.56**	0.24	**0.71**	**0.47**	–0.09	**0.66**	**0.85**	**0.74**	**0.93**	**1.00**											
Methyl Heptanoate	**0.46**	**0.50**	0.22	**0.68**	**0.38**	–0.31	0.22	**0.86**	**0.91**	**0.71**	**0.78**	**1.00**										
Limonene	**0.45**	**0.50**	0.15	**0.69**	**0.43**	–0.34	**0.36**	**0.93**	**0.94**	**0.84**	**0.87**	**0.92**	**1.00**									
Linalool	**0.38**	**0.38**	0.16	**0.42**	0.23	0.33	**0.65**	0.18	0.06	**0.47**	0.31	0.26	0.24	**1.00**								
Nerol	0.28	0.32	0.06	0.33	0.20	0.10	0.26	0.21	0.13	0.25	0.10	0.27	0.21	**0.67**	**1.00**							
Neral	0.01	0.07	–0.06	–0.04	0.09	0.21	0.16	–0.18	–0.28	–0.10	–0.27	–0.20	–0.22	**0.47**	**0.61**	**1.00**						
Geraniol	0.12	0.28	–0.23	0.34	0.18	**–0.47**	0.12	**0.65**	**0.66**	**0.46**	**0.44**	**0.64**	**0.62**	**0.35**	**0.53**	0.14	**1.00**					
Geranial	–0.05	–0.13	0.13	–0.28	–0.13	**0.64**	0.18	**–0.69**	**–0.81**	**–0.37**	**–0.48**	**–0.69**	**–0.66**	0.33	0.15	**0.37**	**–0.55**	**1.00**				
Geranyl acetate	0.20	0.13	0.17	0.00	0.12	**0.65**	**0.46**	**–0.39**	**–0.62**	–0.08	–0.19	**–0.50**	**–0.42**	**0.42**	0.33	**0.49**	–0.33	**0.80**	**1.00**			
β-caryophyllene	0.27	0.23	0.10	**0.43**	0.18	–0.11	0.24	**0.37**	**0.41**	**0.41**	0.32	**0.42**	**0.49**	**0.47**	**0.53**	0.28	**0.41**	–0.04	0.11	**1.00**		
α-humulene	0.14	0.14	–0.07	0.31	0.15	–0.26	0.12	**0.38**	**0.41**	0.30	0.23	**0.36**	**0.43**	**0.38**	**0.55**	**0.40**	**0.52**	–0.12	0.07	**0.94**	**1.00**	
Caryophyllene Oxide	–0.02	–0.08	0.11	–0.24	–0.07	**0.50**	–0.05	**–0.62**	**–0.64**	**–0.42**	**–0.60**	**–0.56**	**–0.56**	0.26	0.20	**0.47**	**–0.37**	**0.70**	**0.60**	0.00	–0.03	**1.00**

Values in **bold** are different from 0 with a significance level alpha = 0.05.
Pine/resinous/dank-P/R/D.
Tropical-T/Catty & T/Fruity

Table S11 Concentrations of 16 volatiles in hydrodistilled hop oil for the 2014 Cascade samples

Sample ID	Isobutyl Isobutyrate	α-Pinene	β-Pinene	β-myrcene	Methyl Heptanoate	Limonene	Linalool	Nerol	Neral	Geraniol	Geranial	Geranyl acetate	β-caryophyllene	α-humulene	β-farnesene	Caryophyllene Oxide
CAS_01_14	0.24	0.26	2.36	151	0.22	0.73	1.20	1.02	0.00	0.81	0.13	0.07	43.4	125	26.8	1.49
CAS_02_14	0.52	0.45	3.78	222	0.89	1.20	4.95	1.93	0.00	2.36	0.13	0.12	66.7	188	70.2	5.73
CAS_03_14	2.15	1.36	12.3	815	1.90	4.75	10.4	3.06	6.76	5.25	0.09	0.26	109	265	117	2.40
CAS_04_14	1.83	1.90	15.9	1010	2.59	6.17	11.1	3.94	5.60	3.50	0.93	0.38	136	341	156	3.31
CAS_05_14	0.52	0.61	5.66	411	1.09	1.78	6.77	3.25	0.00	7.67	0.84	0.00	110	277	156	5.26
CAS_06_14	0.49	0.64	5.89	432	0.81	1.86	6.00	2.91	0.00	3.88	0.66	0.00	105	262	147	1.71
CAS_07_14	1.28	1.55	13.2	888	1.46	5.04	8.39	2.60	5.54	3.35	0.33	0.47	97.0	241	114	1.75
CAS_08_14	2.20	1.97	17.0	1100	3.34	6.44	14.1	3.96	9.32	5.36	1.18	0.74	146	353	151	2.01
CAS_09_14	1.46	1.41	10.8	651	2.17	4.54	8.12	1.95	7.57	2.46	0.13	0.36	72.1	174	73.8	4.88
CAS_10_14	1.90	1.55	13.6	934	1.84	4.20	9.32	3.06	6.89	4.13	0.38	0.72	107	266	140	1.69
CAS_11_14	0.30	0.27	3.26	244	0.43	1.13	3.40	2.42	0.00	2.77	0.38	0.00	91.6	213	132	2.40
CAS_12_14	1.02	0.65	6.33	403	0.68	1.77	4.95	1.94	2.16	3.68	0.21	0.34	69.8	189	89.4	4.19
CAS_13_14	1.92	2.08	17.2	1130	2.01	4.37	10.9	3.25	7.54	5.35	0.10	0.67	110	265	126	4.11
CAS_14_14	1.22	1.25	11.3	738	1.49	3.31	7.10	2.23	3.48	4.17	0.36	0.40	87.9	237	108	2.90
CAS_15_14	2.10	1.90	16.7	1110	2.54	5.05	10.5	3.21	9.39	4.15	0.14	0.57	110	275	136	3.29
CAS_16_14	1.86	1.89	16.4	1140	2.33	7.08	10.5	3.04	8.41	4.41	0.43	0.56	124	301	144	1.93
CAS_17_14	2.18	1.78	15.5	1100	2.43	4.85	9.82	3.08	9.08	3.53	0.15	0.59	111	268	131	4.26
CAS_18_14	0.28	0.57	4.65	286	0.48	1.43	1.96	2.14	0.00	1.16	0.36	0.16	88.8	232	82.6	3.76
CAS_20_14	0.33	0.75	7.11	483	0.91	2.07	2.96	2.09	0.00	1.55	0.38	0.28	81.2	222	74.7	2.72
CAS_21_14	0.60	1.10	9.43	592	1.31	3.52	4.51	2.12	2.37	1.87	0.34	0.31	82.6	220	76.9	5.09
CAS_22_14	2.08	2.40	22.2	1520	2.89	8.40	8.05	3.17	9.46	2.30	0.33	0.52	120	294	118	3.55
CAS_24_14	1.28	1.62	16.3	1120	1.63	4.24	5.55	2.34	8.83	2.58	0.13	0.21	93.1	241	82.8	2.43

Concentrations (mg/100g) of the hop volatiles are heat mapped: green cells represent the highest concentration and red cells represent the lowest concentrations

Table S12 Concentrations of 16 volatiles in hydrodistilled hop oil for the 2015 Cascade samples

Sample ID	Isobutyl Isobutyrate	α-Pinene	β-Pinene	β-myrcene	Methyl Heptanoate	Limonene	Linalool	Nerol	Neral	Geraniol	Geranial	Geranyl acetate	β-caryophyllene	α-humulene	β-farnesene	Caryophyllene Oxide
CAS_01_15	w	6.64	15.4	572	8.45	9.09	5.17	0.69	0.00	2.17	0.25	19.4	81.2	152	62.2	0.00
CAS_02_15	6.19	5.25	11.1	402	7.26	7.32	5.94	0.60	0.15	2.92	0.22	17.9	83.3	166	61.3	0.00
CAS_03_15	5.77	4.30	9.67	359	5.57	6.54	1.82	0.31	0.00	1.71	0.20	14.2	53.5	110	40.5	0.44
CAS_04_15	3.57	2.78	4.60	165	3.89	3.94	1.42	0.44	0.12	1.37	0.14	11.1	44.0	93.9	40.9	0.00
CAS_05_15	4.67	3.66	7.18	283	5.28	5.23	2.84	0.54	0.00	1.44	0.15	11.8	51.2	109	47.3	0.00
CAS_06_15	3.83	3.49	7.91	236	4.68	4.74	2.15	0.32	0.03	1.93	0.35	9.13	54.2	111	35.3	0.13
CAS_07_15	2.74	2.37	4.28	134	3.10	3.45	1.86	0.25	0.00	1.44	0.14	12.0	59.5	156	61.5	2.76
CAS_08_15	7.15	5.39	11.5	430	7.48	8.10	3.88	0.61	0.07	3.09	0.15	18.1	71.0	156	37.1	1.54
CAS_09_15	4.56	2.71	5.38	215	3.46	3.95	2.19	0.10	0.00	1.82	0.17	6.95	33.8	76.5	28.5	0.00
CAS_10_15	6.36	5.72	13.7	509	7.42	8.43	4.15	0.30	0.00	2.13	0.32	10.4	77.3	167	47.3	0.00
CAS_11_15	4.09	3.76	7.99	275	4.95	5.39	1.79	0.22	0.00	1.26	0.13	4.97	60.4	137	36.5	1.72
CAS_12_15	1.78	1.56	2.49	69.6	2.01	2.27	0.49	0.00	0.00	0.32	0.03	0.58	30.8	79.8	14.2	1.12
CAS_13_15	6.51	5.69	13.6	521	7.72	8.27	4.26	0.38	0.00	1.84	0.25	11.2	76.9	163	49.5	0.00
CAS_14_15	14.3	10.5	25.8	1130	15.7	15.2	8.58	2.14	0.17	3.76	0.39	24.3	108	241	85.9	0.00
CAS_15_15	6.84	4.41	10.8	363	5.98	6.55	4.59	0.69	0.00	3.82	0.12	16.2	53.6	103	29.5	1.36
CAS_16_15	5.12	3.90	8.04	279	5.35	5.64	3.51	0.29	0.16	2.50	0.26	17.8	72.5	165	60.5	1.64
CAS_17_15	5.46	4.11	9.42	314	5.64	6.41	5.25	0.45	0.00	4.07	0.40	13.9	56.0	114	34.7	1.97
CAS_18_15	9.84	6.62	15.5	579	9.15	9.71	5.78	0.69	0.08	1.99	0.32	17.0	69.1	132	44.7	0.00
CAS_19_15	3.18	2.78	4.99	167	3.73	3.99	1.68	0.36	0.00	1.48	0.17	8.68	60.3	160	53.9	1.28
CAS_20_15	5.61	4.81	12.1	383	6.26	7.22	4.80	0.38	0.03	2.98	0.29	10.9	63.1	128	35.2	0.59
CAS_21_15	2.57	2.20	4.21	119	2.81	3.01	1.45	0.19	0.00	1.09	0.06	5.36	50.5	133	38.0	2.93
CAS_22_15	2.51	2.18	4.36	124	2.85	3.22	1.75	0.28	0.03	1.67	0.23	6.17	53.6	127	25.0	4.02
CAS_23_15	5.29	4.23	8.50	270	5.91	6.19	2.99	0.37	0.00	2.46	0.21	17.6	72.7	182	74.9	9.44
CAS_24_15	2.70	2.24	4.09	125	2.97	3.15	0.94	0.16	0.00	0.70	0.10	5.80	38.4	78.7	26.4	1.03
CAS_25_15	4.06	3.04	6.85	201	4.00	4.32	2.96	0.22	0.03	2.56	0.18	12.3	48.0	104	27.6	1.03
CAS_26_15	3.84	3.20	6.71	205	4.73	4.70	3.12	0.60	0.04	2.61	0.41	17.3	72.1	187	54.6	3.67
CAS_27_15	2.64	2.11	3.59	129	2.84	2.92	1.42	0.21	0.00	1.13	0.09	6.20	29.5	63.2	26.4	1.41
CAS_28_15	7.34	5.17	11.5	436	7.39	7.58	3.92	0.72	0.14	1.66	0.30	13.8	59.6	121	50.1	0.30
CAS_29_15	6.81	5.29	12.6	403	6.93	7.69	5.08	0.28	0.00	3.16	0.32	15.1	73.8	143	37.1	1.20

Concentrations (mg/100g) of the hop volatiles are heat mapped: green cells represent the highest concentration and red cells represent the lowest concentrations

Table S13 Concentrations of 16 volatiles in hydrodistilled hop oil for the 2015 and 2016 Centennial samples

Sample ID	Isobutyl Isobutyrate	α-Pinene	β-Pinene	β-myrcene	Methyl Heptanoate	Limonene	Linalool	Nerol	Neral	Geraniol	Geranial	Geranyl acetate	β-caryophyllene	α-humulene	β-farnesene	Caryophyllene Oxide
Cent_01_15	5.31	5.06	12.5	450	6.22	6.89	6.88	0.88	0.15	56.2	0.87	0.00	72.6	141	n.d	0.00
Cent_02_15	8.82	6.96	18.8	637	11.4	10.9	14.0	6.25	5.34	97.5	2.70	0.77	154	347	n.d	7.22
Cent_03_15	10.6	7.94	23.3	850	11.6	11.3	13.2	4.32	0.87	88.3	2.04	0.24	90.5	152	n.d	0.00
Cent_04_15	12.3	8.30	21.6	751	12.4	12.3	14.5	8.38	2.17	143	2.55	1.15	138	291	n.d	3.19
Cent_05_15	10.4	7.23	21.2	649	10.7	11.0	13.9	5.57	2.08	82.6	2.82	0.90	123	238	n.d	9.44
Cent_06_15	11.9	8.27	23.1	721	12.2	11.9	14.1	4.06	1.88	74.6	3.05	0.34	106	197	n.d	3.90
Cent_07_15	10.2	7.17	20.2	629	10.5	11.0	13.7	6.61	2.23	114	3.48	1.27	141	296	n.d	6.62
Cent_08_15	7.76	5.61	15.8	428	7.53	8.10	9.46	4.56	1.68	82.1	3.05	0.32	118	246	n.d	8.60
Cent_09_15	9.87	7.57	19.9	823	12.2	11.5	10.3	4.16	0.58	70.3	1.75	0.32	110	211	n.d	0.59
Cent_10_15	9.68	7.42	18.4	675	11.3	11.4	6.20	3.59	0.18	62.4	0.95	0.25	118	223	n.d	0.00
Cent_11_15	12.4	8.68	23.6	940	12.9	12.8	8.89	3.22	0.88	34.4	1.67	1.25	96.1	167	n.d	0.00
Cent_12_15	9.62	8.34	22.2	774	11.7	13.3	14.6	5.00	1.01	52.7	10.2	1.15	208	377	n.d	7.02
Cent_01_16	3.25	0.93	13.6	331	4.85	4.66	12.0	4.02	1.95	43.4	11.6	1.18	93.6	174	n.d	17.4
Cent_02_16	2.62	0.70	13.6	384	3.98	5.32	12.8	4.31	2.48	40.8	11.0	1.96	113	201	n.d	27.0
Cent_03_16	0.72	0.60	9.04	266	2.96	2.88	9.17	2.93	1.43	27.2	6.60	0.90	94.4	168	n.d	13.0
Cent_04_16	1.92	0.80	11.9	400	3.02	4.75	10.7	3.26	1.47	41.5	11.2	1.36	91.1	174	n.d	13.1
Cent_05_16	4.59	1.91	19.1	559	2.04	7.80	12.9	4.49	2.02	45.9	11.2	1.58	97.0	168	n.d	10.3
Cent_06_16	6.03	1.40	20.8	698	7.53	6.66	13.1	3.63	1.74	58.0	10.7	1.63	93.7	151	n.d	6.27
Cent_07_16	1.04	0.38	6.20	211	2.43	2.55	6.68	3.88	1.35	34.6	7.42	0.80	81.6	165	n.d	5.01
Cent_08_16	2.21	0.59	10.7	353	2.47	4.26	8.69	2.59	1.64	34.6	9.29	0.95	75.1	143	n.d	10.5
Cent_09_16	3.48	0.89	18.5	615	6.86	7.22	14.0	5.99	2.27	46.3	11.2	1.81	108	197	n.d	14.1
Cent_10_16	2.06	0.95	12.6	365	3.57	5.57	12.8	4.80	2.55	47.3	13.6	1.76	105	198	n.d	16.6
Cent_11_16	0.93	0.45	8.42	298	2.93	3.34	10.6	3.99	1.81	60.7	9.37	1.52	117	239	n.d	9.06
Cent_12_16	5.57	1.37	15.4	401	6.32	5.18	15.6	7.09	3.15	55.4	12.3	1.80	112	230	n.d	12.0
Cent_13_16	7.67	1.46	20.4	649	1.59	6.28	10.9	3.85	2.57	50.3	11.0	2.15	119	261	n.d	10.5
Cent_14_16	6.75	1.87	20.8	772	8.29	7.51	15.7	5.08	1.84	45.8	10.2	1.81	111	186	n.d	4.85
Cent_15_16	1.54	0.57	10.6	348	3.12	3.72	11.4	4.21	2.53	41.8	7.98	1.34	105	216	n.d	11.3
Cent_16_16	3.06	1.18	17.7	496	4.93	6.54	10.6	4.66	2.59	47.5	8.29	1.58	118	205	n.d	9.04
Cent_17_16	6.78	1.46	18.2	548	1.10	5.32	9.73	3.42	2.13	41.5	7.97	1.49	104	226	n.d	4.31
Cent_18_16	3.10	0.64	9.69	250	3.35	3.22	11.6	7.17	3.56	46.8	13.3	1.61	99.1	194	n.d	14.1
Cent_19_16	1.29	0.84	12.5	361	4.21	4.43	12.9	5.46	2.73	51.2	10.9	1.43	132	236	n.d	9.03
Cent_20_16	3.58	1.64	19.2	664	5.50	6.74	15.3	4.30	1.57	64.1	10.4	1.16	110	202	n.d	6.63
Cent_21_16	3.91	1.79	20.7	500	5.52	6.82	14.1	6.37	2.27	45.7	9.11	1.37	126	225	n.d	15.1

Concentrations (mg/100g) of the hop volatiles are heat mapped: green cells represent the highest concentration and red cells represent the lowest concentrations.
(n.d) – not detected