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Ambient orchard volatiles from California almonds

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ABSTRACT

The volatile emissions of various plant parts of almonds have been studied via various techniques in the past. These analyses have typically been performed on single cultivars and hence may not be representative of the volatiles found in an entire almond orchard. Recent reports suggest some almond volatiles exhibit semiochemical activities for the navel orangeworm (NOW), a major insect pest of almonds; thus, the volatile composition of the comprehensive almond orchard would be helpful to research concerning NOW. The ambient volatile emissions of an almond orchard containing the cultivar Nonpareil and associated pollenizers were collected at four intervals during the 2009 growing season from orchards in the south Central Valley of California. The volatiles hexanal, octanal, nonanal, benzaldehyde, acetophenone, ethyl benzoate, methyl salicylate, and phenol were consistent in their presence and in relatively high amounts. The orchard volatile composition was analyzed via electroantennogram (EAG) analysis, which produced strong responses from NOW antennae.
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1. Introduction

The Central Valley of California is the world's top producer of almonds, *Prunus dulcis* (P. Mill) D.A. Webb, with 710,000 bearing acres (USDA-NASS, 2010) and supplies nearly 80% of the world's almond demands. The Nonpareil almond variety represents the most widely planted cultivar in the Central Valley and comprises ca. 37% of the total acres of varieties grown. Other cultivars and pollenizers such as Butte, Carmel, Padre, Sonora, Monterey, and Aldrich combined comprise ca. 54% of the total almond acreage (USDA-NASS, 2009).

The volatile emissions of almonds and corresponding plant parts have been investigated with reports on the steam distillation of dried almond hulls (Buttery et al., 1980), *ex situ* whole damaged and undamaged almonds (Beck et al., 2008), and the *in situ* emission of Nonpareil almonds over a growing season (Beck et al., 2009), among others. However, little is known regarding the general atmospheric bouquet emitted from an orchard and what affect the orchard bouquet may have on host-plant locating behavior of insects.

The navel orangeworm (NOW), *Amyelois transitella* (Walker) (Lepidoptera: Pyralidae), is a major insect pest of California tree nuts, almonds in particular. Feeding damage by NOW larvae reduces nut kernel quality resulting in wide-spread economic loss to the almond industry. In addition to the direct feeding damage, NOW larvae have been shown to contribute to contamination by *Aspergillus flavus*, a ubiquitous fungus of tree nut orchards that is capable of producing aflatoxins, which represent a serious food safety problem due to their carcinogenic and teratogenic attributes (Campbell et al., 2003).

Host-plant location by an insect is in part dependent upon its ability to detect specific semiochemicals, and a complex mixture of ubiquitous plant volatiles may be necessary to elicit an appropriate response from insects to their host-plant (Bruce et al., 2005).

The goals of this investigation were to: collect the ambient volatile emission of almond orchards from the southern Central Valley of California during a typical growing season (ca. April through August); identify the major volatiles emitted and their relative quantities; and, determine the general chemoreceptivity of female NOW adult moths to the collected volatile bouquet.

2. Results and discussion

A total of 25 volatiles were collected in minor to major amounts, separated via GC–MS, and identified (Table 1). Once desorbed, the volatiles were quantified using an internal standard and the relative amount of each was calculated. Of the 25 principal volatiles collected from the almond orchards, eight were consistent throughout the spring to summer collection periods, and in relatively high (>20 ng m^{-3}) amounts: hexanal, octanal, nonanal, benzaldehyde, acetophenone, ethyl benzoate, methyl salicylate, and phenol. A number of other identified volatiles were either

Abbreviations: EAG, electroantennogram; NOW, navel orangeworm; RIs, retention indices.

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Table 1
Ambient almond orchard volatile amounts from Kern County, California collected during the 2009 growing season.

#	Compound ID	DB-Wax[a]			Ambient almond				Avg	s.e.
		RT	RI		Volatile amounts (ng m^{-3})[b]					
			Calc'd	Lit	Collection 1	Collection 2	Collection 3	Collection 4		
1	Hexanal	6.49	1077	1077	26.8	49.3	31.1	23.3	32.6	5.8
2	Undecane	6.76	1088	1100	0.0	0.0	0.0	7.0	1.8	1.8
3	Cumene	8.77	1167	1168	3.0	5.3	0.0	3.5	3.0	1.1
4	Heptanal	9.11	1180	1180	12.2	13.1	11.4	13.1	12.4	0.4
5	Limonene	9.48	1194	1195	3.7	0.6	0.0	0.0	1.1	0.9
6	p-Cymene	11.59	1266	1264	1.8	4.8	4.5	6.9	4.5	1.0
7	Octanal	12.17	1285	1284	78.1	108.2	49.6	50.1	71.5	13.9
8	Nonanal	15.42	1390	1389	237.4	338.4	161.2	169.4	226.6	41.0
9	Acetic acid	17.29	1451	1447	11.1	3.9	13.9	11.2	10.0	2.1
10	Decanal	18.65	1495	1495	3.8	0.0	18.1	21.7	10.9	5.3
11	Benzaldehyde	19.20	1515	1516	306.8	165.3	306.6	1971.5	687.5	429.3
12	Benzonitrile	21.63	1595	1597	3.9	1.7	3.5	10.0	4.8	1.8
13	γ-Pentanolactone	21.78	1601	1600	3.4	8.1	10.8	6.2	7.1	1.5
14	Methyl benzoate	22.19	1615	1616	7.7	9.3	14.8	7.0	9.7	1.8
15	Sabina ketone[c]	22.51	1626	n/a	12.6	0.0	5.3	3.2	5.3	2.7
16	Phenylacetaldehyde	22.70	1633	1636	11.9	10.4	19.0	25.9	16.8	3.6
17	Acetophenone	22.98	1642	1645	151.5	224.8	263.8	355.4	248.9	42.5
18	Ethyl benzoate	23.51	1661	1661	51.9	59.7	23.3	31.8	41.7	8.5
19	Salicylaldehyde	23.72	1668	1673	5.4	7.2	5.3	9.8	6.9	1.1
20	γ-Hexanolactone	24.39	1691	1699	4.3	9.6	13.9	13.5	10.3	2.2
21	Naphthalene	25.44	1730	1734	0.0	0.0	1.4	3.0	1.1	0.7
22	Methyl salicylate	26.46	1767	1771	122.7	191.7	76.7	77.5	117.2	27.1
23	1-Methylnaphthalene	29.35	1876	1884	0.0	11.8	14.8	0.0	6.6	3.9
24	Phenol	32.48	2002	2000	74.7	83.7	74.4	87.8	80.2	3.4
25	p-Anisaldehyde	32.84	2017	2024	3.5	0.0	0.0	11.3	3.7	2.7
	Collection dates				4/23–5/5	6/30–7/7	7/7–7/15	8/11–8/21		
	Relative nut phenology				kernel filling	hull split[d]	hull split[d,e]	hull split[f]		

[a] RI calculated relative to *n*-alkanes on DB-Wax and compared to literature and internally generated data base values.
[b] Ambient volatile amount calculated using total analyzed relative amount of each volatile per volume of air collected (total number of minutes × flow rate for each Tenax cartridge).
[c] Tentative assignment, compound not available for authentication.
[d] Primarily relative to Nonpareil.
[e] Start of hull split for pollenizers.
[f] Primarily relative to pollenizers, late for Nonpareil.

transient and/or at a very low relative concentration within the ambient orchard environment. The average values (Avg) shown in Table 1 provide a quick reference for relatively high amount of volatiles (a large Avg value), and the standard error (s.e.) describes either consistent or transient emission over the four collections. For instance, a low s.e. may indicate consistent emission of that volatile (*e.g.*, heptanal with an average emission of 12.4 ± 0.4 ng m^{-3}); whereas a larger s.e. may indicate either an upward or downward trend in volatile emission (*e.g.*, phenylacetaldehyde, which increases over time, with an average emission of 16.8 ± 3.6 ng m^{-3}). It should be noted that alkyl aromatics were also detected and were identified components from orchard maintenance pesticide sprays; however, these residual volatile amounts were not evaluated for this report.

Benzaldehyde, a ubiquitous plant volatile known as a primary component of bitter almond oil (Arctander, 1960), was detected as the most prevalent volatile with a range of 165–1972 ng m^{-3}. Benzaldehyde, as well as all of the aldehydes, was detected as both the aldehyde and the corresponding acid. This is presumably due to air oxidation of the aldehydes while absorbed on the Tenax medium. To verify this assumption, the aldehydes detected in this study were loaded onto a cartridge of Tenax and placed in an oven at 38 °C with airflow of 4 l min^{-1}. The components were desorbed after one week and the corresponding acids were detected in varying amounts. Thus, the aldehyde amounts shown in Table 1 are understood to be a combination of both the aldehyde and acid form, and include the relative amounts for their detected associated acids.

The C_6–C_{10} alkyl aldehydes, of which hexanal, octanal, and nonanal were consistently detected and in relatively large amounts, along with lesser amounts for heptanal and decanal, are known as fatty acid breakdown products (Frankel, 1982). Nonanal, the volatile with the third highest presence, has been detected in other almond volatile investigations (Buttery et al., 1980; Beck et al., 2008, 2009), yet the studies by Beck et al. did not report finding the other alkyl aldehydes shown in Table 1. The presence of the C_6–C_{10} alkyl aldehydes in a previous report by Buttery et al. bring to question the specific reason for presence and/or increased emission of this class of compounds. It should also be emphasized that the ambient volatiles collected during this study may be representative of what insects encounter while present in the orchards, and are not necessarily only from the almond tissues, but may also originate from soil, microbes, and/or weeds. The volatiles noted earlier from orchard maintenance sprays provide a good example of other orchard content odors.

Another consistent and major volatile was acetophenone followed by other aryl compounds with moderate volatile amounts—ethyl benzoate, methyl salicylate, and phenol. Acetophenone, a ubiquitous volatile from several plant families (El-Sayed, 2010), showed a progressive increase in ambient volatile presence (Table 1) over the growing season. Ethyl benzoate is a ubiquitous volatile emitted from numerous plants (El-Sayed, 2010), including almonds (Beck et al., 2008). Ethyl benzoate has been reported as possessing some ability to attract NOW, in addition to the structurally similar methyl benzoate (Price et al., 1967), a minor but consistent volatile in this study. Similarly, the ubiquitous plant volatile methyl salicylate has demonstrated semiochemical activity (El-Sayed, 2010) for a number of species. A surprising volatile detected was phenol, for which this would be the first report of its detection in almonds. Though this report does