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TECHNICAL PAPER

Identification and evaluation of volatile organic compounds evolved during solarization with almond hull and shell amendments

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ABSTRACT

Biosolarization is a fumigation alternative that combines solarization with organic amendments to suppress pests and pathogens in agricultural soils. The generation of volatile biopesticides in the soil, stemming from biodegradation of carbon-rich amendments, contributes to pest inactivation. The purpose of this study was to (1) profile volatiles that may contribute to pest control under field conditions and (2) measure volatile compounds that may present nuisance or exposure risks for humans near biosolarized fields where larger-scale anaerobic degradation of residues occurs. Biosolarization was performed using prominent agricultural waste products, hulls and shells from several almond varieties as soil amendments. After 8 days of biosolarization, soil samples were analyzed using solid phase microextraction-gas chromatography coupled to mass spectrometry. Volatile fatty acids and ketones made up 85% of biosolarized soil headspace, but terpenes, alcohols, aldehydes, esters, and sulfides were detected as well. Different almond variety residues produced distinct volatile profiles, and nonpareil-amended soils had a much richer and more diverse profile, as well as a fivefold greater VOC abundance, than pollinator-amended soil. Identified volatiles with low US recommended exposure limits were quantified via internal and external standards, including acetic acid, 2-butanone, butanal, hexanal, and phenylethyl alcohol. Across biosolarization treatments, headspace concentrations of selected compounds did not exceed 1 mg/m^3. This study demonstrates that almond processing residues recycled into the soil as biosolarization substrates produce a high diversity of bioactive degradation compounds on a field scale, with low potential of non-target risks to humans.

Implications: This manuscript has implications for two policy goals in the state of California: to reduce landfill disposal of organic waste, and to reduce emissions from soil fumigants. Almond hulls and shells are an increasing source of organic waste, and novel recycling strategies must be developed. Here, recycling almond residues as soil amendments promoted the rapid formation of VOCs which may act as alternatives to chemical fumigants. Headspace concentrations of potentially deleterious VOCs produced from treated soil were low, on the order of parts per billion. These results will help achieve policy goals by expanding waste usage and fumigation alternatives.

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Introduction

Soil-borne pathogens, including parasitic nematodes, fungi, and bacteria, jeopardize crop production. Historically, pest management has been achieved via chemical fumigants, including methyl bromide, 1,3-dichloropropene, chloropicrin, and metam sodium, which are applied to soil before the planting season (EPA 1993). Fumigants are characterized by high toxicity and volatility, allowing quick diffusion into soil and elimination of pests within days when applied under plastic tarps (EPA 2005). Usage of these pesticides in California is high; almost 13 thousand combined tons were applied statewide in 2017 (DPR 2018). High toxicity and volatility make fumigants particularly hazardous to farm workers (Burgess et al. 2000; Oriel et al. 2009) and communities near fields (Lee et al. 2002; O'Malley et al. 2004). Despite regulations that aim to reduce this safety risk (EPA 2016), persistent ambient levels of fumigants and their breakdown products have been detected in the California Central Valley (Baker et al. 1996; Wofford et al. 2014), and accidental exposure risk can never be fully eliminated.

Certain biogenic volatiles may contribute to similar pest control without the toxicity of conventional soil fumigants. Plants, fungi, and microbes generate diverse profiles of volatile organic compounds (VOCs) for a variety of purposes, including cell-cell signaling, interspecific communication, carbon release, and as defense against pathogens or competitors (Campos, Pinho, and De, Freire 2010; Schulz-Bohm et al. 2018). Common biogenic VOCs include alcohols, volatile fatty acids (VFAs), aldehydes, ketones, sulfides, terpenes, esters, and aromatic compounds. VOCs can travel through the soil in both water and air fractions, and

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can easily cross cell membranes where they may enact toxicological effects on pathogens (Gray, Monson, and Fierer 2010; Terra et al. 2017).

Stimulating the activity of native microbes can be an effective strategy to introduce microbial VOCs (mVOCs) to the soil. In this case, fresh or processed organic residues are incorporated directly into the soil where they can be metabolized by native saprophytes. Under microaerobic conditions, this degradation process can emit a diverse array of fermentative mVOCs; decomposition may also emit more VOCs than fresh residues alone (Gray, Monson, and Fierer 2010). This method can also take advantage of low-value biomass as soil amendments, which can be available near field sites in high volumes (Achmon et al. 2016; Matteson and Jenkins 2007; Oldfield et al. 2017). Despite potential economic benefits, VOC emissions from soil amended with organic residues have been studied less than living plant tissue.

Biosolarization is one method that uses the anaerobic degradation of plant residues to improve the efficacy of traditional soil solarization (Gamliel and Stapleton 1997). Solarization, which disinfests soil by heating through a plastic tarp, requires fallow soil for 4–6 weeks and is climate dependent (Katan 1981). During biosolarization, soils are amended with biomass and covered with a clear tarp to maximize both anaerobic degradation and soil heating (Blok et al. 2000). These two modes of action work synergistically to increase efficacy and to decrease treatment time from weeks to days (Simmons et al. 2016). Previous field studies have established effective biosolarization using low-cost food processing waste: for example, tomato pomace amendments to control weeds, and anaerobic digestate to control both weeds and fungal pathogens (Achmon et al. 2017; Fernández-Bayo et al. 2018). Almond processing residues (hulls and shells) have immense promise in biosolarization for several reasons: these residues are rich in soluble sugars, so rapid degradation is expected (Holtman et al. 2015; Offeman et al. 2014); lab studies have found that extracts from soils that were biosolarized using almond residues were toxic to phytoparasitic nematodes (Fernández-Bayo et al. 2020); residues are increasingly abundant and can be supplied at low cost; and almond hulling is typically co-located geographically with other fruit, nut, and vegetable production in CA that historically rely on fumigation reducing transport cost (ABC 2020).

The increased performance of biosolarization over traditional solarization has been linked to VFA accumulation (Simmons et al. 2016), though other VOCs may be present. To date, few studies have characterized the VOC profile of solarized soil. One study found sulfides, alcohols, and aldehydes were emitted from solarized soil amended with brassica crops, however, many other VOCs were unable to be identified due to the analytical method used (Gamliel and Stapleton 1993). While low in toxicity, these VOCs may be associated with some risk to environmental health and safety; biogenic volatiles such as alcohols and aldehydes can be more reactive than anthropogenic VOCs, thus a potentially significant source of air pollution (Cadena et al. 2009; Malkina et al. 2011). Worker health and safety has also been of concern in cases where microbial degradation occurs on a large scale, such as composting facilities and dairy silages (Davidson et al. 2018; Domingo and Nadal 2009).

The goal of this study was to characterize VOCs produced during biosolarization. Field biosolarization was established using almond residue amendments sourced from nonpareil and associated pollinator varieties. Volatiles were identified in biosolarized soils, non-amended solarized soil, and the non-solarized soil mixtures using headspace solid phase microextraction coupled to gas chromatography and mass spectrometry (SPME-GC-MS). Differences in volatile profile between residue types were evaluated qualitatively, and the detected volatiles were reviewed for documented pesticidal activity. In addition to identifying pest-control-promoting VOCs produced during biosolarization, other potential health and safety risks were identified by quantifying select volatiles of occupational health concern.

Materials and methods

Microcosm preparation

The field site was located in Davis, CA (USA), and soil properties were previously reported (Fernández-Bayo et al. 2017). Air-dry soil from the top 15 cm was sieved (2.0 mm) and stored at room temperature. Almond residues for soil amendments including hulls and shell from two varieties, nonpareil (NPL) and a pollinator variety mix (PLM), were received whole (North State hulling Coop, Chico CA); properties were previously reported (Fernández-Bayo et al. 2020). A subset of each residue was ground using a laboratory blender and sieved (2.0 mm). Sieved soil was amended with 1.75–2.5% sieved NPL or PLM (dry weight) and wetted to field capacity (20% moisture content, wet basis). Non-amended (NA) soil was wetted to field capacity but received no residues. Soil was aliquoted into 100 mL plastic sample bags with 50 g each of wetted soil and sealed. Microcosms were equilibrated overnight at 4 °C.

Field treatment

The 38.4 × 16.8 m field site was subdivided into 4.9 × 1.8 m plots and randomly assigned one of five treatments, with three replicates each: solarization with no amendment (NA), biosolarization using 1.75% or 2.5% NPL, or biosolarization using 1.75% or 2.5% PLM. Biosolarized plots were amended and tilled down to 15 cm to achieve amendment rates of 1.75% or 2.5% dry weight (22.6 or 32.6 tons/acre). Mesocosms were embedded 7 cm deep into plots corresponding to the same amendment rate and residue type in triplicate. Three microcosms were collocated in each plot. Plots were set with surface drip-irrigation tape and sealed with total impermeable film (TIF, TriCal, Hollister, CA). Additional control plots were established (CON), which received no amendment and no TIF. With the exception of controls, all plots and mesocosms underwent solarization under plastic film for 8 days, after which they were retrieved and stored airtight at 4°C until analysis. Soil from mesocosms that had not underwent field exposure (non-solarized) and soil from the microcosms that had been treated for 8 days (solarized and controls) underwent VOC analysis.

HS-SPME-GC-MS analysis

Soil (10 g) from mesocosms was transferred to 20-mL glass amber headspace vials (Agilent, Santa Clara CA). An internal standard (IS), cyclohexanol-D_{12} in milli-Q water, was pipetted onto the soil surface immediately before the PTFE cap was sealed to achieve a concentration of 10 μg/L. Cyclohexanol-D_{12} was chosen because it was functionally similar to the analytes of interest, soluble in water, and was not an expected analyte of the sample. VOCs were analyzed on an 7890A gas chromatograph coupled to an Agilent 7000 triple quadrupole mass spectrometer operated in scan mode and fitted with a multipurpose autosampler (Gerstel, Linthicum MD). To extract volatiles into the headspace, soil vials were incubated at 60 °C and agitated at 500 rpm for 35 mins. A 1 cm DVB/CAR/PDMS (divinylbenzene, carboxen, and polydimethylsiloxane) solid phase microextraction (SPME) fiber (Sigma–Aldrich, St. Louis MO) was then exposed to the soil headspace for 15 mins at 60 °C. The fiber was desorbed into the GC inlet at 250 °C for 10 mins on splitless mode. VOCs were separated on a polar VF-WAXms column (30 m x 250 μm x 0.25 μm, Agilent) using He as a carrier gas at column flow rate of 1.0 mL/min. The oven was held at 35 °C for 5 mins, increased at a rate of 6 °C per min from 35° C to 250 °C, and was then held at 250 °C for 5 mins. Experimental Kováts retention indices (KI) were obtained by injecting a homologous series of alkanes (C_9 – C_{18}). To identify the VOCs, the mass spectrum of each peak was obtained via the Agilent Unknowns Analysis software.

VOC identification

Volatiles were identified by comparing the mass spectra fragment patterns to those in the NIST library using the Mass Spectral Search Program software, and the experimentally obtained KI was compared to those reported in the literature (Linstrom and Mallard 2014). Spectra that were at least an 80% match and had KI within ± 20 literature values were considered. Compounds were classified into chemical class based on functional group (alcohols, aldehydes, ketones, organic acids, sulfides, esters, aromatics, or terpenes) and identified as present or absent for each soil treatment. The relative peak area (RPA, Equation (1)) was determined for each peak to normalize for instrument and matrix variation according to previous methods; while these values do not correspond to headspace concentration, the obtained relative values can be used to compare the difference in volatile profiles among different treatments (Xiao et al. 2014). The RPA was used to determine the relative abundance (Equation (2)) for each compound in a given sample, and values of co-located mesocosms were averaged to determine the RPA and relative abundance of each compound for each replicate plot.

$$\begin{aligned}&\mathit{Relative\ Peak\ Area}\\&\quad=(\mathit{Peak\ Area})/(\mathit{Internal\ Standard\ Peak\ Area})\end{aligned}\tag{1}$$

$$\begin{aligned}&\mathit{Relative\ Abundance}\\&\quad=(\mathit{RPA\ of\ compound})/(\mathit{Total\ RPA\ for\ sample})\end{aligned}\tag{2}$$

VOC quantification

Identified compounds with low recommended exposure limits (REL) according to the US National Institute of Occupational Safety and Health (NIOSH 2005) were selected and quantified. For these select compounds, an external calibration curve of pure standards (≥98%, 20–400 μg/L in methanol) were injected onto devolatilized soil. These compounds included butanal, hexanal, benzaldehyde, phenylethyl alcohol, acetic acid, 2-butanone, and 2,3-butanedione (Sigma–Aldrich, St. Louis MO). An internal standard (IS), cyclohexanol-D_{12} in milli-Q water, was pipetted onto the soil surface immediately before the PTFE cap was sealed to achieve a concentration of 10 μg/L. Spiked soils were analyzed using the same methods as the samples. The relative peak area of the standards was calculated and compared to the relative peak area of the samples. This assumed the following regarding VOC concentration: (1) tarp removal after 8 days of solarization represented the maximum concentration, as volatiles will emit or decompose quickly under aerobic conditions according to previous studies

(Achmon et al. 2017, 2016); (2) the headspace concentration detected in SPME vial represents a maximum headspace concentration of each compound due to the extreme extraction conditions (high heat, rapid shaking, high incubation time); (3) amendment rates used in the field trial are representative, or higher than, what will typically be applied in the field to control pests.

Statistical analysis

All data analysis was performed in R Studio (2010, version 1.2.1335). To characterize the VOC profile for the soil, first the alpha diversity (richness) and Shannon diversity were quantified according to compound relative abundance. To further characterize volatile profile, Bray–Curtis differences in compound composition were calculated using the vegan package in R (Oksanen 2008) from relative abundance and plotted using nonmetric multidimensional scaling (NMDS). Analysis of variance using distance matrices (Adonis) analysis determined how the factor (residue, solarization) effected the volatile profile, and similarity percentage analysis (SIMPER) followed by t-test were used to determine which compounds contributed to differences in VOC profile. ANOVA and Tukey's HSD compared differences in richness, diversity, and compound class abundance between treatments. Finally, the RPA of the most prevalent VOCs, as well as total VOCs, were compared using nonparametric Kruskal Wallis and Dunn's test due to non-normality in volatile distribution.

Results

Compound identification

A total of 56 VOCs was identified on the basis of 80% match to the NIST library and comparison to the KIs from literature values (Table 1). These included 6 alcohols, 3 aldehydes, 5 aromatics, 5 esters, 21 ketones, 7 VFAs, 1 sulfide, and 8 terpenes. The presence and absence of each compound was determined for each of the soil treatments (Table 2). A maximum of 15 compounds were detected in non-solarized soil, mainly terpenes and some aromatics, ketones, and volatile fatty acids; all 56 were detected in solarized soil.

Volatile profiling

Compound richness and diversity were determined for each treatment (Table 3). Residue type affected the richness and diversity of volatiles ($P < .001$ for both), and overall NPL amended soils were richer and more diverse than PLM and NA soil ($P < .001$ for both). Solarization resulted in increased compound richness and diversity ($P < .001$ for both) compared to the pre-treatment, non-solarized samples of the same composition. Amendment rate had no significant effect ($P = .295$, 0.745 for richness, diversity).

Nonmetric multidimensional scaling (NMDS) was used to visualize the Bray–Curtis dissimilarity between amended soil treatments according to the relative peak area of VOCs detected in each sample (Figure 1); due to low compound frequency, NA soils were omitted. Adonis analysis indicated that residue type and solarization explained difference in dissimilarity between treatments ($P < .001$ for both), but not amendment rate ($p = .842$).

Compositional differences in amended soils were compared using SIMPER analysis for the four treatments indicated in the NMDS biplot (Figure 1). Of the 56 compounds analyzed, 21 compounds represented over 90% of the dissimilarity between the four clusters, mainly terpenes, ketones, and organic acids (Table 4). Amended soils that had not undergone solarization completely overlapped regardless of PLM or NPL amendment; t-tests indicated no significant difference between compound relative abundances ($P > .05$ for all). The same was observed for amended samples that underwent solarization ($P > .05$ for all). The NPL residues pre- and post-solarization were the only clusters to separate completely: solarized soil had greater 2-butanone and isobutyric acid ($P = .008$, 0.007), but non-solarized soil had greater 2-carene abundance ($P = .011$). Finally, non-solarized and solarized soils amended with PLM residues had little separation, no significant differences were found in compound relative abundance ($P > .05$ for all).

Compound class relative abundance was also analyzed, and further compositional differences were observed. Non-solarized soil headspace was dominated by terpenes, aromatic compounds, and ketones, with trace VFAs: 80–89, 3–11, 0–15, and 0–2%, respectively, and did not significantly vary by soil amendment composition (Figure 2).

After solarization (Figure 3), terpene abundance decreased significantly ($P < .001$), and VFA and ketone abundance significantly increased ($P = .001$ and 0.047, respectively). VFAs dominated the solarized soil profile in all treatments (50–94%), but levels were highly variable and not statistically different between residue treatments. Ketone abundance was significantly affected by residue ($P = .002$), with NPL-amended soil having higher ketone abundance in solarized plots (42%) than both PLM (10%) and non-amended control (0%). Terpenes were also significantly affected by residue ($P = .031$), with PLM-amended soils having higher terpene abundance in solarized plots (18%) than nonpareil-amended soils (1%). More functional group classes were observed among amended solarized soils, including

Table 1. Compounds identified in headspace of soil biosolarized with almond hulls and shells using solid phase microextraction gas chromatography coupled to mass spectrometry.

Compound	MP[a]	rt[b]	KI exp[c]	KI std[d]	KI lit[e]	Compound	MP[a]	rt[b]	KI exp[c]	KI std[d]	KI lit[e]
Alcohols						*Ketones*					
1-Heptanol	86	16.9	1454		1443	2-Butanone*	90	2.7	929	929	914
1-Hexanol	90	14.7	1357		1357	2-Decanone	85	17.5	1483		1482
2-Butanol	87	5.3	1009		1028	2-Heptanone	90	9.9	1165		1174
2-Butanol (R)	87	5.3	1009		1028	2-Hexanone	89	7.0	1062		1075
2-Ethylhexanol	85	17.7	1489		1488	2-Nonanone	87	15.2	1375		1388
Isoamyl alcohol	92	11.4	1223		1229	2-Pentanone	90	4.0	967		972
Aldehydes						2-Undecanone	88	19.7	1590		1600
3-Methyl-butanal	84	2.9	935		917	2,3-Butanedione	89	4.1	971	967	964
Butanal*	91	2.5	921	922	905	2,3-Hexanedione	97	8.6	1118		1138
Hexanal*	90	7.0	1063	1063	1078	2,5-Hexanedione	88	18.0	1505		1515
Aromatics						3-Methyl-2-Butanone	88	3.1	940		925
Acetophenone	88	20.8	1643		1645	3-Methyl-2-Pentanone	94	4.9	996		1016
Benzaldehyde	87	18.2	1515	1517	1508	3-Octanone	91	11.7	1234		1240
Guaiacol	87	24.7	1862		1862	4-methyl-2-Heptanone	81	10.5	1187		1206
Phenol	85	27.2	2015		2008	5-Methyl-2-Heptanone	86	11.8	1238		1256
Phenylethylalcohol*	88	25.6	1916	1922	1912	5-methyl-2-Hexanone	87	8.7	1124		1141
Esters						6-methyl-2-Heptanone	85	11.3	1219		1236
Butyl acetate	92	6.8	1056		1064	Acetoin	94	13.3	1297		1283
Butyl butyrate	92	10.7	1193		1205	Methyl isobutyl ketone	90	4.7	988		1006
Ethyl Acetate	94	2.6	925		921	Methyl vinyl ketone	88	3.4	949		948
Ethyl pentanoate	87	8.5	1116		1128	Sulcanone	87	14.0	1328		1339
Ethyl propionate	86	3.6	956		956	*Terpenes*					
Volatile Fatty Acid						1-Decene	92	5.8	1024		1039
Acetic acid*	90	17.0	1459	1467	1452	2-methylisoborneol	90	19.6	1585		1602
Butyric acid	94	20.6	1632		1628	3-Carene	87	8.5	1114		1112
Hexanoic acid	90	24.6	1853		1849	a-Copaene	91	17.2	1469		1475
Isobutyric acid	91	19.4	1572		1555	camphor	88	17.9	1500		1509
Isovaleric acid	88	21.3	1673		1680	camphor (S)	89	17.9	1501		1490
Propanoic acid	90	18.8	1543		1550	Limonene	98	10.1	1172		1189
Valeric acid	90	22.7	1743		1744	o-Cymene	89	11.8	1239		1254
Sulfides											
Dimethyl disulfide	89	6.6	1050		1061						

*Compounds selected for quantification.
[a] Mean percentage match (MP) with NIST library.
[b] Retention times (rt) of compounds (mins).
[c] Kovat's indices calculated for compounds found in this study (KI exp).
[c] Kovat's indices calculated for select pure standards (KI std), n = 5.
[d] Kovat's indices obtained from previous studies (KI lit) indexed in the NIST database (Linstrom and Mallard 2014).

alcohols, aldehydes, esters, and sulfides, but these classes were lower in relative abundance (<5%).

To better understand differences in VOC quantity, treatments were then compared by peak area, normalized across runs using the internal standard (RPA). Ten compounds represented 85% of the total RPA in the analysis and were found primarily in solarized soil. These included the VFAs acetic, butyric, isobutyric, valeric, isovaleric, and hexanoic acid, and the ketones 2-butanone, 2-pentanone 2,3-butanedione, and acetoin (Figure 4). According to the Kruskal–Wallace test, isobutyric acid, 2-butanone, valeric acid, 2,3-butanedione, and isovaleric acid were all elevated in NPL-amended soils compared to PLM- and non-amended soil (P = .024, 0.005, 0.037, 0.005, 0.037, respectively). Butyric acid, acetic acid, 2-pentanone, and hexanoic acid levels were not significantly affected by residue type (P = .201, 0.183, 0.075, 0.201, respectively). Acetoin was only detected in one plot of the NPA soils, and thus could not be analyzed despite having high RPA. The total VOC peak area was also significantly affected by residue type ($P < .001$), where NPL soils had fivefold greater total VOC peak area than the PLM, and 11-fold greater VOC peak area than NA soils. There were no significant differences between the PLM and the NA soil for either total RPA or individual compound RPA.

VOC quantification

The quantity of certain compounds considered potentially hazardous based on NIOSH recommended exposure limits (REL) was estimated by comparison to relative peak areas of pure standards. These included acetic acid, 2-butanone, butanal, hexanal, and phenylethyl alcohol. Only acetic acid headspace concentrations were within the range of the calibration curve used (>0.05 mg/m^3). Soil headspace reached concentration maximums between 0.07 and 0.38 mg/m^3 acetic acid, depending on treatment, and were higher for the nonpareil residues and 2.5% amendment rate (Table 5).

Table 2. Compounds identified in headspace of soil biosolarized with almond hulls and shells using solid phase microextraction gas chromatography coupled to mass spectrometry.

	Non-Solarized[a]						Solarized[b]				
Compound	NA[c]	PLM[d] 1.75	PLM[d] 2.5	NPL[e] 1.75	NPL[e] 2.5	CON[f]	NA[c]	PLM[d] 1.75	PLM[d] 2.5	NPL[e] 1.75	NPL[e] 2.5
Alcohol											
1-Heptanol	-	-	-	-	-	-	-	-	+	-	-
1-Hexanol	-	-	-	-	-	-	-	-	+	+	+
2-Butanol	-	-	-	-	-	-	-	-	-	+	-
2-Butanol (R)	-	-	-	-	-	-	-	-	-	+	+
2-Ethylhexanol	-	-	-	-	-	-	-	-	-	+	+
Isoamyl alcohol	-	-	-	-	-	-	-	-	-	+	+
Aldehyde											
3-Methyl-butanal	-	-	-	-	-	-	-	-	-	+	+
Butanal*	-	-	-	-	-	-	-	-	-	+	+
Hexanal*	-	-	-	-	-	-	-	+	+	-	+
Aromatic											
Acetophenone	-	-	-	-	-	-	-	-	+	+	+
Benzaldehyde	+	-	-	+	-	+	+	+	+	+	+
Guaiacol	-	-	-	-	-	-	-	-	+	+	+
Phenol	-	-	+	-	-	-	-	-	+	+	+
Phenylethylalcohol*	-	-	+	-	-	-	-	+	+	+	+
Ester											
Butyl acetate	-	-	-	-	-	-	-	-	-	+	+
Butyl butyrate	-	-	-	-	-	-	-	-	-	+	+
Ethyl Acetate	-	-	-	-	-	-	-	-	-	+	+
Ethyl pentanoate	-	-	-	-	-	-	-	-	-	+	+
Ethyl propionate	-	-	-	-	-	-	-	-	-	+	+
Ketone											
2-Butanone*	-	-	+	-	-	-	-	+	+	+	+
2-Decanone	-	-	-	-	-	-	-	-	+	+	+
2-Heptanone	-	-	-	-	-	-	-	-	+	+	+
2-Hexanone	-	-	-	-	-	-	-	-	-	+	+
2-Nonanone	-	-	-	-	-	-	-	-	+	+	+
2-Pentanone	-	-	-	-	-	-	-	-	+	+	+
2-Undecanone	-	-	-	-	-	-	-	-	+	+	+
2,3-Butanedione*	-	-	-	-	-	-	-	-	+	+	+
2,3-Hexanedione	-	-	-	-	-	-	-	-	-	+	+
2,5-Hexanedione	-	-	-	-	-	-	-	-	-	+	+
3-Methyl-2-butanone	-	-	+	-	-	-	-	-	+	+	+
3-Methyl-2-Pentanone	-	-	-	-	-	-	-	-	-	+	+
3-Octanone	-	-	+	+	-	-	-	+	+	+	+
4-Methyl-2-Heptanone	-	-	-	-	-	-	-	-	-	+	+
5-Methyl-2-Heptanone	-	-	-	-	-	-	-	-	-	+	+
5-Methyl-2-Hexanone	-	-	-	-	-	-	-	-	-	+	+
6-Methyl-2-Heptanone	-	-	-	-	-	-	-	-	-	+	+
Acetoin	-	-	-	-	-	-	-	-	-	+	-
Methyl isobutyl ketone	-	-	-	+	-	-	-	-	-	+	+
Methyl vinyl ketone	-	-	-	-	-	-	-	-	-	-	+
Sulcanone	-	-	-	-	-	-	-	-	+	+	+
Volatile Fatty Acid											
Acetic acid*	-	-	+	-	-	+	+	-	+	+	+
Butyric acid	-	-	-	-	-	+	+	+	+	+	+
Hexanoic acid	-	-	+	-	-	-	-	-	-	+	+
Isobutyric acid	-	-	-	-	-	+	+	+	-	+	+
Isovaleric acid	-	-	-	-	-	-	-	-	-	+	+
Propanoic acid	-	-	-	-	-	-	-	-	-	+	+
Valeric acid	-	-	-	-	-	-	-	+	-	+	+
Sulfide											
Dimethyl disulfide	-	-	-	-	-	-	-	+	+	+	+
Terpene											
1-Decene	-	-	-	-	-	-	-	-	+	-	-
2-methylisoborneol	-	-	-	-	-	-	-	+	+	-	+
3-Carene	-	+	+	+	+	-	-	-	+	+	+
a-Copaene	+	-	+	+	-	+	+	+	+	+	-
Camphor	-	-	+	-	-	-	-	+	+	+	-
Camphor (S)	-	-	+	-	-	-	-	+	+	+	+
Limonene	-	-	+	-	-	-	+	-	-	-	-
o-Cymene	-	-	+	-	+	+	+	+	+	+	+

Presence (+) or absence (-) is indicated for detected compounds and all soils treatments.
*Compounds selected for quantification.
[a] Soil mixtures that did not undergo solarization.
[b] Soil mesocosms embedded in the field 7 cm deep and solarized for 8 days.
[c] Soil receiving no amendment (NA).
[d] Soil amended with a hulls and shells from a pollinator variety mixture (PLM), 1.75 or 2.5% dry weight.
[e] Soil amended with a hulls and shells from Nonpareil variety (NPL), 1.75 or 2.5% dry weight.
[f] Soil mesocosms embedded field soil for 8 days, but received no amendment and no solarization (CON).

Table 3. Richness and diversity of volatiles detected in biosolarized soil headspace according to compound relative abundance.

	Richness		Diversity	
Soil Treatment	Non-Solarized[a]	Solarized[b]	Non-Solarized[a]	Solarized[b]
NA[c]	1 a	3.3 ± 3 a	0 c	0.57 ± 0.6 bc
PLM[d]	3.8 ± 3 a	10.8 ± 6 a	0.74 ± 0.8 bc	1.47 ± 0.5 ab
NPL[e]	2.3 ± 1 a	33.2 ± 10 b	0.61 ± 0.5 bc	2.1 ± 0.5 a

Values indicate mean ± standard deviation. Lowercase letters indicate treatments are significantly different according to two-way ANOVA using soil amendment and solarization as factors, followed by Tukey's HSD ($P < 0.05$).

[a] Soil mixtures that did not undergo solarization.

[b] *Soil mesocosms embedded in the field 7 cm deep and solarized for 8 days.*

[c] *Soil receiving no amendment (NA), n = 3.*

[d] *Soil amended with a hulls and shells from a pollinator variety mixture (PLM), 1.75 or 2.5% dry weight, n = 3 each.*

[e] *Soil amended with a hulls and shells from Nonpareil variety (NPL), 1.75 or 2.5% dry weight, n = 3 each.*

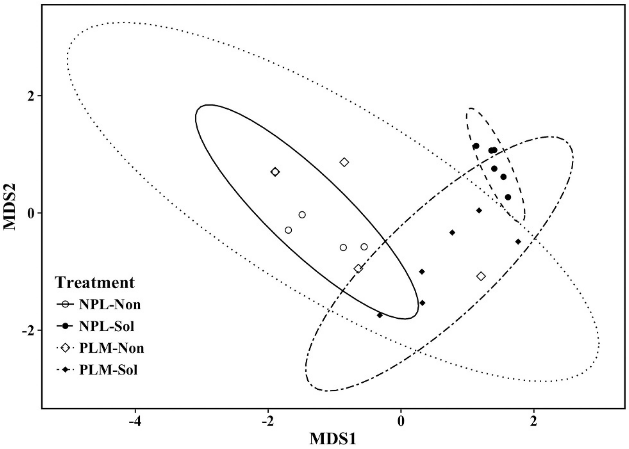

Figure 1. Nonmetric multidimensional scaling biplot. Points represent individual amended soil plots separated according to Bray–Curtis dissimilarity based on individual compound relative abundance. Treatments include non-solarized (Non) and solarized (Sol) soils for soil amended with pollinator (PLM) or nonpareil (NPL) hulls. Amendment rates (1.75 vs 2.5%) are indicated by shape but did not have a significant effect on dissimilarity and were clustered together. Ellipses surround 95% confidence interval for clusters.

Discussion

Volatile profile

Non-solarized soils had very low compound richness, diversity, and overall peak area. Previous studies have noted that VOC levels are low at the time of amendment, as VOCs need to diffuse through the soils, a process which takes 1 week to 10 days (Estupiñan-López et al. 2017; Grimme et al. 2007). This coincides with the timing in both the current and previous biosolarization research, in which the treatment disinfested weeds in 8 days (Achmon et al. 2017). The high heat from solarization in addition to time can stimulate degradation and increase volatile emissions (Gamliel and Stapleton 1993; Malkina et al. 2011; Terra et al. 2017).

Despite similar carbon content, both the relative abundance and quantity of certain compounds were distinct based on amendment composition. Biosolarized soils amended with nonpareil residues had higher VOC richness, diversity, and fivefold greater quantity compared to soil biosolarized with pollinator residues. In fact, soil biosolarized with pollinator residues had a similar VOC richness and quantity to the non-amended solarized treatments. The volatile profiles of pollinator-amended soil were similar before and after biosolarization, enriched in terpenes. In contrast, profiles of nonpareil-amended soils were distinct before and after biosolarization, where biosolarization significantly diminished initial terpene abundance and enriched for oxygenated VOCs, ketones, and VFAs. Nonpareil residues may undergo more robust soil fermentation than pollinator residues due to their higher content of fermentable sugars that can quickly leach into the soil. Several studies have also established a relationship between residue type and VOC profile, which also correlated to pest-control performance (Bruggen and Semenov 2000; Hewavitharana, Ruddell, and Mazzola 2014; Pedroso et al. 2019). Even with the same microbial community, difference in initial plant residue composition may yield different degradation products (Gray, Monson, and Fierer 2010). Residues often also harbor their own decomposer communities (Moorhead and Sinsabaugh 2006; Strickland et al. 2009), and these different bacterial communities can produce different VOC profiles even with similar substrates (Bunge et al. 2008; Lechner et al. 2005). The current study

Table 4. Relative abundance (%) of the 21 compounds that contributed to 90% volatile Bray–Curtis dissimilarity according to similarity percentage analysis (SIMPER).

	Non-Solarized[a]		Solarized[b]	
Compound	PLM[c]	NPL[d]	PLM[c]	NPL[d]
Ketones				
2-Butanone	9%	0%*	5%	13%*
2-Pentanone	0%	0%	1%	12%
2,3-Butanedione	0%	0%	1%	8%
3-Octanone	5%	11%	1%	1%
Acetoin	0%	0%	0%	6%
VFAs				
Acetic acid	1%	0%	5%	11%
Butyric acid	0%	0%	46%	15%
Hexanoic acid	1%	0%	0%	3%
Isobutyric acid	0%	0%*	9%	9%*
Isovaleric acid	0%	0%	0%	3%
Valeric acid	0%	0%	5%	6%
Terpenes				
2-methylisoborneol	0%	0%	8%	0%
3-Carene	14%	42%*	0%	0%*
a-Copaene	5%	34%	6%	0%
Camphor	9%	0%	2%	0%
Camphor (S)	1%	0%	1%	0%
Limonene	47%	0%	0%	0%
o-Cymene	5%	8%	1%	0%
Others				
Benzaldehyde	0%	3%	1%	1%
Dimethyl disulfide	0%	0%	1%	0%
Hexanal	0%	0%	2%	0%
% Abundance	96%	97%	95%	89%

*significantly different in relative abundance of the two compared treatments according to t-test.

[a] Soil mixtures that did not undergo solarization.

[b] *Soil mesocosms embedded in the field 7 cm deep and solarized for 8 days.*

[c] *Soil amended with a hulls and shells from a pollinator variety mixture (PLM), 1.75 or 2.5% dry weight, n = 3 each.*

[d] *Soil amended with a hulls and shells from Nonpareil variety (NPL), 1.75 or 2.5% dry weight, n = 3 each.*

underscores this, as despite similarities in residue source and carbon content, differences in hull and shell composition yielded distinct volatile emissions.

No difference in VOC diversity, profile, or magnitude was found between soils amended with 1.75 or 2.5% biomass. Previous studies found that organic matter content increases VOC magnitude (van Agtmaal et al. 2018), but others found that only a weak correlation between emissions and biomass content (Gray, Monson, and Fierer 2010). Further research using more residue types and levels is needed to further elucidate the relationship between biosolarization amendments and VOC profile, especially as variation can be high.

VOC identification

Volatile fatty acids had the highest abundance in biosolarized soils, particularly acetic, butyric, isobutyric, valeric, isovaleric, and hexanoic acid. These were found in both biosolarized treatments, but nonpareil-amended soils had greater quantities of isobutyric, isovaleric, and valeric acid. Lab-scale simulated biosolarization using these residues detected acetic acid as a major product, with butyric, isobutyric, and propionic as minor products (Fernández-Bayo et al. 2020), but valeric, isovaleric, and hexanoic acids were not previously identified in soil biosolarized with almond residues. Organic acids are formed by bacterial fermentation during biomass degradation (Gray, Monson, and Fierer 2010; Hafner et al. 2013) and are broad spectrum biocides (Campos, Pinho, and De, Freire 2010; Grimme et al. 2007). VFAs are found in high concentrations in dairy silage, but due to low volatility are generally not of concern as environmental pollutants (Alanis et al. 2008; Hafner et al. 2013).

Ketones were abundant in nonpareil-amended soils and represented the most diverse class of compounds. These are highly volatile and bioactive compounds produced by plants, fungi, and bacteria, many of which have been observed biocides. For example, methyl ketones (2-butanones, 2-pentanones, 2-hexanones, 2-heptanones, 2-nonanone, and 2-undecanone) found in nonpareil-biosolarized soil were also observed in previous studies with demonstrated fungicidal (Chuankun et al. 2004; Mülner et al. 2019; van Agtmaal et al. 2015) and nematicidal (Barros et al. 2014; Gu et al. 2007; van Agtmaal et al. 2015) effects. Three ketones identified in particularly high levels in nonpareil-amended samples – 2-butanone, 2,3-butanedione, and acetoin – are associated with the

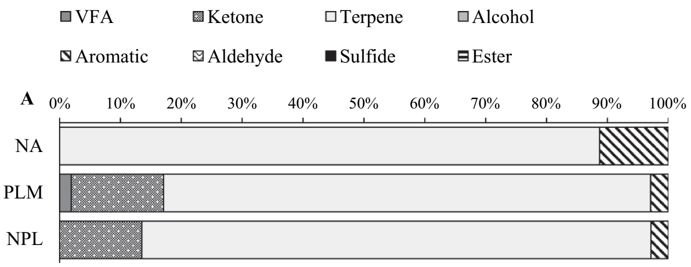

Figure 2. Relative abundance of volatile classes detected in non-solarized soil headspace. The mean total relative abundance of sulfides, aldehydes, esters, alcohols, aromatics, ketones, terpenes, and VFAs were determined for non-solarized, non-amended (NA) soil (n = 3), soil amended with 1.75% or 2.5% pollinator hulls (PLM, n = 6), and soil biosolarized with 1.75 or 2.5% nonpareil hulls (NPL, n = 6).

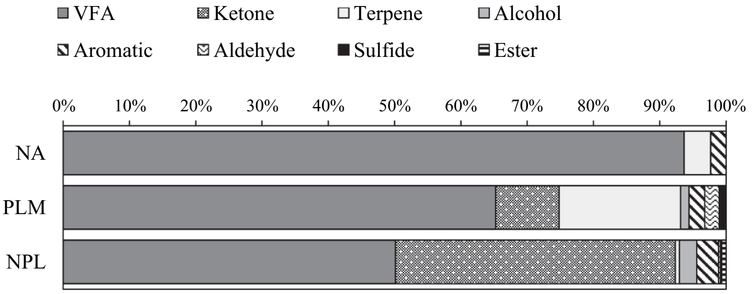

Figure 3. Relative abundance of volatile classes detected in solarized soil headspace. The mean total relative abundance of sulfides, aldehydes, esters, alcohols, aromatics, ketones, terpenes, and VFAs were determined for solarized soil with no amendments (NA) soil (n = 3), soil biosolarized with 1.75% or 2.5% pollinator hulls (PLM, n = 6), and soil biosolarized with 1.75 or 2.5% nonpareil hulls (NPL, n = 6).

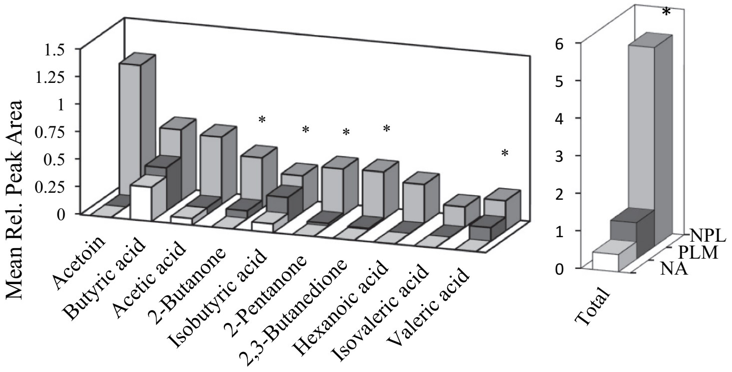

Figure 4. Relative peak area of the ten most abundant compounds in biosolarized samples. Values indicate mean relative peak area in soil headspace of the 10 most abundant compounds as well as the total relative peak area found in the three different solarization treatments: soil biosolarized with 1.75% or 2.5% pollinator hulls (PLM, n = 6), soil biosolarized with 1.75 or 2.5% nonpareil hulls (NPL, n = 6), and soil solarized with no amendment (NA). Asterisk (*) indicates significant difference from other treatments according to the Dunn's test (P < .05).

Table 5. Headspace concentration ranges (mg/m^3) of select compounds in biosolarized soil.

	PLM[a]		NPL[b]		
Compound	1.75%	2.50%	1.75%	2.50%	REL
Acetic acid	<0.05	0.05–0.07	0.08–0.28	0.18–0.38	25
2-Butanone	<0.05	<0.05	< 0.05	<0.05	590
Butanal	<0.05	<0.05	< 0.05	<0.05	175[d]
Hexanal	<0.05	<0.05	< 0.05	<0.05	174[d]
Phenylethyl alcohol	<0.05	<0.05	< 0.05	<0.05	5

Values indicate mean min-max mg/m^3 atmosphere (n = 3) for soils measured after 8 days of biosolarization.

[a] *Soil amended with a hulls and shells from a pollinator variety mixture (PLM), 1.75 or 2.5% dry weight, n = 3 each.*

[b] *Soil amended with a hulls and shells from Nonpareil variety (NPL), 1.75 or 2.5% dry weight, n = 3 each.*

[c] *Recommended exposure limit according to United States National Institute of Health and Safety (NIOSH) guidelines (mg/m^3).*

[d] *RELs for valeraldehyde; the CDC control recommends reducing exposure to similar aldehydes* (NIOSH 1991).

same lactic acid bacterial fermentation pathway (Hafner et al. 2013; Keen and Walker 1974). Acetoin has been observed as an intermediate that can quickly convert to and from 2,3-butanedione, which may explain why its highly variable abundance in this study (Hafner et al. 2013); *Bacilli* in soil may emit these compounds as a mechanism to maintain internal pH during VFA accumulation (Härtig and Jahn 2012) and so the presence of these compounds relate to the high VFA levels found in nonpareil-biosolarized soil. These compounds are plant growth promoters, but can also act as nematicides (Barros et al. 2014; Terra et al. 2017).

Other degradation volatiles such as alcohols, aldehydes, esters, and sulfides were detected in lower abundances in biosolarized soils but may still offer mechanistic importance to the system. Alcohols are endogenous to certain plant residues (Barros et al. 2014), as well as a common by-product of yeast and lactic acid bacterial fermentation (Malkina et al. 2011). Isoamyl alcohol was particularly prevalent in soil biosolarized with nonpareil residues, and has known broad spectrum pest control (Barros et al. 2014; Estupiñan-López et al. 2017; Grimme et al. 2007; Terra et al. 2017). Low alcohol emissions from fermented almond hull and shells were observed in silage; this was a benefit, as alcohols risk greater ozone formation than other fermentative VOCs (Hafner et al. 2013; Malkina et al. 2011). Aldehydes were also identified in both biosolarized treatments, included butanal isomers, and hexanal. Aldehydes are highly reactive and volatile which can make them important to consider at even low levels in terms of ozone formation (Hafner et al. 2013; Howard et al. 2010), and human health (NIOSH 1991). Several esters were observed in nonpareil biosolarized soils in low abundance, including ethyl acetate, butyl acetate, butyl butyrate, ethyl valerate, and ethyl propionate. While esters can act as nematicides on their own (Barros et al. 2014; Terra et al. 2017), they are of interest to fumigation alternatives research as they are significantly more volatile than VFAs, but quickly degrade into their analogous acids when dissolved in water (Coetzee et al. 2019). This may be a reason that they were observed in low abundance, as the moist soil environment may quickly facilitate this conversion. Finally, dimethyl disulfide was the singular sulfurous compound identified, where it was observed in all amended samples. Due to its high toxicity, dimethyl disulfide is currently used as a commercial preplant soil fumigant being for the control of nematodes, weeds, and soil-borne plant pathogens (Ajwa et al. 2010). It has been detected in high levels in insufficiently aerated compost, but was not found to be a risk for compost facility workers (Tolvanen et al. 2005).

Prior to solarization, amended soils headspaces were enriched in terpenes and aromatic compounds. Terpenes are common in microbial and plant signaling (Schulz-Bohm et al. 2018) and are one of the most highly emitted VOCs in nature. For example, 2-methylisoborneol was abundant in solarized soils, and is often associated with the aroma of soil emitted by cyanobacteria (Zamyadi et al. 2015). Others, including limonene, camphor, 3-carene, and o-cymene were more abundant in pre-solarized samples. These are common degradation products of leaf litter (Gray, Monson, and Fierer 2010) and composting (Tolvanen et al. 2005), and may be derived from plant essential oil degradation. Infected plants may release terpenes into the soil as a mechanism of recruiting antagonistic bacteria (Gray, Monson, and Fierer 2010), but the direct role of terpenes in pest inactivation requires further elucidation. Prominent aromatic compounds detected included benzaldehyde and phenylethyl alcohol. These compounds are highly volatile and bioactive, and have been shown to act as fungicides and nematicides in soil (Campos, Pinho, and De, Freire 2010; Gu et al. 2007), which may translate to amendment-driven pest control without fermentation.

VOC quantification

The volatility and bioactivity of the VOCs identified make them of potential concern to human health if inhaled (Curtis et al. 2006; Kampa and Castanas 2008; Müller et al. 2004a, 2004b; Rumchev, Brown, and Spickett 2007). Even naturally occurring VOCs can be irritants, and on a long enough time scale can cause more serious damage. Selected compounds emitted from biosolarization sites were quantified, but only acetic acid reached the threshold of quantification for this study >0.05 mg/m^3. Here, acetic acid maximums were between 0.7 and 0.38 mg/m^3 depending on treatment, but these levels likely pose no risk as they are between 2 and 3 orders of magnitude below the NIOSH limit (NIOSH 2005). These levels are on par with studies measuring outdoor VOC levels close to composting facilities, which were at most 1 mg/m^3, and were also determined to pose no risk to communities (Domingo and Nadal 2009). Recent research suggests emissions of VFAs have likely been over-estimated in previous air quality research. Due to low volatility and high degradation rate, very low concentrations of VFAs actually enter the atmosphere; they argue the largest risk to humans and the environment would come instead from alcohols and aldehydes (Alanis et al. 2008; Howard et al. 2010), which were minor components of the VOCs detected in this field trial.

Worker exposure to VOC mixtures in composting plants have generally found little occupational exposure risks from organic acids, ketones, aldehydes, esters, and sulfides (Domingo and Nadal 2009; Mølhave, Grønkjær, and Larsen 1991; Nadal et al. 2009). However, these studies also note that emissions are extremely variable and therefore difficult to estimate. The additive or synergistic effect of all VOCs and their impact on health is not understood (Rumchev, Brown, and Spickett 2007). In addition, potentially harmful VOCs have no REL, making quantification difficult. For example, nonpareil-amended soils generated high abundances of 2,3-butanedione (diacetyl), a flavoring known to cause respiratory illness to workers (CDC 2003); while no illness has been linked to naturally-occurring 2,3-butanedione to date, steps can be taken to reduce potential exposure to biosolarized soil.

Emissions from biosolarized soil, though low, may be managed with irrigation. Previous studies have observed that high moisture content soils trap VOCs in the aqueous phase, preventing volatilization into the atmosphere (Barros et al. 2014; Pedroso et al. 2019; Terra et al. 2017). Employing this phenomenon would have a twofold benefit, as it would minimize or eliminate human exposure, while increasing the bio-pesticidal efficacy due to longer retention in soil. Future work aims to model how VOCs are transported through the soil profile during irrigation events. Other research in this area should include targeted and time-series methods for quantifying the emissions of potentially harmful VOCs including VFAs, diketones, and aldehydes.

Conclusion

This non-target analytical method identified dozens of compounds not previously characterized during biosolarization, primarily VFAs and ketones, but also terpenes, alcohols, aldehydes, esters, sulfides, and aromatic compounds. Differences in the volatile profile were found between amendments applied, in which nonpareil-amended soils had very different VOC profiles before and after biosolarization. Soil biosolarized with nonpareil residues also had higher total VOCs, and higher abundance of certain VFAs and ketones than pollinator-amended soil. Many of the compounds identified in this soil could potentially act as biopesticides while presenting low risk to human and environmental health. Future research should determine how these individual compounds or compound mixture may affect different target pests.

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