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In-field yellow starthistle (*Centaurea solstitialis*) volatile composition under elevated temperature and CO_2 and implications for future control

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Abstract Abiotic stressors may affect biogenic volatile organic compounds (BVOCs) involved in plant communication. We examined how certain environmental conditions affect plant signaling via BVOC emission. Specifically, we investigated the effects of elevated CO_2 and temperature in situ on BVOCs produced by mechanically damaged leaves of *Centaurea solstitialis* L. (yellow starthistle), a major invasive weed in western North America, grown in grassland plots in the foothills of northern California. The headspace BVOCs of *C. solstitialis* were collected in situ by a customized Teflon® bag and solid-phase microextraction and analyzed by gas chromatography–mass spectroscopy. Damaging leaves led to the release of 14 volatile compounds, predominantly sesquiterpenes. The co-occurrence of five compound pairs was highly significant across all treatments, which may be explained through synthesis by the same enzyme. We found no significant effect of treatment on the levels of individual or total volatiles. The stability of volatile profile for this invasive under future conditions should therefore (1) not alter indirect defense signaling and (2) support the selection of biological controls on the basis of their specificity to the identified in-field host plant BVOCs.

Keywords *Centaurea solstitialis* (yellow starthistle) · Abiotic stressors · Invasive species · Biogenic volatile organic compound (BVOC) · Elevated CO_2 · Elevated temperature

Introduction

Global climate change is expected to increase in the current century and is shifting environment dynamics, invasive species abundance, and plant–insect communication (McFrederick et al. 2009; IPCC 2013a). Ecosystem response to climate change driven abiotic stressors is occurring in both terrestrial and marine communities around the world (IPCC 2014b). The consequences of anthropogenic CO_2 and rising temperatures are affecting ecosystems and community composition (IPCC 2014a). Species restricted to a certain range have seen a dramatic range reduction, and due to recent climate change, have been the first to experience whole species extinctions (Beever et al. 2003; Descimon et al. 2005). Such stressors have disrupted synchronicity between interacting species at the flowering and breeding interface (Visser and Both 2005).

Because environmental changes involve multiple factors that may occur simultaneously, it is important to examine the potential for inhibitory or promoting effects of CO_2 and temperature stressors both individually and in concert in the field. Such factors alter plant physiological properties, modifying herbivore consumption and influencing plant community composition (Peters et al. 2006). Generally, elevating mean temperature increases biomass production in natural systems in colder regions, either by speeding up metabolism or extending the growing season (Rustad et al.

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2001). Increasing atmospheric CO_2 often leads to increased net primary production and above-ground biomass (Norby et al. 2005; Field et al. 2007), though not always (Shaw et al. 2002; Norby et al. 2010). In general, increased decomposition offsets some or all of the increase in net primary production (van Groenigen et al. 2014). Focusing treatments on specific plant species in the field will complement work at the community level and provide further insight.

Invasive plant species continue to threaten ecosystem biodiversity and stability both regionally and globally (Mooney and Drake 1986; James et al. 2010; Groom et al. 2014). Their adaptive flexibility along with their ability to competitively exclude and displace native species has allowed them to flourish in new environments (Mooney and Cleland 2001). The growth of invasives could be favored under climatic change by increasing expansion rates through their inherent temperature tolerance and adaptability to extreme weather events (Dukes and Mooney 1999; Bradley et al. 2010; Wheeler and Schaffner 2013). Identifying specific factors that facilitate invasive success, such as elevated CO_2, is key (Dukes 2000; Verlinden et al. 2014).

Yellow starthistle (YST), *Centaurea solstitialis* L. (Asteraceae), a winter annual native to the Mediterranean region, has established in North America and covers over 7 million hectares in at least 23 states. YST is most widespread in California (Wilson et al. 2003; DiTomaso et al. 2006; Pitcairn et al. 2006). This invasive weed is highly competitive and its thorny spines around the flowerhead are detrimental to grazing cattle. The establishment of YST in North America coincides with recent rapid increase of CO_2 levels (Wilson et al. 2003). In a 40-year time period (1960–2000), atmospheric CO_2 has increased by approximately 50 ppm, during which YST expansion grew exponentially from 1 to 14 million acres (IPCC 2014a; Pitcairn et al. 2006). CO_2 positively affects YST growth. The invasive grew up to six times larger under elevated CO_2 in grassland plots (Dukes et al. 2011). It also has great potential for displacing native species and reducing biodiversity, making effective biological control a top priority (Van Driesche et al. 2008).

Biogenic volatile organic compounds (BVOCs) provide multiple ecological functions (Tholl et al. 2006) where sesquiterpenes can figure prominently in some plant–insect signaling (Yuan et al. 2009). BVOC responses can also include plant communication during herbivory or abiotic stress responses such as heat and oxidative pressure (Sharkey et al. 2001; Dudareva et al. 2006; Peñuelas and Staudt 2010). No broad conclusive patterns have been demonstrated for climate change effects on plant direct defense via BVOCs (Peñuelas and Staudt 2010). However, a plant's BVOC response depends on multiple factors such as the degree of temperature increase, time of day, season, plant species examined (Yuan et al. 2009), and method of collection (Beck et al. 2014). Several studies have detected and identified a suite of BVOCs emitted from YST (Buttery et al. 1986; Binder et al. 1990; Beck et al. 2008; Smith and Beck 2013). Buttery and Binder originally collected and examined ex situ volatiles from YST plants and detected compounds that may be unique to harvested plant parts and thus will not be discussed (Buttery et al. 1986; Binder et al. 1990). Yellow starthistle studies discussed in this paper have found mechanical leaf damage to generate a broad profile of volatile compounds (Beck et al. 2008; Smith and Beck 2013). A future comparison of methodology, plant part, and corresponding volatiles may be of benefit.

Volatiles induced during leaf herbivory, such as sesquiterpenes, attract natural predators and parasitoids by signaling that a plant is being consumed (Turlings et al. 1990; Dicke et al. 1990; Vet and Dicke 1992; Heil 2004). This plant–herbivore–carnivore interaction involving plant volatiles is known as indirect defense (Price et al. 1980; Dudareva et al. 2006). For YST, this defense mechanism may play a crucial role during the early growth stages when physical defense is low. During this time, gastropod herbivores such as *Deroceras reticulatum* (gray garden slug) have been shown to consume nearly half of above ground production (Peters et al. 2006). *D. reticulatum* feeding on young YST elicits BVOC emissions attractive to the predatory ground beetle *Pterostichus melanarius* (Oster et al. 2014). This dynamic between a natural control, its host, and predator may change if environmental conditions such as temperature and CO_2 are altered (Thompson 2005; Wheeler and Schaffner 2013).

Studying indirect defenses through plant volatile response to abiotic stressors, such as climate change conditions, is a relatively unique approach. This is the first known report of the volatile composition of *C. solstitialis* grown under climate change treatments in the field. Our aims were to (1) determine if YST growth under elevated CO_2 or temperature is associated with a change in BVOC emissions, thereby influencing plant–insect signaling, (2) compile a broad BVOC profile emitted from damaged YST, and (3) add to a growing volatile library which will assist in the selection of species-specific biological controls for invasive weeds.

Materials and methods

YST growth site

Plants were grown in the Jasper Ridge Global Change Experiment located in the Jasper Ridge Biological Preserve of Stanford University near the eastern foothills of the Santa Cruz Mountains (Latitude: 37.40524|Longitude: −122.2421). The Global Change Experiment explores responses of grassland to four environmental factors: warming, elevated CO_2, increased precipitation, and increased nitrogen deposition. The study site contains 32 circular plots two meters in diameter, divided into four randomly distributed treatment quadrants exposed to ambient or elevated CO_2 (additional 300 ppm for a total of 700 ppm, or twice the ambient level), elevated N (additional 7 g N per m^2 per year), elevated precipitation (adding half of ambient rainfall shortly after the event), and elevated temperature (temperature raised an approximate 3 °C with infrared heaters) with all 16 possible combinations interspersed among the global change landblocks (Fig. 1). These treatments reflect a mid-range scenario expected globally for the twenty-first century (IPCC 2013b). The effects of two factors (temperature only, CO_2 only, and temperature and CO_2 combined) and an ambient control group on YST were studied.

Seedling growth and transfer

Seeds from wild YST collected from Jasper Ridge were germinated in November on petri dishes for 7 days and transferred to growth trays, which were placed into the greenhouse for 8 days with final transfer to the Global Change Experiment at 17 days after germination (December 11th, 2012). Seedlings were planted into established grassland in each quadrant (ambient, temp, CO_2, temp + CO_2) and allowed to grow until rosette stage. Beginning in April 2013, seedlings were given 20 ml of water once a week until 1 week prior to sampling.

Volatile sampling

The in situ volatile collection experiments were performed as described by Beck et al. (2008) and Smith and Beck (2013). Plants were sampled for volatiles upon reaching uniform physiological maturity, i.e. when reaching the rosette growth stage. Plants were sampled from ambient plots ($N = 8$), elevated CO_2 plots ($N = 15$), elevated temperature ($N = 9$), elevated CO_2 and temperature combined ($N = 23$); additional damaged plants were utilized for further compound verification via a second gas chromatography–mass spectroscopy (GC–MS) column. The 2-month sampling time spanned June 7th–August 7th. Sampling took place between 6:00 and 9:00 each morning to capture volatiles during a time of natural herbivore activity and to prevent condensation in the volatile collection medium at higher ambient temperatures. Prior to volatile collection, each plant was punctured a total of 30 times (leaves only) with a B-D 16G syringe needle. Control experiments were performed to determine the background volatile profiles of plants with undamaged leaves ($N = 6$) and empty bags ($N = 6$) using the same collection protocol described. Leaf puncture was chosen for consistency in damage amounts.

A 10.2 × 25.4 cm customized Teflon® bag (Welch Fluorocarbon, Dover, New Hampshire; heat sealed on three sides, with two Kynar portals) (Beck et al. 2008) was utilized for volatile collection. A solid-phase microextraction

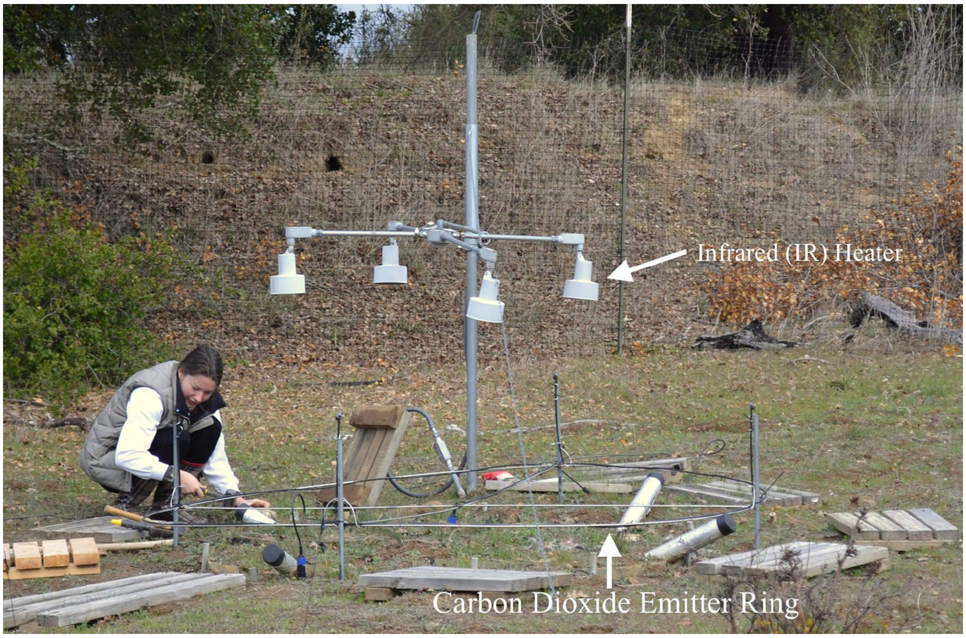

Fig. 1 Photograph of global change field experiment plot. Elevated temperature achieved through an infrared heater lamp; elevated CO_2 emitted via mini-FACE system

(SPME, Supelco, Bellefonte, PA; 100 µm, polydimethylsiloxane fiber) needle was inserted through the port septum and allowed to adsorb volatiles for an exposure period of 2 h (Fig. 2). At the end of exposure time, the fiber was retracted into the SPME and removed from the outlet port. The SPME was placed in an individual Kimax® 70 ml culture tube, sealed with a stopper, and tightly wrapped with Parafilm® sealing film. The tube was placed in a 3.79-L Ziploc® bag and stored upright in ice and transported to the lab for analysis. Storage time of the fiber prior to injection time onto the GC ranged between 2 and 8 h. All SPME cartridges remained in the cooler until injection time.

Volatile analysis

Collected volatiles were thermally desorbed on either a J & W Scientific (Folsom, CA) DB-Wax or DB-1 column (60 m × 0.32 mm i.d. × 0.25 µm) on a HP-6890N gas chromatograph (GC) coupled to HP-5975B mass selective detectors (MSD) (MS; Palo Alto, CA). Desorbed volatiles were analyzed using methods previously published (Beck et al. 2008; Smith and Beck 2013). NIST, Wiley, and internally generated databases were used for fragmentation pattern identification. The retention indices (RIs) were calculated using a homologous series of *n*-alkanes on DB-Wax and DB-1 columns. Volatile identifications were verified by injection of commercially available or isolated laboratory standard samples for comparison to retention times and fragmentation patterns while tentatively identified compounds were verified from comparison of RI values to elution from two different columns.

Statistical analysis

To test the presence of a relationship between treatment and peak relative abundance of both individual volatiles and the total sum of volatiles within each treatment, we used a non-parametric multivariate ANOVA: Manly's method of unrestricted permutation (Manly 2007) and Edgington's method of restricted permutation (Edgington and Onghena 2007). We performed a linear regression to test for the effect of sampling period on the relative abundance of each compound. Presence of compound co-occurrence was calculated with the Spearman correlation coefficient in R-project using the rcorr function.

Results

The in situ volatile emission profile of damaged *C. solstitialis* comprised 14 compounds of which 13 were sesquiterpenes (incl. two unidentified) and one was an alkene (Table 1). The compound germacrene D had a relative abundance greater than all other compounds by more than one order of magnitude (Fig. 3). Even without controlling for multiple testing, both Manly's and Edgington's methods revealed no significant relationship between treatment and relative abundance of volatiles either individually or as a total signal ($P > 0.05$). In-field control experiments of undamaged plants detected no volatile compounds, lending support to either trace level presence below detection limits in the field or an absence of volatiles for undamaged YST (the latter seen by Beck et al. 2008 for YST and its sister species). There were four compounds not detected in the ambient treatment but present in other

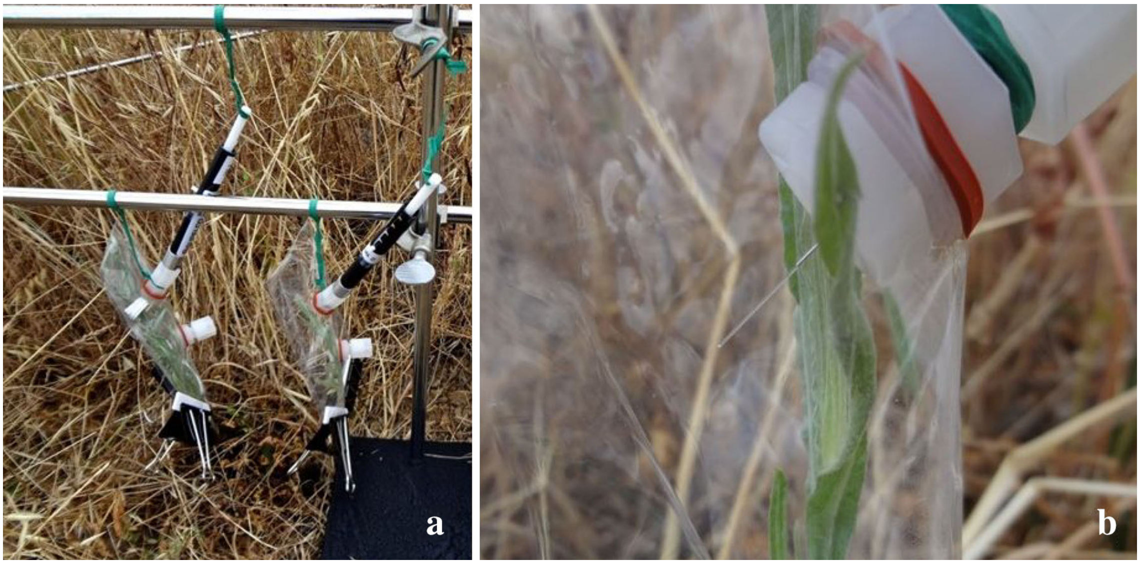

Fig. 2 Field setup: **a** in situ volatile collection of *C. solstitialis* using a Teflon® Bag and SPME, **b** close-up photo of exposed SPME fiber

Table 1 Volatile compound identities

Cmpd	RI	Library/ID	Fragment pattern
1	1490	α-Copaene	161(100), 105(79), 119(77), 93(46), 91(38)
2	1518	β-Bourbonene (*Tent*)	81(100), 80(65), 123(51), 79(27), 161(25)
3	1528	α-Gurjunene	204(100), 105(95), 161(84), 189(70), 41(58)
4	1545	1-Pentadecene	41(100), 43(75), 55(72), 57(67), 69(65)
5	1574	Unk sesquiterpene	161(100), 120(85), 105(65), 91(55), 41(55)
6	1591	Unk sesquiterpene	161(100), 91(45), 105(35), 119(25), 162(15)
7	1594	β-Caryophyllene	41(100), 93(83), 69(70), 91(65), 79(63)
8	1662	*Trans*-β-farnesene	69(100), 41(80), 93(55), 67(25), 79(20)
9	1666	α-Humulene (*Tent*)	93(100), 80(34), 121(30), 41(27), 147(25)
10	1707	Germacrene D	161(100), 105(55), 91(50), 41(40), 81(37)
11	1724	β-Bisabolene	69(100), 41(85), 93(81), 67(51), 79(40)
12	1732	Bicyclogermacrene	121(100), 93(90), 41(55), 92(50), 107(47)
13	1767	β-Sesquiphellandrene	69(100), 41(76), 93(57), 91(49), 77(48)
14	1801	1,5,9-Trimethyl-1,5,9-cyclododecatriene	68(100), 67(50), 93(40), 189(39), 107(33)

RI compound retention index, *fragment pattern* 5 largest fragments with relative sizes, *(Tent)* tentative

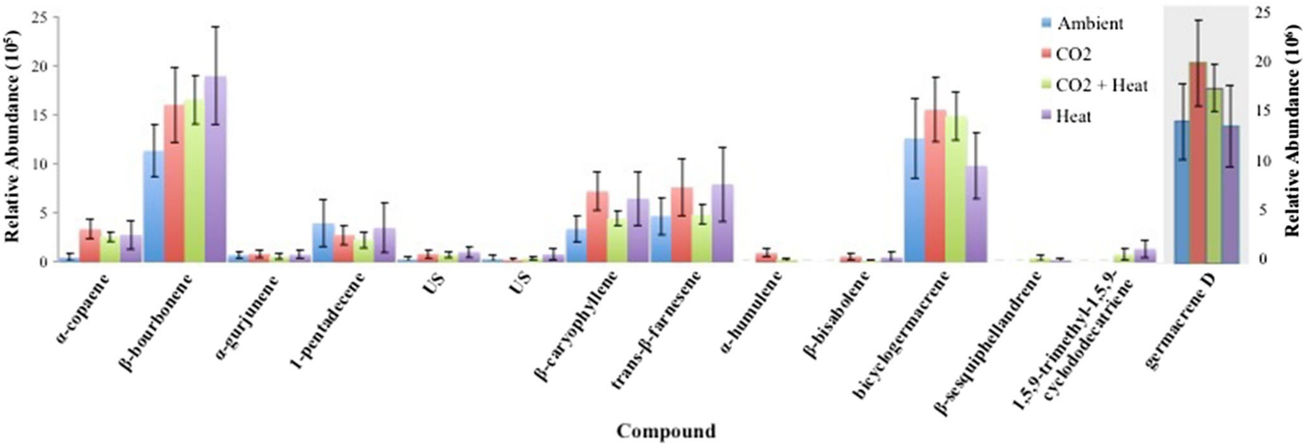

Fig. 3 Relative volatile abundances across four treatments for all compounds (10^5), including germacrene D (10^6)

treatments: α-humulene, present in both CO_2 treatments; β-bisabolene, present in the CO_2 and temperature treatments; β-sesquiphellandrene, only present in the temperature treatment; and 1,5,9-trimethyl-1,5,9-cyclododecatriene, present in the temperature and interaction treatments. However, the compounds were only detected for a few samples in these treatments; therefore, the treatments did not show a significant effect on the presence/absence of the compounds using a multivariate logistic regression. Using the full sample, multiple volatile compounds were significantly correlated (Spearman's correlation coefficient (corr) >0.5, based on a conservative significance level of 0.0001). Five compound pairs exhibited highly significant co-occurrence (corr > 0.75): germacrene D with bicyclogermacrene (corr = 0.87), germacrene D with β-bourbonene (corr = 0.82), germacrene D with β-caryophyllene (corr = 0.80), β-caryophyllene with β-bourbonene (corr = 0.78), and β-bourbonene with an unknown sesquiterpene with RI of 1574 (corr = 0.76), as seen in Fig. 4.

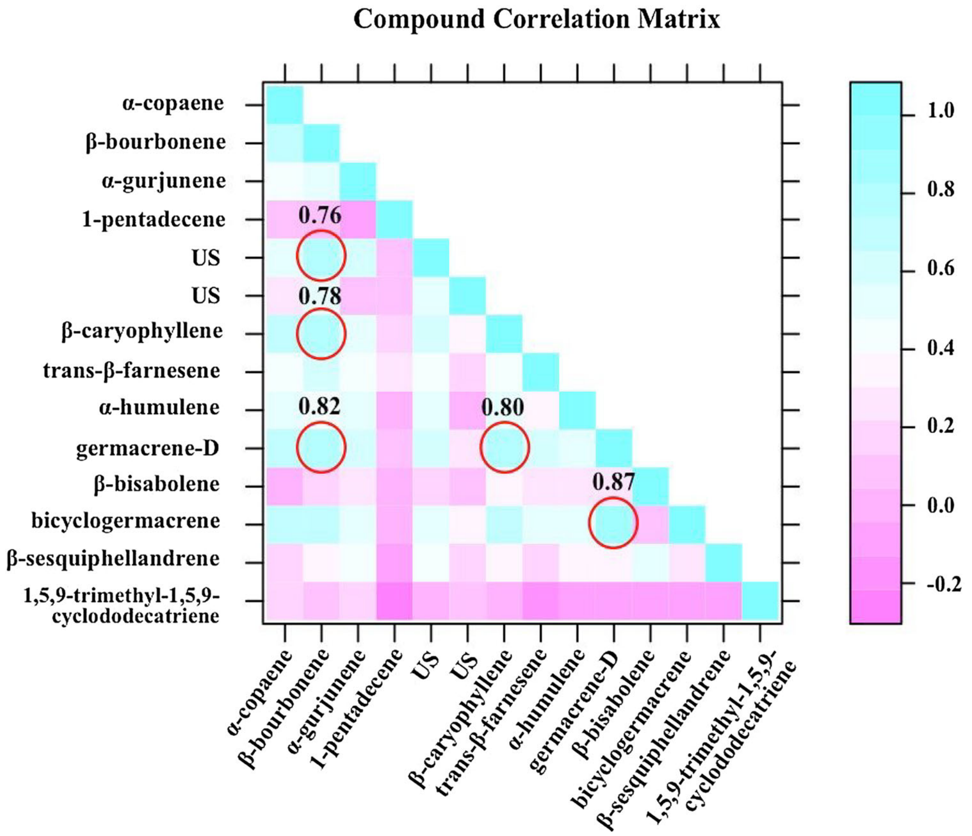

Fig. 4 Correlation of volatile compounds. Gradient legend shows Spearman correlation coefficient (corr) value; corr > 0.5 shows significance (*P* value <0.0001). Five compound pairs (*circled*) exhibited highly significant co-occurrence (corr > 0.75): germacrene D with bicyclogermacrene (corr = 0.87), germacrene D with β-bourbonene (corr = 0.82), germacrene D with β-caryophyllene (corr = 0.80), β-caryophyllene with β-bourbonene (corr = 0.78), and β-bourbonene with an unknown sesquiterpene with RI of 1574 (corr = 0.76)

Discussion

Treatment effects

The absence of significant treatment effects of elevated temperature and CO_2 on volatile emission in YST may be the result of both a species-specific and terpene-specific response. In addition, natural environmental conditions acting as limiting factors and abiotic stressors may have also influenced emission. Different plant species display substantial variability in sesquiterpene emission even under similar treatment conditions (Duhl et al. 2008). Generally, elevated temperature tends to positively affect BVOC emission by increasing diffusion and enhancing enzymatic activity (Guenther et al. 1993). However, Mediterranean species such as yellow starthistle tend to be water rather than temperature limited (Monson et al. 2007; Fortunati et al. 2008; Llusià et al. 2008, 2009) and, under conditions of water stress, their terpene emissions have been shown to decrease (Vallat et al. 2005; Monson et al. 2007; Omeno 2007). Thus, either the temperature treatment did not influence volatile emission or the dry growing season experienced in this study may have acted in compensation to a possible elevation in emissions due to the temperature treatment, resulting in an apparently conserved emission signal.

CO_2 concentration in the atmosphere is vital for plant carbon fixation and sequestration and one of the many effects of its elevation is often increased standing biomass, when acting as a limiting resource (Körner 2006; Peñuelas and Staudt 2010). Although it has been suggested that such productivity may increase BVOC synthesis and emission (Lerdau et al. 1994) in light of the carbon-nutrient balance hypothesis (Gershenzon 1994; Waterman and Mole 1989), there is conflicting evidence (Yuan et al. 2009). In fact, terpenoid emissions have not only been seen to decrease under elevated CO_2, pointing to inhibited terpene synthase activity (Loreto et al. 2001; Rosenstiel et al. 2003), but have also shown no significant effects (Constable et al. 1999). In the latter case, a steady state of emission per unit biomass may be maintained due to lower stomatal density on the resulting larger-grown leaves (Woodward et al. 2002; Vuorinen et al. 2004). While elevated CO_2 provides additional carbon for the production of secondary metabolites, terpene production is cost intensive and requires sufficient nutrients for the production of biosynthetic enzymes and storage structures (Gershenzon 1994). In fact, the naturally poor soil quality and the absence of fertilization in the field result in lower volatile emissions than from plants grown in nutrient rich greenhouse soil (Gouinguené and Turlings 2002). Additionally, terpene production may not only depend on carbohydrate or substrate supply, but also on terpene synthase enzyme activity (Chappell et al. 1991; Iijima et al. 2004). Hence, the BVOC emission response under elevated temperature and CO_2 in yellow starthistle may be limited by precipitation and nutrient conditions in the field and may, therefore, not be directly coupled to the strong growth response of YST observed under elevated CO_2 in other studies (Dukes et al. 2011).

Many of the existing studies have been performed under artificial conditions, yet free air CO_2 enrichment (FACE) experiments are very limited (Yuan et al. 2009). Therefore, the complex dynamic of biotic and abiotic factors in the field may dampen the effects of treatment, providing a more accurate picture of their collective influence. Plants under laboratory conditions grow without competition for space, light, water, etc.—all of which in the field may represent a resource more limiting than carbon and of stronger effect than the treatment itself (Körner 2006).

Volatile compounds

In response to mechanical damage, field-grown YST released an array of volatiles, dominated by sesquiterpenes (Table 1; Fig. 3)—compounds known for their semiochemical activity in plants (Yuan et al. 2009). The absence of other volatiles, such as green leaf volatiles (GLVs), may be attributed to a species-specific response as well as to plant growth conditions: both Beck et al. (2008) and Smith and Beck (2013) also found a major presence of sesquiterpenes with only trace or minor levels of GLVs and monoterpenes. The most abundant volatile from all treatments was germacrene D, followed by β-bourbonene and bicyclogermacrene. These three compounds have been identified as semiochemicals in other systems (Weissbecker et al. 2000; Light and Knight 2005; Sidney et al. 2006; Ghirardo et al. 2012). The compounds α-gurjunene and the two unknown sesquiterpenes had the lowest relative abundance. Terpene production is a regulated response and plants may only emit enough volatiles to elicit a reaction from predators (Tholl 2006).

Sesquiterpenes are from the terpenoid family group comprised of three isoprene units and are synthesized by the mevalonate (MVA) pathway in the cytosol (Lichtenthaler 1999), possibly utilizing universal terpenoid intermediates from the parallel methylerythritol phosphate (MEP) pathway located in the plastid (Hemmerlin et al. 2012). Regulation of terpenoid biosynthesis is generally spatial and temporal. Spatially, sesquiterpene biosynthesis can be sequestered in glandular structures often found on leaves while temporally, volatile emission and enzyme activity have been shown to peak and decline during plant growth (Gershenzon et al. 1989; Grinspoon et al. 1991; McGarvey and Croteau 1995). A study examining terpenoid biosynthesis found that suites of enzymes are responsible for terpenoid formation in ginger and turmeric. In fact, nearly all sesquiterpenes identified by Koo and Gang (2012) were found to be produced by multiple terpene synthases, including eight of the thirteen sequiterpenes detected in our study. For example, one terpene synthase produced β-caryophyllene and 1,5,9-trimethyl-1,5,9-cyclododecatriene, in addition to α-humulene as a major product, while three enzymes produced both β-caryophyllene and germacrene D (Koo and Gang 2012).

Multiple pairs of compounds correlated across all treatments including the ambient treatment. The volatiles germacrene D and bicyclogermacrene had the highest correlation (corr = 0.87). These two compounds are candidates as signals in indirect defense based on their presence in slug-damaged YST (Oster et al. 2014). Both compounds belong to the germacrane family of sesquiterpenes (McMurry and Bosch 1985; Bülow and König 2000). Additionally, the third strongest co-occurring pair (corr = 0.80), germacrene D and β-caryophyllene, has been shown to be synthesized by the same enzymes in other plants (Koo and Gang 2012). Therefore, compound co-occurrence may be explained by synthesis from the same terpene synthases in general (Bohlmann et al. 1998; Steele et al. 1998). In fact, the formation of multiple products by a single terpene synthase is often seen in this enzyme family (Chen et al. 2003; Tholl et al. 2005) and may be due to the production of reaction intermediates with multiple metabolic destinies (Crock et al. 1997).

Several of the BVOCs emitted by YST in response to damage under simulated global changes are associated with indirect defense in other species. Colorado beetle-damaged potato plants emit β-caryophyllene, α-humulene, *trans*-β-farnesene, bicyclogermacrene, and germacrene D. These compounds are implicated in indirect defense by attracting the predaceous stinkbug *Perillus bioculatus* (Weissbecker et al. 2000). In other indirect defense systems, α-copaene attracts predatory mites to spider-mite-infested lima bean plants (Dicke 2009). The compounds *trans*-β-farnesene and α-copaene have been shown to arise from the same precursors during biosynthesis in grape berries (May et al. 2013). The eulophid wasp parasitoid of elm leaf beetle eggs is attracted to a *trans*-β-farnesene and α-humulene containing mixture released by egg-infested elms (Büchel et al. 2011). Finally, α-gurjunene, β-bisabolene, and β-sesquiphellandrene possess insect repellent properties in low doses (Wang and Kays 2002; Conti et al. 2011; Ray et al. 2012). Several of the detected sesquiterpenes have been reported as pheromones from various aphid species. For instance, *trans*-β-farnesene and α-gurjunene are minor components of *Brevicoryne brassicae*, and germacrene D, β-bourbonene, and α-copaene comprise the blend of pheromones of *Euceraphis punctipennis* (Francis et al. 2005).

Four of the compounds detected here were also observed in our earlier study using slug-damaged plants: *trans*-β-farnesene, germacrene D, bicyclogermacrene, and 1,5,9-trimethyl-1,5,9-cyclododecatriene (Oster et al. 2014). The compound *trans*-β-farnesene may play a role in indirect defense by attracting the predatory *P. melanarius* ground beetle to its slug prey (Oster et al. 2014). This compound has been shown to attract *P. melanarius* in other studies and is the main constituent of the alarm pheromone emitted from its aphid prey (Kielty et al. 1996). A compound of note was the detection of 1,5,9-trimethyl-1,5,9-cyclododecatriene. Reports of this unique sesquiterpene as a plant volatile are limited. One investigation lists it as a component of water lily flowers (Yuan et al. 2014) and a second investigation detects a minor amount of the compound in ginger and turmeric tissues (Koo and Gang 2012). No reports of semiochemical activity of this compound have been published to date.

Eight of the compounds detected in this experiment were in the portfolio for damaged YST described by Beck and Smith (who found a similar number of total volatiles): α-copaene, α-gurjunene, β-caryophyllene, *trans*-β-farnesene, α-humulene, germacrene D, bicyclogermacrene, and pentadecene (Beck et al. 2008; Smith and Beck 2013; Beck et al. 2014). The detected alkene, pentadecene, possesses a wide range of activities. It acts as a trail pheromone for seed harvesting ants (Co et al. 2003) and is also found in beetle sex pheromones (Keville and Kannowski 1975). Additionally, pentadecene is a major component in volatiles emitted from the buds and flowers of plants in the *Centaurea* genus upon damage (Senatore et al. 2003).

The other six compounds, all sesquiterpenes, were not detected in the previous YST studies and include β-bourbonene, two unknowns, β-bisabolene, β-sesquiphellandrene, and 1,5,9-trimethyl-1,5,9-cyclododecatriene. Most notable was the relatively large amount of β-bourbonene produced in the current study and across all treatments, yet not detected by Smith and Beck (2013). Since β-bourbonene was detected in the ambient treatment, the only possible explanation for its appearance includes either the age of the plant (our study sampled younger plants than Smith and Beck (2013) or its growth under field conditions. Both β-bourbonene and α-copaene are reported pheromones for the European birch aphid (Francis et al. 2005) and β-bourbonene has exhibited semiochemical behavior for Lepidoptera (Sidney et al. 2006). The large amount of the sesquiterpene detected and the limited, but strong evidence for semiochemical activity in other systems warrant further investigation of this compound. Non-identical experimental conditions may contribute to these differences. Smith and Beck (2013) performed their experiment under lab conditions whereas our collection was performed in the field. In addition, year to year climate variation has been documented for this region (Zavaleta et al. 2003; Dukes et al. 2011); our experimental year experienced little precipitation and a dry spring.

Centaurea solstitialis is a dominant invasive weed that poses a growing challenge to land managers, farmers, and grassland diversity in North America (Wilson et al. 2003; DiTomaso et al. 2006). The stability in volatile profile should not directly affect YST control during early growth by its chief herbivore and recruitment of predators via indirect defense. Thus, for natural control purposes, attention should be given to monitoring both herbivore and predator populations during early growth of this weed, while supporting the selection of biological controls on the basis of their specificity to the identified in-field host plant BVOCs.

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Compliance with ethical standards

Conflict of interest The authors have no conflict of interest to declare.

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