


# The effects of climate change associated abiotic stresses on maize phytochemical defenses

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**Abstract** Reliable large-scale maize production is an essential component of global food security; however, sustained efforts are needed to ensure optimized resilience under diverse crop stress conditions. Climate changes are expected to increase the frequency and intensity of both abiotic and biotic stress. Protective phytochemicals play an important role in both abiotic stress resilience and resistance to biotic challenges, yet the concentration and composition of these phytochemicals are also dependent on climate variables. We review the research on the effects of climate change associated abiotic stresses on three classes of maize defense metabolites, including benzoxazinoids, volatile organic compounds, and terpenoid phytoalexins. Despite significant knowledge gaps that still exist, it is evident that climate change will influence maize phytochemicals associated with

resilient productivity. While broad generalizations are not yet possible, climate induced changes in phytochemicals are context specific and dependent upon developmental stage and tissue type. Under conditions of drought, maize modulates different classes of defense phytochemicals to protect the above- and belowground tissues. Aboveground the benzoxazinoid defenses are stimulated, but belowground terpenoid phytoalexins are predominantly deployed. Changes in the allocation or distribution of the different classes of defense metabolites or signaling molecules have the potential to further shape the biodiversity and abundance of pests within the maize agroecosystem. A better understanding of the underlying genetics, biosynthetic pathways, regulation and precise biological roles of maize phytochemicals modulated by arrays of climatic conditions will be required to ensure

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optimal plant resilience and productivity in the face of combined biotic and abiotic stresses.

**Keywords** Maize · Abiotic and biotic stress · Benzoxazinoids · Volatile organic compounds · Terpenoid phytoalexins · Climate resilience

## Introduction

Maize (*Zea mays*) is the most produced grain crop on earth. As an integral component of the world's food supply, maize supports an exponentially growing human population either directly through consumption or indirectly through livestock feed. As an additional demand, there is also increasing use of maize for the production of bio-ethanol as a renewable source of energy and alternative to fossil fuels. To meet growing demands, the U.S. planted roughly 400,000 km<sup>2</sup> of maize in 2012 which was the largest planting in nearly eight decades (Barton and Clark 2014). However, aberrant weather conditions consistent with climate change reduced the yield to the smallest crop harvest per unit area planted in over 20 years. The devastating effects of extreme heat and drought were exacerbated by the outbreak of corn rootworm (Petzold-Maxwell et al. 2013; Zukoff et al. 2016), and increased incidence of fungal infection resulting in mycotoxin contamination of the surviving grain (Bienkowski 2012; Schultz 2012; Smith and Mitchell 2012).

Extreme weather events and the negative impacts of abiotic stress on crop yields are increasing in frequency and intensity (Hatfield et al. 2011). With the continuous burning of fossil fuels and deforestation, the atmospheric carbon dioxide concentration ([CO<sub>2</sub>]) has risen from a pre-industrial concentration of 280 μmol CO<sub>2</sub> mol<sup>-1</sup> air to a current concentration of 400 μmol CO<sub>2</sub> mol<sup>-1</sup> air (1 × [CO<sub>2</sub>]) and is projected to reach 800 μmol CO<sub>2</sub> mol<sup>-1</sup> air (2 × [CO<sub>2</sub>]) before the end of this century (Solomon et al. 2007; Karl et al. 2009). Changes in the composition of atmospheric gases, such as CO<sub>2</sub>, are largely responsible for the greenhouse effect, leading to warmer temperatures and more severe precipitation events. While rising [CO<sub>2</sub>] benefits the photosynthetic activity of C3 plants, only relatively modest increases in C4 plant productivity have been observed at elevated [CO<sub>2</sub>] (Leakey et al. 2006; Kim et al.

2007). As a C4 plant, the modest increase in growth is likely due to the indirect enhancement of water-use efficiency through reduced stomatal conductance and transpiration rather than a direct increase in photosynthesis (Leakey et al. 2006; Allen et al. 2011; Prior et al. 2011). Because of the CO<sub>2</sub>-concentrating mechanism in C4 plants that mitigates the limitations of high photorespiration, maize is already functioning at near-saturated photosynthetic capacity and does not directly benefit from CO<sub>2</sub> fertilization. Nevertheless, since maize is a summer grown crop and is anticipated to experience more frequent episodes of drought, enhanced water-use efficiency will benefit vegetative growth. However, this benefit will not likely compensate for the detrimental physiological costs of warmer temperatures and severe drought on maize productivity because the adverse impacts of these stresses are greatest on the plants reproductive processes (Prasad et al. 2006; Hatfield 2016).

In addition to the impact of abiotic stress on maize, climate change is also predicted to alter the geographical distribution, population dynamics, abundance, and aggressiveness of many important agricultural pests (Elad and Pertot 2014; Sharma 2014). For example, populations of corn earworm (*Helicoverpa zea*), European corn borer (*Ostinia nubilalis*), and corn rootworm (*Diabrotica* spp.) are projected to become more widespread (Porter et al. 1991; Aragón and Lobo 2012; Sharma 2014). Warmer temperatures combined with extreme precipitation or drought are also projected to increase incidence of maize fungal infection and mycotoxin contamination further reducing yield quantity and quality (Diffenbaugh et al. 2008; Wu et al. 2011; Sharma 2014). *Aspergillus flavus* and *Fusarium verticillioides* are of particular concern because they are most aggressive under warmer, dry conditions (Paterson and Lima 2010, 2011). Another concern is that a new *Fusarium graminearum* population, which may be more resilient to extreme weather conditions, appears to be spreading throughout some regions of the U.S. and Canada (Ward et al. 2008; Vujanovic et al. 2012; Vaughan et al. 2016a). Insect pests, pathogens and weeds typically have shorter life cycles and higher reproductive rates that enable them to adapt faster to climate changes than planted crops (Diffenbaugh et al. 2008; Manea et al. 2011; Runion et al. 2014; Sharma 2014). Consequently, future maize crops will be challenged

by intensified biotic stress as well as abiotic stress (Hatfield et al. 2011).

In order to cope with the multitude of abiotic and biotic stress factors in the surrounding environment, plants have evolved sophisticated phytochemical defenses that contribute to resilience. The elucidation of plant defense efficacy requires an understanding of the precise spatial and temporal context in which the diverse protective phytochemicals are synthesized and accumulated. Upon stress perception, conserved signal transduction cascades, including specific ion channels, kinase cascades, reactive oxygen species and phytohormone signaling pathways, are activated and lead to molecular modifications that in turn activate or repress specific phytochemical biosynthetic machinery. The phytohormone abscisic acid (ABA) predominantly controls abiotic stress responses, while salicylic acid (SA) and jasmonic acid (JA)/ethylene signaling pathways mediate biotic stress resistance. The interactions between stress signaling pathways have been the focus of extensive scientific studies and reviews (Fujita et al. 2006, 2009; Robert-Seilaniantz et al. 2011; Atkinson and Urwin 2012; Rejeb et al. 2014; Foyer et al. 2016; Verma et al. 2016). An individual stressor can activate common or antagonistic pathways, resulting in cross-tolerance or cross-talk with other stress responses (Foyer et al. 2016). For example, SA usually has an antagonistic effect on JA defense responses, while ABA frequently has a positive effect on JA mediated defenses. Recent findings also suggest that ABA is central in the fine-tuning of observed responses to simultaneous biotic and abiotic stresses. Nevertheless, it is evident that the efficacy of the defense response depends on the plant species and developmental stage, as well as the nature, timing, and degree of the interacting stress stimuli (Rejeb et al. 2014).

Maize produces many different types of resilience/resistance compounds including defense-related proteins, flavonoids, and cell wall components such as lignin. However, in the present paper, we focus on three specific classes of maize defense metabolites, namely, benzoxazinoids, volatile organic compounds, and terpenoid phytoalexins. We review what is known about how abiotic stress conditions influence these maize defense metabolites and discuss knowledge gaps and potential future challenges facing maize productivity.

## Benzoxazinoids

The most extensively studied class of defense-related phytochemicals in maize are the benzoxazinoids. Benzoxazinoids are nitrogen containing, indole-derived compounds based on a 2-hydroxy-2H-1,4-benzoxazin-3(4H)-one skeleton and are associated with a wide variety of general defense activities against bacteria, fungi, insect herbivores and competing plants (Niemeyer 2009; Wouters et al. 2016). In addition to direct defense activity, benzoxazinoids have also been implicated in endogenous signaling functions regulating innate immunity and callose deposition (Ahmad et al. 2011). Benzoxazinoids accumulate as glucoside conjugates with 2-(2,4-dihydroxy-7-methoxy-1,4-benzoxazin-3-one)-beta-D-glucopyranose (DIMBOA-Glc) and 2-(2-hydroxy-4,7-dimethoxy-1,4-benzoxazin-3-one)-beta-D-glucopyranose (HDMBOA-Glc) predominating (Niemeyer 2009; Wouters et al. 2016). These benzoxazinoid glucosides are largely considered phytoanticipins due to their accumulation in young tissues where they serve as a defensive reserve that can be quickly activated upon attack. However, consistent with inducible defenses, HDMBOA-Glc rapidly accumulates following caterpillar herbivory and pathogen infection via both de novo biosynthesis and the O-methylation of existing DIMBOA-Glc pools (Oikawa et al. 2004; Dafoe et al. 2011; Huffaker et al. 2011a). In response to cellular damage, plastid-localized glucosidases come into contact with the vacuole-localized  $\beta$ -glycosides to liberate the corresponding aglycones (Glenn et al. 2002; Niemeyer 2009). Both DIMBOA and HDMBOA aglycones have a short *in planta* half-life and quickly degrade into a complex array of further reactive products. Among the stable and quantifiable breakdown products, 6-methoxy-benzoxazolin-2-one (MBOA) is considered an effective insect-deterrent and antibiotic compound (Richardson and Bacon 1993; Bravo et al. 1997; Glenn et al. 2002; Meihls et al. 2012).

The concentration and composition of benzoxazinoids varies with maize genotype, organ and age, but is also dependent on weather conditions such as those associated with climate change (Niemeyer 2009). Warmer temperatures increase the rate of maize growth and development (Hatfield and Prueger 2015), which can influence tissue benzoxazinoid content because concentrations are highest in

seedlings and continually decline with plant maturity (Cambier et al. 2000). Correspondingly, studies conducted in wheat indicate that temperature induced changes in growth rate influenced both constitutive and inducible benzoxazinoid defenses (Gianoli and Niemeyer 1996, 1997). Warmer soil temperatures and changes in moisture content also have the potential to expedite the degradation of maize root benzoxazinoid exudates leading to changes in allelopathic potential, belowground organ susceptibility and microbial communities of the rhizosphere (Woodward et al. 1978; Neal et al. 2012). Conditions of drought that restrict maize growth have been shown to increase total seedling DIMBOA concentrations (Richardson and Bacon 1993). Furthermore, Erb et al., demonstrated that drought induced ABA signaling leads to the accumulation of DIMBOA and other phenolic compounds in maize leaves (Erb et al. 2009a; b; 2011). On the other hand, conditions of drought in combination elevated [CO<sub>2</sub>] resulted in reduced constitutive levels of DIMBOA-Glc and HDMBOA-Glc in maize stem tissues (Vaughan et al. 2016b), but the aglycones were not measured in this study so direct comparisons are not possible. Further research is needed to determine how differences in the composition and quantities of individual benzoxazinoids will ultimately influence maize susceptibility to pests.

The production potential of nitrogen containing metabolites such as benzoxazinoids are dependent on soil nitrogen availability, and future climate conditions are projected to increase soil erosion and deplete fertility (Brevik 2013). However, while soil nitrogen deficiency reduces maize leaf DIMBOA content, low phosphorous increases the amount of DIMBOA (Schlüter et al. 2013). In the absence of significant fertilizer applications, both nitrogen and phosphorous are projected to become increasingly limited under conditions of elevated [CO<sub>2</sub>] (Niklaus and Körner 2004). Additional research investigating the interactive effects of both low nitrogen and phosphorous on benzoxazinoids will be necessary to fully understand the potential impact of depleted soil fertility in the context of climate change.

Given the limited amount of data available, it is difficult to predict the impact of future climate conditions on maize benzoxazinoid defenses. Obviously the timing and location of pathogen or insect herbivore attack influences the outcome, but under conditions of drought benzoxazinoid defenses will

likely be stimulated in maize leaf tissues. Even under warmer temperatures the growth rate of maize will be limited by water availability. A stimulation in benzoxazinoids, may provide enhanced protection against insect and pathogen invaders which are sensitive to these compounds. However, the drought stimulated enhancement of benzoxazinoids and other phenolic compounds alone were not sufficient to induce resistance against the generalist herbivore *Spodoptera littoralis*, nor the necrotrophic pathogen *Setosphaeria turcica* (Erb et al. 2011). Furthermore, it is unclear how the interaction between elevated [CO<sub>2</sub>] and drought will influence the entire array of benzoxazinoid metabolites and complex pathway regulation.

### Volatile organic compounds

Maize has been widely studied as a model for the production of volatile organic compounds (VOCs) that function as an airborne plant intra- and interspecies communication system (Turlings et al. 1990; Engelberth et al. 2004; Ton et al. 2007). Maize VOCs are structurally diverse and include indole, C6 green leaf volatiles (GLVs), and multiple terpenoids: C10 monoterpenes, C15 sesquiterpenes, homoterpenes (comprising C11 (3E)-4,8-dimethyl-1,3,7-nonatriene (DMNT) and C16 (3E,7E)-4,8,12-trimethyl-1,3,7,11-tridecatetraene (TMTT)), and C20 diterpenes. Plants constitutively emit low levels of specific volatiles, but unique blends are induced by different types of stress and play an important role in both defense signaling and resistance. For example, the emission of GLVs and indole from herbivore damaged maize leaves has been shown to prime the defenses of distal tissues or neighboring plants resulting in a stronger and/or faster defense response upon subsequent attack (Engelberth et al. 2004; Erb et al. 2015). Additionally, herbivore-induced volatiles function in indirect defense via the attraction of natural enemies of the herbivore. For instance, maize leaves damaged by *Spodoptera exigua* (beet armyworm) larvae emit VOCs that attract female *Cotesia marginiventris* parasitic wasps, which lay eggs in the larvae causing their untimely death and consequently reduced plant damage/consumption (Turlings et al. 1990, 1991). Nevertheless, since VOCs are indiscriminately released into the plants surroundings they can also be recognized and used by insects to locate preferred host plants. For example, gravid

female moths of *Ostrinia nubilalis* (European corn borer) are attracted to the maize GLVs nonanal and decanal (Molnar et al. 2015).

There is a large amount of variability in the composition and quantity of constitutive and inducible VOCs produced by different maize cultivars and lines (Turlings et al. 1998; Kollner et al. 2009; Degen et al. 2012); however, environmental conditions can also contribute to variation in VOC emissions. Soil moisture, air humidity, temperature, and light intensity all have been shown to influence maize VOCs. In response to induction by *Spodoptera littoralis* oral secretions, volatile emissions from young maize leaves were greatest at 60% relative air humidity and between 22 and 27 °C (Gouinguene and Turlings 2002). However, the relative abundance of individual volatile compounds varied at different temperatures (Gouinguene and Turlings 2002). Although temperature can affect the vapor pressure of volatiles, it was speculated that changes in emission of the induced volatiles with temperature and humidity was due to changes in stomatal aperture. Indeed, stomata are thought to be the main route of exit for many leaf volatiles (Widhalm et al. 2015). In support of this hypothesis, maize leaf treatment with ABA or dark exposure at midday (two treatments that reduce stomatal aperture) reduced the emission of *E*- $\beta$ -farnesene (Seidl-Adams et al. 2015). However, the effect of stomatal conductance on volatile release depends on the chemical properties of the individual volatile, and emission of some volatiles have been found to be more dependent on stomatal aperture than others (Fall and Monson 1992; Nemecek-Marshall et al. 1995). Interestingly, Gouinguene and Turlings (2002) reported that elicited maize volatiles were greater from plants in dry soils than in wet soils; however, while the amount of DMNT and indole emitted was greatest at 20–40% soil moisture, the concentration of (*E*)- $\beta$ -caryophyllene and bergamotene was greatest at 80–100% soil moisture. Nevertheless, given that a natural physiological stress response of plants to elevated [CO<sub>2</sub>] and drought is the reduction of stomata aperture, these abiotic stress conditions likely hinder the release of numerous maize volatiles that regulate multi-trophic interactions.

Volatile organic compounds are also emitted from maize roots. In response to root attack by the specialist maize herbivore *Diabrotica virgifera virgifera* (Western corn rootworm), roots produce the

sesquiterpene (*E*)- $\beta$ -caryophyllene that attracts the entomopathogenic nematode *Heterorhabditis megidis* (Rasmann et al. 2005). However, *D. virgifera* can also use maize root volatiles, specifically the gaseous hormone ethylene and (*E*)- $\beta$ -caryophyllene, to select the most suitable host plants (Robert et al. 2012). Therefore, herbivore-induced volatiles in maize roots play similar roles as their aboveground counterparts. (*E*)- $\beta$ -caryophyllene diffuses through the soil in the gas phase and predictably low soil moisture facilitates diffusion. However, at extremely low levels of soil moisture, (*E*)- $\beta$ -caryophyllene is rapidly lost into the atmosphere through vertical diffusion (Hiltpold and Turlings 2008). Drought and warmer soil temperatures will likely increase the rapid loss of root-derived volatile signals leading to changes in belowground multi-trophic interactions and defenses.

As discussed in the context of benzoxazinoids, the indirect influence of future climate conditions on soil fertility may also reduce maize VOC production. Maize supplemented with a complete nutrient solution released significantly more constitutive and induced volatile organic compounds (Gouinguene and Turlings 2002). Therefore, without increased fertilization, soil erosion may further compromise maize VOC based defenses.

Given that different weather conditions can have profound effects on the emission and dispersal of VOCs, understanding the impact of climate variability on the biosynthesis of these VOCs is more complex. For example, the measurement of emitted volatiles from the head space alone may not represent the total quantity synthesized under the different environmental conditions. A more comprehensive approach is necessary. Such as the methods used by Seidl-Adams et al. (2015) that included analyses of biosynthetic gene expression and quantification of both volatiles emitted and intracellular volatile accumulation. Further studies using this approach are required to fully differentiate between environmental effects on volatile biosynthesis with respect to measured volatile emission.

In addition to effecting volatile production and release, weather conditions can also affect the unique chemistry of VOCs. Many abiotic stresses lead to enhanced oxidative stress that may result in oxidation of certain volatiles changing their ability to act as airborne signals (Niinemets et al. 2014). Furthermore, changes in atmospheric gases, particularly the

presence of pollutants impacts the chemistry of many volatiles after they have been released from the plant. For instance, moderately enhanced atmospheric ozone levels result in the degradation of many herbivore induced terpenes and GLVs (Pinto et al. 2007). The potential effects of climate change on volatiles from a variety of plant species were recently reviewed (Blande et al. 2014).

Despite the insights provided by published research, additional information is still required to determine how the interactions of multiple simultaneous abiotic and biotic stress factors will influence maize VOC production and emission. Furthermore, it remains unclear how climate induced changes in VOC production will influence the web of ecological interactions with maize. While climate can directly shape the community structure surrounding maize crops, it can also indirectly alter plant produced signals that are involved in the attraction and/or repellence of interacting insects and microbes, both which in turn can further dictate community structure and influence maize productivity. Therefore, ecological studies paired with genetic mechanisms and resources are an essential combination to fully understand and demonstrate how climate induced changes in maize VOCs relate to field relevant resilience. An added layer of complexity is the ability of insects to learn chemical cues through positive and negative associations (Paré and Tumlinson 1999; Jones and Agrawal 2017). Altered differences in the rates of development, thermal tolerance and associative learning between parasitoids, predators and herbivores could have further consequences during climate change (Eigenbrode et al. 2015).

### Terpenoid phytoalexins

Compared to the maize benzoxazinoid pathway, similarly complex arrays of non-volatile terpenoid phytoalexins exist yet were first discovered only recently in 2011 (Huffaker et al. 2011b; Schmelz et al. 2011). Recent analyses of pathway mutants suggest important and unexpected roles in maize resilience (Vaughan et al. 2015). To date, maize terpenoid phytoalexins consist of zealexins, which are sesquiterpene acids on a  $\beta$ -macrocarpene carbon skeleton and kauralexins which are acidic diterpenoid *ent*-kaura(e)ne derivatives. Both zealexin and kauralexins contain numerous related family members that display

significant antifungal activity against various maize pathogenic fungi (Huffaker et al. 2011b; Schmelz et al. 2011, 2014). Additionally, kauralexins can be induced by *O. nubilalis* stem tunneling and function as local insect antifeedants (Schmelz et al. 2011). While strongly pathogen-inducible, kauralexins are also unexpectedly produced in roots during drought stress and play a measurable role in drought tolerance (Vaughan et al. 2015). Furthermore, the abundance of zealexin and kauralexin phytoalexins can vary dependent upon the type of stress. For instance, the concentration of total zealexins is greatest in response to pathogen infection, but in response to herbivore damage or drought the kauralexins comparatively predominate (Huffaker et al. 2011b; Schmelz et al. 2011; Vaughan et al. 2015).

As inducible defense metabolites synthesized *de novo* in response to stimuli, the accumulation of terpenoid phytoalexins is subject to cross-talk between signaling pathways during conditions of multiple stress factors. In maize stalks, the biosynthesis of the terpenoid phytoalexins is promoted by the synergistic interactions between of jasmonic acid (JA) and ethylene (Schmelz et al. 2011, 2014). However, belowground treatment with ABA alone is sufficient to induce the accumulation of terpenoid phytoalexins of maize roots (Vaughan et al. 2015), suggesting that regulation may vary among organs. Further research is needed to verify the organ specific involvement of the different phytohormone pathways regulating terpenoid phytoalexin production.

Several publications investigating the influence of elevated [CO<sub>2</sub>] and drought on the accumulation maize terpenoid phytoalexins have recently been published (Vaughan et al. 2014, 2015, 2016b). Since multiple variables were evaluated in these studies, the data obtained from maize stem inoculations with *Fusarium verticillioides* under the different abiotic stress conditions have been compiled into a heat map (Fig. 1). Interestingly, growth at elevated [CO<sub>2</sub>] compromised the induction of both jasmonic acid (JA) and salicylic acid (SA) in maize (Vaughan et al. 2014). This is unlike soybean plants that exhibit an increase in SA while JA signaling is dampened (Casteel et al. 2012). Consistent with compromised JA signaling, the accumulation of downstream terpenoid phytoalexins was also reduced at elevated [CO<sub>2</sub>], and the maize plants were more susceptible to pathogen proliferation.

Although drought has the potential to enhance JA signaling (Riemann et al. 2015; Vaughan et al. 2016b), the addition of drought stress did not negate the compromising effects of elevated  $[\text{CO}_2]$  on the maize defense response. Despite the more rapid and higher accumulation of JA under conditions of drought, maize under conditions of elevated  $[\text{CO}_2]$  with and without drought stress accumulated less terpenoid phytoalexins than irrigated plants at ambient  $[\text{CO}_2]$ . Interestingly, there were also significantly less terpenoid phytoalexins in the inoculated tissue of drought stressed plants at ambient  $[\text{CO}_2]$  in comparison to irrigated plants at ambient  $[\text{CO}_2]$  (Vaughan et al. 2016b). However, since the accumulation of terpenoid phytoalexins is also dependent on the concentration and early progression of the inoculum (Huffaker et al. 2011b), this result may be attributed to less pathogen proliferation due to drought-related hydraulic changes in the stem tissue that were non-conductive to the pathogen growth (Vaughan et al. 2016b). Comparative works with heat killed fungal spores could resolve innate differences in basal defense elicitation caused by abiotic variables.

Belowground kauralexin accumulation in response to *Diabrotica balteata* larval feeding damage was also reduced at elevated  $[\text{CO}_2]$  under well-watered conditions (Vaughan et al. 2014). However, given that terpenoid phytoalexins are induced in root tissues by drought stress and this induction is mediated by ABA, the compromising effects of elevated  $[\text{CO}_2]$  on JA and kauralexin accumulation in response to *D. balteata* larval feeding damage was negated under the combined conditions of elevated  $[\text{CO}_2]$  and drought (Vaughan et al. 2016b).

Vast knowledge gaps remain in our understanding of how future climate variability will impact inducible maize defenses, such as terpenoid phytoalexins. Additional research is needed to evaluate the role of terpenoid phytoalexins in abiotic stress and determine the mechanism(s) involved in kauralexin mediated drought stress tolerance. The impact of warmer temperatures on maize terpenoid phytoalexins also remains to be determined. JA signaling can be upregulated in response to heat stress and is thought to play a role in thermotolerance of some plants (Sharma and Laxmi 2016). The impact of individual and combined abiotic and biotic stress factors on ethylene signaling is another area of research worthy of consideration. It is possible that the induction of JA

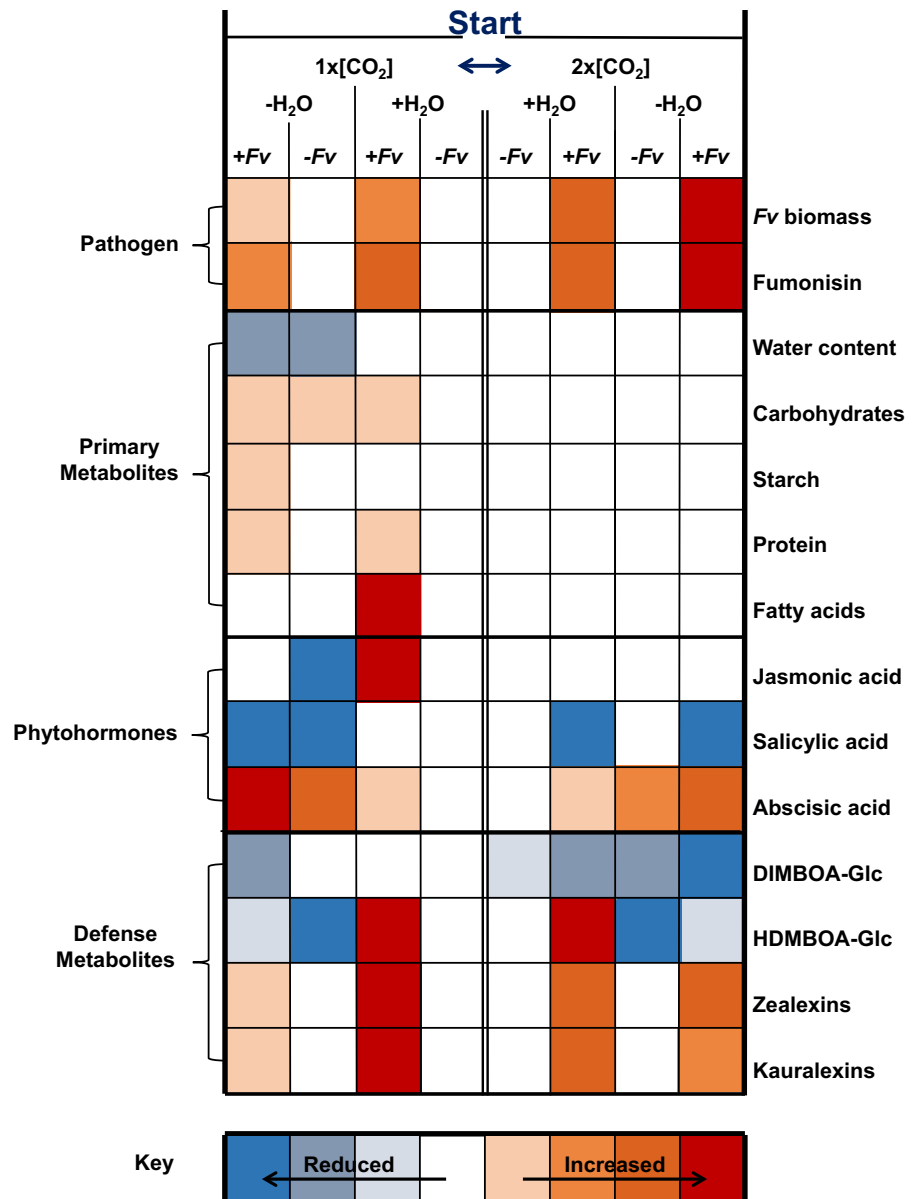
and ethylene with heat stress will negate the effects of elevated  $[\text{CO}_2]$  alone and in interaction with drought.

## Knowledge gaps and conclusions

A simplified summary of the effects of individual and combined abiotic stress factors on maize phytochemical defenses was constructed (Fig. 2). This overview integrates both constitutive and induced defense responses to broadly capture empirical data relating to the potential impact of various abiotic stressors associated with climate change on the listed classes of phytochemicals. At first glance, it is evident that numerous knowledge gaps exist, particularly in understanding the interactive effects of multiple simultaneous abiotic stress conditions on maize phytochemicals. This is of particular concern given that future climate predictions suggest that our agricultural systems will more frequently be challenged by a combination of multiple abiotic stressors (elevated  $[\text{CO}_2]$ , drought, and heat). Additionally, the influence of the abiotic stress on maize phytochemicals will further depend on the organ type and developmental stage. Research has primarily focused on the aboveground portions of younger maize plant tissues, and extrapolations to other tissues or mature maize plants may not be possible at this time.

While an individual maize plant is likely to experience multiple abiotic stress conditions in a given year, changes in atmospheric composition will be the most consistent stress. Overall, elevated  $[\text{CO}_2]$  appears to compromise maize phytochemical defenses suggesting that future maize plants will be more susceptible to biotic stress. Drought and heat stress have a positive to mixed effect on the phytochemical defenses depending in part upon on the degree of the stress. Under conditions of drought, maize appears to modulate its phytochemical defenses by organ type. Aboveground the benzoxazinoid defenses are stimulated, but belowground in the roots terpenoid phytoalexins are predominantly deployed. The susceptibility or resistance of drought stressed maize will ultimately depend on the sensitivity of the pest or pathogen to the major class of defenses deployed within that particular tissue. For example, the strategy of enhanced aboveground benzoxazinoid defenses will not protect maize against the mycotoxigenic fungus *F. verticillioides*, which is capable of

**Fig. 1** Heat map of compiled data from (Vaughan et al. 2014, 2016b). Starting at the top center of the map, the main control is the uninfected ( $-Fv$ , damaged and mock-inoculated stems) maize at ambient  $[CO_2]$  ( $1 \times [CO_2]$ ) with irrigation ( $+H_2O$ ). All comparisons are relative to the value of this main control, designated white. Factors that deviate from control are either increased (orange/red) or reduced (blue); the color key at the bottom of the map indicates the magnitude of the either an increase or decrease relative to the concentration of the control. The data has been arranged so that the comparisons can be made starting from the center where the  $-Fv$ ,  $+H_2O$  maize plants at  $1 \times [CO_2]$  and elevated  $[CO_2]$  ( $2 \times [CO_2]$ ) are side by side and the addition of pathogen infection ( $+Fv$ ) and drought ( $-H_2O$ ) radiate out from the center. The  $2 \times [CO_2]$  is inverted and extends to the right, while the respective comparisons at  $1 \times [CO_2]$  extends to the left. (Color figure online)




detoxifying benzoxazinoids (Glenn et al. 2001, 2002), but displays reduced growth in the presence of terpenoid phytoalexins (Vaughan et al. 2014). Indeed, *F. verticillioides* has been shown to thrive on drought stressed maize (Miller 2001). Likewise, maize plants containing high levels of HDMBOA-Glc are susceptible to maize leaf aphid (*Rhopalosiphum maidis*) due to the reduced presence of free DIMBOA and less effective promotion of callose deposition around the feeding site (Meihls et al. 2013). Thus the fine tuning

of defense modulation will shape the biodiversity and abundance of pests within the maize agroecosystem.

Interestingly, the abiotic stress in direct contact with a tissue type appears to have the most influence on that tissue type, and the impact of that particular stress factor takes precedence over the other stress factors. Elevated  $[CO_2]$  is in direct contact with the aboveground tissues, and reduced soil moisture is directly associated with the roots. Aboveground the compromising effects of elevated  $[CO_2]$  on maize



	Elevated [CO <sub>2</sub> ]	Drought	Heat	Elevated [CO <sub>2</sub> ] x Drought	Elevated [CO <sub>2</sub> ] x Heat	Elevated [CO <sub>2</sub> ] x Drought x Heat	
BXs	↓ <sup>1</sup>	↑ <sup>2</sup>	↑↓ <sup>3</sup>	↓ <sup>1</sup>	?	?	Shoot
VOCs	↓ <sup>4</sup>	↑ <sup>5</sup>	↑↓ <sup>5</sup>	?	?	?	
Z+Ks	↓ <sup>6</sup>	↓ <sup>1</sup>	?	↓ <sup>1</sup>	?	?	
BXs	?	— <sup>2</sup>	↓ <sup>7</sup>	?	?	?	Root
VOCs	?	↑↓ <sup>8</sup>	?	?	?	?	
Z+Ks	↓ <sup>1</sup>	↑ <sup>1</sup>	?	↑ <sup>1</sup>	?	?	



**Fig. 2** Review summary: effects of individual and combined abiotic stress factors on maize benzoxazinoids (BXs), volatile organic compounds (VOCs), and terpenoid phytoalexins (zealexins and kauralexins; Z + Ks) in both the shoots (*top*) and roots (*bottom*). This simplified illustration does not distinguish between constitutive and induced defense phytochemical concentrations, but very broadly displays the potential impacts that can be predicted based on the reviewed literature. With respect to maize not experiencing abiotic stress, the *red arrow* pointing up indicates that the condition is stimulating and the *blue arrow* pointing down indicates that the condition is compromising to the class of phytochemicals. Both a *red* and

*blue arrow* indicates that the effect depends on the timing and degree of the abiotic stress imposed. A *dash* indicates no influence. A question mark suggests that there is not enough available data to predict the potential influence of the abiotic stress condition(s). The numbers in the right hand corner of the boxes indicate corresponding references that support the prediction: <sup>1</sup>(Vaughan et al. 2016b), <sup>2</sup>(Erb et al. 2009b), <sup>3</sup>Prediction based on analysis in wheat (Gianoli and Niemeyer 1996, 1997), <sup>4</sup>(Block et al. 2017), <sup>5</sup>(Gouinguene and Turlings 2002), <sup>6</sup>(Vaughan et al. 2014), <sup>7</sup>(Woodward et al. 1978), <sup>8</sup>(Hiltpold and Turlings 2008). (Color figure online)

phytochemicals takes precedence over any potential stimulation caused by drought. Belowground, the influence of drought on roots appears to supersede the impact of elevated [CO<sub>2</sub>]. While additional research including other interacting abiotic stress factors will be necessary to test this hypothesis, it is consistent with the ‘optimal defense theory’ which predicts that defense-related phytochemicals will be allocated to tissues of greatest value or risk of attack (Zangerl and Rutledge 1996). The assignment of which tissue is of greatest value or risk is not necessarily fixed and can be adjusted based on the plant’s status. Therefore, the outcome of defense signaling cross-talk in different tissues may also depend on the status of that particular tissue and its association to the interacting stress factors.

Understanding the effects of climate changes on maize phytochemicals and the ultimate impact of these effects on maize productivity remains challenging as

integrated interactions are quite complex. The interactive effects of elevated [CO<sub>2</sub>], drought, and heat on maize constitutive and induced phytochemical defenses have not been investigated. Furthermore, induced phytochemical responses may vary with the type of biotic stress interacting with the abiotic stress factors.

Nevertheless, it is evident that weather induced changes in maize phytochemical defense responses will ultimately influence maize productivity. Given that climate simulation models predict a 15–50% decrease in maize yields from the twentieth to the twenty-first century (Xu et al. 2016), and most of these models do not account for the potential impact of extra biotic stress (Chakraborty and Newton 2011), filling the many knowledge gaps is a well merited urgent task. Despite advancements in crop protection methods, pests (including weeds, herbivores, and pathogens) are estimated to account for approximately 30%

of global maize crops losses (Oerke 2006). Maize losses related to herbivores and pathogens display large regional variability. This is thought to be due to the climate restricted geographical distribution of aggressive pests (downy mildews, corn borers) that localize to particular hot spots (Oerke 2006). Climate change will not only widen the area of such potential hot spots, but also compromise natural maize phytochemical defenses that have the potential to limit crop losses to pests.

Effective strategies to improve the resilience of maize productivity in the face of climate changes will have to incorporate knowledge of both abiotic and biotic stress tolerance mechanisms. Although the phytochemicals discussed here, were classically referred to as ‘secondary metabolites’ as they did not appear to have any fundamental roles in plant growth, they are now viewed as specialized metabolites that are essential in plant-environment interactions that mediate adaptation, defense, long-term survival (Ramakrishna and Ravishankar 2011). Therefore, defense metabolites will be a critical component of climate resilience of maize. The recently discovered terpenoid phytoalexins are promising metabolites that function in both abiotic and biotic stress tolerance (Vaughan et al. 2015) and may aid in improving maize resilience to both drought and mycotoxigenic pathogens. Nevertheless, a deeper understanding of diverse maize phytochemical responses to combined abiotic and biotic stress will be required for ensuring and improving future maize productivity.

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