Chapter 8
Influence of Atmospheric and Climate Change on Tree Defence Chemicals

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Abstract Environmental factors associated with atmospheric and climate change can potentially modify the structure and function of the world's forests. An important indirect effect of environmental variables such as elevated carbon dioxide (CO_2), air temperature, ozone (O_3), UV radiation, and water-related stress on forests results from the response of tree secondary metabolism. In particular, the concentrations of defence chemicals displayed by trees can change in response to certain climate change factors, and this may influence interactions with herbivores and pathogens, and the broader forest community. An evaluation of the literature relating to climate change effects on tree defence chemicals shows variable results in both direction and magnitude of concentration changes and a dearth of studies on chemicals other than carbon-based phenolics and terpenes. Nevertheless, some generalities are evident. Elevated CO_2, O_3, and UV-B tend to increase tree phenolics, while mono- and sesquiterpenes remain unchanged. Elevated temperature increases volatile terpene emissions and often foliar terpene concentrations, whereas phenolics are largely unaffected. Water stress tends to increase phenolic concentrations and mild stress can also increase terpene emissions, but the effect of excess water availability remains largely unknown. A greater understanding of the implications of global climate change factors on the defence chemistry of the world's forest trees would benefit from increasing the classes of defence chemicals examined, expanding the diversity of tree species and biomes studied, and incorporating long-term, multi-factor experiments. Clearly much more work is required to fully understand how the complexity of factors involved in global climate change influence defence chemistry in the world's forest trees, and how this in turn will influence future tree growth and fitness and forest ecosystem functioning.

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8.1 Introduction

Forests of one form or another extend over some 30 % of the earth's 14.9 billion ha land area. In terms of cover, tropical forests are the most abundant (49 %) followed by boreal forests (24 %), temperate forests (13 %), sub-tropical forests (8 %) and plantations (5 %). These forests are an important and relatively stable pool in the global carbon cycle, storing some 45 % of terrestrial carbon. They are also important for a range of other ecological, economic and social services, including the conservation of biological diversity. Not surprisingly, primary (old growth) forests, which make up some 36 % of all forests, generally contain the greatest biological diversity. However, these forests are being either lost or transformed, for example, by selective logging at a rate of six million ha per year. Nevertheless, it is heartening that in 2005 some 400 million ha (11 % of total forested land) was designated worldwide for the conservation of biological diversity as the primary function (FAO 2006).

Conservation of biological diversity and a range of other services may, however, be under increasing threat from a set of forces that can potentially modify the structure and function of forests. These include factors such as land use changes and invasive species and pest outbreaks, which almost always have negative effects on forests. They also include highly pervasive factors associated with atmospheric and climate change, including elevated carbon dioxide (CO_2), air temperature, ozone (O_3), UV radiation, and water-related stress. Not all of these latter factors have negative effects on forests (e. g. CO_2), but they do all have a series of direct and indirect effects on trees which, taken together, are not straightforward to predict. For example, elevated CO_2 is known to promote plant growth by stimulating photosynthesis, but it also causes a dilution of nitrogen in foliage, which can in turn lead to at least two effects that can retard growth (Leakey et al. 2009). The first involves a slowing of the litter decay rate and thus the rate of return of nitrogen and other minerals to the soil and eventually to growing plants (see review by Lukac et al. 2010). The second involves an increase in the amount of foliage consumed by herbivory, which often consume sufficient plant material to satisfy their nitrogen demands. The balance between growth promotion on the one hand and retardation on the other is not easy to predict, and will certainly vary between species and environment.

Another important indirect effect of these environmental variables on forest structure and function results from the response of secondary metabolism and in particular, the concentrations of compounds that moderate interactions with herbivores and pathogens (i.e. defence chemicals). It is clear that maximisation of growth and reproductive fitness in trees requires an astute investment of limited energy and resources in chemical defence versus primary growth processes. Despite recent evidence suggesting that plant defence chemicals can share both primary and defensive roles (see Neilson et al. 2013), it remains logical that the optimal balance between these two investments will vary under different environmental conditions, both stressful and favourable to plant growth. Many theories have sought to predict such responses (e.g. Bryant et al. 1983; Herms and Mattson 1992). It is not our intention here to examine these theories. In this chapter, we will review recent work examining how changes in CO_2, air temperature, ozone, UV radiation, and water-related stress affect defence chemicals in trees. Trees can legitimately be treated separately from annuals, such as the model species *Arabidopsis,* because it is likely that selection has favoured quite different responses in long-lived species that cannot easily escape herbivores by quickly completing their lifecycle.

8.2 Carbon Dioxide

Forests play an important role in the global carbon cycle especially through their capacity for net CO_2 assimilation and for storage of large amounts of carbon in a relatively inert form (i.e. lignified tissues that are persistent and relatively resistant to decomposition). Indeed, it is the return to the atmosphere of carbon that has been sequestered by forests, both living (e.g. deforestation) and dead (e.g. coal), that account for much of the rise in atmospheric CO_2 from a pre-industrial level of some 280 ppm to the current annual average of close to 400 ppm. Such a rise in CO_2 has two primary effects on trees, which in turn effect changes in the concentration of defence chemicals. The first effect is a reduction in stomatal conductance (aperture). Interestingly, despite its importance for plant water and energy balances, and for CO_2 uptake, the mechanism by which guard cells respond to CO_2 is still unknown, but it is apparently a ubiquitous response in higher plants (Mott 2009). The second effect of CO_2 enhancement on trees, and C_3 plants generally (n.b. almost all trees have a C_3 photosynthetic system), is on the CO_2 fixing enzyme of photosynthesis, ribulose bisphosphate carboxylase/oxygenase (Rubisco). The ratio of carboxylation (photosynthesis) to oxygenation (photorespiration) catalysed by this enzyme is directly proportional to the CO_2 to O_2 ratio (Woodrow and Berry 1988), so any increase in CO_2 will increase the rate of net CO_2 assimilation. It will also increase the nitrogen use efficiency of CO_2 fixation because more CO_2 can be fixed per unit Rubisco, which itself comprises an appreciable proportion of leaf nitrogen in trees.

8.2.1 Effects of CO_2 Enrichment

The primary and secondary effects of CO_2 enrichment on the carbon and nitrogen metabolism of trees have been quantified in many experiments in glasshouses, open-topped chambers, and FACE (free air CO_2 enrichment) rings. A recent review of FACE studies (Leakey et al. 2009) made six general observations, including that in C_3 plants carbon uptake is enhanced by high CO_2 despite a reduction in Rubisco concentration, and that photosynthetic nitrogen and water use efficiency increases. Effects are, however, quite variable. For example, (Körner et al. 2005), reported little if any affect of high CO_2 exposure on growth in a mature deciduous forest in Europe, whereas Cole et al. (2010) estimated that natural increases in atmospheric CO_2 have caused a 53 % increase in the growth of quaking aspen (*Populus tremuloides*). It is not surprising, therefore, that chemical defence metabolism, which is influenced both by carbon and nitrogen supply (Fritz et al. 2006), responds to high CO_2 to establish a new balance between growth and chemical defence. It is also not surprising that such a balance will vary with many factors, including plant type, chemical defence compound (type and location), plant age, and the prevailing environmental conditions. With regard to plant type, research on high CO_2 effects on trees has focussed on representatives of very few genera (namely, *Acer*, *Betula*, *Citrus*, *Eucalyptus*, *Fagus*, *Picea*, *Pinus*, *Populus, Pseudotsuga, Quercus* and *Salix*). Importantly, four of these genera make up a sizeable proportion of the species reported as being the most common in a recent inventory of the world's forest (FAO 2006). Notably, species from some of the world's largest and most species-rich forests (i.e. wet tropical forests of Africa and South America) were not well represented in the survey.

One of the most important frameworks for interpreting the results of studies of the response of defence chemicals to high CO_2 involves the assumption that the concentrations of these chemicals are sensitive to substrate (i.e. carbon) supply. In other words, if carbon supply rises through rising photosynthesis, as is the case in most high CO_2 studies, then carbon-based defence chemicals (i.e. those that do not contain nitrogen) should also rise (Bryant et al. 1983; Herms and Mattson 1992). Implicit in this thinking is the assumption that metabolic pathways involved in the synthesis of carbon-based defence chemicals have extra capacity – i.e. that feedback inhibition deriving from a lack of biosynthetic capacity or a lack of capacity to store additional defence chemicals does not negate completely the effects of increased carbon supply. If there is indeed extra capacity, then it is unlikely that it will be even across all of the defence chemicals, and it is unlikely that it will be the same across all species and conditions. Put another way, different species or groups of species will likely have different evolutionary strategies for balancing chemical defence, growth and reproduction (Lindroth 2010).

8.2.2 Carbon-Based Defence Chemicals

Measurements of numerous carbon-based defence chemicals from a range of tree species have largely agreed with the aforementioned ideas, and several generalisations can be made. These relate mainly to studies of photosynthetic tissues. First, mass-based measurements of total carbon-based defence chemicals generally show an increase in concentration (e.g. see meta-analysis by (Koricheva et al. 1998). This increase has generally been found to mirror increases in the carbon to nitrogen ratio, which is driven largely by a reduction in photosynthetic nitrogen and an increase in carbohydrates. Second, different classes of compounds (i.e. those that are synthesised by different metabolic pathways; see Fig. 8.1) often respond

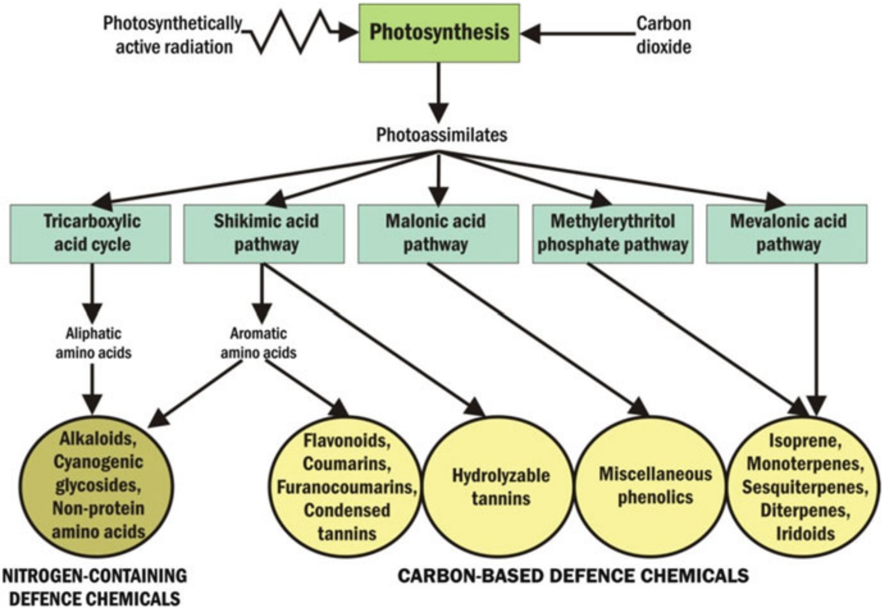

Fig. 8.1 Generalized scheme representing the flow of carbon from photosynthesis through to the major pathways of chemical defence biosynthesis in plants

quantitatively differently to high CO_2. For example, the meta-analyses of trees by Stiling and Cornellisen (2007) and Koricheva et al. (1998) found significant increases in both phenolics and tannins across a range of species. Furthermore, Koricheva et al. (1998) separated measurements of hydrolysable tannins from those of other phenolic compounds derived from phenylpropanoid metabolism, and found both groups to rise significantly under high CO_2. It should be noted that phenolics are a chemically diverse group of compounds involved in both primary and secondary metabolism, and many do not have a clear link to chemical defence.

Terpenoids, on the other hand, have proved much less responsive to high CO_2, with several studies recording a decrease in concentration under high CO_2 (see meta-analysis by Zvereva and Kozlov (2006). This is despite a recent FACE study on a 27-year-old loblolly pine (*Pinus taeda*) plantation finding mono- and diterpene resin mass flow increased by an average of 140 % under elevated CO_2 in trees growing on low-nitrogen soils (Novick et al. 2012). In general, the results of meta-analyses across tree species suggest terpenoids do not show significant responses to elevated CO_2 (Koricheva et al. 1998; Lindroth 2010; Stiling and Cornellisen 2007). It is noteworthy that Novick and co-workers did not detect a significant increase in loblolly pine resin flow under elevated CO_2 for fertilized or carbohydrate-limited trees, supporting the aforementioned importance of the carbon to nitrogen ratio in carbon-based defence responses.

Finally, as noted above, considerable variation has been found in the responses of carbon-based defence chemicals of different species and groupings of species to elevated CO_2. For example, in their meta-analysis, Zvereva and Kozlov (2006) examined studies on the effect of high CO_2 on carbon-based defence chemicals and found a significant rise in angiosperms but a decline in gymnosperms. In a similar manner, Cseke et al. (2009) measured gene expression in two clones of quaking aspen, one being more responsive to high CO_2 in terms of growth than the other. They found evidence of clear differences in the way in which a higher carbon flux is allocated amongst the pathways of secondary metabolism.

8.2.3 Nitrogen-Containing Defence Chemicals

In contrast to the plethora of studies of carbon-based defence chemicals, there has been remarkably little research on those chemicals that contain nitrogen, such as alkaloids and cyanogenic glycosides (see Fig. 8.2). In fact, there has been only one study of this type, on saplings of sugar gum (*Eucalyptus cladocalyx*), which contains relatively high amounts of the cyanogenic glycoside prunasin (Gleadow et al. 1998). It was found that both leaf nitrogen and prunasin concentration declined under high CO_2, but the proportion of nitrogen allocated to prunasin actually increased. Thus, it could be argued that nitrogen was effectively reallocated from photosynthesis to defence.

8.3 Temperature

Global temperatures are predicted to rise during the course of the twenty-first century and beyond. The average global temperature increased by 0.76 °C during the twentieth century, and a further increase of up to 4.0 °C is projected during the twenty-first century (Solomon et al. 2007). Temperature increases are expected to be greatest over land and at most high northern latitudes, thereby influencing the world's forests and those in the Northern hemisphere in particular. Although this section focuses on the direct effects of temperature on tree defence chemicals, it should be noted that temperature changes can also influence herbivore ranges and expansions, and may have large consequences for tree species that lack coevolved defences. For instance, a recent study suggests that global warming has increased the range of mountain pine beetles (*Dendroctonus ponderosae*) so that they now encounter the high-elevation whitebark pine (*Pinus albicaulis*), which is more susceptible to beetle attack than the lower-elevation host species lodgepole pine (*Pinus contorta*; Raffa 2013).

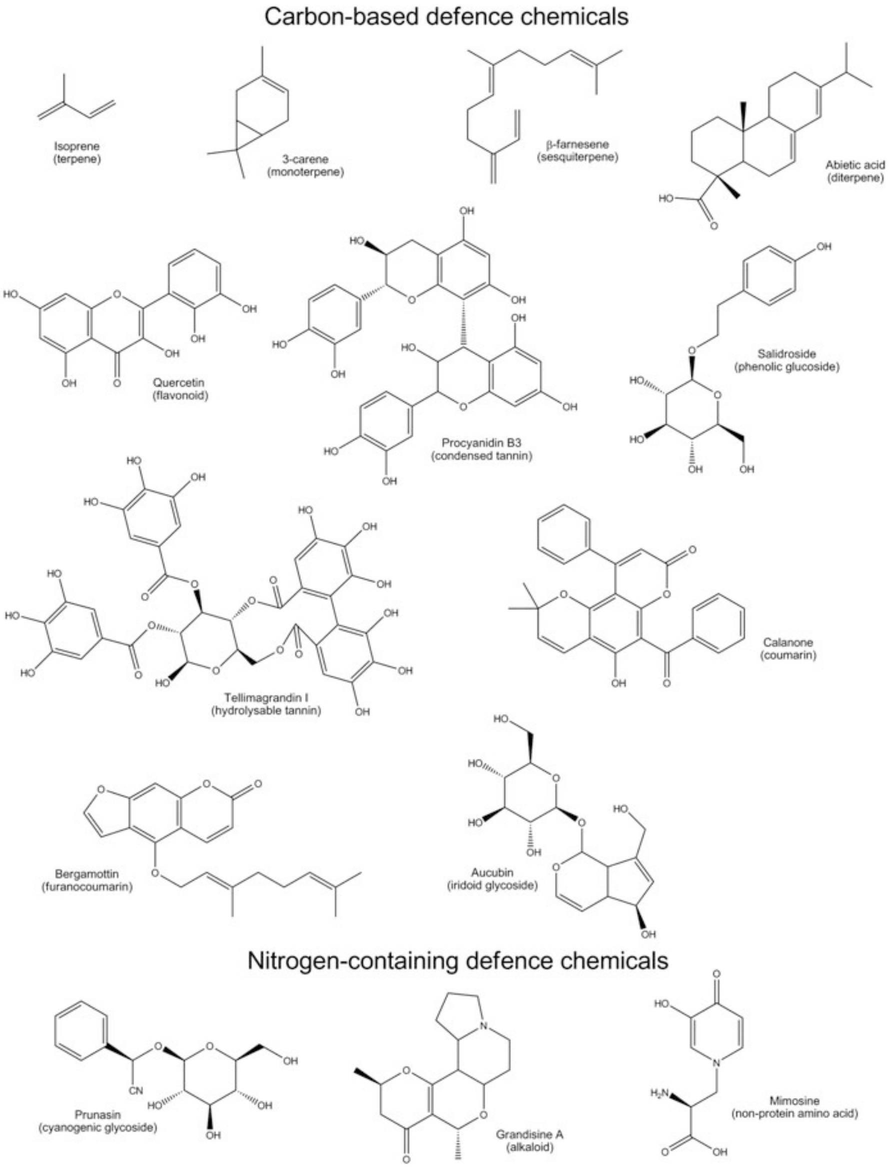

Fig. 8.2 Examples of some of the chemical defences found in trees. The general chemical class of each compound is given in *parentheses*

8.3.1 Temperature Effects on Volatile Defence Chemicals

The key effect of rising temperatures on tree defence chemicals is likely to relate to their volatile emissions. Trees emit a vast array and substantial quantities of volatile organic compounds, including terpenoids (e.g. isoprene, monoterpenes and sesquiterpenes; see Fig. 8.2) and oxygenated hydrocarbons (e.g. alcohols, aldehydes and ketones; Kesselmeier and Saudt 1999). The rate of emission of such volatiles is generally highly correlated with, and apparently dependent on, air temperature. This relationship was exemplified by early work on slash pine (*Pinus elliottii*) that showed that a linear increase in temperature could result in an exponential increase in monoterpene emissions (Tingey et al. 1980). Since then, similar increases in emissions with temperature have been observed for a variety of different terpenoids from numerous tree species, including isoprene from quaking aspen (Fuentes et al. 1999) and white oak (*Quercus alba*; Sharkey et al. 1996), monoterpenes from holm oak (*Quercus ilex*; Loreto et al. 1996) and sesquiterpenes from loblolly pine (Helmig et al. 2006).

The simplest terpenoid is isoprene and it is produced in leaf chloroplasts from photosynthetic intermediates. Although not generally considered a plant defence chemical, isoprene has recently been shown to have deterrent properties towards insect herbivores (Laothawornkitkul et al. 2008). The proportion of fixed carbon emitted as isoprene rapidly increases with temperature via *de novo* biosynthesis. For example, a study on holm oak found that at 30 °C, 2 % of carbon fixed by photosynthesis was emitted as isoprene, but at 40 °C, 15 % was emitted (Loreto et al. 1996). This large proportional increase is attributed to the fact that photosynthesis remains constant or declines at temperatures above 30 °C while isoprene biosynthesis and emission increases. Thus it appears likely that isoprene biosynthesis and emission will increase as global temperatures rise. Given the high proportion of fixed carbon lost as isoprene from the world's forests under global warming, the process of isoprene emission may offset some of the photosynthetic advantages of increased atmospheric CO_2. Moreover, higher isoprene emissions from trees will play an increasingly important role in the atmospheric hydrocarbon budget, influencing air quality and, in particular, contributing to tropospheric ozone depletion episodes (Sharkey et al. 1996).

Monoterpenes and sesquiterpenes are polymers of isoprene and are relatively well characterised as defence chemicals. They are stored predominantly in specialized secretory structures such as resin ducts, secretory cavities, or trichomes which are commonly housed in photosynthetic tissues of trees. The emission of these terpenes is largely dependent on their volatility or on damage to the secretory structures. Generally, terpene emission from trees is assumed to originate via evaporative processes acting on the terpene pools of secretory structures (Grote and Niinemets 2008) and may protect membranes from denaturation during heat stress, thereby increasing the thermotolerance of photosynthesis (Sallas et al. 2003). Evaporation depends mostly on terpene saturation vapour pressure, which is directly related to leaf or needle temperature. Consequently, terpene emissions from trees are commonly calculated by temperature-dependent algorithms (Guenther et al. 1993), and are predicted to increase as global temperature rises. Unlike the situation for isoprene, increases in evaporative emission rates of terpenes have generally been assumed to be independent of de novo biosynthesis. If this assumption is correct, increased emissions may not be balanced by increased biosynthesis. This could potentially lead to decreased foliar terpene concentrations, with subsequent implications for herbivory given their role in chemical defence. Nonetheless, recent work has cast doubt on the assumption that tree monoterpene emission is independent of de novo biosynthesis. The results of a study on four common boreal and alpine forest species showed that at least some monoterpene emissions do result from de novo biosynthesis in all studied species (Ghirardo et al. 2010). In fact, the study showed the proportion of monoterpene emissions that originate directly from de novo biosynthesis to range from 10 % in European larch (*Larix decidua*), to 34 % in Norway spruce (*Picea abies*), 58 % in Scots pine (*Pinus sylvestris*), and to a remarkable 100 % in silver birch (*Betula pendula*; (Ghirardo et al. 2010). If the relationship between terpene emission and concomitant biosynthesis proves to be more general, then increased emissions of mono- and sesquiterpenes with global warming may further offset photosynthetic advantages of increased atmospheric CO_2, especially in species such as silver birch.

Research that has focussed on the concentration of terpenes in foliage of trees subjected to elevated temperatures has produced mixed results. For example, a study on Scots pine seedlings found monoterpene concentrations in needles were not affected by elevated temperature (Holopainen and Kainulainen 2004). In contrast, a study involving both Scots pine and Norway spruce seedlings found the concentrations of almost all examined monoterpenes to increase in both needles and stems (Sallas et al. 2003). In the latter study, the authors suggested that the increase in terpene production might compensate potential terpene emission increases at elevated temperatures. Despite such variable results, a meta-analysis of studies on herbaceous and woody plant species, including a number of tree species, found concentrations of terpenes to generally increase in both green and woody plant parts when plants were subjected to elevated temperature treatments (Zvereva and Kozlov 2006). If the general response of trees to global warming is an increase in terpene concentrations, and if this increase is not counteracted by increased emission rates, then the increased herbivore deterrence and/or toxicity of terpenes may have serious implications not only for herbivores, but also for the wider forest communities that depend on them.

8.3.2 Temperature Effects on Non-volatile Defence Chemicals

The influence of global warming on the numerous non-volatile defence chemicals that trees produce is less clear. Most of the research related to this topic has been conducted on foliar phenolics. By definition, phenolics possess one or more phenol groups (aromatic rings with at least one hydroxyl functional group attached), and common examples include condensed tannins and flavonoids (see Fig. 8.2). Most work has been conducted on the phenolics of northern hemisphere forest species subjected to elevated temperature treatments, but even within this relatively restricted group, few consistent trends have been observed. The aforementioned meta-analysis of studies on herbaceous and woody plant species found a general trend of decreased phenolic concentrations in both green and woody plant parts under elevated temperature (Zvereva and Kozlov 2006). Nevertheless, some studies have observed no change in total phenolics with elevated temperature, such as those on red maple (*Acer rubrum*) saplings (Williams et al. 2003) and Scots pine seedlings (Holopainen and Kainulainen 2004).

Despite inconsistency in the direction and magnitude of changes in phenolic concentration with temperature treatments, the most common observation reported is a reduction in total foliar phenolic concentrations with increasing temperature, although this is not necessarily representative of all individual phenolics in such studies. For example, a study on seedlings of white birch (*Betula pubescens*), silver birch, and dark-leaved willow (*Salix myrsinifolia*) found elevated temperature generally resulted in decreased concentrations of phenolic acids, salicylates and flavonoids, but only condensed tannin concentration decreased in silver birch (Veteli et al. 2007). Similarly, a study on silver birch seedlings at elevated temperature found decreased total phenolics in the leaves, due largely to a decrease in flavonol glycosides and cinnamoylquinic acids, and a decrease in condensed tannins due to a decrease in their precursor (+)-catechin (Kuokkanen et al. 2001). Nevertheless, in that study, the concentration of phenolic glucosides such as salidroside was observed to increase. Furthermore, a study using dark-leaved willow cuttings found the concentration of total phenolics significantly decreased by 25 % under elevated temperatures, and in particular the concentration of chlorogenic acid decreased by 25 %, salicylic alcohol by 27 %, salicortin by 26 % and eriodikytol-di-glucoside by 100 %. However, quercetin and condensed tannin concentrations were unaffected by the elevated temperature treatment (Veteli et al. 2002).

It remains unclear whether temperature has a direct influence on the biosynthesis of tree phenolics or if confounding variables can explain some of the observed changes in phenolic concentrations at elevated temperatures. For instance, a study using saplings of Scots pine found a slight decrease in the concentration of 20 different phenolics at elevated temperature, but the authors concluded that this could be due to mass-based dilution given the greater needle biomass observed in the elevated temperature treated plants (Raisanen et al. 2008). Furthermore, a study on 4-year-old English oak (*Quercus robur*) found an increase in condensed tannins with temperature treatment, but the authors suggested that this result may be confounded by the fact that elevated temperature induced earlier bud burst and that condensed tannins increase with age (Dury et al. 1998). Similarly, the apparent decline in phenolic glucosides in elevated temperature-treated willows could also be an ontogenetic response due to accelerated physiological ageing in the treated trees, and the fact that phenolic glucosides decrease with ontogeny (Veteli et al. 2002). Thus the inherent difficulty of separating biomass and ontogenetic effects from those of elevated temperature may confound interpretation of results in many studies.

Nevertheless, a number of different mechanistic explanations have been proposed to explain a decrease in the foliar concentration of particular phenolics with predicted global temperature rise. First, a decrease in phenolic biosynthesis could be due to differences in activity of enzymes within the biosynthetic pathway at different temperatures (Veteli et al. 2002). Second, elevated temperatures may result in greater losses of carbon via maintenance respiration and, consequently, the biosynthesis of phenolic compounds, especially the glycosylation of flavonoids, would be retarded (Kuokkanen et al. 2001). Third, elevated temperatures may enhance enzymatic breakdown of certain phenolics, especially phenolic glucosides (Veteli et al. 2002). Whether due to one or a combination of these mechanisms, a general reduction in phenolic concentrations is likely due to impact on tree fitness, because of the many and varied primary and secondary roles of phenolics in trees.

Only a few other non-volatile defence chemicals of trees have been examined in the context of global warming. They include the triterpenoid, papyriferic acid, which has been observed to increase in stems of silver birch seedlings subjected to elevated temperature (Kuokkanen et al. 2001), and resin acids which have shown variable responses to temperature treatments. With respect to the latter, a study on Scots pine seedlings found the concentrations of pimaric and dehydroabietic acids in needles, and sandaracopimaric and isopimaric acids in stems to vary significantly across five different temperature treatments (Holopainen and Kainulainen 2004). Despite the significant variation in that study, there was no clear trend of an increase or decrease with increasing temperature. Directionally more consistent results were found in a study on seedlings of two boreal tree species, where elevated temperature increased concentrations of some resin acids in Scots pine needles and total resin acids in Norway spruce needles (Sallas et al. 2003).

8.3.3 Interactive Effects of Elevated CO_2 and Temperature

Potential interactions between rising temperatures and increasing atmospheric CO_2 may have important effects on tree secondary metabolism. Nonetheless, relatively few studies have explored the effects of both parameters in such a way that both their individual and combined effects on tree defence chemicals can be evaluated (Zvereva and Kozlov 2006). A meta-analysis of the studies that have examined the effect of both parameters on plant quality, including terpenes and phenolics, found the results to be taxon-specific and variable depending on the compound analysed (Zvereva and Kozlov 2006). Despite this, the authors generalised that responses to enriched CO_2 can either be independent of temperature, offset by elevated temperature, or apparent only with elevated temperature. These ostensibly contrasting generalisations were based on the fact that several studies concluded temperature does not influence tree secondary metabolism under CO_2 elevation, while others demonstrated clear interactive effects of elevated temperature and CO_2. For example, no significant interaction was found between temperature and CO_2 for phenolic concentrations in leaves of red maple saplings (Williams et al. 2003) or in leaves or stems of silver birch seedlings (Kuokkanen et al. 2001). Indeed, the authors of the latter study suggested that increasing either temperature or CO_2 alone may affect tree secondary metabolism more than a combination of the two factors (Kuokkanen et al. 2001). Moreover, a study on seedlings of three boreal tree species found that phenolic concentration decreased under elevated temperature, increased under elevated CO_2, but was unchanged under a combination of the two factors (Veteli et al. 2007). The study revealed the combined effects of elevated temperature and CO_2 were additive, thereby cancelling out their individual effects (Veteli et al. 2007). A similar trend was found for terpenes and resin acids in a study on Scots pine and Norway spruce seedlings, where significant interactive effects of elevated temperature and CO_2 on needle and stem concentrations of some individual compounds were observed. In that study, the effect of elevated temperature alone was opposite to and much greater than elevated CO_2 (Sallas et al. 2003). Nevertheless, the effect of the combined treatments was generally intermediate between the two factors, again suggesting that temperature and CO_2 have an additive effect on tree defence chemicals.

8.3.4 Phenological Effects of Elevated CO_2 and Temperature

Arguably one of the greatest effects of global warming on forest-herbivore interactions may relate to phenology rather than defence chemicals. Elevated temperatures can lead to phenological mismatches between trees and their insect herbivores (Bidard-Bouzat and Imeh-Nathaniel 2008). Many insects have evolved life histories in which their maximum nutritional demands coincide with the season when developing tree tissue is maximally available. For example, approximately 50 % of forest insect pest species are early-season specialists consuming immature plant tissue when it is generally easier to digest, more nutritious and lower in defence chemicals (Ayres 1993). Increased global temperatures may speed up leaf development rates thus reducing the time that immature foliage is available to these herbivores. Such a phenological mismatch, even on the scale of a few days, can halve herbivore fecundity and therefore greatly impact forest-herbivore communities (Ayres 1993). Rising temperatures, however, are likely to affect insect herbivores similarly by speeding up development, thereby counteracting any such phenological mismatch. In fact, increased insect growth rates may result in increased rates of feeding over shorter time periods, potentially tipping the balance in favour of the herbivores with dramatic impacts for the forest trees.

As with tree defence chemicals, elevated CO_2 is likely to interact with elevated temperature to influence any potential phenological effects. For example, elevated temperatures generally result in accelerated development and enhanced growth and reproductive performance of insects, but elevated CO_2 tends to result in the opposite (Lindroth 2010). Indeed, it has been suggested that temperature increases are likely to mitigate predicted negative effects of enriched CO_2 on insects (Zvereva and Kozlov 2006). Hence, in a similar manner to the combined effects of these factors on tree defence chemicals, elevated temperature and CO_2 may have additive phenological effects.

8.4 Ozone

Unlike CO_2, variations in the O_3 concentration of the lower atmosphere are relatively regional, although there has been an increase in the global background level of some 40 % since the industrial revolution (Solomon et al. 2007). The reason for regional increases in O_3 relates to the mechanism of production of this gas. O_3 is largely produced through the oxidation of atmospheric hydrocarbons in the presence of light and nitrogen oxides. All three of the components of this reaction are highly variable. Hydrocarbon and nitrogen oxide concentrations depend on the intensity of industrial activities, and hydrocarbon concentrations can be further increased by plant emissions (see Sect. 8.3.1). Light intensity varies diurnally, seasonally and regionally. Not surprisingly, therefore, it is predicted that the largest increases in O_3 concentration will occur in the Northern hemisphere, and that globally O_3 will rise to an average concentration of just under 70 ppb by 2050 (Karnosky et al. 2005). Moreover, it is estimated that by the end of the century some 60 % of the world's forests will be significantly affected by O_3 (Vingarzan 2004).

8.4.1 *Effects of Enhanced O_3*

The main mechanism by which O_3 affects plants involves diffusion of the gas through the stomata and into the liquid phase of cells around the intercellular air spaces. O_3 readily reacts with especially lipids and proteins in both the cell wall and plasma membrane, resulting in damage and the release of products such as reactive oxygen species and hydrogen peroxide (Kangasjärvi et al. 2005). This leads to a number of responses, including stomatal closure, production of antioxidants, programmed cell death and other defence responses. Overall, enhanced O_3 causes reductions in photosynthesis and leaf area, and accelerated senescence of leaves, which together result in lower productivity. Wittig et al. (2009), in their meta-analysis of a large number of studies, estimated that the current average ambient level of O_3 of 40 ppb has resulted in a 7 % reduction in the biomass (compared to pre-industrial conditions) of the temperate and boreal forests of the Northern hemisphere. Interestingly, they found that like some CO_2 effects (see Sect. 8.2), gymnosperms were significantly less sensitive to O_3 than angiosperms.

Given that O_3 elicits defence and stress responses involving, amongst other things, the production of reactive oxygen species; it is not surprising that changes in the concentrations of secondary metabolites occur. Indeed, recent work on European beech (*Fagus sylvatica*) saplings showed that elevated O_3 effects an increase in the transcript abundance of genes that are involved in the shikimate pathway (Betz et al. 2009a), which in turn causes an increase in a range of flavonoids and simple phenolics with antioxidant properties. Interestingly, changes in the monomeric composition of lignin were also measured under the enhanced O_3 conditions (Betz et al. 2009b). Most studies of the effects of high O_3 on defence chemicals have, however, not focussed on the mechanisms of the response; rather they have determined the concentration of these chemicals. Like the research on CO_2 effects (see Sect. 8.2), studies have involved a range of tree species, conditions and experimental designs, and the defence chemicals measured have come almost exclusively from the phenolic and terpenoid groups. No studies of, for example, nitrogen-based defence chemicals have apparently been undertaken. Also, like the CO_2 studies, considerable variability – both qualitative and quantitative – has been recorded, depending on species, conditions, and chemical type examined.

In order to make generalisations about these studies of defence chemicals, (Valkama et al. 2007) undertook a meta-analysis of 63 studies of enhanced O_3 effects involving 22 tree species and a range of phenolic and terpenoid compounds. They found that medium- and long-term exposure (i.e. $>$6 months) to enhanced O_3 (i.e. $>$1.5 times ambient) caused an increase in total levels of terpenes and phenolics of 8 % and 16 %, respectively. However, there was considerable variability within these groups of compounds. For example, consistent with the findings of Betz et al. (2009), flavanoids and phenolic acids were found to increase significantly across species, whereas tannins were not. Of the terpenes, a significant increase in concentration was detected for diterpene resin acids, but not for mono- or sesquiterpenes. The analysis of terpene studies also showed that the tree's ontogeny can determine the magnitude of the O_3 response. It was found that mature trees were more responsive than both saplings and seedlings. The authors also drew attention to the considerable variability between species and groups of species. For example, angiosperms were more responsive overall than gymnosperms with respect to the total level of phenolics. There was, however, considerable variability in the responses of individuals within these groups, as summarised in several recent reviews (Bidard-Bouzat and Imeh-Nathaniel 2008; Lindroth 2010; Valkama et al. 2007).

8.4.2 *Interactive Effects of Enhanced CO_2 and O_3*

While both O_3 and CO_2 enhancement have been shown to be able to increase the concentrations of defence chemicals in many tree species, there is reason to propose that concurrent increases in these gas concentrations may show a more complex interactive effect. First, stomatal conductance is reduced under high CO_2, which may decrease the amount of O_3 that can diffuse into leaves. Second, the higher rates of photosynthesis and carbohydrate production under high CO_2 may also increase the capacity of plants to cope with the adverse effects of O_3. Studies of the interactive effects of O_3 and CO_2 were recently reviewed by Valkama et al. (2007) and Lindroth (2010). They concluded that there is evidence of both additive and interactive effects, depending on both the species and the type of defence chemicals examined. In some cases, CO_2 was found to be able to negate the positive effects on a defence chemical of O_3 (e.g. some phenolics; Peltonen et al. 2005), while in other cases there was synergy, with the effect of both gases being greater than the sum of each treatment (e.g. terpenes; Valkama et al. 2007).

8.5 Ultraviolet-B Radiation

In contrast to tropospheric O_3, which is gradually increasing worldwide (see Sect. 8.4.1), stratospheric O_3 has been decreasing, particularly over the last few decades due largely to a marked rise in the concentration of chemicals such as chlorofluorocarbons (CFCs). While trees are not directly affected by events in the stratosphere, the depletion of O_3 has indirect effects, which derive from the fact that O_3 is a strong absorber of UV-B radiation. Modeling has recently shown that there has been a significant rise in the intensity of UV-B at the earth's surface over the last three decades at all latitudes other than the equatorial region (McKenzie et al. 2011). This rise is, moreover, predicted to stabilise, then decline due to reductions in the outputs of O_3-depleting chemicals, with full recovery to the 1980s level likely sometime in the middle of this century (Schrope 2000). Nevertheless, the kinetics of recovery of O_3 levels are dependent on other relatively unpredictable factors such as atmospheric temperature, and UV-B levels can be further influenced by other factors such as cloudiness and aerosol concentration (McKenzie et al. 2011). Clearly, forests will be subjected to enhanced UV-B radiation for some time to come.

8.5.1 Effects of UV-B Enhancement

UV-B radiation affects trees because it is strongly absorbed by macromolecules, including functionally important ones such as proteins and nucleic acids. Absorbance of UV-B radiation causes structural changes in these molecules, which can then lead to deleterious effects including genetic mutations, loss of function of proteins and oxidative stress involving production of active oxygen species. Many studies have sought to examine the effect of enhanced UV-B on overall growth and development of plants, including many tree species. For example, the recent meta-analysis by Li et al. (2010) of studies of enhanced UV-B effects on plants found that some 38 different woody species had been examined. Overall, most evidence suggests that when plants are grown under natural conditions with enhanced UV-B radiation, photosynthetic capacity (i.e. the area based rate of photosynthesis) is not significantly affected, but growth is retarded by small changes in leaf expansion (Ballaré et al. 2011). Trees are generally less sensitive than herbaceous plants, but there is still considerable variation between species (Li et al. 2010). Much of this variation probably relates to differences in UV-B tolerance under normal conditions and differences in the way in which plants acclimate to enhanced UV-B radiation. This latter process is complex and involves UV-B specific and non-specific signalling pathways that moderate a series of processes including morphological changes, accumulation of UV screening compounds (e.g. flavonoids), enhancement of DNA repair, and production of antioxidants (Jenkins 2009).

It is not surprising, therefore, that increases in UV-B radiation are associated with changes in plant defence chemicals, given that up-regulation of especially phenolic metabolism is required to sustain any increase in UV screening and antioxidant compounds, and that many of these compounds also function in defence (e.g. some flavonoids are feeding and oviposition deterrents). Such a diversion of carbon flux could also affect other pathways such as terpene metabolism. Studies of bulk extracts of UV screening compounds from a wide range of species have indeed shown an increase in ability to absorb UV-B radiation, with an average increase of about 10 % for field based studies (Searles et al. 2001). Consistent with this, Li et al. (2010) found that tree species showed a significant increase in UV-B absorbing compounds, especially phenolics, when subjected to both low (18–40 % of ambient UV-B) and high (>40 % of ambient UV-B) radiation treatments. They also noted considerable variation in the response level between species. Overall, tree species show a relatively consistent increase of phenolic metabolism under UV-B enhancement, with increases in a broad range of compounds reported, including flavonoids such as anthocyanins, isoflavonoids and flavonol glycosides, coumarins, tannins and phenolic acids (Bidard-Bouzat and Imeh-Nathaniel 2008). Responses can, however, be complex and few clear patterns have yet to emerge. For example, in a study of 11 phenolic compounds in silver birch leaves, it was found that three compounds increased in concentration while one decreased (Lavola et al. 1997). Similarly, in rough lemon (*Citrus jambhiri*), the concentration of furanocoumarins (which like the flavonoids also absorb strongly in the UV-B) was found to decrease under enhanced levels of UV-B radiation (Asthana et al. 1993).

Relatively few studies of the effect of enhanced UV-B radiation on other groups of defence compounds have been undertaken. For example, it has been reported that terpenoid levels in the bark of silver birch are unaffected by enhanced UV-B radiation (Tegelberg et al. 2002), whereas the level of terpene-derived carotenoids, which serve a photoprotection role, was higher in leaves of holm oak trees growing at high compared to low elevations (Filella and Penuelas 1999). There have been a few studies of nitrogen-based defence chemicals (alkaloid and cyanogenic glycosides) in herbaceous plants, but as yet no tree species have been examined. This is clearly an area that needs additional research because, like high CO_2 effects, UV-B alters both carbon and nitrogen fluxes so it is likely that changes across all groups of defence chemicals will occur (see Fig. 8.1).

8.5.2 Interactive Effects of UV-B and Climate Factors

Globally, increases in UV-B radiation are likely to be combined with rises in CO_2, O_3 and temperature, and changes in water availability. Thus, in order to understand how ecosystems will respond to these changes, it is important to undertake factorial experiments in which the effects of combinations of changes are measured. Studies of the interactive effects of UV-B enhancement and drought have generally shown that the overall growth effect is less than the additive effect of both factors – i.e. UV-B sensitivity is reduced under drought (Caldwell et al. 2007). In contrast, there is little evidence of interactions between UV-B enhancement and either temperature (Day et al. 1999) or elevated CO_2 (Zhao et al. 2003), although most of this work has involved herbaceous species. A recent study of four clones of dark-leaved willow examined the combined effects of UV-B, CO_2 and temperature on both growth and levels of phenolics (Paajanen et al. 2011). No clear results regarding interactive effects emerged from this study largely because the clones had high constitutive levels of phenolics and were thus quite resistant to the UV-B treatment.

8.6 Water-Related Stress

A warmer atmosphere is capable of carrying greater quantities of gaseous water. The subsequent convergence of moisture-laden air masses leads to air uplift, cloud formation and precipitation as rain, hail or snow (O'Gorman and Schneider 2009). Therefore global warming is predicted to result in increased precipitation. The predicted precipitation increases, however, are likely to be regionally specific and not uniform across the earth. Indeed, simulations based on predicted temperature increases in the twenty-first century suggest mean precipitation will generally increase in the deep tropics and extra-tropics, but decrease in the sub-tropics (Sun et al. 2007). Such regional contrasts are due to intense rainfall being an inherently local event that is a direct consequence of the supply of atmospheric moisture from farther afield, where it may otherwise have contributed to more moderate rainfall (O'Gorman and Schneider 2009). Thus rapid increases in precipitation intensity in one region imply a decrease in intensity, duration and/or frequency in other regions (Trenberth et al. 2003). In addition, precipitation extremes are widely held to increase proportionately to the mean atmospheric water vapour content (Pall et al. 2007). Therefore, global warming is also predicted to increase the frequency and intensity of precipitation extremes such as flooding and drought, and this phenomenon is predicted to affect almost all regions of the earth (Kharin et al. 2007). Any changes in precipitation patterns directly influence soil water availability, which in turn affects tree water status and can impact on tree secondary metabolism.

8.6.1 Effects of Excess Water

The most recent models for the influence of global warming on precipitation predict increased intensity of rain and snow in much of the Northern hemisphere (Min et al. 2011), including an increased risk of severe flooding episodes (Pall et al. 2011). In fact, analysis of meteorological data suggests increases in greenhouse-gas concentrations have already resulted in intensification of heavy precipitation events over large swathes of land in the Northern hemisphere during the latter half of the twentieth century (Min et al. 2011). Despite the likelihood of increased soil moisture in such regions, surprisingly few studies have examined the influence of excess water availability on tree secondary metabolism, although its effect on tree nutrition, which may indirectly influence defence chemicals, has received more attention (for review see Kreuzwieser and Gessler 2010).

One of the few studies addressing this topic examined foliar phenolics in tea-leafed willow (*Salix phylicifolia*) trees growing in three different natural habitats: one with permanently water-logged soil, one subjected to regular periods of flooding annually and one growing on well-drained soil, never subjected to water-logging (Sipura et al. 2002). The study found concentrations of condensed tannins and their precursor (+)-catechin, together with ampelopsin and a myricetin derivative, were all highest in the water-logged trees, intermediate in the periodically flooded trees, and significantly lowest in the dry zone trees. These results suggest that the degree of excess water stress can increase the concentration of foliar phenolics, although it should be noted that leaf size (and possibly LMA which is well correlated with phenolics) decreased significantly as the habitats became wetter. In contrast, a study on silky willow (*Salix sericea*) seedlings grown in a common garden experiment found that flooding decreased the concentration of the phenolic glycoside salicortin, but had no effect on $2'$-cinnamoylsalicortin concentration (Lower et al. 2003). Given that global warming is predicted to result in increased precipitation in many regions with an increased likelihood of extreme precipitation events such as flooding, research on the effect of excess water stress on tree defence chemicals is required.

8.6.2 Effects of Drought Stress

In contrast to excess water availability, the influence of limited water availability or drought on tree defence chemicals, particularly carbon-based chemicals, has received more attention. It has been predicted that secondary metabolism should increase under moderate drought stress due to tree growth being limited more than photosynthesis, resulting in the accumulation of carbohydrates and an increase in carbon-based defence chemicals (Ayres 1993). In support of this prediction, a study on black poplar (*Populus nigra*) saplings found that total phenolic glycoside concentrations were 89 % higher in the drought-stressed trees relative to the well-watered control (Hale et al. 2005). Nonetheless, the results of a recent study on apple (*Malus x domestica*) seedlings found that the soluble sugars sorbitol, glucose and fructose increase with low and moderate drought stress as predicted, but the concentrations of defence phenolics did not match predictions as phloridzin decreased with increasing stress while phloretin showed no changes (Gutbrodt et al. 2012). Similarly, in a study of quaking aspen and sugar maple (*Acer saccharum*) seedlings, the concentration of condensed tannins were not altered by drought treatment in either species, nor were those of the hydrolyzable tannins, gallotannin and ellagitannin, which are limited to maples (Roth et al. 1997). In fact, the only defence chemicals that were altered by drought treatment in that study were the aspen phenolic glycosides salicortin and tremulacin, which were significantly reduced by 21 and 14 %, respectively (Roth et al. 1997).

Roth and co-workers attributed their lack of parity with predictions to the following factors. First, drought may have suppressed activity of enzymes required for phenolic biosynthesis, preventing an increase in production. Second, the drought treatment may have been severe enough to retard photosynthesis more than nutrient uptake, leading ultimately to reductions in secondary metabolism due to carbon limitations. In support of this latter notion, a study on Douglas fir (*Pseudotsuga menziesii*) growing different distances from a water source found a non-linear relationship between water stress and condensed tannin concentration, whereby tannin concentrations initially increased under mild water stress, but then levelled off under moderate stress before decreasing under severe stress (Horner 1990). Such non-linear relationships may explain some of the variability observed in studies on drought stress and tree defence chemicals, as most studies have employed only one stress treatment compared to a well-watered control. Thus, to describe potential non-linear relationships between water stress and tree defence chemicals, studies may need to employ additional treatments covering a range of stress levels or multiple harvests during progressive drought.

The influence of drought stress on volatile emissions from trees has also received attention (Kesselmeier and Saudt 1999; Rennenberg et al. 2006) for reviews). In general, emission rates of monoterpenes are mostly unaffected under moderate water stress, when CO_2 and water gas exchange decline, but are reduced under severe water stress. Monoterpene emissions can then increase substantially after rewatering during stress recovery (Kesselmeier and Gessler 1999). With respect to isoprene emissions, a 3 month study on two Eastern cottonwood (*Populus deltoides*) plantations showed emissions were decreased under severe water stress, but stimulated under short term water stress (Pegoraro et al. 2005). These results suggest that moderate soil water stress has the potential to counteract the effect of elevated CO_2 on isoprene by increasing production while decreasing CO_2 assimilation. Global warming is expected to result in mean temperature increases and localised reductions in precipitation in some regions of the world. In these regions, increased isoprene emissions may have negative air-quality impacts on regional atmospheric chemistry (Rosenstiel et al. 2003).

As with the other climate change factors; there has been remarkably little research on the influence of drought stress on nitrogen-containing defence chemicals in trees. One study compared mean foliar cyanogenic glycoside (prunasin) concentration between two sugar gum populations growing in areas with contrasting rainfall (Woodrow et al. 2002). In that study, mean prunasin concentration was found to be higher in the population from the drier site, although the authors attributed this to a concomitant increase in foliar nitrogen. Nevertheless, in a subsequent greenhouse study using sugar gum seedlings, foliar prunasin concentration increased markedly under water stress, and this was independent of changes in leaf nitrogen or any other identifiable variable (Gleadow and Woodrow 2002).

8.7 Conclusions

Factors related to current and predicted climate change are likely to influence at least some of the many defence chemicals produced by the world's forest trees. Climate change factors can act directly and/or indirectly on tree defence chemicals in a number of ways. Direct effects on the concentration of a given defence chemical include changes in biosynthetic enzyme activity, substrate availability, catabolic activity (enzymatic or otherwise) and volatile emission rates. Indirect effects include changes in nutrient availability, which can have flow-on effects on the rate of biosynthesis of particular defence chemicals. The key climate change factors likely to influence tree foliar enzyme biosynthesis are atmospheric CO_2 concentrations, global temperatures, ozone stress, UV levels and water availability, and these factors may act independently or interactively. The direction and magnitude of the effect of these factors on tree defence chemicals appears to be species- and possibly genotype-specific, as well as dependent on the types of defence chemicals produced. Despite the complexity of climatic factors and tree responses, some general trends for defence chemicals under a changing climate are apparent from the research conducted to date:

- Elevated CO_2 consistently results in increased phenolic concentrations, whilst terpenes generally remain unchanged. Nitrogen-containing chemicals have rarely been examined, but in a single study, cyanogenic glycoside content was observed to decrease.
- Elevated temperature consistently results in increased isoprene emissions and may also increase mono- and sesquiterpene emissions. Foliar terpene concentrations may also increase, but phenolic concentrations often remain unchanged, or may decrease. Nitrogen-containing chemicals have not been examined.
- Drought stress can result in increased phenolic concentrations and mild stress can increase terpene emissions. Nitrogen-containing chemicals have rarely been examined, but the cyanogenic glycoside content has been observed to increase under drought stress. The influence of excess water availability is largely unknown, but increased phenolic concentrations have been observed.

- Enhanced O_3 tends to increase phenolics and diterpene resin acids, but appears to have no effect on mono- and sesquiterpenes. Nitrogen-containing chemicals have not been examined.
- UV-B consistently increases phenolics, whereas terpenes remain unchanged. Nitrogen-containing chemicals have not been examined.

8.7.1 Future Directions

A greater understanding of the implications of global climate change for defence chemistry in the world's forest trees would benefit from extending research in a number of clear directions. As outlined succinctly by Lindroth (2010), future research in this area should aim to increase the classes of defence chemicals quantified, expand the diversity of tree species and biomes studied, and incorporate long-term, multi-factor experiments.

The number and type of chemicals examined to date has been restricted to only a few classes of chemical compounds, primarily the carbon-based phenolics and terpenoids, and commonly only select compounds within each class. The influence of global climate change on other classes of carbon-based defence chemicals such as iridoid glycosides is unknown, despite their importance in some tree species. Moreover, nitrogen-containing compounds such as alkaloids, cyanogenic glycosides, and non-protein amino acids can be very important in certain forest ecosystems, but have received scant attention. Irrespective of chemical class, the influence of climate change on the mode of expression of chemical defence, i.e. whether inducible or constitutive, also requires greater attention in the future. For example, a recent study on a non-tree species, *Brassica napus*, found the inducibility of glucosinolates could be altered by both elevated CO_2 and changes in ozone levels (Himanen et al. 2008). Similar changes in tree species could have great implications for forest ecosystems.

The number of species and biomes studied to date has also been relatively restricted and has resulted in much of the world's forests being under-represented. The majority of research has focused on a select group of deciduous and coniferous tree species from particular Northern hemisphere biomes. Future studies should incorporate a greater number of boreal and tropical forests, as both are critically important to the global carbon cycle and a range of other ecosystem services, but neither has received much attention; a problem that is particularly acute for understanding effects on ecosystem services. Similarly, Southern hemisphere forests have rarely been investigated in the context of defence chemistry and climate change, despite the increasing importance and prevalence of plantation forests of genera such as *Eucalyptus* throughout the world.

Arguably the most important improvement to future experimentation in this field will relate to the simultaneous examination of multiple climatic factors. In a recent review, Bidart-Bouzat and Imeh-Nathaniel (2008) concluded that future studies should focus on simultaneously testing the effects of multiple climate change factors to gain a more realistic perspective of how climate change may impact defence chemical production. The evaluation of one or two factors at a time, which has been the general strategy to date, makes predicting the response of trees to changes in the complexity of climate factors very difficult. This is because climatic factors can induce differential responses in trees, in terms of both direction and magnitude of defence chemical changes, and future scenarios affecting the world's forests will be the result of these complex interactions, not single factor changes. According to Lindroth (2010), a better understanding of the ways the various atmospheric and climatic factors interact is needed to more realistically approximate future environments, and to provide a diversity of conditions under which to test the effects of individual factors on tree defence chemicals.

In addition to the inclusion of multiple factors, future experimental designs also need to take into consideration the developmental stage of trees used and the length of experiments. The majority of published studies have been performed on seedlings and saplings, but these immature stages may respond in a very different manner to adult trees and represent a relatively small proportion of the lifespan of tree species. Moreover, the majority of studies to date have been performed over relatively short time periods (months to several years), which are considerably less than the lifespan of forest trees, and do not provide knowledge on the perpetuation of effects over time. Furthermore, short-term experiments with few sampling times can fail to detect non-linear effects of climatic factors on tree defence chemicals. Future research should attempt to overcome logistic and funding constraints to focus more on long-term effects of global change factors on tree defence chemicals. Long-term experiments will also enable studies on indirect effects of climate change on tree defence chemistry such as nutrient cycling at the ecosystem level, potential evolutionary responses of herbivorous insects, as well as effects on mutualistic associations of trees with pollinators and mycorrhizae.

Clearly much more work is required to fully understand how the complexity of factors involved in global climate change will influence the defence chemistry of the world's forest trees and how this in turn will influence future tree growth and fitness in the face of predation.

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