Chapter 1
Diversification of Volatile Isoprenoid Emissions from Trees: Evolutionary and Ecological Perspectives

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Abstract Not all tree species are strong constitutive volatile compound emitters, and a variety of hypotheses have been put forward to explain the evolution and the function of the emissions of volatile compounds. This chapter reviews the evolutionary and ecological aspects of volatile compound production in trees, specifically asking how and in which tree species the capacity for constitutive volatile production has evolved. The capacity for volatile emissions is a polyphyletic trait present in several diverse plant groups, but the presence of emission capacity is not directly related to phylogenetic distance among the species and species genera, demonstrating that the trait has evolved multiple times during evolution. We here review present volatile emission inventories highlighting the need for more worldwide, coordinated efforts to obtain realistic data of geographical and taxonomic patterns. We thereafter discuss the past evolution of isoprenoid emissions, and pose the questions of why isoprene emission is particularly widespread in hygrophytes, why it is a characteristic of mostly fast-growing perennial plants and why it is stimulated by low concentrations of CO_2. Finally, we discuss the future, how climate and global change and the corresponding ecological constraints impact the diversification and emission of volatile organic compounds from plants.

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Ü. Niinemets and R.K. Monson (eds.), *Biology, Controls and Models of Tree Volatile Organic Compound Emissions*, Tree Physiology 5, DOI 10.1007/978-94-007-6606-8_1,

1.1 Introduction: The Spectrum of Volatile Organic Compounds in Plants and the Importance of Constitutive Volatile Isoprenoids

The emission of biogenic volatile organic compounds (BVOCs) by plants was first reported in the 1950s and 1960s (see the Preface; Rasmussen and Went 1965; Sanadze and Kalandaze 1966) and has been studied since by plant biologists and atmospheric chemists. The amount of hydrocarbons emitted into the atmosphere by plants as BVOCs far exceeds the levels from human activity (Sharkey et al. 2008; Peñuelas and Staudt 2010). The large scale of emission, the reactive properties, and the large capacity of many organisms to sense them render several of these products of secondary plant metabolism as particularly important for the chemical and physical properties of the atmosphere. BVOCs also play a critical role in the interaction between the biosphere and atmosphere, in addition to their role in communication amongst organisms (Peñuelas et al. 2009a, b; Dicke and Loreto 2010).

Plants produce several secondary metabolites, which can be classified in three main groups: isoprenoids, phenolics, and nitrogenous compounds. Volatile isoprenoids (isoprene, monoterpenes, and some sesquiterpenes) can be either directly emitted, as is always the case for isoprene, or stored in resin ducts or in glandular trichomes for later release, especially upon mechanical stress. All plant organs can emit isoprenoids; vegetative organs such as leaves and branches (Loreto and Schnitzler 2010), flowers (Knudsen et al. 1993), and roots can all emit volatiles (Steeghs et al. 2004). Volatile isoprenoids are generally easily smelled (e.g., the typical fragrance of flowers, resin, and conifer needles), but isoprene, at its natural concentration, cannot be detected by human olfactory system. Plants release a very large amount of carbon as isoprene, estimated to be more than 500 Tg isoprene year^{-1} (Arneth et al. 2008; Ashworth et al. 2013), more than an order of magnitude of the amount of isoprene emitted by animals (Sharkey and Loreto 1993). The emission of volatile isoprenoids is widespread in terrestrial plants, with no apparent evolutionary or ecological gradient (see below), but high isoprene emitters are generally only trees or perennials. For the purposes of this book on tree physiology, we will therefore present evolutionary and ecological considerations related mostly to isoprene emission.

The reason why plants re-emit up to 10 % of their fixed carbon as isoprenoids (and a much larger proportion under conditions of stress that substantially inhibit photosynthesis) remains a debated issue (Sharkey and Yeh 2001; Peñuelas and Llusià 2004; Vickers et al. 2009) despite the many studies of isoprenoid emission. Plants very likely invest such high metabolic costs to protect vital organs from both biotic (insects and pathogens) and abiotic (especially extreme temperatures and atmospheric pollutants) stresses (Possell and Loreto 2013). Emissions, however, appear to be "specialized", because not all isoprenoids function in plant defence. Isoprene was not believed to have a role in defence against biotic stressors until two independent reports indicated its capacity to repel insects (Laothawornkitkul et al. 2008; Loivamäki et al. 2008). On the other hand, the finding that isoprene (and volatile isoprenoids) protects against abiotic stressors, especially high temperatures (Sharkey and Singsaas 1995; Peñuelas et al. 2005; Velikova et al. 2011) and oxidative stress (Loreto and Velikova 2001; Peñuelas and Llusià 2002; Vickers et al. 2009; Possell and Loreto 2013), has repeatedly been confirmed experimentally. The mechanisms by which isoprene produces its protective effects are also topics of debate. The ideas that isoprene strengthens thylakoid membranes or scavenges reactive oxygen species have been discussed (reviewed by Loreto and Schnitzler 2010). Velikova et al. (2012) have recently suggested that membrane stabilisation may also reduce the production of reactive oxygen and nitrogen species under conditions of stress, thus, reconciling the two putative roles of isoprene. Despite the prominent role of isoprene in plant protection against abiotic stressors, only a relatively few extant plants emit large amounts of isoprene (less than 30 % of the woody species examined to date), the trait having been lost multiple times during the course of evolution (Harley et al. 1999, see below). Another intriguing observation is that plants do not generally emit both isoprene and monoterpenes, but with exceptions, especially in isoprenoid-storing plants. This feature has often been observed and was discussed in detail by Harrison et al. (2013). Even within a single plant species, leaves specialize in emitting either monoterpenes or isoprene at different times during ontogeny, with an apparent trade-off of carbon between the different biosynthetic pathways (Brilli et al. 2009).

Constitutive emissions of monoterpenes may have the same role as that of isoprene. If the mechanism of membrane stabilisation is through lipid solubility and the capacity to delocalize electrons by conjugated double bonds (Loreto and Schnitzler 2010), then several monoterpenes can replace isoprene, as is often seen (e.g., Loreto et al. 2004). Monoterpenes, though, are possibly formed at lower rates, an issue difficult to resolve due to the frequent accumulation of monoterpenes in storage pools and despite the fact that twice as much carbon is required to construct monoterpene skeletons as isoprene skeletons.

Plants that emit monoterpenes and sesquiterpenes, however, accumulate isoprenoids in specialized organs in leaves, stems, or trunks and then massively release them after wounding. The main role of these compounds is thus to act as powerful deterrents to pathogens and herbivores (Dicke and Baldwin 2010) and to contribute to the sealing of wounds (Loreto et al. 2008). Constitutive and induced emissions of volatile isoprenoids may be stimulated by mechanical stresses and metabolic changes in plants attacked by herbivores. The emitted isoprenoids can directly attract or deter herbivores (*direct defence*) or attract parasitoids or predators of herbivores, thus, eliciting an *indirectly induced defence* resulting from the interaction of plants with insects of the third trophic level, i.e., carnivores (Llusià and Peñuelas 2001; Dicke et al. 2003a, b; Matthes et al. 2010; Dicke and Baldwin 2010; Trowbridge and Stoy 2013). After the first report of the interactions amongst the three trophic levels (Price et al. 1980), these relationships became an attractive area for interdisciplinary research involving evolutionary biology, ecology, and plant physiology. Volatile isoprenoids may also activate mutualisms, e.g., with pollinators or ants (Farré-Armengol et al. 2013). In insect-plant mutualisms, the partners involved play different roles. The sedentary partner (the plant) must be easily located and must offer rewards (mostly food) to the mobile partner (the insect), who offers a service but who also has a choice whether or not to visit a particular individual (Farré-Armengol et al. 2013). This relationship implies that plants have evolved particular traits contributing to mutualism, whereas insects have not. In fact, the behavioral repertoire of mutualistic insects is no different from that of their non-mutualistic relatives. Such an asymmetry in trait evolution is particularly evident in more generalized insect-plant mutualisms (Bronstein et al. 2006).

Phylogenetic studies suggest that insect-plant mutualisms, despite their ecological importance, may have appeared and disappeared several times throughout evolutionary history, as has isoprene emission (see below). Pollination and seed dispersal, where physical factors such as wind, water, or gravity have replaced insect- and bird-facilitated dispersal (Bronstein et al. 2006), clearly illustrate this adaptability. Whether changes in BVOC emissions have also played a role in these shifts is not clear, but is a very interesting question. Notably, in the evolution of plants, interactions with pollinators and seed dispersers appeared after herbivory and environmental stresses had already shaped evolution of plants (Farré-Armengol et al. 2013). More generally, understanding the trade-offs between the costs and benefits of emitting volatiles is challenging and important from the viewpoint of evolutionary ecology.

1.2 The Present: Inventories of Volatile Isoprenoids

1.2.1 State-of-the-Art of Emission Inventories

Numerous screening studies have been performed since the 1970s to identify plant species that emit BVOCs. Beginning in North America but later rapidly expanding to Europe and other continents, most of these studies have focused on isoprene, the most abundant BVOC. The results of these species inventories, together with data on canopy densities and species abundances, were used to calculate BVOC-emission capacities of landscapes that were further integrated into emission models to estimate BVOC fluxes at regional, continental, and global scales (Guenther et al. 2006; Ashworth et al. 2013; Guenther 2013).

In addition to their usefulness in estimating emission inventories, data of the relative abundancies of isoprene-emitting species in regional floras may improve our understanding of the evolutionary origins and ecological significance of isoprene emissions. If isoprene production confers significant protection against stresses at non-negligible metabolic costs, then the patterns of species abundance and species dominance of isoprene emitters may vary worldwide according to site-specific conditions. Terrestrial ecosystems, though, differ greatly in age. While communities of tropical forests may be many millions of years old, those at higher latitudes emerged from ice-age refugia only a few thousand years ago and they may still be far from equilibrium. The adaptive significance of isoprene production in younger, often oligospecific plant communities may differ from that in older, often highly diversified communities, independent of differences in the occurrence of abiotic stresses associated with each climate. Furthermore, isoprene emissions may have initially evolved in only a limited number of plant taxa whose distributions depend not only on their competitiveness and the potential role of isoprene production therein, but also on the extent of their past geographical isolation that was governed by geological events such as continental drift and changes in sea level.

Monson and co-workers (2013) recently combined a large dataset of isoprene emission with DNA sequence data to reconstruct the taxonomic distribution and evolutionary history of isoprene emitters throughout the plant kingdom. Their compilation found that all major groups of Gymnosperms (Pinophyta) and Angiosperms (Magnoliophyta) contain both isoprene-emitting and non-emitting species, with perhaps a few exceptions. Isoprene emitters seem to be particularly rare in the subclass Asteridae that consists of modern and highly derived plant clades, many of which are herbaceous species. Isoprene emitters are also rare in the subclass Magnoliidae, which is considered a rather ancient clade within the Magnoliophyta comprising numerous trees and shrubs in tropical and subtropical areas around the world. Nevertheless, isoprene-emission capacity appears to be associated with the perennial lifestyle and to be particularly frequent in woody plant species. Isoprene emission is also present in Pinophyta trees, but emissions appear to be generally low and limited to a few genera (e.g., *Abies*).

We examined about 30 emission inventories for the presence of isoprene-emitting species in the floras form various ecosystems and biomes. From each inventory, we calculated the fraction of isoprene-emitting species per vegetation type, defining isoprene emitters as species with reported emission rates clearly exceeding 1 $\mu g\ g^{-1}\ h^{-1}$ (ca. 4 pmol $g^{-1}\ s^{-1}$). We did not include species with taxonomically assigned emission properties unless we found reliable corroborating information from other sources. Figure 1.1 displays the mean fraction of emitters per biome. These results imply a relatively homogenous presence of isoprene emitters throughout the world's major biomes, with mean fractions only ranging between about 20–35 %. The range is, however, considerably larger when comparing individual screening studies. For example, the fraction of isoprene-emitting species reported at various locales in China (Fig. 1.2) extends from 10 %, reported by Klinger et al. (2002) amongst 67 species in the humid forests of the Ailao Mountains, to 46 %, observed by Geron et al. (2006a) amongst 95 species screened in the tropical Biological Gardens of Xishuangbanna. Worldwide, the average fraction of isoprene-emitting species across all screening studies considered here is 29 %, which is close to the values we have extracted from the global BVOC databases of NCAR and Lancaster University (approximately 32 and 33 %, respectively, for isoprene-emission potentials $>1\ \mu g\ g^{-1}\ h^{-1}$).

Inferring trends from the geographical variation of the fractions displayed in Figs. 1.1 and 1.2 is appealing. For example, the relative presence of isoprene emitters in the floras of tropical and subtropical America tends to decrease from wet to dry forests, savannas, and desert shrublands. The forests of cold highlands and boreal regions seem to have fewer isoprene emitters than temperate forests (Figs. 1.1 and 1.2), whereas the flora of suburban areas may be particularly rich in isoprene

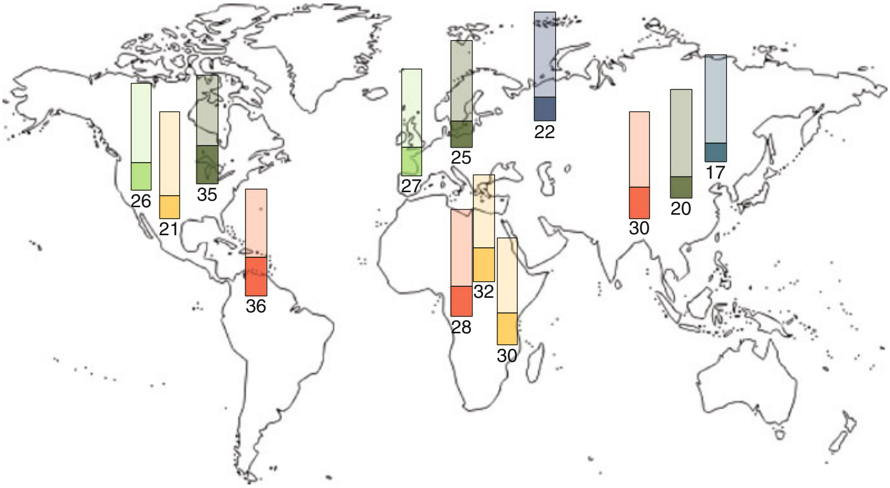

Fig. 1.1 Mean fraction of isoprene-emitting plant species in the floras of various ecosystems around the world (numbers are percentages of isoprene emitters). The colours roughly denote climate classes. *Red*: moist tropical; *yellow*: dry (sub)tropical; *light green*: dry temperate; *dark green*: moist temperate; *blue*: cold (References: Arey et al. 1995; Bracho-Nunez et al. 2012; Chang et al. 2012; Geron et al. 2002, 2006a, b; Guenther et al. 1996a, b, 1999; Harley et al. 2003, 2004; Isebrands et al. 1999; Helmig et al. 1999; Karl et al. 2009; Karlik and Winer 2001; Keenan et al. 2009; Keller and Lerdau 1999; Klinger et al. 1998, 2002; Lerdau and Keller 1997; Lerdau and Throop 1999; Lindfors et al. 2000; Owen et al. 2001; Parra et al. 2004; Rinne et al. 2009; Singh et al. 2008; Tsui et al. 2009; Wang et al. 2003; Xiaoshan et al. 2000; BVOC emission databases of the National Center for Atmospheric Research (http://bvoc.acd.ucar.edu) and the Lancaster University (http://www.es.lancs.ac.uk/cnhgroup/iso-emissions.pdf))

emitters (Beijing, Hangzhou, and Hong Kong in Fig. 1.2). Many ornamental shrubs and trees used for private gardening and urban shading are isoprene emitters that contribute to the atmospheric load of BVOCs in these areas (Niinemets and Peñuelas 2008). Few studies have examined the abundance of isoprene emitters along geographical, climatic/edaphic, and successional gradients in different continents and biomes (Klinger et al. 1994, 1998, 2002; Martin and Guenther 1995). The results of these studies collectively suggest that isoprene emitters, often associated with fast-growing woody species, are more frequent in transitional, mid-successional forests than in late “climax” forests that are dominated by evergreen monoterpene-emitting plants (Harrison et al. 2013).

1.2.2 What Are We Missing in Emission Inventories?

The current species inventories, however, can only be taken as rough estimates of the true prevalence of isoprene emitters in terrestrial ecosystems. The fraction of isoprene emitters determined by screening studies at one location can differ by as

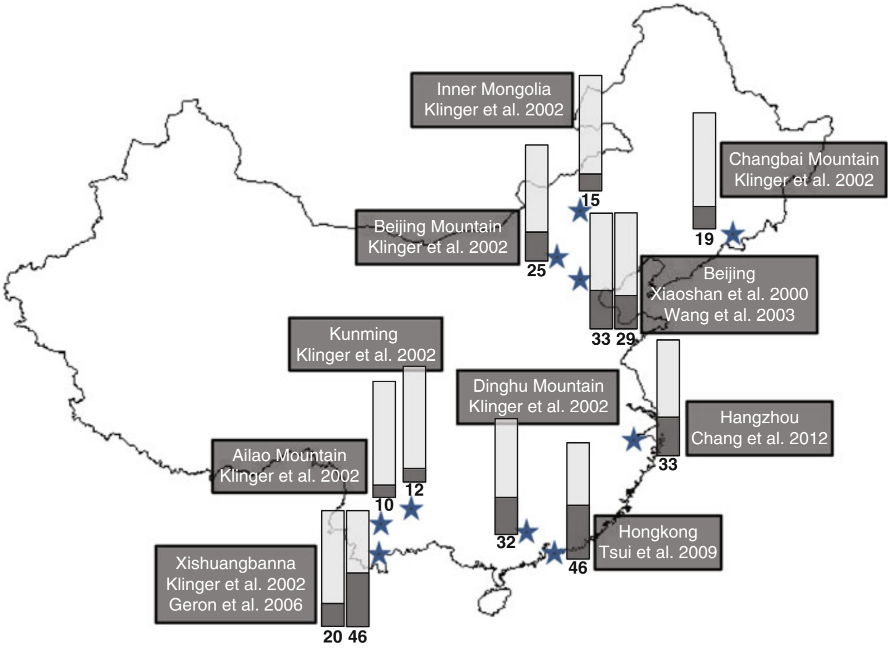

Fig. 1.2 Fractions of isoprene-emitting plant species observed in screening studies conducted in various regions of China (*numbers* are percentages). *Asterisks* indicate the approximate locations of the studies

much as a factor of two (for example, see the inventories of the Xishuangbanna region in southern China in Fig. 1.2). Inventories are unreliable for several reasons. First, fewer than 2,000 woody species have been screened for isoprene emission, and in many inventories, only few species have been measured in particularly species-rich floras that are composed of thousands of vascular plant species. Second, screening studies have usually focused on large woody plant species, neglecting small herbaceous species, probably because the latter are difficult to measure with current enclosure systems and are considered to contribute less biomass to the vegetation cover. Thus, if isoprene emission is indeed mostly confined to woody perennial growth habits, then the real fraction of isoprene-emitting species present in the world's floras is likely much lower than those inferred from current emission inventories (Figs. 1.1 and 1.2) in which annual and biennial plant species are largely underrepresented. Third, inventories are usually conducted at a single time of year (generally in summer), but the biosynthesis of constitutive volatile isoprenoids is under strong ontogenetic, seasonal, and even circadian control (for overviews, see Loreto and Schnitzler 2010; Niinemets et al. 2010). The situation is particularly complicated for monoterpenes, amongst which are some compounds such as the β-ocimenes that are known to be induced by stress and/or to occur only during a limited time of the year (Staudt et al. 1997, 2000, 2003; Grote et al.

2013). Fourth, inventories are usually conducted on only a few individuals and ignore the possibility of intra- and inter-population variability in the emission of isoprenoids. For example, the emission of volatile isoprenoids by the Mediterranean oak species *Quercus ilex* and *Q. suber* can change qualitatively, and can also be absent amongst individuals and populations (Loreto et al. 2009; Staudt et al. 2001, 2004, 2008). Fifth, screening studies differ greatly in their applied methods (i.e., enclosure systems and analytical facilities), although some efforts have been made to develop standardized methods and measuring protocols (for an overview, see Niinemets et al. 2011). Optimal identification and quantification of different classes of BVOCs require the use of several different sampling and analytical techniques. Consequently, the same plants, which have been screened for the emission of isoprene, have often not been screened for the emission of other volatile isoprenoids. Finally, many plant species previously classified as isoprenoid non-emitters now emerge as emitters when monitored with more sensitive methods of detection (e.g., Peñuelas et al. 2009b).

Our knowledge of the present distribution of BVOC-producing plants in terrestrial ecosystems has rapidly progressed in recent decades, but more worldwide coordinated efforts are needed to obtain realistic data on geographical and taxonomic patterns of volatile isoprenoid production by plants. These systematically gained data are a prerequisite for understanding and reliable assessment of the past and future evolution of volatile isoprenoid production.

1.3 The Past: Evolution of Volatile Isoprenoids

1.3.1 Volatile Isoprenoids: "Secondary" or "Primary" Metabolites?

The evolution of volatile isoprenoids is currently being intensively investigated. Using the traditional definitions of "secondary metabolites", volatile isoprenoids should not be essential for plants. The production of volatile isoprenoids has been proposed to take advantage of dimethylallyl diphosphate (DMADP) and its isomer, isopentenyl diphosphate (IDP), both of which are synthesized primarily to produce essential isoprenoids. Conditions affecting synthesis of the higher isoprenoids will thus affect the production and emission of volatile isoprenoids (Owen and Peñuelas 2005). According to Peñuelas and Llusià (2004), every BVOC emitted does not necessarily have a specific role, given that their emission is unavoidable due to their volatility. In many cases, however, natural selection has taken advantage of this volatility and conferred upon them important roles in defence or communication (Peñuelas and Llusià 2004).

Thus, volatile isoprenoids, while traditionally classified as secondary metabolites, are in fact key molecules that require large fractions of fixed carbon (Sharkey and Yeh 2001) and serve multiple very important physiological and ecological functions, especially those related to communication and protection against biotic and abiotic stressors (Loreto and Schnitzler 2010; Possell and Loreto 2013). Evolution forced by selection can work on available genotypic diversity and modify the roles of isoprenoids to serve a broad diversity of adaptive roles (Peñuelas and Llusià 2004), e.g., due to high levels of ozone (Lerdau 2007; Calfapietra et al. 2013) or low levels of CO_2 (Way et al. 2011). The human factor may also be an important driver of evolution by selection, at least after plant domestication. Non-volatile terpenes, which are also considered as "secondary metabolites", are often not "secondary" for humans. For example, morphine and codeine, two alkaloids produced by *Papaver somniferum*, link "ecology, evolution, and human affairs" very well, as noted by Theis and Lerdau (2003). In other cases, intraspecific differences in the emission of volatile isoprenoids may have no evolutionary significance *per se*, but are associated with suitable traits for cultivation. A similar hypothesis has been invoked by Loreto et al. (2009) to explain why Portuguese cork oaks that have been selected for the quality of cork also emit a blend of constitutive monoterpenes characterized by a much higher emission of limonene compared to the blend emitted elsewhere in the range of this plant species.

The "raison d'être of secondary plant substances" has been investigated for more than 50 years (Fraenkel 1959) and is still being discussed (Berenbaum and Zangerl 2008), but we now believe that plants synthesize their secondary compounds, including volatile isoprenoids, to fulfill specific needs. Just as floral scents and pigments were selected to attract pollinators, or toxic non-volatile secondary compounds to repel herbivores and pathogens, evolution may have selected the biosynthesis of volatiles emitted from leaves. Thus, research into the ecological and physiological roles of isoprenoids have led us to question the firm meaning of the term "secondary plant compound". In fact, secondary and primary roles are often indistinguishable with regard to enhancing plant fitness.

1.3.2 Loss and Gain of Isoprene Emission Capacity: When and Why?

Past inventories suggest that the emission of isoprene and monoterpenes is scattered across plant divisions (Harley et al. 1999; Kesselmeier and Staudt 1999; Bagnoli et al. 2012). In fact, isoprene emission occurs in Bryophyta (mosses), Pteridophyta (ferns), Pinophyta (conifers), and Magnoliophyta (angiosperms), both monocots and dicots, independent of phylogeny. This evidence has suggested, as commented above, that the capacity for isoprene emission may have been gained and lost several times during the evolutionary history of plants (Sharkey et al. 2008; Monson et al. 2013).

If isoprenoid emission is under evolutionary control, then an evolutionary perspective can help us to understand why only some plants emit isoprene or monoterpenes. According to Harley et al. (1999), the enzyme responsible for isoprene biosynthesis, isoprene synthase (IspS), may have evolved several times independently, but Hanson et al. (1999) proposed that the trait of isoprene emission evolved only once and was lost many times, accounting for its heterogeneous distribution among taxa. More recently, Lerdau and Gray (2003) suggested an independent origin of isoprene emission in Pinophyta and Magnoliophyta, with multiple losses of the trait accounting for the distribution of isoprene emission within Magnoliophyta. In fact, recurrent losses and neo-formations of isoprenoid synthase genes have been indicated by several independent studies. For example, Welter et al. (2012) observed that the production of isoprenoids by *Q. afares*, an oak species resulting from an ancient hybridization between an isoprene-emitting and a monoterpene-emitting oak, has strongly diverged from its parental species, including the complete suppression of isoprene production. The most recent examination of phylogenetic relationships (Monson et al. 2013) has: (i) confirmed the “multiple gain – multiple loss” model of isoprene evolution in both Pteridophyta (ferns) and Magnoliophyta, (ii) suggested that isoprene synthase genes arose frequently from mutations of terpene synthase genes (incidentally, this origin is reminiscent of the finding that mono- and sesquiterpene synthases in Pinophyta and Magnoliophyta have evolved from an ancestral diterpene synthase (Chen et al. 2011)), and (iii) indicated that isoprene production has been widely lost, and retained only under a few conditions. Sharkey et al. (2013), basing their analysis on the chronology of rosid evolution, suggest that isoprene-emitters appeared during the Cretaceous, and that the trait was subsequently lost multiple times until present. Monson et al. (2013) hypothesize that the loss of isoprene may have had different causes depending on whether isoprene emission was an adaptive or neutral trait. The idea that the trait is adaptive is more appealing, because the trait would be lost whenever the cost of isoprene biosynthesis exceeded its adaptive value. The frequency of loss during evolution suggests only a narrow range of conditions in which isoprene has adaptive value.

If isoprene has adaptive significance, what are the conditions under which the trait is retained?

(a) Isoprene emission is particularly widespread in hygrophytes. Hanson et al. (1999) and Vickers et al. (2009) therefore suggested that isoprene evolution could be beneficial when plants are under more recurrent and stronger oxidative stress in terrestrial than in aquatic environments. About 80 % of European hygrophytes emit isoprene, a figure significantly higher than in xerophytes (Loreto et al. unpublished data). However, it may be possible that hygrophytes diversified less than other plant functional types in which the trait was lost more often. Even resurrection plants that can survive in extremely dry environments have recently been found to emit isoprene (Beckett et al. 2012).

(b) Isoprene emission is a characteristic of perennial plants. This restriction may suggest a relationship with the phloem-loading type, being active phloem loading widespread in trees, and associated with lower concentration of leaf non-structural carbohydrates, which are then made available for growth (Turgeon 2010). However, it was also suggested that high sugar content in the mesophyll is needed to provide substrate for isoprene (Logan et al. 2000;

Kerstiens and Possell 2001). A relationship between isoprene emission and sugar accumulation has not yet been demonstrated.

(c) Isoprene emission is a characteristic of fast-growing perennial plants. Again, this restriction postulates a direct link between the rapid metabolism of carbon and the need to produce isoprene. In both cases, the benefit of producing isoprene is unclear, unless plants need to release extra carbon and energy when the machinery of carbon metabolism is maximally active, an idea reminiscent of the "overflow valve" hypothesis (Logan et al. 2000) and consistent with the idea that unstressed plants produce more isoprene because the carbon is not needed for structural or defensive compounds (the "opportunistic hypothesis", Owen and Peñuelas 2005). Not all strong isoprene emitters, though, are fast-growing (e.g., some deciduous oaks are slow-growing), and even amongst fast-growing plants, no clear relationship has been found between primary metabolism (photosynthesis) and isoprene emission (Guidolotti et al. 2011). Nevertheless, there is evidence of prevalence of isoprene emission among early-successional trees that typically grow in high light environments and have greater growth rates than late-successional species (Niinemets and Valladares 2006; Valladares and Niinemets 2008; Harrison et al. 2013).

(d) Isoprene emission is stimulated by low concentrations of CO_2. This characteristic has been interpreted as evidence that isoprene may have had an adaptive advantage during those epochs in geological history when atmospheric CO_2 concentration was low (Way et al. 2011). Epochs characterized by low levels of CO_2, however, were also cold, whereas isoprene emission is stimulated by high temperatures, and its function is associated with foliar thermotolerance (Sharkey and Yeh 2001). The evolution of the isoprene trait in epochs with low concentrations of CO_2 would be difficult to explain within this scenario. However, it may be argued that even in cold epochs, parts of the globe experienced a temperate climate. On more physiological grounds, isoprene might be needed when photosynthesis is constrained by low CO_2, and associated with environmental stresses (Possell and Loreto 2013). This would explain why isoprene evolved under low CO_2 but does not explain why isoprene is today a widespread trait in fast-growing trees (see (c) above).

1.4 The Future: Impacts of Climate Change and Ecological Constraints on the Diversification and Emission of Volatile Organic Compounds

The pace and extent of climate change will affect isoprenoid emissions. Temperature and CO_2 are key climate change factors controlling isoprene emissions. Light, water availability, and pollution, are also likely going to interfere with isoprene production and emission capacity by plants (Calfapietra et al. 2013; Holopainen et al. 2013). Because of the well-known dependence of synthesis and volatilization of volatile isoprenoids on temperature (Niinemets et al. 2004), any further increase in temperature (as foreseen by IPCC 2007) will cause an increase in isoprenoid emission by plants, thus, inducing (alluding to monoterpene odor) ‘a more fragrant world’ (Peñuelas and Staudt 2010). Indeed, rising temperatures since the late nineteenth century may have already induced higher emissions worldwide.

Higher temperatures are mainly due to the accumulation of greenhouse gases, primarily CO_2. Rising levels of CO_2 have a negative effect on isoprene, documented by many reports since Sanadze (1964) and reviewed elsewhere (Loreto and Schnitzler 2010; but see Sun et al. 2012; Calfapietra et al. 2013; Monson 2013). The impacts of simultaneous increases in temperature and CO_2 levels on isoprene emission may thus virtually cancel out, with a residual stimulatory effect due to higher CO_2-driven biomass production and leaf area index (Arneth et al. 2008). A similar conclusion was reached by Heald et al. (2009) using a different algorithm, and therefore, this scenario is rather probable. Rising levels of CO_2 appear not to have a similar inhibitory effect on monoterpenes, so the future impact of rising CO_2 levels on these compounds cannot be predicted using the same parameterization as for isoprene (Arneth et al. 2008). Although clearly there are more data needed on $[CO_2]$ effects on monoterpene emissions. More importantly, volatile isoprenoid emissions can be transiently enhanced by high temperatures that are repeatedly occurring worldwide (Rennenberg et al. 2006). In the absence of a concurrent increase in CO_2 levels, this effect appears to be much more dramatic and deserves thorough analysis, especially if the frequency of episodic extremely high temperatures will indeed increase in the future.

In areas where rising temperatures and enhanced evapotranspiration will reduce water availability, isoprenoid emission may also be affected by drought. Stress from drought appears to have a complex impact on isoprenoids, but isoprene biosynthesis is generally resistant to drought and increases the metabolic cost of isoprenoids when carbon acquisition by photosynthesis is inhibited (Loreto and Schnitzler 2010; Possell and Loreto 2013). Interestingly, the dependence of isoprenoid emission on temperature changes in leaves severely stressed by, or recovering from drought, suggesting that a further feedback operates on the main driver of isoprene emission; this can be a possible additional factor reducing isoprenoid emission in a warmer world (Bertin and Staudt 1996; Fortunati et al. 2008).

Changes in incident light, for example through an increase in the atmospheric load of aerosols that increase the fraction of diffuse light (Mercado et al. 2009), may have large impacts on the future release of isoprenoids from vegetation (Kulmala et al. 2013). Foliar isoprenoid emissions normally increase with increasing incident radiation. Combined with extreme temperatures or drought, though, strong radiation amplifies oxidative stress inside leaves, which can efficiently reduce the total amount, alter the composition, and modify the thermal responses of isoprenoid emissions (Staudt and Lhoutellier 2011). Such unaccounted interactive effects of environmental drivers on isoprenoid emissions may explain some of the observed variability in the response of emissions to single factors. For example, monoterpene emissions from Mediterranean oaks appear to be much more resistant to drought when studied in controlled mono-factorial laboratory and greenhouse conditions

(Bertin and Staudt 1996; Staudt et al. 2008) than under field conditions (Staudt et al. 2002; Lavoir et al. 2009). More studies of the interactions caused by stress are certainly needed to reliably predict the future evolution of isoprenoid emissions.

The impact of pollutants on isoprenoid emission is controversial. Air pollution appears to stimulate or maintain isoprenoid biosynthesis and emission, although not always (Peñuelas et al. 1999; Loreto et al. 2004; Calfapietra et al. 2009, 2013; Holopainen et al. 2013). Calfapietra et al. (2009) hypothesized a hormetic response, with pollution stimulating isoprenoid emission until the inhibition of photosynthesis no longer allows for a sufficient production of isoprenoid substrates. Again, as in the case of drought, pollutants will increase the costs of carbon and energy of isoprenoid formation. Why is this? We suggest that this results from the circumstance that isoprenoids interact with reactive oxidative species, thereby reducing membrane damage and stabilising photosynthesis (Loreto and Schnitzler 2010). Enhanced isoprenoid emission may thus reflect the activation of a defensive system by plants against stress.

If volatile isoprenoids protect plants against high temperatures and oxidative stresses, then high emitters should be fitter in a warmer, drier and more polluted world. In fact, because most natural ecosystems are composed of both emitters and non-emitters of volatile isoprenoids, emitters may ultimately be selectively favored by evolution (Lerdau 2007). On the other hand, because most isoprene emitters are woody species, man- and climate-driven conversion of forested areas to cropland, savanna, arid shrubland, and grassland may dramatically change the pattern of emission and reduce the emission of isoprene (Wiedinmyer et al. 2006). Moreover, because many isoprene emitters are deciduous, and warming will favor evergreen plants, isoprene emitters may be disfavored, e.g., in boreal areas that will experience milder temperatures. Another important alteration in the agro-ecosystems may come from changes in land use involving intensive cultivation of fast-growth plantations. Most of these fast-growing plants including poplars (*Populus* spp.), willows (*Salix* spp.), eucalypts (*Eucalyptus* spp.), oil palm (*Elaeis guineensis*), and reed (*Phragmites australis*), are all strong isoprene emitters, with eucalypts also emitting monoterpenes from storage organs. An expansion of plantations of these species worldwide is thus expected to vastly increase the biogenic emission of isoprene. For example, very large areas of rainforest in China, Malaysia, and neighboring countries have been converted to plantations of rubber trees (*Hevea brasiliensis*) or oil palms, which release five to ten times more monoterpenes or isoprene than the natural vegetation (Wang et al. 2007; Hewitt et al. 2009). In contrast, biofuel-producing C_4 plants do not emit isoprenoids in large amounts (Graus et al. 2011), though low emissions of isoprene and monoterpenes have been reported in switchgrass (*Panicum virgatum*) (Eller et al. 2012) and corn (*Zea mays*) may emit several isoprenoids, predominantly sesquiterpenes, when and after enduring pest attacks (Ton et al. 2007). The massive cultivation of C_4 biofuel plants in the future may thus not affect or may decrease regional fluxes of isoprene. These crops, though, release significant amounts of oxygenated BVOCs of low molecular weight, such as methanol, accounting for several grams per liter of biofuel produced. These BVOCs are less reactive than volatile isoprenoids and are therefore less efficient as drivers of atmospheric chemistry.

As is evident from all of the above, the way the emissions of volatile isoprenoids respond to future conditions is still unclear. The overall emission of isoprene may increase if large forested areas are converted to tree plantations at the current pace, and if a "greening of the world" would occur because of photosynthesis stimulation by rising CO_2 levels (unlikely given the accompanying warming and drying; Peñuelas et al. 2011). In any case, the combined effect of climatic and anthropogenic factors, in particular, the interaction between rising temperature, CO_2, drought, and pollution, may offset the predicted (Lerdau 2007) evolutionary shift in favor of isoprene emitters in natural ecosystems. Rather, monoterpene-emitting plants, which are often evergreens and resistant to drought, with substantial limitations to CO_2 entry in the leaves, may take the highest advantage in terms of photosynthesis and growth from rising CO_2 levels (Niinemets et al. 2011). Because monoterpene emission is stimulated by rising temperatures and levels of pollutants, and is not inhibited by rising levels of CO_2, monoterpene emitters may have the largest evolutionary advantage, making a warmer world indeed more "fragrant".

Acknowledgements JP is indebted to the Spanish government projects Consolider Ingenio MONTES (CSD2008-00040) and CGL2010-17172 and the Catalan government project SGR2009-458.

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