Isoprene emission by plants in polluted environments

Manuel Bellucci[1,2], Vittoria Locato[1], Thomas D. Sharkey[3] , Laura De Gara[1], Francesco Loreto[2,4*]

[1]Unit of Food Science and Human Nutrition, Department of Science and Technology for Humans and the Environment, Campus Bio-Medico University, Rome, Italy

[2]Department of Biology, Agriculture and Food Science, National Research Council of Italy, Rome, Italy

[3]MSU-DOE Plant Research Laboratory, Plant resilience Institute and Department of Biochemistry and Molecular Biology, Michigan State University, East Lansing, MI, USA.

[4]Department of Biology, University of Naples Federico II, Naples, Italy

*** Corresponding author**

Manuel Bellucci (m.bellucci@unicampus.it); Francesco Loreto (francesco.loreto@unina.it)

ORCID

Manuel Bellucci: 0000-0002-7902-2522

Laura De Gara 0000-0001-5938-7113

Vittoria Locato 0000-0003-0267-5039

Francesco Loreto: 0000-0002-9171-2681

Thomas D Sharkey 0000-0002-4423-3223

Abstract

In recent years, anthropogenic activities and climate change have significantly increased exposure of plants to environmental stresses (single or multiple) and pollutants, with negative consequences for the survival and productivity of vegetation. Plants may activate an armament of defenses against stresses. Isoprene, the most abundant biogenic volatile organic compound (BVOC) emitted by plants, is supposed to have a direct or indirect antioxidant role by quenching reactive oxygen species (ROS) or by reprogramming gene expression for antioxidant activation. On the other hand, isoprene is involved in the chemistry of troposphere, further contributing to a build up of pollutants when mixing with anthropogenic gases. In this review, we summarize present knowledge on the impact of air and soil pollutants on isoprene emission by plants, indicating possible feedback and feedforward mechanisms that may affect whole ecosystem functioning and evolution of plant species.

Keywords: Isoprene emission; biogenic volatile compounds; environmental stress; air chemistry, soil pollution; belowground communications, climate change

Introduction

Plants are sessile but not passive components of the ecosystems, and they interact with the environment in several ways. Biogenic volatile organic compounds (BVOCs) are gases that are emitted by organisms in all terrestrial and marine ecosystems (Loreto et al. 2014). Plants emit worldwide more than 1 Pg C per year as BVOCs (Guenther et al. 1995, 2012), about half of which is isoprene (Guenther et al. 2006). Leaf BVOCs may be constitutively emitted (generally leaf life-long) or induced by abiotic and biotic stresses (Loreto and Schnitzler 2010). Some constitutive BVOCs may also be induced by stresses (Harrison et al. 2013). More than 1700 BVOCs have been identified, which are emitted by 90 different plant families belonging to both angiosperms and gymnosperms (Knudsen et al. 2006), and including also ferns and mosses (Hanson et al. 1999). As the detection systems get more accurate and high-throughput, the idea that all plants emit BVOCs is becoming realistic.

Synthesis of most significant BVOCs occurs through three pathways: the lipoxygenase (LOX), the shikimic acid, and the terpenoid pathways (Pichersky and Gershenzon 2002). Terpenoids or isoprenoids are the largest group of specialized plant metabolites and derive from two precursors: isopentenyl pyrophosphate (IPP) and dimethylallyl pyrophosphate (DMAPP) (McGarvey and Croteau 1995). Among terpenoids, isoprene (C_5H_8) is the simplest and most volatile BVOC. Isoprene is formed by the chloroplastic methyl erythritol 4-phosphate (MEP) pathway through isoprene synthase (IspS), which catalyzes the removal of pyrophosphate (PPi) from DMAPP. Constitutive, light-dependent emissions of volatile isoprenoids are generally limited to large amounts of isoprene, especially from fast-growing plants (Loreto and Fineschi 2015), and of monoterpenes from some families of trees and bushes (Loreto and Schnitzler 2010). Emission of isoprene is a metabolic cost for plants, but benefits may outweigh the cost, especially under high temperature (Jardine et al. 2012) and oxidative stress (Vickers et al. 2009). Isoprene was thought to quench reactive oxidative species (ROS) such as hydrogen peroxide (H_2O_2) (Loreto and Velikova 2001), singlet oxygen ($^1O_2$), (Affek and Yakir 2002) or reactive nitrogen species (RNS) (Velikova et al. 2005), and to stabilize chloroplast membranes (Velikova et al. 2011a) facilitating photosynthetic electron transport rate (Pollastri et al. 2019). The antioxidant role of isoprene is now revised, as the capacity of isoprene emission induces a reprogramming of the entire genome and metabolome (Monson et al., 2021; Dani and Loreto,

2022) that improve the ability of plants to tolerate various stresses. The general role of isoprene as a stress protective agent remains unquestioned.

Stress tolerance is improved because of carbon allocated for constitutive BVOC biosynthesis but also because of stress-induced BVOCs (Paré and Tumlinson 1999; Mithöfer and Boland 2012), especially after herbivores or pathogens attacks (Dicke and Baldwin 2010), or after abiotic stresses such as drought, high temperatures, or oxidative pollutants (Loreto and Schnitzler 2010).

Isoprene plays several roles in atmosphere chemistry, all of which are due to its oxidation (Heald et al. 2009; Archibald et al. 2010). When anthropogenic volatile pollutants such as nitrogen oxides (NO_x) are absent, isoprene further cleanses the atmosphere of ozone. In the presence of NO_x, however, isoprene participates in reactions leading to increased ozone formation (Fehsenfeld et al. 1992) under a well-established stoichiometry (Kanakidou et al. 2005). As the emission of isoprene to the atmosphere is so prevalent, the impact of environmental factors such as light intensity, atmospheric CO_2 concentration, temperature, relative humidity, and nutrient status on isoprene emission has attracted great attention (Loreto and Schnitzler 2010; Harrison et al. 2013). Climate change impact on isoprene emission has been mainly attributed to positive long-term (enzyme-driven) and short-term (substrate-driven) feedback of rising temperature (Lehning et al. 2001; Rennenberg et al. 2006), implying that future emissions of isoprene will also increase (Arneth et al. 2008). This may be counteracted by an often large (and largely unexplained) inhibition of isoprene in rising CO_2 (Rosenstiel et al. 2003; Guidolotti et al. 2011). However, the inhibitory impact of rising CO_2 seems to be lost as the temperature gets higher, and the overall impact of climate change is therefore expected to lead to a heavier load of isoprene in the atmosphere (Sharkey and Monson 2017). It may be also hypothesized that, in response to increasing environmental stresses and global warming, a shift of native plants toward species and genotypes able to emit isoprene constitutively or an induced manner will occur (Lerdau 2007). Here, we focus on reviewing anthropogenic atmospheric and soil pollutants and climate change that could also affect isoprene emission by natural vegetation and thus alter further the load of isoprene in the atmosphere.

Focus on isoprene and air pollution

a) Isoprene and the chemistry of the troposphere.

Most of the plant BVOCs have relatively short lifetimes in the atmosphere ranging from less than a minute to few hours depending on the atmospheric conditions (Blande et al. 2014). In the case of isoprene, rapid reaction with NO_x leads not only to ozone production, but also to the appearance of secondary products of isoprene oxidation, mainly methylvinyl-ketone (MVK), methacrolein (MACR) and 2-methyltetrols like 2-methylthreitol and 2-methylerythritol that have been found in the natural aerosol of Amazonia forest (Claeys et al. 2004).

Formaldehyde is also produced by isoprene oxidation and, despite the low yield (<10%), this BVOC has been used as an important proxy of isoprene natural planetary sources by satellite inspection (Palmer et al. 2006). MVK and MACR are markers of isoprene oxidation also *in planta* and therefore it is possible for these secondary BVOCs to be directly emitted by plants and not only formed by isoprene reactions in the atmosphere (Jardine et al. 2012). Recent results, however, suggest that MVK and MACR might be produced *in planta* by pathways other than isoprene oxidation (Kai et al. 2012), and that MVK may even be further oxidized to methyl ethyl ketone (MEK), making the pattern of interactions between plant BVOCs and atmospheric chemistry even more complex (Cappellin et al. 2019).

Indeed, ozonolysis (Pinto-Zevallos et al. 2010) results in the formation of many secondary organic aerosols (SOAs) (Seinfeld and Pandis 2006; Laothawornkitkul et al. 2009) with relevant climatic impacts (Claeys et al. 2004; Paulot et al. 2009). Isoprene, monoterpenes, and other terpenoids characterized by high emission rates and high reactivity with the atmospheric oxidants that are present in polluted and urban areas (NO_3^-, ozone, hydroxyl radical ($OH\cdot$), are major contributors of SOA burden (Kanakidou et al. 2005; Goldstein and Galbally 2007). Field studies have shown that under conditions with moderate to high BVOC levels, NO_3^- predominantly reacts with BVOCs (Brown and Stutz 2012) to produce multifunctional compounds such as organic nitrates (ONs) (Nah et al. 2015; Faxon et al. 2017).

b) Impact of main atmospheric determinants of climate change on isoprene.

The two main atmospheric constituents affecting isoprene emission are carbon dioxide (CO_2) and ozone (O_3). Anthropogenic CO_2 emission is the most important forcing variable affecting changes in climate since the beginning of the industrial era. Over time, CO_2 concentrations have continued to increase in the atmosphere, reaching 417 ppm (IPCC 2021) with further increases each year. A recent meta-analysis (Feng et al. 2019) summarized decades of experimental data (e.g. Possell, Hewitt, and Beerling 2004; Rosenstiel et al. 2003) showing a largely negative

impact of rising CO_2 on isoprene emission, while emission of monoterpenes is substantially unaffected by CO_2 accumulation. The negative impact of rising CO_2 on isoprene has surprised scientists, as isoprene is almost totally made by photosynthetic carbon (Delwiche and Sharkey 1993), and photosynthesis is stimulated by CO_2 (Long et al. 2004). It has been suggested that the decrease of isoprene emission when CO_2 increases is related to i) photorespiration inhibition, and to the consequent reduction of pyruvate available to the MEP pathway (Rosenstiel et al. 2003); or ii) to competition for phosphoenol pyruvate (PEP) a cytosolic substrate that may support chloroplastic demand (Loreto and Fares 2007); or iii) to an inhibitory effect on IspS activity (Scholefield et al. 2004). A hypothesis that the CO_2 inhibition was related to a triose phosphate utlilization limitation of photosynthesis was recently ruled out (Lantz et al.) Guidolotti et al. (2011) found an inverse relationship between isoprene and intercellular CO_2 concentration (C_i), which holds even at currently ambient CO_2 concentration (> 400 ppm). This supports the notion that the CO_2-dependent reduction of isoprene reflects fine biochemical adjustments. However, the inhibitory impact of rising CO_2 seems to be lost as the temperature gets higher (a necessary consequence of CO_2 accumulation as CO_2 is a greenhouse gas), and the overall impact of climate change is therefore expected to lead to a heavier load of isoprene in the atmosphere (Sharkey and Monson 2017). Moreover, CO_2 may also indirectly stimulate isoprene emission at whole canopy and ecosystem level, because of higher photosynthesis, growth rate and biomass accumulation, made possible by the increase in CO_2 availability (Arneth et al. 2007). However, several lines of evidence indicate that CO_2 does not always increase linearly with an increase in photosynthesis and plant growth/productivity. Moreover, there is a significant interspecific variability in [CO_2]-responsiveness of isoprene emission that is unexplained. Such variability in emission reduction could be caused by a significant variation in the size, composition of the precursor pools responsible for isoprene emissions (Niinemets et al. 2021). Squire et al. (2014) found that climate change, which includes both rising temperature and CO_2, increased isoprene emissions by natural vegetation and the effect is expected to continue as long as CO_2 overfertilizes plants (Squire et al. 2014). Future increase of isoprene emission by natural vegetation is expected when accounting for rising temperature only (Sanderson et al. 2003; Lathière et al. 2005; Wu et al. 2012). By modelling temperature and CO_2 interaction (which includes direct and indirect CO_2 effects) indeed it is confirmed that isoprene emissions will be stimulated over the 21st century (Arneth et al. 2007; Heald et al. 2009). A framework modeling study based on a scenario where

180 the effect of climate and natural vegetation changes (driven by the rising of temperature and by
181 the expansion of broadleaf forests respectively) co-occur, suggests an increase of isoprene
182 emission by ~42% by 2050, which drops to ~4% if CO_2 inhibition of isoprene emission is also
183 included (Tai et al. 2013).
184 We speculate that both effects of climate change and environmental stress could lead to
185 an increase of isoprene-emitting species in polluted environments in response to the negative
186 effects (e.g oxidative stress) resulting from increased air and soil contaminants (Figure 1).
187 The other gas that has received large attention for its feedback on isoprene is ozone. While
188 generally, CO_2 improves plant growth (Long et al. 2004), ozone is a serious environmental stress
189 that causes heavy damage to photosynthesis. Indeed, when ozone enters the leaf, it is degraded to
190 other ROS, which can cause oxidative stress and damage to lipo-proteic bilayer of the
191 photosynthetic membranes, with consequent rapid chloroplast degradation (Loreto et al. 2001).
192 High doses of ozone could cause an initial stimulation of isoprene emission (Velikova et
193 al. 2005) due to higher expression of IspS and its activity (Fares et al. 2006). It seems that this
194 upregulation is more evident in leaves developing under enriched O_3 atmosphere and that build
195 up a better resistance to pollutants (Fares et al. 2006). However, plants adapted to high O_3 are not
196 able to further stimulate isoprene emission when exposed to a following stimulus (Calfapietra et
197 al. 2008). If O_3 does not damage photosynthesis, isoprene emission is maintained and as already
198 mentioned, often stimulated. Under these conditions, isoprene may scavenge ROS made by O_3
199 (Velikova et al. 2004) or may make the photosynthetic membranes more resistant to ROS-
200 dependent oxidation (Pollastri et al. 2019; Velikova et al. 2011a). As isoprene is also stimulated
201 by high temperatures, when high O_3 episodes are more frequent, the antioxidant role of isoprene
202 becomes more relevant when associated with heat waves (Jardine et al. 2012). A first line of
203 defense against O_3 is stomatal closure. Loreto and Fares (2007) showed that leaf damage is
204 associated to O_3 concentration inside leaves rather than to the atmospheric O_3. However, under
205 prolonged or chronic exposure to O_3 that overcomes the epidermal barrier, photosynthesis is
206 severely impaired and consequently also isoprene emission is restrained. Indeed, O_3 often
207 irreversibly damages plant tissues leading to reduced crop yields and forest growth (Mills et al.
208 2010). The uptake of O_3 inside mesophyll causes oxidation of cell wall components, damages
209 photosynthetic apparatus with detrimental effects on growth rate and biomass production, and
210 accelerates leaf senescence (Ashmore 2005; Fares et al. 2006; Wittig et al. 2009). Meta-analysis

data show that isoprene and photosynthesis are reduced to similar extent (10%) by high O_3 exposure (Feng et al. 2019). However, isoprene emission is significantly increased by exposure of leaves to high UV-b (Harley et al. 2006; Tiiva et al. 2007) and UV-a (Pallozzi et al. 2013) radiation, which is a requisite for O_3 formation in the atmosphere. Thus, the overall impact of air pollution on isoprene emission needs additional field testing where all factors dynamically interact together.

Figure 1 summarizes the interaction between plant isoprene and atmospheric pollutants in cities and industrial areas, which may have two effects: on one hand this interaction may increase the O_3 load and high O_3 episodes may exacerbate environmental stresses; on the other hand, this same interaction may favor evolution of a vegetation that is resistant to O_3 pollution and associated oxidative stresses. As isoprene is involved in antioxidant protection (Loreto and Schnitzler 2010) this may lead to higher isoprene emission by both native and alien (invasive) species (Lerdau 2007). The two effects may feedback on each other, and the loop may cause unpredictable consequences. Llusìa et al. (2010) suggested that protection against multiple environmental stress conferred by high capacity to emit terpenoids accounted for the success of invasive plant species in Hawaii. Similarly, establishment and proliferation of *Artemisia vulgaris* in a new habitat seems to be related to its capacity to emit BVOCs (Barney et al. 2005). On the other hand, it is also conceivable that human-driven land use change, by replacing natural vegetation with agricultural crops, has also selected against high isoprene emitters (Loreto and Fineschi 2015). Changes in natural vegetation (reduction of isoprene emitting species) could affect air quality (Tai et al. 2013; Hantson et al. 2017). Clearly, understanding the future effects of climate change on isoprene emission is a very complex task, because of the wide range of multiple and concomitant environmental factors that could have synergistic or antagonistic effects.

The future rising of environmental stresses (known to trigger oxidative stresses) related to anthropogenic processes could lead to a positive feedback for isoprene (both constitutive and induced, Figure 1) and other BVOCs biosynthesis and emission, acting as a plant-defense-system in response to climate change and warming (Peñuelas and Llusià 2003). For example, field measurements showed that white oak tree canopies have higher isoprene emission rates when exposed to more sunlight, reduced water availability, and high temperature (Sharkey et al. 1996). Interestingly, these plants did not show any anomalies in their growth and an increased

thermotolerance (Singsaas et al. 1997) and it is suggested that the quenching of ROS by isoprene could be an effective way to reduce the negative effects of oxidative stress compounds (Velikova et al. 2005).

Focus on isoprene and soil pollution

Soils may also contribute to the exchange of BVOCs, as sinks or sources, depending on the very diverse soil composition in terms of microorganisms, flora and fauna, thus expanding functional considerations on trophic interactions from the aboveground to the belowground plant compartment (Penuelas et al. 2014). While the complex relationships between isoprene and atmospheric pollution have been largely investigated, much less is known about the impact of soil pollution on isoprene. One could speculate that isoprene antioxidant action also improves resistance to soil pollution. “Soil pollution” refers to the presence of a chemical or substance out of place and/or present at a higher-than-normal concentration that has adverse effects on any non-targeted organism (FAO and ITPS 2015). Soil pollution acts as an abiotic stress on plants. It triggers ROS production, leading to adaptive plant responses including the improvement of the primary antioxidant redox system and the increase of the biosynthesis of secondary metabolites.

Except natural areas with specific geological conditions, the major soil pollutants are related to anthropogenic (industrial) activities that release different kinds of pollutants, from complex hydrocarbons released by oil industries to very simple chemical elements such as heavy metals released as byproducts of several processes or nutrient elements such as nitrates from excess fertilization or phosphates from commercial cleaning industries.

Heavy metals soil pollution is a problem of major importance for plant productivity and survival (Salt et al. 1998; Foy et al. 2003; Fargasová and Molnárová 2010). There are several cases in which the effect of heavy metal pollution on BVOC emissions has been investigated. Velikova et al. (2011b) suggested that heavy metal (Ni) pollution increases both constitutive (isoprene) and induced (monoterpenes and sesquiterpenes) isoprenoid emissions. Indeed, other reports indicate that high doses of Cu could induce BVOCs (Obara et al. 2003; Mithöfer et al. 2004) some of which characterize the interplay plants-herbivores (Winter et al. 2012). Soil cadmium stress seems to increase total leaf VOC emission (Lin et al. 2022). A time course with cadmium stress induced an upregulation of isoprene synthase (Li et al. 2017). Moreover, isoprene affects heavy metals detoxification transcriptome (Zuo et al. 2019).

The impact of nutrients on isoprene emission has received even wider coverage. Nutrient excess is often a consequence of pollution and over-fertilization, and finally eutrophication (Shortall 2013). Nitrates seem to generally elicit production and emission of isoprene, possibly making more N available for isoprene synthase biosynthesis (Litvak et al. 1996; Fernández-Martínez et al. 2017). On the other hand, excess of phosphorus in soils has a clear inhibitory effect on isoprene emission, assessed in different experiments (Fares et al. 2008; Cocozza et al. 2019, 2020) but never explained physiologically. Intuitively, high phosphorous should be beneficial for the synthesis of a molecule that requires large inputs of phosphorylated substrates, like ATP and NADPH (Sharkey and Yeh 2001). High phosphorous also stimulates photosynthesis which supplies carbon for isoprene synthesis. However, uncoupling of isoprene synthesis and photosynthesis is often observed, for example under elevated CO_2 (cfr. see above), or under water and salt stress (Loreto and Schnitzler 2010). It was proposed that competition with mitochondrial respiration for pyruvate or phosphoenolpyruvate is responsible for the inhibition of isoprene emission under high phosphorous nutrition (Fares et al. 2008), similar to what may occur under elevated CO_2 (Rosenstiel et al. 2003), although we think that all pyruvate for isoprene synthesis comes from the Calvin-Benson cycle Sharkey et al. 2020.

While different nutrients may have opposite effects on isoprene emission, a reduction of the intensity of emitted BVOCs in plants cultivated under high level of fertilization seems to be a convergent result (Fernández-Martínez et al. 2017), which may also explain why storage of BVOCs into reservoirs is a lost trait in recently evolved angiosperm crops. Evolution against emission of BVOCs may have an important trade-off in terms of improved plant productivity in absence of stress, but losing the capacity to synthesize and emit BVOCs may not pay off when plants must defend themselves from abiotic stresses or must communicate with other organisms. We eventually hypothesize that native and pioneer plants of polluted areas emit more isoprene (constitutive and induced) and speculate that the capacity to produce large amounts of isoprene may confer an adaptive advantage in a rapidly changing climate characterized by more frequent extreme events and pollution episodes.

Water and salt are important components of soils. Isoprene synthesis and emission continues even under drought or high salinity, despite concurrent photosynthesis inhibition (Brilli et al. 2007). The massive literature covering the impact of these stresses on isoprene was

often reviewed (e.g. Loreto and Schnitzler 2010) and the topic is beyond the scope of this work aiming at reviewing only impacts of soil pollutants.

Soil structure and composition influence the development and morphology of the root system. The root is the anchorage system of plants and is critical for the uptake of nutrients required for plant growth and physiology, including the isoprene pathway. If for the aboveground part of plants (leaves) there is much scientific evidence on the effects and activities of in-situ emission of isoprene, less well studied is whether belowground heterotrophic tissues (roots) can also emit isoprene, and if roots are also influenced when plants acquire or enhance their capacity to emit isoprene. Although it is mainly emitted from leaves, there is evidence that the root systems of poplar (Ghirardo et al. 2011) and transgenic Arabidopsis (Loivamäki et al. 2007; Miloradovic van Doorn et al. 2020) emit a small amount of isoprene. It is shown that the constitutive promoter of isoprene synthase (PcISPS) is present and active in specific regions of roots (Cinege et al. 2009; Miloradovic van Doorn et al. 2020).

There are reports of isoprene affecting root development. Miloradovic van Doorn et al. (2020) recently proposed a ROS-related role of isoprene in roots, showing an altered lateral root development and differences in ROS accumulation in roots. ROS are known to be involved in many pathways, especially under a challenging environment, being signals able to activate defenses responses also coordinating the developmental processes with environmental conditions (Locato et al. 2018). An interplay between ROS and hormones, in particular auxin, ethylene, and abscisic acid has also been reported (Xia et al. 2015). Isoprene also seems to interfere with many hormones, especially those sharing the same MEP pathway (cytokinins and abscisic acid) but possibly also with auxins (Dani and Loreto 2022). The effect of these interactions on roots is unknown, but a possible scheme of signaling function of internal isoprene in roots in relation with ROS was proposed (Miloradovic van Doorn et al. 2020). ROS signaling affects hormonal networks and signaling processes that regulate response to environmental drivers (Mittler 2017). It was proposed that isoprene could adjust ROS by quenching (direct) or changing gene expression (indirect) and so regulate all ROS–related pathways, including those involved phyto-hormones. Even if the molecular mechanism of this interplay is still relatively unknown, this could influence the growth of the root system in particular the lateral roots (Miloradovic van Doorn et al. 2020). Isoprene affects also root proteome and many of the proteins affected are involved in redox and stress responses (Miloradovic van Doorn et al. 2020).

Soil pollutants directly affect root development and the determinants of root system architecture (Lombardi et al. 2021) and this might also contribute to change BVOC emission by aboveground and belowground plant organs (Figure 1,2), in turn altering plant capacity to cope with pollution and environmental constraints (e.g. drought stress). Finally, root volatiles often are key elements of plant-plant communication and for interactions of plants with soil microbiome (Figure 2), with positive consequences on priming defensive responses, facilitating root nutrient uptake or counteracting the negative effects of pollutants. For example, BVOCs emitted from roots may facilitate interactions with arbuscular mycorrhizal fungi, expanding their beneficial functions, from improving resistance to soil stresses to enhancing nutrient availability (Asensio et al. 2012). However, whether these same functions may be attributed to isoprene is unclear. We hypothesize that this beneficial interaction (BVOCs-soil microbiome) could lead to better plant tolerance to soil stress and have positive feedback on plant biomass (Figure 2). In leaves, isoprene does not seem to be a messenger able to induce priming of receiving plants (Giordano et al. 2021), and does not influence insect feeding (Brilli et al. 2009). This may very well be the case in roots as well, where the emission of isoprene by plants is also elusive, and possibly tiny.

Soil constraints increase ROS formation, and it was shown that ROS, and ROS scavenging enzymes, play crucial roles in early-stage root-mycorrhiza interaction (Baptista et al. 2007; Nanda et al. 2010; Ditengou et al. 2015). Several studies shown that the intensity of ROS burst is important for root-microbes (mutualistic or pathogen) interaction and contact (Baptista et al. 2007; Nanda et al. 2010) and plant redox balance could be fundamental to differentiate between the various microbes. ROS adjustment by isoprene (direct or indirect) could be crucial for regulating root redox balance and root isoprene emission could facilitate the interaction and communication with soil microbiome (Figure 2). It is known that volatiles are a signal for aboveground plant communication (Ninkovic et al. 2021) but it was reviewed that root volatiles might play a role in belowground communication (plant-plant; plant-soil microbiome) (Abbas et al. 2022).

The role of isoprene in belowground communication is unclear and unknown while for root volatiles (BVOCs) with their diversity and their specificity are have been extensively analyzed in the belowground communication (Schenkel et al. 2015; Abbas et al. 2022). So, we suggest that in polluted environments, root-induced BVOCs might lead to a further increase in

this communication between plants via belowground, and thus they might ameliorate the negative effect of soil constraints (Figure 2).

Conclusion and future directions

Over the past few years, isoprene emission has been well-studied for its effects on atmospheric pollution and on plant defense, but the reciprocal impact of isoprene, soil and atmospheric pollutants is more elusive and complicated, especially when considering that direct measurements of isoprene emission are missing (soil) and that long-term responses at whole plant and community level have not been extensively investigated (both in soil and air).

Future studies should evaluate the long-term effect of pollutants, including evolutionary impacts on the composition of natural and semi-natural forests around cities and industrial areas where anthropogenic pollution may be persistent over time. This allows a better evaluation on how policies of re-forestation and afforestation of these areas may impact on air quality, considering climate change pressures, which may lead to regional expansion of broadleaf forests, the main emitters of isoprene (Wu et al. 2012), and in boreal areas. Finally, soil pollution impacts on isoprene is largely uninvestigated, and the impact of soil microorganisms is also basically unknown, although preliminary experiments indicate that beneficial microorganisms such as mycorrhiza (Pollastri et al. 2018) and plant growth-promoting rhizobacteria (Brunetti et al. 2021) may stimulate isoprene emission.

Author contribution: **Conceptualization:** Manuel Bellucci and Francesco Loreto; **Writing original-draft preparation:** Manuel Bellucci and Francesco Loreto; **Writing review and editing:** Manuel Bellucci, Laura de Gara, Vittoria Locato, Francesco Loreto and Thomas D Sharkey **Funding acquisition:** Laura De Gara and Francesco Loreto **Supervision:** Laura De Gara, Vittoria Locato, Francesco Loreto, and Thomas D Sharkey. All authors read and approved the final manuscript.

Funding: This work was supported by the Project PRIN 2017 by the Italian Ministry of University and Research): 'Plant multitROphic interactions for bioinspired Strategies of PEst ConTrol (PROSPECT)'; Consiglio Nazionale delle Ricerche (CNR) fellowship to Manuel Bellucci and by 'The Company of Biologists' Travel Fellowship award number DEVTF2210892. Funding at Michigan State University was from the U.S. National Science

Foundation, award number IOS-2022495. Michigan AgBioResearch provided partion support for T.D.S.

Data availability: Not applicable

Code availability: Not applicable

Declarations

Ethic approval: All authors have approved the submission of this paper

Consent to participate: Not applicable

Consent to publication: All authors consent to the submission of this paper

Competing interest: The authors have no competing interests

References

Abbas F, O'Neill Rothenberg D, Zhou Y, et al (2022) Volatile organic compounds as mediators of plant communication and adaptation to climate change. Physiol Plant 174:e13840. https://doi.org/10.1111/ppl.13840

Affek H, Yakir D (2002) Protection by Isoprene against Singlet Oxygen in Leaves. Plant Physiol 129:269–277. https://doi.org/10.1104/pp.010909

Archibald A, Cooke M, Utembe S, et al (2010) Impacts of mechanistic changes on HOx formation and recycling in the oxidation of isoprene. Atmos Chem Phys 10:. https://doi.org/10.5194/acp-10-8097-2010

Arneth A, Miller P, Scholze M, et al (2007) CO2 inhibition of global terrestrial isoprene emissions: Potential implications for atmospheric chemistry. Geophys Res Lett 34:. https://doi.org/10.1029/2007GL030615

Arneth A, Schurgers G, Hickler T, Miller P (2008) Effects of species composition, land surface cover, CO2 concentration and climate on isoprene emissions from European Forests. Plant Biol (Stuttg) 10:150–162. https://doi.org/10.1055/s-2007-965247

Asensio D, Rapparini F, Penuelas J (2012) AM fungi root colonization increases the production of essential isoprenoids vs. nonessential isoprenoids especially under drought stress conditions or after jasmonic acid application. Phytochemistry 77:149–161. https://doi.org/10.1016/j.phytochem.2011.12.012

421 Ashmore M (2005) Assessing the future global impacts of ozone on vegetation. Plant Cell
422 Environ 28:949–964. https://doi.org/10.1111/j.1365-3040.2005.01341.x

423 Baptista P, Martins A, Pais MS, et al (2007) Involvement of reactive oxygen species during early
424 stages of ectomycorrhiza establishment between Castanea sativa and Pisolithus tinctorius.
425 Mycorrhiza 17:185–193. https://doi.org/10.1007/s00572-006-0091-4

426 Barney J, Hay A, Weston L (2005) Isolation and characterization of allelopathic volatiles from
427 mugwort (Artemisia vulgaris). J Chem Ecol 31:247–265. https://doi.org/10.1007/s10886-
428 005-1339-8

429 Blande J, Holopainen J, Niinemets Ü (2014) Plant volatiles in polluted atmospheres: Stress
430 responses and signal degradation. Plant Cell Environ 37:. https://doi.org/10.1111/pce.12352

431 Brilli F, Barta C, Fortunati A, et al (2007) Response of isoprene emission and carbon metabolism
432 to drought in white poplar (Populus alba) saplings. New Phytol 175:244–254.
433 https://doi.org/https://doi.org/10.1111/j.1469-8137.2007.02094.x

434 Brilli F, Ciccioli P, Frattoni M, et al (2009) Constitutive and herbivore-induced monoterpenes
435 emitted by Populus × euroamericana leaves are key volatiles that orient Chrysomela populi
436 beetles. Plant Cell Environ 32:542–552. https://doi.org/https://doi.org/10.1111/j.1365-
437 3040.2009.01948.x

438 Brown S, Stutz J (2012) Nighttime Radical Observations and Chemistry. Chem Soc Rev
439 41:6405–6447. https://doi.org/10.1039/c2cs35181a

440 Brunetti C, Saleem AR, Della Rocca G, et al (2021) Effects of plant growth-promoting
441 rhizobacteria strains producing ACC deaminase on photosynthesis, isoprene emission,
442 ethylene formation and growth of Mucuna pruriens (L.) DC. in response to water deficit. J
443 Biotechnol 331:53–62. https://doi.org/https://doi.org/10.1016/j.jbiotec.2021.03.008

444 Calfapietra C, Scarascia Mugnozza G, Karnosky DF, et al (2008) Isoprene emission rates under
445 elevated CO2 and O3 in two field-grown aspen clones differing in their sensitivity to O3.
446 New Phytol 179:55–61. https://doi.org/10.1111/j.1469-8137.2008.02493.x

447 Cappellin L, Loreto F, Biasioli F, et al (2019) A mechanism for biogenic production and
448 emission of MEK from MVK decoupled from isoprene biosynthesis. Atmos Chem Phys

19:3125–3135. https://doi.org/10.5194/acp-19-3125-2019

Cinege G, Louis S, Hänsch R, Schnitzler J-P (2009) Regulation of isoprene synthase promoter by environmental and internal factors. Plant Mol Biol 69:593–604. https://doi.org/10.1007/s11103-008-9441-2

Claeys M, Graham B, Vas G, et al (2004) Formation of Secondary Organic Aerosols Through Photooxidation of Isoprene. Science 303:1173–1176. https://doi.org/10.1126/science.1092805

Cocozza C, Brilli F, Miozzi L, et al (2019) Impact of high or low levels of phosphorus and high sodium in soils on productivity and stress tolerance of Arundo donax plants. Plant Sci 289:110260. https://doi.org/10.1016/j.plantsci.2019.110260

Cocozza C, Brilli F, Pignattelli S, et al (2020) The excess of phosphorus in soil reduces physiological performances over time but enhances prompt recovery of salt-stressed Arundo donax plants. Plant Physiol Biochem PPB 151:556–565. https://doi.org/10.1016/j.plaphy.2020.04.011

Dani KGS, Loreto F (2022) Plant volatiles as regulators of hormone homeostasis. New Phytol 234:804–812. https://doi.org/https://doi.org/10.1111/nph.18035

Delwiche C, Sharkey T (1993) Rapid appearance of 13C in biogenic isoprene when 13CO2 is fed to intact leaves. Plant Cell Environ 16:587–591

Dicke M, Baldwin IT (2010) The evolutionary context for herbivore-induced plant volatiles: beyond the "cry for help". Trends Plant Sci 15:167–175. https://doi.org/10.1016/j.tplants.2009.12.002

Ditengou FA, Müller A, Rosenkranz M, et al (2015) Volatile signalling by sesquiterpenes from ectomycorrhizal fungi reprogrammes root architecture. Nat Commun 6:6279. https://doi.org/10.1038/ncomms7279

FAO, ITPS (2015) Status of the World's Soil Resources (SWSR) - Main Report. Rome, Italy

Fares S, Barta C, Brilli F, et al (2006) Impact of high ozone on isoprene emission, photosynthesis and histology of developing Populus alba leaves directly or indirectly exposed to the

476 pollutant. Physiol Plant 128:456–465. https://doi.org/10.1111/j.1399-3054.2006.00750.x

477 Fares S, Brilli F, Nogues I, et al (2008) Isoprene emission and primary metabolism in Phragmites
478 australis grown under different phosphorus levels. Plant Biol (Stuttg) 10:38–43.
479 https://doi.org/10.1055/s-2007-965429

480 Fargasová A, Molnárová M (2010) Assessment of Cr and Ni phytotoxicity from cutlery-washing
481 waste-waters using biomass and chlorophyll production tests on mustard Sinapis alba L.
482 seedlings. Environ Sci Pollut Res Int 17:187–194. https://doi.org/10.1007/s11356-009-
483 0136-2

484 Faxon C, Hammes J, Pathak R, Hallquist M (2017) Characterization of organic nitrate
485 constituents of secondary organic aerosol (SOA) from nitrate-radical-initiated oxidation of
486 limonene using High-Resolution Chemical Ionization Mass Spectrometry. Atmos Chem
487 Phys Discuss 18:1–25. https://doi.org/10.5194/acp-18-5467-2018

488 Fehsenfeld F, Calvert J, Fall R, et al (1992) Emissions of volatile organic compounds from
489 vegetation and the implications for atmospheric chemistry. Global Biogeochem Cycles
490 6:389–430

491 Feng Z, Yuan X, Fares S, et al (2019) Isoprene is more affected by climate drivers than
492 monoterpenes: A meta-analytic review on plant isoprenoid emissions. Plant Cell Environ
493 42:1939–1949. https://doi.org/10.1111/pce.13535

494 Fernández-Martínez M, Llusia J, Filella I, et al (2017) Nutrient-rich plants emit a less intense
495 blend of volatile isoprenoids. New Phytol 220:. https://doi.org/10.1111/nph.14889

496 Foy CD, Chaney R, White M (2003) The Physiology of Metal Toxicity in Plants. Annu Rev
497 Plant Physiol 29:511–566. https://doi.org/10.1146/annurev.pp.29.060178.002455

498 Ghirardo A, Gutknecht J, Zimmer I, et al (2011) Biogenic Volatile Organic Compound and
499 Respiratory CO2 Emissions after 13C-Labeling: Online Tracing of C Translocation
500 Dynamics in Poplar Plants. PLoS One 6:e17393

501 Giordano D, Facchiano A, D'Auria S, Loreto F (2021) A hypothesis on the capacity of plant
502 odorant-binding proteins to bind volatile isoprenoids based on in silico evidences. Elife
503 10:e66741. https://doi.org/10.7554/eLife.66741

Goldstein AH, Galbally IE (2007) Known and unknown organic constituents in the Earth' s atmosphere. Environ Sci Technol 41:1514–1521. https://doi.org/10.1021/es072476p

Guenther A, Hewitt CN, Erickson D, et al (1995) A global model of natural volatile organic compound emissions. J Geophys Res 100:8873–8892. https://doi.org/10.1029/94JD02950

Guenther A, Jiang X, Heald C, et al (2012) The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2.1): an extended and updated framework for modeling biogenic emissions. Geosci Model Dev Discuss 5:. https://doi.org/10.5194/gmdd-5-1503-2012

Guenther A, Karl T, Harley P, et al (2006) Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature). Atmos Chem Phys 6:3181–3210. https://doi.org/10.5194/acp-6-3181-2006

Guidolotti G, Calfapietra C, Loreto F (2011) The relationship between isoprene emission, CO2 assimilation and water use efficiency across a range of poplar genotypes. Physiol Plant 142:297–304. https://doi.org/10.1111/j.1399-3054.2011.01463.x

Hanson DT, Swanson S, Graham LE, Sharkey TD (1999) Evolutionary significance of isopreneemission from mosses. Am J Bot 86:634–639. https://doi.org/https://doi.org/10.2307/2656571

Hantson S, Knorr W, Schurgers G, et al (2017) Global isoprene and monoterpene emissions under changing climate, vegetation, CO2 and land use. Atmos Environ 155:35–45. https://doi.org/https://doi.org/10.1016/j.atmosenv.2017.02.010

Harley P, Deem G, Flint S, Caldwell M (2006) Effects of growth under elevated UV-B on photosynthesis and isoprene emission in Quercus gambelii and Mucuna pruriens. Glob Chang Biol 2:149–154. https://doi.org/10.1111/j.1365-2486.1996.tb00060.x

Harrison SP, Morfopoulos C, Dani KGS, et al (2013) Volatile isoprenoid emissions from plastid to planet. New Phytol 197:49–57. https://doi.org/10.1111/nph.12021

Heald C, Wilkinson M, Monson RK, et al (2009) Response of isoprene emission to ambient CO2 changes and implications for global budgets. Glob Chang Biol 15:1127–1140. https://doi.org/10.1111/j.1365-2486.2008.01802.x

IPCC (2021) Intergovernmental Panel on Climate Change sixth assessment report on climate change 2021: AR6 Climate Change 2021: The Physical Science Basis synthesis report

Jardine K, Monson R, Abrell L, et al (2012) Within-plant isoprene oxidation confirmed by direct emissions of oxidation products methyl vinyl ketone and methacrolein. Glob Chang Biol 18:973–984. https://doi.org/10.1111/j.1365-2486.2011.02610.x

Kai H, Hirashima K, Matsuda O, et al (2012) Thermotolerant cyclamen with reduced acrolein and methyl vinyl ketone. J Exp Bot 63:4143–4150. https://doi.org/10.1093/jxb/ers110

Kanakidou M, Seinfeld J, Pandis S, et al (2005) Organic aerosol and global climate modelling: a review. Atmos Chem Phys 5:1053–1123

Knudsen J, Eriksson R, Gershenzon J, Ståhl B (2006) Diversity and Distribution of Floral Scent. Bot Rev 72:1–120. https://doi.org/10.1663/0006-8101(2006)72[1:DADOFS]2.0.CO;2

Laothawornkitkul J, Taylor JE, Paul ND, Hewitt CN (2009) Biogenic volatile organic compounds in the Earth system. New Phytol 183:27–51. https://doi.org/10.1111/j.1469-8137.2009.02859.x

Lathière J, Hauglustaine DA, de Noblet N, et al (2005) Past and future changes in biogenic volatile organic compound emissions simulated with a global dynamic vegetation model. Geophys Res Lett 32:. https://doi.org/10.1029/2005GL024164

Lehning A, Zimmer W, Zimmer I, Schnitzler J-P (2001) Modeling of annual variations of oak (Quercus robur L.) isoprene synthase activity to predict isoprene emission rates. J Geophys Res 106:3157–3166. https://doi.org/10.1029/2000JD900631

Lerdau M (2007) ECOLOGY: A Positive Feedback with Negative Consequences. Science 316:212–213. https://doi.org/10.1126/science.1141486

Li M, Xu J, Algarra Alarcon A, et al (2017) In Planta Recapitulation of Isoprene Synthase Evolution from Ocimene Synthases. Mol Biol Evol 34:2583–2599. https://doi.org/10.1093/molbev/msx178

Lin T, Zhu G, He W, et al (2022) Soil cadmium stress reduced host plant odor selection and oviposition preference of leaf herbivores through the changes in leaf volatile emissions. Sci

559 Total Environ 814:152728. https://doi.org/https://doi.org/10.1016/j.scitotenv.2021.152728

560 Litvak M, Loreto F, Harley P, et al (1996) The response of isoprene emission rate and
561 photosynthetic rate to photon flux and nitrogen supply in aspen and white oak trees. Plant
562 Cell Environ 19:549–559

563 Locato V, Cimini S, De Gara L (2018) ROS and redox balance as multifaceted players of cross-
564 tolerance: epigenetic and retrograde control of gene expression. J Exp Bot 69:3373–3391.
565 https://doi.org/10.1093/jxb/ery168

566 Loivamäki M, Gilmer F, Fischbach RJ, et al (2007) Arabidopsis, a Model to Study Biological
567 Functions of Isoprene Emission? Plant Physiol 144:1066–1078.
568 https://doi.org/10.1104/pp.107.098509

569 Lombardi M, De Gara L, Loreto F (2021) Determinants of root system architecture for future-
570 ready, stress-resilient crops. Physiol Plant 172:2090–2097.
571 https://doi.org/https://doi.org/10.1111/ppl.13439

572 Long SP, Ainsworth EA, Rogers A, Ort DR (2004) Rising atmospheric carbon dioxide: plants
573 FACE the future. Annu Rev Plant Biol 55:591–628.
574 https://doi.org/10.1146/annurev.arplant.55.031903.141610

575 Loreto F, Dicke M, Schnitzler J-P, Turlings TCJ (2014) Plant volatiles and the environment.
576 Plant Cell Environ 37:1905–1908. https://doi.org/10.1111/pce.12369

577 Loreto F, Fares S (2007) Is Ozone Flux Inside Leaves Only a Damage Indicator? Clues from
578 Volatile Isoprenoid Studies. Plant Physiol 143:1096–1100.
579 https://doi.org/10.1104/pp.106.091892

580 Loreto F, Fineschi S (2015) Reconciling functions and evolution of isoprene emission in higher
581 plants. New Phytol 206:578–582. https://doi.org/10.1111/nph.13242

582 Loreto F, Schnitzler J-P (2010) Abiotic stresses and induced BVOCs. Trends Plant Sci 15:154–
583 166. https://doi.org/10.1016/j.tplants.2009.12.006

584 Loreto F, Velikova V (2001) Isoprene produced by leaves protects the photosynthetic apparatus
585 against ozone damage, quenches ozone products, and reduces lipid peroxidation of cellular

membranes. Plant Physiol 127:1781–1787

McGarvey DJ, Croteau R (1995) Terpenoid metabolism. Plant Cell 7:1015–1026. https://doi.org/10.1105/tpc.7.7.1015

Mills G, Hayes F, Simpson D, et al (2010) Evidence of widespread effects of ozone on crops and (semi-)natural vegetation in Europe (1990–2006) in relation to AOT40- and flux-based risk maps. Glob Chang Biol 17:592–613. https://doi.org/10.1111/j.1365-2486.2010.02217.x

Miloradovic van Doorn M, Merl-Pham J, Ghirardo A, et al (2020) Root isoprene formation alters lateral root development. Plant Cell Environ 43:2207–2223. https://doi.org/https://doi.org/10.1111/pce.13814

Mithöfer A, Boland W (2012) Plant Defense Against Herbivores: Chemical Aspects. Annu Rev Plant Biol 63:431–450. https://doi.org/10.1146/annurev-arplant-042110-103854

Mithöfer A, Schulze B, Boland W (2004) Biotic and heavy metal stress response in plants: evidence for common signals. FEBS Lett 566:1–5. https://doi.org/10.1016/j.febslet.2004.04.011

Mittler R (2017) ROS Are Good. Trends Plant Sci 22:11–19. https://doi.org/10.1016/j.tplants.2016.08.002

Monson RK, Weraduwage SM, Rosenkranz M, et al (2021) Leaf isoprene emission as a trait that mediates the growth-defense tradeoff in the face of climate stress. Oecologia 197:885–902. https://doi.org/10.1007/s00442-020-04813-7

Nah T, Sanchez J, Boyd C, Ng N (2015) Photochemical Aging of α-pinene and β-pinene Secondary Organic Aerosol formed from Nitrate Radical Oxidation. Environ Sci Technol 50:. https://doi.org/10.1021/acs.est.5b04594

Nanda AK, Andrio E, Marino D, et al (2010) Reactive oxygen species during plant-microorganism early interactions. J Integr Plant Biol 52:195–204. https://doi.org/10.1111/j.1744-7909.2010.00933.x

Niinemets Ü, Rasulov B, Talts E (2021) CO(2) -responsiveness of leaf isoprene emission: Why do species differ? Plant Cell Environ 44:3049–3063. https://doi.org/10.1111/pce.14131

613 Ninkovic V, Markovic D, Rensing M (2021) Plant volatiles as cues and signals in plant
614 communication. Plant, Cell \& Environ 44:1030–1043.
615 https://doi.org/https://doi.org/10.1111/pce.13910

616 Obara N, Hasegawa M, Kodama O (2003) Induced Volatiles in Elicitor-treated and Rice Blast
617 Fungus-inoculated Rice Leaves. Biosci Biotechnol Biochem 66:2549–2559.
618 https://doi.org/10.1271/bbb.66.2549

619 Pallozzi E, Marino G, Fortunati A, et al (2013) Effect of Exposure to UVA Radiation on
620 Photosynthesis and Isoprene Emission in Populus × Euroamericana. In: Kuang T, Lu C,
621 Lixin Z (eds) Photosynthesis research for food, fuel and the future. Springer, Berlin,
622 Germany, pp 763–767

623 Palmer P, Abbot D, Fu T-M, et al (2006) Quantifying the Seasonal and Interannual Variability of
624 North American Isoprene Emissions Using Satellite Observations of the Formaldehyde
625 Column. J Geophys Res Atmos 111:. https://doi.org/10.1029/2005JD006689

626 Paré PW, Tumlinson JH (1999) Plant Volatiles as a Defense against Insect Herbivores. Plant
627 Physiol 121:325–332. https://doi.org/10.1104/pp.121.2.325

628 Paulot F, Crounse JD, Kjaergaard HG, et al (2009) Unexpected epoxide formation in the gas-
629 phase photooxidation of isoprene. Science 325:730–733.
630 https://doi.org/10.1126/science.1172910

631 Penuelas J, Asensio D, Tholl D, et al (2014) Biogenic volatile emissions from the soil. Plant Cell
632 Environ 37:. https://doi.org/10.1111/pce.12340

633 Peñuelas J, Llusià J (2003) BVOCs: plant defense against climate warming? Trends Plant Sci
634 8:105–109. https://doi.org/10.1016/S1360-1385(03)00008-6

635 Pichersky E, Gershenzon J (2002) The formation and function of plant volatiles: perfumes for
636 pollinator attraction and defense. Curr Opin Plant Biol 5:237–243.
637 https://doi.org/10.1016/s1369-5266(02)00251-0

638 Pinto-Zevallos D, Blande J, Souza S, et al (2010) Plant Volatile Organic Compounds (VOCs) in
639 Ozone (O3) Polluted Atmospheres: The Ecological Effects. J Chem Ecol 36:22–34.
640 https://doi.org/10.1007/s10886-009-9732-3

641 Pollastri S, Jorba I, Hawkins TJ, et al (2019) Leaves of isoprene-emitting tobacco plants
642 maintain PSII stability at high temperatures. New Phytol 223:1307–1318.
643 https://doi.org/10.1111/nph.15847

644 Pollastri S, Savvides A, Pesando M, et al (2018) Impact of two arbuscular mycorrhizal fungi on
645 Arundo donax L. response to salt stress. Planta 247:573–585.
646 https://doi.org/10.1007/s00425-017-2808-3

647 Possell M, Hewitt CN, Beerling D (2004) The effects of glacial atmospheric CO2 concentrations
648 and climate on isoprene emissions by vascular plants. Glob Chang Biol 11:60–69.
649 https://doi.org/10.1111/j.1365-2486.2004.00889.x

650 Rennenberg H, Loreto F, Polle A, et al (2006) Physiological responses of forest trees to heat and
651 drought. Plant Biol (Stuttg) 8:556–571. https://doi.org/10.1055/s-2006-924084

652 Rosenstiel TN, Potosnak MJ, Griffin KL, et al (2003) Increased CO2 uncouples growth from
653 isoprene emission in an agriforest ecosystem. Nature 421:256–259.
654 https://doi.org/10.1038/nature01312

655 Salt DE, Smith RD, Raskin I (1998) PHYTOREMEDIATION. Annu Rev Plant Physiol Plant
656 Mol Biol 49:643–668. https://doi.org/10.1146/annurev.arplant.49.1.643

657 Sanderson M, Jones CD, Collins W, et al (2003) Effect of Climate Change on Isoprene
658 Emissions and Surface Ozone Levels. Geophys Res Lett 30:1936

659 Schenkel D, Lemfack MC, Piechulla B, Splivallo R (2015) A meta-analysis approach for
660 assessing the diversity and specificity of belowground root and microbial volatiles. Front
661 Plant Sci 6:707. https://doi.org/10.3389/fpls.2015.00707

662 Scholefield P, Doick K, Herbert B, et al (2004) Impact of rising CO2 on emissions of volatile
663 organic compounds: Isoprene emission from Phragmites australis growing at elevated CO2
664 in a natural carbon dioxide spring. Plant Cell Environ 27:393–401.
665 https://doi.org/10.1111/j.1365-3040.2003.01155.x

666 Seinfeld JH, Pandis S (2006) Atmospheric Chemistry and Physics: From Air Pollution to
667 Climate Change, 2nd edn.

668 Sharkey T, Yeh S (2001) Isoprene emission from plants. Annu Rev Plant Physiol Plant Mol Biol.
669 Annu Rev Plant Physiol Plant Mol Biol 52:407–436.
670 https://doi.org/10.1146/annurev.arplant.52.1.407

671 Sharkey TD, Monson RK (2017) Isoprene research - 60 years later, the biology is still enigmatic.
672 Plant Cell Environ 40:1671–1678. https://doi.org/10.1111/pce.12930

673 Sharkey TD, Singsaas EL, Vanderveer PJ, Geron C (1996) Field measurements of isoprene
674 emission from trees in response to temperature and light. Tree Physiol 16:649–654.
675 https://doi.org/10.1093/treephys/16.7.649

676 Shortall OK (2013) "Marginal land" for energy crops: Exploring definitions and embedded
677 assumptions. Energy Policy 62:19–27.
678 https://doi.org/https://doi.org/10.1016/j.enpol.2013.07.048

679 Singsaas EL, Lerdau M, Winter K, Sharkey TD (1997) Isoprene Increases Thermotolerance of
680 Isoprene-Emitting Species. Plant Physiol 115:1413–1420.
681 https://doi.org/10.1104/pp.115.4.1413

682 Squire OJ, Archibald AT, Abraham NL, et al (2014) Influence of future climate and cropland
683 expansion on isoprene emissions and tropospheric ozone. Atmos Chem Phys 14:1011–1024.
684 https://doi.org/10.5194/acp-14-1011-2014

685 Srikanta Dani KG, Loreto F (2022) Plant volatiles as regulators of hormone homeostasis. New
686 Phytol. https://doi.org/10.1111/nph.18035

687 Tai A, Mickley L, Heald C, Wu S (2013) Effect of CO2 inhibition on biogenic isoprene
688 emission: Implications for air quality under 2000 to 2050 changes in climate, vegetation,
689 and land use. Geophys Res Lett 40:. https://doi.org/10.1002/grl.50650

690 Tiiva P, Rinnan R, Faubert P, et al (2007) Isoprene emission from a subarctic peatland under
691 enhanced UV-B radiation. New Phytol 176:346–355. https://doi.org/10.1111/j.1469-
692 8137.2007.02164.x

693 Velikova V, Edreva A, Loreto F (2004) Endogenous isoprene protects Phragmites australis
694 leaves against singlet oxygen. Physiol Plant - PHYSIOL PLANT 122:219–225.
695 https://doi.org/10.1111/j.0031-9317.2004.00392.x

Velikova V, Pinelli P, Pasqualini S, et al (2005) Isoprene decreases the concentration of nitric oxide in leaves exposed to elevated ozone. New Phytol 166:419–425. https://doi.org/10.1111/j.1469-8137.2005.01409.x

Velikova V, Tsonev T, Loreto F, Centritto M (2011a) Changes in photosynthesis, mesophyll conductance to CO2, and isoprenoid emissions in Populus nigra plants exposed to excess nickel. Environ Pollut 159:1058–1066. https://doi.org/10.1016/j.envpol.2010.10.032

Velikova V, Várkonyi Z, Szabó M, et al (2011b) Increased thermostability of thylakoid membranes in isoprene-emitting leaves probed with three biophysical techniques. Plant Physiol 157:905–916. https://doi.org/10.1104/pp.111.182519

Vickers C, Possell M, Cojocariu C, et al (2009) Isoprene synthase protects transgenic tobacco plants from oxidative stress. Plant Cell Environ 32:520–531. https://doi.org/10.1111/j.1365-3040.2009.01946.x

Winter TR, Borkowski L, Zeier J, Rostás M (2012) Heavy metal stress can prime for herbivore-induced plant volatile emission. Plant Cell Environ 35:1287–1298. https://doi.org/10.1111/j.1365-3040.2012.02489.x

Wittig V, Ainsworth E, Naidu S, et al (2009) Quantifying the impact of current and future tropospheric ozone on tree biomass, growth, physiology and biochemistry: A quantitative meta-analysis. Glob Chang Biol 15:. https://doi.org/10.1111/j.1365-2486.2008.01774.x

Wu S, Mickley L, Kaplan J, Jacob D (2012) Impacts of changes in land use and land cover on atmospheric chemistry and air quality over the 21st century. Atmos Chem Phys 12:. https://doi.org/10.5194/acp-12-1597-2012

Xia X-J, Zhou Y-H, Shi K, et al (2015) Interplay between reactive oxygen species and hormones in the control of plant development and stress tolerance. J Exp Bot 66:2839–2856. https://doi.org/10.1093/jxb/erv089

Zuo Z, Weraduwage SM, Lantz AT, et al (2019) Isoprene Acts as a Signaling Molecule in Gene Networks Important for Stress Responses and Plant Growth. Plant Physiol 180:124–152. https://doi.org/10.1104/pp.18.01391

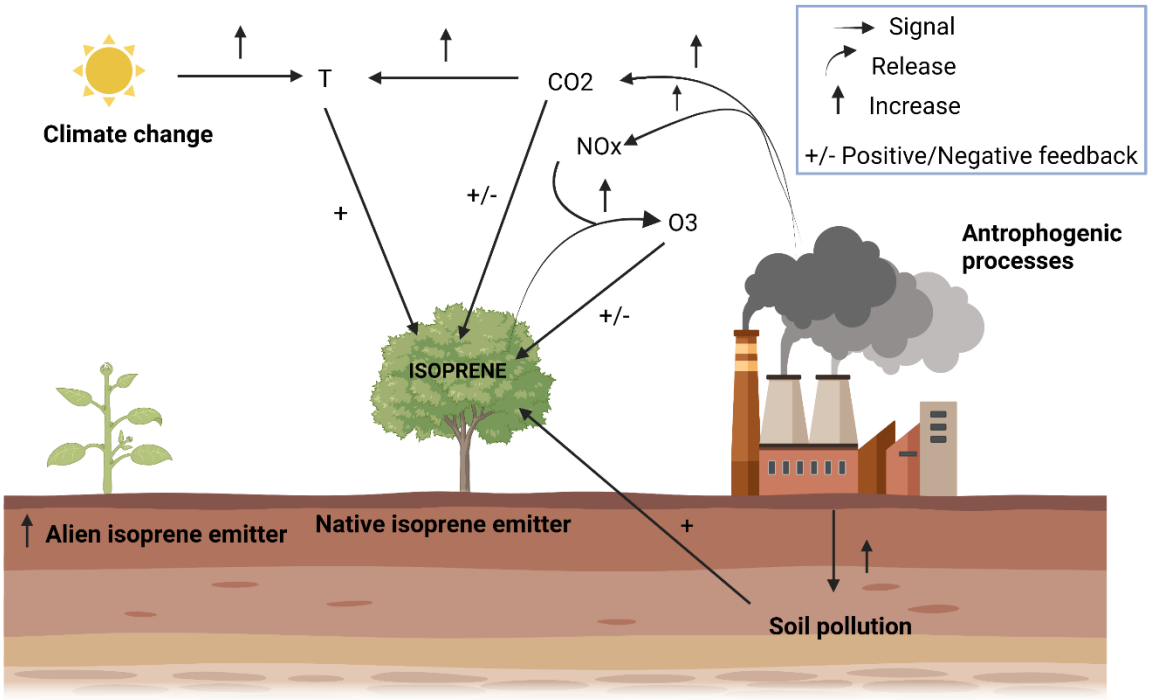
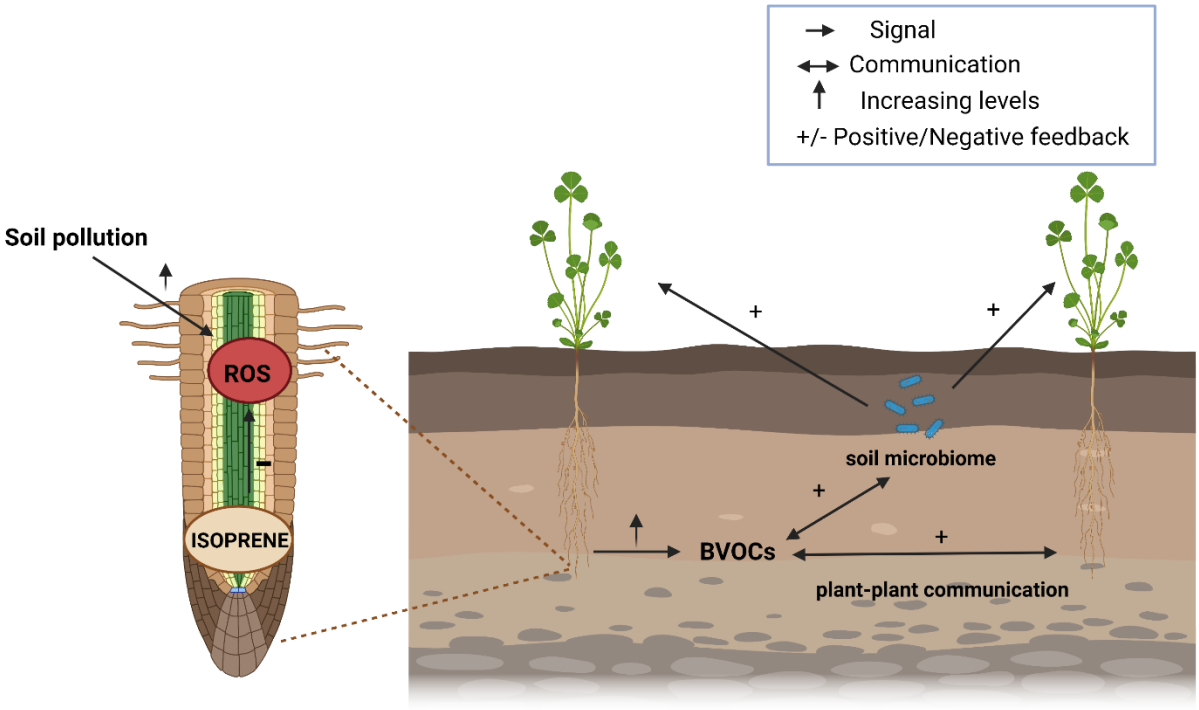


Fig. 1 Dynamic of plant isoprene emission and settlement of alien isoprene-emitting species induced by anthropogenic processes determining environmental stresses or by climate change. Positive or negative feedback (+/-) refers to the direct effects of pollutants on the isoprene emission capacity. ↑ represent the direct effects of anthropogenic processes and climate change

736 on the increasing of air and soil determinants and settlement of new isoprene emitter species.
737 Figure was created with *BioRender.com*.



738

739 **Fig. 2** Soil pollutants effects on root ROS generation and root-related BVOCs and the
740 communication plant-plant and plant-microbiome through the soil. + or – refer to the direct
741 effect of isoprene or BVOCs while ↑ to the direct effects of soil pollution. Only for this purpose
742 we refer to BVOCs only for unclear evidence of isoprene belowground communication. *Figure*
743 *was c*reated with BioRender.com.

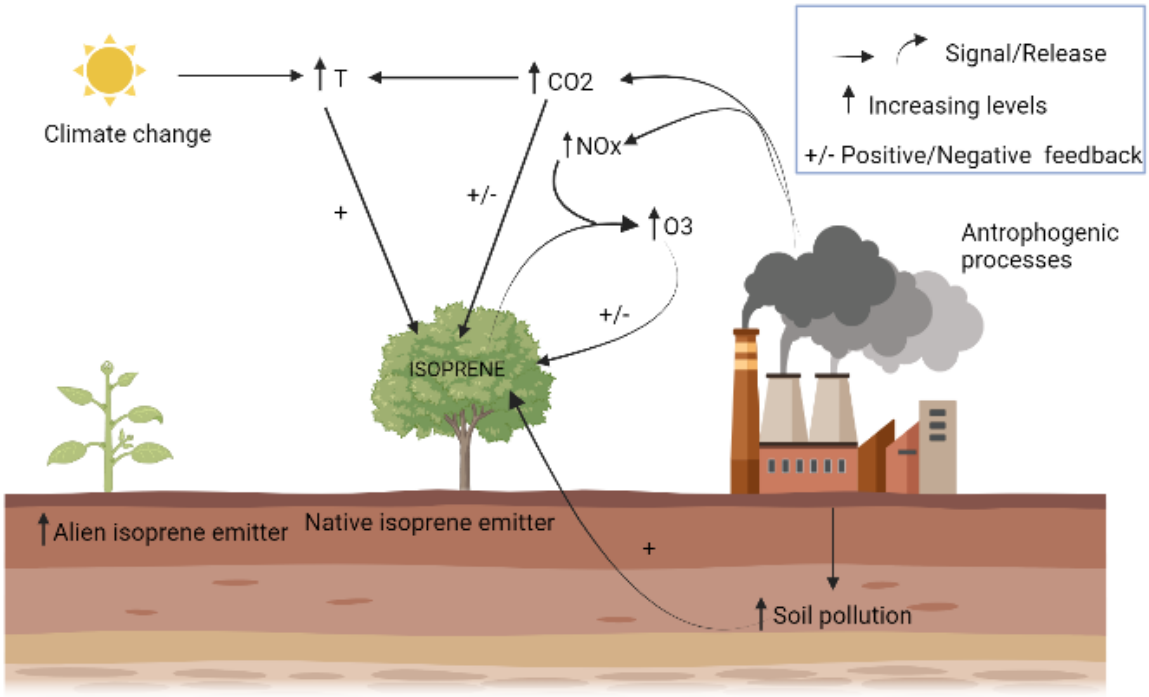


Figure 1 Dynamic of plant isoprene emission and settlement of alien isoprene emitting species induced by anthropogenic processes determining environmental stresses or by climate change. + or – refer to the direct effects of contaminants on the emission of isoprene while ↑ represent the effects of anthropogenic processes and climate change on air and soil determinants and settlement of alien species.

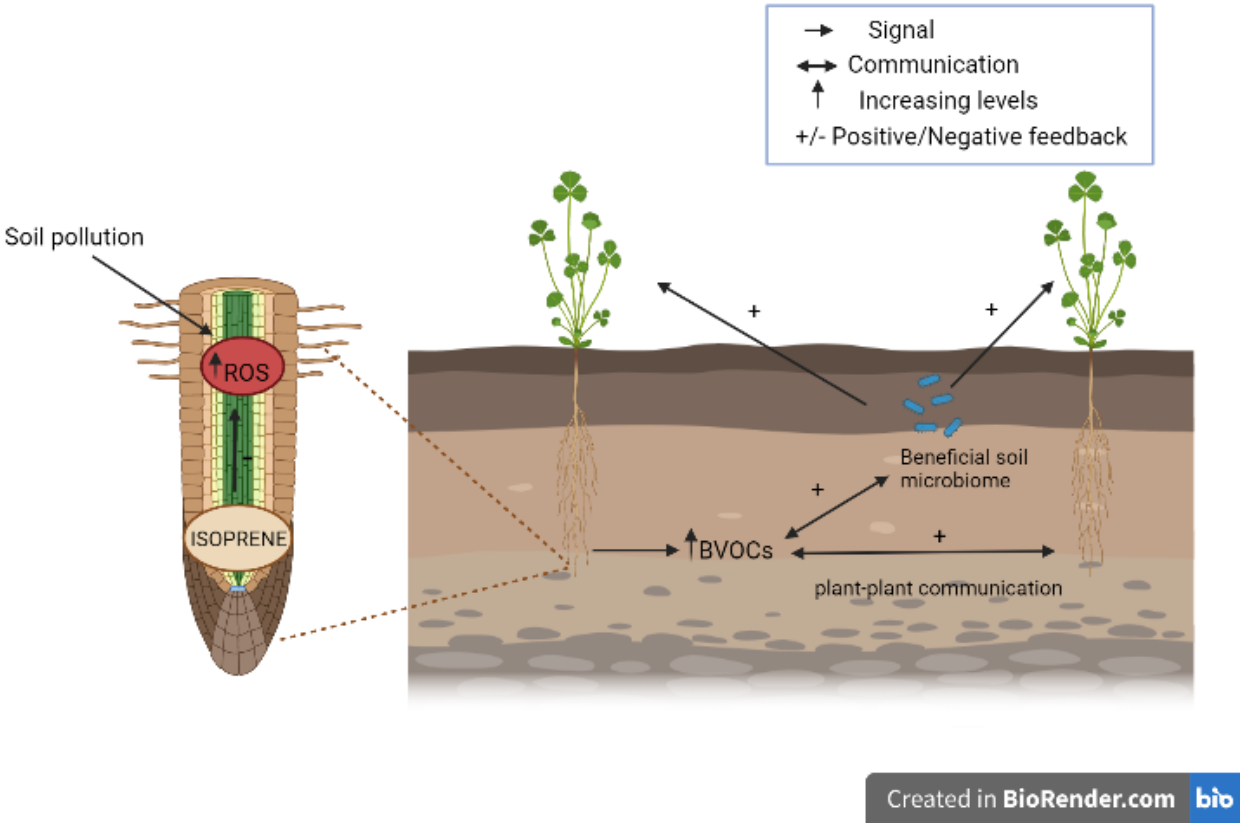


Figure 2 Soil pollutants effects on root ROS generation and root-related BVOCs and the communication plant-plant and plant-microbiome through the soil. + or – refers to the direct effect of isoprene or BVOCs while ↑ to the direct effects of soil pollution.