

# Impact of Air Pollution on Terrestrial Ecosystems



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**Abstract** This chapter summarizes the current state of knowledge on the impacts of air pollution on terrestrial vegetation in general and in the Mediterranean region. These impacts occur either indirectly through changes in the physical state of the atmosphere, such as increase in the temperature (caused by greenhouse gases), and in the diffuse radiation (caused by aerosols) that reaches vegetation, or directly through phytotoxicity resulting from ozone, sulfur, nitrogen, and other pollutants' stomatal and non-stomatal uptake by the plants, nutrient balance modification by atmospheric deposition, transfer of plant diseases by aerosols, and pollution by

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persistent pollutants and metals. Abiotic and biotic stresses can also alter the composition, amounts, and functioning of volatile organic compounds that are emitted by the plants and play known ecological roles. These impacts are summarized, and plant physiological responses to an excess of critical nutrient levels are presented and discussed.

## 1 Introduction

The Mediterranean Basin is among the world's regions hosting the highest biodiversity of both marine and terrestrial ecosystems. The Mediterranean's flora is highly diverse with 15,000–25,000 species, among which 60% are native and endemic species unique to the region (Vlachogianni et al., 2012). Globally, terrestrial vegetation is responsible for more than half of the atmospheric oxygen production. Regionally, vegetation interacts with the atmospheric water cycle through photosynthesis, respiration, and transpiration. In urban regions, vegetation has the capacity to partially counterbalance the heat island effect and improve microclimate through the reduction of both noise and intensity of atmospheric ionization. Furthermore, vegetation is an efficient recycling energy source, and plant products provide raw material for various constructions, clothing, as well as nutrients for humans and fauna.

Due to the mild weather conditions and the fertility of most soils, agriculture has always been an integral part of human activities and an important contributor to the economy of the Mediterranean countries. However, vegetation in the region is at risk due to land use changes and the occurrence of environmental stresses and air pollution combined with climate change. Mediterranean vegetation is known to be highly resilient to disturbances, which is tentatively attributed to its historical evolution under various stresses and to its increased biodiversity, although the mechanisms associated with the resilience of ecosystems remain to be understood (Lavorel, 1999). Severe man-driven land use changes, like urban extension, agricultural abandonment, and afforestation, have led to flora redistribution within the Mediterranean region and to the increase of invasive alien plant species (Mosher et al., 2009; Vilà et al., 2003). In addition, human interference to nature has resulted to several side effects such as extreme climatic events, including prolonged droughts and increased occurrence of wildfires, along with elevated ozone (O<sub>3</sub>) and particulate matter levels (Avila et al., 1997; Kanakidou et al., 2011).

Air pollutants affect the physiology of the plants in several ways and through different pathways: (a) by absorption through the leaf stomata or epidermis (Heath, 2008; Hill, 1971), (b) through the root system after air pollutant deposition onto the soils (Cataldo & Wildung, 1978; Gandois & Probst, 2012), (c) by adsorption of aerosols onto the leaves thus reducing the penetrating light and blocking the opening of stomata (Gheorghe & Ion, 2011), and (d) by changing the Photosynthetically Active Radiation (PAR) that reaches the plant (Rap et al., 2015). Air pollutants can

also cause acute damage to the vegetation whenever absorption of high pollutant concentrations is performed in a relatively short time interval, while chronic injuries occur due to long-term absorption of pollutants at sublethal concentrations (Gheorghe & Ion, 2011). In addition, plants (both above- and below-ground plant components) emit a variety of volatile organic compounds (VOC) (Agathokleous et al., 2020; Guenther et al., 2012; Yuan et al., 2009) that have several ecological functions in the plant cycle, serving, for instance, for pollinator attraction, plant defense against insects, plant-plant communication, thermotolerance, and removing reactive oxygen species like ozone (Yuan et al., 2009). Biotic and abiotic stresses to the plants can lead to changes in the emitted VOC composition (e.g., VOCs emitted as a plant response to pathogen or herbivore attacks; Hopke et al., 1994), and thus in their contribution to the abovementioned functions (Yuan et al., 2009). Mills et al. (2018) estimated a global loss in wheat yields due to exposure to O<sub>3</sub> of 6–9% on average in the south and north hemisphere, respectively, that results in actual total grain losses of approximately 85 Tg per year.

In the 80s, acid rain emerged as a major problem for European forests (Grennfelt et al., 2020). The acid rain facilitated solubilization and leaching of mineral elements, like calcium (Ca), potassium (K), and magnesium (Mg), from the soil and led to the removal of vital minerals and nutrients for plant growth resulting in profound yellowing of the leaves due to deficiencies (Landmann & Bonneau, 1995). The applied legislation for air pollution abatement resulted in the reduction of pollutants' emissions (Lamarque et al., 2013) that subsequently led to substantial decrease of sulfate concentrations in atmospheric aerosols over the past 30 years (Aas et al., 2019) and reduced atmospheric deposition to distant forests (Pierret et al., 2019). However, deposition fluxes of reactive nitrogen remain high and affect ecosystem's health (Aguillaume et al., 2016; Im et al., 2013; Kanakidou et al., 2020; Markaki et al., 2010; Ochoa-Hueso et al., 2011). Nevertheless, eutrophication and acidification issues persist, and they are of high concern since they affect biodiversity leading to a loss of species richness (Duprè et al., 2010). Analyzing 70 years of species richness in acidic grasslands of Northern Europe, Duprè et al. (2010) found that changes in vegetation species spatial distribution were mainly related to soil acidity, which affects solubilization of metal oxides and releases toxic metal ions, and to the cumulative amounts of nitrogen (N) and sulfur (S) deposition. It is worth noting that N atmospheric deposition has been proposed to be the main driver for variation in plant species richness (Stevens et al., 2004), phytocommunity composition (Bobbink et al., 2010), and relative plant species abundance (Gilliam, 2006). The interaction between N deposition and air temperature increase under climate change has been predicted to impact soil functioning and to cause vegetation species and spatial changes for the next decades (Gaudio et al., 2015; Rizzetto et al., 2016).

Furthermore, aerosol pollution also affects vegetation by scattering light and thus increasing the fraction of diffuse radiation and the efficiency of photosynthesis (Rap et al., 2015) and by providing nutrients and/or toxic substances to the ecosystem through dry or wet deposition (Kanakidou et al., 2018; Ochoa-Hueso et al., 2011). Adsorption of aerosols on the leaf surface causes negative effects to the

plants since aerosols cover the leaves surface, reduce the penetrating light, and block the opening of stomata (Gheorghe & Ion, 2011). The vicinity of the Mediterranean Basin with the African desert results in frequent dust outbreaks that increase aerosol levels and nutrient deposition over the Mediterranean (Kanakidou et al., 2020; Guieu and Ridame, 2022). In addition, dust outbreaks can also carry pathogens to Mediterranean (Polymenakou et al., 2008) and other ecosystems causing them to degrade as has been suggested for Caribbean ecosystems (Garrison et al., 2003, 2006).

Finally, intensification of agriculture activities so as to cover human needs for nutrition has led to soil contamination through the excessive use of fertilizers and pesticides. Spraying of several pesticides in the atmosphere against insects, plant pathogens, or other pests in order to improve product quality and to increase the yields of various crops has contributed to air pollution of agricultural regions. Pesticides include a wide range of compounds: insecticides, herbicides, fungicides, plant growth regulators, and others (Aktar et al., 2009). They are sprayed on the crops, and thus they partially remain in the atmosphere, transported by the wind, and deposited to the nearby soils, thus expanding contamination and providing an additional pathway for pesticides to penetrate into the plants through the soil. Toxic metals form another category of important air pollutant present in the atmosphere in low concentrations, which once are deposited can accumulate in the soils (Hernandez et al., 2003), sediments (N'Guessan et al., 2009), and organisms (EMEP, 2018; Kabata-Pendias, 2010). Persistent organic compounds and toxic metals tend to accumulate in plants, resulting in an increase of their concentration within the tissues of organisms at successively higher levels, entering the food chain (Liu et al., 2005). Metal enrichments of soils in agricultural and urban areas of Greece (Kelepertzis, 2014) and Spain (Acosta et al., 2011) have been attributed to accumulation processes resulting from prolonged applications of large amounts of fertilizers and pesticides–fungicides (copper (Cu), zinc (Zn), cadmium (Cd), lead (Pb), and arsenic (As)), as well as from industrial activities, and metal deposition due to the high volume of vehicular traffic (Pb and Cd). Pollution of vegetation both by metals and pesticides can be harmful to human health since these pollutants can penetrate in the food chain (Nasreddine & Parent-Massin, 2002). Finally, more or less biodegradable detergents that are discharged into the sea can then be transported to the atmosphere through the production of sea spray leading to air pollution. The deposition of sea spray loaded with detergent on the leaves of the plants promotes the penetration of salt into the plants causing their death. Impacts of the aforementioned pollution can be observed on certain coastal forests around the Mediterranean Sea (Garrec, 2019).

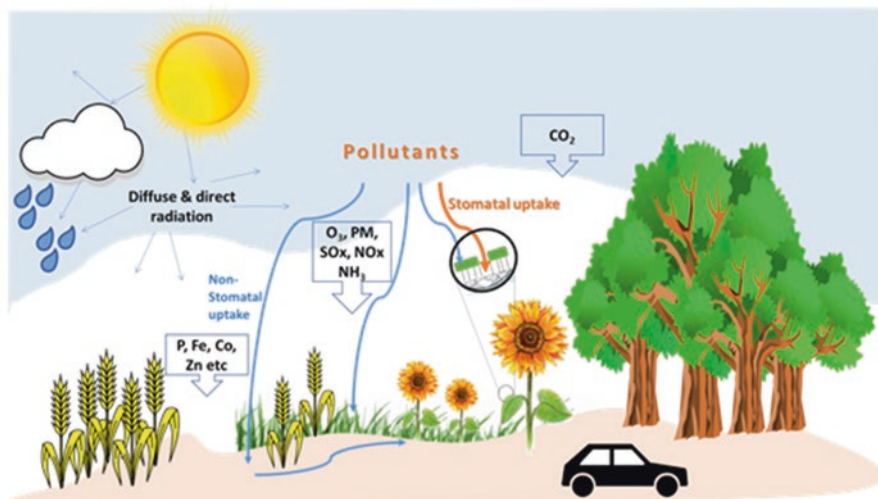
In this chapter, we first outline general information regarding the mechanisms of air pollutants pathways into the plants and the phytotoxicity effects caused by the most common atmospheric pollutants. Subsequently, we discuss the impact of the major pollutants, namely, ozone, sulfur, nitrogen, and metals on the vegetation, spanning from forests to crops in the Mediterranean region.

## 2 Pollutant Uptake by the Plants

Penetration of air pollutants into the plant occurs either from the aerial or from the underground organs of the plants. From the aerial organs, air pollutant absorption into plants occurs mainly through the leaves, although a slight absorption through stems and trunk might also be possible (Garrec, 2019; Kabata-Pendias, 2010). Air pollutants can also be absorbed by the roots of the plants after being deposited onto the soil in their deposited chemical form or after being chemically transformed. Before reaching the cuticle of the leaf, the pollutant passes through a thin zone of calm air that surrounds each leaf, the atmospheric interfacial leaf/atmosphere sub-layer. The resistance to air pollution absorption through the interfacial atmospheric layer varies according to numerous parameters, such as leaf size, shape, and orientation, presence and shape of trichomes, and wind speed (Garrec, 2019; Gupta, 2016; Heath et al., 2009).

The interfacial leaf/atmosphere layer contains three phases: (a) the gas phase, where the air pollutants reaching the plant are present together with the emissions of the leaf; (b) the aqueous phase, which contains the water film located at the surface of the leaf and water that is bound to the cuticle through its polar groups; and (c) the lipid phase, which contains the waxes that are located on the surface of or inside the cuticle. The pollutant may react in one of these phases and could produce additional secondary phytotoxic products to the initial pollutant itself (Percy et al., 1994). Organic matter exudation by the leaves can lead to a complete dissolution of dry deposition of metals at the leaf surface and make them easier to be absorbed by the leaves (Hou et al., 2005).

The air pollutants can be transported into the plant following various pathways (Fig. 1): penetration mainly by stomata (*gases*), which are present in the leaf surface (Gupta, 2016), surface deposits (aerosols), and trapping in epicuticular waxes (lipophilic and high molecular weight gases). Following dry and wet atmospheric deposition, *metals* can be found in wax and inside the coniferous needles depending on the metal and its particulate or dissolved form (Gandois & Probst, 2012). The main plant absorption route for *organic pollutants* is via the lipid structure of the cuticle. However, from the pollutant concentration found in the interfacial leaf/atmosphere layer, only a small portion will finally enter into the plant. There, they will react within the different plant compartments, both in the outer and the inner sides of the plasma membrane (apoplast and symplast) (Faulkner, 2018; Garrec, 2019; Kundu et al., 2018; Oparka, 2005). Meteorological conditions such as amount of sun irradiance, wind, and rain, as well as leaf microstructure and vegetation macrostructure, influence the characteristics of *aerosol deposition* on the surface of the leaves (Leonard et al., 2016). Moreover, O<sub>3</sub> absorption by stomata depends on water availability during the growing season, plant morphological characteristics such as the existence and the shape of the leaf trichomes, and also on the sensitivity of the plants, which may vary strongly according to both the species and the varieties (Lombard et al., 2015; Saitanis et al., 2014; Saitanis & Karandinos, 2002). The physiological response of plants to air pollutants after their absorption will depend



**Fig. 1** Gaseous and particulate atmospheric pollutants are transported in the plants through stomatal and non-stomatal uptake by the leaves as well as via deposition onto the soil and subsequent uptake by the roots

on both the characteristics of the plant and the nature of the air pollutant (Wolfenden & Mansfield, 1990).

### 3 Pollutant Reactions Inside the Plant

Once the pollutant enters the plant, it causes an oxidative stress producing reactive oxygen species (ROS), including free hydroxyl radicals, which can cause damage to the plants at different levels. ROS induce oxidative damage to lipids, proteins, and DNA (Sharma et al., 2012). The pollutant will cause specific stress to the plant depending on its physicochemical characteristics (Table 1).

Ozone enters the plants through stomatal and non-stomatal uptake from the leaf cuticle via thermal decomposition or aqueous reactions in water films on plant surfaces (Fowler et al., 2009; Heath, 2008). Inside the plant,  $O_3$  contributes to ROS production, but since it is very short-lived, it is quickly converted to more stable ROS, such as hydrogen peroxide, superoxide, and hydroxyl radical (Health 2008). If  $O_3$  concentration exceeds the detoxification capacity of the apoplastic antioxidants, it will negatively affect plant's physiological processes, such as photosynthesis and/or respiration (Emberson et al., 2018; Musselman et al., 2006).

Nitrogen dioxide ( $NO_2$ ) dissolved in cells produces nitrite ions ( $NO_2^-$ ), which are toxic at high concentrations and nitrate ions ( $NO_3^-$ ) that enter nitrogen metabolism. Nitrogen dioxide pollution is detectable on leaves and seedlings and is more

**Table 1** Main categories of atmospheric short-lived pollutants, the pathways through which they enter into the plants, and their main effects on the plants

Pollutant	Transport pathway	Effects on plant
Ozone (O <sub>3</sub> )	Stomata, non-stomatal pathway, deposition on leaves	Increase in reactive oxygen species Changes in plant's physiological processes Reduction of photosynthesis Reduction of crop yields Emissions of VOC, plant reproduction, plant-to-plant and plant-soil-microbe interactions Changes in C and N cycling Changes in Diversity of plant communities
Reactive nitrogen (N) (mainly NO <sub>x</sub> , NH <sub>3</sub> , HNO <sub>3</sub> , ammonium, and nitrate)	Stomata, deposition on leaves	Low levels → amino acids/protein synthesis High levels → reduced photosynthetic activity Changes in plant and soil stoichiometry (N/P) N-induced P limitation Soil and water eutrophication leading to plant toxicities or deficiencies and biodiversity losses
Sulfur (S) (mainly SO <sub>2</sub> , H <sub>2</sub> SO <sub>4</sub> , sulfate)	Stomata, deposition on leaves	Low levels → protein synthesis High levels → stomata opening reduction, water stress, O <sub>2</sub> replacement in cellular material Chlorophyll degradation Acidification after deposition to plants and soils Soil acidification/nutrient losses
Acid deposition (mainly N, S)	Deposition on leaves and soil	Acidification of soil: nutrient losses through leaching of plant growth minerals and nutrients, resulting in yellowing of leaves, increase vulnerability of plants, dying trees, and solubilization of toxic metals; loss of plant diversity
Aerosols (also containing S, N, and metals)	Deposition on leaves and soil	Diffuse radiation, closing of stomata Acidification of soils, leaching of minerals, mineral and nutrient deficiency Accumulation of pollutants into plants Carriers of plant diseases
Trace metals	Deposition on leaves and soil, with uptake by the roots	Accumulation into plants and leave edges Disturbance of plant's physiological processes depending on the metal Contamination of food chain
Pesticides	Deposition on leaves and soil, with uptake by roots	Accumulation into plants Contamination of food chains
Halogens (Cl <sub>2</sub> , HCl, HF)	Stomata, deposition on leaves	Interfere with enzymes activity Damage cell membranes of plants Disruption of the cellular metabolism of calcium Necrosis, plant death

profound in conifer older needles where tipburn is observed. It forms crystalloid structures in the stroma of chloroplasts and bloats the thylakoid membrane within the plant cells, resulting in the reduction of photosynthetic activity (Gheorghe & Ion, 2011).

Sulfur enters the leaves as sulfur dioxide ( $\text{SO}_2$ ) through the stomata. Sulfur, at low concentrations, is used by the plant in protein synthesis, but at high concentrations, it interferes with electron transport chain, leading to stomatal opening reduction, water stress, and oxygen replacement in cellular material (Mudd, 1975). It also affects structural proteins in the cell membrane leading to alterations in the permeability of the membranes (Nieboer et al., 1976). In high concentrations,  $\text{SO}_2$  will lead to chlorophyll's degradation (Brahmachari & Kundu, 2017).

Halogens ( $\text{Cl}_2$ ,  $\text{HCl}$ ,  $\text{HF}$ ) enter the plants through the stomata and move to the margins and edges of the leaves, where they tend to accumulate. Inside the plants, fluorides interfere with the activity of many enzymes, by inhibiting the functioning of proteins through combination with the metal components of the proteins or otherwise (Gheorghie & Ion, 2011). It is worth mentioning that hydrofluoric acid ( $\text{HF}$ ) pollution is also inducing a disruption of the cellular metabolism of calcium (Garrec, 2019).

The phytotoxicity of the various pollutants depends on their chemical identity (Table 1). The main air pollutants have been classified by laboratory experiments according to their decreasing phytotoxicity impact as follows:

Hydrofluoric acid ( $\text{HF}$ ) > ozone ( $\text{O}_3$ ) > sulfur dioxide ( $\text{SO}_2$ ) > nitrogen dioxide ( $\text{NO}_2$ ).

However, this trend is only indicative, since different plants have different sensitivity to the various pollutants (Smith et al., 1989; Yu et al., 2011). In addition to the phytotoxic potential of the pollutant, the plant's response depends on the cumulative amount of the pollutant that entered the plant. Furthermore, the time period over which a certain amount of pollutant is transported into the plant is also important for its phytotoxic response. For the same amount of pollutant, a shorter transportation time will result in a greater pollutant impact. The so-called peak effect is usually explained by the fact that over short periods of time, the plant does not have adequate time to acclimatize, adapt, and initiate its defense systems response.

The large number of pollutants (e.g.,  $\text{HF}$ ,  $\text{O}_3$ ,  $\text{SO}_2$ ,  $\text{NO}_2$ , aerosols, metals) that affect plants can also be classified according to the extent of their impact zone, which depends on their lifetime in the atmosphere and thus on the distance in which they can affect vegetation after emission or formation and transport in the atmosphere (Garrec, 2019). Short-lived pollutants, like nitrogen oxides and ammonia, with lifetimes of a few hours to a day exhibit impacts on the plants within a radius of a few tens of kilometers from their emission sources. Nitrogen oxides ( $\text{NO}_x$ ) are mainly originating from transport and other combustion sources, while ammonia ( $\text{NH}_3$ ) is mainly from agriculture and transport. In contrast, pollutants with atmospheric lifetimes ranging from few days to weeks can have impacts over several hundred kilometers around their emission sources. These include mainly acidic compounds, such as sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and nitric acid ( $\text{HNO}_3$ ), deposited by dry or wet removal processes. Since these acids are formed via the oxidation of primary pollutants ( $\text{SO}_2$  and  $\text{NO}_2$ ) by oxidants like ozone, hydroxyl radicals, and nitrate radicals, they are considered as secondary pollutants (Graedel & Crutzen, 1993). Pollutants with lifetime of several years have global impacts and mainly include carbon dioxide ( $\text{CO}_2$ ), which is linked to the massive use of fossil fuels by transport



and industry. Carbon dioxide has direct beneficial effects on plant growth via its essential role in photosynthesis, while at the same time, it has indirect harmful effects on plants through enhancing the greenhouse effect that results in climate change (Farquhar, 1997). Other global pollutants, which have an indirect effect on vegetation via their contribution to the greenhouse effect, include: methane ( $\text{CH}_4$ ), a component of natural gas, which is also produced by ruminants and in anaerobic environments such as wetlands and rice fields and which has phytotoxic effects on plants whenever its concentration is increased such as in the case of landfills (Peer et al., 1993); nitrous oxide ( $\text{N}_2\text{O}$ ), resulting from the massive use of fertilizers in agriculture; halocarbons, having several applications such as solvents, refrigerants and in insulation materials; or even soil disinfectants such as methyl bromide which was in use until the beginning of the century. Halocarbons are also ozone-depleting gases with the possibility of an additional negative impact on plants as a result of the increased UV-B solar flux that reaches Earth's surface due to their contribution to the enlargement of the ozone hole.

#### 4 Plant's Response to Pollution Exposure

Plants respond to air pollution by developing different defensive mechanisms through anatomical, morphological, and physiological changes (Darrall, 1989; Dineva, 2004; Gravano et al., 2003), aiming to limit the uptake of the pollutant and thus increase plant's tolerance to the pollutant. Such mechanisms can be physiological (i.e., falling leaves, closing stomata) or chemical and biochemical (i.e., production of insoluble precipitates, emission of reduced forms of pollutant (e.g.,  $\text{H}_2\text{S}$ ,  $\text{NH}_3$ ), enzymatic degradations or on-enzymatic antioxidant compounds) (Heck et al., 1988). When the plant confronts pollution stress, these additional defense mechanisms are activated and added to the existing ones, in an effort to strengthen the plant's tolerance to imposed pollution stress.

Damages caused by air pollution can be irreversible, such as cell death and leaf necrosis of the plant, which correspond to the so-called visible injury. In contrast, the injuries could be "invisible" whenever the defense system of the plants manages to limit the damage or the pollution impact is low. In those cases, either a physiological plant change is observed, such as decreases in size and yield (Guderian, 1985; Garrec, 2019), or changes in phenology (Honour et al., 2009).

Wang et al. (2003) suggested that the impact of abiotic stresses related to climate and air pollution, such as heat, drought, cold, salinity, and nutrient deficiencies or toxicity, can cause a reduction on worldwide agriculture average yields by >50% for most major crop plants. Imposition of stress conditions may also alter the emissions of biogenic volatile compounds from the vegetation (Guenther et al., 2012; Rinnan et al., 2014). Each emitted compound has a specific role in the plant tolerance and defense (Yuan et al., 2009). For instance, isoprene emissions from plants were found to attribute an antioxidant role in the presence of high  $\text{O}_3$  levels (Loreto et al., 2001) and to contribute to the thermotolerance of the plants (Hanson et al., 1999;

Velikova & Loreto, 2005). Furthermore, plant exposure to high  $O_3$  levels affects the above- and below-ground analogy of plant biomass, generally inhibiting the allocation to roots and decreasing C cycling and N fixation (Agathokleous et al., 2020). Tiiva et al. (2007) also found that exposure of subarctic fens to high UV-B radiation resulting from stratospheric  $O_3$  depletion was leading to isoprene emissions increase.

## 5 Symptomatology of Plants Affected by Air Pollution

Upon air pollution imposition, a variety of symptoms are induced and expressed by plants. Therefore, the symptomatology, which is the analysis of such symptoms, could serve as the basis of air quality biomonitoring methods by utilizing plants' responses to pollutants.

### 5.1 Symptoms

Depending on the plant species and the type of pollutant, the injury symptoms are different. Generally, air or soil pollution by pesticides have similar symptoms on vegetation, which are mainly expressed on foliage in the form of chlorosis, necrosis, burns, and twisting of leaves (Sharma et al., 2018). Reactive nitrogen species, in the form of nitrate ( $NO_3^-$ ) and ammonium ( $NH_4^+$ ), act as fertilizers promoting plant's growth. However, they can also have a negative impact on vegetation (and fauna) when they accumulate inducing ecosystems eutrophication, acidification, and mineral deficiencies. The latter affects biodiversity and leads to a decrease in resilience resistance to various stresses (European Commission, 2013; European Environment Agency, 2019; Garrec, 2019). In most cases, injury by  $NO_2$  is shown as burn at the edge of the conifer needle and chlorosis in the leaves of angiosperms. Leaves first exhibit water-soaked areas that at later stages become necrotic (Gheorghe & Ion, 2011). Injury by halogens is commonly visible on conifers by chlorosis, which later on is changing to red/brown discoloration and burns of the edges of the needles, eventually evolving to necrosis of the entire needle. Similar symptoms are common in the leaves of angiosperms (Gheorghe & Ion, 2011). In most cases, plants' injury by  $SO_2$  is initially seen by the appearance of water-soaked leaves, which later become necrotic, changing into brown spots (Gheorghe & Ion, 2011). Yellowing of conifer needles and decrease in tree vitality are the impacts of acid deposition on plants (Altshuller & Linthurst, 1984). This is mainly an indirect effect of acid atmospheric deposition on soil acidification, which leads to soil base cation depletion and, consequently, to needle magnesium deficiency evidenced by needle yellowing (Landmann & Bonneau, 1995). Acidity is mainly induced by  $HNO_3$  and  $H_2SO_4$  acids and releases soluble forms of metals into the environment, which may be in toxic forms. For instance, Cu toxicity is increased in acidic environments and affects primarily the plant roots leading to growth reduction and chlorosis of mature leaves

(Alva et al., 1995). Finally, Pb and Cd affect the biodiversity of soil fauna species and microorganisms and reduce plant growth (European Environment Agency, 2019).

Injury due to exposure to elevated concentrations of O<sub>3</sub> is commonly expressed by necrotic spots on the leaves of the plants that have irregular shape and are often tan, brown, or black colored. Some of the leaves change their color to bronze or red, which is usually a precursor sign to necrosis. Ozone is the most worrying pollutant currently affecting vegetation and ecosystems, since it is well established that it causes leaf necrosis and results in yield losses reaching 5–19% (Feng & Kobayashi, 2009). Ozone also has indirect effects on vegetation since it is a greenhouse gas linked to climate change (see the chapter by Mallet et al., 2022). Holland et al. (2006) estimated that ozone is responsible for 90% of the plants yield losses related to air pollution. However, the negative effects of ozone are very often masked by the positive effects on photosynthesis due to CO<sub>2</sub> increase in the atmosphere.

## 5.2 *Biotic and Abiotic Indicators and Biomonitoring of Air Quality*

Due to this significant role of O<sub>3</sub>, a number of indicators have been developed in order to describe the sensitivity of plants to O<sub>3</sub> in different natural or anthropogenic environments (forests, grasslands, field crops, etc.), depending on the climatic zones (Western and Central Europe, Mediterranean coast of Europe, and other). The most used indicator for plant's exposure to O<sub>3</sub> is AOT40, which is a measure of the accumulated daylight ozone concentrations in excess above a threshold of 80 µg m<sup>-3</sup> (40 ppbv), using only the daily O<sub>3</sub> levels per hour between 8:00 and 20:00 (CET) in the months of the growth season. This is also used for legislation purposes in European Union (EU Directive 2008/50/EC). Other O<sub>3</sub> metrics include the daylight average ozone concentrations during the growing season (M7 for 7 hours daylight period or M12 for 12 hours daylight period) or cumulative exposure indexes over the growing season with weights on hourly average O<sub>3</sub> concentrations that favor the higher hourly average concentrations, while retaining the mid and lower concentrations (Emberson et al., 2018).

Plants can also be used as indicators of metals air pollution. Riga-Karandinos and Saitanis (2004) suggested that trace metal concentration measurements in the leaves of Laurel (*Laurus nobilis* L.) could be used as indicators of urban traffic in Athens. Riga-Karandinos et al. (2006) have further found high concentrations of platinum (Pt) and Pb, known to be used in catalytic converters, together with other traffic metals (Pb, Cu, and Zn) at roadside topsoil in the greater Athens area where pollutants can penetrate the plants through their roots. Furthermore, Rodríguez Martín et al. (2018) suggested that metal content in tree rings could be used as a pollution registry.

Biomonitoring is using both the visible (by observing necroses) or invisible (by biochemical analyses) disturbances of the plants caused by air pollution to deduce

air pollutant levels (de Temmerman et al., 2004; Garrec & Van Haluwyn, 2002). The use of bioindicators might be complicated by the nonlinear response of ecosystems to air pollution and climate change. In addition, it requires an unambiguous relationship between the cause and the bioindicator symptom.

Cryptogams (lichens and bryophytes), which are important components of the Mediterranean vegetation, are often used as indicators of air pollution and climate change relative to a set of contaminants (Agnan et al., 2015; Gandois et al., 2014; Loppi et al., 1997). Due to their high sensitivity to environmental changes, they are often employed as early-warning indicators of such impacts in particular for N (Ochoa-Hueso et al., 2017). In addition, the potential utility of the N content in mosses as an indicator of total N deposition has been demonstrated by Munzi et al. (2012), and they have also been used as critical load indicators for nitrogen (Geiser et al., 2010). However, cryptogams in the Mediterranean are not effective biomarkers for changes in water availability induced by climate change because they are affected by several stress factors in similar ways (Pirintsos et al., 2011). Lichens have been efficiently used to identify local sources of atmospheric contamination in urban or highly contaminated industrial sites of the Mediterranean countries (Llop et al., 2017; Paoli et al., 2006; Ratier et al., 2018). More rarely used in distant areas, lichen and mosses were successfully used as metal biomonitors in various environmental situations in France and over the last century. This allowed identification of present-day and past sources of contaminants and dust, and their variation in time and space (Agnan et al., 2014, 2015), revealing a regional atmospheric signal, including both soils derived and industrially influenced atmospheric deposition. Moreover, in three different mountainous forest sites in France, lichens and mosses contents in trace metals, of which Rare Earth Elements, were compared to various compartments of the forest ecosystem (bulk deposition and throughfall, soil, and bedrock) (Gandois et al., 2014). The different accumulation of trace metals as monitored by lichens and mosses indicated a different influence of forest ecosystems. Mosses were representative of local throughfall content, since they were enriched in elements from the accumulation of dry deposition inside the canopy, either due to leaching (Mn), direct uptake (Ni), or dry deposition dissolution (Pb, Cu, Cs) contrary to lichens growing on tree barks where transfer was observed only for major elements. Agnan et al. (2017) has improved the bioindication scale using lichens collected in eight distinct French and Swiss forest areas. This also enabled the evaluation of the metal resistance or sensitivity of lichens. Furthermore, the index of atmospheric purity and the lichen diversity value were calculated based on the estimation of various ecological variables (including lichen diversity and abundance) and average ecological features for each site and variable (light, temperature, humidity, substrate pH, and eutrophication) that corresponded to lichen communities. Furthermore, tobacco plant varieties have been used as O<sub>3</sub> bioindicators in Greece (Saitanis, 2008; Saitanis et al., 2003) and have shown high injuries in all studied regions indicating high phytotoxicity by O<sub>3</sub> levels.

### 5.3 *Eutrophication, Acidification, Critical Loads*

Eutrophication refers to ecosystem conditions with an excess in nutrients (often referring to N compounds) resulting from increased input rates. Nitrate and ammonium inputs through atmospheric deposition are of particular interest in the present section. In concern to air pollution, eutrophication is related to the ability of an ecosystem to optimally use the reactive nitrogen atmospheric deposition fluxes for its growth. Eutrophication happens when the ecosystem is saturated in N, and thus additional N input is not leading to further growth optimization but instead is leading to N and biodiversity losses (Bobbink et al., 2010; Schmitz et al., 2019). Acidification is related to eutrophication and refers to the lowering of the soil pH due to deposition of acidic compounds, such as  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  that are produced from the oxidation of  $\text{NO}_x$  and  $\text{SO}_x$  emissions. Under the Convention of Long-Range Transboundary Air Pollution (LRTAP) within the United Nations, the critical loads of S and N have been used as indicators for ecosystem sensitivity to acidification and eutrophication (Reinds et al., 2008). Thus, critical N load levels are the threshold values above which damage occurs to the ecosystem (Hettelingh et al., 2001). These thresholds were initially determined using mass balance steady-state models or from empirical models. The latter are experimentally derived models studying different types of vegetation and are specific to habitat classes. Ammonia and  $\text{NO}_x$  critical levels are based on the response of vegetation types like lichens and bryophytes (Ochoa-Hueso et al., 2017), often based on very little information. Thus, for European-Mediterranean habitats, empirical critical N loads have been proposed to vary between 3 and 25  $\text{Kg N ha}^{-1} \text{ yr}^{-1}$  for four different ecosystems with the highest values corresponding to xeric grasslands and the lowest ones to the *Pinus* woodlands (Bobbink & Hettelingh, 2011).

Recently, it was stated that while steady-state models are compatible with the critical loads concept (CLRTAP, 2015), they are not suitable for simulating temporal air pollutant changes, particularly for nitrogen. Therefore, dynamic biogeochemical-ecological coupled models have been developed (de Vries et al., 2010; Rowe et al., 2015; Wallman et al., 2005), based on the impact of atmospheric deposition of S and N on soil functioning and in cascade to forest underground vegetation, using the loss of biodiversity as an indicator of change (Belyazid et al., 2011; Probst et al., 2015). However, the adequacy of critical loads as indicators of N deposition effects has been recently questioned by Payne et al. (2019), who proposed that the cumulative deposition over a 30-year window should be considered as the metric for the ecological damage caused by nitrogen deposition. This suggestion was further supported by the observed slow recovery of ecosystems from N deposition effects (Schmitz et al., 2019). Similarly, although N deposition has decreased in several regions over Europe due to declined  $\text{NO}_x$  and  $\text{NH}_3$  emissions (>50% and < 30%, respectively, between 1990 and 2015), the required timescale to observe the effect of these changes on the ecosystems is uncertain. Dirnböck et al. (2018) investigated 23 European forest research sites, including sites in Italy and the Balkans, and they concluded that reduction of  $\text{NO}_x$  and  $\text{NH}_3$  emissions have to be

significantly higher than projected under current legislation scenarios to allow recovery from chronically high N deposition. Thus, current reduction in N deposition is expected to lead only to limited species recovery in European forests.

## 6 Interactions and Covariates Between Plants, Air Pollutants, and Environment

Air pollution and climate have concurrent impacts on vegetation. Temperature increases accelerate the dryness of vegetated soils, which retain less water for evapotranspiration, and, thus, cannot effectively contribute to the cooling of the atmosphere. In a warmer and dryer environment, plants close their stomata in order to reduce their water losses, thus minimizing the entrance of O<sub>3</sub> within the plant, therefore reducing O<sub>3</sub> uptake and subsequent reactive oxygen species formation. Gao et al. (2017) suggested that accounting for water stress effects on stomatal O<sub>3</sub> flux can better explain biomass losses on poplar (*Populus deltoides* Marsh) than without consideration of such effects. Lin et al. (2020) pointed out the significant O<sub>3</sub>/vegetation/climate interactions since reduced O<sub>3</sub> absorption or uptake by vegetation is increasing surface O<sub>3</sub> concentrations, leading to further atmosphere warming through escalation of greenhouse effect by O<sub>3</sub>. They further discussed the importance of soil moisture effect on O<sub>3</sub> reduction by stomatal uptake and its consequent increase for the overall O<sub>3</sub> dry deposition. These effects are currently not considered in O<sub>3</sub> deposition modeling although they could help to improve our understanding of the observed O<sub>3</sub> concentration trends. Lin et al. (2020) have used measurements of O<sub>3</sub> fluxes by eddy correlation and derived O<sub>3</sub> deposition velocities over an oak forest in Italy, and over a spruce-dominated forest in Denmark. These observations were performed for two different study periods: 1 year characterized by heat wave and drought and a second year with normal precipitation events. They reported significant decreases in O<sub>3</sub> deposition velocity during the year characterized by heat waves and drought periods. More specifically, in the Mediterranean study site, a 70% reduction in O<sub>3</sub> deposition velocity was reported and was attributed to plants' stomatal response to the reduced soil moisture, suggesting that vegetation response is expected to worsen peak O<sub>3</sub> episodes during mega-droughts periods. However, multiple stresses on vegetation do not result in additive effects since, for instance, the signalling pathways of biotic and abiotic stresses can act antagonistically as reported by Atkinson and Urwin (2012). Therefore, understanding the mechanisms of the interactions of the responses to various stress factors at a molecular level is fundamental for future development of stress-tolerant crop plants (Atkinson & Urwin, 2012).

Ainsworth (2008) meta-analysis of vegetation response to combined increases in temperature, CO<sub>2</sub>, and O<sub>3</sub> showed that high temperature damage negated any yield benefits resulting from elevated CO<sub>2</sub>. A large number of studies have been conducted in major food crops (potato, barley, wheat, rice, bean and soybean) to

investigate concurrent effects of drought and ozone on vegetation (see Feng and Kobayashi (2009) for a comprehensive review). Such studies have exhibited that the positive impact of O<sub>3</sub> limitation by stomata closing was often outweighed by the damages on yield due to drought stress (Fangmeier et al., 1994). High temperatures induce faster maturation and hence a shorter grain fill period, reducing the overall yield (Erda et al., 2005), and can induce floret sterility in cereals such as rice (Matsui et al., 2014), wheat, and maize (Craufurd & Wheeler, 2009; Wheeler et al., 1996). However, physiological responses differ among crops (Eyshi Rezaei et al., 2015). Yield losses varied from 5.3% for potato to 19% for beans and soya beans when exposed to O<sub>3</sub> concentrations between 30 and 50 ppbv compared to 26 ppbv or less (Feng & Kobayashi, 2009). Avnery et al. (2011) evaluated crop losses reaching up to 15% for the year 2000 due to O<sub>3</sub> exposure, corresponding to an annual loss of 79–121 million metric tons of global crop yields or 11–18 billion dollars annually, while Mills et al. (2018) estimated that exposure to O<sub>3</sub> led to wheat grain losses to cost 24.2 billion dollars annually for the period 2010–2012.

In addition to O<sub>3</sub>, climate is affecting other pivotal air pollutants (such as SO<sub>2</sub>, N reactive species, and aerosols), due to their temperature-dependent photochemical production or depletion and their deposition dependence on precipitation and wind patterns. In particular, atmospheric N deposition due to the semi-volatile character of NH<sub>4</sub>NO<sub>3</sub> is strongly dependent on relative humidity and temperature conditions (Fowler et al., 2009; Nenes et al., 2021). Thus, atmospheric deposition of nitrogen is affected by climatic changes and will impact vegetation habitats (Dirnböck et al., 2003). Dynamic biogeochemical-ecological chain models for critical loads have thus tested these covariant effects. They were able to detect the joined influence of climate and nitrogen deposition on biodiversity loss, following scenarios of current legislation or maximum feasible reduction of N emissions or/and temperature increase (Gaudio et al., 2015; Rizzetto et al., 2016).

## **7 Impacts of Air Pollutants on Terrestrial Vegetation of the Mediterranean Region**

The natural and seminatural ecosystems in the Mediterranean Basin have much higher plant biodiversity (hosting 4.3% of the global endemic plants) and biologically relevant heterogeneity in space and time compared to those in temperate and boreal areas of Europe (Myers et al., 2000; Ochoa-Hueso et al., 2017). The Mediterranean climate, characterized by drought summer periods and mild winter temperatures, plays a critical role in the behavior of plants, allowing their growing season to be extended over the whole course of the calendar year. Therefore, it has been suggested that the entire ecosystem exposure to pollutants should be calculated based on an annual basis, while the actual growing season period is more suitable for determining single species exposure to pollutants (Schenone, 1993). These particularities support a separate discussion of air pollution impact on Mediterranean vegetation. This separation is further supported by the existence of multiple plant

adaptation mechanisms to the climatic conditions of the Mediterranean Basin, where heat waves and droughts are occurring frequently. Such mechanisms include foliage loss during the water stress periods; physiological responses such as closing of the stomata to limit water losses; changes in the metabolic pathways such as instead of  $C_3$  photosynthesis utilizing the Crassulacean acid metabolism (CAM), which is a typical ecophysiological adaptation of plants to arid conditions (Grams & Thiel, 2002); and changes in the depth and distribution pattern of the root systems. All the above mechanisms develop plant adaptation and ensure their survival under stressful climatic extremes (Schenone, 1993). Furthermore, due to natural evolution and adaptation to their environment, the Mediterranean forests have developed cross-tolerance to the environmental conditions dominating the region (Paoletti, 2006).

### ***7.1 Vegetation Exposure to Ground Level Ozone***

Due to the sunny and warm weather conditions of the Mediterranean region, there is a potential for high  $O_3$  deposition rates throughout the year (Kanakidou et al., 2011). Consequently, higher  $O_3$  stomatal uptake may take place during winter than summer months, in spite of the lower winter ozone concentrations (Cieslik, 2009; Gerasopoulos et al., 2006). In addition, plants emit different compositions of VOC, which are oxidized by ozone reducing the oxidative stress and thereby protecting the plants (Yuan et al., 2009). However, these reactions are also reducing the distance to which VOC can be transported to enable plant communication and pollinator attraction. Ozone pollution can also alter the timing of flowering, the number and biomass of flowers, and weed development. The susceptibility of plants to  $O_3$  levels depends on genotype and varies among plant functional groups (Agathokleous et al., 2020). Therefore, exposure to high  $O_3$  levels affects plant community composition and also threatens terrestrial biodiversity at various trophic levels. Agathokleous et al. (2020) using climate scenarios for 2100 warned that the Mediterranean Basin, one of the higher endemic richness regions globally, is among the most threatened regions by high  $O_3$  levels. Gerosa et al. (2005) found that in an Italian oak forest, which represented a typical Mediterranean ecosystem, the average  $O_3$  stomatal uptake was less than half of the total  $O_3$  deposition flux and that non-stomatal deposition was increasing with leaf wetness and air humidity during the fall season. The increased non-stomatal fluxes of  $O_3$  observed in Mediterranean forests (Gerosa et al., 2005, 2009) and their diurnal and seasonal variations were different in many aspects when compared to those observed in the northern European forests (Fowler et al., 2009). Furthermore, measurements above oak forests in central Italy (Gerosa et al., 2005, 2009; Cieslik, 2009) and southeastern France (Michou et al., 2005) showed that dry and hot conditions can significantly affect the diurnal variation of  $O_3$  deposition velocity. The Mediterranean vegetation is more tolerant to high  $O_3$  levels than the mesophillic broad-leaf trees (Paoletti, 2006) because of its better antioxidant defense (Nali et al., 2004), although biomass losses and changes



in biomass distribution in the various plant compartments due to exposure to high O<sub>3</sub> cannot be excluded. However, deciduous broad-leaf trees are less tolerant to oxidative stress compared to evergreen broad-leaf trees due to their physiology with higher stomatal conductance and thinner leaves (Calatayud et al., 2010). Indeed, Calatayud et al. (2007) investigated the sensitivity to O<sub>3</sub> of four maple trees (*A. campestre*, *Acer opalus subsp. granatense*, *A. monspessulanum*, and *A. pseudoplatanus*), which are present in humid parts of the Mediterranean. They found differences (e.g., in CO<sub>2</sub> assimilation, stomatal conductance, transpiration rate, and water use efficiency), which may be partly related to higher stomatal conductance. On the other hand, Li et al. (2016) examining the O<sub>3</sub> sensitivity of 29 deciduous and evergreen species in China detected correlation to both low leaf mass per area and low leaf area-based antioxidant levels, but not to stomatal conductance. Moreover, Manes et al. (2007) evidenced that O<sub>3</sub> uptake varies within a Holm oak (*Quercus ilex* L.) canopy and attributed this fluctuation to the influence of microclimatic conditions on plants' physiological activity related to stomatal opening, which in turn is affected by internal and external effectors (e.g., plant hormones, water availability, hydraulic conductance). Sanz and Millan (2000) suggested a complex interaction between high radiation, drought, and O<sub>3</sub> response in Mediterranean tree species such as Aleppo pine (*Pinus halepensis* Mill.). Tree species sensitivity to O<sub>3</sub> as revealed by functional leaf traits has to be considered (Calatayud et al., 2011). Saitanis et al. (2003) observed stomatal conductance in leaves of tobacco, grape wines, and needles of Aleppo pine at various locations in Greece and found them peaking in midday hours when O<sub>3</sub> was high. They also observed injuries due to O<sub>3</sub> air pollution which were more severe at the high-altitude location. Fumagalli et al. (2001) performed studies with open-top chambers in 24 agricultural and horticultural crops grown in commercial fields in the Mediterranean. They reported that ambient O<sub>3</sub> resulted in 17–39% yield loss in crops such as wheat, bean, watermelon, and tomato. Nitrogen fixing legumes were also found to be less tolerant to O<sub>3</sub> exposure compared to grasses, which could eventually reduce their economic value (Sanz et al., 2007).

## 7.2 Vegetation Exposure to Nitrogen Oxides

Dry deposition onto the ecosystems can contribute up to 58–67% of the total N deposition in the Mediterranean Basin (Rodà et al., 2002). Due to the difficulty of measuring the actual dry deposition, this flux is commonly inferred from observations of atmospheric concentrations from representative stations (Sanz et al., 2002) coupled with deposition modeling (García-Gómez et al., 2018). Nitrogen is deposited in the forms of reduced or oxidized, inorganic, or organic N. The contribution of organic N was found to vary between 34% and 56% of total deposition (Im et al., 2013; Izquieta-Rojano et al., 2016; Kanakidou et al., 2020; Mace et al., 2003; Violaki et al., 2010) and can be a substantial contributor to N critical loads in

Mediterranean agricultural areas. Several studies have been performed in the Mediterranean to investigate the impact of N deposition on individual plants, lichens, and soil properties as reviewed by Ochoa-Hueso et al. (2017). Few studies, such as NitroMed (Ochoa-Hueso & Manrique, 2011), investigated the integrated responses at the ecosystem level using statistical methods. Their results indicate that N availability in soils is increased by N deposition, but concurrently, soil becomes more acidic, which affects the microbial community by reducing the fungi to bacteria ratio and impact the overall enzymatic activity (Ochoa-Hueso et al., 2017). Changes in the stoichiometry of the plants (higher N/P ratio of the leaves) (Sardans et al., 2016) as well as changes in biomass partitioning and allometric ratios (Cambui et al., 2011) have been observed as a response to the increased N deposition. Furthermore, the effect of concurrent O<sub>3</sub> and N deposition in the Mediterranean can change composition and reproductive structure of the annual pastures (Gonzalez-Fernandez et al., 2013).

### 7.3 *Accumulation of Toxic Metal Air Pollutants on Vegetation and Soil*

Only limited number of studies have investigated metals in agricultural soils in the Mediterranean region (Stanners & Bourdeau, 1995) and mainly at regional level in some countries such as Greece (Stalikas et al., 1997), Italy (Abollino et al., 2002; Facchinelli et al., 2001), and Spain (Andreu & Gimeno-García, 1996; Boluda et al., 1988). Riga-Karandinos et al. (2006) measurements of trace metals at roadside top-soil in the greater Athens area indicated the penetration of pollution metals into the soils, from where they can be potentially transferred to the plants (Gandois et al., 2010). Evergreen shrubs were tested for their capacity to accumulate a large set of metals on the surface of their current season leaves in a Mediterranean environment. The results showed a common temporal pattern with elements increasing from early summer to midsummer and then decreasing to early autumn. Deposition was also linked to meteorological parameters. Rain decreased the accumulation of metals on leaves, while increasing wind speed was enhancing the presence of elements on leaves (Mori et al., 2015).

Furthermore, Rodríguez Martín et al. (2018) have found significant enrichments of metals in Aleppo pine wood compared to the natural environment. More specifically, they measured 2.5 times higher Pb in tree wood close to burning power plants and 25 times higher Cd near mining areas compared to natural areas. Based on measurements of aerosols deposited on the leaves of *Platanus acerifolia* tree from 23 European cities over 20 countries, Baldacchini et al. (2017) concluded that this tree could be used to monitor aerosols, using the morphology and elemental composition of leaf-deposited particles, together with the leaf magnetic content, i.e., in ferromagnetic minerals coming from dust deposited on the leaves (Leng et al., 2018).

#### 7.4 *Plant Nutrient Uptake Limitations Induced by Air Pollution*

Ochoa-Hueso et al. (2011) suggested that the effect of N deposition inputs and the susceptibility of the Mediterranean ecosystems to exotic plant invasion may be controlled by P availability. In their study, Herut et al. (1999) indicated that atmospheric inputs of bioavailable N and P represent an imbalanced contribution to the new carbon production and reinforce the unusual N:P ratios ( $\sim 27$ ) and possible P limitation in the southeast Mediterranean Sea. Ochoa-Hueso and Manrique (2013) and Ochoa-Hueso et al. (2017) reported a shift from N to P limitation in the terricolous moss *Tortella squarrosa* in the Iberian Peninsula due to increased N deposition. In addition, the epiphytic lichen communities in Portugal and Spain have shifted from oligotrophic-dominated to nitrophytic-dominated species (Aguillaume, 2016; Pinho et al., 2008). The impact of anthropogenic N emissions on these shifts is supported by the  $^{15}\text{N}$  isotopic signature of the N composition of mosses, which is shifted to more positive  $\delta^{15}\text{N}$  values, while the agricultural activities are reducing  $\delta^{15}\text{N}$  (e.g., Delgado et al., 2013). Human-induced imbalance in N and P deposition has been also reported for other regions and ecosystems, like the Chinese forests, leading to P limitation of the forest ecosystem (Du et al., 2016).

### 8 Conclusions and Perspectives

Air pollution has significant direct (after uptake by the plant) and indirect (through changes in climate and diffuse solar radiation) effects on terrestrial vegetation that lead to visible and invisible vegetation damages. These effects, mostly from exposure to high  $\text{O}_3$ , have been observed to reduce crop yields, thus affecting agriculture effectiveness and its ability to feed the Earth's population. Plant phenology, functional type, and the seasonality of  $\text{O}_3$  have to be taken into account when evaluating the impact of air pollution on the Mediterranean vegetation. Understanding of the interaction between the various stress factors, in particular climate (temperature, droughts, and other extremes) and air pollution ( $\text{O}_3$ , aerosol,  $\text{CO}_2$ ) and how these factors once combined affect vegetation, is critical for the definition of actions in order to preserve biodiversity and sustain agricultural production.

Atmospheric deposition of pollutants provides nutrients and toxic compounds or their products to the vegetation via either direct uptake by the foliage or by indirect uptake through plants' roots. Accumulation of pollutants in the environment has long-term effects on vegetation and soil; thus, it demands long recovery periods after the accumulation has stopped. This is particularly true for N deposition, which leads to N accumulation more than the optimal ecosystem levels in the soils, implies soil acidification, leads to biodiversity reduction, and changes the composition of phytocommunities. Indeed, changes in nutrient stoichiometry have been observed in plants exposed to excessively high N levels in the soil resulting from deposition

of anthropogenic reactive nitrogen. As in other locations, human-induced P limitation has been observed in Europe and the Mediterranean due to anthropogenic N deposition. Such alterations of the ecosystem's composition must be carefully evaluated, particularly under conditions of climate change that are potentially increasing the occurrence of severe drought events. Indeed, interactive effects between climate change and N deposition on vegetation have been shown and predicted.

Finally, plants' response to air pollution is expressed by symptoms that vary depending on the plant species and variety and the type of pollutant. Thus, plant disturbances caused by air pollution can be utilized to deduce air pollution levels, through the so-called biomonitoring procedure. However, since the use of bioindicators requires an unambiguous relationship between the cause and the plant response, this approach becomes complicated by the nonlinear response of ecosystems to air pollution and climate change. Despite this complexity, the power of biomonitoring to reconstruct past pollution influence, by using, for example, well-preserved herbariums compared with present-day situations, can contribute to the effort to obtain a spatial view of the impact of atmospheric pollution around the Mediterranean regions.

Further research is needed in all abovementioned fields. Observatories for long-term monitoring of all compartments of the environment and key drivers are essential to understand and evaluate the impact of air pollution on Earth's vegetation. This need is specifically urgent for the Mediterranean region, due to its susceptibility to various stresses induced either by climate change or air pollution or by other expressions of human activities footprint on the environment.

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