

EMISSION AND ROLE OF BIOGENIC VOLATILE ORGANIC COMPOUNDS IN BIOSPHERE

Aansa Rukya Saleem^{*†},
Tariq Mahmood^{*}, Waqar-un-Nisa^{*}
and Madiha Aslam^{*}

ABSTRACT

Plants are an essential part of the biosphere. Under the influence of climate change, plants respond in multiple ways within the ecosystem. One such way is the release of assimilated carbon back to the atmosphere in form of biogenic volatile organic compounds (BVOCs), which are produced by plants and are involved in plant growth, reproduction, defense and other interactions. These compounds are emitted from vegetation into the atmosphere under different environmental situations. Plants produce an extensive range of BVOCs, including isoprenoids, sesquiterpenes, aldehydes, alcohols and terpenes in different tissues above and below the ground. The emission rates vary with various environmental conditions and the plant growth stage in its life span. BVOCs are released under biotic and abiotic stress changes, like heat, drought, land-use changes, higher atmospheric CO₂ concentrations, increased UV radiation and insect or disease attack. Plants emit BVOCs in atmosphere in order to avoid stress, and adapt to harsh circumstances. These compounds also have a significant role in plant-plant interaction, communication and competition.

BVOCs have the ability to alter atmospheric chemistry; they readily react with atmospheric pollutant gases under high temperature and form tropospheric ozone, which is a potent air pollutant for global warming and disease occurrence. BVOCs may be a cause of photochemical smog and increase the stay of other GHGs in the atmosphere. Therefore, further study is required to assess the behavior of BVOCs in the biosphere as well as the atmosphere.

Keywords: BVOCs, Abiotic, Biotic, Atmosphere and Stress

1. INTRODUCTION

The planet Earth has an integrated and self-sustaining system that is composed of multiple biotic and abiotic components. The Earth system comprises of various sub regions, i.e., biosphere, lithosphere, hydrosphere and atmosphere, in which all components interact and are able to perform chemical, physical and biological reactions in the system. Biosphere is the main region on earth with a range of ecosystems with all bio/geo/chemical cycles [1-2]. It is also accredited that biological processes on land system widely influence the atmospheric system and associated climate,

because it exchanges many gases among the land and gaseous spheres, although only CO₂ attains most attention though. Similarly, carbon-related living processes like immobilization and mineralization of carbon capture more consideration [3-5] because of its momentous role in climate system. Beside natural processes, many anthropogenic activities boost up the carbon concentration in atmosphere that induce global warming and climatic shift [3].

Accordingly, the 21st century climate models predicted that overall mean temperature of the globe will rise 1-6°C [6]. This may result in continuous increase CO₂ concentrations in the atmosphere. Furthermore, uplift in temperatures alters the weather pattern, precipitation distribution and rainfall intensity, which cause water scarce conditions, such as drought. Drought occurs when abrupt rain fall patterns bring water scarce situation and high temperatures cause soil water loss through transpiration and evaporation [7].

These all natural and anthropogenic changes exert pressure on ecosystem values that changes altering plant-species distribution and characteristics. Plants being immobile cannot evade environmental stresses in the same way as mobile organisms can [8]. These weather shifts directly affect plant growth, biochemical activity and the length of the active growing season [9], thus plants exhibit varied responses to environmental stresses. Plants adopt various mechanisms to work with increased CO₂ concentration, high temperature and restricted water supply by maximizing water uptake and reducing water loss from the above ground vegetative body. Plant body modifies its biochemical processes to become more tolerant. In such circumstances, plants release certain chemical compounds in atmosphere to defeat environmental stresses. These are known as biogenic volatile organic compounds [2, 10, 11].

2. BIOGENIC VOLATILE ORGANIC COMPOUNDS (BVOCs)

Biogenic volatile organic compounds (BVOCs) constituted one of nature's many biodiversity treasures. These biogenic compounds are released from natural sources at an estimated rate of 1.1-1.5 Pg C per year globally [16-23], which is greater than anthropogenic emissions [24] and their concentration varies from several ppt (parts per trillion) to ppb (parts per billion), and reactivity span from minutes to hours

^{*} Department of Environmental Sciences, PMAS Arid Agriculture University, Rawalpindi, Pakistan. [†] Email: rukayya583@gmail.com

Emission and Role of Biogenic Volatile Organic Compounds in Biosphere

Table-1: Major BVOCs Categories Emitted from Plants

BVOCs group	Average Global Emission (10^{12} gC)	Atmospheric reactivity lifetime (hour)	Atmosphere concentration	Example
Isoprene	175–503	4.8	pmol mol ⁻¹ to several nmol mol ⁻¹	Limonene, 2-Methyl-3-buten-2-ol, hexenal, acetaldehyde Methanol, ethanol, formic acid, acetic acid, acetone
Monoterpenes	127–480	2.4 – 4.8	pmol mol ⁻¹ to several nmol mol ⁻¹	
Other reactive BVOCs	~ 260	<24.0	to several nmol mol ⁻¹ 1–3 nmol mol ⁻¹	
Other reactive BVOCs	~ 260	>24.0	2–30 nmol mol ⁻¹	
Ethylene	1 – 20	45.6	pmol mol ⁻¹ to several nmol mol ⁻¹	

Source: [2, 3, 25]

[15-25]. In harsh environment, plants produce and emit a large number of biogenic volatile organic compounds to reduce stress and to ensure survival for themselves [12-14]. BVOCs cover a wide range of organic species (Table-1), including isoprene, terpenes, hemiterpenes, monoterpenes, sesquiterpenes, isoprenoids and other oxygenated compounds [13,15,16]. Also a variety of low-molecular weight ($C < 5$) BVOCs are released by plants, for example methanol, ethylene, formaldehyde, ethanol, and acetaldehyde [17,19]. So far, almost 1,700 substances have been found that release from various plant body parts [20]. Pluralities of biogenic compounds are lipophilic and, with ample vapour pressure, are capable of entering into the atmosphere significant concentrations. Plants in unfavorable severe conditions release photosynthetic assimilated carbon back to the environment in the form of BVOCs. In normal circumstances, plants give out upto 2% of their assimilated carbon from leaves in gas exchange [21]. For dealing with multiple stresses, increase in assimilated carbon release may be upto 10 to even 67% in BVOCs production, while the concentrations vary throughout the whole life cycle of a plant [22].

In BVOCs group Isoprenoid (Isoprene and monoterpenes) is considered dominant member emitted by plants [16, 26]. Isoprene is a 2-methyl-1,3-butadiene, which is mostly produced by few herbaceous and several woody plant species [25]. Isoprene (C_5H_8) and monoterpenes ($C_{10}H_{16}$) are major emitted compounds from vegetation [15,27]. Isoprene

production and emission by plants were first described by Sanadze [28] and its effect on the physico chemistry of the atmosphere was first described by Went [29]. Isoprene is quantitatively the most important of the non-methane BVOCs (NMBVOCs), with an annual emission of about 400–600 TgC; about 90% of this is emitted by terrestrial plants. The main environmental controls on isoprene emission are light, temperature and atmospheric CO_2 concentration [30].

3. REGULATION OF BVOCs EMISSION

A broad range of BVOCs are produced of the above in several tissues in above- and below-ground parts of plants. Nearly all parts from vegetative body, as well as flowers and roots [11] emit these compounds in all life stages but their concentrations vary from more obvious at specific developmental stages to their peak on maturation [1,31-33]. Plant leaves have the maximum emission rates throughout a life cycle. Woody plants are more capable of releasing vast mixture of terpenoids, including isoprene, monoterpenes, sesquiterpenes along few diterpenes [34].

BVOCs do not store in plant body, these directly release in atmosphere as produced [12], while in some plants, BVOCs, after production, are accumulated in leaves and stem compartment in high concentrations that may be able to diffuse out of the plant body under biotic and abiotic stress conditions. Thus emission concentration generally relies on existence of leaves and storage compartments [35]. A

few plant species, like Pinus, Abies, Eucalyptus and other members in *Rutaceae* family, accumulate Terpenes in specific storage sections (for example, resin ducts, cavities, oil glands or glandular trichomes). While many others, like some oak species (*Quercus spp.*) are not able to store BVOCs [37]. Isoprene is a major compound emitted from vegetation but it does not get accumulated in plant body, consequently isoprene is not stored in the leaf. Isoprene emission rate thus accurately reflects its instantaneous rate of synthesis [36]. In addition the emission rates of BVOCs are determined by their synthesis rates and by their physicochemical characteristics, including solubility, volatility and diffusivity. However, BVOCs release is attributable to enzymatic activities in both optimum and stress environment [1,38,39].

Emissions of BVOCs are biosynthetically regulated by both environmental and genetic factors [19, 40]. Environmental stresses may induce change in BVOCs composition, concentration, either by inducing or quenching the emissions [11]. Soil water availability, carbon dioxide (CO₂) concentration, light, temperature and other environmental stresses may therefore affect the production and emission of some BVOCs by altering plant physiology, the substrate availability and limiting the enzyme activity. Other BVOCs are produced after injury and feeding by herbivores or after certain environmental stresses. Biotic and abiotic stresses induce BVOC production from leaves, such as terpenes, methyl jasmonate (MeJA) and methyl salicylate (MeSA), and their composition and quantity rely on magnitude and type of stress [1,41, 42]

4. EFFECTS OF ABIOTIC STRESSES

Abiotic stresses prompt and influence BVOC release for plant protection, defense and directly signal the environmental constraint [11]. General stress conditions tend to prohibit photosynthesis by minimizing the CO₂ uptake and diffusion to the fixation site inside leaves. Stress conditions alter biochemical reactions, photosynthetic cycles, and primary or secondary metabolites formation in multiple ways.

Drought: The drought phenomenon is often the natural outcome of heat waves, summer climate, low rain fall and high transpiration rate [11]. Anomalous rain fall pattern and intensity depict more drastic climatic change [43]. Water conservation to evade drought condition in plant body is managed by stomatal closure, reduction in leaf area, root extension for increased water uptake, reduced plant height,

controlled transpiration and limited photosynthesis [44-46]. Thus change in abiotic stresses directly influences stomatal conductance and triggers various biochemical and gas diffusion constraints for photosynthetic pathway and production a range of BVOCs [11]. Drought impinges the vegetation in many areas by altering biochemical processes. Modest drought may abate or augment the isoprene and monoterpene emissions. Whereas, prolonged and stern drought conditions result in partial or full inhibition of photosynthetic processes and, eventually, in prominent decline in BVOCs emissions [40]. The diverse behavior in BVOCs release to mild drought may be attributable to leaf physiology; BVOCs biochemistry and plant species. Although, the abatement in photosynthesis and stomatal conductance are anticipated to pose negative effect on BVOCs release by shifting carbon supply into the non-mevalonate pathway. Eventually, volatile terpenes' emission is resistant to stress but it is also known that the emission is often elicited by stress occurrence. Generally, drought situation provokes isoprene synthesis and release [48]. However, it does not reduce with increase in drought [11], either it seems to be unaffected by mild stress for limited time until the stress becomes severe, which almost completely inhibits photosynthesis [48, 49, 50]. On reversing stress conditions opposite results have been observed in BVOCs release pattern.

Temperature: The BVOCs liberation rate is partly determined by leaf temperature. However, leaves emission concentration is not considerably sensitive to leaf physiological attributes, yet it is affected by physiochemical limitations owing to temperature, stomatal conductance, leaf structure and enzymatic chemistry [51]. Temperature is an instantaneous and potent factor which causes enzyme degradation that is involved in BVOCs synthesis. High temperatures create physiological changes in leaf that influence BVOCs emission pattern [12, 16]. Thus, temperature is another influencing abiotic factor that can boost up BVOCs to higher emission level. BVOCs release strongly relies on temperature, since increased temperatures catalyze chemical reaction, cellular diffusion and also raise vapour pressure of BVOCs [52-53]. The balance among gaseous and aqueous chemical phases is regulated by temperature and hence it is assumed that more BVOCs enter the gas phase and are the emitted at high temperatures [11]. This was depicted by Penuelas & Llusia [12] that 2-3°C rise in mean global temperature can surge global BVOCs release by 25-45%. Isoprene synthesis has shown sensitivity to temperature [53] and this

Emission and Role of Biogenic Volatile Organic Compounds in Biosphere

response remains similar to almost all species, though basal emission varies with leaf age of specific species because young leaves do not emit isoprene [54]. It was indicated in a case study from the Great Britain that a unit elevation in temperature increase isoprene emissions by 14% in summers and 3°C shift could raise emission by 50%. Isoprene emission shows decrease in concentration with rise in temperature. Generally high temperatures (more than 40°C), show steep drop in concentration of isoprene emissions. It is shown that high temperature promotes photorespiration and stimulate biochemical restriction of photosynthesis. However, physiological factors (stomatal and mesophyll conductance and resistance to CO₂) influence the leaf carbon fixation and effusion (photorespiration, respiration, BVOCs) process [55-56]. Beside this, the plant species that do not store BVOCs into specific storing pools in leaf mesophyll, easily release BVOCs against the concentration gradient along the leaf. Here the only limitation is the stomatal conductance for gas exchange. Rise in mean temperatures often influences the leaf stomatal behavior.

Elevated CO₂: Present and anticipated climatic changes are responsible for raising CO₂ concentration that further brings a rise in temperature, water scarcity and drastic meteorological events [6, 58]. From pre-industrial time to the present, the atmospheric CO₂ concentration has raised nearly 35%. It is projected that this increase will double within the 21st century [6]. CO₂ is considered a basic reason of global warming. However, for short time periods the mounting CO₂ concentration can possibly improve plant vegetative growth and photosynthetic efficiency. The primary factor of better growth is the increased substrate availability for Rubisco in photo biochemical processes, consequently bringing enhancement in photosynthesis [11]. At higher concentrations plants release their assimilated carbon in the form of BVOCs, however elevated CO₂ level may cause rise [59], decline [60] or may have no prominent effects on [61] BVOC production and emission at the leaf. Several aspects like plant species, age, experimental duration and CO₂ concentration, may cause shift in the results. Generally, CO₂ is one important factor that uncouples terpenoid formation and release during photosynthesis [11]. It, thus, assists the production and emission of BVOCs.

Atmospheric CO₂ concentration shows influence on major isoprene emissions. A high level of CO₂ induces the photosynthesis process, beside this, isoprene

emission is restricted at elevated CO₂ concentration and emission increases at low CO₂ level. Studies on various plant species have revealed the limited isoprene biosynthesis under higher than ambient CO₂ concentrations [11,61]. Regardless of the lower isoprene emission at higher CO₂ level, on balance it may be offset because high CO₂ increases plant biomass and leaf area, which ultimately results in release of more or equal isoprene in atmosphere

5. EFFECT OF BIOTIC STRESSES

Alongwith all abiotic stress factors, various biotic factors induce BVOCs production in plants. Competition among plants of same and different species for biotic resources, like light, water soil nutrients, is one of the most important stress factors. This struggling link among plant communities shapes vegetation composition and regulates biodiversity [1-2]. To get success in competition, plants release a wide range of phenotypical signals to enhance resource capture and, thus, increase their fitness during competition [10]. Apart from plant competition, plant tolerance behaves as another biotic stress. BVOCs release and have capability to modulate tolerance level of plants toward light, heat, oxidative and abiotic stresses, pollutants and can influence plant-plant interaction [3, 10, 40, 62]. BVOCs may also trigger some responses in neighboring plants [10]. The inducible BVOCs also behave as alleles and info chemicals involved in plant-insect and plant-plant interactions in community, while its emission depend on the plant species and genotype as well as on the type of insect inducer [2]. Both biotic and abiotic circumstances both have an impact on BVOCs concentration. Plants that proliferate on limited nutrient soil produce lesser BVOCs concentration than nutrient rich soil upon any herbivore attack [10].

Similarly, photo irradiance influences the emission rate, dense canopies receive less light and it is highly correlated with BVOCs emission [19]. Total BVOC emissions of healthy, undamaged plants are only mildly affected by light intensity, whereas BVOC emissions of herbivore-attacked plants are strongly light dependent [40].

6. ROLE OF BVOCs IN ECOSYSTEM

BVOCs are produced under stressed and non-stressed situations to make plant tolerant and competent. These compounds play significant role in plant growth, metabolism, reproduction, protection and defence [1]. Indeed, their concentration alter by

global climatic alterations, hence affecting the structure and biochemical functions of organisms as well as the communities and system. The previous five years have shown basic modifications in plant, physiology, community interaction and competition. It is seen that volatile hormone ethylene work as an indicator for [10] competing plants and non-competing individuals, both in quality and quantity concern. BVOCs affect plant community in two ways:

- compounds behave as allelopathic that inhibits the plant development; and
- release from plants to give some clue about competitor presence or to exhibit clue about opposing strength.

7. BVOCs ROLE TO ALTER ATMOSPHERIC CHEMISTRY

BVOC have prominent role in biosphere and atmospheric interactions. Plant biologists show interest in BVOCs functions in the biosphere as well as their role in plant biology and ecology [3,5,11].

Atmospheric Chemistry: One of the important considerations of BVOCs is their role in atmospheric chemistry [63, 36] because of their possible interference in the carbon cycle. Among different BVOCs emitted, non-methanic biogenic compounds are of important concern because of their higher reactivity to many important atmospheric oxidants viz: $\text{OH}\cdot$, O_3 , $\text{NO}_3\cdot$ radicals and also due to their high emission rate, estimated at $\sim 1150 \text{ TgC year}^{-1}$, globally [64]. Specifically, isoprene is known for its role in the formation of blue haze, which are visible over dense forests [29]. Further isoprenes are also involved in the formation of different organic acids and carbon monoxide.

Ozone Formation: Globally, in the form of background concentrations or air pollution the concentration of ozone in the troposphere is likely to increase in coming decades [2]. BVOCs have dual interaction with the ozone in troposphere, such that the effect of ozone on BVOCs emission of the plants is usually dependent on other experimental factors, like temperature and applied ozone concentration, plant species, season and type of BVOCs. The oxidizing potential of many species in the troposphere is also effected by the BVOC emission. Reportedly, the breakdown of BVOCs results in the formation of ground level ozone, known to be major component of photochemical smog [1,2] and also the third most potent GHG (green house gas). At the same time,

BVOCs also react with ozone and thus are also crucial in ozone dissociation. Since the formation of ozone at ground level is also dependent upon the presence of NO_x in certain areas, and NO_x are usually present as pollutant in urban areas, therefore the concentration of ozone can readily increase in such areas. Recently, role of BVOCs in formation of ozone has been discussed on continental scale. Important contemplations related to the emission of NO_x , photochemical activity and reduction in ozone through transportation and dry deposition [3,11] have also been made.

BVOCs also result in atmospheric pollution even on un-polluted sites, where the emission of BVOCs has enhanced the concentration of other green house gases, primarily methane. This issue of BVOCs is often linked with their role in decreasing the oxidation capacity of troposphere by interference with $\text{OH}\cdot$ (hydroxyl) radicals, known for their role in atmospheric cleansing through series of oxidation reaction [1, 2,12]. So the change in BVOCs concentration results in differential oxidation in troposphere. Increased level of BVOCs would result in increased the level of ozone and instantaneously the level of methane in the atmosphere. The formation of ozone in the atmosphere by BVOCs emission is usually linked with the presence of unsaturated compounds present in BVOCs, that react with $\text{OH}\cdot$ or NO_3 radicals during day and night, respectively. The resultant product is peroxy radical that oxidizes NO to NO_2 . The photolysis of NO_2 is initiator of ozone formation thus biogenic volatile organic compounds directly form ozone at polluted sites [64, 65].

Secondary aerosols: Other biogenic compounds usually terpenes (monoterpenes ($\text{C}_{10}\text{H}_{16}$), sesquiterpenes ($\text{C}_{15}\text{H}_{24}$) and oxygenated aromatic methyl chavicol ($\text{C}_{10}\text{H}_{12}\text{O}$) also play critical role in atmospheric chemistry because they result in formation of secondary aerosols (SOA), thus contributing to the changing oxidative potential of atmosphere. An important property of BVOCs, to act as cloud condensation nuclei, make them crucial in SOA formation [12] as they produce large quantities of organic aerosols [35]. BVOCs are regarded important in production of SOA [12], as the oxygenated and sized BVOCs emitted from certain species play their role in increasing the size of particles [40]. Among many BVOCs, the emitted terpenoids react rapidly with the oxidants in the atmosphere and result in the formation of aerosols. On lab scale limited number of volatile compounds are known to be produced by ozonolysis of terpenes. This property may be critically

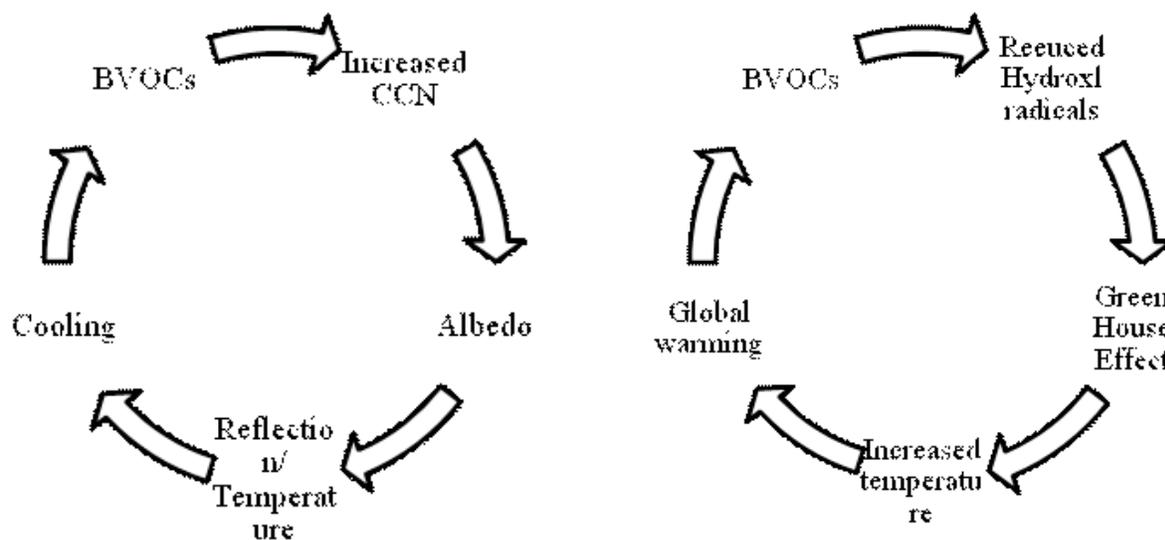


Figure-1: Positive and Negative Feedback Mechanism for Global Warming through BVOCs Emissions

important in the SOA formation due to their role in gas to particle conversion. Under increased concentrations of ozone through anthropogenic activities the problem could further aggravate. Compared to previous decades, BVOCs are now more concentrated in the formation of condensable vapours, SOA and cloud condensation nuclei (CCN) in small duration. The increased level of CCN would lead to cooling of the earth surface as the high concentration of CCN in clouds reduces the opacity of clouds therefore lesser radiations will reach Earth surface. High level of CCN would either directly reduce the albedo of the clouds or affect in the total GHE (green house effect). Thus resulting in overall cooling of Earth's surface, because of reduced net energy budget of solar radiations.

8. BVOCs AND GLOBAL WARMING

Although a probable cooling effect of the SOA is there; the emission of BVOCs is still an impending source of global warming. As discussed previously, BVOCs play their role in production of ozone and increase the lifespan of methane in atmosphere [1,2,12,40], hence exhibiting a positive and negative feedback mechanism (Figure-1).

ACKNOWLEDGEMENT

After Allah Almighty, I pay sincere gratitude to my honorable teachers and loads of thanks to all fellows who are always present beside me and supported me.

REFERENCES

1. Laothawornkitkul, J., Nigel, J. E., Paul, D., and Hewitt, C. N., 2009. Biogenic volatile organic compounds in the Earth system. *New Phytologist*, (183)2009, pp.27-51.
2. Penuelas, J., and Staudt, M., 2009. Induced biogenic volatile organic compounds from plants BVOCs and global change. *Trends in Plant Science*, 15(3)2009, pp. 133-144.
3. Peñuelas, J., Rutishauser, T., Filella, I., 2009. Phenology feedbacks on climate change. *Science*, (324)2009, pp. 887-888.
4. Bonan, G.B., 2008. Forests and climate change: forcings, feedbacks, and the climate benefits of forests. *Science*, (320)2008, pp. 1444-1449.
5. Heimann, M., and Reichstein, M., 2008. Terrestrial ecosystem carbon dynamics and climate feedbacks. *Nature*, (451)2008, pp. 289-292.
6. IPCC, 2007. Climate change the physical science basis. Summary for policy makers. Geneva, Switzerland: IPCC Secretariat, 2007: Cambridge University Press.
7. Jaleel, C. A., Manivannan, P., Sankar, B., et al., 2007. Water deficit stress mitigation by calcium chloride in *Catharanthus roseus*: effects on oxidative stress, proline metabolism and indole alkaloid accumulation. *Colloids and Surfaces B-Biointerfaces*, 60(1)2007, pp. 110-116.
8. Yordanov, I., Velikova, V., and Tsonev, T., 2003. Plant responses to drought and stress tolerance. *Bulgarian Journal of Plant Physiology*, 2003, pp. 187-206.

9. Myneni, R. B., Keeling, C. D., Tucker, C. J., et al., 1997. Increased plant growth in the northern high latitudes from 1981 to 1991. *Nature*, (386)1997, pp. 698-702.
10. Kegge, W., Pierik, R., 2003. Biogenic volatile organic compounds and plant competition Special Issue: Induced biogenic volatile organic compounds from plants *Cell press*, 15(3) 2003. pp. 126-132.
11. Loreto, F., & Jorg-Peter S., 2010. Special Issue: Induced biogenic volatile organic compounds from plants, Abiotic stresses and induced BVOCs *Cell press*, 15(3) 2003, pp. 154-166.
12. Penuelas, J., and Llusia, J., 2003. BVOCs: plant defense against climate warming. *TRENDS in Plant Sciences*, 3 (8)2003, pp. 105-109.
13. Simpraga, M., Verbeeck, H. M., Demarcke, E., et al., 2011. Clear link between drought stress, photosynthesis and biogenic volatile organic compounds in *Fagus sylvatica* L. *Journal of Atmosphere and Environment*, (45)2011, pp. 5254-5259.
14. Velikova, V., Tsonev, T., Barta, C., et al., 2009. BVOC emissions, photosynthetic characteristics, and changes in chloroplast ultrastructure of *Platanus orientalis* L. Exposed to elevated CO₂ and high temperature. *Environmental Pollution*, (157)2009, pp. 2629-2637.
15. Zemankova, K., and Brechler, J., et al., 2010. Emissions of biogenic VOC from forest ecosystems in central Europe: Estimation and comparison with anthropogenic emission inventory. *Journal of Environmental Pollution*, (158)2010, pp. 462-469.
16. Guenther, A., Hewitt, N., Erickson, D., et al., 1995. Global model of natural organic compound emissions. *Journal of Geophysical Research*, (100)1995, pp. 8873-8892.
17. Fall, R., 2003. Abundant oxygenates in the atmosphere: a biochemical perspective. *Chemical Reviews*, (103)2003, pp. 4941-4951.
18. Argueso, C., Hansen, M., and Kieber, J., 2007. Regulation of ethylene biosynthesis. *Journal of Plant Growth Regulation* (26)2007, pp. 92-105.
19. Kreuzwieser, J., Schnitzler, J. P., Steinbrecher, R., 1999. Biosynthesis of organic compounds emitted by plants. *Plant Biology*, (1)1999, pp. 149-159.
20. Knudsen, J.T and Gershenzon, J., 2010. The chemical diversity of floral scent. In *Biology of Floral Scent* (Dudareva, N. and Pichersky, E., eds), pp. 27-52, 2010. Taylor & Francis
21. Simpraga, M., Verbeeck, H., Demarcke, M., et al., 2011. Comparing monoterpene emissions and net photosynthesis of beech (*Fagus sylvatica* L.) in controlled and natural conditions. *Atmospheric Environment*, (45)2011, pp. 2922-2928.
22. Fares, S., Gentner, D. R., Park, J. H., et al., 2011. Biogenic emissions from Citrus species in California. *Journal of Atmospheric Environment*, (45)2011, pp. 4557-4568.
23. Kreuzwieser, J., Rennenberg, H., and Steinbrecher, R., 2006. Impact of short-term and long-term elevated CO₂ on emission of carbonyls from adult *Quercus petraea* and *Carpinus betulus* trees. *Journal of Environmental Pollution*, (142)2006, pp. 246-253.
24. Owen, S. M., Mackenzie, A. R., Stewart, H., et al., 2003. Biogenic Volatile Organic Compound (BVOC) Emission Estimates from an Urban Tree Canopy. *Journal of Ecological Applications*, 13(4) 2003, pp.927-938.
25. Kesselmeier, J., and Staudt, M., 1999. Biogenic volatile organic compounds (VOC): an overview on emission, physiology and ecology. *Journal of Atmospheric Chemistry*, (33)1999, pp. 23-88.
26. Magel, E., Mayrhofer, S., Mullera, A., et al., 2006. Photosynthesis and substrate supply for isoprene biosynthesis in poplar leaves. *Journal of Atmospheric Environment*, (40)2006, 138-S151.
27. Atkinson, R., and Arey, J., 2003. Gas-phase tropospheric chemistry of biogenic volatile organic compounds: a review. *Journal of Atmospheric Environment*, (37)2003, pp. 197-219.
28. Sanadze, G. A., 1956. Emission of gaseous organic substance from plants. *Repertuar Akademiia Nauk Gruzinskoi SSR*, (17)1956, pp. 429-433.
29. Went, F. W., 1960. Blue hazes in the atmosphere. *Nature*, (187)1960, pp.641-643.
30. Sanadze, G. A., 2004. Biogenic isoprene-(a review). *Russian Journal of Plant Physiology*, (51)2004, pp. 729-741.
31. Dixon, J., and Hewett, E. W., 2000. Factors affecting apple aroma/flavour volatile concentration: a review. *New Zealand Journal of Crop and Horticultural Science* (28)2000, pp. 155-173
32. Knudsen, J. T., Eriksson, R., Gershenzon, J., and Stahl, B., 2006. Diversity and distribution of floral scent. *Botanical Review*, (72)2006, pp. 1-120
33. Soares, F. D., Pereira, T., Maio Marques, M. O., Monteiro, A. R., 2007. Volatile and non-volatile chemical composition of the white guava fruit (*Psidium guajava*) at different stages of maturity. *Food Chemistry*, (100)2007, pp.15-21.
34. Owen, S. M., Boissard, C., and Hewitt, C. N., 2001. Volatile organic compounds (VOCs) emitted from 40 Mediterranean plant species:

Emission and Role of Biogenic Volatile Organic Compounds in Biosphere

- VOC speciation and extrapolation to habitat scale. *Atmospheric Environment*, (35)2001, pp. 5393-5409.
35. Pichersky, E., and Gershenzon, J., 2002. The formation and function of plant volatiles: perfumes for pollinator attraction and defense. *Plant Biology*, (5)2002, pp. 237-243.
 36. Pacifico, F., Harrison, S. P., Jones, C. D., Sitch, S., 2009. Review Isoprene emissions and climate. *Atmospheric Environment*, (43)2009, pp. 6121-6135.
 37. Loreto, F., Ciccioli, P., Brancaleoni, E., et al., 1998a. Measurement of isoprenoid content in leaves of Mediterranean *Quercus* spp. by a novel and sensitive method and estimation of the isoprenoid partition between liquid and gas phase inside the leaves. *Plant Science*, (136)1998a, pp. 25-30.
 38. Loreto, F., and Velikova, V., 2001. Isoprene produced by leaves protects the photosynthetic apparatus against ozone damage, quenches ozone products, and reduces lipid peroxidation of cellular membranes. *Plant Physiology*, (127)2001, pp. 1781-1787
 39. Fischbach, R. J., Staudt, M., Zimmer, I., et al., 2002. Seasonal pattern of monoterpene synthase activities in leaves of the evergreen tree *Quercus ilex*. *Physiologia Plantarum*, (114)2002, pp. 354-360.
 40. Penuelas, J., and Llusia, J., 2001. The complexity of factors driving volatile organic compound emissions by plants. *Biologia Plantarum*, (44)2001, pp. 481-487.
 41. Mithofer, A., Wanner, G., and Boland, W., 2005. Effects of feeding *Spodoptera littoralis* on Lima bean leaves. II. Continuous mechanical wounding resembling insect feeding is sufficient to elicit herbivory-related volatile emission. *Plant Physiology*, 137: 2005, pp. 1160-1168.
 42. Laothawornkitkul, J., Moore, J.P., Taylor, J.E., et al., 2008a. Discrimination of plant volatile signatures by an electronic nose: a potential technology for plant pest and disease monitoring. *Environmental Science & Technology*, 42 2008a, pp. 8433-8439.
 43. IPCC, 2007. *Climate change 2007: the physical science basis. Summary for policy makers.* Geneva, Switzerland: IPCC Secretariat, Cambridge University Press, 2007.
 44. Arndt, S.K., Clifford, S.C., Wanek, W., et al., 2001. Physiological and morphological adaptations of the fruit tree *Ziziphus rotundifolia* in response to progressive drought stress. *Tree Physiology*, 21 2001, pp. 705-715.
 45. Arndt, S.K., Wanek, W., Clifford, S.C., and Pop, M., 2000. Contrasting adaptations to drought stress in field-grown *Ziziphus mauritiana* and *Prunus persica* trees: water relations, osmotic adjustment and carbon isotope composition. *Australian Journal of Plant Physiology*, 27 2000, pp. 985-996.
 46. Wilkinson, S., and Davies, W.J., 2010. Drought, ozone, ABA and ethylene: new insights from cell to plant to community. *Plant, cell and environment*, 33 2010, pp. 510-525.
 47. Ormeno, E., Mevy, J.P., Vila, B., et al., 2007. Water deficit stress induces different monoterpene and sesquiterpene emission changes in Mediterranean species. Relationship between terpene emissions and plant water potential. *Chemosphere*, 67 2007, pp. 276-284.
 48. Thomas, D., and Loreto, S.F., 1993. Water stress, temperature, and light effects on the capacity for isoprene emission and photosynthesis of kudzu leaves. *Oecologia*, 95 1993, pp. 328-333.
 49. Brilli, F., Barta, C., Fortunati, A., 2007. Response of isoprene emission and carbon metabolism to drought in white poplar (*Populus alba*) saplings. *New Phytologist*, 175 2007, pp. 244-254.
 50. Funk, J.L., Mak, J.E., and Lerdau, M.T., 2004. Stress-induced changes in carbon sources for isoprene production in *Populus deltoids*. *Plant, Cell & Environment*, 27 2004, pp. 747-755.
 51. Niinemets, U., and Reichstein, M., 2003. Controls on the emission of plant volatiles through stomata: differential sensitivity of emission rates to stomatal closure explained. *Journal of Geophysical Research*, 108 2003, ACH2_1-ACH_10.
 52. Fuentes, J.D., Lerdau, M., Atkinson, R., et al., 2000. Biogenic hydrocarbons in the atmospheric boundary layer: a review. *Bulletin of the American Meteorological Society*, 81 2000, 1537-1575.
 53. Sharkey, T.D., and Yeh, S.S. Isoprene emission from plants. *Annual Review of Plant Physiology and Plant Molecular Biology*, 52 2001, pp. 407-436.
 54. Centritto, M., Nascetti, P., Petrilli, L., et al., 2004. Profiles of isoprene emission and photosynthetic parameters in hybrid poplars exposed to free-air CO₂ enrichment. *Plant, Cell and Environment*, 27 2004, pp. 403-441.
 55. Fares, S., Mahmood, T., Liu, S., et al., 2010. Influence of growth temperature and measuring temperature on isoprene emission, diffusive limitations of photosynthesis and respiration in hybrid poplars. *Journal of Atmospheric Environment*, 45(1) 2010, pp. 155-161.
 56. Niinemets, U., Díaz-Espejo, A., Flexas, J., et al.,

2009. Role of mesophyll diffusion conductance in constraining potential photosynthetic productivity in the field. *Journal of Experimental Botany*, 60 2009, pp. 2249-2270.
57. Centritto, M., Loreto, F., and Chartzoulakis, K., 2003. The use of low [CO₂] to estimate diffusional and non-diffusional limitations of photosynthetic capacity of salt stressed olive saplings. *Plant, Cell and Environment*, 26 2003, pp. 585-594.
58. Ciais, P.H., Reichstein, M., Viovy, et al., 2005. Europe-wide reduction in primary productivity caused by the heat and drought in 2003. *Nature*, 437 2005, pp. 529-533.
59. Staudt, M., Joffre, R., Rambal, S., and Kesselmeier, J., 2001. Effect of elevated CO₂ on monoterpene emission of young *Quercus ilex* trees and its relation to structural and ecophysiological parameters. *Tree Physiology*, 21 2001, pp. 437-445.
60. Loreto, F., Fischbach, R.J., Schnitzler, et al., 2001a. Monoterpene emission and monoterpene synthase activities in the Mediterranean evergreen oak *Quercus ilex* L. grown at elevated CO₂ concentrations. *Global Change Biology*, 7 2001a, pp. 709-717
61. Centritto, M., Nascetti, P., Pettrilli, R.A., and Loreto, F. Profiles of isoprene emission and photosynthetic parameters in hybrid poplars exposed to free-air CO₂ enrichment. *Plant Cell and Environment*, 27 2004, pp. 403-412.
62. Loreto, F., and Velikova, V., 2001. Isoprene produced by leaves protects the photosynthetic apparatus against ozone damage, quenches ozone products, and reduces lipid peroxidation of cellular membranes. *Plant Physiology*, 127 2001, pp. 1781-1787.
63. Yassaa, N., Meklati, B.Y., and Cecinato, A., 2000. Evaluation of monoterpene biogenic volatile organic compounds in ambient air around *Eucalyptus globulus*, *Pinus halepensis* and *Cedrus atlantica* trees growing in Algiers city area by chiral and achiral capillary gas chromatography. *Journal of Atmospheric Environment*, 34 2000, pp. 2809-2816.
64. Demarcke, M., Amelynck, C., Schoon, N., et al., 2010. Laboratory studies in support of the detection of biogenic unsaturated alcohols by proton transfer reaction-mass spectrometry. *International Journal of Mass Spectrometry*, 290 2010, pp. 14-21.
65. Seinfeld, J.H., and Pandis, S.N., 1998. *Atmospheric Chemistry and Physics*. John Wiley and Sons Inc., USA.

