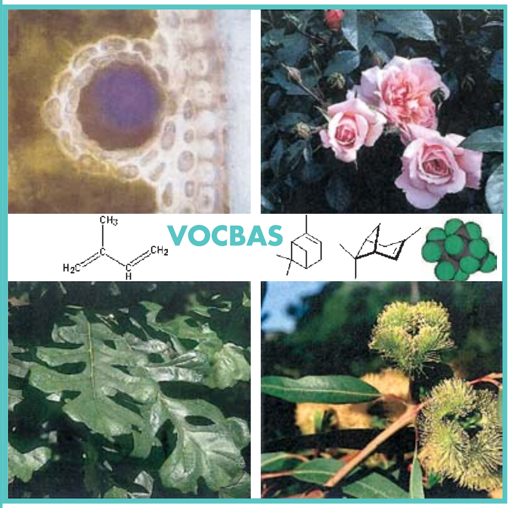
Volatile Organic Compounds in the Biosphere-Atmosphere System (VOCBAS)

An ESF scientific programme

Plants and animals emit VOCs (isoprenoids, and oxygenated compounds) and the release of these gaseous compounds has been demonstrated to affect the chemical and physical properties of the atmosphere (Chameides et al. 1988). In the presence of NO_x, produced by fossil fuel combustion and natural processes, biogenic VOCs react in the atmosphere to form tropospheric ozone, an important pollutant. These reactions may also cause a decrease in the concentrations of the hydroxyl radical (OH) and so lead to the accumulation of methane and other greenhouse gases. A further consequence of these reactions is the formation of secondary organic aerosol particles, a component of PM10 in the atmosphere, which has known adverse effects on human health.
VOC emissions take place on the continental scale and can therefore play a role in atmospheric chemistry even in remote areas. The interactions between the biosphere and the atmosphere mediated by the production and emission of reactive trace gases are a crucial and central component of the study of Earth System Science. Their importance to the functioning of the Earth's climate is only now beginning to be appreciated, and there is wide acknowledgement that this is an area needing concerted scientific effort on a large scale.



The European Science Foundation acts as a catalyst for the development of science by bringing together leading scientists and funding agencies to debate, plan and implement pan-European initiatives.

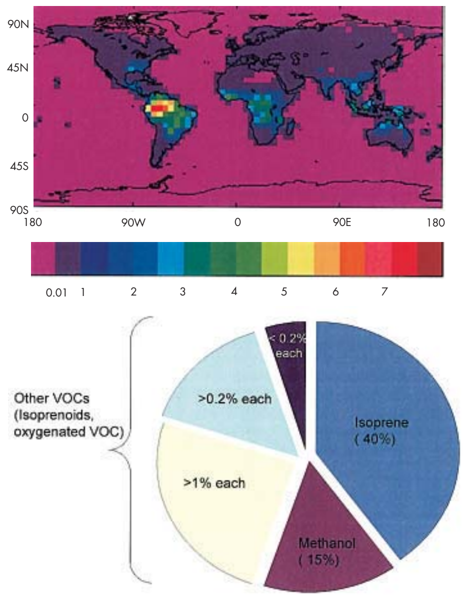


Figure 1. Estimated global production of Biogenic VOC (upper panel) and of the relative abundance of chemical species emitted (pie graph). Note the estimated large emission by tropical forests and the predominant contribution of isoprene to biogenic VOC emissions.
Data from A. Guenther available at www.atm.helsinki.fi/ILEAPS/presentations/talks/Alex_Guenther.ppt

Introduction

Plants and animals emit VOCs (isoprenoids, and oxygenated compounds, *Figure 1*) and the release of these gaseous compounds affects the chemical and physical properties of the atmosphere. In the presence of NO_x, produced by fossil fuel combustion and natural processes, biogenic VOCs react in the atmosphere to form tropospheric ozone, an important pollutant. These reactions may also cause a decrease in the concentrations of the hydroxyl radical (OH) and so lead to the accumulation of methane and other greenhouse gases. A further consequence of these reactions is the formation of secondary organic aerosol particles, a component of PM10 in the atmosphere, which has known adverse effects on human health. VOC emissions take place on the continental scale and can therefore play a role in atmospheric chemistry even in remote areas.

The emissions of VOCs by plants are several orders of magnitude higher than by animals and account for a relevant amount of carbon fixed by photosynthesis, especially under stress conditions. From a plant biology standpoint, VOC emissions therefore may substantially reduce the amount of carbon fixed by vegetation and may consequently strongly affect plant productivity. Why plants give away such a relevant amount of resources is still a matter of debate.

When VOCs accumulate in specialised organs of leaves, stems or trunks, they are massively released after wounding. These emissions are thought to act as a powerful deterrent against pathogens and herbivores, and to contribute to wound sealing. VOCs accumulated in flowers, on the other hand, attract pollinators. More studies are needed to understand the role of VOCs in tritrophic relationships and in possible plant-plant communications.

VOCs may also be involved in protection against environmental stresses since experiments have recently shown that VOC-emitting plants are less damaged by ozone and elevated temperature. The mechanism by which this protection occurs is still unknown.

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Scope

Biogenic VOCs impact on two very important fields: plant protection against biotic and abiotic stresses, and air pollution and climate change. VOCBAS implements, supports, and coordinates a series of research activities involving atmospheric chemists, plant biologists, pathologists, entomologists, agronomists and foresters, to determine how biogenic volatile organic compound (VOC) emissions affect the relationship between the biosphere and the atmosphere.

VOCBAS brings together this scientific community who carries out internationally recognised research into the production and emissions of VOCs by plants in the context of global change and ecosystems from a wide range of disciplines. The programme spans plant processes, genetics, and ecosystem functioning, environmental controls on VOC emission fluxes, flux measurements and modelling on the leaf, canopy, ecosystem and regional scales, and the emission of these compounds into the atmosphere. VOCBAS addresses the European Research Area (ERA) priority 1.6.3 "Global change and ecosystems" reducing the considerable fragmentation that exists at present in this multi-disciplinary field of research, and will spread excellence through and beyond the programme. VOCBAS will establish European research at the forefront of this area of international importance and will foster pan-European research leading to a better understanding of how biogenic VOC emissions affect the present and future relationship between the biosphere and the atmosphere.

Scientific objectives

The following five specific research areas have been identified, and within each area *specific scientific objectives* will be pursued during the programme:

1) VOCs and the chemical and physical properties of atmosphere

VOCs are formed and emitted by plants at an estimated 1.1-1.5 Pg C per year on the global scale *(Figure 1)*. Although this emission accounts for approximately 2% of the total C-exchange of 69 Pg between the biota and the atmosphere, it has not been considered in global C-cycling so far. Forests emit a wide range of VOCs, mainly isoprenoids. Biogenic VOC emission rates can have both direct and indirect effects on the carbon cycle.

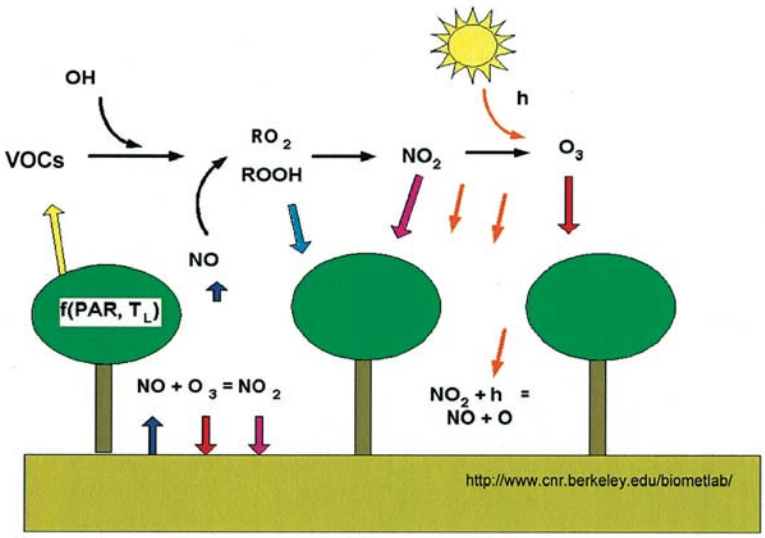

Figure 2. VOCs in the biosphere-atmosphere system. Biogenic, highly reactive VOCs scavenge ubiquitous hydroxyl radical and in presence of anthropogenic pollutants are involved in the mechanisms of formation of tropospheric ozone

Direct effects are caused by the emission of assimilated carbon by plants in the form of these organic compounds. Indirect effects occur because these compounds play a role in the oxidative chemistry of the lower atmosphere. Biogenic VOCs rapidly react with anthropogenic and natural compounds (mainly NO_x) leading to high ozone episodes and photochemical smog, particularly during periods of high radiation and temperature at low wind speeds, when biogenic VOC emissions are usually high *(Figure 2).*

Moreover, by altering the concentrations of the hydroxyl radical in the atmosphere, VOCs may subsequently alter the lifetime of radiatively active trace gases, including methane, in the atmosphere.

The interaction between anthropogenic and biogenic chemical species present in the atmosphere and the consequent formation of ozone and photochemical smog have now been demonstrated in several case-studies in the USA. In Europe, these findings have fostered studies on VOC emissions by natural vegetation over the Mediterranean area and from boreal forests as well as on the control of environmental factors over biogenic emissions. These studies demonstrated that *European vegetation is rich in species emitting VOCs and that the range of VOCs emitted is far greater than in some other areas of the world.* Therefore, plant species specific changes in VOC emission triggered by a changed environment strongly affect emission quality and emission source strength in Europe *with so far unknown consequences for C-cycling and air chemistry.*

2) VOCs in biotic stress interactions

During the process of evolution other organisms have 'learned' to use the chemical cues released by plants. Multitrophic interactions between plants (first trophic level), herbivorous arthropods (second trophic level) and their parasitoids and predators (third trophic level) are mediated by VOCs formed in damaged host plants and/or induced by elicitors that are present in regurgitants of herbivorous insects *(Figure 3).*

Figure 3. Biogenic VOCs in plant-host interactions. Feeding damage by herbivores increase isoprenoid emissions from plants. In this case Diamondback Moth feeding on oil seed rape leaf induces de novo synthesis of VOCs and elicits emission of constitutive and induced VOCs. Photo courtesy of J. Holopainen

It has long been known that plants that store isoprenoids accumulate these substances in a variety of ducts, glands and cavities, and that the synthesis itself occurs in the cells lining these specialised structures. These VOCs, in particular, are believed to serve defence purposes against insect, fungi, herbivores, other plants and, when volatilised, are signals for pollinators, can mediate tritrophic interactions, and act as signals for conspecific herbivores. Their synthesis is generally constitutive, but it may also be induced by herbivores or pathogen attacks. The synthesis may initiate at different times after the attack, denoting a different role for monoterpenes, sesquiterpenes and diterpenes. The pathway of synthesis of these isoprenoids may be plastydic or cytoplasmic and does not strictly require the use of carbon freshly fixed by photosynthesis, being the carbon supplied from the classic mevalonate pathway. The aerial information network between different trophic levels is complicated and only few interactions, like the one mentioned above, have been exemplified at the moment. *How and to which extent these actions are exerted, is therefore largely unknown*. To get a functional and mechanistic understanding of food webs and their information web, simple natural, forest or agricultural systems with few interactions should be studied. It is known that environmental (light, temperature, water and nutrient stresses, mechanical stresses, seasonality, see following section) factors strongly control VOC emission rates from plants. A few reports suggest that elevated CO_2, ozone and UV-B could severely disturb VOC-based multitrophic communication. When these systems are artificially exposed to environmental stress factors, *better estimates of global change on ecosystem vulnerability can be assessed*.

3) VOCs in the plant-environment interaction

The control of VOC emissions by the main environmental factors has been investigated in great detail because of its importance. Parameterisation on the basis of their dependence on a few environmental variables has provided good estimates of the actual emission rates of biogenic VOCs though it is now under scrutiny for its inaccuracy in some environmental conditions, such as under future levels of CO_2 and other pollutants, and for compounds other than isoprene.

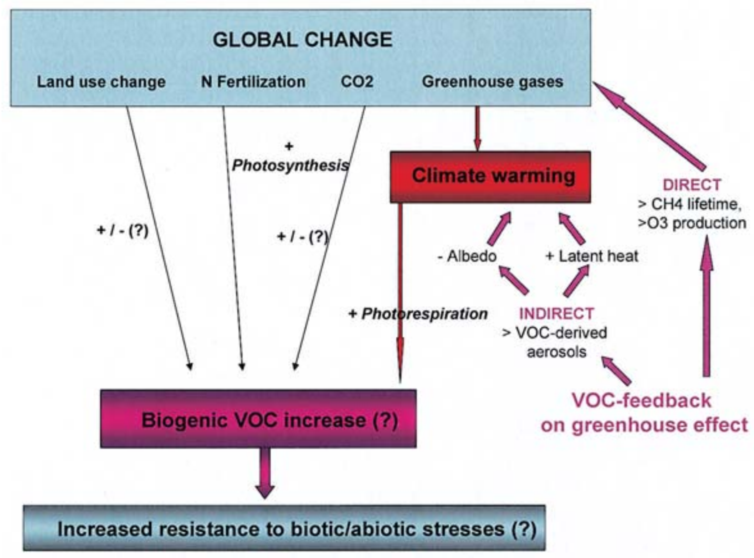

Figure 4. Proposed feedback – feedforward interactions between global change factors and biogenic VOC. By influencing primary processes (photosynthesis, photorespiration) feeding carbon to secondary metabolite synthesis, or by directly controlling biogenic VOC synthesis (e.g. rising temperature), global change factors may elicit (+) or inhibit (-) VOC emissions and consequently impact on plant resistance to stress factors.
Redrawn from Penuelas and Llusia, Trends in Plant Science

Numerous studies have been and are now addressing the effects of environmental changes driven by global warming and CO_2 rising *(Figure 4).* The controversial results of these preliminary studies underline the necessity of further investigations centred on key plant species of European ecosystems. Such studies are necessary for providing realistic emission inventories under future climate conditions leading to a sound basis for estimating carbon exchange processes between biosphere and atmosphere.

The study of VOC-dependence on environmental factors has given insights about the yet unknown function(s) of these compounds. It has been demonstrated that certain volatile isoprenoids protect leaves against thermal stresses and ozone damages. *The mechanism by which this protective action occurs is unclear and needs further research*. Presently, the most likely explanation is that isoprenoids are embedded in the organelle membranes and prevent membrane lipid denaturation following oxidative stress.

4) VOC biosynthesis

Early studies on the environmental control on isoprenoid emission, and on the labelling of isoprenoid molecules by ^{13}C indicated that most of the emitted isoprenoids are formed directly from carbon recently fixed by photosynthesis, probably inside the chloroplasts and are not stored in specialised structures. Isoprene-synthase, the enzyme catalysing the last step in isoprene formation from its immediate precursor, dimethyl-allyl diphosphate (DMADP) has been found in the chloroplasts of isoprene-emitting plants and recently the isoprene synthase gene was cloned from poplar. The deduced amino acid sequence showed about 49% identity to monoterpene synthases of dicots. Recently, a new pathway leading to isoprenoid synthesis from photosynthesis intermediates has been demonstrated in bacteria and plants. This chloroplastidic pathway (named also 2-methyl-erythritol 4-phosphate = MEP pathway from its first committed intermediate), requiring photosynthetic intermediates, is active in all of those species that emit isoprenoids without storing them in specialised structures, but recent studies demonstrated that it is also present in pine. This pathway is likely responsible for the synthesis of most of the volatile isoprenoids (isoprene, monoterpenes, and some sesquiterpenes) as well as of higher isoprenoids, such as the carotenoids, located and having a functional role in chloroplasts *(Figure 5)*.

Apparently, a relatively small number of isoprenoid synthases, with very similar chemical properties and structures, can catalyse the synthesis of many isoprenoids which are produced by redox modification of the parent skeleton. This finding has received confirmation by molecular cloning of isoprenoid synthase genes. cDNA cloning proved that isoprenoid synthases form multiple products in a very conservative ratio. Subdivision of isoprenoid synthases in families on the basis of amino acids sequences has also led to the observation that functional diversity may be evolved with few changes in enzyme structures. Isoprenoid biosynthetic genes are ideal tools not only to unravel the mechanisms of formations of these isoprenoids, but also to improve our understanding about their functions. Macro and micro array techniques may be used for identification of genes involved in processes related to plant-pathogen and plant-herbivore interactions. In addition, identified mutants or transformants with altered levels of individual isoprenoids or ratio between isoprenoids, or defective for isoprenoid synthesis, can be employed to rigorously test isoprenoid protective functions against abiotic stresses.

5) VOC modelling

Until now the emission of biogenic VOCs has been parameterised on the basis of their dependence on a few environmental variables. This approach yielded an empirical model that proved its usefulness in modelling exercises and provided good estimates of the global emission levels of the most important VOCs, with emphasis on isoprene. However, the model is now under scrutiny for its inaccuracy in many environmental conditions, under future levels of CO_2 and other gases, and for compounds other than isoprene *(Figure 6)*. It is necessary to integrate measurements at larger temporal and spatial scales to improve estimation and modelling of VOCs and to accurately predict biogenic VOC load in the atmosphere as a consequence of global change factors.

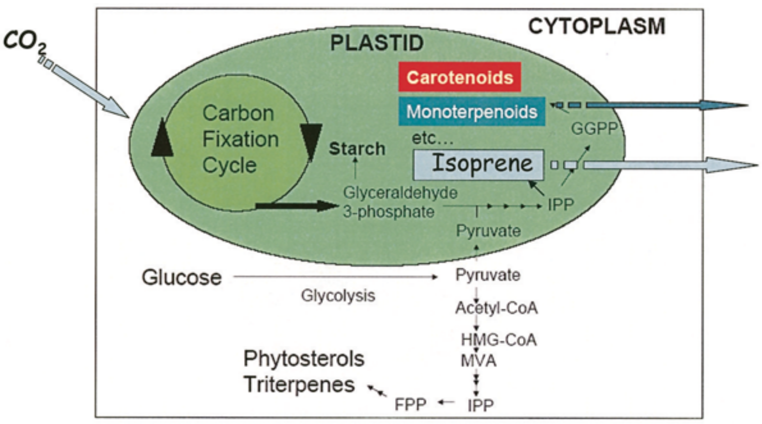

Figure 5. The chloroplastic and cytosolic pathways of isoprenoid formation in plants. Emitted isoprenoids mainly come from the chloroplastic pathway. The two pathways share and potentially compete for metabolites. However cooperation/competition in biosynthesis of chloroplastic vs extrachloroplastic isoprenoids is unknown and needs to be studied. Redrawn from W. Gruissem, http://www.pb.ipw.biol.ethz.ch

On the other hand, by studying the molecular and biochemical basis of isoprenoid synthesis, it is now possible to provide the background to *generate detailed mechanistic predictions of isoprenoid emissions currently and in response to future climate changes.* The recently described biochemical-based BIM (biochemical isoprene emission model) and the phenological-based model SIM (seasonal isoprene synthase model) can be used as a basis for further developments.

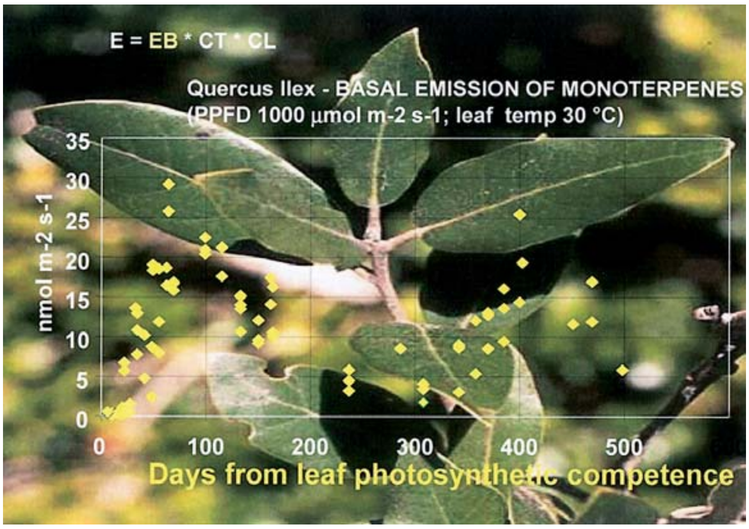

Figure 6. Biogenic VOC emission algorithms. Emissions of isoprenoids are estimated by algorithms on the basis of isoprenoid light- (CT) and temperature (CL)-dependence (Guenther algorithm). However, physiological factors (age, seasonality) that strongly influence the emissions are not taken into account and may significantly impair predictions. The basal emission (EB) of holm oak leaves changes dramatically over the two-year life of the leaves. A better understanding of isoprenoid synthesis makes increasingly available data to build process-based algorithms.
Unpublished data by F. Loreto.

Programme activities

VOCBAS will run for five years and during this time the programme will

- coordinate and integrate studies carried out by European laboratories on the ecological role of biogenic VOCs and their fate in the atmosphere, and
- support collaborative research projects between laboratories working on the biosynthesis, ecology, chemistry and modelling of biogenic VOCs. These objectives will be pursued by carrying on the following activities:

1) Training (courses and exchange visits)
2) Workshop and conference organisation
3) Communication and interactions with other programmes

More information is available at: www.esf.org/vocbas

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For the latest information on this programme consult the *VOCBAS* home page: www.esf.org/vocbas

Cover picture:
Volatile organic compounds (VOC) are synthesized in a variety of structures such as ducts (a) or flowers (b) and are emitted in the atmosphere principally by leaves (c) and flowers (d)

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