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A MODEL TO ASSESS THE EMISSION OF INDIVIDUAL ISOPRENOIDS EMITTED FROM ITALIAN ECOSYSTEMS

settore scientifico-disciplinare AGR/05

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INTRODUCTION

Biogenic volatile organic compounds (BVOC) are organic trace gases other than carbon dioxide and carbon monoxide released from above- and below-ground plant organs.

BVOC emissions can affect directly or indirectly the atmospheric concentrations of air pollutants and greenhouse gases such as ozone and carbon monoxide, as well as the formation of aerosols (Andreae, et al., 1997); (Atkinson, 1990); (Fehsenfeld, et al., 1992); (Graedel, 1979). The term BVOC is used to identify isoprenoids (isoprene, monoterpenes, sequiterpenes and oxygenated terpenes) but also alkanes, alkenes, carbonyls, alcohols, esters, ethers and acids also emitted by plants.

Isoprenoid compound emitted by terrestrial vegetation can be classified mainly into three classes: hemiterpene compounds, such as isoprenene having 5 carbon atoms in the molecule, monoterpenes with 10 carbon atoms in the molecule, and sesquiterpenes with 15 carbon in the molecule. In general, isoprene and monoterpenes are, by far, the most abundant BVOC released by plants (Karl, et al., 2009).

The main factor determining the type and quantity of BVOC emissions in the atmosphere is the distribution of plant species covering the land surface. Within each vegetation type BVOC emission are mainly influenced by the photosynthetically active photon flux density (PPFD) reaching the leaf surface, the leaf temperature and the soil moisture (Karl, et al., 2009). Among these environmental factors, temperature and light are, by far, the principal parameters determining short-term BVOC emissions (Guenther, et al., 2000); (Kesselmeier, et al., 1999). Isoprenoids compounds are emitted from coniferous, deciduous as well as broadleaved evergreen trees as a function of temperature, or both temperature and light (Kesselmeier, et al., 1999).

Once emitted into the atmosphere BVOC react producing tropospheric ozone and other photochemical oxidants in the presence of sufficient amounts of nitrogen oxides (NOx) and UV light (Kanakidou, et al., 2005), oxidation products from several monoterpenes are also known to undergo gas-particle partitioning, and they have been found in atmospheric particles (Yu, et al., 1999); (Kavouras, et al., 1999a). BVOC are generally more reactive than the anthropogenic ones (AVOC): as they react faster with OH radicals to produce ozone, and with ozone to produce secondary organic aerosols (SOA). The atmospheric lifetimes of many isoprenoids range from minutes to few hours (Atkinson, et al., 2003). On a global scale, BVOC emissions from terrestrial vegetation are one order of magnitude higher than those of AVOC) (Guenther, et al., 1995). Although they occur most in tropical areas, they are also important in temperate regions: in many industrialized countries of Europe, BVOC emissions are comparable to AVOC emissions in terms of mass (Friedrich, et al., 1999).

The Italian landscape is characterized by the presence of different forest types, spanning from alpine to semiarid environment, within the Alpine, Continental, Mediterranean and Mediterranean-Temperate climate. The Italian territory shows a strong seasonal variability in the amount of BVOC emissions, mainly related to the high temperature and solar radiation characterizing the summer in the Mediterranean area.

So far, national and international emission inventories have been expressed in terms of isoprene and the whole content of monoterpenes. This approach has several limits: the most important one is that the class of monoterpenes is composed by several compounds, the most abundant are about 10-12, of which make up 22% of the total, all displaying different reactivity toward OH radicals and ozone (Atkinson, et al., 2003), and different potentials of SOA productions (Hoffmann, et al., 1997). Indeed, differences in the chemical behavior of monoterpenes are sometimes larger than that between some monoterpenes and isoprene.

While BVOC-specific emission inventories might appear not so important for plant physiologist, they are extremely important for modeling tropospheric ozone and SOA formation. Their estimate is, however, not so easy because it requires a knowledge of the emissions of the different BVOC from the different vegetation species. Furthermore the species specific dependence of isoprenoids emission on biological processes is also required. To get reliable data, the development of plant-specific emission models derived from both laboratory and field observations are needed.

While short term emission responses to temperature or light and temperature- are adequately described by the emission algorithms (Guenther, et al., 1995), seasonality terms were recently introduced to account for changes in the emission caused by phenological variations of plants physiology (Ciccioli, et al., 2003); (Staudt, et al., 2000); (Schnitzler, et al., 1997).

This work presents a novel method to derive BVOC-specific emission inventories starting from vegetation maps. Using laboratory and field data, BVOC-specific maximum emission factors were estimated for the main forest species in Italy. Proper algorithms were developed to predict diurnal and seasonal variations of isoprene and individual monoterpene emissions from these species. BVOC-specific emission maps for 20 vegetation species in Italian ecosystems were obtained by creating an emission model in a GIS environment. The model has been created for the year 2006, with a 1 km x 1 km spatial and 1 h temporal resolutions. Data provided by the model are particularly suitable to be used for the prediction of tropospheric ozone and photochemical oxidants with mathematical models in areas, such as the Italian peninsula, where the large biodiversity leads to complex compositions of BVOC emissions. The model resolution allows to predict photochemical smog pollution at local as well as meso- and global scale. Results are compatible most with Lagrangian models but they can also be used in Eulerian models providing that prediction is made at a mesoscale level.

OBJECTIVES OF THE STUDY

The aim of the study is to develop a GIS-based model to estimate the emission of Biogenic Volatile Organic Compounds (BVOC) from forest ecosystems in Italy. The purpose of the model is to generate a species-specific emission inventory for isoprene and individual monoterpenes with validation on experimental data collected in selected sites of the CARBOITALY project.

The work was subdivided in several topics according to the following specific objectives and methodological approaches used for their attainment:

- ✓ To develop a detailed and flexible methodology that could be used in conjunction to photochemical models to assess the production of Ozone e secondary organic aerosol (SOA).
- ✓ To create updated maps of vegetation to estimate specie-specific BVOC emissions, through the intersection of information from CORINE IV Land Cover maps and from National Forest Inventory (INFC) data.
- ✓ To create maps of density of foliar biomass, source of BVOCs, combining the maps previously created with maps of Leaf Area Index (LAI) provided by the CARBOITALY project.
- ✓ To generate maps of photosynthetic active radiation (PAR) and leaf temperature considering sunshine hours from daily averages.
- ✓ To produce specie-specific maps of daily, monthly and annual emissions of BVOCs for the study case of year 2006.

A further source of information will come from the study of land cover changes in burned areas in Southern Europe, that are potentially relevant for the model assessment of BVOC emissions caused by biomass burning in Italy.

Details on the used methodological approaches will be discussed in the respective chapters.

1. BIOSYNTHESIS OF BIOGENIC VOLATILE ORGANIC COMPOUNDS (BVOC) BY TERRESTRIAL ITALIAN ECOSYSTEM

1.1 The plant as a BVOC factory

Plants are multifaceted chemical factories that produce a multitude of compounds ranging from ethylene and methanol to complex terpenoids and nitrogen containing alkaloids. More than 100,000 chemical products are known to be produced by plants and at least 1700 of these are known to be volatile (Dicke, et al., 2010), as shown schematically in Figure 1-1. Over the earth, terrestrial vegetation is, by far, the most important natural source for BVOC. Their short-term emissions are driven by in temperature or temperature and PAR (Guenther, et al., 1995). Terrestrial vegetation produces and releases a wide spectrum of BVOC, amongst which isoprenoid components (isoprene, monoterpenes and sesquiterpenes) are the most abundant and, very often, the most reactive. In addition to isoprenoids, other VOC (OVOC), such as methanol and carbonyl compounds are produced and released (Winer, et al., 1992); (Kesselmeier, et al., 1997); (Helmig, et al., 1999). Depending on emission quantity and quality, the atmospheric degradation of volatile isoprenoids affects directly or indirectly the atmospheric concentrations of ozone and particulate matter that are important air pollutants and species relevant to earth warming, (Andreae, et al., 1997); (Atkinson, 1990); (Fehsenfeld, et al., 1992); (Graedel, 1979). Global scale emissions of BVOC from terrestrial vegetation are estimated to be in the range of 1.000 Tg C yr^{-1} (Guenther, et al., 1995), whereas those from man-made activities are calculated to be 150 Tg C yr^{-1} (Muller, 1992); (Piccot, et al., 1992); (Veldt, et al., 1993); (Steinbrecher, 1994).

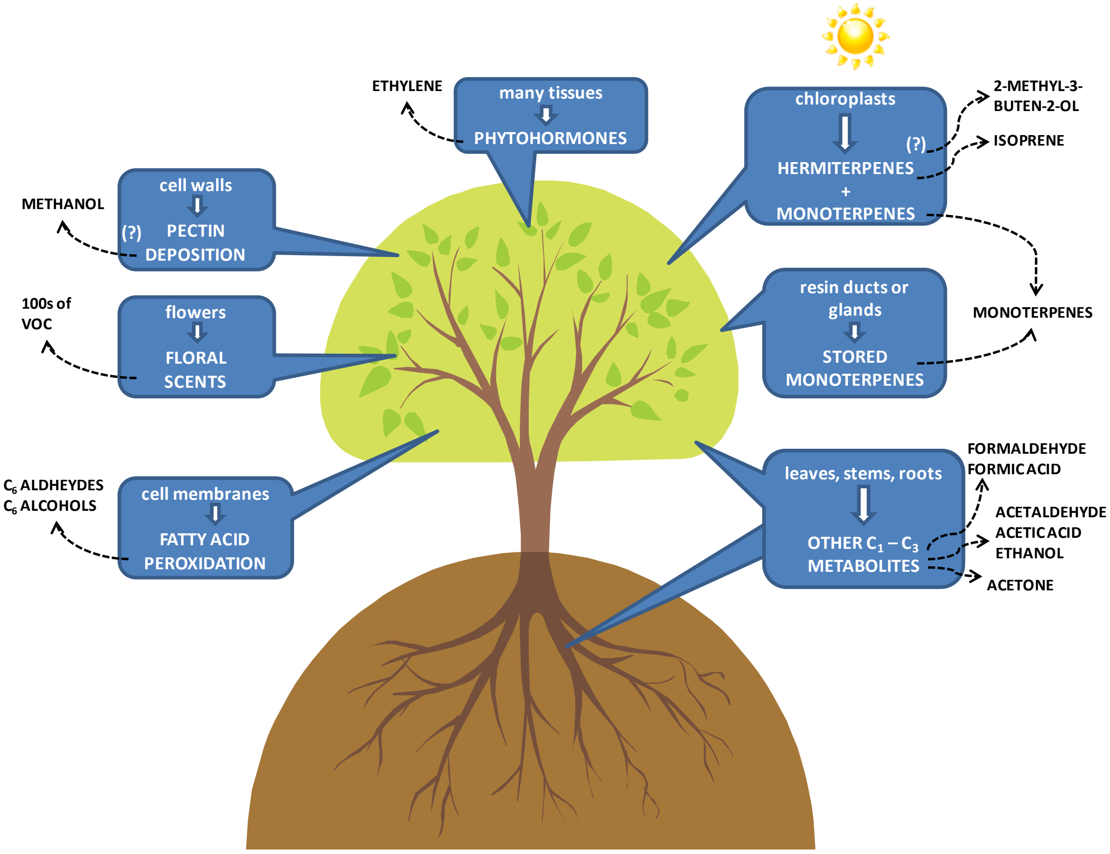


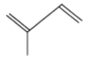
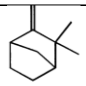
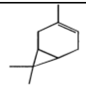
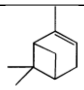
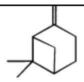
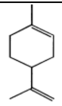
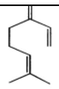
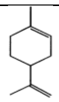
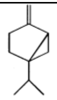
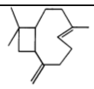
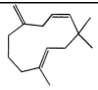
Figure 1-1 A”VOC tree” illustrates that plants have the metabolic potential to produce and emit a variety of VOCs. In this scheme a hypothetical tree emits all known major plant VOCs plus floral scents. The probable plant tissues and compartments for VOC formation are indicated

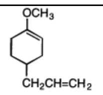
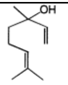
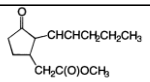
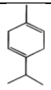
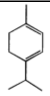
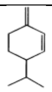
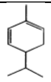
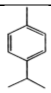
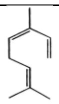
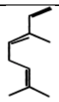
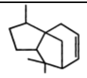
BVOCs are released from above- and below-ground plant organs. In general, flowers and fruits release the widest variety of BVOCs, with emission rates peaking at maturation (Dixon, et al., 2000); (Knudsen, et al., 2006); (Knudsen, et al., 2006); (Soares, et al., 2007). Leaves represent the most important BVOC sources in terrestrial plants. The vegetative parts of woody plants are more likely to release diverse mixtures of terpenoids, including isoprene, monoterpenes, sesquiterpenes and some diterpenes (Owen, et al., 2001); (Keeling, et al., 2006), whereas grass species emit relatively large amounts of oxygenated BVOCs and some monoterpenes (Kirstine, et al., 1998); (Fukui, et al., 2000).

1.2 Molecular and chemical aspects of BVOC synthesis

Little is known about the regulation of BVOC synthesis rates, with probably more than 90% of the genes involved in their biosynthesis still unidentified (Laothawornkitkul, et al., 2009). Terpenes have many volatile representatives. Monoterpenes and isoprene belong to the biochemical class of isoprenoids (or terpenoids), whose carbon skeletons are composed of characteristic C_5 units (McGarvey, et al., 1995). According to the number of C_5 units, they are subdivided into hemiterpenes (C_5, e.g., isoprene, prenylresidue of cytokinene), monoterpenes (C_{10}, e.g., sabinene, a-pinene, limonene) and sesquiterpene (C_{15}, e.g., b-caryophyllene, abscisic acid). Table 1-1 reports some of the most common isoprenoids found in plant emission together the chemical formula, chemical structure, molecular weight and boiling point (Winer, et al., 1992).

Table 1-1 Common isoprenoids detected in terrestrial vegetation emission vegetation. (Fuentes, et al., 2000).

Compound name	Chemical formula	Molecular weight (g mol^{-1})	Boiling point (K)	Chemical structure
Isoprene	C_5H_8	68.12	307	
Camphene	$C_{10}H_{16}$	136.24	320	
3-Carene	$C_{10}H_{16}$	136.24	441	
α-Pinene	$C_{10}H_{16}$	136.24	428	
β-Pinene	$C_{10}H_{16}$	136.24	436	
Limonene	$C_{10}H_{16}$	136.24	448	
Myrcene	$C_{10}H_{16}$	136.24	440	
Terpinolene	$C_{10}H_{16}$	136.24	459	
Sabinene	$C_{10}H_{16}$	136.24	437	
β-Caryophyllene	$C_{15}H_{24}$	204.35	396	
α-Humulene	$C_{15}H_{24}$	204.35	396	

Methyl chavicol		148.20	489	
Linalool	$C_{10}H_{18}O$	154.25	469	
Methyl jasmonate		224.30	383	
γ-Terpinene	$C_{10}H_{16}$	136.24	455	
α-Terpinene	$C_{10}H_{16}$	136.24	447	
β-Phellandrene	$C_{10}H_{16}$	136.24	446	
α- Phellandrene	$C_{10}H_{16}$	136.24	447	
p-Cymene		134.22	450	
c- β-Ocimene		136.24	373	
t- β-Ocimene		136.24	373	
α-Copaene		204.36	397	
α-Cedrene		204.36	534	

There are two pathways for which you get to the synthesis of isoprenoids in plants, and they are shown in Figures 2-1 and 3-1. Both pathways require phosphorylation energy (ATP), reduction power (NADPH, NADH) and a carbon substrate like pyruvate, glyceraldehydes 3-phosphate, or acetate to form isopentenyl pyrophosphate (IPP) and dimethylallyl pyrophosphate (DMAPP) that are the isoprene precursors. One of the pathways is the so-called DXP pathway, the other the classic Mevalonate pathway. Synthesis of isoprene from IPP and DMAPP requires a specific enzyme, called isoprene synthase.

Today it is believed that most of the isoprene formation occurs in the chloroplast through the DXP pathway, and the formation through the mevalonate pathway is smaller and it occurs most in the cytosol.

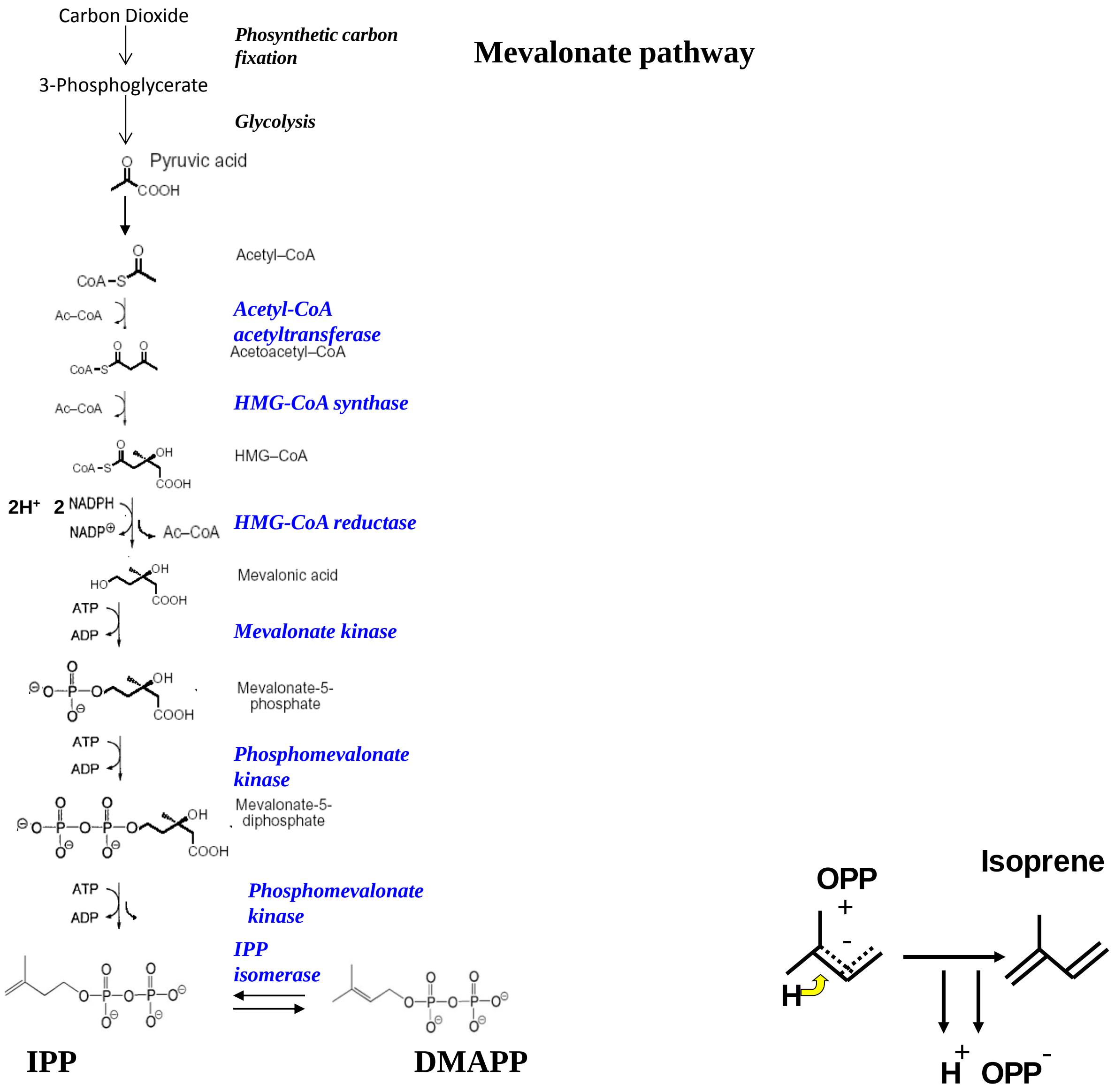


Figure 2-1 Biosynthetic pathway for isoprene production plants and Isoprene synthase. In the last step in isoprene synthesis is catalyzed by the enzyme isoprene synthase.

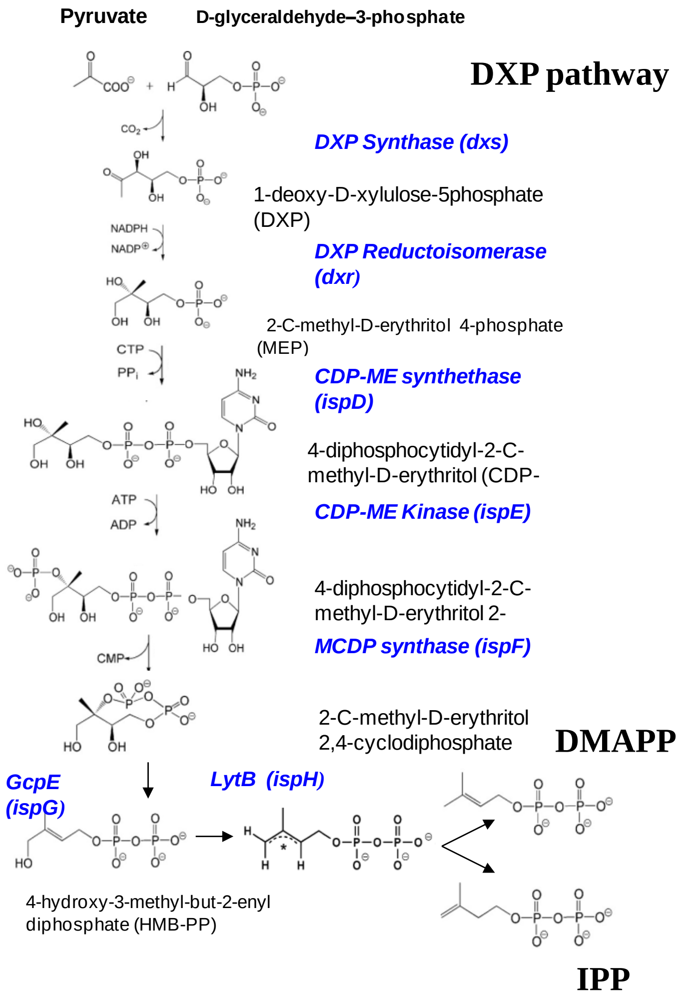


Figure 3-1 Schematic of the DXP pathway of biogenic volatile organic compound (BVOC) biosynthesis in plants.

Terpenes and sesquiterpenes are formed by a mechanism similar to that of isoprene, but a preliminary synthesis of geranyl pyrophosphate (GPP) and farnesyl pyrophosphate (FPP) is required. The final compounds are formed by proper enzymes either cyclases or synthases. Figure 4-1 shows the steps for the formation of some monoterpenes through limonene synthase.

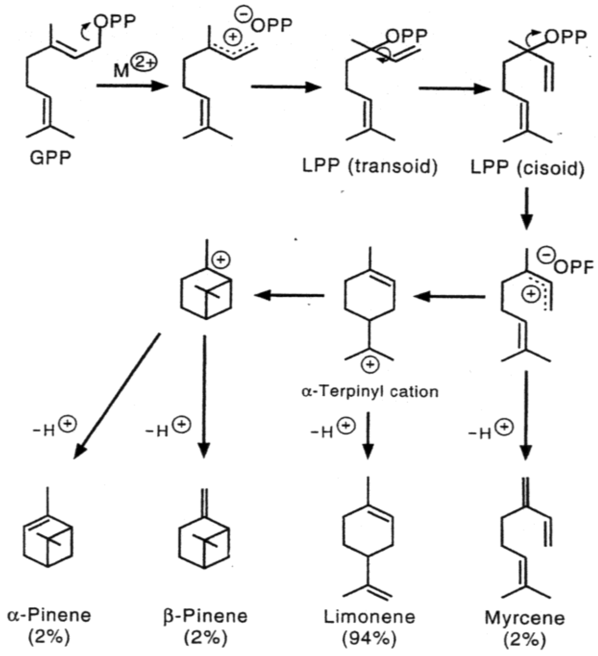


Figure 4-1 Production of terpenes from GPP as performed by limonene.

The scheme was obtained from a limonene synthase isolated from glandular trichomes of peppermint. The steps involves first isomerisation of GPP to linalyl diphosphate (LPP and than cyclization to limonene via a carbocation intermediate (α-terpinyl cation). In the active site of the enzyme, various other carbocation intermediates can form, and proton abstraction from each leads to release of small amounts of myrcene, α-pinene, and β-pinene from (McGarvey, et al., 1995). Similarly to isoprene, the synthesis of monoterpenes occurs most inside chloroplasts, although a minor contribution comes from reactions in the cytosol. There is still a debate about the site where the bulk of sesquiterpnes is produced.

1.3 Storage BVOC and emission process

Isoprenoids produced in the chloroplasts and cytosol may escape through the air passing through the stomata or they can accumulate in storage organs located inside (resin ducts) or outside the plant (glandular trichomas). In the latter case emission occurs much later after the synthesis because compounds need to across strong cellular barrier before they reach the stomatal chamber or the atmosphere. The rate determining step for the emission is diffusion through membranes which is a process solely dependent from temperature (Tingey, et al., 1990); (Guenther, et al., 1995). If synthesized isoprenoids are not stored in specialized organs, their emission occurs few minutes after their formation in the chloroplasts and cytosol. The emission is thus strictly related to the photosynthesis, and is dependent from the light and temperature. Temperature increases the emission because the activity of the enzymes for the production of isoprenoid and their precursors increases exponentially with the temperature according to the well known Arrhenius equation.

1.3.1 Algorithms utilized

This different emission behaviour of isoprenoids has been has been formalized into different empirical equations called short-term emission algorithm.

For the light and temperature dependent emission of isoprene, the following algorithm has been proposed and validated by (Guenther, 1997) in many isoprene emitting plants.

$$\mathrm{E} = E^{\circ}_{L+T}\; C_T * \; C_L \tag{1-1}$$

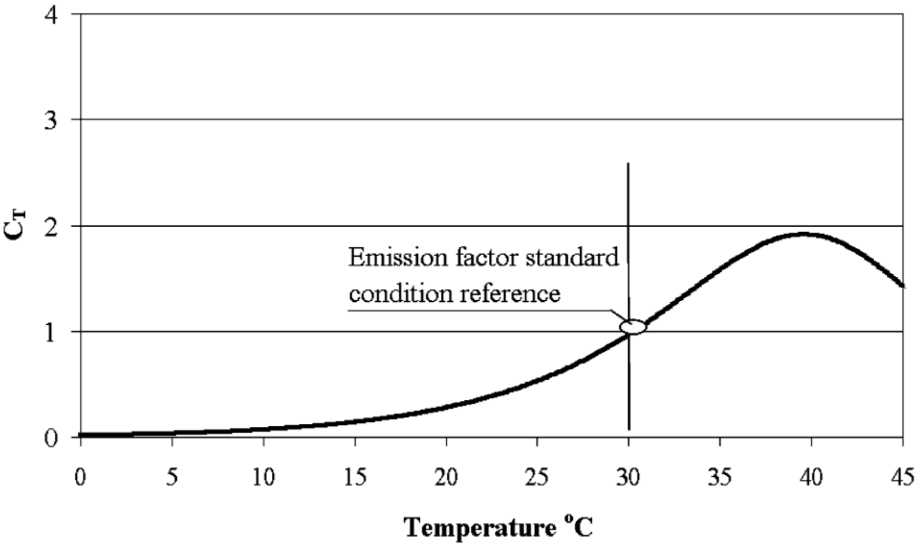
The equation allows to predict the emission E° knowledge of the value of the basal emission ($E°_{L+T}$) measured at light saturation conditions (1000 µmol gDW^{-1} h^{-1}) and a standard temperature of 30°C.

$$C_T \;=\; \frac{exp^{\frac{C_{T1}\,(T-T_S)}{R\,T_S\,T}}}{C_{T3}+exp^{\frac{C_{T2}\,(T-T_M)}{R\,T_S\,T}}} \tag{2-1}$$

and

$$\mathrm{C_L} = \frac{\alpha * \mathrm{C_{L1}} * \mathrm{PAR}}{\sqrt{1+\alpha^2 * \mathrm{PAR}^2}} \tag{3-1}$$

where α=0.0027, C_{L1}=1.066, C_{T1}=95.000 J mol^{-1}, C_{T2}=230.000 J mol^{-1}, C_{T3}=0.961, L= PAR (µmol m^{-2} s^{-1}), T=Leaf temperature (°K), T_M=314 °K, T_S=303 °K).



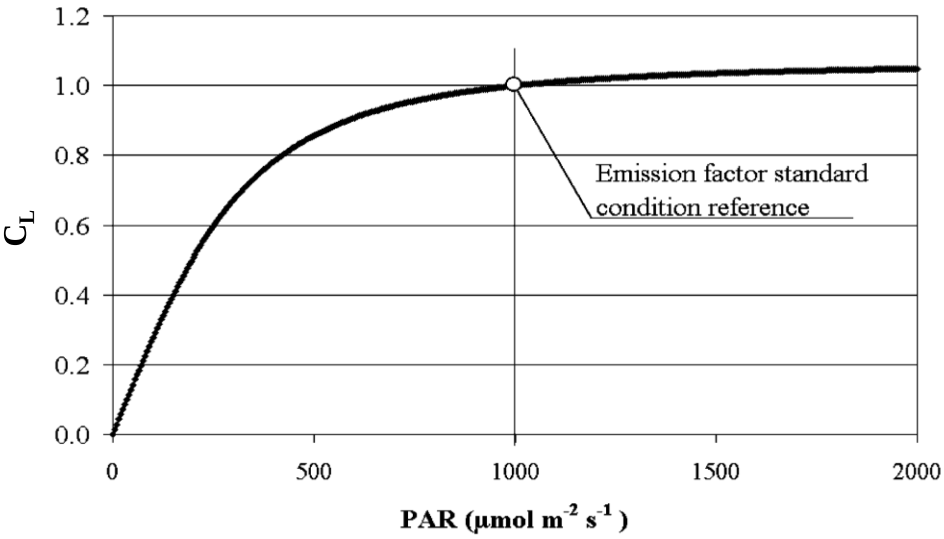


Figura 5-1 Behavior of C_T and C_L for algorithm “L+T” (adimensional) (modificated by Parra et al. (2004)

Figure 5-1 shows that C_T is almost zero for a temperature of O°C and exponentially increases with temperature up to a value of 1,9 at 40°C. For higher temperatures the value of this term decreases quite rapidly. The exponential part of the C_T is defined by the increase in the catalytic activity of the isoprene synthesis with the temperature, as it follows the classical Arrhenius trend. The decline above a certain temperature indicates that the enzyme starts to denaturants. C_L increases with an asymptotic trend and reaches a value of reach 1,1 at 1000 μmol m^{-2} s^{-1}. The trend of this term is analogous to that of the photosynthesis. In the algorithm both C_T and C_L are 1 in standard conditions.

In recent years, it has been found that this algorithm is also suitable to describe the emission of monoterpenes from some evergreen and deciduous plants, such as *Quercus ilex* (Ciccioli, et al., 1997), *Fagus sylvatica* (Dindorf, et al., 2005), *Quercus suber* (Pio, et al., 2005) and some tropical plants (Kuhn, et al., 2004). It appears to be suitable to describe the emission of all isoprenoids from the pool directly related to the photosynthesis (L+T pool).

In the case of plants that store mono and sesquiterpenes in specialized organs (resin ducts or glandular trycoma) the emission is decoupled from the photosynthesis and the process driving the emission is diffusion through the organ membranes. The process is only dependent on temperature and only the term C_T is considered. It is generally described by the following equation:

$$C_T = e^{-\beta(T-Ts)} \tag{4-1}$$

where β , which is the diffusion term, is a term ranging between 0,07 and 0,9, although (Guenther, 1997) has proposed the use on an value of 0,09.

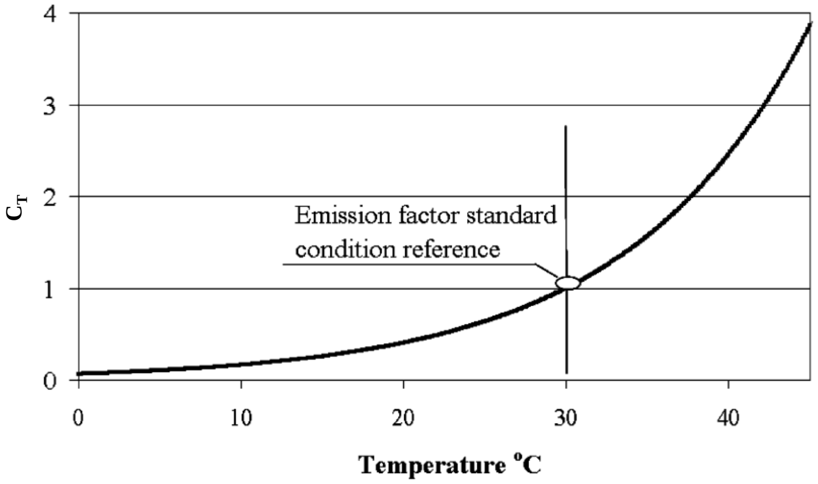


Figure 6-1 Behavior of C_T for algorithm "T" (adimensional) (modificated by (Parra, et al., 2004)

For monoterpene with dependence on temperature only (MTpool), C_T is almost zero for an leaf temperature of 0°C, increased until almost 2.5 at 40°C and keeps rising for higher temperatures (Figure 6-1).

These algorithms can be successfully applied if the value of the basal is known. One important problem is that the value of this parameter has been found to change through the year and empirical correction terms need to be used to estimate the monthly value of E°, starting from the maximum value measured in the year. Results obtained by various authors have shown that seasonal variations of E° occurs in evergreen oak species (Ciccioli, et al., 2003) and conifers (Staudt, et al., 2000) as well as in broadleaf trees (Schnitzler, et al., 1997). (Ciccioli, et al., 2003) have shown that the seasonality trend of the basal emission is the same as that followed by the photosynthesis, and it seems to be related to real changes in the physiological conditions caused by the natural cycle followed by the plants, due to environmental conditions as well as phenological processes of leaves. (Schnitzler, et al., 1997) has shown that changes in E° are related to the the production and activity of the synthases in leaves.

Another important aspect to consider, is that in some plants both pools can be active, so we may have vegetation species emitting isoprene in the L+T mode and monoterpenes in the T and L+T mode. This is the case, for instance, of *Picea abies* Karst (Grabmer, et al., 2006).

Measurements of isoprene emissions from *Quercus virginiana* (Tingey, et al., 1981), *Populus tremuloides* (Monson, et al., 1989), *Eucalyptus globulus* (Guenther, et al., 1991); *Populus tremuloides, Quercus alba, Populus fremonlii* (Fall, et al., 1992) and *Pueraria lobata* (Sharkey, et al., 1993) besides monoterpene emissions from *Eucalyptus globulus* (Guenther, et al., 1991), *Quercus ilex* (Loreto, et al., 1996), *Picea abies* (Steinbrecher, 1989); (Staudt, 1997) and *Pinus pinea* (Staudt, 1997) showed no significant influence of stomatal conductance on emission rate. Investigations on the localization of isoprene release from single leaves, discerning the abaxial from the adaxial surface by the use of microcuvettes (*Quercus virginiana, Platanus occidentalis*, (Tingey, et al., 1981); *Quercus rubra*, (Loreto, et al., 1990); *Eucalyptus globules*, (Guenther, et al., 1991); *Populus tremuloides*, *Quercus alba*, *Populus fremonlii*, (Fall, et al., 1992), clearly showed that a significant isoprene emission rate was only detectable on that leaf side containing the stomatal pores.

For monoterpene emissions, similar experiments were reported for two plant species only by (Loreto, et al., 1996) founding a monoterpene emission only from the abaxial side of *Quercus ilex* leaves, whereas (Guenther, et al., 1991) reported emissions from the adaxial side of *Eucalyptus* leaves. The apparent non-dependence of stomatal closure and isoprenoid emissions has been explained by the low, unsaturated VOC concentrations in the intercellular air spaces of the leaf mesophyll, which increase when stomata close. The decrease in stomatal conductance would, hence, be compensated by an increase in the concentration gradient between in- and outside the leaf (Monson, et al., 1991); (Sharkey, et al., 1991); (Fall, et al., 1992); (Bertin, et al., 1996); (Sharkey, et al., 1996); (Staudt, 1997).

Monoterpenes are potentially able to permeate through the cuticles, as showed by (Schmid, et al., 1992); (Schmid, et al., 1991) and (Estell, et al., 1994), as well as other gases such as CO_2, SO_2, and O_2 having a 2-3 fold higher permeability than water (Schonherr, 1982); (Lendzian, 1987). Moreover, evidence exists that monoterpene emissions from leaves are strongly influenced by cuticula hydratation (Croteau, 1977); (Lamb, et al., 1985); (Staudt, 1997). However, the results obtained with isoprenoids should not be transferred to all trace gas species. In a recent study on *Populus sp.*, (Guidolotti, et al., 2011) found an inverse correlation between isoprene emission and intercellular CO_2 concentration and a positive correlation between isoprene emission and instantaneous water use efficiency. This could indicate an indirect stomatal control on isoprene emission, mediated by a constitutively reduced intercellular CO_2 concentration.

1.4 Emission Mechanism

The BVOC emissions from leaves are not only limited by physiological factors, but also by physico-chemical constrains caused by temperature, stomatal conductance and leaf structure (Niinemets, et al., 2004). Therefore, physico-chemical characteristics such as low volatility or diffusion can also control the emission, interacting with physiological limitations. Among the most important physicochemical features, we may mention: i) volatility, determined by gas phase partial pressure, and aqueous and lipid phase concentrations; ii) the diffusion through the gas, aqueous and lipid phases within the leaves and iii) the diffusion from the leaf surface. According to (Grote, et al., 2008), the capacity for compound storage inside the plants, is depending on the control of emissions by differently, shared physiological and physic-chemical factors (Figura 7-1). In species with large storage pools such as conifers, the synthesis (I) and emission (E) rates could be effectively decoupled (**I** ≠ **E**). Instead when a storage pools is small, as in the case of isoprene, the synthesis and emission rates are essentially equal (**I** = **E**).

Gas phase diffusion at the leaf-air interface, determined by stomatal conductance, can influence significantly the synthesis and the emission of BVOCs with low Henry's law constants, such as formic acid, formaldehyde and methanol that primarily partition to the aqueous phase (Laothawornkitkul, et al., 2009). This does not apply to the less water-soluble compounds, such as isoprene and non-oxygenated terpenes that partition mainly to the gas phase (Niinemets, et al., 2004), with emission rates generally independent of stomatal conductance. The isoprene, for example, is not stored at all and is highly volatile with a small storage capacity within the leaves: therefore, its emission rate only depends on temperature and light (Laothawornkitkul, et al., 2009).

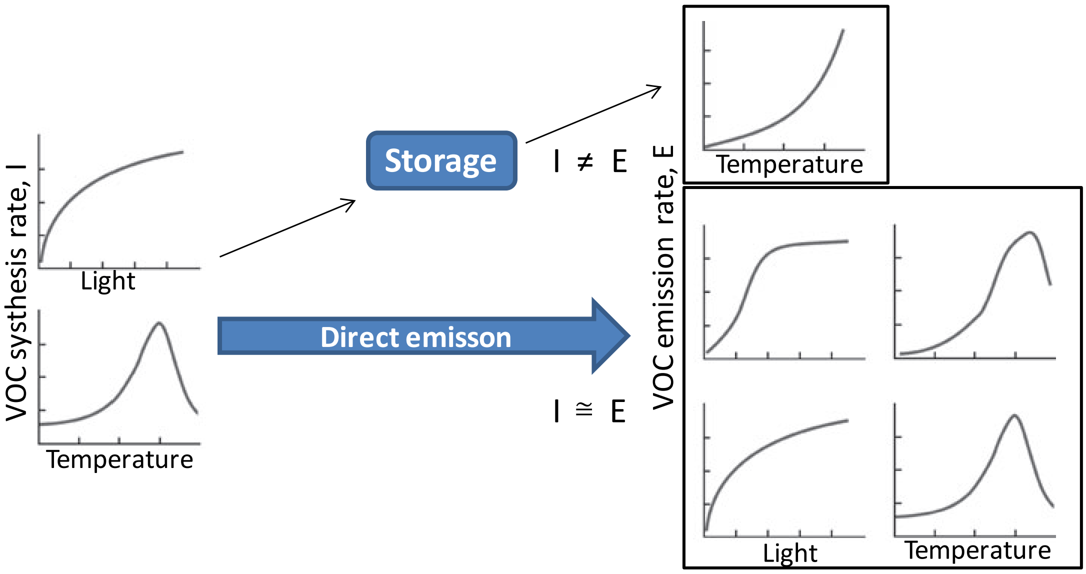


Figure 7-1 Schematic about the relationship between light and temperature controls of BVOC synthesis rates (I), and light and temperature controls of BVOC emission rates (E) (Grote, et al., 2008).

(Guenther, et al., 2000) investigated on the different mechanisms that regulate the BVOC emission from vegetation. Two of these processes have been described: (a) Synthesis in Chloroplasts and (b) Defense in specialized tissues. In the latter case, the algorithm to derive emission activity is an exponential increase with the temperature such that proposed by Guenther and colleagues (Guenther, et al., 1993), previously shown (see section 1.3). The processes occuring in chloroplasts, including emissions of isoprene (Guenther, et al., 1993), 2-methyl-3-buten-2-ol (MBO) (Harley, et al., 1998) and some monoterpenes (Kesselmeier, et al., 1996); (Ciccioli, et al., 1997), can be described as the product of temperature and the light (photosynthetic photon flux density (PPFD) (Guenther, et al., 1993). Such environmental responses were included in empirical emission algorithms that predicted plant emissions with high predictive power in some, but not in all, situations (Guenther, et al., 2000).

Until recently, it was believed that monoterpenes were emitted only by conifers and their release controlled by the needle temperature. All other vegetation species were believed to emit isoprene with a mechanism that was dependent on light and leaf temperature (Fall, 1999). Recent studies performed on European evergreen oaks (Ciccioli, et al., 1997); (Pio, et al., 2005) and deciduous species of Europe (Dindorf, et al., 2006) as well as Amazonia (Kuhn, et al., 2002) have clearly shown that both evergreen and deciduous species can emit monoterpenes with the same light and temperature dependent mechanism followed by isoprene-emitting plant. Other studies have also shown that not all conifers emit monoterpenes in a temperature-dependent mode. Some conifers (such as spruce), myrtle and eucalyptus that are common in Europe emit isoprene and monoterpenes in light and temperature dependent way (Grabmer, et al., 2006); (Staudt, et al., 2000); (Kesselmeier, et al., 1999).

The Mediterranean area includes a large number of forest ecosystems, and most of these produce and release large amounts and mixtures of terpenoids. Some species, such as *Quercus ilex* L. release terpenes directly after their synthesis (Staudt, et al., 2001). Instead, others store these biogenic volatile organic compounds prior to release, like *Pinus halepensis* Mill. (Llusià, et al., 2000).

The above studies of *Quercus ilex* demonstrated that the production and release of high amounts of monoterpenes by plants are not necessarily restricted to species storing essential oils in glandular organs. Moreover, oak forests can also constitute an important source not only of isoprene but also of monoterpenes. Nevertheless, not all oaks are isoprene emitters, with *Quercus cerris* that is a negligible emitter (Steinbrecher, et al., 1997).

According to (Niinemets, et al., 2002), monoterpene emissions respond to environmental modifications, but the emissions do not respond instantly to changes in the synthesis rates because of low volatility and low diffusion within the leaves.

In general, all studies on the emission of isoprene and monoterpenes show clear temperature dependence. Additionally, isoprene emissions have been shown to be triggered by light, as a result of the link between isoprene emission and synthesis from photosynthetic products. As no large isoprene pool exists, synthesis and hence emission will cease within minutes under dark conditions (Ciccioli, et al., 2003); (Evans, et al., 1985); (Guenther, et al., 1991); (Kesselmeier, et al., 1999); (Monson, et al., 1991); (Sanadze, 1991); (Sharkey, et al., 1991); (Tingey, et al., 1981).

2. RELEVANCE OF BVOC IN PHOTOCHEMICAL SMOG POLLUTION AND GLOBAL CLIMATE CHANGES

2.1 Global scale

Emissions inventories are based on emission factors, data on climate, land use, and/or vegetation types as well as biomass distribution. The emission factor specifies the basic emission or emission capacity of a plant species under standard conditions, usually at a temperature of 30°C and a photosynthetically active radiation (PPFD) of 1000 µmol photons m^{-2} s^{-1}. Some models cover specific climatic conditions within the vegetation canopy (Lamb, et al., 1993). Regional and global emission inventories for hydrocarbons include the most important monoterpenes and isoprene (Zimmerman, 1979); (Lamb, et al., 1993); (Graedel, et al., 1993); (Guenther, et al., 1995); (Simpson, et al., 1995). Estimates for the global carbon input by these compounds range between 127 and 480 Tg C yr^{-1} for monoterpenes and between 175 and 503 Tg C yr^{-1} (Guenther, et al., 1995) for isoprene: these values are in the same range of methane release (ca. 500 Tg C yr^{-1}, (Crutzen, 1991)) and significantly higher than anthropogenic nonmethane hydrocarbon emissions (ca. 100 Tg C yr^{-1}, (Singh, et al., 1992).

Therefore, the emissions of BVOC far exceed the global anthropogenic VOC. Though many BVOC species have been identified to be emitted from plants, much of the global flux and subsequent effect on atmospheric chemistry is probably caused by a relativity small number of compounds. Isoprene makes the largest contribution, followed by the monoterpene family (Levis, et al., 2003).

Sesquiterpenes are important precursors to secondary organic aerosols (SOAs) (Hoffmann, et al., 1997); (Bonn, et al., 2003), but estimating their emission rate and related compounds is difficult because of their reactivity and low vapour pressures. Furthermore, some oxygenated compounds, such as methanol, acetone and acetaldehyde, can play an important role in the atmosphere chemistry (Guenther, et al., 1995); (Kesselmeier, et al., 1999); (Fuentes, et al., 2000).

2.2 Lifetime of Isoprene and reactions with OH and O_3

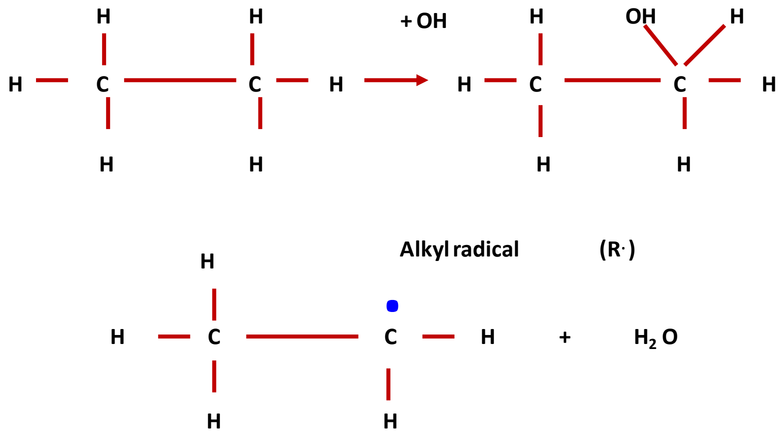
When reactive BVOCs are released into the atmosphere, they are subject to oxidation reactions, potentially leading to the ultimate products of CO_2 and water (Laothawornkitkul, et al., 2009).

Many gas-phase oxidation products have been identified from the ozonolysis of terpenes, including low molecular weight compounds, for example formaldehyde, acetone, and formic acid, and higher molecular weight products such as nopinone and pinonaldehyde, as well as other multifunctional compounds with carbonyl, carboxyl or hydroxyl groups (Calogirou, et al., 1999); (Jang, et al., 1999).

The VOC can rapidly react with the hydroxyl radicals (OH) resulting from the UV photolysis of tropospheric ozone (O_3) and other photochemical products, such as low molecular weight carbonyls, mentioned above. The initial products of the VOC-OH reaction can be further oxidized to form peroxyradicals (RO_2). This can be produced through two types of reactions:

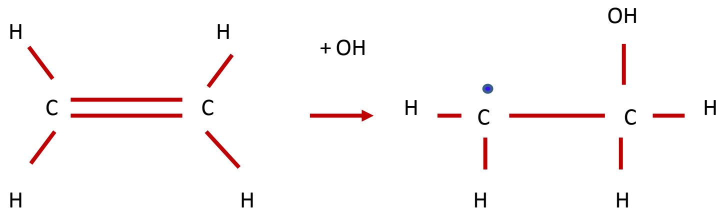
(a) Hydrogen abstraction to a saturated hydrocarbon

HYDROGEN ABSTRACTION



(b) Hydroxyl radical addition to an unsaturated hydrocarbon

HYDROXYL RADICAL ADDITION



Hydroxyalkyl radical (HOR·)

Both organic radicals react with oxygen to produce peroxyalkylradicals:

$$\begin{tikzcd} R\cdot + O_2 \arrow[r] & ROO\cdot \arrow[dr] & \\ & & RO_2\cdot \\ HOR\cdot + O_2 \arrow[r] & HOROO\cdot \arrow[ur] & \end{tikzcd}$$

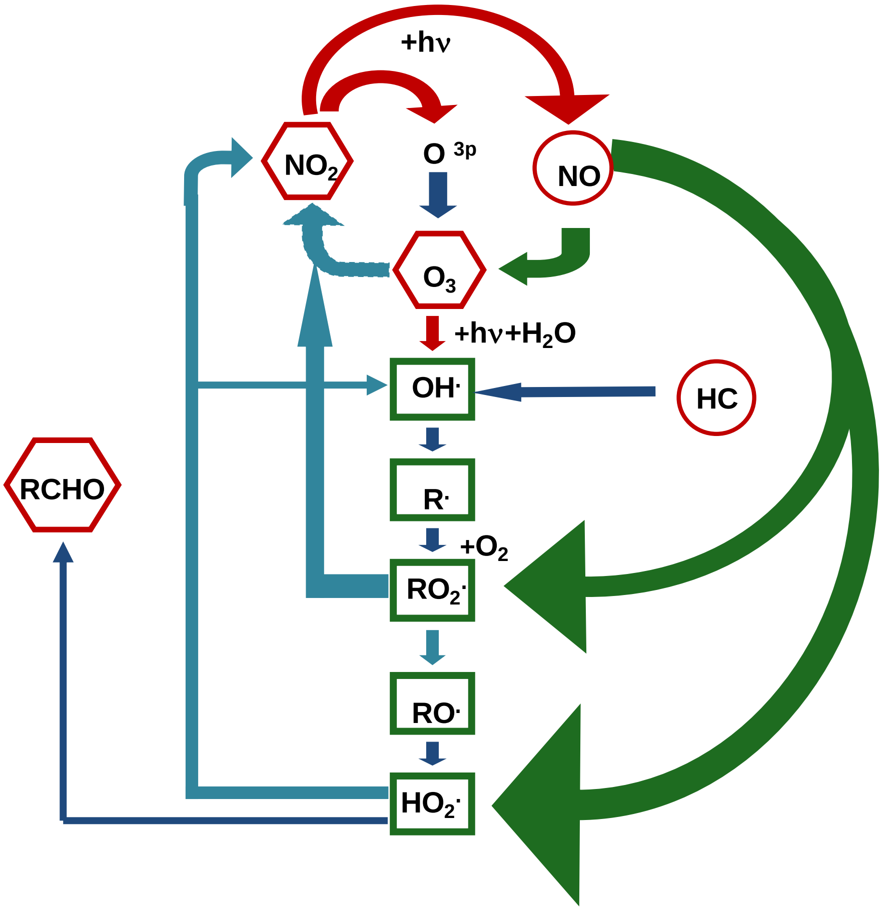


Figure 1-2 Schematic diagram summarizing of VOC to produce peroxyradicals ($RO_2^{\cdot}$).

In the presence of sufficient oxides of nitrogen, these RO_2 species may oxidize NO to NO_2, which can, in turn, be photodissociated, leading to the formation of O_3 and the regeneration of OH (Figure 1-2). Hydroperoxyradicals can also convert NO to NO_2 re-introducing OH radicals into the photochemical cycle. Therefore OH removed by VOC can be eventually regenerated. With low NO_x concentrations, $RO_2^{\cdot}$ may react with hydroperoxy radicals ($HO_2^{\cdot}$) to form less reactive peroxides, which may be removed from the atmosphere by deposition processes which lead to the net consumption of O_3 (Fehsenfeld, et al., 1992).

Besides OH, O_3 can themselves act as an oxidant for unsaturated BVOCs (Fehsenfeld, et al., 1992). The addition of O_3 to carbon-carbon double bonds leads to the formation of ozonides, which are unstable free radicals that can form OH and RO_2.

At night, when OH concentrations are effectively zero, BVOC oxidation may be driven by reaction with the nitrate radical (NO_3) (Wayne, 2000). Because of its rapid reaction with NO and its short lifetime (~5 s) in sunlight as a result of photolysis, NO_3 concentrations are low during the day but can increase substantially at night (Figure 2-2). This may lead to the removal of BVOCs that would otherwise be available for daytime O_3 formation. However, the reaction rate of NO_3 with most BVOCs are quite low (one-fifth of that with OH in the case of isoprene), and so reaction with OH is normally the dominant route of oxidation.

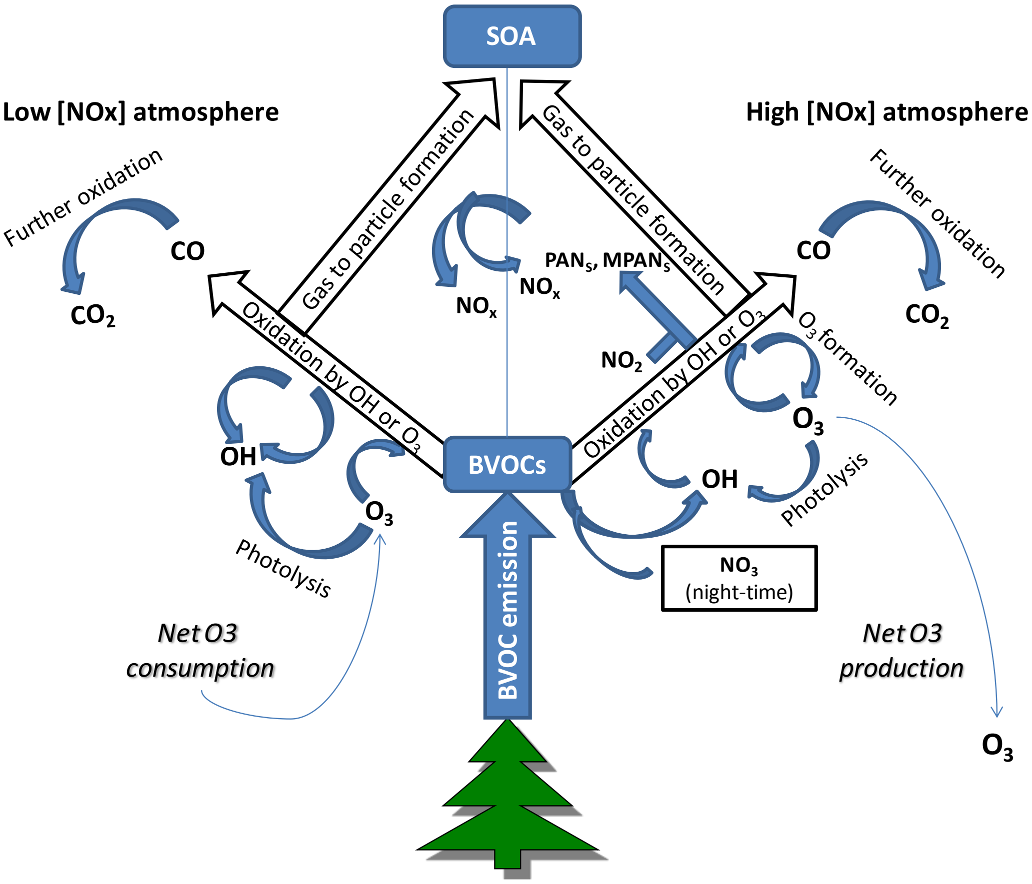


Figure 2-2 Schematic diagram summarizing the current understanding of the roles of biogenic volatile organic compounds (BVOCs) in the chemical components of the Earth system (Laothawornkitkul et al., 2009).

Carbon Monoxide (CO) influences the oxidative capacity of the atmosphere in the same way as isoprene by functioning as a sink for OH (Logan, et al., 1981). Therefore, the oxidation of CO can act as a source or sink of O_3, depending on the availability of NO_x. Once generated, CO can be transported over large distances because of its relatively long atmospheric lifetime (several months). BVOCs can therefore, in this way, influence atmospheric chemistry at global scale (Fehsenfeld, et al., 1992); (Lerdau, et al., 1997); (Lerdau, et al., 2002). According to (Calfapietra, et al., 2008), the combination of elevated concentrations of CO_2 and O_3 resulted in a strong decrease of isoprene emission in open field conditions.

Atmospheric oxidation of BVOCs and their primary oxidation products (e.g. methyl vinyl ketone and methacrolein in the case of isoprene) can, in the presence of NO_x, result in the formation of organic nitrates, including peroxyacetylnitrates (PANs) and peroxymethacrylic nitric anhydrides (MPANs) (Fehsenfeld, et al., 1992). PANs and MPANs have longer atmospheric lifetimes than NO_x (days to months) and hence can be transported over greater distances, allowing them to act as carriers of reactive nitrogen (Figure 2-2).

Several studies evidence that a broad variety of trees emit reactive BVOCs that either do not escape the ecosystem canopy, or are not typically measured by current analytical techniques. (Ciccioli, et al., 1999). Ciccioli and colleagues (1999) argued that terpenes can be oxidized within a forest canopy. These measures were realized within a forest canopy before detection by above-canopy flux techniques in an orange orchard in Spain in 1995 and 1996. This species emitted large amounts of b-caryophyllene during the summer. This compound, a reactive sesquiterpene, was observed in leaf enclosures that were not observed in simultaneous above canopy measurements, and suggested they were oxidized before escaping the orchard canopy.

2.3 Formation of aerosols

In recent years biogenic VOCs have been identified as the major precursor substances to the formation of secondary organic aerosols (SOAs) in the atmosphere (Kavauras, et al., 1999b); (Pandis, et al., 1992); (Yu, et al., 1999). The anthropogenic contribution to the SOA formation is small on a global scale, although it can be important in polluted regions (Kanakidou, et al., 2005).

Different laboratory and outdoor chamber experiments, evidence that monoterpenes, isoprenes and sesquiterpenes emitted by vegetation have a high potential to form SOAs, such as also anthropogenic species like aromatic compounds, long-chain alkaenes and alkanes can form SOA (Kroll, et al., 2008); (Surratt, et al., 2006). However, studies over tropical forests have not always found significant SOA production to the expected degree, indicating that further work is needed in this area (Rizzo, et al., 2006).

Many details in the formations process of SOA are still unknown, probably by the lack of knowledge of gaseous secondary organics involved in gas/particle partitioning. Kanakidou and colleagues (Kanakidou, et al., 2005) argued that one of chemical mechanism that form SOA is linked to the heterogeneous reactions: this processes result in the decrease of the volatility of the semi-volatile compounds that are partitioned between aerosol and gas phase. Figure 3-2 give an example of SOA formation: VOC are oxidized in the atmosphere mainly by O_3, NO_3 and OH. The oxidation process adds functional groups to the organic gas molecules and thus lowers their vapour pressure. This process partly results in gases that are again volatile and do not contribute to the aerosol formation. Another part of the reaction products however might be semi-volatile and condense to form aerosol particle, if ambient conditions are favourable (Dusek, 2000). Thus, SOA formation involves a multiplicity of semi-volatile organic compounds (SVOC) having complex molecular structures. Their low atmospheric concentrations cause analytical difficulties (Jacobson, et al., 2000); (Turpin, et al., 2000); (Kanakidou, et al., 2005). The SVOCs, which evaporate during the emission-dilution process, could condense back to the particulate phase after oxidation. The exact physical and chemical pathways to SOA formation are still not fully understood for most parent hydrocarbons.

Almost all organic material associated with the condensed phase should be regarded as semi-volatile. The SVOCs include any compound with more than 1% of its mass in both the condensed and vapour phases somewhere in the atmosphere. Given the atmospheric range of organic aerosol (OA) mass concentrations of between 0.1 and 100 $\mu g\ m^{-3}$ (Chung, et al., 2002); (Cabada, et al., 2004), compounds with effective saturation concentrations between 0.001 and 10000 $\mu g\ m^{-3}$ should be considered semi-volatile under even the most narrow definition of the term.

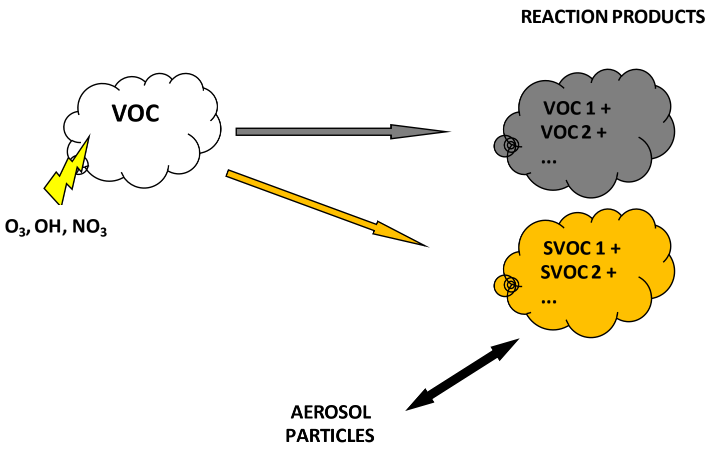


Figure 3-2 Schematic overview of SOA formation

Although it is known that a substantial fraction of the aerosol particles in remote regions is made of organic material, and that the oxidation of BVOCs may lead to the formation of SOAs, it is not yet clear how important is SOA formation in altering the climate system (Laothawornkitkul, et al., 2009).

Aerosols directly affect climate by scattering solar radiation. They also indirectly alter the Earth's radiative balance by acting as cloud condensation nuclei, changing cloud albedo and the degree of cloud cover, so potentially leading to net cooling of the Earth's surface during the day. Nevertheless increased cloud cover may also reduce the occurrence of low night-time surface temperatures, which can damage plants (Hayden, 1998) or increase average night temperature by reflecting inside infrared radiation.

Isoprene accounts for about half of all natural VOC emission, and several studies detected the presence of humic-like substances (glycol aldehyde, hydroxyl acetone and methyltetrols), indicating the involvement of isoprene as source for SOA (Jang, et al., 2003); (Claeys, et al., 2004a); (Claeys, et al., 2004b); (Limbeck, et al., 2003); (Matsunaga, et al., 2003). Claeys and colleagues (2004b) proposed that a small (0.2%) fraction of all isoprene emissions may be converted into SOA, corresponding to emissions of 2 $Tgyr^{-1}$.

The VOC potential for SOA formation depends on their lifetime; VOCs such as terpenoid ketones, terpenoid alcohols, and higher olefins, have a lifetime <1 day while less reactive VOC such as methanol and various aldehydes and ketones, have lifetimes longer than 1 day.

According to (Griffin, et al., 1999), only about 30% of the so far described VOC, have the potential to form SOA. In contrast, some monoterpenes and all sesquiterpenes have large potential for SOA formation, because of their high reactivity, with atmospheric lifetime of only a few minutes (see Table 1-2.a,b) (see the square in green) (Hoffmann, et al., 1997); (Jaoui, et al., 2003). According to (Bonn, et al., 2003), the atmospheric new particle formation observed in remote areas and generally attributed to low-volatility oxidation products of monoterpenes, may be actually initiated by products of sesquiterpenes reactions with O_3. Other studies, report that carbonyls (>C7) may be important contributors to SOA (Matsunaga, et al., 2003). Estimates indicate that SOA can be responsible for about 10-40% of the global organic aerosol (OA) mass (Kanakidou, et al., 2005); this is the sum of primary organic aerosol (POA) and SOA. In the latter case, about 90% of SOA is currently believed due to biogenic VOCs (Kanakidou, et al., 2005). .

Table 1-2.a Chemical lifetimes of Terpenes and their oxidation products. Data obtained by (Atkinson, et al., 2003).

Monocyclic	**OH radicals $2.0\ 10^{6}$ molecules cm^{3}**	**O_3 $7\ 10^{11}$ molecules cm^{3}**
limonene	50 min	2 hr
limonene ketone	1 hr	2.6 hr
limonene aldehyde	1.26 hr	2 day
terpinolene	30 min	30 min
4-methyl-3-cyclonexenone	1.5 hr	non reactive
α-pinene	2.6 hr	4.6 hr
pinonaldehyde	2.9 hr	> 2.3 yr
pinaketone	12 hr	> 8 yr
b-pinene	1.8 hr	1.1 day
Nopinone	10 hr	
3-carene	1.6 hr	11 hr
caronaldehyde	2.9 hr	> 2.3 yr
sabinene	1.2 hr	4.6 hr
sabinaketone	2.3 day	> 0.9 yr
camphene	2.6 hr	18 day
camphenilone	2.3 day	

Table 1-2.b Chemical Lifetimes of other biogenic compounds than monoterpenes and their oxidation products. Data obtained by (Atkinson, et al., 2003).

Monocyclic	**OH radicals** **2.0 10^6** **molecules cm^3**	**O_3** **7 10^{11}** **molecules cm^3**
Isoprene	1.4 hr	1.3 day
Isoprene oxidation products		
methacrolein	4.1 hr	15 day
methyl vinyl ketone	6.8 hr	3.6 day
3-methylfuran	1.5 hr	19 hr
Sesquiterpenes		
b-caryophyllene	40 min	2 min
a-humulene	27 min	2 min
a-cedraene	1.9 hr	14 hr
a-copaene	1.4 hr	2.5 hr
Alcohols		
methanol	12 day	> 4.5 yr
2-methyl-3-buten-2-ol	2.1 hr	1.7 day
Cis-3-hexem-1-ol	1.3 hr	6 hr
linalool	50 min	55 min

Table 1-2.a shows as most of the VOCs emitted from biogenic sources are highly reactive in the troposphere, with calculated lifetimes of few hours or less. Moreover some sesquiterpenes, such as b-caryophyllene and a-humulene, can shows an even shorter lifetime in presence of O3 (Table 1-2.b), and they are therefore rapidly removed by oxidation reaction once emitted from vegetation, leading to very low concentrations in the atmosphere (Atkinson, et al., 2003).

2.4 The relationship between VOC and Organic Aerosol and VOC and NO_x

The ratio of VOC to NO_x is one of the most important parameters in the behaviour of the VOC-NOx-O_3 system. Moreover, it has a major effect on how reductions in VOC and NO_x affect ozone concentrations (Committee on Tropspheric Ozone, National Research Council (CGER), 1991).

The availability of VOCs and NO_x in the morning along with their different reaction rates with the OH radical can greatly influence how much ozone is formed on a given site in a day (Seinfeld, et al., 1998).

The evaluation of the potential for photochemical ozone production of a BVOC compound has to be made for different VOC and NO_x concentrations because the production of ozone and photooxidants is strongly dependent on the VOC/NO_x regime established in the air mass (Finnlayson-Pitts, et al., 1999).

The O_3 – NO_x – VOC connection can be illustrated by a plot (Figure 4-2) generated applying to VOC and NO_x concentrations a basic ozone model called “Empirical Kinetic Modeling Approach” (EKMA) (Finnlayson-Pitts, et al., 1999). This graph shows peak of ozone formation as a function of the ratio of VOC to NO_x concentrations. It identifies threes regimes with different O_3 – NO_x – VOC sensitivities. The straight line in the centre of Figure 4-2, represents a constant VOC/NO_x = 8. The values between 5 and 15 are considered transitional, with an “optimal” production of O_3 is estimated in correspondence of VOC/NO_x ratio around 8 (Derwent, et al., 1996).

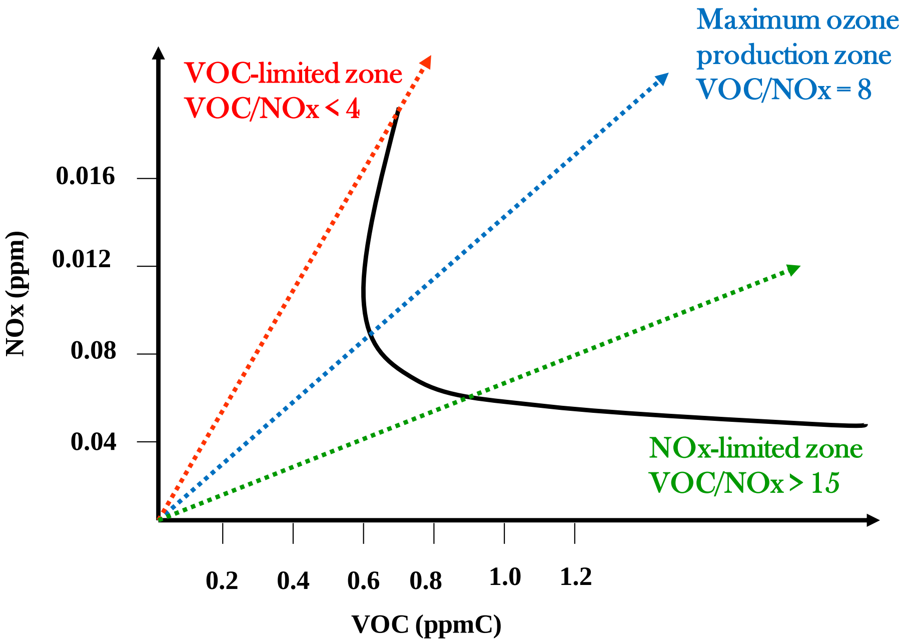


Figura 4-2 Ozone formation in three different zones of the plot as a function of the VOC/NO_X ratio.

In the urban area, (see the dotted line in red), is observed a typical situation of strong polluted areas, characterized by a low VOC/NO_x ratio, where NO_x emissions have much greater influence, the ozone synthesis is limited by VOCs concentration.

Instead for the dotted line in green, there is observed a typical situation of low polluted areas (rural). Therefore, we find a NO_x sensitive regime for ozone production, because of the higher production of biogenic VOC with respect to NO_x. In this way, in the rural air masses the ozone concentrations are most efficiently lowered by reducing NO_x, shifting in this way the VOC/NO_x ratio to less favourable value for ozone production (The VOC/NO_x ratio for maximum ozone production), while in the urban ones the same goal can be achieved by reducing the VOC concentration.

Moreover, in blue we can see the maximum ozone production zone, while the continue line in black shown a typical trend observed in suburban sites located downwind, such as an urban plume.

3. PROBLEM OF MODELLING

An important application of air quality models is to determine how pollutant concentrations respond to changes in emissions. For this type of applications, accurate emission inputs are pivotal to good model performance. Emissions inputs are developed to be compatible with both the chemical mechanism used in the photochemical models, and the model resolution (Russell, et al., 2000). Detailed and speciated VOC emissions should be lumped into the appropriate chemical mechanism categories. Emissions estimates (or inventories) need to be processed into a form used by air quality models via emissions processors that are part of the air quality modelling system.

It is generally believed that emissions are one of, if not the most, uncertain inputs into air quality models, and certainly one of the most important. Biogenic emissions are believed to be very uncertain as well, with scientists often suggesting an uncertainty of a factor of three or more (e.g. (Simpson, et al., 1995)). A recent study, found that the uncertainty in the regionally averaged impact of BVOC on ozone build-up in Europe is estimated to be ± 50%. Evaluating the impact of biogenic VOCs on atmospheric chemistry is subject at least to three types of major uncertainties: emission inventory, modelling of chemical pathways, and ambient NO_x abundance (Curci, et al., 2009).

Biogenic emissions uncertainty appears to be the dominant limitation in the current ability to accurately predict the dynamics of ozone over urban and regional scales, as well as for the impact of control strategies.

Although trends in BVOC emission rates as the Earth's climate changes are still uncertain, reactive BVOCs are of obvious concern, as they may give rise to species-specific feedbacks between plants and the atmosphere (Shallcross, et al., 2000); (Fuentes, et al., 2001); (Lerdau, 2007); (Arneth, et al., 2008). Simplistically, it may be expected that climate warming will increase BVOC emissions due to their strong temperature dependence, and so it will increase their atmospheric concentrations, causing a decrease in the concentration of OH, and so leading to a reduction in the capacity of the atmosphere to remove tropospheric methane and CO, resulting in even further global warming. Enhancement of isoprene emissions in response to rising temperatures may also have the dual effect of promoting tropospheric O_3 production in NO_x -polluted air, whilst contributing to reduced O_3 damage of leaves from isoprene-emitting species (Loreto, et al., 2001b); (Velikova, et al., 2005).

However, such simplistic models require considerable elaboration, as many BVOCs serve to protect plants against biotic stress such as insect attacks (Miller, et al., 2005); (Poecke, et al., 2004) and because of their role in enhancing plant abiotic stress resistence as well, such as against heat stress and oxidative stress generated by ozone exposure (Affek, et al., 2002); (Loreto, et al., 2001b); (Penuelas, et al., 2005); (Sharkey, et al., 2001); (Sharkey, 2005); (Velikova, et al., 2005). Greater stress resistance induced by BVOC emissions can be of particular significance in a globally changing environment that is characterized by amplification of many abiotic stresses.

Present models are unable to adequately predict these possible interactions and feedbacks, partly because the combined effect of global warming with other global environmental drivers on BVOC emissions may not always give straightforward outcomes. For example, drought episodes may remove the positive effect of warming on isoprene emissions (Fortunati, et al., 2008), whereas enhanced UVB radiation, together with warming, may actually increase emissions (Tiiva, et al., 2007). In addition, changes in cloudiness driven by BVOC emissions and subsequent SOA formation could change the intensity of the impact of photosynthetically active radiations, hence changing the emission rates of some light-dependent BVOCs.

4. EXPERIMENTAL

The research carried out over the last years within the framework of the European projects BEMA (Biogenic Emissions in the Mediterranean Area) (Seufert, et al., 1997), BIPHOREP (Biogenic VOC emissions and PHOtochemistry in the boreal regions of Europe) (Laurila, 1999), ECOVOC and VOCAMOD, have shown that many plants present in Southern and Central Europe exhibit an emission behaviour different from plants of the same family growing in North America. In particular, some Mediterranean species are strong monoterpene emitters, but they release them with the mechanism followed by isoprene emitting plant species. Moreover, some common deciduous species are basically non-BVOC emitters. Moreover, the emission-factors of many Mediterranean species are still affected by large uncertainties in terms of emission rates and iosoprenoid composition, and their dependence from environmental factors is still unknown. Emission variations can be induced by differences in latitude, climate and soil type. For some oaks, the tendency to form hybrid may change the emission behaviour. A reliable model for predicting the BVOC emission over the Italian territory requires that all the various parameters influencing the plant emission are taken into a due account. Given the complexity of plant physiology, parameterization procedures were developed in this work to describe as better as possible the effect produced by environmental factors and physiological and phonological processes. Due to the large biodiversity of the Italian forest ecosystems, different parameterization procedures were adopted for the different plant species. The estimate was also complicated by the fact that values of some environmental factors to predict the emission were required at the same spatial and temporal resolution requested by the model.

In this section we summarize the approaches that were developed and adopted to build up the BVOC emission model needed to predict the emission of isoprene and individual monoterpenes from the Italian forest ecosystems at a high spatial (1km x1km) and temporal resolution (daily basis).

4.1 Vegetation maps

4.1.1 Land cover maps

The digital land use map produced by the CORINE IV Land Cover (CLC) for the year 2006 was used in this study. The map, provided by the partners of the CARBOITALY Project, covers 301,330 km^2 with a spatial resolution (grid cell size) of 1 km^2. The UTM coordinates (North West corner) are the following: X (longitude) = 313,000 m, Y (latitude) = 5,230,000 m. Based on the coverage, the following classes and sub-classes were selected in this study.
2.2 Permanent Culture
Subdived into:

2.2.3 Olive grove
2.2.4 Wood arboriculture
Subdived into:
2.2.4.1 *Poplar culture*
2.2.4.3 *Eucalyptus*
3.1.1 Forest areas covered by broadleaf species
Subdived into:
3.1.1.1 Forest areas covered by evergreen oaks and evergreen broadleaf species (mainly *Q. ilex, Q. suber, Q. cocifera*)
3.1.1.2 Forest covered by deciduous oaks (mainly *Q. cerris, Q. pubescens, Q. frainetto, Q. petraea, Q. robur*)
3.1.1.3 Mixed forest areas covered by autoctonous broadleaf species (*Acer platanoides, Fraxinus excelsior, Fraxinus ornus, Ostrya Carpinifolia*)
3.1.1.4 Forest area covered by *Castanea sativa*
3.1.1.5 Forest areas covered by *Fagus sylvatica*
3.1.1.6 Wooden areas covered by hygrophillic plants (*Salix sp., Populus sp., Alnus sp.*)
3.1.1.7 Wooden areas covered by exotic broadleaf trees (*Robinia pseudoacacia, Ailanthus altissima*)

3.1.2 Forest areas covered by conifers
Subdived in:
3.1.2.1 Forest covered Mediterranean pines and Cypress trees (*P. Pinea, P. Pinaster, P. Halepensis*)
3.1.2.2 Mixed forest covered by Mountain pines (*P. Nigra, P. Sylvestris*)
3.1.2.3. Forest covered by Norway spruce (*Abies alba, Picea abies*)
3.1.2.4 Mixed forest covered by *Larix decidua* and *Pinus Cembra*
3.1.2.5 Forest areas covered by exotic conifers (*Pseudotsuga menziesi, P. Radiate, P. Strobes*)

According to these maps, the surface covered by deciduous, coniferous and broad leaf forests was 18.20%, 5.09% and 1.09% of the entire territory. Values of the coverage were also provided for each of the subclasses.

These maps, although useful for many forest applications, were not so suitable for estimating species-specific BVOC emission because in many instances, they included forest species exhibiting different emissions and followed different emission algorithms.
The maps, that were originally supplied in the IDRISI format (IDRISI Kilimanjaro, ©Clark Labs, 2006) were converted into an ArcGIS 9.3 (©ESRI, 2008) format, that was used for the model development.

4.2 Meteorological maps

Meteorological data on leaf temperature (in K°) and solar surface radiation (W m^{-2}) from MODIS are the drivers used as input for the BVOC emissions model. The meteorological parameters necessary for estimating the BVOC emissions were the foliar temperature and the PAR. Foliar temperature and solar radiation data were provided in grid format maps by CARBOITALY project, at the spatial resolution of 1 km x 1 km and daily temporal resolution for the year 2006. The PAR was therefore not directly available and it was calculated using a linear correlation to convert the total radiation given in the meteorological maps into PAR; the regression line parameters were given by (Jacovides, et al., 2004).

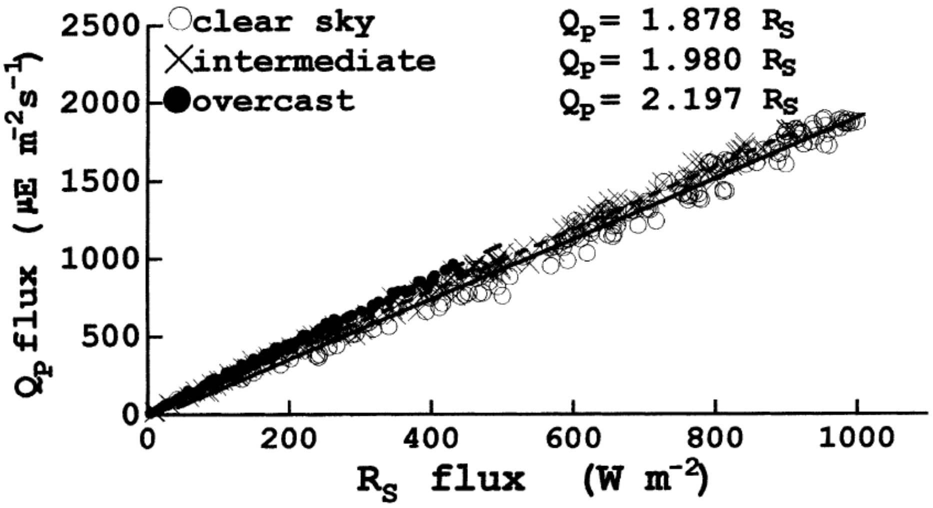


Figure 1-4 Regression lines shown correspond to clear (solid), intermediate (short-dashed) and overcast (long-dashed) skies, respectively (Jacovides et al., 2004).

This correlation is based on hourly data of photosynthetic photon flux density (Q_P) and broad solar irradiance (R_S).The dependence on Q_P by R_S is influenced by the cloudiness, so the angular coefficients of the regression line are given for three different conditions (clear sky, intermediate and overcast) and ranges from 1.878 to 2.197 (μE J^{-1}); the ratio on clear days is 14.5% lower than that on overcast days indicating that the clouds reduce the hourly global solar radiation proportionally more than the spectral PAR portion (Figure 1-4).

Considering the mean Italian climatic characteristics, we chosen the linear regression corresponding to intermediate cloudiness.

The leaf temperature data are available as daily means: in fact we could not obtain from satellite data more accurate. They were therefore derived indirectly approximating the daily trend of leaf temperature to a Gaussian curve (Figure 2-4), whose integral was equal to the area of a rectangle having a side equal to the daily length and a side equal to the mean temperature value. A typical temperature diurnal variation was reproduced assuming that temperature was minimum around 6:00am, increasing linearly to reach the maximum value around 12:00 pm and then decreasing linearly to reach the minimum value again. The daily trend of PAR was obtained in the same way (Figure 3-4).

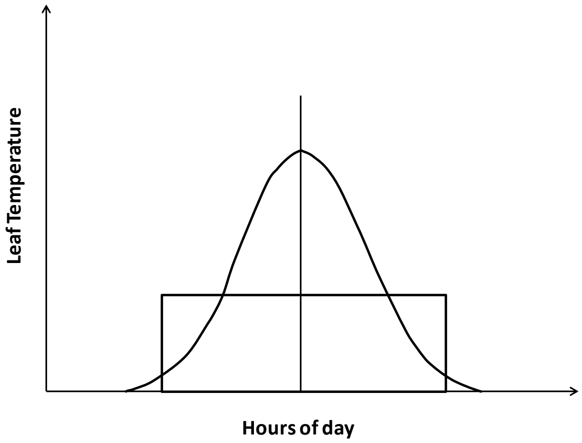


Figure 2-4 Parameterization of the daily trend of the leaf temperature and the PAR, based on mean values obtained from satellite data.

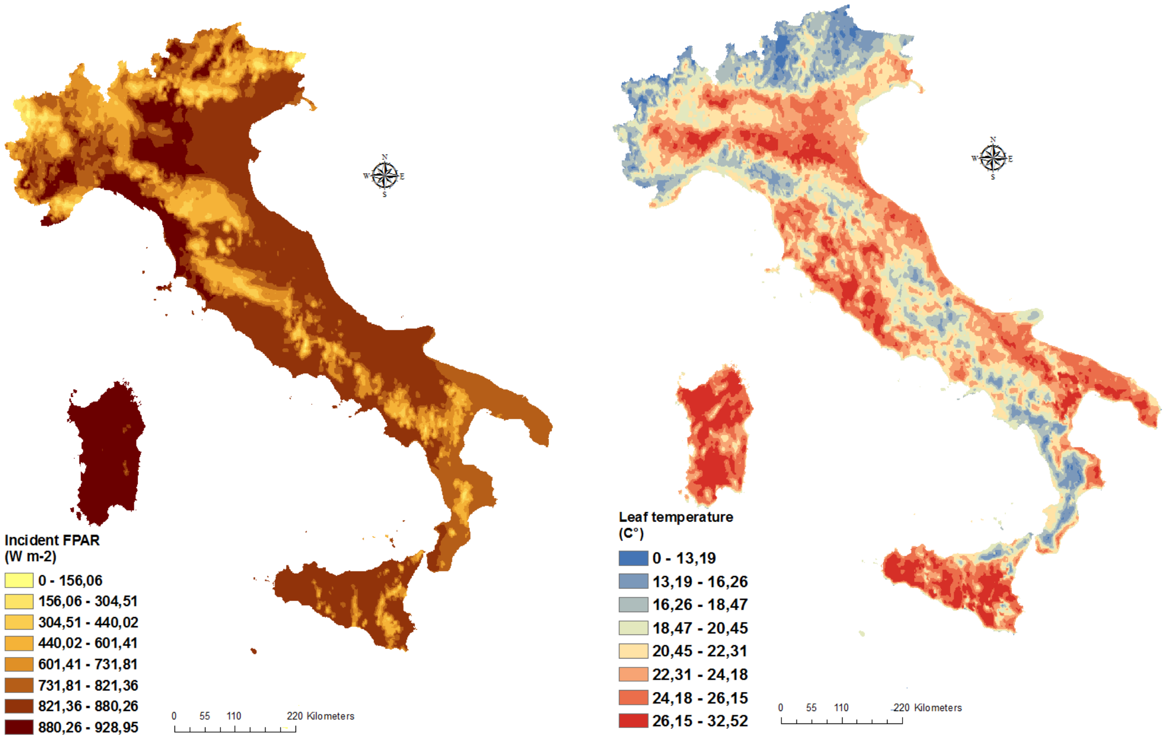
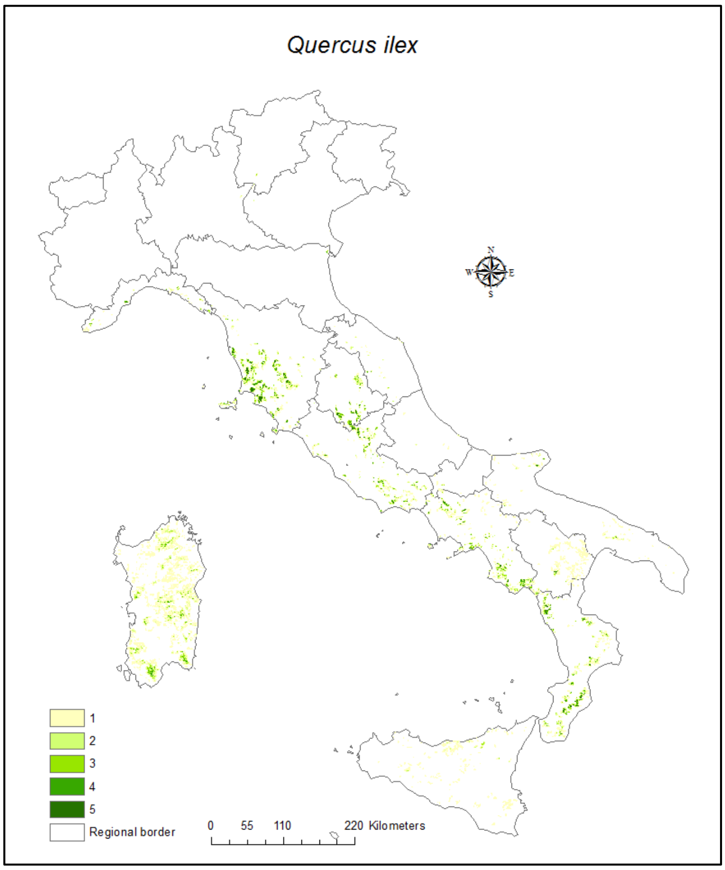


Figure 3-4 Example of the geographic distribution of FPAR and Leaf temperature in Italy obtained for July 29nd, 2006.

4.3 Foliar biomass density

At stand scale the VOC emissions not only depends on the species compositions and the environmental condition, but also on the amount of foliar biomass density present for unit land area. Previous studies considered this parameter as a constant, independently on the phenological estate of the vegetation during the vegetative season. Nevertheless, more information on the seasonal VOC emission dynamics at the national scale can be obtained introducing the LAI as variable: in our work we used the Leaf Area Index (LAI) data for the year 2006, obtained from high resolved satellite observation (MODIS, MODerate-resolution Imaging Spectroradiometer) provided by the partners of the project. The frequency of the satellite observations was 8-day. The foliar biomass density was calculated combining the LAI maps with species-specific value of SLA. To estimate the foliar biomass density we used data collected during recent years along with data previously reported in the literature. For each species the SLA value was considered constant during the year.

Through this procedure we obtained maps of foliar biomass density (D_B) for each class of Table 1-4. The SLA values used for each plant species are reported in Table 3-4 and 4-4. Therefore, the D_B was calculated daily for the year 2006; Figure 4-4 shows an example of D_B for the species *Q. ilex* (Julian day 217, August 07th, 2006). The LAI value with 8-days frequency was integrated in the daily calculation of the emission.



Foliar biomass density [g m-2]		
🟨	1	0 - 240
🟩	2	240 - 480
🟩	3	480 - 720
🟩	4	720 - 960
🟩	5	960 - 1200

Figure 4-4 Geographic distribution of foliar biomass density in Italy for the *Q. ilex* species (Values obtained for August 07th, 2006).

4.4 Method utilized for measuring BVOC fluxes

A commercial tethered balloon (volume 9 m^3, Aerial Products Corp., FL, USA) was used to collect VOC samples. An electric winch was employed during the campaign to raise and pull down the balloon.

Biogenic and anthropogenic VOCs were directly collected into glass cartridges (160 mm length, 3 mm I.D.) packed with 156 mg Tenax TA using automated air sampling systems (pocket pump 210 series, SKC Inc, PA, USA). Samplers were programmable and equipped with flow controls to pass equal amounts of air into the traps. They were programmed to get the simultaneous sampling of VOCs at all levels. Flow rates of 110-120 ml min-1 were used and 7-8 L of air collected into the traps. Temperature and pressure sensors (PCE, Italia) were attached to the pumps recorded with a sampling rate of 1 s. After samplings the cartridges were purged with helium to remove ozone, kept at low temperatures (0°C) and analysed within 30 days after the experiment. The tethered balloon fluxes, with an estimated footprint of several km2, are assumed to be representative of the combination of the characteristic local-scale landscape elements in this area, including plateaus, slopes and valley.

The cartridges were analyzed by thermal desorption gas chromatograph (GC 5890, Hewelett Packard, Palo Alto, CA, USA) with mass spectrometer (MSD 5970, Hewelett Packard) following the methodology described by (Ciccioli, et al., 2002).

4.5 Model Run

The BVOC modelling has been performed in a grid approach with 1 km x 1 km grid in Transverse Mercator projection compatible with meteorological input data. The period estimated was from 1 January to 31 December 2006. In the model daily emissions of isoprene and individual monoterpenes have been estimated for both day and night. In the latter case, we estimated only for species with dependence on temperature (algorithm T), such as, spruce, conifers and broadleaved evergreen species.

Moreover, we estimated the BVOC emissions for winter seasonal. In this case, deciduous species were excluded due of them seasonal trend, that indicate the fall of leaves in this period.

Several software has been used during the development of this study. For the GIS applications we used ArcGIS 9.3 (©ESRI, 2008) software package, to deal with remote sensed data we used to IDRISI Andes (©Clark labs, 2006) software. To write the lines of AML (Arc Macro Language) program, we used EditPad Lite (©Jan Goyvaerts, 2010) software. Thus, the model was written adapting the reading of inputs, the computation and the output creation to the requests of GIS visualization and processing software used in this work.

Therefore, were effected different cartographic processes to obtain the output databases in our work, the mainly are the following:

- Conversion of Idrisi file, from IDRISI grid (rst) to ASCII grid (asc) dataset, for the following files: CORINE IV Land Cover, FPAR, LAI, Leaf temperature, all these were provided by project. For this, we created a file IML (IDRISI Macro Language) that contains the syntax of the command lines for each file to be converted. Moreover, this file contains a list of modules and their parameters to be run the File/Run Macro dialog box into IDRISI. This Macro Language files was created in EDIT and saved with .iml extension.

The ASCII grid is a text file that contains all values of the individual grids, presenting the values for separate cells. In this format the values for the individual cells are stored in rows and columns with a header that describes the format. All the input data of the model are in ASCII grid format and present the same characteristics of extent.

- Exportation of all files, from IDRISI software and import into ArcGIS environment. In relation to import in ArcGIS, we converted the file ASCII (asc) to GIS format through the tool Arctoolbox/Conversion tool/To Raster/ASCII to Raster into ArcGIS environment.

- We masked the areas corresponding to each region of Italy with the aim of realized the reclassification of the CORINE Land Cover (see Table 1-4), this was obtained into Arctoolbox/Spatial Analyst Tool/Extraction/Extract by Mask into ArcGIS environment.

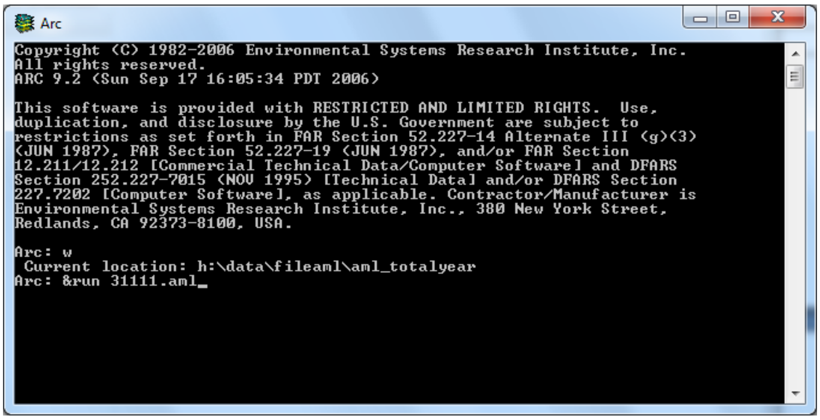
To automate the computation process, we wrote a macro running under ArcGIS (Figure 5-4) that, taken input grids, it process them in order to obtain the final grids of VOC emissions. For each day of the year 2006 simulation, we used the following ArcInfo input grids:

- Land cover database reclassified according to Table 1-4.

- 46 grids reporting the 8-day Leaf Area Index (LAI).

To calculate the algorithms of temperature and light for each day of the year 2006 we used:

- 365 grids reporting foliar Temperature (in °K) and Total Radiation (in W m^{-2}).



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ARC 9.2 (Sun Sep 17 16:05:34 PDT 2006)

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227.7202 [Computer Software], as applicable. Contractor/Manufacturer is
Environmental Systems Research Institute, Inc., 380 New York Street,
Redlands, CA 92373-8100, USA.

Arc: w
 Current location: h:\data\fileaml\aml_totalyear
Arc: &run 31111.aml_
```

Figure 5-4 Window of the ArcInfo tool that allows execute the file AML.

This tool was developed as tool of Arctoolbox into ArcGIS and as AML executable. AML is the language through which communicate in the ARC environment. An AML program might be composed entirely of commands from ARC or any the subsystems. However, there are several other elements of AML that allow for the creation of more powerful and flexible applications. AML is an interpreted language. Each line of an AML passes through the AML processor before be executed by the current arc program.

4.6 Evaluation of model performance

To assess the quantitative performance of the model in the estimation of the species-specific individual isoprenoids emissions, we utilized the coefficient of determination (R^2) and, as described by Collalti (2011), Feikema et al. (2010) and Stape et al. (2004), the main statistics indicators, such as:

Relative average error (e%)

$$e\% = 100 * \left(\frac{P - \bar{O}}{\bar{O}}\right) \tag{1-4}$$

Mean absolute error (MAE%)

$$MAE\% = 100 * \frac{\left(\left(\sum_{i=1}^{n} P_i - O_i\right)/n\right)}{\bar{O}} \tag{2-4}$$

The error (relative or absolute) is an adimensional algebraic quantity, expressed by the relationship between two homogeneous quantities. The relative error is used to quickly estimate the tolerability of the error, comparing it directly with the quantity measured. The lower the value of the relative error, the greater the accuracy of the resultant estimate. Thus, the relative and absolute errors are reported as a percentage.

The coefficients of efficiency (EC, EF)

$$EC\ (ME) = 1.0 - \frac{\sum_{i=1}^{n} (P_i - O_i)^2}{\sum_{i=1}^{n} (O_i - \bar{O})^2} \tag{3-4}$$

$$EF = \frac{\sum_{i=1}^{n} (O_i - \bar{O})^2 - \sum_{i=1}^{n} (P_i - O_i)^2}{\sum_{i=1}^{n} (O_i - \bar{O})^2} \tag{4-4}$$

They provide a quality degree value of the estimate compared with the measured values. Values between 0.6 and 0.8 are considered satisfactory, values above 0.8 good, and are considered excellent values close to the unit.

The root mean square error (RMSE)

$$RMSE = \frac{\sum_{i=1}^{n} (P_i - O_i)^2}{n} \tag{5-4}$$

The root mean square error is a dispersion index of experimental measurements, derived directly from variance values. It has the same units of the observed parameters. When it is value is close to 0, the model can be described as an excellent predictor.

O_i and P_i are the measured and estimated values, respectively $\bar{O}$ and P are their respective averages, and n is the number of observations.

5. MODEL DEVELOPMENT

5.1 General structure of the model

The input data necessary to calculate the various contributions to achieve the final result are summarized in Figure 1-5. The model consists of five different modules where the emission is obtained from the spatial distributions of vegetation species present in Italian forest ecosystems, meteorological data using proper emission algorithms and the speciated basal emissions rates. For each species, the amount of the emitting biomass was obtained by elaborating LAI maps made available for the year 2006 by the CARBOITALY project. Specific parameterization procedures were developed to upscale individual plant emissions to the canopy. Input data needed by the different modules were introduced into the model and mathematically treated using a GIS software able to incorporate all the equations and algorithms needed for the calculations.

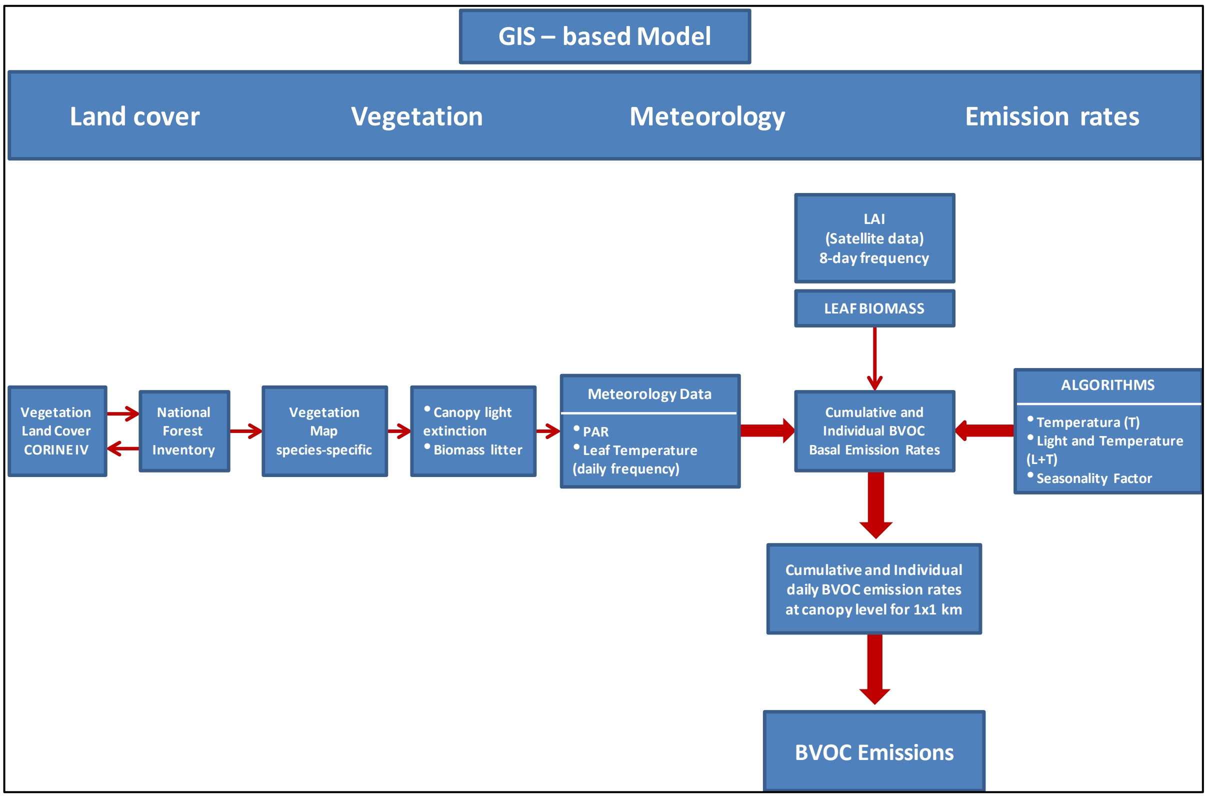


Figure 1-5 Schematic diagram of the various modules of the GIS model.

In the next sections the improvements made to the input data and to the various steps to achieve a species-specific emissions area described.

5.2 Development of species-specific vegetation maps

Since the classification system made by CORINE Land Cover (CLC) often provides surface coverages only for a group of species characterized by different isoprenoid emissions, which also follow different emission algorithms, the only way to get reliable input data for our model was to derive from them species specific vegetation maps.

To achieve this goal, the original land cover maps were compared with those provided by National Forest Inventory (INFC, http://www.infc.it), funded by Ministry for Agriculture and Forestry. While the CLC maps were obtained from satellite observations, the INFC maps were based on data collected in the field by the forestry departments of each Italian region. In many cases species specific-data were provided allowing to derive the land cover from the CLC maps. The only problem with these INFC maps was that the data were not available on a GIS format. By comparing the spatial distribution of vegetation species in the two land cover systems, we were able to derive, by difference or by interpolation, the surface coverage for the species that in the CLC were classified into the same sub-class, but exhibited substantial differences in the emission rates, emission composition and emission algorithms. The procedure followed is illustrated well in Figure 2-5 where the surface coverage of the evergreen species *Quercus ilex* and *Quercus suber* were obtained from those indicated by the CLC as evergreen broadleaf species.

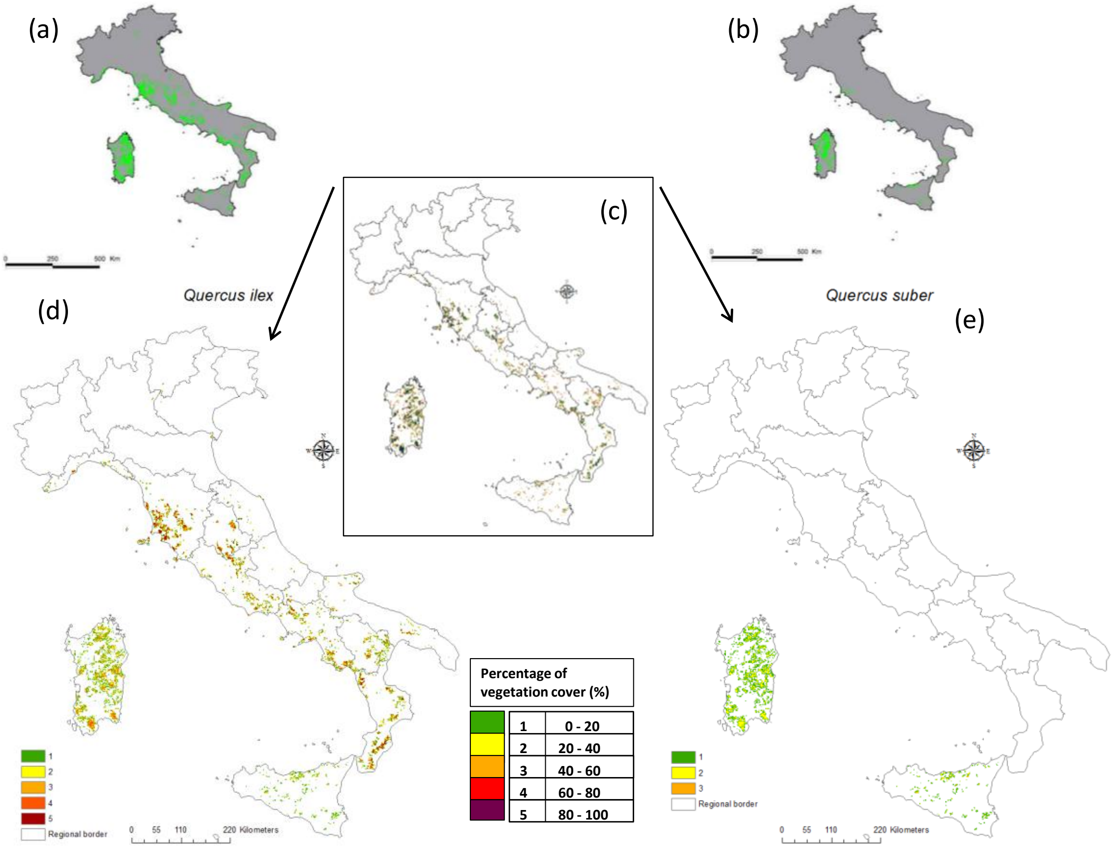


Figure 2-5 Geographical distribution of vegetation species present in Italy. (a) Distribution of the *Q. ilex* in the category of high forest of the INFC; (b) Distribution of the *Q. suber* in the category of high forest of the INFC; (c) Map of vegetational cover of broadleaved evergreen forest (CLC, classes 3111; see section 4.1.1), (d) Map of *Q. ilex* species (CLC, classes 31112) and, (e) *Q. suber* species (CLC, classes 31111).

Table 1-5 reports the comparison between the surface coverage of *Quercus suber* and *Quercus ilex* that were obtained starting from the CLC maps for broadleaf evergreen species.

Table 1-5 Fractional contents of evergreen oak species in Italy

Territorial district	**Broadleaved (*) evergreen (km^2)**	***Quercus ilex* (km^2)**	***Quercus suber* (km^2)**
Piemonte			
Valle d'Aosta			
Lombardia	3,61	3,62	
Trentino A. A.	2,09	2,09	
Veneto	2,23	2,23	
Friuli V. G.			
Liguria	85,40	85,40	
Emilia	7,44	7,44	
Toscana	1.168,86	1.162,86	
Umbria	292,96	292,96	
Marche	48,89	48,89	
Lazio	522,36	522,36	
Abruzzo	10,06	10,06	
Molise	15,44	15,44	
Campania	654,22	654,22	
Puglia	176,65	176,62	
Basilicata	343,91	343,91	
Calabria	816,50	816,50	
Sicilia	413,26	223,4	190,84
Sardegna	2.807,67	1.796,97	1.013,42
Italy	**7.371,55**	**6.165**	**1.204,26**

(*) Data provided by National Forest Inventory (INFC)

By extending this approach to the group of vegetation species differing in emission composition and emission algorithms 20 classes of vegetation species out of the original 10 were produced for modeling purposes and they are listed in Table 2-5.

Table 2-5 Comparison between the vegetation classes given by the CLC and those obtained by combining these data with the National Forest Inventory.

N°	Original classes from CLC	Species specific classification obtained in this work	Species
1	3.1.2.3	3.1.2.3.1	*Abies alba*
2		3.1.2.3.2	*Picea abies*
3	3.1.1.3	3.1.1.3.2	*Carpinus betulus*
4		3.1.1.3.1	*Fraxinus excelsior*
5	3.1.1.4	3.1.1.4	*Castanea sativa*
6	3.1.1.5	3.1.1.5	*Fagus sylvatica*
7	2.2.4.3	2.2.4.3	*Eucalyptus*
8	3.1.2.2	3.1.2.2.1	*Pinus nigra*
9		3.1.2.2.2	*Pinus sylvestris*
10	3.1.2.1	3.1.2.1.1	*Pinus pinea*
11		3.1.2.1.2	*Pinus pinaster*
12		3.1.2.1.3	*Pinus halepensis*
13	3.1.1.2	3.1.1.2.1	*Quercus cerris +Quercus frainetto*
14		3.1.1.2.2	*Quercus pubescens+Quercus petrea+Quercus robur*
15	3.1.1.1	3.1.1.1.1	*Quercus suber*
16		3.1.1.1.2	*Quercus ilex*
17	3.1.2.4	3.1.2.4	*Larix deciduas+ Pinus cembra*
18	2.2.3	2.2.3	*Olea Europaea*
19	2.2.4.1	2.2.4.1	*Populus spp.*
20	3.2.3.2	3.2.3.2	Garrigue

The Table 2-5 shows that, although the numbers of sub-classes were doubled, some of them were still comprised of a combination of species, whose emission was quite homogeneous in terms of composition but sometimes different in terms of emission rates. For some of these sub-classes, such as that composed by *Quercus cerris* and *Quercus frainetto,* the possibility to get reliable maps for individual species is quite difficult as they are often associated even in the inventory maps of tress made for local use. Therefore a parameterization procedure was necessary to work with our model. We considered that the presence of the last two species is negligible in most of the Italian ecosystems and no large errors are introduced in the model by neglecting their contribution to the emission. We also considered that *Quercus cerris* was also much more abundant than *Quercus Frainetto* in many instances, and that assuming a constant ratio of 9:1 for the entire territory would have limited the uncertainty within reasonable values. A similar approach was followed in the case of the sub-class 3.1.2.4 (Mixed forest covered by *Larix decidua* and *Pinus Cembra)* that was composed of *Larix decidua* and *Pinus cembra*. We assumed that these species were in a ratio 4:1 in all cells. For the sub-class composed by *Quercus pubescens, Quercus petrea* and *Quercus robur,* there was no need to generate more detailed maps because, as we will see later, all these oaks emit isoprene at quite similar rates. For the case of the Garrigue, the idea of getting a species-specific emission rate was too complex, and integrated values obtained from ecosystem fluxes recently measured in Castelporziano for isoprene and total monoterpenes were used. The dependence from environmental parameters for monoterpenes was assessed by considering the behaviour of some of the most common vegetation species present in this ecosystem.

5.3 Basal emission rates used in the species-specific model

By considering the results that were recently obtained by various authors (Ciccioli, et al., 2003); (Ciccioli, et al., 1999); (Loreto, et al., 1996); (Seufert, et al., 1997); (Steinbrecher, et al., 1997), the most suitable input for our model was to have basal emission rates of individual compounds for the 20 subclasses listed in Table 2-4, by distinguishing them according to the emission algorithm each compound follows. Therefore the entry in our model was composed by compounds that were classified as L+T and T according to their emission algorithm. The former term was used to indicate those isoprenoids (both isoprene and individual monoterpenes) whose emission was directly related to the synthesis in the chloroplasts, the latter was used to indicate those monoterpenoids whose emission was delayed with respect to the production because of a temporal storage in specialized organs. This approach is formally equivalent to that already used by (Karl, et al., 2009) and (Steinbrecher, et al., 1997) for producing their emission inventories for Europe. However, some substantial differences exist with respect to our approach. (Karl, et al., 2009) still produce their data in terms of BVOC classes, and the results are given as isoprene, total monoterpenes, sesquiterepnes and other VOC. The approach followed by (Steinbrecher, et al., 2009), is much closer to the one developed by us, as these authors made an attempt to quantify the relative emission of the prevalent monoterpenes emitted by various ecosystems. An analysis of the basal emission rates used by these authors showed that in many cases, values used were falling in the upper range reported in the literature and they may overestimate the real emission. The reliability of basal emission values is, however, one of the most critical issues to model isoprenoid emissions. Indeed this value may drastically change with the season, but also from the experimental approach used (Niinemets, et al., 2011). To get reliable emission values with the enclosure approach, it is important that the plant stays in environmental conditions very close to the real world. In the past very little attention has been paid to this aspect, mainly because the photosynthesis was not controlled during the BVOC emission determination. Data have shown that to prevent heat stress, the exchange rate of air in the enclosure should be quite fast (0,5 exchange min^{-1}) and the enclosure well mixed. Moreover, the content of biomass should be such to prevent injuries to the plant and to avoid excessive shading. However, guidelines to get reliable emission values have been only recently proposed, and it is now clear that the large differences in the basal emission of many isoprenoids found in the technical literature may be explained by the improper conditions in which determinations were made. To reduce the uncertainty associated with basal emission rates, two approaches were followed in our study.

For some of the most common plant species present in the Italian forest ecosystems, basal emission determinations were performed with enclosures working in the proper conditions. The species investigated were: Q*uercus cerris, Castanea sativa, Fraxinus ornus, Quercus suber, Acer platanoides, Fagus sylvatica, Carpinus betulus, Fraxinus excelsior* and *Pinus pinaster*. Determinations were carried out in the year 2007 at the time of the year where the highest emission occurred (July-August). To be sure that the plant was not under stress, the emission was measured concurrently with the photosynthesis and water transpiration. The stomatal conductance was also determined during the experiments. The chamber was equipped with a temperature control system to get a value of the temperature equal to 30±1 °C. The enclosure was equipped with a sensor to be sure that the emission was measured at saturation conditions (1000 μmol m^{-2} h^{-1}). Determinations were carried out when the plant was in the dark (emission T dependent) and at 1000 μmol m^{-2} h^{-1} (emission L+T dependent) of PAR. Three dark-light cycles were performed for each plant species, using three different specimens of young plants grown in small pots. The emission was controlled on line with PTR-MS supplied by Ionicon Analytik Ges.m.b.H Innsbruck, Austria. This instrument provided values of isoprene, total monoterpenes and some oxygenated VOC (namely methanol, acetaldehyde and acetone). Parallel sampling of the emission was performed on cartridges filled with solid sorbents (Tenax GC and Carbopack B, supplied by Supelco, USA) able to retain isoprene, monoterpenes and high molecular weight oxygenated BVOC. Six traps for each specimen were collected and they were analysis by two different laboratories using a MSD, 5970 (Hewlett Packard, Palo Alto, Ca, USA) connected to a GC 5890 from the same company. Traps were thermally desorbed and compounds indentified and quantified with the technique described in (Chung, et al., 2002). With this approach we were able to get values of the emission for different isoprenoids, coming from different pools.

Data refer to the time of the year when this parameter reached the maximum value ($\mathring{E}_{max}$). They were checked for consistency by comparing them with those obtained by different authors with enclosures installed in the field. Data obtained on some plant species, such as *Fagus sylvatica* and *Quercus ilex*, were perfectly coherent with those measured in the field (Dindorf, et al., 2005); (Ciccioli, et al., 1997) in various sites of Europe during summer.

For plant species that were not directly measured, basal emission values were obtained from the literature after a critical analysis of the data. The final selection was made by considering the following:

- Proximity to the Mediterranean area. This criteria is important because it has been found that species growing in different climatic and ecological areas can evolve in diverse clones, producing different isoprenoid emissions. For example the BVOC emissions of *Pinus sylvestris* in Scandinavia and Central Europe seems to differ from those located in the Alps.

- Data acquisition in the period of maximum emission.

- Level of speciation of the emitted compound.
- Reliability of the methodology used for the determination as defined in the paper by (Niinemets, et al., 2011).

The selected values of the maximum basal emission for the isoprenoids emitted by the different pools of the plants present in the most relevant Italian forest ecosystems are listed in Table 3-5, 4-5 are reported the detail of the chemical compounds respect to the emissive behavior (algorithm “L+T” and “T”).

Table 3-5. Standard emission potentials (in $\mu g\ g(DW)^{-1}\ h^{-1}$ at 30°C leaf temperature and 1000 µmol $m^{-2}\ s^{-1}$ PPFD) of isoprene and monoterpenes for tree species and Specific Leaf Area (SLA) in cm^2g^{-1}. Algorithm “L+T” are monoterpenes emitted with temperature and light dependence.

ALGORITHM “L+T”					
Species	**Compound**	**Stand. Emission potential**		**SLA (cm^2g^{-1})**	**References**
		Hemiterpenoids $\mu g\ g(DW)^{-1}\ h^{-1}$	**Monoterpenoids $\mu g\ g(DW)^{-1}\ h^{-1}$**		
Abies alba	**Isoprene**	**1**		**52**	**(4)**
Carpinus betulus	**cis-b-Ocimene**		**0,07**	**95**	**(1)**
	tr-b-Ocimene		**1,92**		
	Linalool		**0,13**		
Castanea Sativa	**Thujene**		**0,02**	**122**	**(1)**
	a-Pinene		**0,11**		
	Camphene		**0,03**		
	Sabinene		**2,21**		
	b-Pinene		**0,11**		
	Myrcene		**0,20**		
	1,8-Cineol		**0,02**		
	b-Phellandrene		**0,04**		
	Limonene		**0,07**		
	cis-b-Ocimene		**0,05**		
	tr-b-Ocimene		**0,28**		
	g-Terpinene		**0,01**		

	Terpinolene		**0,01**		
	Linalool		**0,03**		
Fagus Sylvatica	**Thujene**		**0,11**	**162**	**(1)**
	a-Pinene		**0,29**		
	Camphene		**0,02**		
	Sabinene		**9,33**		
	b-Pinene		**0,18**		
	Myrcene		**0,38**		
	a-Phellandrene		**0,03**		
	a-Terpinene		**0,06**		
	p-Cymene		**0,04**		
	1,8-Cineol		**0,03**		
	b-Phellandrene		**0,33**		
	Limonene		**0,26**		
	tr-b-Ocimene		**0,00**		
	g-Terpinene		**0,06**		
	Terpinolene		**0,01**		
	Linalool		**0,04**		
Fraxinus excelsior	**cis-b-Ocimene**		**0,01**	**47**	**(1)**
	tr-b-Ocimene		**0,25**		
Garrigue	α-Pinene		0,16	55	(2)
	Camphene		0,03		
	6-methyll-5 methyl Heptane		0,40		
	Sabinene		0,04		
	β-Pinene		0,13		
	Myrcene		0,02		
	1,8-cineol		0,10		
	Limonene		0,06		
	cis-b-Ocimene		0,02		

	trans-β-Ocimene		0,02		
	Terpineol		0,01		
	trans-β-Caryophyllene		0,01		
Eucaliptus	**Isoprene**	**50**		**130**	**(1), (3)**
	a-Pinene		**2,00**		
	b-Pinene		**0,40**		
	Myrcene		**0,08**		
	1,8-Cineol		**1,20**		
	D-Limonene		**0,24**		
	a-Terpineol		**0,04**		
	g-Terpineol		**0,04**		
Picea Abies	**Isoprene**	**1**		**24**	**(1), (4), (5)**
	a-Pinene		**0,25**		
	Camphene		**0,02**		
	Sabinene		**0,03**		
	b-Pinene		**0,31**		
	Myrcene		**0,06**		
	d-3-Carene		**0,05**		
	1,8-Cineol		**0,09**		
	d-Limonene		**0,12**		
Populus nigra	Isoprene	70		136	(6)
Pinus nigra	a-Pinene		2,15	106	(10), (8), (9)
	Camphene		0,04		
	Sabinene/b-Pinene		0,23		
	Myrcene		0,24		
	3-Carene		0,07		
	Limonene		0,12		
	B-Phellandrene		0,13		

Pinus pinea	a-Pinene		0,11	39	(10)
	Sabinene		0,08		
	1,8 Cineol		0,19		
	g-Terpinene		0,02		
	Limonene		1,59		
	Myrcene		0,09		
	Linalool		0,72		
	trans-b-Ocimene		0,19		
Pinus Sylvestris	a-Pinene		0,36	45	(11), (12)
	Camphene		0,13		
	b-Pinene		0,12		
	Myrcene		0,23		
	1,8-Cineol		0,18		
	cis-b-Ocimene		0,02		
	trans-b-Ocimene		0,09		
	g-Terpinene		0,02		
	Linalool		0,02		
Quercus cerris	**Isoprene**	**0,10**		**80**	**(1), (4)**
	a-Pinene		**0,04**		
	Camphene		**0,01**		
	Sabinene		**0,02**		
	b-Pinene		**0,02**		
	Myrcene		**0,01**		
	p-cymene		**0,01**		
	b-Phellandrene		**0,01**		
	1,8-Cineol		**0,01**		
	D-Limonene		**0,02**		
	g-Terpinene		**0,01**		
Quercus frainetto		60			(13)

Quercus pubescens	Isoprene	70		115	(13), (14)
Quercus patraea		60			(13)
Quercus robur		60			(13)
Quercus ilex	**α-Pinene**		**6,46**	**53**	**(14), (15), (16),**
	Camphene		**1,00**		
	Sabinene		**1,80**		
	b-Pinene		**4,44**		
	Myrcene		**0,48**		
	α-Phellandrene		**0,20**		
	α-Terpinenep		**0,54**		
	p-Cymene		**0,84**		
	1,8-Cineol		**1,64**		
	b-Phellandrene		**0,20**		
	Limonene		**0,82**		
	g-Terpinene		**0,90**		
	Terpinolene		**0,36**		
	Linalool		**0,08**		
	α-Terpinenol		**0,24**		
Quercus suber	**Isoprene**	**0,24**		**59**	**(1)**
	Tricyclene		**0,08**		
	a-Pinene		**10,59**		
	Camphene		**0,77**		
	Sabinene		**12,36**		
	b-Pinene		**8,75**		
	Myrcene		**1,33**		
	α -Phellandrene		**0,12**		

	α -Terpinenep		**0,47**		
	p-Cymene		**0,16**		
	1,8-Cineol		**0,04**		
	b-Phellandrene		**0,83**		
	Limonene		**0,65**		
	g-Terpinene		**0,53**		
	Terpinolene		**0,19**		
	Linalool		**0,04**		

References. (1) Ciccioli et al., unpublished; (2) (Fares, et al., 2009) ; (3) (Ciccioli, et al., 1999); (4) Ciccioli et al., 2004; (5) (Karl, et al., 2009); (6) (Lenz, et al., 1997); (7) (Veldt, 1989); (8) (Mumm, et al., 2004); (9) (Mediavilla, et al., 2003); (10) (Kesselmeier, et al., 1997); (11) (Komenda, et al., 2001); (12) (Mencuccini, et al., 2001); (13) (Seufert, et al., 1997); (14) (Roche, et al., 2004); (15) (Ciccioli, et al., 2003), (16) (Loreto, et al., 1996). The words in blue and in bold indicate the measures taken by our group of work (IMC-CNR and IBAF-CNR, Rome, Italy).

Table 4-5. Standard emission potentials (in $\mathbf{\mu g\ g(DW)^{-1}\ h^{-1}}$ at 30°C leaf temperature and 1000 µmol m^{-2} s^{-1} PPFD) of isoprene and monoterpenes for tree species and Specific Leaf Area (SLA) in cm^{2}g^{-1}. Algorithm "T" are monoterpenes emitted only temperature dependent.

ALGORITHM "T"					
Vegetal species	**Compound**	**Compound class**		**SLA (cm^{2}g^{-1})**	**References**
		Hemiterpenoids $\mu g\ g(DW)^{-1}\ h^{-1}$	**Monoterpenoids** $\mu g\ g(DW)^{-1}\ h^{-1}$		
Abies alba	**a-Pinene**		**0,39**	**52**	**(1)**
	Camphene		**0,41**		
	Sabinene		**0,01**		
	b-Pinene		**0,12**		
	Myrcene		**0,07**		
	a-Phellandrene		**0,00**		
	b-Phellandrene		**0,05**		
	1,8-Cineol		**0,01**		
	D-Limonene		**0,44**		
Carpinus	**cis-b-Ocimene**		**0,01**	**95**	**(1)**

betulus	tr-b-Ocimene		0,36		
	Linalool		0,03		
Fagus Sylvatica	Sabinene		1,04	122	(1)
	Myrcene		0,05		
	b-Phellandrene		0,04		
	Limonene		0,04		
Fraxinus excelsior	cis-b-Ocimene		0,00	47	(1)
	tr-b-Ocimene		0,10		
Larix decidua	a-Pinene		1,01	137	(3), (17)
	Camphene		0,02		
	Sabinene		0,05		
	b-Pinene		0,28		
	Myrcene		0,01		
	D-3-Carene		0,06		
	p-cymene		0,01		
	b-Phellandrene		0,01		
	1,8-Cineol		0,01		
	d-Limonene		0,07		
Pinus cembra	α-Pinene		1,36	137	(3), (17)
	Camphene		0,07		
	Sabinene		0,07		
	β-Pinene		0,27		
	Myrcene		0,08		
	p-cymene		0,01		
	β-Phelandrene		0,36		
	1,8-cineol		0,08		
	d-Limonene		0,18		
Olea	α-pinene		0,09	50	(18), (19)

Europaea	Linalool		0,01		
Picea Abies	**a-Pinene**		**0,25**	**24**	**(1), (3), (6)**
	Camphene		**0,05**		
	Sabinene		**0,01**		
	b-Pinene		**0,05**		
	Myrcene		**0,01**		
	D-3-Carene		**0,05**		
	1,8-Cineol		**0,12**		
	D-Limonene		**0,05**		
Pinus halepensis	**a-Pinene**		**0,80**	**160**	**(3), (14), (20)**
	Camphene		**0,02**		
	b-Pinene		**0,09**		
	Myrcene		**0,49**		
	D-3-Carene		**0,21**		
	D-Limonene		**0,18**		
	cis-b-Ocimene		**0,02**		
	trans-b-Ocimene		**0,17**		
Pinus nigra	Limonene		1,13	106	(10), (8), (9)
	b-Phellandrene		0,69		
	b-Caryophyllene		0,60		
	b-Farnesene		0,14		
	Germacrene		0,44		
Pinus pinaster	**α-pinene**		**0,45**	**50**	**(1)**
	b-pinene		**0,57**		
	Myrcene		**0,24**		
	Δ-3-Carene		**0,16**		
	1,8-Cineol		**0,02**		
	Limonene		**0,06**		

Pinus pinea	α-pinene		0,07	39	(9), (10)
	Sabinene		0,12		
	Limonene		2,70		
	Myrcene		0,11		
Pinus Sylvestris	a-Pinene		0,17	45	(11), (12)
	Camphene		0,04		
	Sabinene		0,09		
	b-Pinene		0,03		
	Myrcene		0,03		
	d-3-Carene		0,16		
	1,8-Cineol		0,01		
	d-Limonene		0,05		

References. (1) Ciccioli et al., unpublished; (2) (Ciccioli, et al., 1999); (3) Ciccioli et al., 2004; (6) (Karl, et al., 2009); (7) (Lenz, et al., 1997); (8) (Mumm, et al., 2004); (9) (Mediavilla, et al., 2003); (10) (Kesselmeier, et al., 1997); (11) (Komenda, et al., 2001); (12) (Mencuccini, et al., 2001); (13) (Seufert, et al., 1997); (14) (Roche, et al., 2004); (15) (Ciccioli, et al., 2003), (16) (Loreto, et al., 1996); (17) (Gower, et al., 1993); (18) (Mariscal, et al., 2000); (19) (Steinbrecher, et al., 2009); (20) (Llusia, et al., 1999). The words in blue and in bold indicate the measures taken by our group of work (IMC-CNR and IBAF-CNR, Rome, Italy).

5.4 Modification of the short-term emission algorithm, to account for the seasonality of isoprenoid emissions

As said in the previous section, short term emission algorithms can be used to predict the all year emission only if proper correction terms are used to account for the seasonal variations of E°. Therefore the general algorithms to be used for the two different isoprenoids pools are:

$$E_{L+T} = E^{\circ}_{L+T\,max} * C_S * C_T * C_L \qquad (10\text{-}5)$$

$$E_T = E^{\circ}_{T\,max} * C_S * C_T \qquad (11\text{-}5)$$

Where C_S is a correction term that allows to derive the monthly basal emission by knowing the maximum values reached through the year.

The total emission of isoprenoids from the different plant pools is thus given by:

$$E_{total} = E_{L+T} + E_T \qquad (12\text{-}5)$$

Although it is known that the maximum value of the basal emission is usually reached in hot months of the year, and the annual trend is described by the Gaussian type of equation, some differences have been observed between conifers, broadleaf evergreen species and deciduous trees. Instead of using a general term for Cs, we have decided to use in our model specific equations for each one of the trees belonging to these classes. The equations are discussed below.

Case 1. Coniferous trees, emitters of isoprene and monoterpenes, following a light and temperature dependent algorithm.

For the calculation of the emission for coniferous trees (except *Larix decidua* that follow the trend of the deciduous species) the equation suggested by (Staudt, et al., 2000) for Cs was used. It states that:

$$C_S = 1 - \rho \left\{ 1 - exp^{[-\frac{(D-D_O)^2}{\tau}]} \right\} \qquad (13\text{-}5)$$

where

D : month of the year (from May to October in the case of the deciduous)

D_o : month with the maximum basal emission $\overset{\circ}{E}_{max}$ $(\div\ 6{,}5;\ 7{,}5)$

$\rho : \frac{(\overset{\circ}{E}_{max} - \overset{\circ}{E}_{min})}{\overset{\circ}{E}_{max}}$

τ: period (in months) of growth of the species $(\div\ 5{,}5;\ 6)$

For practical applications the expression can be simplified if values of 0,8, 7 and 6 are used for ρ, D_O and τ, respectively. This generates the profile shown in Figure 3-5

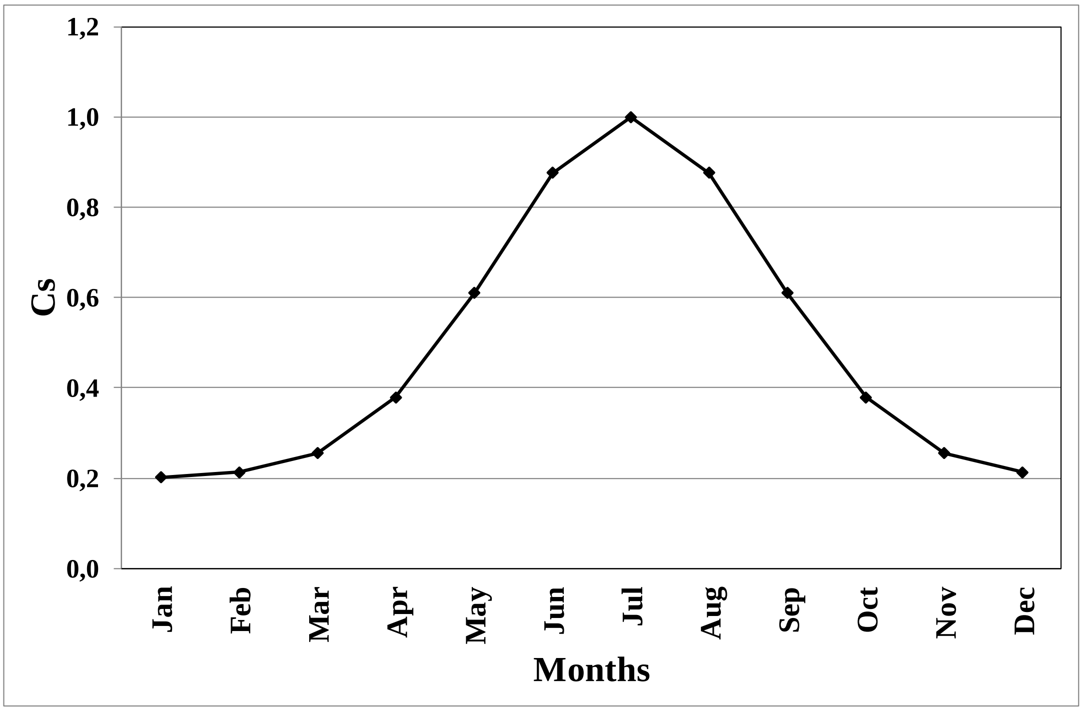


Figure 3-5 Seasonality **c**orrection factor applied to the Coniferous using the algorithm by (Staudt, et al., 2000)

Case 2. Evergreen broadleaf species, emitting isoprene and monoterpenes in a L+T mode.

In this case the experimental algorithm proposed by (Ciccioli, et al., 2002) was used. It has the following mathematical form

$$C_S = exp^{-[\frac{(a-t)^2}{2*b^2}]} \tag{14-5}$$

where

t : Julian day;

a and b: empiric terms with values 170,54 and 75,03 respectively.

The monthly trend obtained is displayed in Figure 4-5.

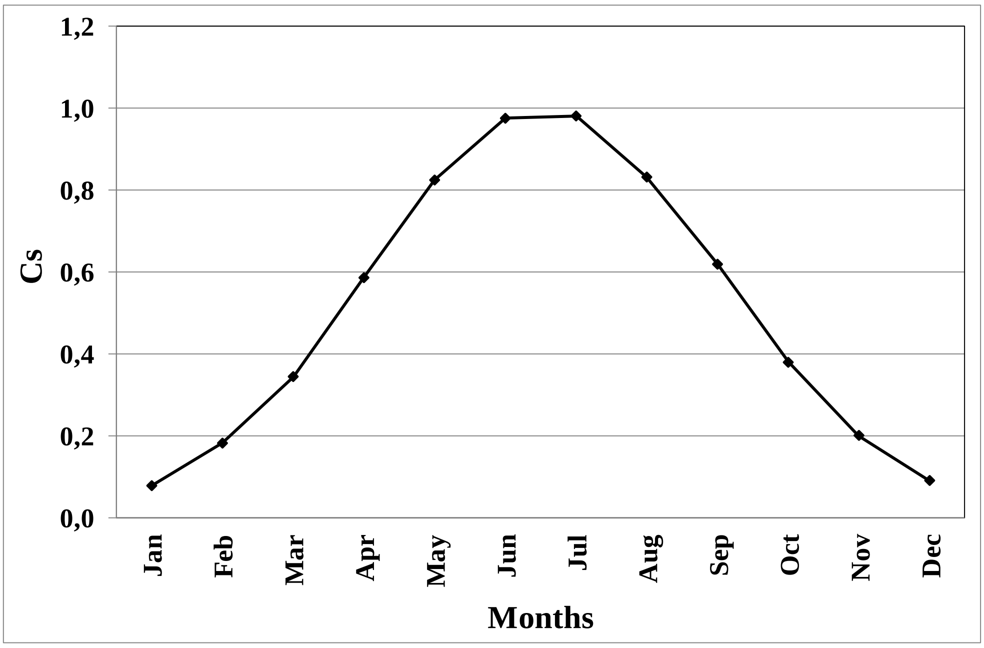


Figure 4-5 Seasonality correction factor applied to the Broadleaved evergreen using the algorithm by (Ciccioli, et al., 2002)

Case 3. Deciduous **species,** emitting isoprene. In this case the seasonality was calculated by using the values shown in Figure 6-5 as the algorithm proposed by (Schnitzler, et al., 1997) was restricting the emission with respect to the actual trends.

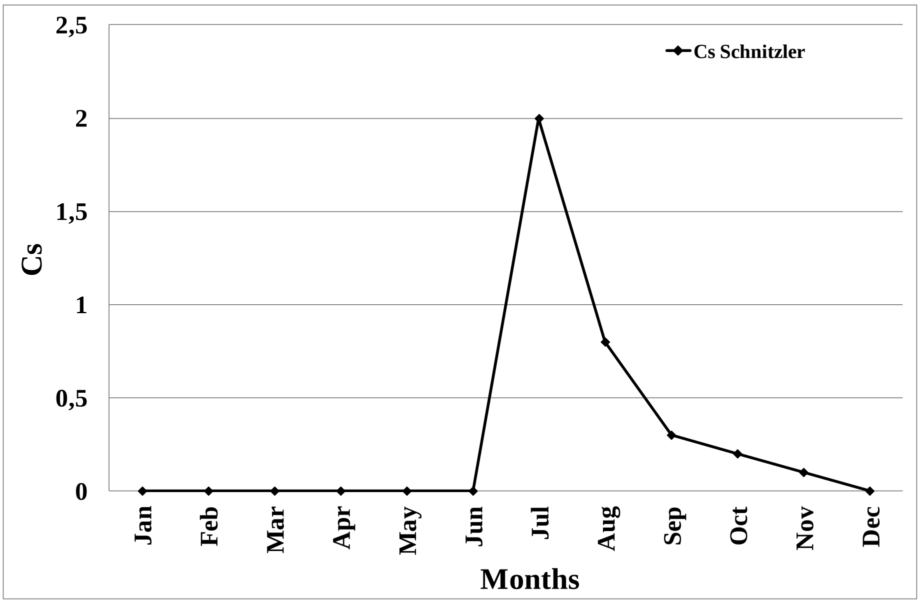


Figure 5-5 Seasonality correction factor applied to the deciduous species.

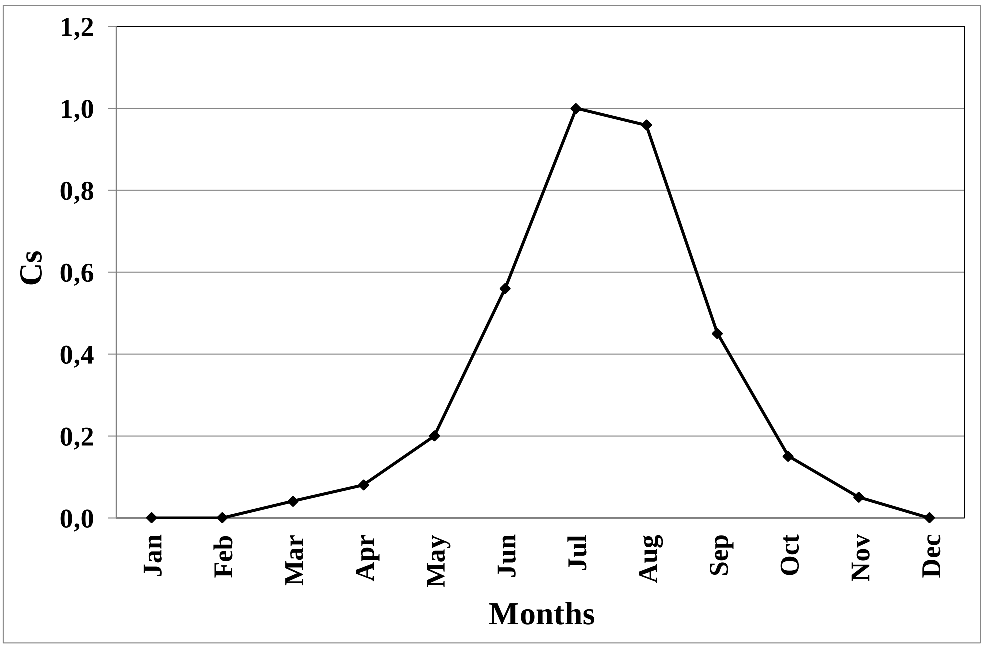


Figure 6-5 Seasonality correction factor applied to the deciduous species.

Seasonal variations described by the empirical values displayed in Figure 6-5 were found to be more appropriate for the type of emission occurring in many parts of Italy.

5.5 Parameterization of processes

In order to take into account the physiological and environmental mechanisms influencing the emissive behavior of the natural ecosystems, it is necessary to correct further the E° values, which is characteristic for each species, by the measured values of the different variables involved in the process.

5.5.1 Canopy light extinction

Since plant emission is usually expressed in mg g^{-1} of dry emitting mass (either leaf or needles) h^{-1}, an estimate of the emitting mass amount should be made per unit of forest surface, and for each ecosystem. The data published by (Lenz, et al., 2002) were used in our model. To account for the different emissive characteristics of the leaves under direct sunlight or under shadows we introduced corrections at $\overset{\circ}{E}_{max}$ (characteristic for each species).

Therefore, to estimate the effective basal emission at level of canopy depending on the light exposure, we used the following expression:

$$\overset{\circ}{E}_{eff}\ (\mu gC\ gDW^{-1}) = E^{\circ} * R_C \qquad (17\text{-}5)$$

where:

E° = basal emission corrected, equal to $\overset{\circ}{E}_{max} * C_S$

R_C = correction factor that takes into account "canopy effect". It takes different values emission depending on the algorithm used.

Algorithm "T"

Assumes that $\overset{\circ}{E}_{max}$ varies for a single species depending on the class of irradiance; this was done according to the measurements by (Lenz, et al., 1997), as follow:

Irradiance (%)	**Leaf $\overset{\circ}{E}_{max}$ fraction**
0-10	0,32
10-40	0,62
40-70	0,78
70-100	1,00

To calculate the total effect, we made the following assumptions for an average closed canopy:

Irradiance (%)	**Biomass fraction estimated (g DW)**
0-10	0,2
10-40	0,3
40-70	0,3
70-100	0,2

In the case of the *Pinus halepensis*, that follows the emissive algorithm "T" for the monoterpenes, the following contributions to the values of $\overset{\circ}{E}_{max}$, equal to 2 μgC $\mathrm{gDW}^{-1}\mathrm{h}^{-1}$ (see Table 4-5) can be obtained:

Irradiance (%)	**Contribution $\overset{\circ}{E}_{max}$**
0-10	0,10
10-40	0,28
40-70	0,35
70-100	0,30

The value of $\overset{\circ}{E}_{eff}$, equal to 1,03 is reduced with respect to original value of around the 30%.

When the estimate of the emission for total ecosystems followed an emission algorithm "T", we utilize a value of $\boldsymbol{R_C}$ equal to **0,68**.

Algorithm "L+T"

In this case, the irradiance assumes a very important effect. Following (Lenz, et al., 1997), we assume that 50% of the biomass has an emission rate equal to $\overset{\circ}{E}_{max}$ (contribution of the illuminated area); to this value we add a value equal to a fixed percentage (25%, the contribution of the shadowed part) of the obtained emission. Thus, we have the following expression:

$$\overset{\circ}{E}_{eff} = \overset{\circ}{E}_{max} * 0{,}5 + \left(\overset{\circ}{E}_{max} * 0{,}5\right) * 0{,}25 \qquad (18\text{-}5)$$

In the case of *Quercus ilex*, that follows the emissive algorithm "L+T" for the monoterpenes, we obtained a value of $\overset{\circ}{E}_{eff}$ of 12,5 compared to the value of $\overset{\circ}{E}_{max}$ 20 μgC gDW^{-1}h^{-1} (see Table 3-5).

When the emission for total ecosystems follows an emission algorithm "L+T", we utilize a value of $\boldsymbol{R_C}$ equal to **0,625**.

5.5.2 Biomass litter

The emission of the litter constituted by the dead biomass accumulated on the soil was also considered.

While the production and the emission of compound following an algorithm "L+T" ends with the end of the photosynthetic process, the emission of the compound following an algorithm "T" continues also after the shedding of the leaf.

To take into account this contribution, we consider an additional contribution equal to 10% of the basal emission for the species that follow an algorithm "T", which have been already corrected with factors C_S and R_C. When the calculation of the emission follows an algorithm "L+T", this value is null (European projects BEMA, unpublished).

5.6 Estimate of the species-specific basal emission

The real basal emission ($\overset{\circ}{E}_{reale}$), which is the emission corrected by the factors mentioned before can be expressed through the following equation:

$$\overset{\circ}{E}_{real}\ (\mu\text{gC gDW}^{-1}\text{h}^{-1}) = \overset{\circ}{E}_{eff} + \overset{\circ}{E}_{eff} * C_E \qquad (19\text{-}5)$$

for:

$$\overset{\circ}{E}_{eff} = \overset{\circ}{E}_{max} * C_S * R_C \qquad (20\text{-}5)$$

where:

C_E: correction factor that takes into account the contribution of the litter, equal to 0,1 (for the biogenic emissions that depend only on temperature, i.e. algorithm "T") and equal to 0 in the other case (algorithm L+T).

C_S: correction factor that takes into account the seasonal distribution of the emissions..

R_C: correction factor that takes into account the "canopy effect".

In the case of the algorithm "L+T", when the correction factor C_E, it is null, $\overset{\circ}{E}_{eff}$ and $\overset{\circ}{E}_{reale}$ will coincide.

Finally, it must be emphasized that E°, as used in all the algorithms previously described, is the Basal Real Emissions, and that it is obtained after the basal emissions corrections, as described previously.

5.7 Calculation of the annual emission

The algorithms previously described allow estimate the annual emission of BVOC for each species in different environmental condition.

Algorithm "L+T"

$$E_{annual} = \sum_{n=12}^{n=1} \overset{\circ}{E}_{L+T} * C_L * C_T * D_B * N_d * N_L$$

Algorithm "T"

$$E_{annual} = \sum_{n=12}^{n=1} \overset{\circ}{E}_{T} * C_T * D_B * N_d * N_L * N_n$$

where:

E°_{L+T} ($\mu g\ g^{-1}\ h^{-1}$): basal emission rate, light and temperature dependence;

E°_{T} ($\mu g\ g^{-1}\ h^{-1}$): basal emission rate, temperature dependence;

C_T and C_L: terms describing the light and temperature dependence;

D_B ($g\ m^{-2}$): foliar biomass density, characteristic of each ecosystem;

N_d: number of days per month;

N_L: number of hours of sunshine during the each day of the year, referred to the mean latitude of the Italy.

N_n: number of night-time hours, only for Algorithm T.

6. RESULTS PROVIDED BY MODEL

For the year 2006, ~70.500 daily maps were generated by our model to get daily values of the emission of individual isoprenoids. From these large data sets different elaborations were made.

6.1 Total annual BVOC emissions from Italian forest ecosystems

As a first step, total annual values were analyzed by separating the contributions of isoprene from those of monoterpenes coming from different pools. On a total of 73,06 Gg (~63,37 Gg C) of isoprenoids; 31,70 Gg (~27,90 Gg C) were represented by isoprene (43,39%); 37,92 Gg (51,90%) by monoterpenes coming from the pool directly related to the photosynthesis (MTsynt), and 3.32 Gg (4,5%) from monoterpenes stored in specialized organs or resin ducts. The large predominance of MTsynt with respect to MTpool, summarizes well the specificity of the Mediterranean regions with respect to those of Central and Northern Europe, where the majority of monoterpenes released in the atmosphere come from specialized pools.

Data reported in Figure 1-6 shows that deciduous vegetations produced 29,98 Gg of isoprene, 5,97 Gg of MTsynt and 0,80 Gg of MTpool, for a total BVOC of 36,75 Gg. Broadleaf evergreen plants produced, 0,04 Gg of isoprene and 30,04 Gg of MTsynt, giving a total of 30,08 Gg of BVOC. Conifers forest emitted 1,09 Gg of isoprene, 1,67 Gg of MTsynt, 2,52 Gg of MTpool, a total of 5,28 Gg BVOC, emission from the garrigue was estimated to be 0,24 Gg of MTsynt, giving a total of 0,24 Gg of BVOC. Finally cultivated trees generated 0,59 Gg of isoprene, 0,005 Gg of MTsynt and 0,001 Gg of MTpool, giving a total of 0,596 Gg of BVOC).

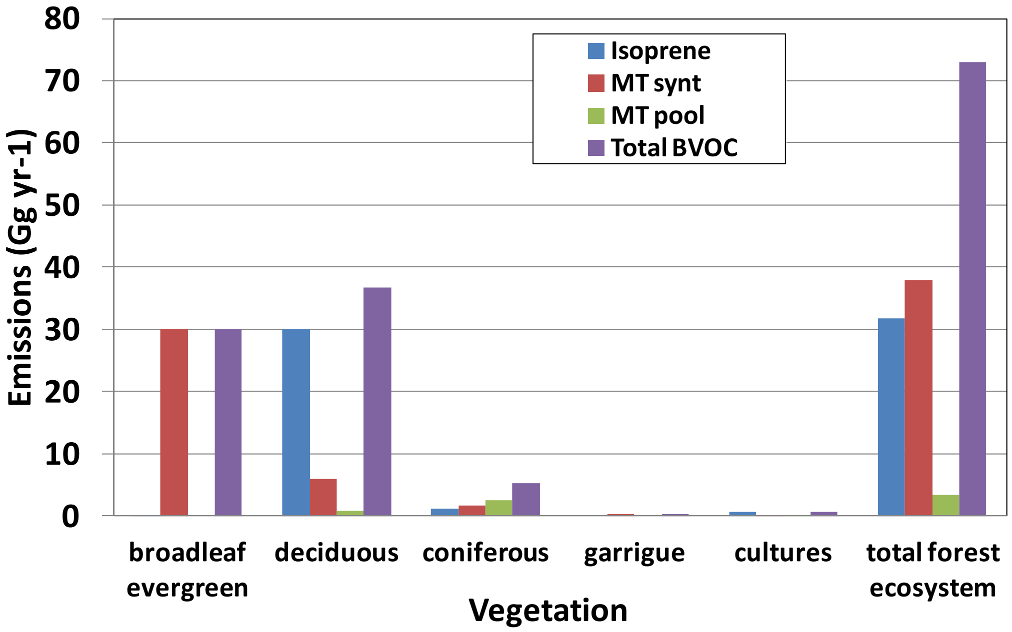
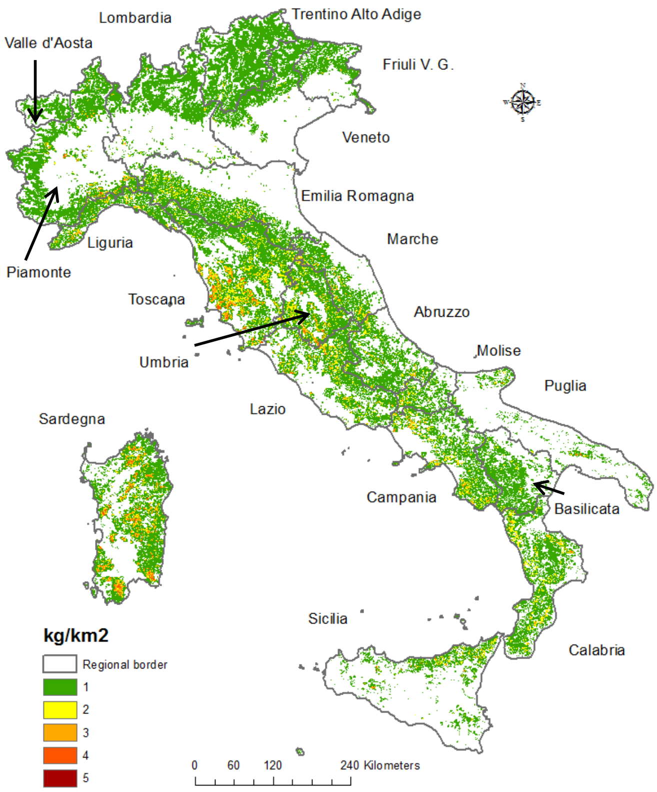


Figure 1-6 BVOC emissions from different ecosystems in the Italian area for 2006 (Gg yr^{-1}).

The most relevant portion of MTsynt was coming from forest ecosystems dominated by broadleaf evergreen vegetation species. As expected, isoprene, that always follows a L+T dependence, was emitted most by forest ecosystems dominated by deciduous trees. However, the values estimated by our model were smaller than the Figures obtained for many European countries, and previous estimated for Italy. This can be attributed to two facts. The first was a more accurate estimate of the area occupied by the only oak species (*Quercus cerris*) that, according to previous (Seufert, et al., 1997) and our experiments to be a very low isoprenoid emitter.

6.2 Distribution of the total isoprenoid emissions among the Italian Regions

The emission of total isoprenoids from the different Italian regions is shown in Figure 2-6, whereas data area reported in Table 1-6. Their knowledge can be important for photochemical modellers as in summer, when the major ozone production occurs, the air circulation is dominated by sea-land breeze regime that is effective most from the coast and the Apennines. Isoprenoid emissions near the coast and downwind large urban areas can increase the levels of ozone, photochemical oxidants and fine organic aerosol coming from the sea, leading to photochemical smog episodes.



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🟨	2	2.400 – 4.800
🟧	3	4.800 – 7.200
🟥	4	7.200 – 9.600
🟫	5	9.600 – 12.000

Figure 2-6 Spatial distribution of total BVOC emissions for the year 2006 divided for regions.

Table 1-6 Estimates of the annual biogenic VOC emission (Gg yr^{-1}) at regional and country scales in the year 2006. Total region and forest area (km^2). Total emissions for km^{-2} of forest (kg km^{-2} yr^{-1})

Territorial district	Monoterpene (MT)	Isoprene (ISO)	Total BVOC	Total (a) forest area	Total (a) region area	Total MT emissions for km^2 of forest	Total ISO emissions for km^2 of forest	Total BVOC emissions for km^2 of forest
Piemonte	1,1	2,0	3,1	9.401	25.399	117	213	330
Valle d'Aosta	0,3	0,2	0,5	1.059	3.263	283	189	472
Lombardia	1,0	0,9	1,9	6.657	23.863	150	135	285
Trentino A. A.	1,1	0,8	1,9	7.797	13.607	141	103	244
Veneto	0,7	0,4	1,1	4.468	18.391	157	89	246
Friuli V. G.	0,6	0,2	0,8	3.572	7.856	168	56	224
Liguria	0,9	1,1	2,0	3.751	5.420	240	293	533
Emilia Romagna	0,8	2,9	3,7	6.088	22.123	131	476	608
Toscana	6,6	5,4	12,0	11.515	22.990	573	469	1.042
Umbria	1,7	2,9	4,6	3.903	8.456	436	743	1.179
Marche	0,5	1,9	2,4	3.081	9.694	162	617	779
Lazio	2,6	2,2	4,8	6.058	17.207	429	363	792
Abruzzo	0,9	1,6	2,5	4.386	10.795	205	364	570
Molise	0,3	0,8	1,1	1.486	4.437	202	538	740
Campania	2,7	1,9	4,6	4.453	13.590	606	427	1.033
Puglia	0,6	0,4	1,0	1.790	19.366	335	223	559
Basilicata	0,8	1,0	1,8	3.564	9.995	224	280	505
Calabria	3,6	2,2	5,8	6.129	15.081	587	359	946
Sicilia	1,3	1,4	2,7	3.382	25.703	384	414	798
Sardegna	12,9	1,1	14,0	12.133	24.090	1.063	91	1.154
Italia	41,0	31,3	72,3	104.673	301.326	6.596	6.444	13.040

(a) Values derived from Italian National Forest Inventary

If we define as low, medium, high and very high the isoprenoid emissions ranging between 0-1, 1-3, 3-5 and 5-13 Gg yr^{-1} respectively. Our model shows that only 2 regions (Tuscany and Sardinia) belong to the very high emission class. 10 regions show instead a low emission. Higher levels of monoterpene emissions (23,1 Gg yr^{-1}) occurs in the central (6,6 Gg yr^{-1}), southern and western (16,5 Gg yr^{-1}) parts of Italy, in regions such as, Tuscany, Calabria and Sardinia. Higher levels of isoprene emission are observed in Tuscany, lower levels occur in 7 regions.

In terms of emission density of total isoprenoids expressed as (kg km^{-2} yr^{-1}), Umbria and Sardinia are the regions with the highest emission density with values of 1.170 and 1.150 kg km^2 yr^{-1}, respectively. The contribute by 9,0% and 8,8% respectively, to the total isoprenoid emission. Substantial emission density was also found for Tuscany, Campania and Calabria with values of 1.040; 1.030 and 940 kg km^2 yr^{-1}, respectively. The contribute to the total isoprenoid emission by 8,0%, 7,9% and 7,3% respectively. The regions contributing most to total isoprene emissions were Umbria, Marches, Molise and Emilia-Romagna, as they accounted for 11,5%, 9,6%, 8,4% and 7,4%, respectively. As far as total monoterpenes are concerned, the major contribution was given by Sardinia (16,1%), Campania (9,2%), Calabria (8,9%) and Tuscany (8,7%).

By considering that the Po valley, which covers a substantial part of Northern Italy, is often experiencing stable conditions either in winter and during summer, whereas the central regions are often affected by long range transport from western countries, it is useful to get some general indications on the isoprenoid emissions occurring in the North, Centre and South of Italy.

North; This area is characterized by an annual emissions of isoprene and monoterpenes of 8,5 Gg yr^{-1} and of 6,5 Gg yr^{-1}, respectively.

Centre; This area shows instead annual emission values for isoprene and monoterpenes of 14,0 yr^{-1} and 12,3 Gg yr^{-1} .

South; This was the area emitting most isoprenoids with values of 8,8 Gg yr^{-1} for isoprene and 22,2 Gg yr^{-1} for monoterpenes.

The main reason why the higher emission of total isoprenoids is observed in the Southern part (31,0 Gg yr^{-1} against values of 26,3Gg yr^{-1} and 15 Gg yr^{-1} estimated for the Central and Northern parts of Italy), is related to the occurrence of higher temperatures through all the year and the more diffuse presence of high emitting oak species (specifically Roverella, Rovere and Farnia) and broadleaf evergreen forests.

6.3 Main isoprenoid species emitted by Italian forest ecosystems

The most relevant result provided by our modelling approach was the annual amounts of individual species that largely dominated the isoprenoid emissions from the Italian forest ecosystems. According to the maps as shown in Figures 3-6a and b the most abundant BVOC after isoprene (31,70 Gg yr^{-1}) were α-pinene (9,10 Gg yr^{-1}) and sabinene (4,34 Gg yr^{-1}). This finding, which reflects the dominance of *Fagus sylvatica* and *Castanea sativa* in the Italian forest ecosystem and has never been reported before, it is of paramount importance in assessing the ozone production in the Italian peninsula as it has been shown before that sabinene reacts much faster with OH radicals than α-pinene and has a comparable reactivity with ozone. In spite of the lower emission, the contribution sabinene to ozone formation can be thus comparable with that of α-pinene.

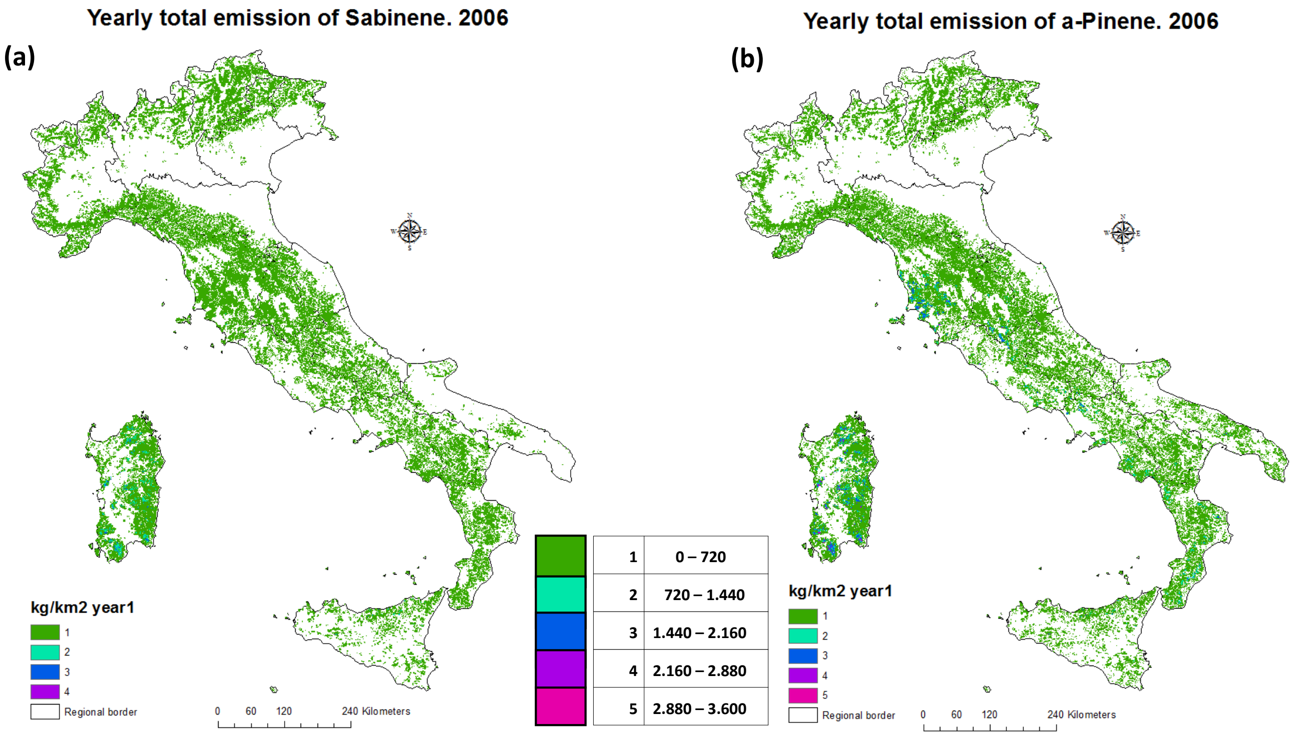


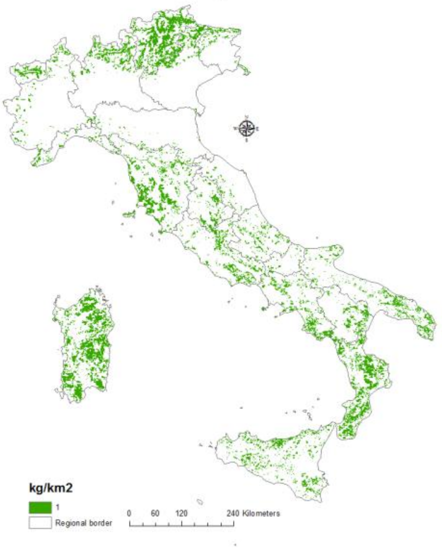
Figure 3-6 (a) spatial distribution of total annual emissions of sabinene in Italy for the year 2006. (b) spatial distribution of total annual emissions of α-pinene in Italy for the year 2006.

6.4 Monthly trends of isoprenoid emissions and complexity of the emission

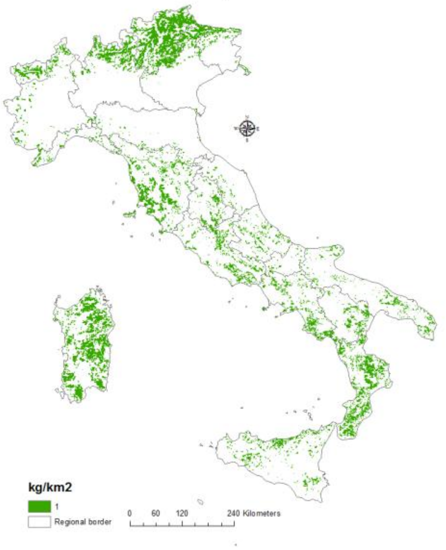
The large dominance of isoprene and monoterpenes, whose emission is directly linked to the photosynthesis in the Italian forest ecosystems, generates also a stronger seasonal variability in the emission than that observed in countries where the emission is more dependent on temperature. This is clearly visible from the monthly maps shown in Figures 4-6 and the data displayed in Figures 5-6. Both data indicate that the time period between May to September is the one where most of the annual emission occurs. It accounts for ca. 94% of the total annual emission.

From September to April monthly emissions of isoprenoids are much lower (500 kg km^{-2} month^{-1}), than those occurring from May to August (with values over 3.500 kg km^{-2} month^{-1}). These data seems to fit well with the seasonal trends measured by (Ciccioli, et al., 2003) in a Mediterranean forest site of Central Italy.

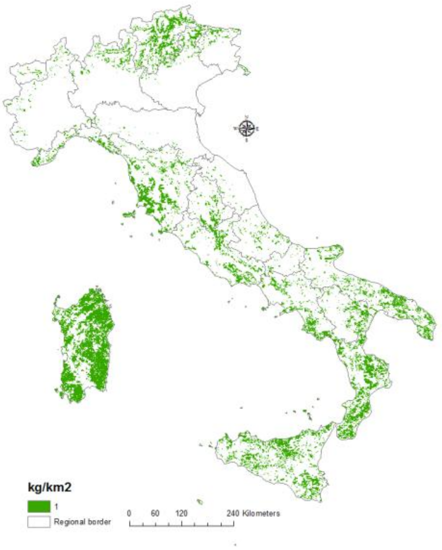
January 2006



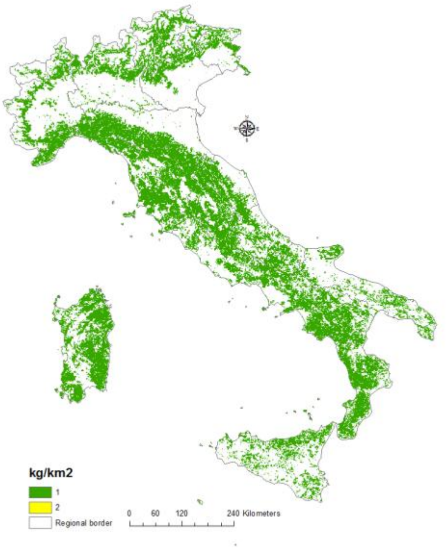
February 2006



March 2006



April 2006



May 2006

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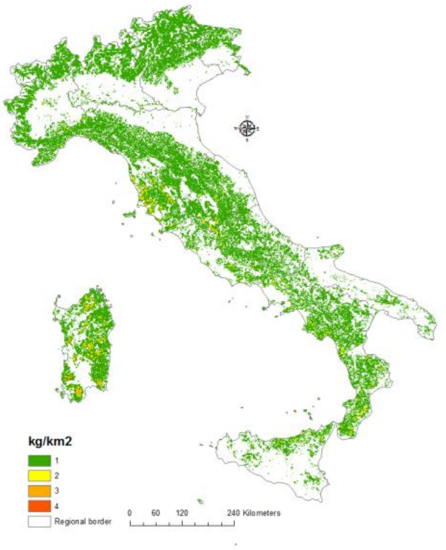
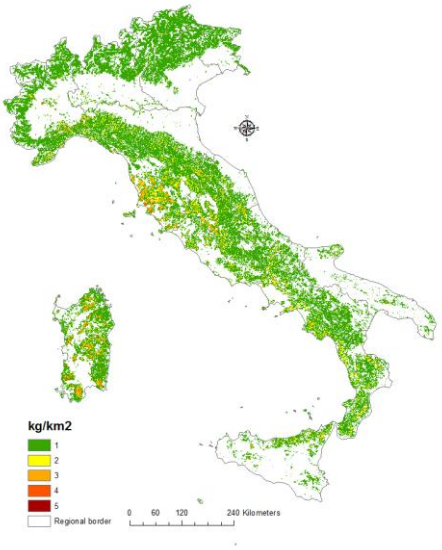
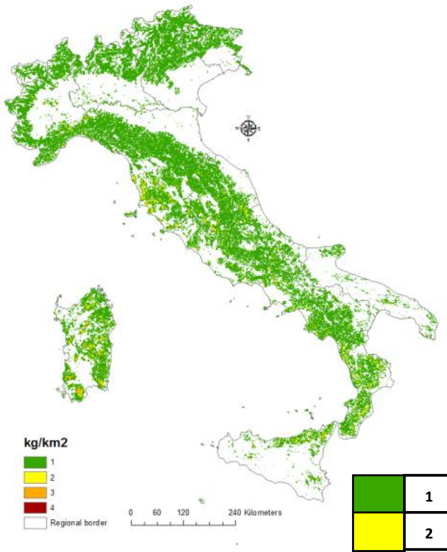


July 2006



August 2006



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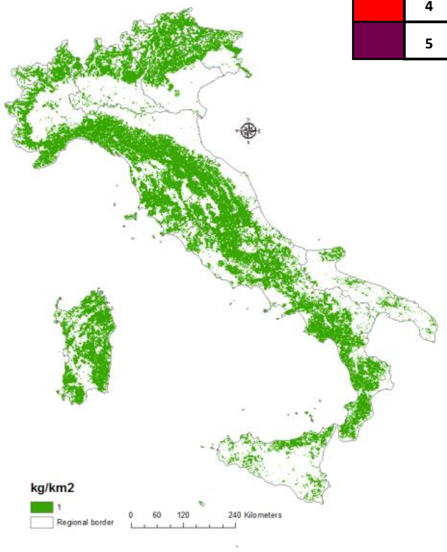
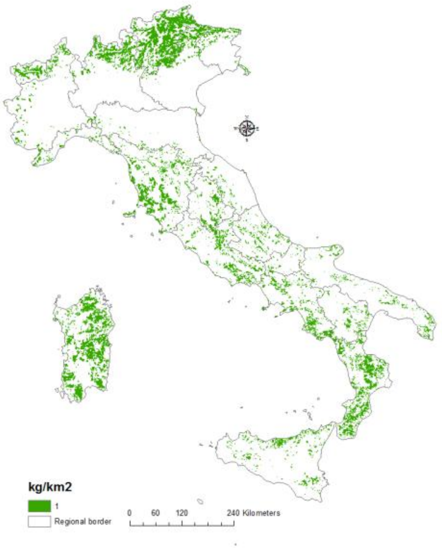
September 2006

October 2006



November 2006



December 2006

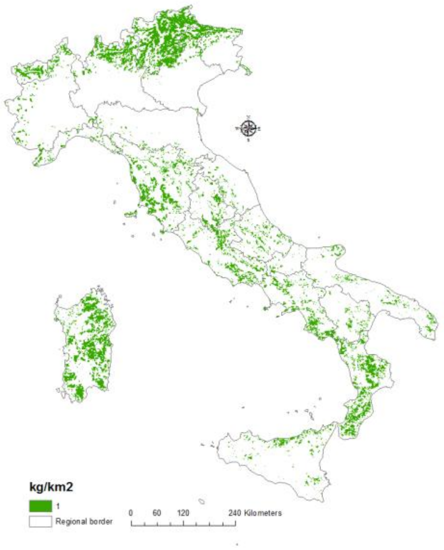
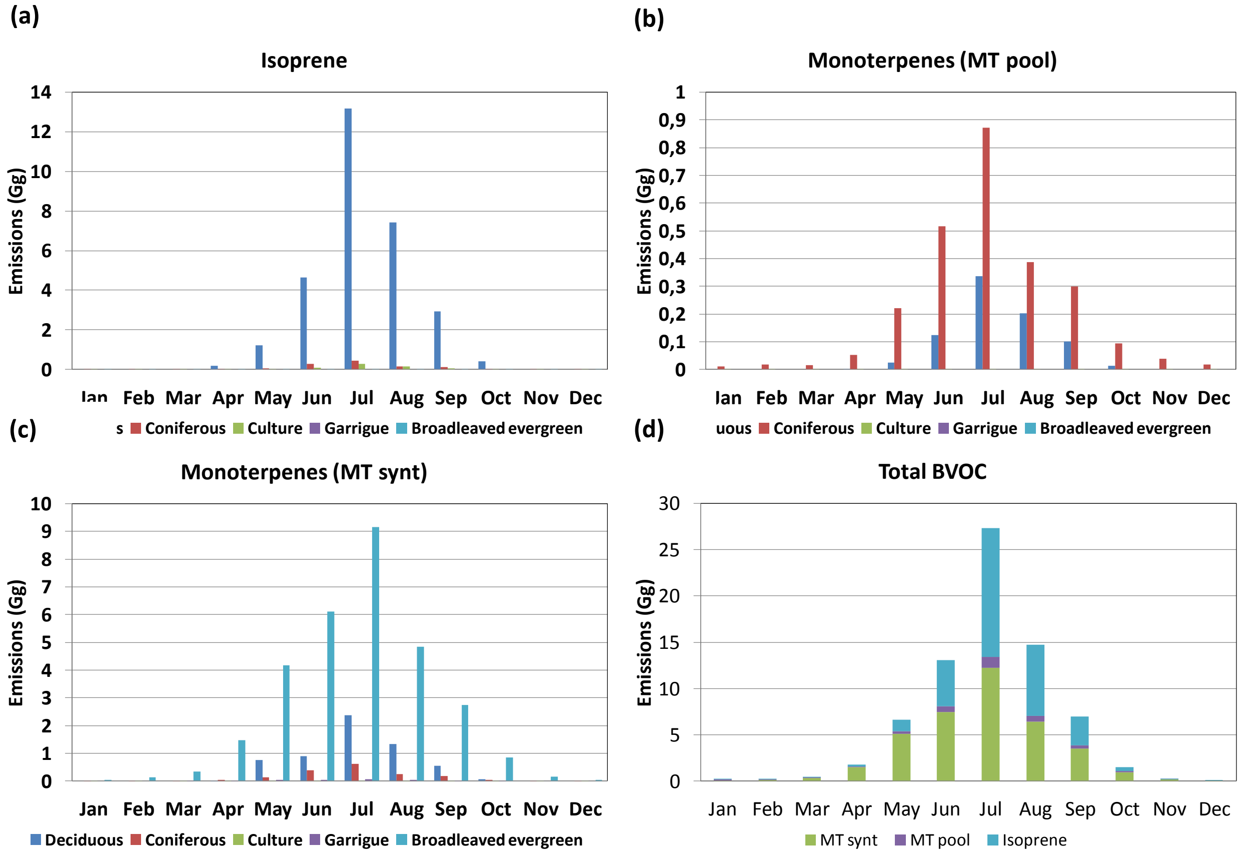


Figure 4-6 Geographical distribution of modeled BVOC fluxes for each month in 2006 in the Italian area: (A) from January to June and (B) from July to December.



Isoprene

Monoterpenes (MT pool)

Monoterpenes (MT synt)

Total BVOC

Figure 5-6 Monthly emissions of isoprene, monoterpenes (MT synt and pool) and total BVOC in the Italian area in 2006.

The once of isoprenoid emissions is regulated by the sprouting or development of new leaves, and increases with their foliar surface until it reaches a maximum in the middle of the summer. At the end of September and through the whole month of October, leaves falls in deciduous trees and reduce their emission in evergreen trees. For the year 2006 our model indicates that the maximum isoprenoid emissions occurred in July, as they accounted for 37,38% of total annual emissions (27,32 Gg).

During this month the 13,17 Gg of isoprene, 2,37 Gg of MTsynt and 0,34 Gg of MTpool (which adds up to 15,88 Gg of total BVOC) were emitted from Deciduous trees; 0,01 Gg of isoprene and 9,16 Gg of MTsynt (totaling 9,18 Gg of BVOC) from Broadleaved evergreen; 0,43 Gg of isoprene, 0,62 Gg of MTsynt and 0,87 Gg of MTpool (adding up to 1,93 Gg of total BVOC) from Coniferous forest; 0,27 Gg of isoprene and 0,001 Gg of MTsynt (summing up to 0,27 Gg of total BVOC) from cultivated forests; and 0,07 Gg of MTsynt from the Garrigue.

In general the major trees contributing to was emitted mainly from *Quercus pubescens*, *Quercus petrea* and *Quercus robur* corresponding to 27,01 Gg (85% of the total). Instead the monoterpenes (specifically MTsynt) were emitted principally from *Quercus ilex*, *Quercus suber* and *Fagus sylvatica* representing each ca. 61,16% (23,19 Gg), 18,06% (6,85 Gg) and 10,03% (3,81 Gg) of the total, respectively.

6.5 Individual isoprenoid emissions for the July 2006

The higher emission coincides with the larger number of different isoprenoids emitted by the different tree species. This aspect is summarized well by the data shown in Figure 6-6, where the fractions of different L+T isoprenoids released in July by different vegetation classes and subclasses present in the Italian forest ecosystems. Data in the Figure indicate that **Isoprene** emission originated most (11,91 Gg) from *Quercus petraea* + *Quercus pubescens* + *Quercus robur; Quercus cerris* + *Quercus frainetto* + *Quercus trojana* + *Quercus macrolepis* produced 1,28 Gg and *Populus nigra* 0,25 Gg; **α-Pinene** emission originated most (2,26 Gg) from *Quercus ilex*, *Quercus suber* produced 0,57 Gg, *Picea abies* emitted 0,11 Gg, *Fagus sylvatica* produced 0,04 Gg and *Pinus sylvestris* 0,02 Gg; **Sabinene** emission produced most (1,15 Gg) from *Fagus sylvatica*, *Castanea sativa produced 0,37 Gg*, *Quercus suber* 0,67 Gg and *Quercus ilex 0,63 Gg*; **β-Pinene** emission originated most (1,56 Gg) from *Quercus ilex*, *Quercus suber* produced 0,48 Gg, *Picea abies* 0,14 Gg, and *Pinus sylvestris* 0,01 Gg; **tr-b-Ocimene** emission originated most (0,32 Gg) from *Carpinus betulus* and *Fraxinus excelsior* 0,03 (Gg); and a **miscellaneous category of monoterpene** emission originated (2,71 Gg) from *Quercus ilex*, *Quercus suber* produced 0,3 Gg, *Fagus sylvatica* 0,15 Gg, *Castanea sativa* 0,1 Gg, *Picea abies* 0,11 Gg and *Pinus pinea* 0,01 Gg. Species emitting mainly isoprene generally emit no other compounds (Figure 6-6). However, *Picea abies* emitted β-pinene, α-pinene and limonene, which contributed 16%, 13% and 6% respectively to total emissions of this species.

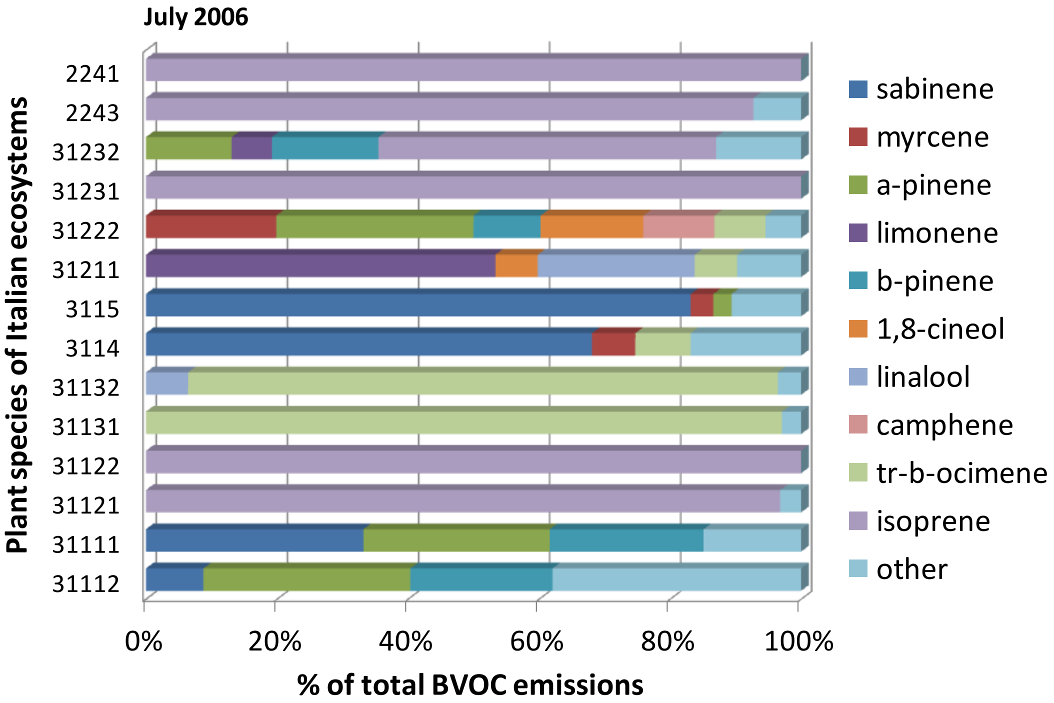


Figure 6-6 Percent composition of BVOC emissions from Italian ecosystems, values obtained for July 2006, for species that follow an algorithm “L+T”, 2006. Codes for plant species are: P*opulus nigra* (2241); *Eucalypus* (2243); *Picea abies* (31232); *Abies alba* (31231); *Pinus sylvestris* (31222); *Pinus pinea* (31211); *Fagus Sylvatica* (3115); *Castanea sativa* (3114); *Carpinus betulus* (31132); *Fraxinus excelsior* (31131); *Quercus petraea* + *Quercus pubescens* + *Quercus robur*

(31122); *Quercus cerris* + *Quercus frainetto* + *Quercus trojana* + *Quercus macrolepis* (31121); *Quercus suber* (31111); *Quercus ilex* (31112)

Obviously monthly trends discussed before result from the integral of the day by day variation run by the model. An example of the results obtained in a day of July (29th) and the contribution to of different vegetation species to the whole compositions are reported in (Figure 7-6). In the Figure tree species responsible for more than 1% of the total emission are indicated. Data show that Oak species (*Quercus pubescens*, *Q. petrea*, *Q. robur*, *Q. ilex*, *Q. suber*) and beech (*Fagus sylvatica*) were those determining the emission. Isoprene mainly originated from *Quercus pubescens*, *Q. petrea* and *Q. robur*, that accounted for ~86% of the total isoprene emission (more than 328 Mg). *Quercus ilex* and *Quercus suber* were the main sources of MTsynt (240 Mg) and accounted for 58% and 16% respectively, of the total MTsyn emission. *Fagus sylvatica* and *Castanea sativa*, contributed to this emission with 39,3 Mg and 15,6 Mg, corresponding to 11,9% and 4,7% of the total. *Picea abies* was the most important forest species emitting isoprenoids of the MTpool. With 5,9 Mg represented 38,5% of the total MTpool emissions.

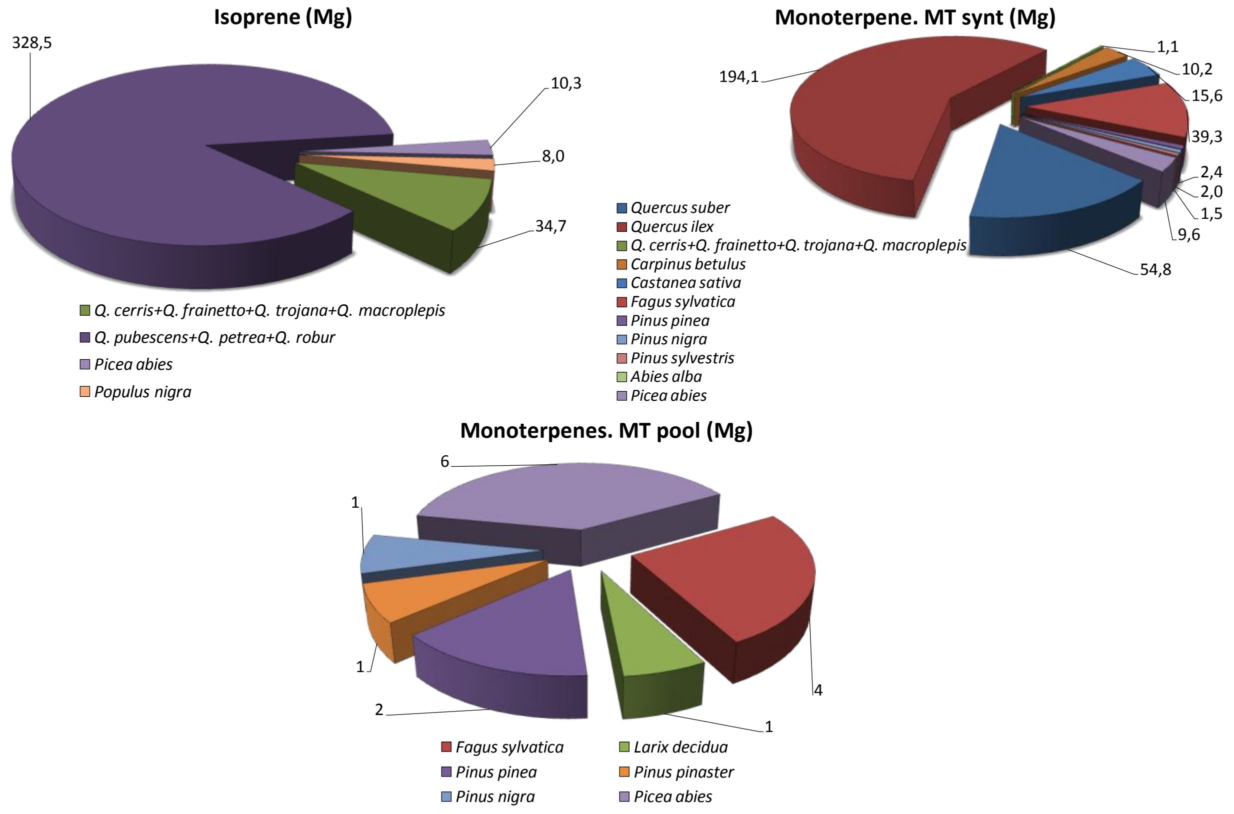


Figure 7-6 Main plant ecosystems responsible of BVOC emissions. Values obtained for July 29nd, 2006.

6.6 Model validation

In addition to provide speciated data for predicting ozone with photochemical models, the species-specific approach used in our model allows a more accurate validation of its results through field measurements. This is possible by selecting areas where specific isoprenoids are emitted by the forest ecosystems. In this study two sites were identified where a good validation of the model could have been performed. The first one was the forest site of Collelongo (Abruzzo, Italy) and the other was the forest site of Castelporziano (Latium, Italy). Both are located in Central Italy. While Collelongo is located in the Apennines range, Castelporziano is located on the Tyrrhenian coasts near Rome. The former site was chosen because is located in a forest area where *Fagus sylvatica* is, by far, the dominant vegetation species. Since no flux determinations have been performed so far in as such ecosystem, a specific field campaign was held in this site. It was performed when the middle of the summer when the highest emission was expected to occur. These experiments allowed also to verify the high sabinene emitting feature of *Fagus sylvatica*, measured in previous years with the enclosures. In the case of the coastal site of Castelporziano, where the higher contribution to the emission was coming from *Quercus ilex*, monthly flux data of single monoterpenes were available for the year 1997. They indicated that α-pinene and β-pinene where the species producing the highest fluxes.

6.6.1 Collelongo site

Figures 8-6 provide an overview of the area where the site is located and the complexity of its morphology. Sites of this type are generally not suitable for measuring fluxes because normally flat areas are used. However, it is impossible to find in Italy flat sites where dense and wide forest of *Fagus sylvatica* exist. Among the various micrometeorological methods available for measuring BVOC fluxes (Relaxed Eddy Accumulation, Gradient method and the Eddy Covariance method), the gradient method using tethered balloons was preferred as it is the one that could have been affected by the lower uncertainty in flux determination. Moreover, a long series of turbulence data were available from a tower built for measuring the fluxes of CO_2 by Eddy Covariance. Since also the tower was located along the edge of a mountain, the balloon was raised in the largest valley nearest the tower. The location of the balloon and the tower are shown in Figures 9-6. The balloon was risen up to 200 m, but it was soon found that, in most instances the mixing height was lower than 150 m, due to the convergence of air from both sides of the mountain where the valley was located. The difference in height between the tower and the flat area was such that turbulent data measured over the tower were representative of the meteorological situation established in the mixing layer. The balloon, filled with helium, was raised up to 200 m from the flat area in order to get the monoterpene concentrations at the highest level as possible.

Figure 8-6 Geographic area where the site Collelongo is localizated.

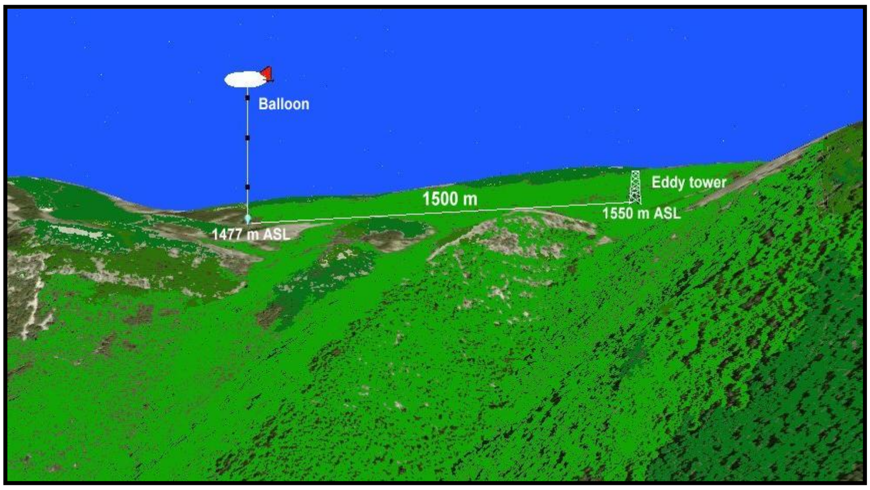


Figure 9-6 Localization of the experimental site, this is situated within a 3000 ha community forest composed by almost a pure high stand of *Fagus sylvatica* L. trees with a mean height of 25 m (Images by Rapparini et al., unpublished).

In spite of the time of the year, a large meteorological variability affected the area during the campaign that was held from July 28 to August 2. After a heavy rain episode, hot and sunny days alterned with cloudy ones with sporadic rain. Although not always easy for the measure of isoprene flux, this situation was good, instead, to check the reliability of our method for measuring fluxes and the light and temperature dependence of monoterpene emission from *Fagus sylvatica*. Data obtained by GC-MS confirmed that the major isoprenoid emitted was sabinene, which accounted for ca. 70-80% of vegetation emission. Other monoterpenes were detected, but seldom were they emitted by the forest. Often they were transported into the site from areas located at the foot of the mountain. For this reason, they are not shown in Figures 10-6 where diurnal variations of sabinene fluxes are compared with those of the incident PAR and the temperature of the canopy. The fair correlation of sabinene fluxes with these two parameters and the limited emission when clouds were passing over the site, fully confirmed the light and temperature dependence of sabinene emission from *Fagus sylvatica* at a canopy scale. The high dependence was also demonstrated by the fact that only tiny fluxes where measured for anthropogenic compounds, such as benzene, Freon 113 and carbon tetrachloride, that were reaching the site by long range transport and were well distributed in the atmospheric boundary layer. The only problems that may affect our flux data are arising from sabinene reactivity. Indeed the presence of sabinene-ketone was found in our traps. By slightly increasing the gradient, this reactivity could lead to some overestimation of sabinene fluxes.

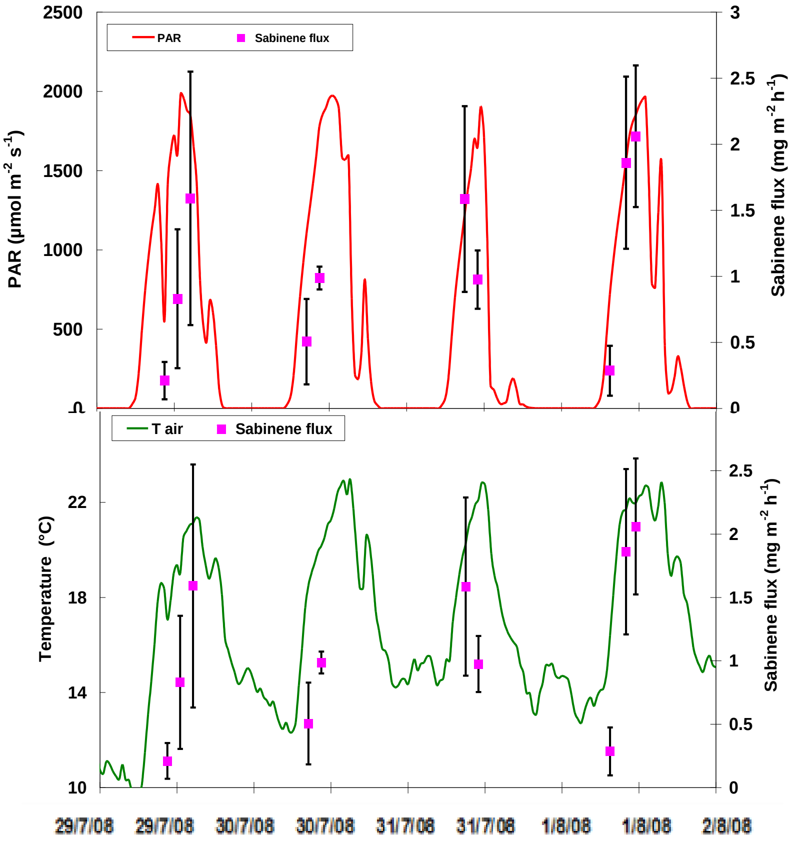
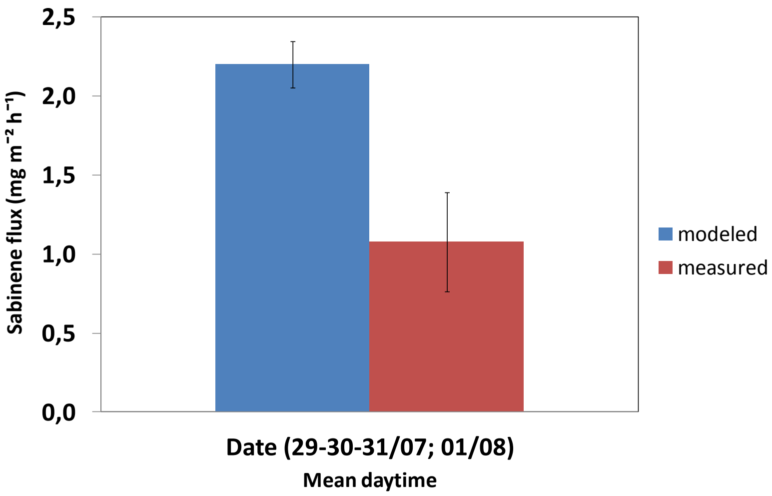


Figure 10-6 Sabinene fluxes (mg m^{-2} h^{-1}) as a function the PAR and Temperature in the period from 29 July to 01 August of the year 2008 (Ciccioli et al., unpublished).

From the Figure 10-6 daytime averages of sabinene fluxes were ranging between 0,5-1,5 mg m^{-2} h^{-1}, with maximum values reaching 2,2 mg m^{-2} h^{-1}. A comparison with the data predicted by the model for the same days is shown in Figure 11-6.



	Average measured (mg m^{-2} h^{-1})	Average modeled (mg m^{-2} h^{-1})
29/07/08	1.21	2.40
30/07/08	0.75	2.10
31/07/08	1.28	2.10
01/08/08	1.40	2.20
daytime	**1.16**	**2.20**

Figure 11-6 Comparison of the modeled and measured mean daytime emissions of Sabinene, *Fagus sylvatica*, from 29-31 July to 1 August 2008, (p = 0.01 and the degrees of freedom is 3)

Data indicate that sabinene fluxes predicted by the model were higher than those measured over the site. It should be noted, however, that differences were not so dramatic. They arise from both the uncertainties in the model as well as by the uncertainty in the flux determination, previously discussed. As far as the model is concerned, the major source of errors comes from the fact that the meteorological parameters used by the model are those obtained by MODIS, and they are averaged in space and time, at a lower resolution that obtained in the flux determinations. For this reason the model is not able to represent some processes that occur at a sub-daily time level, such as the effects of leaf temperature, or hourly changes in solar radiation due to cloud cover

6.6.2 Castelporziano site

The model was also validated for the seasonality and emission rates by comparing the data given by the model with the actual fluxes measured in the *Quercus ilex* stand of Casteporziano in 1997, where the meterorological conditions were not so much different from those occurring in the year 2006.

Figure 12-6 compares the seasonal trends of α-pinene predicted by the model with that reported by (Ciccioli, et al., 2003). Data show that the predicted trend of emission for α-pinene from the *Quercus ilex* stand does not differ too much from the measured one, in spite of the fact that data refer to different years. By considering this, the performance of the model can be considered quite good, because the standard deviation (R^2) was 0,69 and relative errors were e% = -14,7, MAE% = -16,3, EC = 0,7. Particularly important was fact that the value of the RMSE was 0,05 mg m^{-2} h^{-1}

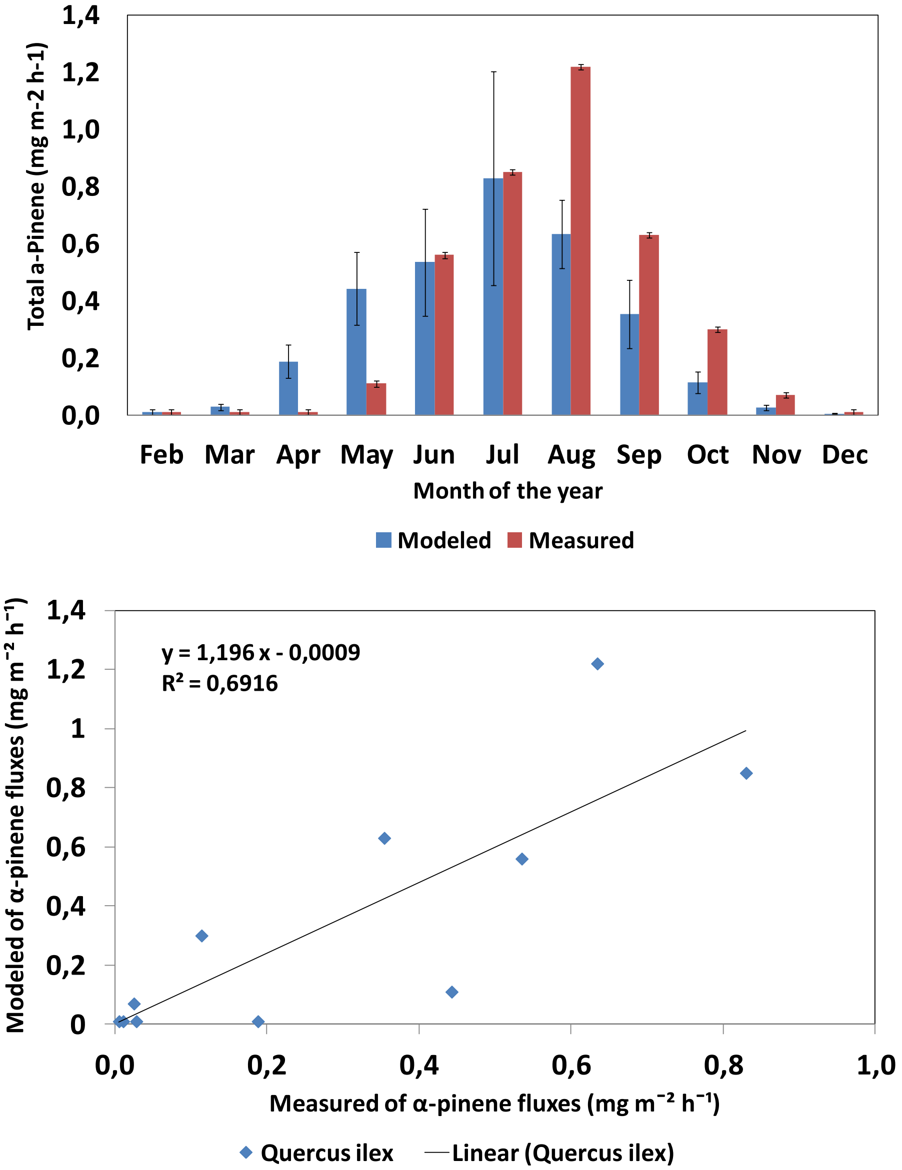


Figure 12-6 Comparison of the modeled and measured monthly estimation of α-pinene, *Quercus ilex* (R^2= 0,69, n= 11, p=0,45 and degrees of freedom is 10)

The efficiency coefficient (EC) of the model measured for α-pinene emitted from *Quercus ilex* was positive and higher (EC=0.7) than that considered satisfactory for a model.

6.7 Comparison with other models

Although a lot of efforts have been paid to assess the BVOC emissions at a European scale, and numerous publications have been produced, few are the numbers given for Italy. In some cases only maps at very low resolution are available. Basically we may refer for comparison with the Table 2-6 given by (Simpson, et al., 1999) and (Lenz, et al., 2002) who reported only the total sum of isoprene and monoterpenes emission for Italy. Our data seem to better approach those reported by Simpson than those of Lenz who considered the different pools as we did. However, none of these authors accounted for the seasonality of the emission and never checked their emission values through flux determinations as we did.

It should be noted that in both studies, the total BVOC emission is given. Although forest emission is the major source, additional emission from cultivated areas may also occur. However, this would not increase our value of a large extent, because many cultivars emit oxygenated BVOC. Even though many of the emission factors used by Lenz et al. (2002) exceed the ones used in our model, their values cannot explain the differences observed. We think that Lenz et al. (2002) largely overestimated the emission of both isoprene and monoterpenes because the type of maps they used were not adequately validated with those provided by National Forest Inventory, and because they did not account for seasonality effect on the emission.

Table 2-6 Comparison of BVOC emissions for forest tree species in Italy (in Gg/yr)

	Sum isoprene	Sum monoterpenes
This study	32	41
Lenz et al. (2002)	245	115
Simpson et al. (1999)	36	32

7. POTENTIAL APPLICATION OF THE MODEL AT THE CHANGE OF LAND USE DUE TO DEFORESTATION AND BURNING

7.1 Land cover changed in burned areas (2000-2006)

The wildfires in Southern Europe burn thousands of squared kilometers of forest, shrub lands, and grasslands every year. They cause extensive economical and ecological losses (C. Quintano et al., 2011). Although fire is an integral component of Mediterranean ecosystems, the dynamics of regimes in Southern Europe is driven mainly by human factors. In fact, humans are responsible for over 95% of the fires taking place in this region (San-Miguel-Ayanz, et al., 2009).

Land cover changes are related to fire hazard through changes in fuel load which, along with topography and weather, are the main drivers of fire intensity and rate of spread (Fernandes, 2009); (Moreira, et al., 2009). Therefore, increased fire hazard is expected where land cover changes promote an increase in plant biomass (fuel load) while decreased fire hazard is linked to changes associated with the removal of biomass (San-Miguel-Ayanz, et al., 2012).

For all this reason, the study of land cover changes in burned areas and of fire regimes in Southern Europe has become fundamental.

Land cover is a fundamental component of fire dynamics. It influences all the phases of the fire, from ignition to fire behavior and post-fire restoration. A depth analysis of land cover changes in areas affected by fires and the effects of fire on land cover dynamics is tackled of follow.

7.2 Methodology

The aim was to carry out a detailed analysis of land cover changes that occurred in areas affected by fires during the period 2000-2006 in several Southern Europe countries. This was done using the CORINE Land Cover maps (CLC maps, hereafter) available for 2000 and 2006, and the European Fire Database (EFFIS) containing the annual forest fire information compiled by EU Member States and other European countries (http://effis.jrc.ec.europa.eu). EFFIS database was used for the period 2000-2006. The countries studied included Portugal, Spain, France and Italy. Greece was excluded from this analysis due to the lack of CORINE 2006 data for this country.

We worked with the second level of CORINE land cover data and when the results of the analysis indicated the occurrence of a major type of transition at a country level, the third level was used. The areas that were burned in each country and for each year throughout the studied period were obtained after the annual fire maps of the EFFIS database. For each country, a set of seven masks (ArcGIS shape layers) was derived from these fire maps; i.e. one mask for each year from 2000 to 2006 (Figure 6-1). All fires smaller than 50 ha were discarded for the creation of the mask (San-Miguel-Ayanz, et al., 2012).

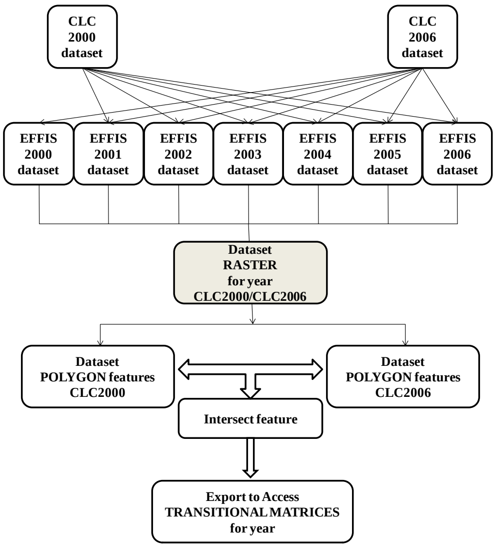


Figure 1-7 Schematic diagram of various modules of the GIS process

Each year the mask was used for extracting two new raster layers from the two CLC maps of each country. The raster layer derived from the CLC 2000 map would represent the land cover pre-fire situation in the areas burned that year, whereas the raster layer derived from the CLC 2006 map would represent the land cover post-fire situation in those same areas. Then, all these raster layers were converted into shape files in ArcGIS. For each year, we combined the two corresponding layers, obtaining a final shape file in which each polygon would correspond to a given transition of land covers between CLC2000 and CLC2006 and would reflect this information in its attribute table. Based on these data, we generated seven transitional matrices for each country (one per year) and selected, in each case, the major transitional classes to be analyzed at the second CLC data level. An overall transition matrix was also calculated by pooling the data from all countries. Land cover transitions representing less than 50 ha were excluded.

7.3 Result and Discussion

During the study period (2000-2006), the total burned area in the four considered countries was 1,395,119 ha (only considering fires larger than 50 ha) (Figure 2-7). Half of this area (51%) consisted of CLC Level 2 class 32 (“Scrub and/or herbaceous associations”), followed by class 31 (“Forests”) (34%). At CLC Level 3 fires affected mainly class 324 (“Transitional woodland-scrub”), corresponding to 23% of the total, class 312 (“Coniferous forest”) (15%), followed by classes 311 (“Broad-leaved forest”) (12%) and classes 313 (“Mixed forest”), 321 (“Natural grassland”), 322 (“Moors and heathland”) and 323 (“Sclerophyllous vegetation”), representing each ca. 9% of the total burned area.

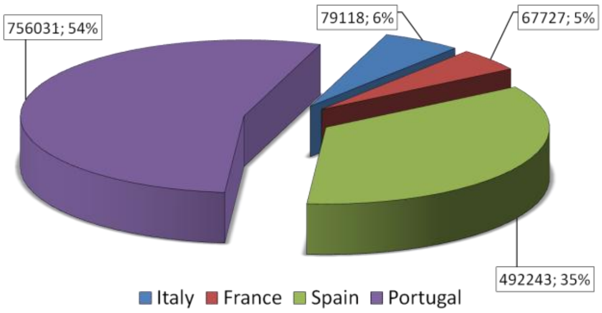


Figure 2-7 Total burned area in Southern Europe (ha) (2000-2006)

Overall, a total of 1,016,055 ha of burned areas (72.8% of the total) did not change their land cover after fire. The land covers with less persistence in burned areas were Forests, Open spaces with little or no vegetation, and Inland wetlands (Table 1-7). Caution should be taken in interpreting the finding for the latter land cover, as the area with this land cover was very small (150 ha) and thus prone to significant proportional changes even with small variations in polygon boundaries. From the remaining 379,064 ha in which changes occurred, 76.9% became class 32 (“Scrub and/or herbaceous associations”) and 19.6% became class 33 (“Open spaces with little or no vegetation”). The transition matrix for the overall burned area (Table 1-7) showed that the main changes driven by fire were the transition from Forests to Scrub and/or herbaceous associations (over 50% of the forests in 2000 suffered this transition). The transition from Open spaces with little or no vegetation to Scrub and/or herbaceous vegetation was also relevant (45%), as well as Inland wetlands to Inland waters (46%). Other important transitions were from Arable land to Artificial, non-agricultural vegetated areas (15%). Of these transitions, only the former can be clearly attributed to fire effects.

Table 1-7 Transition matrix for the period 2000-2006 in the burned areas in Portugal, Spain, France and Italy.

		CLC2006												
		11	12	13	14	21	22	23	24	31	32	33	41	51
CLC2000	11	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	12	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	13	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	14	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	21	0.00	0.00	0.00	0.15	0.82	0.00	0.00	0.01	0.00	0.01	0.00	0.00	0.00
	22	0.00	0.00	0.00	0.00	0.00	0.87	0.01	0.05	0.00	0.07	0.01	0.00	0.00
	23	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00
	24	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.96	0.00	0.02	0.01	0.00	0.00
	31	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.41	0.51	0.07	0.00	0.00
	32	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.94	0.05	0.00	0.00
	33	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.45	0.54	0.00	0.00
	41	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.54	0.46
	51	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00

Note: Each row provides the proportion of the initial land cover (in 2000) that persisted or changed to other land cover in 2006. Light grey cells indicate the persistence values (diagonal) and dark grey cells indicate the main transitions (over 5%). Codes for land cover are: Urban fabric (11); Industrial, commercial and transport units (12); Mine, dump and construction sites (13); Artificial, non-agricultural vegetated areas (14); Arable land (21); Permanent crops (22); Pastures (23); Heterogeneous agricultural areas (24); Forest (31); Scrub and/or herbaceous associations (32); Open spaces with little or no vegetation (33); Inland wetlands (41); Inland waters (51).

In Italy, the total area burned during the study period was 79,118 ha (Figure 2-7) (5.7% of the total burned area in the four countries). Fires affected mainly class 211 "Non-irrigated arable land" (22% of the total area burned in the country), class 321 ("Natural grassland") and class 323 ("Sclerophyllous vegetation") representing each one ca. 19% of the total area burned, and class 311 ("Broad-leaved forest") (15%). 68,621 ha of burned areas (86.7% of the total) did not change land cover after fire (Figure 3-7). From the 10,497 ha that suffered land cover changes, 31% became class 323 ("Sclerophyllous vegetation"), 19% became class 321 ("Natural grassland"), 11% became class 333 ("Sparsely vegetated areas"), 10% became class 243 ("Land principally occupied by agriculture with significant areas of natural vegetation") and 8% became class 334 ("Burned areas").

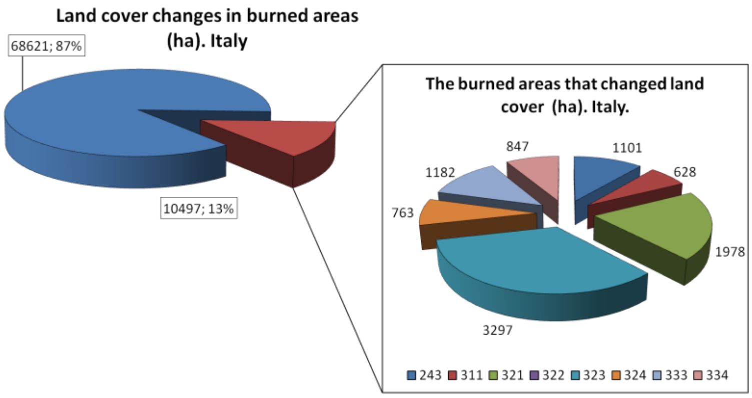


Figure 3-7 Land use change after fire in Italy (ha) (2000-2006)

In France, the total area burned during the study period was 67.727 ha. (Figure 2-7) (4.8% of the total area burned in the four countries). Fires affected mainly classes 323 (“Sclerophyllous vegetation”) and 321 (“Natural grassland”), corresponding to 31% and 17%, respectively, of the total area burned in the country. In addition, fires affected also classes 313 (“Mixed forest”) and 312 (“Coniferous forest”) representing each one ca. 10%. 41,740 ha of the burned areas (61.6% of the total) did not change land cover after fire (Figure 4-7). From the 25,987 ha that changed land cover type, 41% became class 334 (“Burned areas”), 30% became class 324 (“Transitional woodland scrub”) and 20% became class 323 (“Sclerophyllous vegetation”).

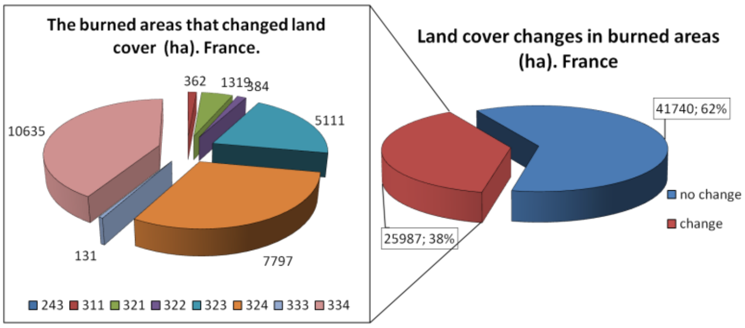


Figure 4-7 Land use change after fire in France (ha) (2000-2006)

In Spain, the total area burned during the study period was 492,243 ha. (Figure 2-7) (35.3% of the total area burned in the four countries). Fires affected mainly class 324 (“Transitional woodland scrub”), corresponding to 27% of the total area burned in the country, and class 323 (“Sclerophyllous vegetation”) (14%). Classes 321 (“Natural grassland”), 312 (“Coniferous forest”) and 313 (“Mixed forest”) were also strongly subjected to fires (12%, 11% and 10%, respectively, of the total burned area). 381,982 ha of the burned areas (77.6% of the total) did not change land cover after fire, whereas 110,261 ha did (Figure 5-7). Among the latter, 47% became class 324 (“Transitional woodland scrub”) and 29% became class 334 (“Burned areas”).

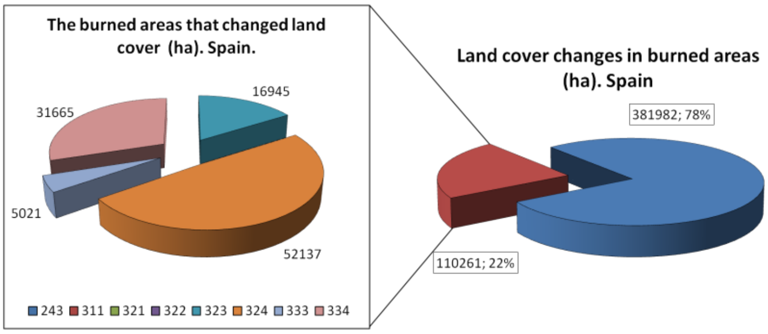


Figure 5-7 Land use change after fire in Spain (ha) (2000-2006)

In Portugal, the total area burned during the study period was 756,031 ha (Figure 2-7). This country had, therefore, the largest proportion (54.2%) over the total area burned in the four countries. Fires affected mainly class 324 (“Transitional woodland scrub”), corresponding to 24% of the burned area, class 312

(“Coniferous forest”) (19%), class 311 (“Broad-leaved forest”) (15%) and class 322 (“Moors and heathland”) (11%). 469,533 ha of burned areas (62.1% of the total) did not change land cover after fire, whereas 286,498 ha did, of which 81% became class 324 (“Transitional woodland scrub”), 7% class 334 (“Burned areas”) and 3% class 322 (“Moors and heathland”) (Figure 6-7).

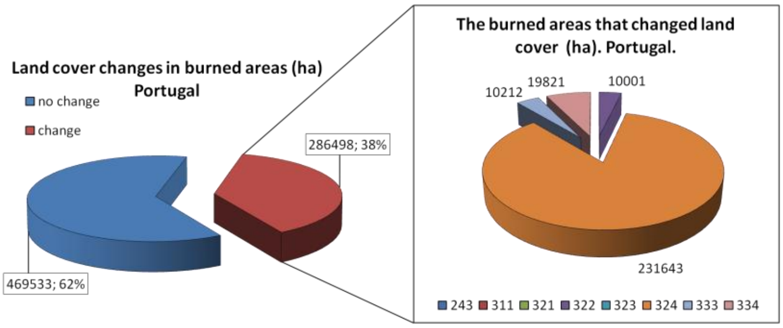


Figure 6-7 Land use change after fire in Portugal (ha) (2000-2006)

Classifying all the CLC transition classes into agradative (any transition resulting in an increase of the vegetation cover or leading to a more advanced successional stage), degradative or stable categories, we found clear differences among the considered countries in the distribution of the total burned area among these three types (Table 2-7). In Portugal, Spain and France, the post-fire land cover changes occurred in areas burned between 2000 and 2006 mostly favoured degradative transitions. This degradation trend was particularly strong in Portugal and Spain. In France, agradative transitions represented a slightly larger area than degradative ones.

Table 2-7 Distribution of the total burned area per country between agradative, degradative and stable land cover transitions.

	Italy		France		Spain		Portugal	
	ha	%	ha	%	ha	%	ha	%
Agradative transitions	4,187	5.3	13,331	19.7	36,736	7.5	42,717	5.7
Degradative transitions	6,308	8.0	12,667	18.7	73,524	14.9	243,774	32.2
Stable transitions	68,621	86.7	41,740	61.6	381,982	77.6	469,533	62.1

These results suggest a slow post-fire vegetation dynamics in most of the countries studied. In all of them, except France, degradative transitions accounted for the largest part of the land cover changes that occurred on burned areas. Moreover, a large part of the areas classified as 33 (“Open spaces with little or no vegetation”) in CLC 2000 had remained in that same class in CLC 2006, not evolving to classes with increased vegetation cover or towards more mature successional stages. This slow dynamics may be due to various factors. First of all, in Spain and Portugal (the two countries with the smallest proportion of agradative transitions), more adverse climatic conditions (i.e. dryer conditions) in many of the areas affected by fires may have caused lower rates of post-fire vegetation recovery. Secondly, in those two countries, a large part of the fires occurred in the last two years of the studied period (2005 and 2006). In Spain and

Portugal, these fires accounted for 38% and 33 %, respectively, of the total burned area in each case, whereas in Italy and France, these values were much lower (26% and 11%, respectively). In the two former countries, thus, a larger extent of burned areas had a very short time to recover, which, obviously, influenced the results.

In general, the length of the study period was short, as the maximum post-fire period that could be monitored was 6 years. We have to highlight, therefore, that in most cases our results are documenting post-fire land cover dynamics on the short (or sometimes medium) term.

7.4 Changes in the BVOC emissions due to biomass burning

To assess the atmospheric impact of biomass burning, and especially to represent it quantitatively in models of atmospheric transport and chemistry, accurate data on the emission of trace gases and aerosols from biomass fires are required.

Emissions must typically be represented in the form of spatiotemporally resolved fields, where the emissions per unit area and time is provided at a specified spatial and temporal resolution. These fields are obtained by multiplying an exposure term, for example, the amount of biomass burned within a grid cell during a time interval, with an emission factor, that is, the amount of the chemical species released per mass of biomass burned (Andreae, et al., 2001).

The atmospheric impact of forest fire mainly depend on two processes: the emission directly connected to the burning of biomass and the changes in the BVOC emissions, related to the land use change after fire, since with the burning biomass disappears a part of the emission of the burned area.

The same approach used in estimating the BVOC emissions from Italian forest ecosystem, could be employed to estimate the emission from forest fire using the burned area maps used in the chapter 5: this estimate however require further data, such as burning efficiency and emission factors.

The burning efficiency could be assessed with a dryness index, based on the relative greenness index (RGI), it derived from the normalized difference vegetation index (NDVI) (Barbosa, et al., 1999).

The emission factor is defined as the amount of a compound released (M_x) per amount of dry fuel consumed ($M_{biomass}$), expressed in units of g kg^{-1}. Calculation of this parameter requires knowledge of the carbon content of the biomass burned and the carbon budget of the fire. The total carbon released is estimated by adding measured concentrations of CO_2, CO, hydrocarbons, and particulate carbon, when this information is available. The emission factor can be expressed as:

$$\boldsymbol{EF_x = \frac{M_x}{M_{biomass}} = \frac{M_x}{M_C}[C]_{biomass}}$$

$$\boldsymbol{EF_x = \frac{[x]}{\Sigma([C_{\mathrm{CO_2}}] + [C_{\mathrm{CO}}] + [C_{\mathrm{CH_4}}] + [C_{\mathrm{VOC}}] + [C_{\mathrm{aeros}}] + \cdots)}[C]_{biomass}}$$

where,

M_c is the mass of carbon emitted, $[\boldsymbol{C}]_{\boldsymbol{biomass}}$ is the carbon concentration in the biomass burned, $[\boldsymbol{x}]$ is the concentration of species *x* in the smoke, and $[\mathbf{C_{CO_2}}]$ etc. Are the concentrations of the various carbon species in the smoke. Alternatively, the carbon budget of the fire can be estimated by multiplying the CO_2 in the smoke with an assumed factor to represented non-CO_2 carbon emissions (i.e., CO, hydrocarbons, and aerosol carbon). Where fuel and residue data at the ground are not available, a fuel carbon content of 45% is usually assumed in order to derive emission factors from emission ratios (Andreae, et al., 2001).

Furthermore, our model is able to detect the changes in the BVOC emissions due to the change in the forest covers after fires.

8. CONCLUSIONS

Although time consuming, the species-specific approach used in our model allows to get reliable Figures of the isoprenoid emissions from the Italian forest ecosystems at a high spatial and temporal resolution. It provides a unique set input data for modelling the photochemical oxidant formation at different scales. In the way it has been designed, it is quite friendly and be improved as soon as more speciated emission data are available. Definitely, a validation on a forest site with conifers should be made, especially in those located in Calabria, where *Pinus nigra* is present. We think that a module is needed to account for changes in emission caused by drought stress. Although we know how to properly correct the emission algorithms for these effects, there is a difficulty to define proper thresholds to which they can be applied. Certainly, it must be combined with a module considering the type of soils where forests are located.

Regarding to the study realized about the land use changes post-fire in Southern Europe, could be important to develop modules to estimates the pyrogenic and biogenic VOC emissions from biomass burning. This aim can be achieved by evaluating BVOC emission factors from biomass burning in Italian forest ecosystems.

References

Affek H. P. and Yakir D. Protection by isoprene against singlet oxygen in leaves. [Journal]. - [s.l.] : Plant Physiology, 2002. - 269-277 : Vol. 129.

Andreae M. O. and Merlet P. Emission of trace gases and aerosols from biomass burning. [Journal]. - [s.l.] : Global Biogeochemical Cycles, 2001. - 955-966 : Vol. 15.

Andreae MO. and Crutzen PJ. Atmospheric aerosols: Biogeochemical sources and role in atmospheric chemistry. [Journal]. - [s.l.] : Science, 1997. - 1052-1058 : Vol. 276.

Arimura G., Huber DPW. and Bohlmann J. Forest tent caterpillars (Malacosoma disstria) induce local and systemic diurnal emissions of terpenoid volatiles in hybrid poplar (Populus trichocarpa x deltoides): cDNA cloning, functional characterization, and patterns of gene expression of (-)-germacr [Journal]. - [s.l.] : Plan Journal, 2004. - 603-616 : Vol. 37.

Arneth A. [et al.] Effects of species composition, land surface cover, CO2 concentration and climate on isoprene emissions from European forests. [Journal]. - [s.l.] : Plant Biology, 2008. - 150-162 : Vol. 10.

Atkinson R. and Arey J. Gas-phase troposperic chemistry of biogenic volatile organic compounds: A review. [Journal]. - [s.l.] : Atmos. Environ., 2003. - S197-S219 : Vol. 37.

Atkinson R. Gas-phase tropospheric chemistry of organic compounds: A review. [Journal]. - [s.l.] : Atmospheric Environment, 1990. - 1-41 : Vol. 24 (A).

Bach TJ. Some new aspects of isoprenoid biosynthesis in plants - a review. [Journal]. - [s.l.] : Lipids, 1995. - 191-202 : Vol. 30.

Barbosa P. M. [et al.] An assessment of vegetation fire in Africa (1981-1991): Burned areas, burned biomass, and atmospheric emissions. [Journal]. - [s.l.] : Global Biochemical Cycles, 1999. - 933-950 : Vol. 13.

Bertin N. and Staudt M. Effect of water stress on monoterpenes emissions from young potted holm oak (Quercus ilex L.) trees. [Journal]. - [s.l.] : Oecologia, 1996. - 456-462 : Vol. 107.

Bessagnet B., Seigneur C. and Laurent M. Impact of dry deposition of semi-volatile organic compounds on secondary organic aerosols. [Journal]. - [s.l.] : Atmospheric Environment, 2010. - 1781-1787 : Vol. 44.

Bonn B. and Moortgat GK. Sesquiterpene ozonolysis: origin of atmospheric new particle formation from biogenic hydrocarbons. [Book]. - [s.l.] : Geophysical Research Letters, 2003. - Vols. 30 (11), 1585. DOI: 10.1029/2003GL017000.

Bonn B. and Moortgat GK. Sesquiterpene ozonolysis: Origin of atmospheric new particle formation from biogenic hydrocarbons. [Journal]. - [s.l.] : Geophys. Res. Lett., 2003. - 1585-1588 : Vol. 30.

Cabada JC. [et al.] Mass size distributions and size resolved chemical composition of fine particulate matter at the Pittsburgh supersite. [Journal]. - [s.l.] : Atmos. Environ., 2004. - 3127-3141 : Vol. 38.

Calfapietra C. [et al.] Isoprene emission rates under elevated CO2 and O3 in two field-grown aspen clones differing for their sensitivity to O3. [Journal]. - [s.l.] : New Phytologist, 2008. - 55-61 : Vol. 179.

Calogirou A., Larsen BR. and Kotzias D. Gas-phase terpene oxidation products: A review. [Journal]. - [s.l.] : Atmos. Environ., 1999. - 1429-1439 : Vol. 33(9).

Cane DE. Sesquiterpene biosynthesis: cyclization mechanisms. [Book Section] // Comphrensive Natural Products Chemistry. Isoprenoids Including Carotenoids and Steroids.. - Oxford : Pergamon Press, 1999. - Vol. 2.

Capolovici L. O. [et al.] The capacity for thermal protection of photosynthetic electron transport varies for different monoterpenes in Quercus ilex. [Journal]. - [s.l.] : Plant Physiology, 2005. - 485-496 : Vol. 139.

Chen F. [et al.] Biosynthesis and Emission of Terpenoid Volatiles from Arabidopsis Flowers. [Journal]. - [s.l.] : American Society of Plant Biologists, 2003. - 481-494 : Vol. 15.

Chung SH. and Seinfeld JH. Global distribution and climate forcing of carbonaceous aerosols. [Journal]. - [s.l.] : J. Geophys. Res., 2002. - 4407 : Vol. 107.

Ciccioli P. [et al.] Emission of reactive terpene compounds from orange orchards and their removal by within-canopy processes. [Journal]. - [s.l.] : Journal of Geophysical Research, 1999. - 8077-8094 : Vol. 104.

Ciccioli P. [et al.] Relaxed eddy accumulation, a new techanique for measuring emission and deposition fluxes of volatile organic compounds by capillary gas chromatography and mass spectrometry. [Journal]. - [s.l.] : J. Chromatogr. A, 2003. - 283-296 : Vol. 985.

Ciccioli P. [et al.] Use of the isoprene algorithm for predicting the monoterpene emission from the Mediterranean holm oak Quercus ilex L.: Performance and limits of this approach. [Journal]. - [s.l.] : J. Geophys. Res. (Atmosphere), 1997. - 319-23,328 : Vol. 102.

Ciccioli P., Brancaleoni E. and Frattoni M. Sampling of atmospheric volatile organic compounds (VOCs) with sorbents tubes and their analysis by GC-MS. [Book]. - New York : Environmental Monitoring Handbook, 2002. - Vols. 21.1-21-85.

Claeys M. [et al.] Formation of secondary organic aerosols from isoprene and its gas-phase oxidation products through reaction eith hydrogen peroxide. [Journal]. - [s.l.] : Atmos. Environ., 2004a. - 4093-4098 : Vol. 38.

Claeys M. [et al.] Formation of secondary organic aerosols through photooxidation of isoprene. [Journal]. - [s.l.] : Science, 2004b. - 1173-1176 : Vol. 303.

Collalti A. Sviluppo di un modello dinamico ecologico-forestale per foreste a struttura complessa. [Libro]. - Viterbo : [s.n.], 2011.

Committee on Tropospheric Ozone Formation and Measurement Rethinking the Ozone Problem in Urban and Regional Air Pollution. [Book]. - Washington, DC : National Academy Press, 1991. - Vols. 0-309-04631-9.

Committee on Tropspheric Ozone, National Research Council (CGER) Rethinking the Ozone Problem in Urban and Regional Air Pollution. [Book]. - Washington, D.C. : The Nathional Academies press, 1991.

Croteau R. Effect of irrigation method on essential oil yield and rate of oil evaporation in mint grown under controlled conditions. [Journal]. - [s.l.] : Hort. Sci., 1977. - 563-565 : Vol. 12.

Crutzen PJ. Methane's sources and sinks. [Journal]. - [s.l.] : Nature, 1991. - 380-381 : Vol. 350.

Curci G. [et al.] Modelling study of the impact of isoprene and terpene biogenic emissions on European ozone levels. [Journal]. - [s.l.] : Atmos. Enirion., 2009. - 1444-1455 : Vol. 43.

Derwent R.G., Jenkin M.E. and Saunders S.M. Photochemical ozone creation potentials for a large number of reactive hydrocarbons under European conditions. [Journal]. - [s.l.] : Atmospheric Environment, 1996. - 181-199 : Vol. 30.

Dicke M. and Loreto F. Induced plant volatiles: from genes to climate change [Journal]. - [s.l.] : Trends in Plant Science, 2010. - 115-117 : Vol. 15.

Dindorf T. [et al.] Emission of monoterpenes from European beech (Fagus sylvatica L.) as a function of light and temperature. [Journal]. - [s.l.] : Biogeosciences Discussions, 2005. - 137-182 : Vol. 2.

Dindorf T. [et al.] Significant light and temperature dependent monoterpent emissions from European beech (Fagus sylvatica L.) and their potential impact on the European volatile organic compound budget. [Journal]. - [s.l.] : J. Geophys. Res. (Atmosphere), 2006. - DOI:10.1029/2005JD006751 : Vol. D16305.

Dixon J. and Hewett EW. Factors affecting apple aroma/flavour volatile concentration: a review. [Journal]. - [s.l.] : New Zealand Journal of Crop and Horticultural Science, 2000. - 155-173 : Vol. 28.

Dudareva N. [et al.] (E)-beta-ocimene and myrcene synthase genes of floral scent biosynthesis in snapdragon: function and expression of three terpene synthase genes of a new terpene synthase subfamily. [Journal]. - [s.l.] : Plant Cell, 2003. - 1227-1241 : Vol. 15.

Dudareva N., Pichersky E. and Gershenzon J. Biochemistry of plant volatiles [Journal]. - [s.l.] : Plant Physiology, 2004. - 1893-1902 : Vol. 135.

Dusek U. Secondary Organic Aerosol - Formation Mechanisms and Source Contributions in Europe. [Report]. - Laxenburg : Science for Global Insight, 2000.

Estell RE. [et al.] Secondary chemistry of the leaf surface of Flourensia cernua. [Journal]. - [s.l.] : Biochem. System. Ecol., 1994. - 73-77 : Vol. 22.

Evans RC., Tingey DT. and Gumpertz ML. Interspecies variation in terpenoid emissions from Engelmann and Sitka spruce seedlings. [Journal]. - [s.l.] : Forest Sci, 1985. - 132-142 : Vol. 31.

Fall R. and Benson A. Leaf methanol - the simplest natural product from plants. [Journal]. - [s.l.] : Trends Plant Sci., 1996. - 296-301 : Vol. 1.

Fall R. and Monson RK. Isoprene emission rate in relation to stomatal distribution and stomatal conductance. [Journal]. - [s.l.] : Plant Physiol., 1992. - 987-992 : Vol. 100.

Fall R. Biogenic Emissions of Volatile Organic Compounds from Higher Plants. [Book Section] // Reactive hydrocarbons in the Atmosphere. / book auth. Hewitt NC.. - New York : Academic Press, 1999. - Vols. 41-96.

Fares S. [et al.] The ACCENT-VOCBAS field campaing on biosphere-atmosphere interactions in a Mediterranean ecosystem of Castelporziano (Rome): site characteristics, climatic and meteorological conditions, and eco-physiology of vegetation. [Journal]. - [s.l.] : Biogeosciences, 2009. - 1043-1058 : Vol. 6.

Fehsenfeld F. [et al.] Emissions of volatile organic compounds from vegetation and the implications for atmospheric chemistry. [Journal]. - [s.l.] : Global Biogeochem., 1992. - 389-430 : Vol. 6.

Feikema P.M. [et al.] Validation of plantation transpiration in south-eastern Australia estimated using the 3PG+ forest growth model. [Journal]. - [s.l.] : Forest Ecology and Management, 2010. - 663-678 : Vol. 260.

Fernandes P. Combining forest structure data and fuel modelling to classify fire hazard in Portugal. [Journal]. - [s.l.] : Ann. For. Sci., 2009. - Vol. 66(4):415.

Finnlayson-Pitts BJ. and Pitts JN. Jr. Chemistry of the lower and upper atmosphere. [Book]. - San Diego, USA : Academic Press, 1999.

Fischbach RJ. [et al.] Seasonal pattern of monoterpene synthase activities in leaves of the evergreen tree Quercus ilex. [Journal]. - [s.l.] : Physiologia Plantarum, 2002. - 354-360 : Vol. 114.

Flesch G. and Rohmer M Prokaryotic triterpenoids. The biosynthesis of the bacteriohopane skeleton: formation of isoprenic units from two distinct acetate pools and a novel type of carbon/carbon linkage between a triterpene and D-ribose. [Journal]. - [s.l.] : Eur. J. Biochem., 1988. - 405-411 : Vol. 175.

Fortunati A. [et al.] Isoprene emission is not temperature-dependent during and after severe drought-stress: a physiological and biochemical analysis. [Journal]. - [s.l.] : Plant Journal, 2008. - 687-697 : Vol. 55.

Friedrich R. and Obermeier A. Anthropogenic Emissions of Volatile Organic Compounds. [Book Section] // Reactive Hydrocarbons in the Atmosphere. / book auth. Hewitt NC.. - New York : Academic Press, 1999. - Vols. 41-96.

Fuentes J.D. [et al.] New directions: VOCs and biosphere-atmosphere feedbacks. [Journal]. - [s.l.] : Atmospheric Environment, 2001. - 189-191 : Vol. 35.

Fuentes JD. [et al.] Biogenic hydrocarbons in the atmospheric boundary layer: a review. [Book]. - [s.l.] : Bulletin of the American Meteorological Society., 2000. - Vols. 81: 1537-1575.

Fukui Y. and Doskey PV. Identification of nonmethane organic compound emissions from grassland vegetation. [Journal]. - [s.l.] : Atmospheric Environment, 2000. - 2947-2956 : Vol. 34.

Gershenzon J., McConkey ME. and Croteau RB. Regulation of monoterpene accumulation in leaves of peppermint. [Journal]. - [s.l.] : Plant. Physiol., 2000. - 205-213 : Vol. 122.

Gower S.T., Reich P.B. and Son Y. Canopy dynamics and aboveground production of five tree species with different leaf longevities. [Journal]. - Victoria, Canada. : Tree Physiology, 1993. - 327-345 : Vol. 12.

Grabmer W. [et al.] VOC emissions from Norway spruce (Picea abies L.[Karts]) twigs in the field - Results of a dynamic enclosure study. [Journal]. - [s.l.] : Atmos. Environ., 2006. - 128-137 : Vol. 40.

Graedel TE. [et al.] A compilation of inventories of emissions to the atmosphere. [Journal]. - [s.l.] : Global Biogeochem. Cycles., 1993. - 1-26 : Vol. 7.

Graedel TE. Terpenoids in the atmosphere. [Journal]. - [s.l.] : Rev. Geophys. Space. Phys., 1979. - 937-947 : Vol. 17.

Griffin RJ., Dabdub D. and JH.Seinfeld Estimate of global atmospheric organic aerosol from oxidation of biogenic hydrocarbons. [Journal]. - [s.l.] : Geophys. Res. Lett., 1999. - 2721-2724 : Vol. 26.

Grote R. and Niinemets U. Modeling volatile isoprenoid emissions - a story with split ends. [Journal]. - [s.l.] : Plant Biology, 2008. - 8-28 : Vol. 10.

Guenther A. [et al.] A global-model of natural volatile organic-compound emissions. [Journal]. - [s.l.] : Journal of Geophysical Research-Atmospheres, 1995. - 8873-8892 : Vol. 100.

Guenther A. [et al.] Natural emissions of non-methane volatile organic compounds, carbon monoxide, and oxides of nitrogen from North America. [Journal]. - [s.l.] : Atmospheric Environment, 2000. - 2205-2230 : Vol. 34.

Guenther A. Seasonal and spatial variations in natural volatile organic compound emissions. [Journal]. - [s.l.] : Ecol. Appl., 1997. - 34-45 : Vol. 7.

Guenther A., Zimmerman PR. and Harley PC. Isoprene and monoterpene emission rate variability: model evaluations and sensitivity analyses. [Journal] // J Geophys Res. - [s.l.] : J. Geophys Res., 1993. - 12609-17 : Vol. 98. - pp. 98:12609-17.

Guenther AB., Monson RK. and Fall R. Isoprene and monoterpene emission rate variability: Observations with Eucalyptus and emission rate algorithm development [Journal]. - [s.l.] : J. Geophis. Res., 1991. - 10799-10808 : Vol. 96.

Guidolotti G., Calfapietra C. and Loreto F. The relationship between isoprene emission, CO2 assimilation and water use efficienty across a range of poplar genotypes. [Journal]. - [s.l.] : Physiologia Plantarum, 2011. - Vols. ISSN 0031-9317.

Harley P. [et al.] Emission of 2-metyl-3-buten-2-ol by pines: a potentially large natural source of reactive carbon to the atmosphere. [Journal]. - [s.l.] : Journal of Geophysical Research, 1998. - 25479-25486 : Vol. 103.

Hayden BP. Ecosystem feedbacks on climate at the landscape scale. [Journal]. - [s.l.] : Philosophical Transactions of the Royal Society of London Series B-Biological Sciences., 1998. - 5-18 : Vol. 353.

Helmig D. [et al.] Biogenic volatile organic compound emissions (BVOC). I. Identifications from three continental sites in the U.S. [Journal]. - [s.l.] : Chemosphere, 1999. - 2163-2187 : Vol. 38 (9).

Hermsmeier D., Schittko U. and Baldwin IT. Molecular interections between the specialist herbivore Manduca sexta (Lepidoptera, Sphingidae) and its natural host Nicotiana attenuata. I. Large-scale changes in the accumulation of growth-and defense-related plant mRNAs. [Journal]. - [s.l.] : Plant Physiology, 2001. - 683-700 : Vol. 125.

Hoffmann T. [et al.] Formation of organic aerosols from the oxidation of biogenic hydrocarbons. [Journal]. - [s.l.] : Journal of Atmospheric Chemistry, 1997. - 189-222 : Vol. 26.

Holzke C. [et al.] Terpene emissions from European beech (Fagus sylvatica L.): pattern and emission behaviour within two vegetation periods. [Journal]. - [s.l.] : Journal of Atmospheric Chemistry, 2006. - 81-102 : Vol. 55.

Jacobson MC. [et al.] Organic atmospheric aerosols: review and state of the science. [Journal]. - [s.l.] : Rev. Geophys., 2000. - 267-294 : Vol. 38.

Jacovides C. P. [et al.] Ratio of PAR to broadband solar radiation measured in Cyprus [Journal]. - [s.l.] : Agricultural and Forest Meteorology, 2004. - 135-140 : Vol. 121.

Jang M. [et al.] Particle growth by acid-catayzed heterogeneous reactions of organic carbonyls on preexisting aerosols. [Journal]. - [s.l.] : Environ. Sci. Technol., 2003. - 3828-3837 : Vol. 37.

Jang M. and Kamens RM. Newly characterized products and composition of secondary aerosols from the reaction of a-pinene with ozone. [Journal]. - [s.l.] : Atmos. Environ., 1999. - 459-474 : Vol. 33.

Jaoui M., Leungsakul S. and Kamens RM. Gas and particle distribution from the reaction of b-caryophyllene with ozno. [Journal]. - [s.l.] : J. Atmos. Chem. , 2003. - 261-287 : Vol. 45.

Jenkin ME. and Hayman GD. Photochemical ozone creation potentials for oxygenated volatile organic compounds: sensitivity to variations in kinetic and mechanistic parameters. [Journal]. - [s.l.] : Atmospheric Environment, 1999. - 1275-1293 : Vol. 33.

Joutsensaari J. [et al.] Nanoparticle formation by ozonolysis of inducible plant volatiles. [Journal]. - [s.l.] : Atmospheric Chemistry and Physics, 2005. - 1489-1495 : Vol. 5.

Kanakidou M. [et al.] Organic aerosol and global climate modelling: a review. [Journal]. - [s.l.] : Atmospheric Chemistry and Physics, 2005. - 1053-1123 : Vol. 5.

Kant MR. [et al.] Differential timing of spider mite-induced direct and indirect defenses in tomato plants. [Journal]. - [s.l.] : Plant Physiology, 2004. - 483-495 : Vol. 135.

Karl M. [et al.] A new European plant-specific emission inventory of biogenic volatile organic compounds for use in atmospheric trasport models. [Journal]. - [s.l.] : Biogeosciences, 2009. - 1059-1087 : Vol. 6.

Kavauras IG., Mihalopoulos N. and Stephanou EG. Secondary organic aerosol formation vs primary organic aerosol emission: In situ evidence for the chemical coupling between monoterpene acidic photooxidation products and new particle formation over forests. [Journal]. - [s.l.] : Environ. Sci. Technol., 1999b. - 1028-1037 : Vol. 33.

Kavouras IG., Mihalopoulos N. and Stephanou EG. Formation and gas/ particle partitioning of monoterpenes photo-oxidation products over forests. [Journal]. - [s.l.] : Geophys. Res. Lett., 1999a. - 55-58 : Vol. 26(1).

Kavouras IG., Mihalopoulos N. and Stephanou EG. Formation of atmospheric particles from organic acids produced by forests. [Journal]. - [s.l.] : Nature, 1998. - 683-686 : Vol. 395.

Keeling CI. and Bohlmann J. Genes, enzimes and chemicals of terpenoid diversity in the constitutive and induced defence of conifers against insects and pathogens. [Journal]. - [s.l.] : New Phytologist, 2006. - 657-675 : Vol. 170.

Kesselmeier J. [et al.] Emission of monoterpenes and isoprene from a Mediterranean oak species Quercus ilex L. measured within the BEMA (biogenic emissions in the Mediterranean Area) project. [Journal]. - [s.l.] : Atmospheric Environment, 1996. - 1841-1850 : Vol. 30.

Kesselmeier J. [et al.] EMISSION OF SHORT CHAINED ORGANIC ACIDS, ALDEHYDES AND MONOTERPENES FROM QUERCUS ILEX L. AND PINUS PINEA L. IN RELATION TO PHYSIOLOGICAL ACTIVITIES, CARBON BUDGET AND EMISSION ALGORITHMS. [Journal]. - Great Britain : Atmos. Environ., 1997. - 119-133 : Vols. 31, No. SI.

Kesselmeier J. and Staudt M. Biogenic Volatile Organic Compounds (VOC): An Overview on Emission, Physiology and Ecology. [Journal]. - [s.l.] : Journal of Atmospheric Chemistry, 1999. - 23-88 : Vol. 33.

Kirstine W. [et al.] Emissions of volatile organic compounds (primarily oxygenated species) from pasture. [Journal]. - [s.l.] : Journal of Geophysical Research-Atmospheres, 1998. - 10 605-10 619 : Vol. 103.

Knudsen JT. [et al.] Diversity and distribution of floral scent. [Journal]. - [s.l.] : Botanical Review, 2006. - 1-120 : Vol. 72.

Knudsen JT. and Gershenzon J. The chemistry diversity of floral scent. [Book Section] // Biology of floral scent / book auth. Dudareva N. and Pichersky E.. - Boca Raton, FL, USA : CRC Press, 2006. - Vols. 27-52.

Komenda M. [et al.] Measurements of biogenic VOC emissions: Sampling, analysis and calibation. [Journal]. - [s.l.] : Atmos. Environ., 2001. - 2069-2080 : Vol. 35.

Komenda M. Investigation of the emissions of monoterpenes from Scots pine, Ph.D. Thesis. [Book]. - Julich, Germany : Universitat zi Koln, Berichte des Forschungszentrums, 2001. - Vols. Jul-3866.

Kourtchev I. [et al.] Observation of 2-methyltetrols and related photo-oxidation products of isoprene in boreal forest aerosols from Hyytiala, Finland. [Journal]. - [s.l.] : Atmos. Chem. Phys., 2005. - 2761-2770 : Vol. 5.

Koyama T. and Ogura K. Isopentenyl diphosphate isomerase and prenyltransferases. [Book Section] // Comprehensive Natural Product Chemistry. Isoprenoids Including Catenoids and Steroids. / book auth. Cane DE.. - Oxford : Pergamon Press, 1999. - Vol. 2.

Kroll J.H. and Seinfeld Chemistry of secondary organic aerosol: Formation and evolution of low-volatility organics in the atmosphere. [Journal]. - [s.l.] : Atmos. Environ., 2008. - 3593-3624 : Vol. 42.

Kroll JH. [et al.] Secondary aerosol from isoprene photooxidation under high-NOx conditions. [Journal]. - [s.l.] : Geophys. Res. Lett., 2005. - L18808, DOI: 10.1029/2005GL023637 : Vol. 32.

Kroll JH. and Seinfeld JH. Review: chemistry of secondary organic aerosol: formation and evolution of low-volatility organics in the atmosphere. [Journal]. - [s.l.] : Atmos. Environ., 2008. - 3593-3624 : Vol. 42.

Kuhn U. [et al.] Isoprene and monoterpene emissions of Amazonian tree species during the wet season: Direct and indirect investigations on controlling encironmental functions. [Journal]. - [s.l.] : J. Geophys. Res. (Atmosphere), 2002. - DOI:10.1029/2001JD000978 : Vols. 107 NO, D20, 8071.

Kuhn U. [et al.] Seasonal differences in isoprene and light-dependent monoterpene emission by Amazonian tree species. [Journal]. - [s.l.] : Global Change Biology, 2004. - 663-682 : Vol. 10.

Kuzma J. and Fall R. Leaf isoprene emission rate is dependent on leaf development and the level of isoprene synthase. [Journal]. - [s.l.] : Plant Physiology, 1993. - 435-440 : Vol. 101.

Lamb B. [et al.] A biogenic hydrocarbon emission inventory for the U.S.A. using a simple forest canopy model. [Journal]. - [s.l.] : Atmos. Environ., 1993. - 1673-1690 : Vol. 27.

Lamb B. [et al.] Biogenic hydrocarbon emissions from deciduos rate and coniferous trees in the United States. [Journal]. - [s.l.] : J. Geophys. Res., 1985. - 2380-2390 : Vol. 90.

Laothawornkitkul J. [et al.] Biogenic volatile organic compounds in the Earth system. [Journal]. - [s.l.] : New Phytologist, 2009. - 27-51 : Vol. 183.

Laurila T. Biogenic VOC emissions and photochemistry in the boreal regions of Europe. [Report] : Final report, contract N° ENV4-CT95-0022. - Helsinki : Summary of Biphorep project. In: Laurila T, Lindfords V, editors. Final report, contract N° ENV4-CT95-0022, 1999.

Leaitch WR. [et al.] A case study of gase-to-particle conversion in an eastern Canadian forest. [Journal]. - [s.l.] : Journal of Geophysical Research-Atmospheres, 1999. - 8095-8111 : Vol. 104.

Lendzian KJ. Aufnahme und zellphysiologische Wirkungen von Luftschadstoffen. [Journal]. - [s.l.] : Naturwissenschaften, 1987. - 282-288 : Vol. 74.

Lenz R., Koble R. and Seufert G. Species-based Mapping of Biogenic Emissions in Europe - Case study Italy. [Report]. - [s.l.] : Atmosphere, 1997.

Lenz R., Koble R. and Seufert G. Species-based Mapping of Biogenic Emissions in Europe - Case Study Italy. [Conference] // Proceedings of the 8th European Symposium on the Physico-Chemical behaviour of Atmospheric Pollutants.. - Ispra : Hjorth J.; Raes F. and Angeletti G., Paper TP 15, Published on CD-ROM by The Institute of Environment and Sustainnability, JRC of Ispra, DG Research, European Commission, 2002.

Lenz R.J.M., Seufert G. and Selige TH. Scaling up the biogenic emissions from test sites at Castelporziano. [Journal]. - [s.l.] : Atmos. Environ., 1997. - 239-250 : Vol. 31 No. SI.

Lerdau M. A positive feedback with negative consequences. [Journal]. - [s.l.] : Science, 2007. - 212-213 : Vol. 316.

Lerdau M. and Slobodkin K. Trace gas emissions and species-dependent ecosystem services. [Journal]. - [s.l.] : Trends in Ecology & Evolution, 2002. - 309-312 : Vol. 17.

Lerdau M., Guenther A. and Monson R. Plant production and emission of volatile organic compounds. [Journal]. - [s.l.] : Bioscience, 1997. - 373-383 : Vol. 47.

Levis S. [et al.] Simulating biogenic volatile organic compound emissions in the Community Climate System Model. [Journal]. - [s.l.] : Journal of Geophysical Research-Atmospheres, 2003. - DOI: 10.1029/2002JD003203 : Vol. 108: 659(D4).

Liang P-H., T-P.Ko and Wang AH-J. Structure, mechanism and function of prenyltransferases. [Journal]. - [s.l.] : Eur J Biochem, 2002. - 3339-3354 : Vol. 269.

Limbeck A., Kulmala M. and Puxbaum H. Secondary organic aerosol formation in the atmosphere via heterogeneous reaction of gaseous isoprene on acidic particles. [Journal]. - [s.l.] : Geophys. Res. Lett., 2003. - DOI: 10.1029/2003GL017738 : Vols. 30(19), 1996.

Llusia J. and Penuelas J. Pinus halepensis and Quercus ilex terpene emission as affected by temperature and humidity. [Journal]. - [s.l.] : Biologia Plantarum, 1999. - 317-320 : Vol. 42 (2).

Llusià J. and Penuelas J. Seasonal patterns of terpene content and emission from seven Mediterranean woody species in field conditions. [Journal]. - [s.l.] : Am. J. Bot., 2000. - 133-140 : Vol. 87.

Logan BA., Monson RS. and Potosnak MJ. Biochemistry and physiology of foliar isoprene production. [Journal]. - [s.l.] : Trends in Plant Science, 2000. - 477-481 : Vol. 5.

Logan JA. [et al.] Tropospheric chemistry - a global perspective. [Journal]. - [s.l.] : Journal of Geophysical Research-Oceans and Atmospheres, 1981. - 7210-7254 : Vol. 86.

Loreto F. [et al.] Influence of environmental factors and air composition on the emission of a-pinene from Quercus ilex leaves. [Journal]. - [s.l.] : Plant Physiol., 1996. - 267-275 : Vol. 110.

Loreto F. [et al.] Monoterpene emission and monoterpene synthase activities in the Mediterranean evergreen oak Quercus ilex L. Grown at elevated CO2 concentrations. [Journal]. - [s.l.] : Global Change Biology, 2001a. - 709-717 : Vol. 7.

Loreto F. [et al.] On the monoterpene emission under heat stress and on the increased thermotolerance of leaves of Quercus ilex L. fumigated with selected monoterpenes. [Journal]. - [s.l.] : Plant Cell and Environment, 1998. - 101-107 : Vol. 21.

Loreto F. [et al.] Ozone quenching properties of isoprene and its antioxidant role in leaves. [Journal]. - [s.l.] : Plant Physiology, 2001b. - 993-1000 : Vol. 126.

Loreto F. and Sharkey TD. A gas-exchange study of photosynthesis and isoprene emissin in Quercus rubra L. [Journal]. - [s.l.] : Planta, 1990. - 523-231 : Vol. 182.

Mariscal M.J., Orgaz F. and Villalobos F.J. Radiation-use efficiency and dry matter partitioning of a young olive (Olea europaea) orchard. [Journal]. - Victoria, Canada. : Tree Physiology, 2000. - 65-72 : Vol. 20.

Matsunaga S., Mochida M. and Kawamura K. Growth of organic aerosols by biogenic semi-volatile carbonyls in the forestal atmosphere. [Journal]. - [s.l.] : Atmos. Environ., 2003. - 2045-2050 : Vol. 37.

McGarvey DJ. and Croteau R. Terpenoids metabolism. [Journal]. - [s.l.] : The Plant Cell, 1995. - 1015-1026 : Vol. 7.

Mediavilla S. and Escudero A. Relative growth rate of leaf biomass and leaf nitrogen content in several mediterranean woody species. [Journal]. - Netherlands : Plant Ecology, 2003. - 321-332 : Vol. 168.

Mencuccini M. and Bonosi L. Leaf/sapwood area ratios in Scots pine show acclimation across Europe. [Journal]. - Canada : Can. J. For. Res. , 2001. - 442-456 : Vol. 31.

Meskhidze N. and Nenes A. Phytoplankton and cloudiness in the Southern Ocean. [Journal]. - [s.l.] : Sicence, 2006. - 1419-1423 : Vol. 314.

Miller B. [et al.] Insect-induced conifer defense. White pine weevil and methyl jasmonate induce traumatic resinosis, de novo formed volatile emissions, and accumulation of terpenoid synthase and putative octadecanoid pathway transcripts in Sitka spruce. [Journal]. - [s.l.] : Plant Physiology, 2005. - 369-382 : Vol. 137.

Monson RK. and Fall R. Isoprene emissions from aspen leaves. Influence of environment and relation to photosynthesis and photorespiration. [Journal]. - [s.l.] : Plant Physiol., 1989. - 267-274 : Vol. 90.

Monson RK., Guenther AB. and Fall R. Physiological reality in relation to ecosystem- and global-level estimates of isoprene emission. [Book Section] // Trace Gas Emissions from Plants. / book auth. Sharkey TD., Holland EA. and Mooney HA.. - San Diego : Academic Press, 1991. - Vols. 185-207.

Moreira F. [et al.] Regional variations in wildfire susceptibility of land cover types in Portugal: implications for landscape management to minimize fire hazard. [Journal]. - [s.l.] : Int. J. Wildland Fire, 2009. - 563-574 : Vol. 18.

Muller JF. Geographical distribution and seasonal variation of surface emission and deposition velocities of atmospheric trace gases. [Journal]. - [s.l.] : Journal of Geophysical Research, 1992. - 3787-3804 : Vol. 97 (D4).

Mumm R. [et al.] Analysis of volatiles from black pine (Pinus nigra): significance of wounding and egg deposition by a herbivorous sawfly. [Journal]. - [s.l.] : Phytochemistry, 2004. - 3221-3230 : Vol. 65.

NESCAUM (Northeast States for Coordinated Air Use Management) Preview of 1994 Ozone Precursor Concentrations in the Northeastern U.S. [Book]. - [s.l.] : Ambient Monitoring and Assessment Committee., 1995. - Vol. Available at http://capita.wustl.edu/nescaum/Reports/PAMS94/.

Niinemets U. [et al.] Estimations of isoprenoid emission capacity from enclosure studies: measurements, data processing, quality and standardized measurement protocols. [Journal]. - [s.l.] : Biogeosciences, 2011. - 2209-2246 : Vol. 8.

Niinemets U. and Reichstein M. Effect of nonspecific monoterpenoid storage in leaf tissues on emission kinetics and composition in Mediterranean sclerophyllous Quercus species: a model analysis. [Journal]. - [s.l.] : Glob. Biogeochem. Cycle, 2002. - DOI: 10.1029/2002GB001927 : Vols. 16, 1110.

Niinemets U., Loreto F. and Reichstein M. Physiological and physiocochemical controls on foliar volatile organic compound emissions. [Journal]. - [s.l.] : Trends in Plant Science, 2004. - 180-186 : Vol. 9.

Noe SM. [et al.] Emissions of monoterpenes linalool and ocimene respond differently to environmental changes due to differences in physico-chemical characteristics. [Journal]. - [s.l.] : Atmospheric Environment, 2006. - 4649-4662 : Vol. 40.

Owen SM., Boissard C. and Hewitt CN. Volatile organic compounds (VOCs) emitted from 40 Mediterranean plant species: VOC speciation and extrapolation to habitat scale. [Journal]. - [s.l.] : Atmospheric Environment, 2001. - 5393-5409 : Vol. 35.

Pandis SN. [et al.] Secondary organic aerosol formation and transport. [Journal]. - [s.l.] : Atmos. Environ., 1992. - 2269-2282 : Vol. 26.

Parra R., Gasso S. and Baldasano J.M. Estimating the biogenic emissions of non-methane volatile organic compounds from the North Western Mediterranean vegetation of Catalonia, Spain. [Journal]. - [s.l.] : Science of the Total Environment, 2004. - 241-259 : Vol. 329.

Penuelas J. [et al.] Linking isoprene with plant thermotolerance, antioxidants and monoterpene emissions. [Journal]. - [s.l.] : Plant, Cell and Environment, 2005. - 278-286 : Vol. 28.

Penuelas J. and Llusià J. BVOCs: plants defences against climate warming? [Journal]. - [s.l.] : Trends Plants Sci., 2003. - 105-109 : Vol. 8.

Piccot SD., Watson JJ. and Jones JW. A global inventory of volatile organic compound emissions from anthropogenic sources. [Journal]. - [s.l.] : Journal of Geophysical Research, 1992. - 9897-9912 : Vol. 97 (D9).

Pio CA. [et al.] Diurnal and seasonal emissions of volatile organic compounds from cork oak (Quercus suber) trees. [Journal]. - [s.l.] : Atmos. Environ., 2005. - 1817-1827 : Vol. 39.

Poecke R. M. van and Dicke M. Indirect defence of plants against herbivores: using Arabidopsis thaliana as a model plant. [Journal]. - [s.l.] : Plant Biology, 2004. - 387-401 : Vol. 6.

Ralph S. [et al.] Genomics of hybrid poplar(populus trichocarpa x deltoides)interacting with forest tent caterpillars(Malacosoma disstria):normalized and full-lenght cDNA libraries,expressed sequencies tags,and a cDNA microarray for the study of insect-induced defences [Journal]. - [s.l.] : Molecular Ecology, 2006. - 1275-1297 : Vol. 15.

Rizzo LV. [et al.] Measurement of aerosol and VOC turbulent fluxes over a pristine forest in Amazonia. [Conference] // Eos trans., Fall Meeting. - [s.l.] : American Geophysical Union, 2006. - Vols. A23A-0931.

Roche P., Diaz-Burlinson N. and Gachet S. Congruency analysis of species ranking based on leaf traits: which traits are the more reliable? [Journal]. - Netherlands : Plant Ecology, 2004. - 37-48 : Vol. 174.

Rodriguez-Concepcion M. and Boronat A. Elucidation of the methylerythritol phosphate pathway for isoprenoid biosyntesis in bacteria and plastids. A metabolic milestone achieved through genomics. [Journal]. - [s.l.] : Plant Physiol, 2002. - 1079-1089 : Vol. 130.

Rohmer M. [et al.] Glyceraldehyde 3-phosphate and pyruvate as precursors of isoprenic units in an alternative non-mevalonate pathway for terpenoid biosynthesis. [Journal]. - [s.l.] : J. Am. Chem. Soc., 1996. - 2564-2566 : Vol. 118.

Rohmer M. [et al.] Isoprenoid biosynthesis in bacteria: A novel pathway for the early steps leading to isopentenyl diphosphate. [Journal]. - [s.l.] : Biochem. J., 1993. - 517-524 : Vol. 295.

Russell A. and Dennis R. NARSTO critical review of photochemical models and modeling. [Journal]. - [s.l.] : Atmos. Environ., 2000. - 283-234 : Vol. 34.

Sanadze GA. Isoprene effect - light dependent emission of isoprene by green parts of plants. [Book Section] // Trace Gas Emissions from Plants. / book auth. Sharkey TD., Holland EA. and Mooney HA.. - San Diego : Academic Press, 1991.

San-Miguel-Ayanz J. [et al.] Land Cover Change and Fire Regime in the European Mediterranean Region. [Book Section] // Post-Fire Management and Restoration of Southern European Forest. / book auth. Moreira F. [et al.]. - [s.l.] : Springer, 2012. - Vol. 2.

San-Miguel-Ayanz J. and Camia A. Forest fire at a glance: facts, figures and trends in the EU. [Book Section] // Living with wildfires: what science can tell us. A contribution to the Science-Policy dialogue. / book auth. Birot Y.. - [s.l.] : European Forest Institute, Discussion paper15, 2009. - Vols. 11-18.

Schmid C. and Ziegler H. Sorptions- und Permeationseigenschaften von Cuticeln fur Monoterpene unter besonderer Berucksichtigung des Einflusses von Schadgasen auf Fichte. [Book]. - Neuherberg : Bericht 26/91, 1991. - Vols. 483-490.

Schmid C., Steinbrecher R. and Ziegler H. Partition coefficients of plant cuticles for monoterpenes. [Journal]. - [s.l.] : Trees, 1992. - 32-36 : Vol. 6.

Schnitzler J.P., Lehning A. and Steinbrecher R. Seasonal pattern of isoprene synthase activity in Quercus Robur leaves and ist significance for modeling isoprene emission rates. [Journal]. - [s.l.] : Bot. Acta, 1997. - 240-243 : Vol. 110.

Schonherr J. Resistance of plant surfaces to water loss: Transport properties of cutin, suberin and associated lipids. [Book Section] // Encyclopedia of Plant / book auth. Pirson A. and Zimmermann MH.. - Berlin : Springer Verlag, 1982. - Vol. 12B.

Seinfeld JH. and Pandis SN. Atmospheric Chemistry and Physics: From Air Pollution to Climate Change. [Book]. - [s.l.] : John Wiley and Sons, Inc., 1998. - Vol. 923.

Seufert G. [et al.] An overview of the Castelporziano experiments. [Journal] // Atmos Environ. - [s.l.] : Atmos. Environ., 1997. - 5-17 : Vol. 31(SI). - pp. 31(SI): 5-17.

Shallcross D.E. and Monks P.S. New directions: a role for isoprene in biosphere-climate-chemistry feedbacks. [Journal]. - [s.l.] : Atmospheric Environment, 2000. - 1659-1660 : Vol. 34.

Sharkey T. D. Effects of moderate heat stress on photosynthesis: importance of thylakoid reactions, rubisco deactivation, reactive oxygen species, and thermotolerance provided by isoprene. [Journal]. - [s.l.] : Plant, Cell and Environment, 2005. - 269-277 : Vol. 28.

Sharkey T. D., Chen X. and Yeh S. Isoprene increases thermotolerance of fosmidomycin-fed leaves. [Journal]. - [s.l.] : Plant Physiology, 2001. - 2001-2006 : Vol. 125.

Sharkey TD. [et al.] Field measurements of isoprene emissions from trees in response to temperature and light. [Journal]. - [s.l.] : Tree Physiol., 1996. - 649-654 : Vol. 16.

Sharkey TD. and Loreto F. Water stress, temperature, and light effects on the capacity for isoprene emission and photosynthesis of kudzu leaves. [Journal]. - [s.l.] : Oecologia, 1993. - 328-333 : Vol. 95.

Sharkey TD., Loreto F. and Delwiche CF. The biochemistry of isoprene emission from leaves during photosynthesis. [Book Section] // Trace Gas Emissions from Plants. / book auth. Sharkey TD., Holland Ea. and Mooney HA.. - San Diego : Academic Press, 1991. - Vols. 153-184.

Simon V. [et al.] Biogenic emissions from Pinus halepensis: a typical species of the Mediterranean area. [Journal]. - [s.l.] : Atmospheric Research, 2005. - 37-48 : Vol. 74.

Simon V. [et al.] The biogenic volatile organic compounds emissions inventory in France Application to plant ecosystems in the Berre-Marseilles area (France) [Journal]. - [s.l.] : Science of the Total Environment, 2006. - 164-182 : Vol. 372.

Simpson D. [et al.] Biogenic emissions in Europe. 1. Estimates and uncertainties. [Journal]. - [s.l.] : J. Geophys. Res., 1995. - 22875-22890 : Vol. 100.

Simpson D. [et al.] Inventorying emissions from nature in Europe. [Journal]. - [s.l.] : Journal of Geophysical Research, 1999. - 8113-8152 : Vol. 104.

Singh HB. and Zimmerman PB. Atmospheric distribution and sources of nonmethane hydrocarbons. [Book Section] // Gaseous Pollutans: Characterization and Cycling. / book auth. Nriagu JO.. - [s.l.] : John Wiley, 1992. - Vols. 177-235.

Soares FD. [et al.] Volatile and non-volatile chemical composition of the white guava fruit (Psidium guajava) at different stages of maturity. [Journal]. - [s.l.] : Food Chemistry, 2007. - 15-21 : Vol. 100.

Stape J.L., Ryan M.G. and Binkley D. Testing the utility of the 3-PG model for growth of Eucalyptus grandis. [Journal]. - [s.l.] : Forest Ecology and Management, 2010.

Staudt M. [et al.] Effect of elevated CO2 on monoterpene emisssion of young Quercus ilex trees and its relation to structural and ecophysiological parameters. [Journal]. - [s.l.] : Tree Physiol., 2001. - 437-445 : Vol. 21.

Staudt M. [et al.] Seasonal variation in amount and composition of monoterpenes emitted by young Pinus Pinea trees - Implications for emission modelling. [Journal]. - [s.l.] : J. Atmos. Chem., 2000. - 77-99 : Vol. 35.

Staudt M. Untersuchungen der Monoterpen-Abgabe an europaischen Nadelbaumarten in Abhangigkeit von Umweltfaktoren. [Book Section] // Dissertation Universitat Hohenheim / book auth. Gregor HJ. and Unger HJ.. - Munchen : Documenta Naturae, 1997. - Vols. 111, ISSN 0723-8428.

Steinbrecher R. [et al.] Intra- and inter-annual variability of VOC emissions from natural and semi-natural vegetation in Europe and neighbouring countries. [Journal]. - [s.l.] : Atmos. Environ., 2009. - 1380-1391 : Vol. 43.

Steinbrecher R. [et al.] Isoprenoid emission of oak species typical for the Mediterranean area: source strength and controlling variables. [Journal]. - [s.l.] : Atmos. Environ., 1997. - 79-88 : Vol. 31(SI).

Steinbrecher R. Emissions of selected European ecoystems: The state of the art. [Conference] // The Proceedings of EUROTRAC Symposium 94. - The Hague, The Netherlands : SPB Academic Publishing BV, 1994. - Vols. 448-454.

Steinbrecher R. Gehald und Emission von Monoterpenen in oberirdischen Organen von Picea abies. [Journal]. - TU Munchen : Dissertation, 1989.

Surratt J. D. [et al.] Chemical composition of secondary organic aerosol formed from the photooxidation of isoprene. [Journal]. - [s.l.] : Phys. Chem. A., 2006. - 9665-9690 : Vol. 110.

Surratt JD. [et al.] Chemical composition of secondary organic aerosol formed from the photooxidation of isoprene. [Journal]. - [s.l.] : J. Phys. Chem., 2006. - 9665-9690 : Vol. 110.

Taiz L. and Zeiger E. PLANT PHYSIOLOGY [Book]. - Sunderland, Massachusetts : Sinauer Associater, Inc., Publishers, 1998. - Vols. ISBN 88-299-1623-4.

Tiiva P. [et al.] Isoprene emission from a subarctic peatland under enhanced UV-B radiation. [Journal]. - [s.l.] : New Phytologist, 2007. - 346-355 : Vol. 176.

Tingey D.T., Turner D.P. and Weber J.A. Factors controlling the emissions of monoterpenes and other volatile organic compounds. [Book Section] // Trace Gas Emissions by Plants. / book auth. Sharkey T.D., Holland E.A. and Mooney H.A.. - New York : Academic Press, 1990. - Vols. 93-119.

Tingey DT., Evans R. and Gumpertz M. Effects of environmental conditions on isoprene emissions from live oak (Quercus virginiana). [Journal]. - [s.l.] : Planta, 1981. - 565-570 : Vol. 152.

Turpin BJ., Saxena P. and Andrews E. Measuring and simulating particulate organics in the atmosphere: problems and prospects. [Journal]. - [s.l.] : Atmos. Environ., 2000. - 2983-3013 : Vol. 34.

Underwood BA. [et al.] Ethylene-regulated floral volatile synthesis in petunia corollas. [Journal]. - [s.l.] : Plant Physiology, 2005. - 255-266 : Vol. 138.

Veldt C. and Most PFJ. Van Der Emission factors: volatile organic compounds from mobile sources. [Book]. - The Hague. The Netherlands : Environmental Protection Inspection, 1993.

Veldt C. Leaf biomass data for the estimations of biogenic VOC emissions. [Report]. - [s.l.] : MTO-TNO 99-306, 1989.

Velikova V. and Loreto F. On the relationship between isoprene emission and thermotolerance in Phragmites australis leaves exposed to high temperatures and during the recovery from a heat stress. [Journal]. - [s.l.] : Plant, Cell and Environment, 2005. - 318-327 : Vol. 28.

Wayne RP. Chemistry of Atmospheres [Book]. - New York, USA : Oxford University Press, 2000. - Vol. 3rd edn.

Winer AM. [et al.] Emission rates of organics from vegetation in California's central valley. [Journal]. - [s.l.] : Atmospheric Environment, 1992. - 2647-2659 : Vol. 26A (14).

Wise ML. and Croteau R. Monoterpene biosynthesis. [Book Section] // Comprehensive Natural Products Chemistry. Isoprenoids Including Carotenoids and Steroids. / book auth. Cane DE.. - Oxford : Pergamon Press, 1999. - Vol. 2.

Yu J. [et al.] Observation of gaseous and particulate products of monoterpene oxidation in forest atmospheres. [Journal]. - [s.l.] : Geophys. Res. Lett., 1999. - 1145-1148 : Vol. 26.

Zimmerman PR. Determination of emission rates of hydrocarbons from indigenous species of vegetation in the Tampa. [Book]. - St. Petersburg Florida : EPA/904/9-77/028, 1979.