Journal of Mediterranean Ecology **vol. 5, No.1, 2004: 41-51**

Emission and flux of terpenoids released from the terrestrial ecosystems present in the Pianosa Island

P. Ciccioli[1], R. Baraldi[2*], M. Mannozzi[3], F. Rapparini[2], M. Nardino[2], F. Miglietta[4], E. Brancaleoni E.[1] & M. Frattoni[1].

[(1)] IMC - CNR Institute of Chemical Methodologies, Via Salaria km 29.300, 00019 Monterotondo Scalo,Italy
[(2)] IBIMET - CNR Institute of Biometeorology, National Research Council, Bologna
[(3)] Institute of Chemical Science, University of Urbino, P.zza Rinascimento 6, 61029 Urbino, Italy
[(4)] IBIMET - CNR Institute of Biometeorology, National Research Council, Firenze

[*] Corresponding author
Rita Baraldi, CNR.IBIMET, Via Gobetti 101, 40129 Bologna, Italy
Tel. +39.051.6399009 - Fax +39.051.6399024 - E-mail: r.baraldi@ibimet.cnr.it

Keywords: branch enclosure, Mediterranean ecosystem, mixed box technique, isoprenoids, tethered balloon.

Abstract

For the first time, the emission of individual BVOC released from a Mediterranean ecosystem has been assessed and the results obtained have been directly compared with fluxes measured with the mixed box (MB) approach. The study was conducted in Pianosa, a very small and flat island located in the Tyrrhenian sea, between the coasts of Central Italy and the Corsica Island. Due to the substantial lack of man-made emission and the restricted access, terrestrial vegetation represents in this island the main source of hydrocarbons. This allows to use simple methodologies to estimate and measure the emission of individual BVOC in the atmosphere. Due to the limited number of emitting species, the total emission was estimated by up-scaling to ecosystem level the information obtained with branch enclosures. Data obtained suggested that the basal emission of total isoprenoids generated from the island was one order of magnitude smaller than that estimated in the pine-oak forest ecosystem of Castelporziano (ca. 0.2 mg C $m^{-2}h^{-1}$). α-Pinene was the major component emitted and accounted, by itself, for more than 40% of the total isoprenoid emission. Daily profiles of emission were calculated for the two days when the air masses were depleted in anthropogenic compounds, after traveling for two days over the open sea. Results obtained in these days indicated that α-pinene was the only component displaying an emission (ca. 0.1 mg C m^{-2} h^{-1}) sufficiently high to generate detectable concentrations (0.01-0.03 μg C Nm^{-3}) in the atmospheric boundary layer (ABL). Fluxes determined using the MB approach substantially confirmed the estimates made by up-scaling to ecosystem level the emission from terrestrial vegetation, although a difference of a factor of two was observed between the calculated emission and the measured fluxes. Reasons explaining these differences will be analyzed and critically discussed.

Introduction

Although CO_2 accounts for the largest portion of trace gases exchanged between the atmosphere and forest ecosystems, small amounts of assimilated carbon are also re-emitted by the plant in the form of BVOC. Dominant components are isoprene and monoterpenes. A recent overview of existing data (Kesselmeier *et al*., 2002), indicates that BVOC emission accounts for less than 1% of the Gross Primary Production (GPP) of terrestrial ecosystems. Although small, such emission is extremely important in determining the oxidizing capacity of the atmosphere and the thermal trapping of solar radiation. This happens because, on a global scale, BVOC emission is much larger (Singh & Zimmerman, 1992) and more reactive (Chameides *et al*., 1992, Fehsenfeld *et al*., 1992) than that of VOC produced by man-made activities. In the presence of sufficient amounts of NOx , isoprene acts as a tropospheric source of tropospheric ozone. In the same conditions, monoterpenes can produce and remove ozone from the atmosphere. In the latter case, they can form secondary organic aerosols (SOA) which can act as cloud condensation nuclei (CCN), whose increase in the atmosphere can drastically affect precipitation at a regional scale (Ramanathan *et al*., 2001). In spite of the fundamental role played by BVOC in the atmosphere, its knowledge is still quite limited. This is particularly true for the Mediterranean region where a large biodiversity of terrestrial ecosystems is combined with intense photochemical production from early spring to late autumn (Ciccioli *et al*., 1999a). So far, most of the existing knowledge relies on the results obtained in the BEMA project, where data collected through physiological investigations were corroborated with flux measurements (Seufert *et al*., 1997).

The Pianosa research Project, launched by the Italian Research Council (CNR), provided a good opportunity to

widen this knowledge. The site that is flat and, very often, not influenced by transport of anthropogenic pollutants coming from the main land, was particularly suitable for studying fluxes by means of the mixed box (MB) technique which has the advantages to estimate fluxes over a spatial scale of tens of kilometers, to quantify all the processes that influence the concentration within a special domain, and is based on robust measurement of the mean mixing ratio (Guenther *et al*., 1996).

In this work, the results of a preliminary study aimed at assessing the emission and fluxes of individual BVOC from Pianosa island are presented. The emission from the dominant vegetation species present in the various ecosystems existing in the island was measured using branch cuvettes. Estimated fluxes obtained by up-scaling emission data to ecosystem level were compared with those obtained by using the MB approach.

Methods

Branch enclosure determinations

Basal emission rates at 30°C and light saturation conditions (i.e. at PAR values higher than 1000 μmol m^{-2} s^{-1}) were determined for the dominant plant species present in the various ecosystems of the Pianosa island using a portable branch enclosure (Rapparini *et al*., 2004). Selection of the plant species was based on the landscape information and vegetation distribution provided by Colom *et al*. (2004, this issue). Samplings were made by enclosing healthy branches containing both young and fully expanded leaves (or needles) in 12 l Teflon cuvettes. During the enclosure process, great attention was paid to prevent damages of the terpene storage structures that could have significantly affected the release of monoterpenes from coniferous species. Branches were allowed to equilibrate within the enclosures for at least 4 hours before sample collection. They were flushed with a 10-11 l min^{-1} flow of air free from hydrocarbons obtained by passing ambient air through a filter filled with active charcoal having a specific surface of 800 $m2g^{-1}$. Although the filter quantitatively retains for several days all BVOC, it allows water and ambient CO_2 to reach the branch enclosure. Teflon FEP lines were used to connect the cuvettes with the pumps. Using these parameters, a residence time of approximately 1 min was achieved inside the cuvettes.

BVOC were sampled by passing 2 to 4 l of air through glass tubes filled with 34 mg of Carbograph 2 and 170 mg of Carbograph 1. Both carbons were supplied by Lara S.r.L., (Rome, Italy). Flow rates ranging between 100 and 200 ml min^{-1} were used during BVOC collection, as a function of the resistance posed by the traps. After samplings, cartridges were immediately capped with Swagelok fittings and stored in glass containers. They were transported to the laboratory and stored in a refrigerator kept at –20°C until they were analysed. Trapped compounds were released by the cartridges by thermal desorption, using a desorption-cryofocusing unit supplied by Chrompack (Middleburg, Netherlands). After the cryofocusing step, gases and vapors were injected into a gas chromatographic (GC) system (HP5890, Hewlett Packard, Palo Alto, CA, USA) connected to mass spectrometric unit (HP5970, also Hewlett Packard) as reported by Baraldi *et al*., (1999). A 60 m capillary column internally coated with 0.4 μm of CP-Sil 5 I.D. 0.35 mm was used for the separation. Positive identification of eluted compounds was achieved by comparing the mass spectra recorded in scan mode with those of authentic standards. Quantification of all isoprenoids was performed using d^{14}-cymene as internal standard.

At the end of experiments, sampled leaves were collected and taken to the laboratory where their area was measured by Video Image system (Rapparini *et al*., 2003). They were dried in the oven at 70°C to obtain the dry-weight of leaf biomass (DW) in grams. The ratio between the dry-weight of leaf biomass and its surface area was also determined for each species in order to derive the specific leaf mass (SLM, g m^{-2}). Actual emission rates were calculated from the differences in concentration at the inlet and at the outlet of the branch enclosure.

Tethered balloon measurements for flux determinations by the MB approach.

A commercial tethered balloon (Volume 9 m^3, Blimp Works, Statesville, NC USA) was used to measure BVOC concentrations within the atmospheric boundary layer (ABL) during the field campaign carried out in June 2003 in the Pianosa Island. The balloon, filled with helium, was risen in a site located at the center of the island (Lat. 42° 35.04' N, Long. 10° 04.82'E) in a position very close to the tower were CO_2, water and heat fluxes were measured by Eddy Covariance. BVOC were collected onto cartridges filled with Carbotrap 1 (118 mg), Carbotrap 2 (60 mg) and Carbograph 5 (115 mg) set in series. Three-stage cartridges were used in this case to retain all isoprenoid compounds in air volumes larger than 5 l (Brancaleoni *et al*., 1999). They were connected to a lightweight air samplers equipped with a timer. These home-made samplers, characterized by a weight of 500 g, were equipped with a battery-powered pump supplied by KNF ITALIA (Milano, Italy). They were fixed to the balloon cable in order to collect samples at 3 heights, ranging from 30 m to 200 m above ground. Timers were programmed to allow the simultaneous sampling of BVOC at the different levels. Cartridges were sampled at flow rates ranging between 300 and 400 ml min^{-1} for 40 minutes in order to enrich sufficient air volumes (between 12 and 16 l) for the analysis of BVOC at trace levels (10-2 mg C Nm^{-3}). The balloon was raised in the ABL using a winch's spool driven by an electric drill. Values of the pressure and temperatures were obtained from balloon soundings performed by another group (Viola *et al*., private communication)

Three-carbon cartridges were stored and analyzed with the same procedures adopted for the traps used for the determination of BVOC emission with branch enclosures.

Results and discussion

Estimates of emission and fluxes of BVOC from the Pianosa Island

Emission compositions and basal emission rates of the most abundant vegetation species present in the various ecosystems of the Pianosa Island are summarized in Table 1. Most of them were monoterpene emitters. Only two shrub species (namely *Rosmarinus officinalis* and *Pistacea lentiscus*) showed a tiny isoprene emission. Values obtained for *Rosmarinus officinalis*, *Pistacea lentiscus* and *Juniperus phoenicea* did not differ too much from the data reported by Lenz *et al*. (1997), Hansen *et al*. (1997), Owen *at al*. (1997,

2001) . Major emitters were *Helicrysum litoreum* and *Pinus halepensis*. Values reported for the pine species were quite consistent with those find in the literature for the summer months (Peñuelas and Llusià, 1999). As it happens for all plant species equipped with specialized organs for the storage of terpenoids, the monoterpene emission (***E***) from the species listed in Table 1 was simply described by the following equation (Guenther *et al.*,1993, 1995):

$$E = E^{\circ} C_i^T$$

where:

$$C_i^T = e^{\beta(Ts-T)}$$

in which *Ts* is 30°C, *T* is the actual leaf temperature, ***E***° is the basal emission and β is an empirical factor having an average value of ca. 0.1. Similarly to what has been observed by Staudt *et al*. (1997), we found that the β value that was better describing the temperature dependence of emission of monoterpenes from the species listed in Table 1 was 0.15.

The up-scaling procedure used to derive BVOC basal emission from the entire island in the summer season is summarized in Table 2, where the case of monoterpenes is reported. With reference to the five natural ecosystems identified by Baraldi *et al*. (2004, this issue), the ecosystem composed by mixed woodland and Mediterranean macchia was assumed to be similar in composition to the two pure ecosystems and the surface of emitting biomass was incorporated into them by assuming an equal distribution of 50% woodland and 50% macchia. The potential emission (called in the Table as the emission without corrections) was simply obtained by multiplying the density of emitting biomass for the basal emission derived from the enclosure studies. These values were than corrected to account for the differences in irradiance, and hence temperature, to which different parts of the canopy are exposed. The correction term (0.7) was directly derived from the experimental measurements made by Lenz *et al*. (1997) under the assumption that only 20% of the emitting biomass was fully exposed to sunlight, whereas 30% experienced an irradiance ranging from 70 and 40% , another 30% an irradiance ranging from 40 to 10% and the remaining biomass was exposed to a solar intensity equal or smaller than 10% of full sunlight. A 10% of emission was added to the basal emission values corrected for the irradiance, to account for the contribution coming from the monoterpene emission from dead biomass accumulated over the soil (soil litter). Also in this case, correction values were obtained from the experimental observations made during the BEMA project (Lenz *et al*., 1997). The last column of Table 2 reports the total monoterpene emission from the island. Data indicate clearly that woodland, composed by a very dense forest dominated by *Pinus halepensis*, was the ecosystem contributing most to the monoterpene emission from the Pianosa island. The overall emission from this ecosystem (2.44 mg C m^{-2} h^{-1}) did not differ too much from the values (ca. 3 mg C m^{-2} h^{-1}) reported for the pine-oak forest in Castelporziano (Lenz *et al*., 1997). Also consistent with the data obtained in the BEMA project were the emissions from the Mediterranean macchia and the coastal area.

The approach used for isoprene was much simpler since the only ecosystem that could have generated isoprene to a some extent was the one composed by pasture and cultivated soil. Although this type of ecosystem can release large isoprene fluxes, substantial emission is observed only from the end of March to the end of May when plants are in the growing phase (Ciccioli *et al.,* 1997). In June, most of these plants are in the senescence phase and their emission is quite limited.

Table 3 summarizes the emission of individual isoprenoids from the terrestrial vegetation in the island and the net expected fluxes originated from them. The differences between the two numbers arises from the fact that not all the emission escapes from the canopy but it is partly deposited to the soil or is depleted by chemical reactions with ozone and OH radicals before it reaches the ABL (Ciccioli *et al*., 1999b). In our specific case, compounds emitted by the woodland, the Mediterranean macchia and the coastal area are also partly

Tab.1 Emission rates of isoprenoids (µgC gDW^{-1} h^{-1}) of the dominant vegetation species present in the Mediterranean ecosystems of the Pianosa Island. Values are given with an uncertainty of ± 0.01µgC gDW^{-1} h^{-1}

Compound	Rosmarinus officinalis	Cistus monspeliensis	Pistacea lentiscus	Juniperus phoenicea	Pinus halepensis	Olea europea	Helicrisum litoreum
isoprene	0,01		0,01				
α-pinene	0,43	0,01	0,17	0,32	1,00	0,14	1,72
camphene	0,19		0,02	0,01	0,03	0,05	
sabinene		0,02	0,05	0,07		0,03	0,52
β-pinene	0,35	0,01	0,04	0,03	0,10	0,08	0,72
myrcene	0,03	0,07	0,01	0,06	0,62		0,02
Δ-3-carene				0,05	0,26		0,01
p-cymene	0,03	0,02	0,01	0,02		0,04	
β-phellandrene			0,01	0,06		0,01	0,05
limonene	0,93	0,02	0,02	0,07	0,22	0,04	0,70
trans-β-ocimene		0,10			0,25		
linalool		0,08					
Other Monoterpenes		0,01	0,02	0,02	0,03	0,01	0,24
Total Monoterpenes	1,94	0,35	0,35	0,71	2,50	0,40	3,98
Total Isoprenoids	1,95	0,35	0,36	0,71	2,50	0,40	3,98

Tab.2 Total monoterpene emission at 30°C and light saturation conditions from the ecosystems present in the Pianosa Island. Estimates were obtained by upscaling to ecosystem levels data obtained eith branch enclosures.

Vegetation Species	Basal emission rate	Density of Emitting Dry Biomass	Emission without corrections	Emission corrected for gradient of E° in the crown	Emission corrected for the contribution from the litter	Total Emission from the Ecosystem
Type	μgC gDW^{-1} h^{-1}	g DW m^{-2}	μg C m^{-2} h^{-1}	μg C m^{-2} h^{-1}	μg C m^{-2} h^{-1}	g C h^{-1}
Ecosystem: Pasture/Cultivated soil				**Surface (ha):**	**482,9**	
Various species (mainly Graminaceae and Leguminosae)	*<0.001*	*not determined*	*<0,01*	*<0,01*	*<0,01*	*0*
Ecosystem: Mediterranean Macchia				**Surface (ha):**	**371,2**	
Rosmarinus officinalis	1,94	158,5	308	215	237	879
Cistus monspeliensis	0,35	105,6	37	26	29	107
Pistacia lentiscus	0,35	104,5	37	26	28	105
Juniperus phoenicea	0,71	89,1	63	44	48	180
Pinus alepensis	2,50	10,1	25	18	20	72
Total		**467,9**	**470**	**329**	**362**	**1344**
Ecosystem: Woodland				**Surface (ha):**	**102,5**	
Pinus alepensis	2,50	1269,0	3172	2221	2443	2504
Olea europea	0,40	2,2	1	1	1	1
Juniperus phoenicea	0,71	1,8	1	1	1	1
Total		**1272,9**	**3175**	**2222**	**2444**	**2506**
Ecosystem: Coastal Area				**Surface (ha):**	**56,6**	
Cistus monspeliensis	0,35	70	25	17	19	11
Pistacia lentiscus	0,35	68	24	17	18	10
Juniperus phoenicea	0,71	58	41	29	32	18
Helicrisum litoreum	3,98	65	259	181	199	113
Rosmarinus officinalis	1,94	13	25	18	19	11
Total		**274,0**	**374**	**262**	**288**	**163**
Total Monoterpene Emission (g h^{-1})						**4012**
Average Monoterpene Emission Rate (μg m^{-2} h^{-1})						**389**

removed by deposition over the pasture and cultivated soil that do not emit monoterpenes. This is clear from the map shown in Figure 1, where the footprint seen by the balloon raised at 200 m during the days of June 22nd and 23rd is overlapped with the map of the island. It is clear that compounds emitted from the forest area located upwind (darker area) can be partly deposited before they reach the sampling site. It is very difficult to account for these processes as no deposition velocities are available for within-canopy processes. We have estimated that dry deposition outside the canopy accounted for no more than 10% of the emission, under the assumption that deposition velocities did not exceed 0.001 cm s^{-1}, a value quite consistent with the one used in transport models. More relevant was the removal (20%) arising from within-canopy processes where the contribution of chemical reactions must be also considered (Ciccioli *et al.*,1999b).

Using the values reported in Table 3, daily profiles of individual components were calculated for the days June 22nd and 23rd using the data reported in Figure 2b. To generate daily trends reported in Figure 2a, we have assumed that the temperature of the canopy, macchia and coastal area was, on the average, 3°C lower than that of the air. This assumption is based on the observation that, in the absence of water stress, water transpiration is able to efficiently cool the needles of coniferous trees at a temperature lower than 5°C. Under the hot conditions experienced during the campaign and in the presence of sea breeze, a difference of 3°C was thus quite reasonable. These days were chosen because were the ones in which no additional inputs from other terrestrial sources located upwind to the island were impacting the sampling site or were disturbing a regular development of the ABL. It should be noted that such effects can occur when prevalent winds come from the west or east direction. Analysis of the back trajectories together with measurements of CO_2 vertical profiles (Magliulo *et al.*, personal communication) suggest that the worse situation is the one when the wind blows from the eastern side of the island, because in this case Pianosa is under the plume of a larger island (Elba island) emitting both biogenic and anthropogenic VOC at higher rates. It has been found (Magliulo *et al.*, personal communication), that a complex stratification of layers above the Pianosa island can be generated probably due to the presence in the Elba island of small mountains reaching 1000 m. This effect makes difficult a good evaluation of the ABL by vertical sounding. Data in Figure 3 show the typical back trajectories that were observed in the two days where favorable conditions for the determination

Tab.1 Emission rates of isoprenoids (μgC gDW^{-1} h^{-1}) of the dominant vegetation species present in the Mediterranean ecosystems of the Pianosa Island. Values are given with an uncertainty of ± 0.01μgC gDW^{-1} h^{-1}

					Entire Island			
Compound	**Mediterranean Macchia**	**Woodland**	**Coastal Area**	**Pasture and Cultivated soil**	**Emission**	**Contribution to total emission**	**Emission rate**	**Net Estimated Flux**
	g C h^{-1}	g C h^{-1}	g C h^{-1}	g C h^{-1}	g C h^{-1}	%	mg C m^{-2} h^{-1}	mg C m^{-2} h^{-1}
isoprene	6		1	500	507	11,2	0,049	0,034
α-pinene	356	1002	61		1419	31,4	0,138	0,096
camphene	94	30	3		128	2,8	0,012	0,009
sabinene	39	0	4		44	1,0	0,004	0,003
β-pinene	182	100	9		291	6,4	0,028	0,020
myrcene	69	619	32		720	15,9	0,070	0,049
Δ-3-carene	21	260	13		294	6,5	0,029	0,020
p-cymene	25	0	1		26	0,6	0,003	0,002
β-phellandrene	19	0	2		21	0,5	0,002	0,001
limonene	459	218	18		695	15,4	0,067	0,047
trans-β-ocimene	39	250	14		303	6,7	0,029	0,021
linalool	25	0	3		27	0,6	0,003	0,002
Others	16	25	3		44	1,0	0,004	0,003
Total Monoterpenes	1344	2506	163		4012	88,8	0,389	0,272
Total Isoprenoids	13050	2506	164	500	4519	100,0	0,438	0,307

of isoprenoid fluxes were established over the site. As it can be seen, the air masses reaching the Pianosa island were never passing over the Italian peninsula and the Sardinia or Corsica islands in the two days before the measurements.

Data displayed in Figure 2b allowed to calculate the volume necessary to detect isoprenoids by tethered balloon. It was estimated that 5 to 10 l were necessary to get enough amount of matter for GC-MS determinations, by considering that a substantial portion of emitted components were removed in the ABL by reaction with ozone and OH radicals.

Tethered balloon measurements and isoprenoid flux determination by the MB approach

The calculation of VOC fluxes with the MB approach requires that concentration measurements are performed within the ABL (Greenberg *et al.*, 1999; Greenberg & Guenther 2002; Boy *et al.*, 2003; Spirig *et al.*, 2003). The method is based on the assumption that a constant concentration C_m is generated in the ABL from a compound emitted by the surface. For a no reactive compounds (such as a CFC) emitted at the surface the net flux is thus given by the product of the concentration C_m (in mg C Nm^{-3}) for the height z_i reached by the ABL during sampling. In the case of a compound (such as isoprene or a monoterpene) rapidly reacting with ozone and OH radicals, the equation becomes:

$$F = z_i C_m \tau^{-1}$$

where τ is the estimated lifetime of the compound investigated (in our case an isoprenoid). To derive reliable values for τ, the concentrations of ozone and OH radicals must be estimated or measured and first-order reaction constants known. Daily trends of ozone during the balloon experiments performed in the Pianosa island were obtained by combining information on the ozone profiles measured in the coasts of Tuscany and data collected in the Pianosa island by using passive samplers. It was found that in the Pianosa island 24 hour averaged ozone concentrations were in the range of 30-40 ppbv. This suggested that maximum values exceeding 50 ppbv were reached in the middle of the day. Since OH radicals come from the photolysis of ozone and formaldehyde, both very abundant in Mediterranean coastal regions (Kalabokas *et al.*, 1996), maximum OH radical concentrations of the order of 1 x 10^7 molecules cm^{-3} were estimated to be reached in the Pianosa island when the maximum intensity of UV radiation was achieved. The rate constants used to calculate the lifetime of isoprenoids were those reported by Atkinson (1990). Since many of them are measured at 25°C and determinations were made at higher temperatures, the use of these reaction constants slightly underestimate the flux of isoprenoids in the lower part of the ABL. However, this is compensated by the lower temperatures established at the top of the ABL. Another important aspect was the evaluation of z_i. In our case, data obtained by using the ISLA bi-dimensional model (Nardino *et al.*, this issue) were combined with data obtained with vertical sounding. They showed that the ABL developed up to 330 m above the island when maximum temperatures of 32°C were reached at the earth surface.

Figure 4 reports the typical profiles of VOC that were obtained in June 23rd when reliable values of C_m were obtained for the all day up to an altitude of 200 m. They show that the only biogenic component detected was α-pinene, whose concentrations were much lower than less reactive compounds, such as benzene or CCl_4 advected by sources located far away from the island or homogeneously distributed in the upper hemisphere. This is not surprising because the other isoprenoids were too small in emission and too reactive (Ciccioli *et al.*, 1999a) to reach detectable concentrations in the ABL.

The data of the Net Ecosystem Exchange (NEE) measured over the site during the same period (data not shown) indicate that isoprenoid fluxes represent ca. 1% of

the CO_2 exchanged during daytime hours. A value 3 times lower than that recorded in Castelporziano (Kesselmeier *et al*. 2002). Although interesting for carbon budget purposes, these data do not add any significant information of the exchange mechanisms of carbon between the atmosphere and the ecosystem. Since the bulk of isoprenoids is comprised of monoterpenes stored in resin ducts, the release from the ecosystem is not directly related to photosynthesis. Although isoprenoid production originates from assimilated carbon, monoterpenes do not reach immediately the stomatal chamber but they are stored in specialized organs having a high resistance toward the exchange of gases and vapors

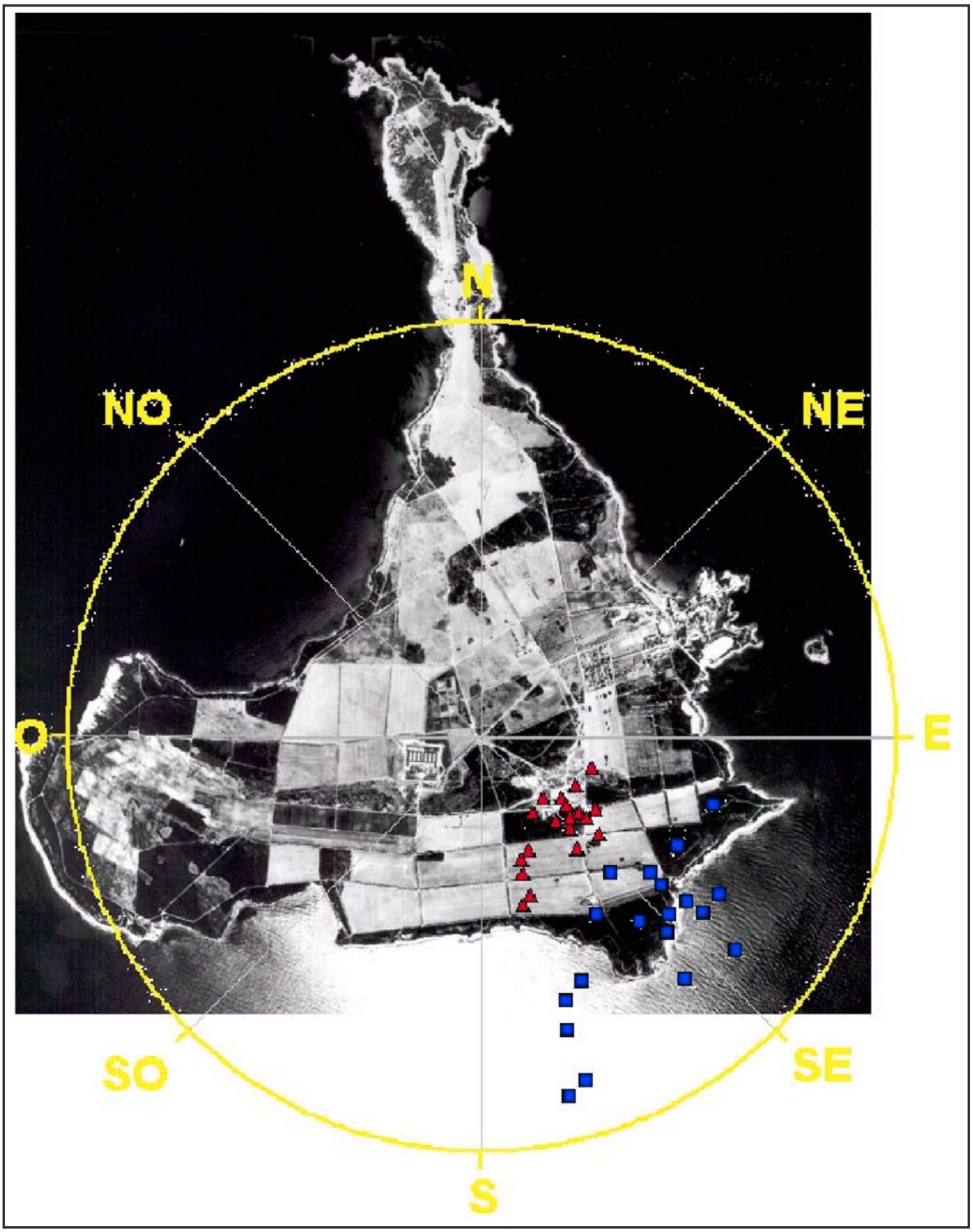
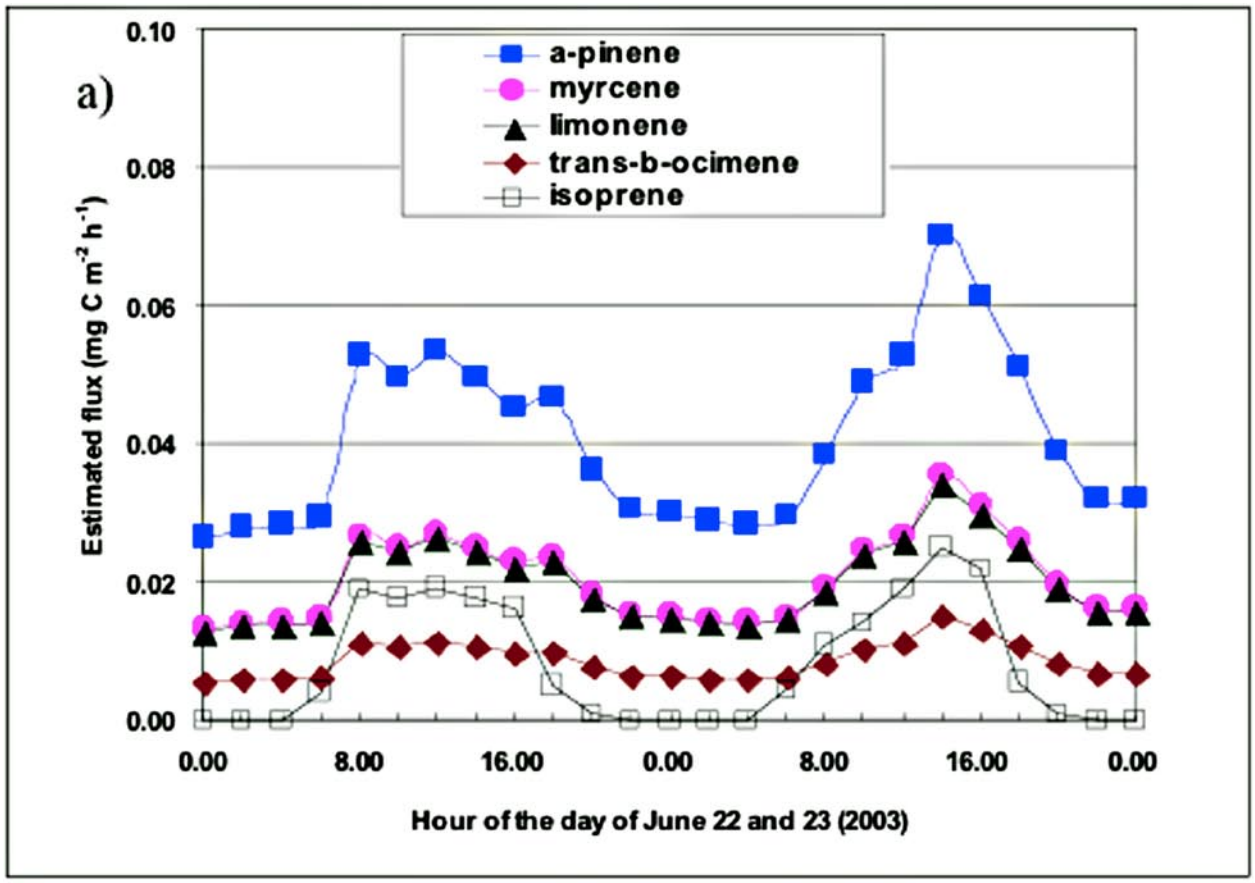


Fig.1 - Aerial view of the Pianosa Island showing the position of the measuring site and the distribution of forest area (dark area) and pasture (light area) in the direction of the prevalent winds observed in June 22nd and 23rd 2003. The footprint seen from the balloon is indicated as 90% (■) and 80% of total flux (▲).



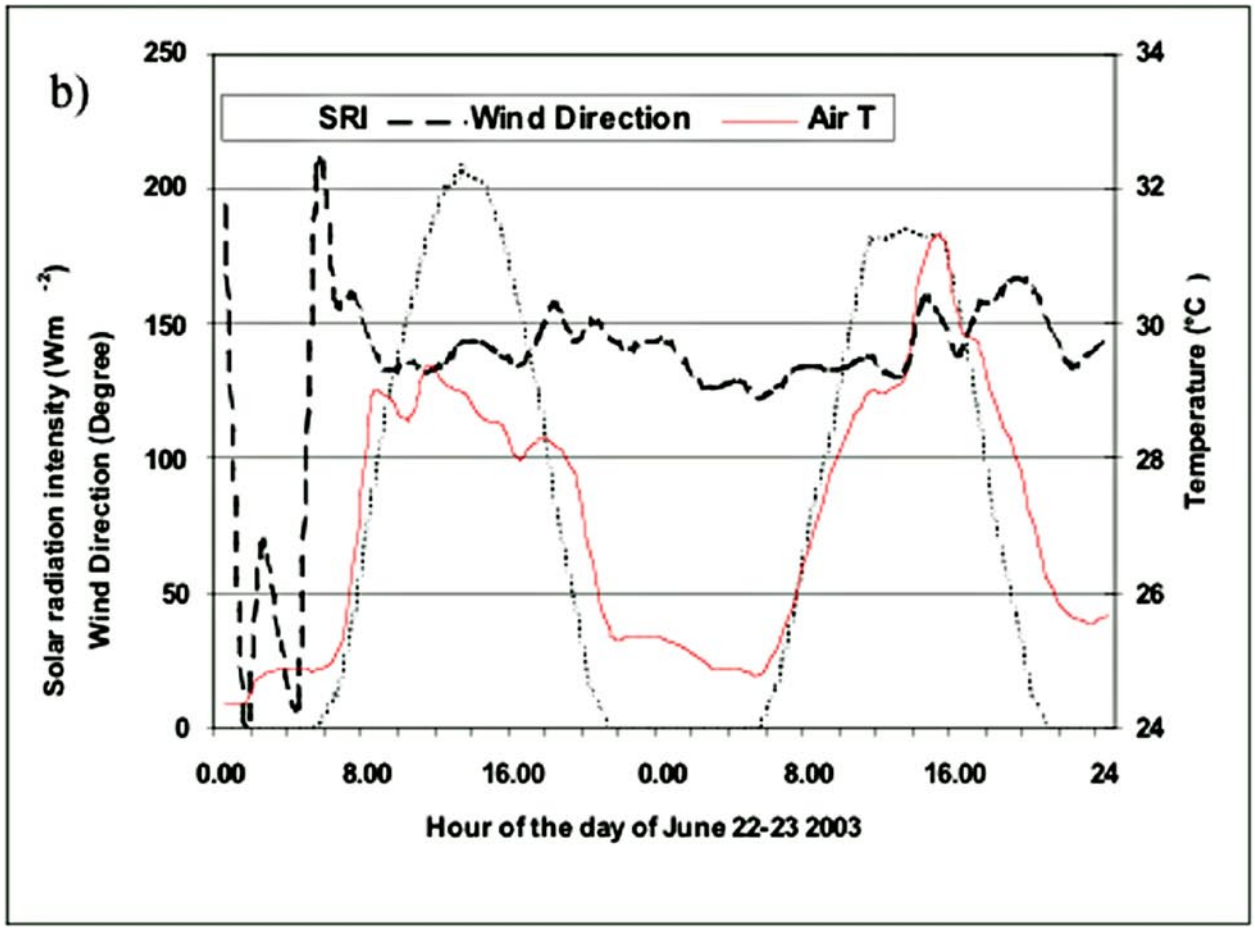


Fig. 2
a) Diurnal variation of individual isoprenoid fluxes from the Pianosa island estimated for the days of June 22nd and 23rd 2003 by using data of Table 3.
b) Solar radiation intensity, air temperature and wind direction measured in the same days.

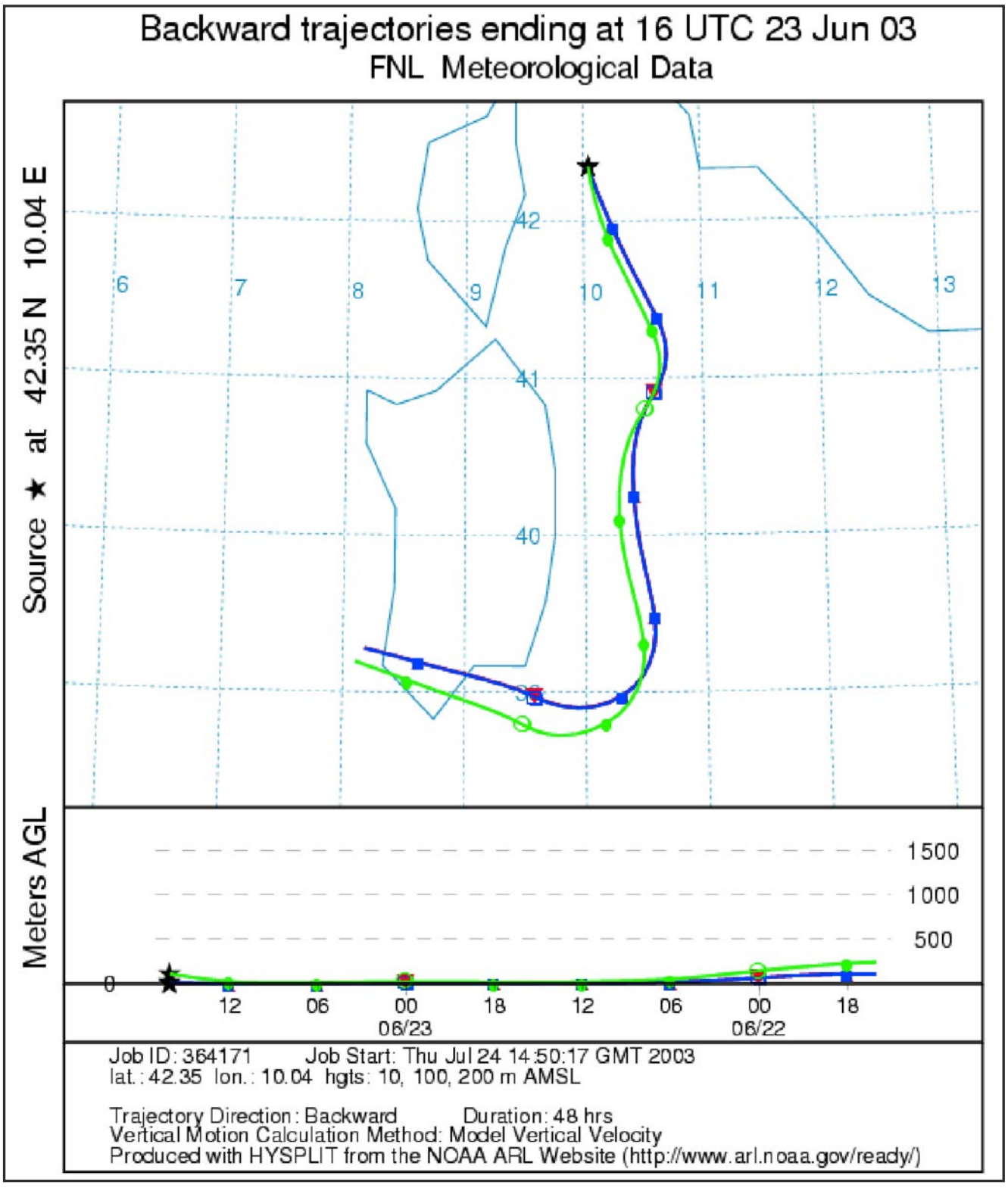


Fig. 3 - Typical 2 days back trajectories followed by the air masses reaching the Pianosa island during the days of June 22nd and 23rd 2003.

(Fall, 1999). The turnover of carbon in conifers can be thus extremely low (days) and the emission takes place also when photosynthesis ceases.

Figures 5a and 5b reports the daily profiles of ozone and OH radicals and the comparison between daily profiles of α-pinene fluxes measured with the MB approach and estimated from the up-scaling procedure previously described. Data refer to the day of June 23rd when sufficient balloon measurements were made to get a daily profile. By considering the large uncertainties associated with the two methods and the tiny concentrations of α-pinene in the ABL, a difference slightly smaller than a factor of 2 between estimates and observations can be considered quite satisfactory. A possible explanation for these differences can arise from several factors. Either up-scaled fluxes are overestimated or measured fluxes are underestimated. The main factor for an overestimation of up-scaled fluxes comes from an underestimation of within canopy removal process and soil deposition. The underestimation of measured fluxes might arise from partial losses of isoprenoids during sampling.

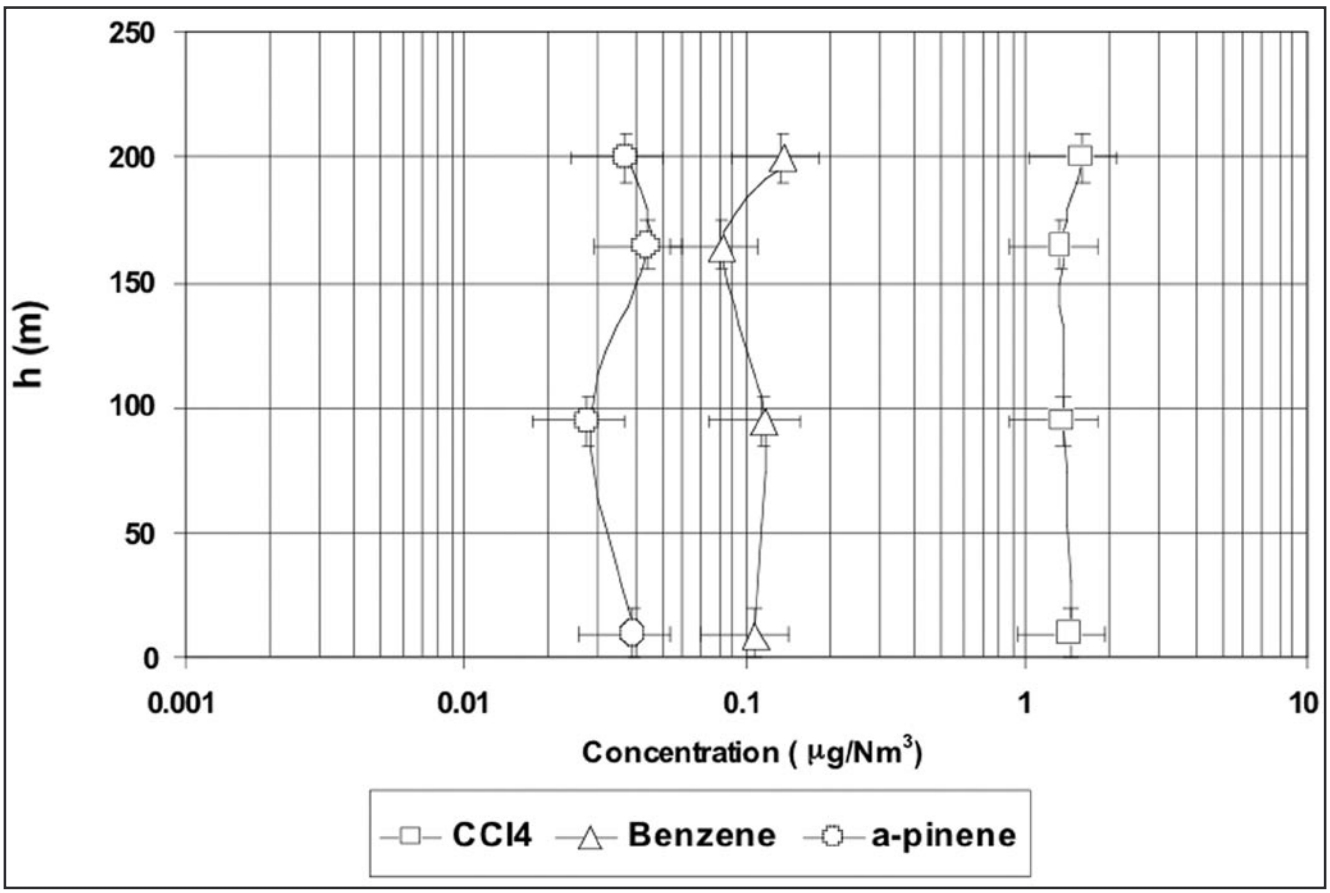


Fig. 4 - Typical vertical profiles of VOC recorded by tethered balloon at the Pianosa island during the day of June 23rd 2003

In conclusion, a simple methodology was developed for estimating the potential emission and expected fluxes of individual BVOC components released from the terrestrial ecosystems present in the Pianosa island. Within a factor of two, estimated values obtained were consistent with those obtained by using the MB approach. Further investigations performed by using the REA approach can be of great help to explain the reasons for the differences observed between calculated and measured fluxes.

Acknowledgments

The author are grateful to Alessandro Zaldei and Matteo Mari for the excellent technical assistance and to Dr Angelo Viola for the boundary layer measurements provided during the 2003 field campaign.

The authors gratefully acknowledge the NOAA Air Resources Laboratory (ARL) for the provision of the HY-SPLIT transport and dispersion and/or ready website (http: www.arl.noaa.gov/ready.html) sed in this publication.

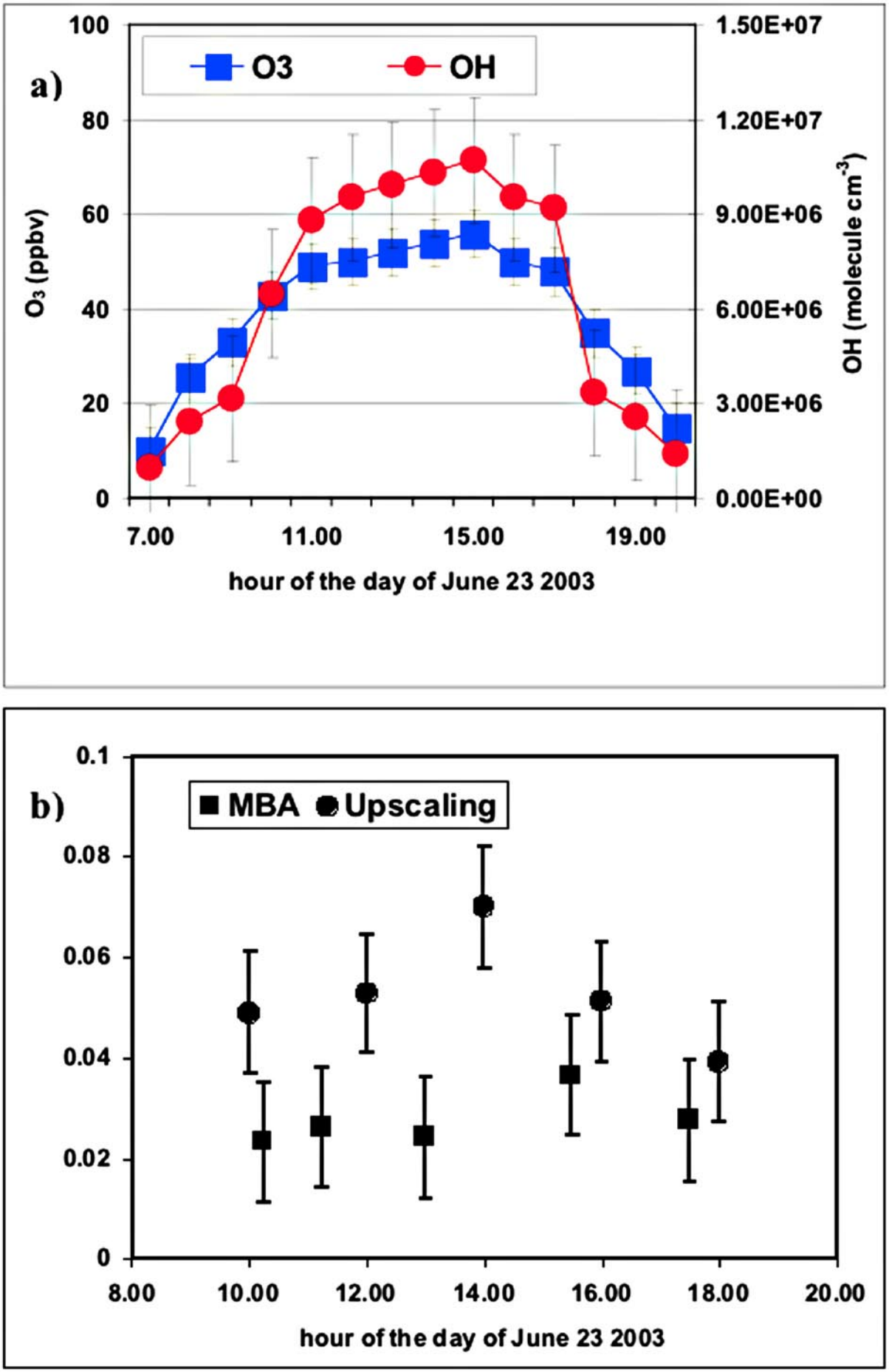


Fig. 5
a) Diurnal variations of ozone and OH radicals used for the calculation of α-pinene fluxes with the MB approach (for detail on the procedure used see the text)
b) Comparison between estimated and measured α-pinene fluxes.

References

Atkinson, R. 1990. Gas-phase tropospheric chemistry of organic compounds: A review, Atmospheric. Environment, 24A:1-41.

Baraldi, R., Rapparini, F., Rossi F., Latella, A. & Ciccioli, P. 1999. Volatile organic compound emissions from flowers of the most occurring and economically important fruit tree species. Physic and Chemistry of the Earth 6: 729-732

Brancaleoni, E., Scovaventi, M., Frattoni, M., Mabilia, R. & Ciccioli, P. 1999. Novel family of multi-layer cartridges filled with a new carbon adsorbent for the quantitative determination of volatile organic compounds in the atmosphere. Journal of Chromatography *A*, 845: 317-328.

Boy, M., Petäjä T., Dal Maso, M., Rannik, Ü., Rinne, J., Aalto, P., Laaksonen, A., Vaattovaara, P., Joutsensaari, J., Hoffmann, T., Warnke,J., Apostolaki, M., Stephanou, EG., Tsapakis, M., Kouvarakis, A., Pio, C., Carvalho, A., Römpp, A., Moortgat ,G., Spirig, C., Guenther, A., Greenberg, J., Ciccioli, P. & Kulmala, M. 2003. Overview of the field measurement campaign in Hyytiälä, August 2001 in the framework of the EU project OSOA. Atmospheric Chemistry and Physics Discussions 3: 3769-3831.

Chameides, WL., Fehesenfeld, F., Rodgers, MO., Cardelino, C., Martinez, J., Parrish, D., Lonneman, W. & Lawson, DR., Rasmussen, RA., Zimmerman, P., Greenberg, J., Middleton, P., Wang, T. 1992. Ozone precursor relationships in the ambient atmosphere. Journal of Geophysical Research, 97:6037-6055.

Ciccioli, P. Fabozzi C., Brancaleoni, E., Cecinato, A., Frattoni, M., Cieslik, S., Kotzias, D., Seufert, G., Foster, P. & Steinbrecher, R. 1997. Biogenic emission from the Mediterranean Pseudo steppe ecosystem present in Castelporziano. Atmospheric Environment 31 (SI):167-175.

Ciccioli, P., Brancaleoni, E., Frattoni, M. 1999a. Reactive hydrocarbons in the atmosphere at urban and regional scales. pp. 159-207.In: Hewitt, C.N. (eds), Reactive hydrocarbons in the atmosphere. Academic Press, San Diego, USA.

Ciccioli, P., Brancaleoni, E., Frattoni, M., Di Palo, V., Valentini, R., Tirone, G., Seufert, G., Bertin, N., Hansen, U., Csiky, O., Lenz, R. & Sharma, M. 1999b. Emission of reactive terpene compounds from orange orchards and their removal by within-canopy processes. Journal of Geophysical Research 104 (D7): 8077-8094.

Colom, M.R., Vaccari, F.P., Scartazza, A., Brugnoli, E., Zerbi, G., Sforzi, S., Baraldi, R., Cotrufo, M.F., D'Acqui, L., Santi, C., Bazzana, C., Vivoli, R. & Spaccini, L. 2004. Pianosa island: structure, functioning and biodiversity of main ecosystems. Journal of Mediterranean Ecology.

Fall, R. 1999. Biogenic Emissions of Volatile Organic Compounds from Higer Plants. pp. 41-96. In Hewitt, N.C. (ed) Reactive Hydrocarbons in the Atmosphere, Academic Press, London, ,

Fehsenfeld, F., Calvert, J., Fall, B., Goldan, P:, Guenther, A.B., Hewitt, C.N., Lamb, B., Shaw, L., Trainer, M., Westberg, H. & Zimmerman, P. 1992. Emission of volatile organic compounds from vegetation and the implication in atmospheric chemistry. Global Biogeochemical Cycles 6:389-430

Greenberg, J.P., Guenther, A., Zimmerman, P., Baugh, W., Geron, C., Davis, K., Helmig, D. & Klinger, L.F. 1999. Tethered balloon measurements of biogenic VOCs in the atmospheric boundary layer. Atmospheric Environment 33: 855-867

Greenberg, J.P. & Guenther, A. 2002. Tethered-balloon profiling for boundary layer atmospheric chemistry. Pp. 20.1-20.13. In: Burden, F.R., McKelvie, I., Förstner, U. & Guenther A.(eds), Environmental monitoring handbook. McGraw-Hill, New York

Guenther, A.B., Monson, R. & Fall, R. 1993a. Isoprene and monoterpene emission rate variability: Observation with eucalyptus and emission rate algorithm development. Journal of Geophysical Research 96: 10799-10808.

Guenther, A.B., Hewitt, C.N., Erickson, D., Fall, R., Geron, C., Graedel, T., Klinger, L., Lerdau, M., McKay, W.A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, J. & Zimmerman, P. 1995. A global model of natural volatile organic compound emissions. Journal of Geophysical Research 100: 8873-8892.

Guenther, A.B., Zimmerman, P., Klinger, L., Greenberg, J., Ennis, C., Davis, K., & Pollock, W. 1995. Estimates of regional natural volatile organic compound fluxes from enclosure and ambient measurements. Journal of Geophysical Research 101: 1345-1359.

Hansen, U., Van Eijk, J., Bertin, N., Staudt, M., Kotzias, D., Seufert, G., Fugit, J.L., Torres, L., Cecinato, A., Brancaleoni, E., Ciccioli, P. & Bomboi, T. 1997. Biogenic emissions and CO2 exchange investigated on four Mediterranean Shrubs. Atmospheric Environment 31(SI): 157-166

Kalabokas, P., Bartzis, J.G., Bomboi, T., Ciccioli, P., Cieslik, S., Dlugi, R., Foster, P., Kotzias, D. & Steinbrecher, R. 1997. Ambient atmospheric gas concentrations and meteorological parameters during the first BEMA measuring campaign on May 1994 at Castelporziano, Italy. Atmospheric Environment 31(SI): 67-77.

Kesselmeier, J., Ciccioli, P., Kuhn, U., Stefani, P., Biesenthal, T., Rottenberger, S., Wolf, A., Vitullo, M., Valentini, R., Nobre, A., Kabat, P. & Andreae, M.O. 2002. Volatile organic compound emissions in relation to plant carbon fixation and the terrestrial carbon budget. Global Biogeochemical Cycles 16: 1126, doi:10.1029/2001GB001813.

Lenz, R., Selige, T. & Seufert, G. 1997. Scaling up the biogenic emissions from test sites at Castelporziano, Atmospheric Environment 31(SI): 239-250

Nardino, M., Facini, O., Georgiadis, T., Rossi, F. & Zaldei A. 2004. Computation of the mixed layer height trough a simplified PBL model for small island (ISLA). Journal of Mediterranean Ecology.

Owen, S., Boissard, C., Street, R.A., Duckham, S.C. & Hewitt, C.N. 1997. The BEMA-project:screening of 18 Mediterranean plant species for volatile organic compound emissions. Atmospheric Environment 31(SI): 101-117

Owen, S., Boissard, C. & Hewitt, C.N. 2001. Volatile organic compounds (VOCs) emitted from 40 Mediterranean plant species: VOC speciation and extrapolation to habitat scale. Atmospheric Environment 35:5393-5409

Peñuelas, J. & Llusià, J. 1999. Short-term responses of terpene emission rates to experimental changes of PFD in *Pinus halepensis* and *Quercus ilex* in summer field conditions. Environmental and Experimental Botany 42: 61-68.

Ramanathan, W., Crutzen, P.J., Kiehl, J.T. & Rosenfeld, D. 2001. Aerosol climate and idrological cycle. Science 294:2119-2124

Rapparini, F., Baraldi, R., Maglietta, F. & Loreto, F. 2004. Isoprenoid emission in trees of *Quercus pubescens* and *Quercus ilex* with lifetime exposure to naturally high CO^2 environment. Plant, Cell & Environment 27:381-391.

Singh, HB. & Zimmerman, P.R. 1992. Atmospheric distribution and source of nonmethane hydrocarbons. pp. In: Nariagu, J.O. (ed), Gaseous Pollutants:Characterization and Cycling. John Wiley, NY.

Seufert, G., Bartzis, J., Bomboi, T., Ciccioli, P., Cieslik, S. , ,Dlugi, R. Foster, P., Hewitt, C.N., Kesselmeier, J., Kotzias, D., Lenz, R., Manes, F. , Perez-Pastor, R., Steinbrecher, R., Torres, L., Valentini, R., & Versino, B. 1997. An overview of the Castelporziano experiment. Atmospheric Environment 31(SI): 5-17.

Staudt, M., Bertin, N., Hansen, U., Seufert, G., Ciccioli, P., Foster, P., Frenzel, B. & Fugit, J.L. 1997. Seasonal and diurnal patterns of monoterpene emissions from *Pinus Pinea* (L.) under field conditions. Atmospheric Environment 31(SI):145-156.

Spririg, C., Guenther, A., Greenberg, J.P., Calanca, P. & Tarvainen, V. 2003. Tethered balloon measurements of biogenic volatile organic compounds at a Boreal forest site. Atmospheric Chemistry and Physics Discussions 3: 5357-5397.