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The ACCENT-VOCBAS field campaign on biosphere-atmosphere interactions in a Mediterranean ecosystem of Castelporziano (Rome): site characteristics, climatic and meteorological conditions, and eco-physiology of vegetation

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Biosphereatmosphere interactions





Abstract

Biosphere-atmosphere interactions were investigated on a sandy dune Mediterranean ecosystem in a field campaign held in 2007 within the frame of the European Projects ACCENT and VOCBAS. The campaign was carried out in the Presidential estate of

- ⁵ Castelporziano, a peri-urban park close to Rome where several investigations on the emission of biogenic volatile organic compounds (BVOC) in Mediterranean area were performed in the past 15 y. While specific aspects of the campaign will be discussed in companion papers, the general climatic and physiological aspects will be presented here together with information regarding BVOC emission from the most common plants
- present in this ecosystem. During the campaign regular air movements were observed, dominated by moderate nocturnal land breeze and diurnal sea breeze. A regular daily increase of ozone concentration in the air was also observed, but daily peaks of ozone were much lower than those measured downwind of the Rome conurbation. The site was ideal as a natural photochemical reactor to observe reaction, transport and de-
- position processes occurring in the Mediterranean basin, where a sea-land breeze circulation system allows a strong mixing between biogenic and anthropogenic emissions and secondary pollutants. The campaign investigated emissions from a poorly studied and largely biodiverse ecosystem, often subjected to a combination of environmental stresses and to anthropogenic pollution. Measurements were run in May,
- when plant physiological conditions were still optimal, in absence of severe drought and heat stress. Foliar rates of photosynthesis and transpiration were as high as generally recorded in unstressed Mediterranean sclerophyllous plants. Most of the plant species emitted high level of monoterpenes, despite measurements being made in a period in which emissions of volatile isoprenoids could be restrained by developmental
- and environmental factors, such as leaf age and relatively low air temperature. No high isoprene emitting plants were found in the ecosystem. It is speculated that environmental stresses limit the emission during summer, differently than in other Mediterranean ecosystems. Accounting for the high spring emission of the dune ecosystem may be



important to correct current algorithms at regional, ecosystem levels, and to interpret measurements of fluxes of volatile isoprenoids and pollutants.

1 Introduction

The Mediterranean ecosystems represent 1% of the Earth's land surface and are concentrated mainly in the Mediterranean basin, where the vegetation community is often named "macchia" or "maquis" and, in its degraded state, "garigue". In Italy, the macchia covers 2–3% of the territory (INFC, 2003) and consists primarily of evergreen shrubs. This vegetation covers the largest part of the dune ecosystem at the interface between lands and the Mediterranean sea, stabilizes coastal sand dunes, and shelters inland vegetation from sea winds and consequent damages due to marine aerosol. Despite the large biodiversity characterizing the macchia vegetation, all plant species show ecological adaptations to the Mediterranean environmental conditions, which are characterized by hot and dry summers, mild and often rainy winters, recurrent exposure to salinity due to sea breeze and saline ground water table, and sandy soil with poor organic fraction and nutrients.

Typically, the morphological and structural adaptations to drought, salinity and high temperatures that are observed in Mediterranean plants include small plant size, globular shape of the canopy, and sclerophytic leaves with thick cuticles and dense mesophyll (Thompson, 2005). The dune vegetation is made by pioneer plant species that need to adapt to rather extreme conditions. To endure recurrent episodes of heat stress, drought, and salt stress plants living in the dunes carry out two alternative ecological strategies. A few plants have a "water spending strategy" with stomata responding strongly to water availability and allowing excellent CO₂ diffusion inside leaves and high rates of photosynthesis when water is available. Most plant species present a "water saving strategy", with stomatal opening permanently restricted by anatomical, morphological and physiological traits, and low rates of carbon assimilation even in the absence of environmental constraints. These plants show a more efficient water use

under harsh conditions (Thompson, 2005).

Another line of defence against biotic and abiotic stresses is constituted by the synthesis and release of trace gases often referred to as biogenic volatile organic compounds (BVOC). The emission of isoprenoids and oxygenated volatiles is common

- in plants and is particularly widespread among the plant species of Mediterranean ecosystems. Isoprenoids are believed to strengthen membranes by protecting leaves against damage caused by heat and oxidative stresses (Sharkey and Yeh, 2001). Oxygenated compounds are indicators of damage occurring at cellular membranes and are released during membrane or cell wall degradation. Methanol and C-6 compounds are
- especially emitted at high rates under these conditions (Loreto et al., 2007). Many of these trace gases are very reactive, and, once emitted in a polluted atmosphere that is enriched by anthropogenic emission of NO_x, may fuel production of ozone (Chameides et al., 1988), secondary organic aerosols and particles (Claeys et al., 2004; Verheggen et al., 2007). These ancillary and unexpected effects of BVOC captured the attention of a multidisciplinary community of scientists that hopes to better understand the possible
 - contribution of biogenic substances to pollution events.

Clearly, the impact of BVOC is expected to be more evident where biogenic and anthropogenic compounds are likely to react, for instance in urban areas, industrial parks and peri-urban green-belts and rural areas. Because some of the oxygenated VOC

- ²⁰ (such as carbonyls) can photolyze quickly and react fast in the atmosphere (Ciccioli and Mannozzi, 2007), sandy dune plants can contribute to ozone and secondary organic aerosol formation to some extent. When the sea breeze circulation is activated over the coast, they are located at the entrance of the photochemical reactor regulating the ozone production downind. When the breeze switches into a land system
- at night, emitted BVOC, can react with primary and secondary pollutants. Some of them, such as monoterpenes or sesquitepenes emitted with a temperature-dependent mechanism, can act as a night time sink of ozone leading to carbonyl and radical formation (Ciccioli and Mannozzi, 2007). Because of the complexity of factors influencing the behaviour of sandy dune plants and their critical location, coastal ecosystems of



the Mediterranean region deserve specific studies, in which emission and deposition of photochemical oxidants and their precursors need to be determined, together with those of primary production and exchange of energy and matter with the atmosphere, namely water, CO_2 and heat. In particular, fluxes of BVOC have been measured so far in Mediterranean ecosystems (such as pseudosteppe and evergreen oak stands) which are different from the dune ecosystem both for the species-specific composition

and for the environmental conditions (Ciccioli et al., 1997, 2003).

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The Presidential Estate of Castelporziano is a large park at the southeastern edge of the large conurbation of Rome. Since 1951, Castelporziano has been an intact and

- ¹⁰ preserved natural laboratory, where climate, ecological, geological and atmospheric researches are carried out by Italian and International research groups. Because of the large biodiversity preserved, the typical Mediterranean climate, and the proximity with urban pollution sources, the park has been a favoured site for the study of the interactions between biosphere and atmosphere in the Mediterranean area. A large
- ¹⁵ campaign was held in Castelporziano more than ten years ago within the framework of the European "Biogenic Emissions in the Mediterranean Area" (BEMA, 1997) project to identify BVOC emitting plants and to estimate fluxes of isoprenoid emission in the atmosphere that could influence the chemistry of the troposphere (BEMA, 1997). Ten years later, two projects, the European Union Network of Excellence on Atmospheric
- ²⁰ Chemistry (ACCENT) and the European Science Foundation programme on Volatile Organic Compounds in the Biosphere-Atmosphere Interactions (VOCBAS) jointly organized a field campaign on the same site. The ACCENT-VOCBAS campaign was performed on May–June 2007 and concentrated on the coastal Mediterranean dune, on a vegetation rich with BVOC-emitting species (Owen et al., 1997), and sensitive to environmental constraints.

Since the pioneering BEMA campaign, outstanding progresses have been made in the inventory and understanding of BVOC emissions by plants. For instance, the advent of the Proton Transfer Reaction-Mass Spectrometry has allowed measurements of fluxes of trace gases with unprecedented speed and sensitivity (Lindinger et al., 1998),

which makes flux measurements possible with eddy covariance techniques (Rinne et al., 2001). Moreover, scientific progresses have demonstrated that the emission of volatile isoprenoids is not only controlled by light and temperature (Guenther et al., 1995) but also change with leaf development (Fuentes and Wang, 1999), and in response to environmental constraints, especially salinity (Loreto and Delfine, 2000) and drought (Brilli et al., 2007).

The field campaign in Castelporziano addressed the following main scientific objectives:

- a) to assess with a new generation of instruments the species-specific BVOC emis-
- sion by dune vegetation;
 - b) to determine, with joint field measurements, BVOC emission rates and physiological conditions from plants that were at the beginning of their growing season, and that were presumably yet unaffected by environmental stressors that strongly limit carbon fixation and allocation to secondary metabolites over dry and hot Mediterranean summers;
 - c) to measure by disjunct eddy covariance (Karl et al., 2002) fluxes of BVOC at the ecosystem level on an ecosystem that has been never investigated previously;
 - d) to integrate concurrent leaf measurements of BVOC, CO₂ and H₂O fluxes driven by physiological processes with ecosystem measurements, supplying information for models of BVOC emissions and reactivity on the macchia vegetation;
 - e) to assess, simultaneously to BVOC measurements and over the same area, the presence of air pollutants, focusing on ozone, NO_x, and particles, in order to estimate whether the possibility exists for BVOC to react with anthropogenic compounds (Atkinson and Arey, 2003), initiating on site the complex chain of reactions that may lead to the formation of secondary pollutants, or protecting plants from pollution damage, as recently reported (Loreto and Fares, 2007);

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- f) to assess, through concurrent measurements of meteorological and climatological parameters, whether the climatic factors may affect BVOC emissions and may explain air mass movements, and the consequent possibility that pollutants be formed or transported on peri-urban and rural areas.
- This paper introduces the general aspects of the campaign, presents biological, climatic and meteorological details of the site, and focuses on the measurements of plant physiological status and BVOC emissions at leaf level. Companion papers will present results obtained during the campaign about specific issues including fluxes and modelling of BVOC emissions, CO₂, water and pollutants, and models of air chemistry and transport of air masses.

2 Material and methods

Site information

The experimental site is located in the Presidential Estate of Castelporziano, 41°40′49.3″ N, 12°23′30.6″ E It covers and area of about 6000 ha located 25 km SE
¹⁵ from the center of Rome, Italy. The Mediterranean ecosystems are well represented and preserved inside the Presidential Estate, which contains more than 1000 plant species. The part of the Estate facing the Tyrrhenian Sea was chosen for the 2007 field campaign (Fig. 1). This area is characterized by sand dunes with vegetation growing in "garigue-type" location and mixed to a humid retrodune area with "maquis" vegetation (Bernetti, 1997; Pignatti et al., 2001). The specific location of the experimental site is 100 m from the coast line, between a first and a second dune layer. An area of 1070 m² was used for the study on vegetation characteristics as described below.

According to phytoclimatic studies (Blasi, 1993), the experimental area belongs to a Thermo-Mediterranaean region, with long and prolonged stress aridity during summer periods, and a moderate cold stress during winter. The soil of the experimental site



is a typical Regosol with a sandy texture and low water-holding capacity, which exacerbates early drought. This soil is not evolved, with an "A" horizon increasing in thickness with the distance from the sea. The chemical properties of the soil are dominated by the strong presence of carbonate elements (0.8% of CaCO₃) that create an alkaline pH of 8.3 (Francaviglia et al., 2006). Organic matter is heterogeneously present in the first horizon of the soil which is also rich in fine roots, reflecting the patched presence of vegetation described in Table 1. The total content of soil organic carbon is in the range of 3.1 g(C) kg⁻¹ soil, with high rates of microbial activity which also favoured a high mineralization rate (Trincheri et al., 1998; Pinzari et al., 1999). The back-dune areas, very close to the experimental site, contain small water-pools, in which water temporarily accumulates, especially during winter, as a function of water-table level and rainfall rate.

Measurement of environmental parameters

Meteorological data were collected during the years 2005–2007 at two stations located inside the Castelporziano estate. The Tor Paterno station was located 6 km to the south of the experimental site, but at a similar distance from the coast. The Carboeurope station (serving the Carboeurope-IP European project, and managed by the University of Tuscia) was located at 500 m NE from the sandy dune site. In Tor Paterno, hourly values of temperature were recorded with a MP100A sensor (Rototronic, Huntington,

- NY, USA). A sonic anemometer (W200P, Vector instruments, Rhyl, UK) was used to instantaneously measure wind speed and directions, and a pluviometer (ARG 100, Environmental measurements, Sunderland, UK) was used to measure daily precipitation. All instruments were connected to a data logger (CR23X, Campbell scientifics, Shepshed, UK). Collected data were downloaded monthly and stored in the data-base of
- the Estate. The Carboeurope station was equipped with similar sensors, but meteorological data were complemented with sensors for the determination of atmospheric pressure and the flux of water and CO₂, by Eddy Covariance.

The Bagnouls-Gaussen's diagrams were used to report the monthly averages of air



temperatures and precipitation. The intersection (grey area) of the precipitation curve with the average temperatures indicates a period of aridity (Bagnouls and Gaussen, 1957).

Minimum and maximum monthly temperatures and precipitation were used to generate the Mitrakos' diagram, which identifies the Monthly Cold Stress (MCS) and the Monthly Drought Stress (MDS) indices, expressed in stress units and calculated according to the intensity and duration of cold and drought stress periods, as described by Mitrakos (1980). In brief, the MCS index was calculated according to Eq. (1):

MCS = 8 * (10 - T)

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¹⁰ Where *T* is the average of the monthly minimal temperatures. For $T = 10^{\circ}$ C, MCS=0 (considering 10°C as a threshold for the vegetative activity for Mediterranean plants); for $T = -2.5^{\circ}$ C, MCS is assumed to be 100 (assuming that minimal values of 2.5 correspond to the maximal cold stress).

The MDS index was calculated according the hypothesis that when monthly precipitation are below 50 mm a drought stress occur in Mediterranean plants (Eq. 2):

MDS = 2 * (50 - P)(2)

Where *P* is the sum of the monthly precipitation (mm). For P=0, MDS=100; for P=50, MDS=0.

Continuous monitoring of ozone was performed during the campaign from above
 canopy using a scaffold (6 m) built in the middle of our experimental area. Air was sampled at a rate of 31 min⁻¹ with a vacuum pump through teflon tubing and passed into a photometric O₃ analyzer (1008 Dasibi Environmental Corp., Glendale, CA, USA) mounted into a cabin 10 m distant from the scaffold. Ozone concentrations in Castel-porziano were compared to those recorded at the EMEP station of Montelibretti lo cated downwind the city of Rome, along the main direction followed by air masses in high pressure summer conditions (sea-land breeze circulation regime) (Ciccioli et al., 1999).

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(1)



Measurement of vegetation composition and distribution

An inventory of the species composition and their distribution in the 1070 m²-wide experimental area around the scaffold where the monitoring devices were positioned was carried out during May. The projected area (PA – m²) of the crown of each plant inside

the experimental plot was obtained by measuring crown radius along the four cardinal axes and averaging the four resulting areas. The sapwood area (SA – m²) was assessed by measuring the stem diameter at 10 cm from the ground on each species, after the cork and phloem were removed, in order to obtain a species-specific sapwood area to projected area ratio (SA/PA). When it was not possible to distinguish to which stem the crowns of plants belonged, height and projected area were measured for the whole patch belonging to the same species. Additionally, the percentage of soil covered by each species was obtained dividing the sum of the PA of each species by the area of the experimental plot.

The basal area of each species was calculated by:

$$BA = \frac{SA}{PA} \times \text{cover}$$

The leaf area of twenty leaves (La_i) per woody species was measured by a computer software (Image Tool Software Roswell, GA). These leaves were dried at 80°C for a week to obtain the leaf mass (LM - g). The leaf mass to area ratio $(LMA - gm^2)$ of each leaf was calculated by:

²⁰ LMA = $\frac{\text{La}_{I}}{\text{IM}}$

The average LMA of each species was calculated.

The leaf area (LA) to sapwood area ratio (LA/SA) of each species was estimated as the slope of the linear fit of the LAb vs. SA regression using thirty branches for each species with diameters ranging between 0.3 and 5 cm. The leaves of each branch were

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(3)

(4)



dried to obtain the total leaf material $(LM_{tot} - g)$ of the branch. The leaf area of each branch (LAb) was estimated by multiplying LMtot by the LMA:

 $LA_b = LM_{tot} \times LMA$

The leaf area index (LAI) of *Quercus ilex*, *Phillyrea latifolia*, *Arbutus unedo*, and *Erica arborea* plants was derived by dividing the LA/SA ratio by the Projected Area (PA)/SA ratio, which yields LA/PA, also called LAI:

$$LAI = \frac{LA}{PA} = \frac{LA}{SA} \times \frac{SA}{PA}$$

The LAI of each species was estimated as the average LAI calculated on at least ten different plants per species. The LAI of *Cistus incanus, Rosmarinus officinalis* and
 Erica multiflora was assessed in a different way because of the elevated number of stems for each bush. For these species the LAI was obtained by multiplying the LMA by the dry weight of the leaves present over 0.25 m² of soil (three samples for each species).

Measurements of plant physiological properties and isoprenoids emission

- Photosynthesis, stomatal conductance and transpiration of all species were measured with a Li-6400-40 gas exchange open portable system (LI-COR, Lincoln, Neb., USA). A leaf was enclosed in a 6 cm² cuvette and an air flow was pumped to the cuvette after being filtered with an active carbon cartridge to scavenge pollutants or BVOC present in the air. The instrument allowed to control light intensity and leaf temperature, which were set, respectively, at 1000 µmol m⁻² s⁻¹ of PAR (Photosynthetic Active Radiation) and 30°C. These are the basal conditions at which isoprenoid emission is commonly measured (Guenther et al., 1995). The outlet from the cuvette was diverted to the Li-6400-40 infrared gas analyzer to measure CO₂ and H₂O exchange, and occasionally diverted to a glass traps (16 cm in length, 4 mm I.D.) filled with 130 g Tenax GC,20–35
- ²⁵ mesh, (Alldrich, USA) and 115 g Carbograph 1, 20-40 mesh, (LARA S.p.A., Rome,

(5)

(6)



Italy) to collect BVOC. Air was passed through the trap at a flow rate of 200 ml min⁻¹, controlled by a pump (Pocket pump, SKC, PA, USA), until a total volume of 101 of air was collected.

- Traps were stored in a refrigerated container until analyzed at CNR laboratory with a gas chromatograph (GC 5890, Hewelett Packard, Palo Alto, CA, USA) connected to a quadrupole mass spectrometer (MSD 5970, Hewelett Packard, Palo Alto, CA, USA). Traps were desorbed by keeping them at a temperature of 250°C for 5 min using helium as carrier gas at a flow rate of 20 ml min⁻¹. Desorbed isoprenoids were concentrated in a empty liner at –190°C under liquid nitrogen and then injected into the GC column by rising the temperature of the liner to 200°C in 5 s. A Chrompack, fused silica capillary column (50 m in length with 0.4 mmm I.D.) coated with a 0.32 μm of CPsil5 (Middelburg, The Netherlands) was used for the chromatographic separation. The elution was carried out by rising the column temperature from 50 to 250°C at a rate of 5°C min⁻¹. Compounds were identified and quantified following the procedure
- described in Ciccioli et al. (2002).

3 Results and discussion

Climate and meteorological data

Meteorological data for the years 2005–2007 showed that the climate of the site is typically Mediterranean with mean monthly temperatures ranging between a minimum of 4°C and a maximum of 27°C, extreme summer temperatures occasionally exceeding 30°C (maximal values of 32°C in August 2007), absence of freezing events, and a pronounced summer drought, with rainfall events concentrated in autumn and spring. In particular, the mean annual precipitation over the years 2005–2007 was 713 mm, but only 480 mm were recorded during 2007. The summer dry period was recorded on each one of the three years, with low monthly rainfalls (<200 mm) clearly shown in Bagnouls-Gaussen's diagrams (Bagnouls and Gaussen, 1957) (Fig. 2). The Mi-





trakos' MCS diagram showed an evident cold stress period in our experimental site from November to March (Fig. 3). More interestingly, the MDS index showed that drought stress was widespread over the entire dry seasons, but particularly strong during the summer periods of years 2006 and 2007 (Fig. 3). A similar climatic regime was
observed after computing the analysis of historical series on the same site, as shown by Manes et al. (1997a).

The year 2007 was in general very warm, with prolonged drought stress also in winter, and monthly precipitation never exceeding 100 mm (Fig. 2). All climatic indices confirmed that the period of the campaign (May 2007) was favourable to vegetative growth, at least when compared to the hot and dry summer. Moreover, the proximity of the site to the sea led to a high humidity regime (with RH rarely below 60%) often even bringing to the formation of dew in the night-time. Based on these climatic data the pe-

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riod between May and June were considered the best to study biosphere-atmosphere exchanges because of the absence of environmental constraints to plant physiology and of the concurrent presence of daily temperature sufficient to induce high emission rates of BVOC.

Under the high pressure conditions prevailing during the campaign, the air mass circlulation was characterized most by a local sea-land breeze circulation, with moderate to strong S-SW winds blowing during the day, and light N-NE winds after 2 a.m. (Figs. 4

- and 6). This type of circulation is typical of the entire coastal area of Latium. Similarly to what observed by Kalabokas at al. (1997) during the BEMA campaign, primary emissions of anthropogenic compounds (e.g. VOC, NO_x, aromatic hydrocarbons) and secondary pollutants (such as ozone and PAN) were advected over the site from the urban area of Rome at night, in the period of time ranging from 2–3 a.m. and 9 a.m.
- ²⁵ Daily variations of the main meteorological parameters recorded in the two meteorological stations of Castelporziano during the field campaign are shown in Fig. 4a–d. Data of the atmospheric pressure show that the weather was characterized by a certain variability, more typical of earlier spring periods. High pressure periods were frequently alternated to short episodes of low pressure, accompanied by precipitations over the



site and high levels of relative humidity in the air. Particularly important was the low pressure episode occurring on 28 May, because it was associated to a front of humid air that generated strong winds blowing from the SW-W sector. Precipitations occurred also at the beginning of the campaign (4 May), but in this case the front was less intense

- and characterized by light winds from the same sector recoreded during the rest of the campaign. Overall, high pressure conditions did not last sufficiently long to generate high temperatures in the air. Only in one case, a maximum daily value of 30°C was reached, whereas for most of the time air temperatures were in the range of 25–26°C. Because of these meteorological conditions, associated with high light intensity levels, we expected to find the vegetation of the sandy dunes on unstressed conditions, and
- we expected to find the vegetation of the sandy dunes on unstressed conditions, and gas-exchanges of CO_2 , H_2O and BVOC yet unconstrained by abiotic stresses typical of the dune Mediterranean ecosystems during summers.

Ozone levels during the field campaign

Wind speeds and temperatures during our measurement period were lower than those
 occurring in the middle of the summer, when the anti-cyclonic weather persists much longer than in spring. Because of this, the input of primary emission (e.g. VOC, NO_x, aromatic hydrocarbons) and the formation of secondary pollution (such as ozone and PAN) along the Tyrrhenian coasts of Latium was expected to be lower than that observed and measured by Kalabokas et al. (1997) in previous campaigns also held
 in Castelporziano. This is also demonstrated by the levels of ozone measured at the

- same time in the sandy-dune site, and at the EMEP station of Montelibretti, located downwind of Rome (Fig. 5). With the only exception of 25 May, when ozone levels as high as 100 ppbv of ozone were recorded, the maximum daily values of the EMEP station in Montelibretti ranged between 60 and 80 ppbv. These ozone values are lower
- than those usually recorded in this station in the middle of the summer, when ozone levels as high as 200 ppbv can be reached under sea-breeze conditions (Ciccioli et al., 1999). Data from these two stations are crucial to understand the ozone formation in the Tiber valley, because levels measured upwind and downwind of Rome provide infor-



mation on the extent to which emission, reactivity and transport contribute to the ozone build-up over the area. Several studies (Ciccioli et al., 1993, 1999; Cantuti et al., 2003) have indeed demonstrated that air masses moving from the coast under sea-breeze conditions become progressively enriched in ozone and photochemical oxidants after

- ⁵ passing through the city centre. This occurs because air masses progressively switch from BVOC-limited conditions, typical of the centre of Rome, to NO_x-limited conditions observed in rural environments dominated by agro-forestry down-wind the urban area. It has been found (Ciccioli et al., 1999) that the maximum photochemical production in the Tiber valley occurs between the city limits of Rome and the suburban areas located
- 10 15 km from the city centre. Under heavy smog conditions, the influx of the city plume of Rome in Montelibretti gives rise to sharp peaks of ozone, peroxyacylnitrates (PAN), sulfates and nitrates whose maximum values can be as twice as the background values (Ciccioli et al., 1993, 1999; Cantuti et al., 1993). However, such photochemical smog events take place when stability conditions last much longer (10–15 days) than during any second stability.
- 15 our campaign.

Long stability periods are needed for the build-up of ozone, because photochemical pollution in the Tiber valley results from a complex recirculation of primary and secondary pollutants occurring over the Mediterranean coasts (Millan-Millan et al., 1996) under high pressure conditions. Under this regime, polluted air masses leaving the city

- ²⁰ of Rome during the day are conveyed back toward the sea by a return flow generated when they reach the Apennine range of Central Italy (Baldi et al., 1993; Mastrantonio et al., 1994). This return flow, moving above the "heat island" of Rome at an altitude from 500 to 900 m above the surface, transport ozone up to 40 km off-shore, where it stratifies into stable layers at night, when little exchange of mass and heat occur
- (Millan-Millan et al., 1996). These layers are often depleted in NO_x and the only potential reservoir of NO₂ is the small amount of PAN (1–2 ppbv) contained in the plume (Ciccioli et al., 1999). Ozone stratified over the sea at night is transported again over the coast after sunrise, when turbulent mixing disrupts the stable layers, and the seabreeze is activated (Millan-Millan et al., 1996). Under summer conditions, transport





normally starts from 11 to 12 a.m. (Baldi et al., 1993; Mastrantonio et al., 1994; Ciccioli et al., 1999) and photochemically polluted air masses reach the Montelibretti site in the early afternoon, between 1–2 p.m. However, only a minor portion of the ozone contained in the return flow of Rome reaches Castelporziano, because the majority of

- the city plume is shifted toward the SE direction by the Corioli's forces. The ozone levels in Castelporziano are thus essentially determined by the photochemical processes occurring in the coastal areas located NW from the site. Data displayed in Fig. 6 substantially confirm the close dependence of the ozone levels in Castelporziano from inland processes, when the sea-breeze is active.
- ¹⁰ It is important to point out here that daily ozone profiles recorded in Castelporziano often substantially differ from those recorded in the stations located in Rome or downwind the city. In urban and suburban stations, the maximum of ozone is generally reached when the maximum production and advection of ozone takes place. This usually occurs in the middle of the day when the temperature, the solar radiation and the
- ¹⁵ speed of the sea-breeze reach the maximum value. This type of profile is observed in Castelporziano only when acute smog episodes takes place all along the Tyrrhenian coasts (Kalabokas et al., 1997). If the return flow rich of ozone is depleted in NO_x, no further ozone production takes place in the early morning over the sea, and the daily ozone profile recorded at the sea shore is characterized by a top-flat peak
- (Millan-Millan et al., 1996). Data displayed in Figs. 5 and 7, indicate clearly that, during the campaign, ozone production in the areas north of Rome was quite limited, and Fig. 7 highlights that production over the sea in the early morning was also limited. The flat profile of ozone in Castelporziano suggests that the ozone levels measured were produced mostly by simple advection of ozone accumulated off-shore.
- Another important difference between the ozone profiles measured in Castelporziano and Montelibretti are the levels reached at night. While ozone was completely removed in the suburban station, substantial levels of ozone still remained in Castelporziano. Since the land-breeze is not activated before 2–3 a.m. (Ciccioli et al., 1999), stable conditions characterize the whole basin of Rome between sunset and the early morn-



ing. In these conditions concentrations of ozone in Castelporziano and Montelibretti are determined by the height of the mixing layer and the removal process occurring in them. The most efficient processes in removing ozone at night are dry depositions, gas-phase reactions with NO, NO₂ and monoterpenes (Finalyson-Pitts and Pitts,

- 1999). Among these processes, the most crucial one is reaction of ozone with NO_{2} , 5 because it leads to the formation of NO3 radicals which can rapidly react with biogenic and anthropogenic VOC (Finalyson-Pitts and Pitts, 1999). Almost complete removal of ozone and VOC at night has been observed in the city centre of Rome, when substantial formation of NO₃ radicals occurred (Ciccioli et al., 1999). In very humid environ-
- ments rich of particles, such as the sandy dune ecosystem, heterogeneous reaction of 10 NO₂ with ozone, leading to nitrous acid, might prevail over NO₃ radical formation, thus limiting the ozone removal from the atmosphere (Lammel and Cape, 1996). Conditions promoting preferential formation of NO₃ radicals and nitrous acid, combined with differences in the mixing height explain why a more complete removal of ozone is observed
- in Montelibretti but not in Castelporziano. 15

Vegetation characteristics

The dune vegetation of the experimental site is composed of patches of Mediterranean "maquis" and "garigue". Following the nomenclature suggested by Pignatti (Pignatti et al., 2001), we named "garigues" the Erico-Rosmarinetum formation, characterized by the abundant presence of low-shrubs species as Rosmarinus officinalis and Er-20 ica multiflora; Arbutus unedo, Phillyrea latifolia and Cistus incanus albidus. The latter are typically located over Regosols soils rich of CaCO₃ from deposited bioclasts. The woody species of these formations are rarely taller than two meters (Table 1). The Mediterranean "maquis" is a variation of the Quercetum-ilicis (Pignatti et al., 2001). which is dominated by *Quercus ilex* from the early developing stages. The early stages 25

of "maguis" are formed by a mixture of *Quercus ilex* and other co-dominant species: Erica arborea, Phillirea latifolia, Juniperus spp. and Arbutus unedo, with canopy level rarely taller than five meters. The increase of below-ground marine water level could



lead to a progressive substitution of actual high "maquis" to plant communities more typical of a degraded "garigue" (e.g. the *Erico-Rosmarinetum*), characterized by low shrubs adapted to very alkaline pH soils. Pignatti et al. (2001) hypothesize that vegetation patches of the two formations (garigue and maquis) observed in the experimental area correspond to an uneven distribution of sea shells which originated the bioclasts.

Future studies should test this hypothesis (Pignatti et al., 2001).

As shown in Table 1, *Quercus ilex* was the tallest plant at the site, reaching the maximum of 3 m height. *Arbutus unedo* has the largest cover (21.9%), followed by *Rosmarinus officinalis* (17.2%), *Quercus ilex* (14.6%), *Phillyrea latifolia* (14%) and *Er*-

- *ica multiflora* (12.3%). The summed percentage coverage shows that the "garigue" (48.2% of the site) was slightly more widespread than the "maquis" (42.1% of the site). In terms of LAI, species as *Erica arborea* (4.5 m² m⁻²), *Arbutus unedo* (2.9 m² m⁻²), *Quercus ilex* (2.9 m² m⁻²), *Rosmarinus officinalis* (2.5 m² m⁻²) mostly contributed to the average LAI of the site, which was 2.3 m² m⁻². Only 5% of the experimental site
 ¹⁵ was assessed to be constituted by bare soil, and another 5% was covered with dead plant materials, i.e. fallen branches and leaves of annual herbs.
 - Changes in quality and depth of the water table of the sandy dune ecosystem can strongly affect biosphere-atmosphere exchanges. The waterpools present in the experimental site have an important ecological role, since they preserve a high floral and fau-
- nal biodiversity. However, a dramatic decrease of the water table level was observed in the last years (Bucci, 2006). This process is very common in the Mediterranean coastal areas, being caused mostly by increasing water demand by agricultural activities and coastal inurbation. As a consequence, marine water infiltrates on the freshwater table, reaching more superficial levels and salinizing the root environment of dune and retro-
- ²⁵ dune plants. If this occurs, shrubs species belonging to the *Erico-Rosmarinetum* with less deep rooting system could be favoured with respect to woody species. Models predict a complete salinization of the soil by 2050 (Bucci, 2006) for the coastal area of Castelporziano. We measured the depth of the water table two times, in the middle of the test site. The water table depth was found to be 210 and 290 cm, respectively,



when measured on 27 May and 4 August. It is therefore suggested that the sinking depth of the water table could be the main cause of abiotic stress during the dry periods. A strong physiological dependence of schlerophylls plants on the freshwater table level was also observed, in our same experimental site, with a study of isotopic fractionation in xylematic water (Alessio et al., 2004). In particular, the shrubs examined 5 in our study, and particularly A. unedo, P. latifolia and, Q. ilex, showed negative values of ¹⁸O₂ values of xylematic water that are associated with high discrimination (Δ) values, even under very dry conditions. This indicates low long-term water use efficiency, especially when compared to the opposite behaviour of some other dune species (e.g. Smilax aspera). Interestingly, no species of the coastal dune system used marine wa-

10 ter or mixtures of marine and freshwater, indicating that in this site marine intrusion was absent.

3.0.1 Physiology

Plants showed an excellent physiological status during the experimental period. Rates of photosynthesis and stomatal conductance measured in mid May (Table 2) were 15 comparable to data reported in the literature for unstressed leaves and higher than rates measured at the same experimental site during previous campaigns held in full summer (Manes et al., 1997b).

Since the measured ozone levels often exceeded 40 ppb during the day-time

- (Figs. 5–7), and this is considered a threshold after which plants can be damaged by 20 the pollutant (UNECE, 2004), we also checked for possible ozone injuries to vegetation. No reduction of chlorophyll content, photosynthesis, chlorophyll fluorescence, nor visible injuries that could be directly attributed to ozone damage were found (data not shown). Most of the schlerophyllous species growing in the experimental site (Quercus
- ilex, Arbutus unedo, Pistacia lentiscus) are known to be resistant to chronic or pro-25 longed ozone exposures (Vitale et al., 2008; Nali et al., 2004). This can be attributed to: i) low stomatal opening which reduces the amount of ozone taken up by leaves (Loreto and Fares, 2007), especially when stomata are further shut down because of





concurrent drought stress; ii) thick cuticular waxes and mesophylls that reduce nonstomatal ozone entry, and increase the chance of ozone reaction inside mesophyll before reaching target sensible organelles (Loreto and Velikova, 2001); iii) detoxification of ozone by reaction of the pollutant with BVOC (especially isoprenoids) emitted

- ⁵ by plants. Loreto and Fares (2007) demonstrated that ozone damage is considerably reduced in high isoprenoid emitters, although ozone uptake is higher in these plants, and products of putative reactions of ozone with isoprenoids were not described *in planta*. Since many Mediterranean species do emit high levels of isoprenoids (see below and also Kesselmeier and Staudt, 1999, for a comprehensive review), isoprenoids
- ¹⁰ and other reactive molecules may be key players in driving ozone uptake and efficient detoxification thus limiting dangerous effects of pollution in peri-urban areas.

Beside being exposed to recurrent high ozone episodes, the entire area of Castelporziano is endangered by acid atmospheric depositions, another typical stress factor in periurban areas. The uptake of acid rain by dune vegetation was evaluated to be up to 434 eq H⁺ ha⁻¹ y⁻¹, near to the critical load (500 eq H⁺ ha⁻¹ y⁻¹), but the risk of acidification was low in comparison with that assessed on pine and oak woods growing near the experimental area (Francaviglia et al., 2006).

3.1 Isoprenoid emission

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As also shown by photosynthesis measurements, plants were actively growing dur-²⁰ ing the experimental campaign. Growth occurs only when environmental constraints are low, and, in dry ecosystems of the Mediterranean area, it takes place mostly in two flushes during spring and fall (Reichstein et al., 2002). High photosynthesis is expected to drive high emissions of BVOC during spring, as some of these compounds, such as the main volatile isoprenoids, are formed by carbon directly shunted from photosynthetic carbon metabolism (Sharkey and Yeh, 2001). However, a strong seasonality has been observed for many BVOC, constraining biosynthesis and emissions of these compounds during spring. Isoprene emission is under developmental control, being very low in expanding leaves, and uncoupled from photosynthesis development



(Sharkey and Loreto, 1993). A seasonal pattern of monoterpene emissions was also observed as depending diurnally and seasonally by light and temperature (Sabillon and Cremades, 2001) and phenology (Staudt et al. 1997, 2000; Ciccioli et al., 2003). This uncoupling is attributed to slow development of the capacity to synthesize iso-

- ⁵ prenoid synthases, the enzymes catalyzing the formation of isoprene (Wiberley et al., 2005) or monoterpenes (Fischbach et al., 2002). Thus, a low emission of isoprene and monoterpenes may be expected early in the season. However, Wiberley et al. (2005) pointed out that the development of the trait (i.e. the transcriptional and translational limitation to isoprene synthase biosynthesis) are in turn controlled by growth tempera-
- ¹⁰ ture. Therefore, in the Mediterranean area, whose climate is characterized by already rather high spring temperatures, a sustained emission of isoprenoids could be seen already in spring.

Table 2 shows that emission of isoprene was low in the Mediterranean dunal ecosystem, confirming data previously obtained by Owen et al. (1997) at the same site, and

- ¹⁵ by the whole previous campaign in the Mediterranean area (BEMA, 1997). However, monoterpene emission by some dune plants was relevant, despite the early season of measurement. *Quercus ilex*, in particular, was confirmed to be a high monoterpene emitter, with α and β -Pinene the most emitted compounds. The total emission of monoterpenes by *Q. ilex* leaves was around 10 µg(C) g⁻¹ DW h⁻¹, a rate comparable
- to those measured in other field measurements (Loreto et al., 2001a). Monoterpene emissions were about 30% lower than those reported by Bertin and Staudt (1996) and Kesselmeier et al. (1997) in Castelporziano but in full summer (i.e. with higher temperatures and more complete leaf development) and on a different site, character-ized by more structured soil and higher water availability. Both mature (second year)
- ²⁵ leaves, and young, still expanding leaves, emitted similar rates of total monoterpenes, which suggests that the rate of biosynthesis and emission is not under developmental control, and that monoterpene emission is also rapidly induced in young leaves that were grown at rather elevated spring temperatures, confirming the indications of Wiberley et al. (2005). Interestingly, however, the composition of the emitted monoter-



pene blend was different in mature and developing *Q. ilex* leaves, with trans and cis- β -ocimene only emitted by mature leaves. We surmise that ocimene biosynthesis is under developmental control. Trans- β -ocimene seasonal emission was observed in pines (Loreto et al., 2000; Staudt et al., 2000). Emission of trans- β -ocimene and other acyclic monoterpenes may be also induced by herbivore feeding (Heil and Silva Bueno, 2007), and may therefore reveal induction caused by past stress occurrence in mature leaves. However, trans and cis- β -ocimene emissions were also measured in *Q. ilex* leaves that were grown in absence of abiotic and biotic stress (Loreto et al., 1996).

Rosmarinus officinalis and Juniperus oxycedrus also emitted monoterpenes at high
rates, but with different emission patterns. β-Pinene and 1,8-cineol were the main compounds emitted by *R. officinalis*, whereas the emission of *J. oxycedrus* was mainly characterized by α-pinene. The total monoterpenes emission by rosemary leaves was 18.89 µg(C) g⁻¹ DW h⁻¹, largely more than reported by Hansen et al. (1997). Contrary to *Q. ilex*, *R. officinalis* and *J. oxycedrus* store monoterpenes in large pools in specialized glandular organs (Ormeno et al., 2007; Salido et al., 2002). The emission by monoterpene-storing species is generally not light-dependent, and a long time is needed to extinguish the pool once biosynthesis has been turned off (Guenther et al., 1993). Llusia and Penuelas (1998, 2000) observed that monoterpene emission by monoterpene storing species is more dependent on temperature than in non-storing

- ²⁰ species, which may drive relevant summer emissions of monoterpenes, even when photosynthesis is environmentally constrained. These authors also found an accumulation of monoterpenes in storage organs of Mediterranean species at increasing drought conditions, with maximal levels in the autumn. These findings suggest that in our measuring period we did not observe the maximal monoterpene emission and
- ²⁵ that even higher emissions can be detected during warmest periods and when the pools of monoterpenes are completely filled. However, the temperature dependence of monoterpenes stored in pools is not always that high. For instance in *Pinus pinea* emission of stored monoterpenes is less dependent on temperature than emission of non-stored monoterpenes (Staudt et al., 1997). In addition, it should be mentioned



that rough handling can drive large emissions from storage pools (Loreto et al., 2000). We paid special attention to avoid breakage of storage pools in our measurements, but cannot exclude altogether that some of the abundant emission observed were also contributed by unwanted mechanical stress.

- ⁵ Owen et al. (1997), reported *Cistus* spp. as a weak isoprene and monoterpenes emitter of the Castelporziano sandy dune ecosystem. However, we found values of monoterpene emission (1.35 μg(C) g⁻¹ DW h⁻¹) much larger than previously reported. Llusia and Penuelas (2000) detected in Cataluna high emissions from *Cistus incanus*, more in line with our indications. Monoterpene emission by *Cistus incanus* is probably
- ¹⁰ under seasonal control. The emission rates detected in our campaign from *Cistus in-canus* leaves were more similar to rates measured in October than to those measured in May in *Cistus incanus* plants growing in the Pianosa island (Baraldi et al., 2001), but Llusia and Penuelas (2000) also measured maximal emissions in May. The Pianosa experiment indicated a strong dependency of *Cistus incanus* emission on water avail-
- ¹⁵ ability, as October sampling was done after a period of rainfalls (Baraldi et al., 2001). Indeed, we observed a further increase of the emission of both isoprene (>80%) and monoterpenes (>40% with respect to controls) in few *Cistus incanus* plants that were artificially irrigated during our experiment. Since stomata opening should not regulate isoprenoid emissions, with few exceptions (Niinemets et al., 2004), our finding indicates
- ²⁰ a strong control of water availability over the synthesis of isoprenoids in this species. This finding is in contrast with recent conclusions that isoprenoid biosynthesis is resistant to drought stress (Pegoraro et al., 2004; Brilli et al., 2007). However, *Cistus* spp. are water-spending plants characterized by low stomatal control on water content and very dramatic changes of leaf water status, especially when living in an environment subjected to fast changes of soil water content, as is the case of the sandy soil of
- Castelporziano site.

A detectable emission of isoprene and monoterpenes was also observed from *Erica* multiflora leaves (1.48 and $2.4 \,\mu g(C) \, g^{-1} \, DWh^{-1}$, respectively). Again, this is a higher emission than previously measured by Owen et al. (1997) at the same site. However,



strong isoprene-emitters are characterized by rates of emissions ten times higher than in monoterpene emitters. Thus, on the basis of our spring measurements and of the summer measurements of Owen et al (1997), *E. multiflora* can only be categorized as a low isoprene emitter.

The other two screened species emitted low amount of monoterpenes. The weak emission of monoterpenes by *Arbutus unedo* (0.29 μg(C) g⁻¹ DW h⁻¹), was also observed by Owen et al. (1997), and Pio et al. (1993). Alessio et al. (2004) also reported inconspicuous emissions of isoprenoids by *Arbutus unedo* and *Phyllirea latifolia*. It is therefore confirmed that these plants do not have the capacity to produce and emit relevant amounts of isoprenoids.

After measuring the basal emission at leaf level of each representative species of the stand (Table 2), an upscaling procedure was developed to estimate isoprenoid emission at ecosystem level. The species representativeness, and the species-specific leaf biomass over the experimental site (the parameters shown in column 4 and 5 of Table 1) were considered. The basal emission of isoprene for the whole stand

of Table 1) were considered. The basal emission of isoprene for the whole stand (normalized at 30°C and a light intensity of 1000 μmol photons m⁻² s⁻¹, according to Guenther's algorithm – 1995) was 0.31 μg(C) g⁻¹ DW h⁻¹. This emission is lower than the emission suggested for Mediterranean ecosystems by Guenther et al. (1995) (16 μg(C) g⁻¹ DW h⁻¹) and by Owen et al. (1997) (14.88 μg(C) g⁻¹ DW h⁻¹). It should be mentioned that these two studies concentrated on Mediterranean ecosystems more abundant of isoprene emitting species (*Myrtus communis* and *Cistus* spp.) than the

dune ecosystem investigated here.

The same averaging procedure was adopted for monoterpenes, and yielded a basal emission rate of $4.7 \,\mu g(C) \,g^{-1} \,DW \,h^{-1}$. For monoterpenes, Guenther et al. (1995) suggested a basal emission value of $1.2 \,\mu g(C) \,g^{-1} \,DW \,h^{-1}$, and a similar indication was

gested a basal emission value of 1.2 μg(C) g⁻¹ DW h⁻¹, and a similar indication was given by Owen et al. (1997) (2.2 μg(C) g⁻¹ DW h⁻¹). Thus it is concluded that the Mediterranean dune vegetation is an important source of monoterpene emission, and a less important source of isoprene emission than other Mediterranean ecosystems. Emissions are also likely different in the macchia ecosystems growing on a less sandy



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soil, under a less dramatic water limitation. Our estimate about stand emission rate may be lower than actual if integrated over the whole vegetative period. It has been shown that isoprene emission is controlled by seasonal temperatures (Sharkey et al., 1999) and a similar control may also occur in monoterpene-emitters (Ciccioli et al., 2003). Unless emissions are drastically restrained by stress episodes (Baraldi et al., 2001; Loreto et al., 2001b) emissions of dune vegetation might therefore increase when

the stand is exposed to high summer temperatures for long periods.

4 Conclusions

The experimental area of Castelporziano is an ideal site to test the interactions between biosphere and atmosphere in an environment that is made fragile by heavy anthropogenic pressure and by climate change drivers. This situation is unfortunately typical of the entire Mediterranean coastal area, where plant ecosystems are particularly perturbed by a combination of anthropic impacts and natural climate changes (van Der Meulen and Salaman, 1997; IPCC, 2007).

- The interdisciplinary effort of the ACCENT-VOCBAS campaign was concentrated on studying the source strength of BVOC emitted by Mediterranean dune vegetation, and the impact of BVOC on the physical and chemical properties of the atmosphere. We characterized the weather, climate and vegetation properties at the site, providing indispensable information for the correct interpretation of the results obtained by teams
- ²⁰ participating to the campaign. We showed that the campaign was run under generally good weather conditions, interrupted by episodic irruptions of cold air, which made easier measurements of chemical species at ecosystem level, and inspection of their sources. Our measurements of ozone concentrations also showed a regular trend that could be interpreted on the basis of the available climatic information. The sea-land
- ²⁵ breeze circulation system was often activated, transporting precursors and products of photochemical pollution along the Thyrrenian coast of Latium. The levels of ozone advected from the sea were lower than those usually observed in the middle of the





summer season when photochemical smog episodes often occur. The ozone profiles were characterized by a top-flat peak reaching the maximum values late in the afternoon.

Plants were in good physiological conditions during the campaign, and showed
⁵ BVOC emission factors higher than previously reported and not constrained by stress effects. The dune vegetation was dominated by monoterpene emitting species, while isoprene emitters were scarcely represented. Monoterpene emission was already quite high during spring, when the biosynthesis of volatile isoprenoids is believed to be limited by developmental causes both in species that do not store or do store these compounds. It is suggested that during summer, the emission may further increase as temperature rises, except than in water-spending plants such as *Cistus incanus*.

These measurements might be of interest to construct inventories and models of isoprenoid emissions at the ecosystem level, since the Mediterranean ecosystem may escape the generalizations that volatile isoprenoids are dominated by isoprene emissions and are under strong developmental control. Finally, we set the background to upscale measurements from leaf to whole ecosystem level, and to interpret concurrent measurements of BVOC fluxes (Davison et al., 2008) and ozone fluxes (Gerosa et al.,

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Table 1. Physiognomic measurements of plant features and estimation of the plant cover of the dune ecosystem at Castelporziano experimental site, Rome, central Italy. H_{max} and H_{min} indicate the maximal and the mean height of plants, respectively. LAI is the Leaf Area Index. Leaf biomass, and the area covered by each species, in the two different ecosystems ("Garigue" and "Maquis"), is reported as a percentage and as total. Missing data are not available.

Species	H _{max} (cm)	H _{mean} (cm)	LAI (m ² m ⁻²)	Leaf biom. $(kg m^{-2})$	Tota (m ²)	al cover (%) (m ²)	"Garigi (%)	ue" cover (m ²)	"Maqui (%)	s cover"
Arbutus unedo	230	137	2.9	0.17	224.2	21.9	55.5	5.4	168.7	16.5
Rosmarinum officinalis	150	77	2.5	0.13	175.7	17.2	175.7	17.2		
Quercus ilex	300	187	2.9	0.20	149.1	14.6	12.1	1.2	137.0	13.4
Phillyrea angustifolia	220	116	1.3	0.23	144.2	14.1	41.0	4.0	103.2	10.1
Erica multiflora	160	93	1.9	0.18	126.7	12.4	121.9	11.9	4.8	0.5
Cistus incanus	150	68	0.6	0.16	46.9	4.6	46.9	4.6		
Erica arborea	220	212	4.5	0.19	15.7	1.5	15.7	1.5		
Pistacia lentiscus	143	90	2.2	0.29	12.2	1.2	12.2	1.2		
Smilax aspera	150	80	2.4	0.11	10.7	1.0	10.7	1.0		
Daphne gnidium	150	98	0.9	0.09	5.6	0.5	5.6	0.5		
Helicrisum litoreum	40	26	1.5	0.16	4.3	0.4	4.3	0.4		
Juneperus Phoenicea	170	120	3.1	0.27	5.4	0.5	0.9	0.1	4.6	0.4
Oxicedrus macrocarpa	40 32	3.1	0.27	0.9	0.1	0.9	0.1			
Mean	163	103	2.3							

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Table 2. Measurements of isoprenoids emitted by the different plant species of the dune vegetation of the experimental area of Castelporziano, Rome, central Italy. Photosynthesis and stomatal conductance are also reported. Missing values are undetected compounds. All values indicates means (n=4), standard deviations are reported in parenthesis for isoprene, total of monoterpenes, photosynthesis and stomatal conductance.

	Isoprenoids	 Quercus ilex 	 Quercus ilex 	 Cistus spp. 	 Cistus spp. 	 Arbutus 	– Phyllirea	 Rosmarinus 	– Erica	– Juniperus
Isoprene 0.33 (0.54) 0.31 (0.4) 0.05 (0.04) 0.32 (0.02) 0.02 (0.01) 1.48 (0.4) 0.02 (0.01) Tricyclene 0.01 0.02 - - - 0.12 - 0.02 alpha-Thipiene 2.39 3.58 0.18 0.31 0.04 0.23 2.44 0.29 5.54 Camphene 0.09 0.14 0.01 0.02 - 0.01 2.81 0.14 0.88 Gamphene 0.39 0.36 0.36 0.31 0.14 0.32 0.56 0.54 0.37 Sabinene 1.66 2.49 0.14 0.12 0.02 0.09 0.66 0.10	(µg(C) g ⁻¹ DW h ⁻¹)	(adult leaves)	(young leaves)	(control)	(irrigated)	unedo	latifolia	officinalis	multiflora	oxycedrus
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Isoprene	0.33 (0.54)	0.31 (0.4)	0.05 (0.04)	0.38 (0.91)	0.02 (0.02)	0.05 (0.04)	0.02 (0.01)	1.48 (0.4)	0.02 (0.01)
alpha-Thujene0.050.070.12-0.01alpha-Pinene2.393.580.180.310.040.232.440.295.54Camphene0.090.140.010.02-0.012.810.140.086-metil-5 metil Eptane0.390.360.360.310.140.220.560.540.37Sabinene1.662.290.140.120.020.090.060.010.10beta-Pinene1.652.430.120.170.030.114.090.260.19Myrcene0.390.650.030.060.010.060.540.050.58alpha-Phellandrene0.010.01 <t< td=""><td>Tricyclene</td><td>0.01</td><td>0.02</td><td>-</td><td>-</td><td>-</td><td>-</td><td>0.12</td><td>-</td><td>0.02</td></t<>	Tricyclene	0.01	0.02	-	-	-	-	0.12	-	0.02
	alpha-Thujene	0.05	0.07	-	-	-	-	0.12	-	0.01
	alpha-Pinene	2.39	3.58	0.18	0.31	0.04	0.23	2.44	0.29	5.54
6-metil-5 metil Eptane 0.39 0.36 0.36 0.31 0.14 0.12 0.56 0.54 0.37 Sabinene 1.66 2.29 0.14 0.12 0.02 0.09 0.06 0.01 0.10 Myrcene 0.39 0.65 0.03 0.06 0.01 0.06 0.54 0.05 0.58 Japha-Phelladrene 0.01 0.01 0.02 - 0.02 - 0.38 D-3-Carene - 0.01 0.04 - 0.01 0.04 - 0.01 0.04 - 0.01 0.04 - - 0.02 0.04 0.01	Camphene	0.09	0.14	0.01	0.02	-	0.01	2.81	0.14	0.08
Sabinene1.662.290.140.120.020.090.060.010.10beta-Pinene1.652.430.120.170.030.114.090.260.19Myrcene0.390.650.030.060.010.060.540.050.58alpha-Phellandrene0.010.01 $ 0.02$ $ 0.38$ $D-3-Carene -$	6-metil-5 metil Eptane	0.39	0.36	0.36	0.31	0.14	0.32	0.56	0.54	0.37
beta-Pinene 1.65 2.43 0.12 0.17 0.03 0.11 4.09 0.26 0.19 Myrcene 0.39 0.65 0.03 0.06 0.01 0.06 0.54 0.05 0.58 D-3-Carene - - - - - 0.02 - 0.38 D-3-Carene - - - - - - - 0.02 - 0.38 D-3-Carene - - - - - - - - - - - - - - - - 0.01 0.02 - 0.01 0.04 - 0.01 0.04 0.01 0.03 - 1.50 Limone 0.22 0.26 0.09 0.28 0.05 0.09 1.41 0.18 0.19 timosh-Crimene 0.77 0.03 0.04 0.23 0.00 0.03 0.25 0.03 0.02 timash-Ca	Sabinene	1.66	2.29	0.14	0.12	0.02	0.09	0.06	0.01	0.10
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	beta-Pinene	1.65	2.43	0.12	0.17	0.03	0.11	4.09	0.26	0.19
alpha-Phellandrene 0.01 0.01 - - - - 0.02 - 0.38 D-3-Garene - - - - - - - - - - - 0.02 - <td>Myrcene</td> <td>0.39</td> <td>0.65</td> <td>0.03</td> <td>0.06</td> <td>0.01</td> <td>0.06</td> <td>0.54</td> <td>0.05</td> <td>0.58</td>	Myrcene	0.39	0.65	0.03	0.06	0.01	0.06	0.54	0.05	0.58
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	alpha-Phellandrene	0.01	0.01	-	-	-	-	0.02	-	0.38
	D-3-Carene	-	-	-	-	-	-	-	-	-
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	alpha-Terpinolene	0.01	0.02	-	-	-	-	0.04	-	0.01
1,8-Cineol 0.10 0.34 0.01 0.02 - 0.02 4.94 0.58 0.15 beta-Phellandrene 0.09 0.08 0.01 0.04 0.01 0.01 0.03 - 1.50 Limonene 0.22 0.26 0.09 0.28 0.05 0.09 1.41 0.18 0.19 cis-b-Ocimene 1.77 0.03 0.04 0.23 0.00 0.03 0.25 0.03 0.02 garmar-Terpinolene 0.02 0.04 - - - 0.10 0.01 0.01 0.01 Unalobo - 0.01 0.02 0.04 - - 0.04 0.01 0.01 0.01 Unalobo - 0.01 - - - 0.04 0.01 0.01 4-Terpinolene 0.01 - - - 0.47 0.09 0.13 trans-b-Carpophylicene - - - - 0.46	para-Cymene	0.02	0.02	-	0.01	-	0.01	0.07	0.01	0.04
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1,8-Cineol	0.10	0.34	0.01	0.02	-	0.02	4.94	0.58	0.15
$ \begin{array}{ccccccc} Linonene & 0.22 & 0.26 & 0.09 & 0.28 & 0.05 & 0.09 & 1.41 & 0.18 & 0.19 \\ cis-b-Ocimene & 1.77 & 0.03 & 0.04 & 0.23 & 0.00 & 0.03 & 0.25 & 0.03 & 0.02 \\ trans-b-Ocimene & 0.52 & 0.02 & 0.02 & 0.07 & 0.01 & 0.02 & 0.06 & 0.16 & 0.09 \\ garma-Terpinolene & 0.01 & 0.02 & - & 0.01 & - & - & 0.10 & 0.01 & 0.01 \\ Terpinolene & 0.01 & 0.02 & - & 0.01 & - & - & 0.04 & 0.01 & 0.01 \\ Linalool & - & 0.01 & - & - & - & 0.04 & 0.01 & 0.00 \\ 4-Terpineol & - & 0.02 & - & - & - & - & 0.48 & 0.03 & 0.00 \\ a+g-Terpineol & - & 0.02 & - & - & - & - & 0.48 & 0.03 & 0.00 \\ a+g-Terpineol & - & 0.02 & - & - & - & - & 0.48 & 0.03 & 0.00 \\ - & - & 0.02 & - & - & - & - & 0.47 & 0.09 & 0.13 \\ trans-b-Caryophyllene & - & - & - & - & 0.46 & - & - \\ Total of Monoterpenes & 9.39 (4.5) & 10.4 (1.91) & 1.01 (0.7) & 1.66 (1.00) & 0.29 (0.20) & 0.98 (0.30) & 18.89 (5.00) & 2.40 (1.00) & 9.57 (2.50 \\ Photosynthesis & 5.28 (0.75) & 3.2 (0.60) & 10.41 (1.09) & 14.35 (1.25) & 9.22 (0.97) & 5.35 (2.61) & 8.58 (1.00) & 0.48 (0.10) & 6.73 (1.20 \\ (mol m^{-2} s^{-1}) & & & & & & & & & & & & & & & & & & &$	beta-Phellandrene	0.09	0.08	0.01	0.04	0.01	0.01	0.03	-	1.50
	Limonene	0.22	0.26	0.09	0.28	0.05	0.09	1.41	0.18	0.19
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	cis-b-Ocimene	1.77	0.03	0.04	0.23	0.00	0.03	0.25	0.03	0.02
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	trans-b-Ocimene	0.52	0.02	0.02	0.07	0.01	0.02	0.06	0.16	0.09
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	gamma-Terpinolene	0.02	0.04	-	-	-	-	0.10	0.01	0.01
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Terpinolene	0.01	0.02	-	0.01	-	-	0.04	0.01	0.11
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Linalool	-	0.01	-	-	-	-	0.07	0.01	0.00
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	4-Terpineol	-	-	-	-	-	-	0.18	0.03	0.00
trans-b-Caryophyllene - - - - - - 0.46 - - - - - - - 0.46 - - - - - - - - - - 0.46 - - - - - - - - - - - - - - 0.46 - - - - - - - - - - - - - - - 0.46 - - - - - 0.46 - - - - - 0.46 - - - - - 0.46 - - - - - 0.46 - - - - - 0.46 - - - - - 0.46 0.33 0.00 9.57 (2.50 0.29 (0.20) 0.38 (0.30) 18.89 (5.00) 0.48 (0.10)	a+g-Terpineol	-	0.02	-	-	-	-	0.47	0.09	0.13
Total of Monoterpenes 9.39 (4.5) 10.4 (1.91) 1.01 (0.7) 1.66 (1.00) 0.29 (0.20) 0.98 (0.30) 18.89 (5.00) 2.40 (1.00) 9.57 (2.50) Photosynthesis 5.28 (0.75) 3.2 (0.60) 10.41 (1.09) 14.35 (1.25) 9.22 (0.97) 5.35 (2.61) 8.58 (1.00) 0.48 (0.10) 6.73 (1.20) $(\mu mol m^{-2} s^{-1})$ Stomatal conductance 0.03 (0.001) 0.038 (0.01) 0.1245 (0.02) 0.204 (0.04) 0.0994 (0.02) 0.073 (0.05) 0.111 (0.06) 0.012 (0.008) 0.056 (0.0	trans-b-Caryophyllene	-	-	-	-	-	-	0.46	-	-
Photosynthesis 5.28 (0.75) 3.2 (0.60) 10.41 (1.09) 14.35 (1.25) 9.22 (0.97) 5.35 (2.61) 8.58 (1.00) 0.48 (0.10) 6.73 (1.20 (1.20)) (µmolm ⁻² s ⁻¹) Stomatal conductance 0.03 (0.001) 0.038 (0.01) 0.1245 (0.02) 0.204 (0.04) 0.0994 (0.02) 0.073 (0.05) 0.111 (0.06) 0.012 (0.008) 0.056 (0.0	Total of Monoterpenes	9.39 (4.5)	10.4 (1.91)	1.01 (0.7)	1.66 (1.00)	0.29 (0.20)	0.98 (0.30)	18.89 (5.00)	2.40 (1.00)	9.57 (2.50)
Stomatal conductance 0.03 (0.001) 0.038 (0.01) 0.1245 (0.02) 0.204 (0.04) 0.0994 (0.02) 0.073 (0.05) 0.111 (0.06) 0.012 (0.008) 0.056 (0.0 (mol m ⁻² s ⁻¹)	Photosynthesis $(\mu \text{mol m}^{-2} \text{ s}^{-1})$	5.28 (0.75)	3.2 (0.60)	10.41 (1.09)	14.35 (1.25)	9.22 (0.97)	5.35 (2.61)	8.58 (1.00)	0.48 (0.10)	6.73 (1.20)
······································	Stomatal conductance $(mol m^{-2} s^{-1})$	0.03 (0.001)	0.038 (0.01)	0.1245 (0.02)	0.204 (0.04)	0.0994 (0.02)	0.073 (0.05)	0.111 (0.06)	0.012 (0.008)	0.056 (0.02)

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Fig. 1. Overview of the experimental site located in Castelporziano. From the right to the left: the Italian peninsula, the Lazio region including Rome, the Castelporziano estate, the picture of the coastal experimental area. The experimental area used for flux measurements is defined by the circle.

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Fig. 2. Bagnouls Gaussens' diagrams for the years 2005–2007 at Castelporziano Estate. The graphs report the sum of monthly rainfall. Monthly temperatures are shown as daily mean (solid line), daily maximum (dotted pattern) and daily minimum (dashed pattern). The grey zone represents a drought period. The bar in 2007 graph shows our measuring period.







Fig. 3. Mitrakos' diagrams for monthly cold stress (MCS) and monthly drought stress (MDS) in the years 2005 (black bars), 2006 (grey bars), 2007 (dark grey bars) at Castelporziano Estate.

















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Fig. 6. Panel **(A)**: Polar plot showing percentage of wind distribution during night (21:00–06:00, solid line) and day hours (06:00–21:00, dashed line) in Castelporziano Estate, central Italy. Panel **(B)**: Polar plot showing ozone concentration (ppbv) during day (black circles) and night hours (white circles) in the same experimental area.









