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Observations of Diurnal to Weekly Variations of Monoterpene-Dominated Fluxes of Volatile Organic Compounds from Mediterranean Forests: Implications for Regional Modeling

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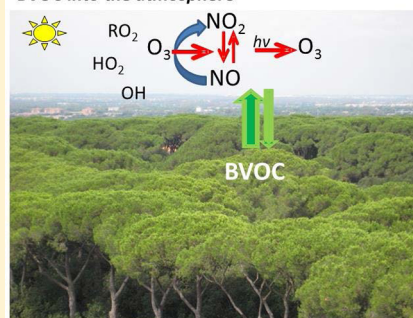
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ABSTRACT: The Estate of Castelporziano (Rome, Italy) hosts many ecosystems representative of Mediterranean vegetation, especially holm oak and pine forests and dune vegetation. In this work, basal emission factors (BEFs) of biogenic volatile organic compounds (BVOCs) obtained by Eddy Covariance in a field campaign using a proton transfer reaction–time-of-flight–mass spectrometer (PTR-TOF-MS) were compared to BEFs reported in previous studies that could not measure fluxes in real-time. Globally, broadleaf forests are dominated by isoprene emissions, but these Mediterranean ecosystems are dominated by strong monoterpene emitters, as shown by the new BEFs. The original and new BEFs were used to parametrize the model of emissions of gases and aerosols from nature (MEGAN v2.1), and model outputs were compared with measured fluxes. Results showed good agreement between modeled and measured fluxes when a model was used to predict radiative transfer and energy balance across the canopy. We then evaluated whether changes in BVOC emissions can affect the chemistry of the atmosphere and climate at a regional level. MEGAN was run together with the land surface model (community land model, CLM v4.0) of the community earth system model (CESM v1.0). Results highlighted that tropospheric ozone concentration and air temperature predicted from the model are sensitive to the magnitude of BVOC emissions, thus demonstrating the importance of adopting the proper BEF values for model parametrization.

Mediterranean forest ecosystems emit reactive BVOC into the atmosphere



INTRODUCTION

Most vascular plants species, especially trees, emit biogenic volatile organic compounds (BVOC). Global estimates of BVOC emissions from plants range from 1 to 1.5 Pg C yr⁻¹. Mediterranean forest trees have been described as high BVOC emitters,^{2–4} with emission depending primarily on light and temperature, and therefore being promoted by the warm Mediterranean climate. In the presence of sufficient sunlight and nitrogen oxides (NO_x), the oxidation of BVOCs can lead to the formation of tropospheric ozone,⁵ a greenhouse gas with detrimental effects on plant health, crop yields, and human health.⁶ BVOCs are also precursors for aerosol formation,⁷ accounting for a significant fraction of secondary organic aerosol (SOA) produced in the atmosphere.⁸

The presidential Estate of Castelporziano covers an area of about 6000 ha located 25 km SW from the center of Rome, Italy (Figure 1) and hosts representative forest ecosystems typical of Mediterranean areas: holm oak forests, pine forests, dune vegetation, mixed oak and pine forests.

Between 1995 and 2011, three intensive field campaigns were carried out on Mediterranean-type ecosystems inside the

Estate. These campaigns were aimed at measuring BVOC emissions and environmental parameters, to improve formulation of basal emission factors (BEFs), that is, standardized emissions at 30 °C and 1000 μmol m⁻²s⁻¹ of photosynthetic active radiation (PAR).¹¹ BEFs are key input parameters of emission models.¹ The first campaign in Castelporziano was a pioneering integrated study on biogenic emissions (1993–1996⁴). BVOC fluxes from different forest ecosystems were mainly investigated using plant- and leaf enclosures connected to adsorption tubes followed by GC–MS analysis in the laboratory. This allowed a first screening of Mediterranean species with respect to their BVOC emission potential, environmental control, and emission algorithms.⁹ In particular, deciduous oak species revealed high isoprene emissions (*Quercus frainetto*, *Quercus petraea*, *Quercus pubescens*), while evergreen oaks emitted monoterpenes only, for example,

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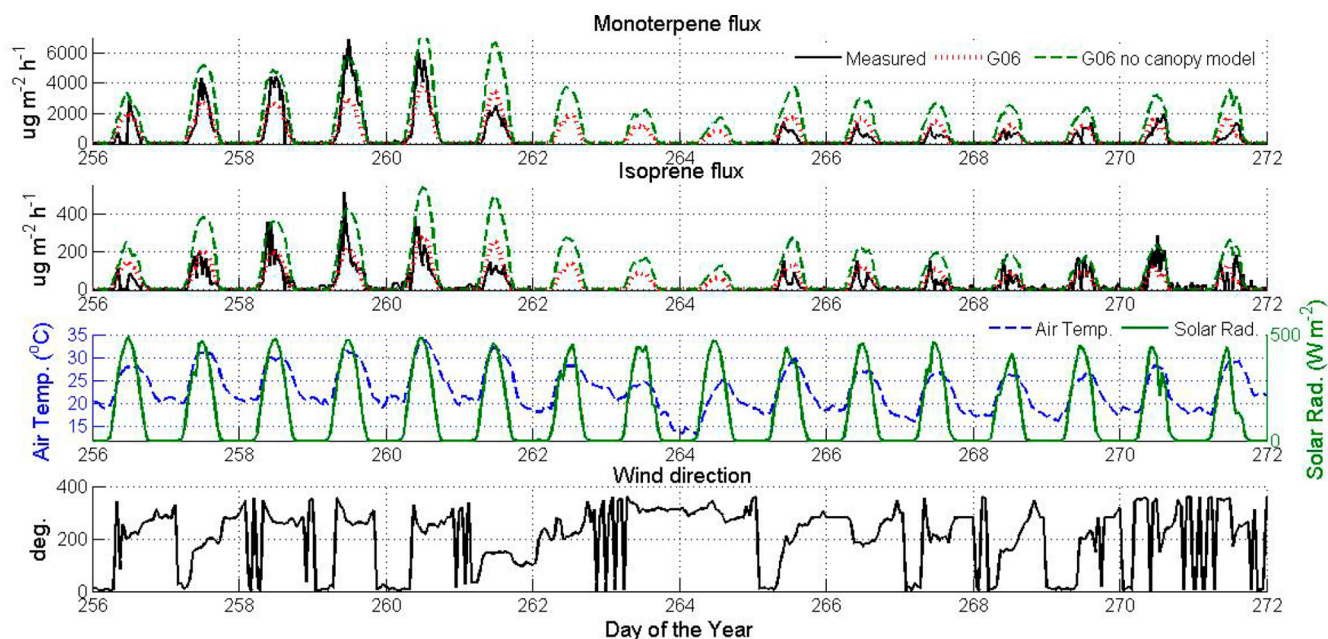


Figure 1. Measured (gap-filled) and modeled BVOC fluxes (with and without the use of a canopy model in the G06 MEGAN 2.1 version) of isoprene and monoterpenes. Air temperature and wind direction are also shown.

Quercus ilex = holm oak. Differences in constitutive emission patterns discovered in Castelporziano supplied basic information to discriminate oak biodiversity in following studies.¹⁰

Ten years later, a second experimental campaign took place in spring and summer 2007 on a dune-shrubland experimental site.^{2,13} In this campaign, the use of a proton transfer reaction mass spectrometer (PTR-MS¹⁴) provided the fast BVOC observations necessary for quasi-real-time flux measurements using Disjunct Eddy Covariance.¹⁵ This allowed for the first time continuous measurements and BEFs calculation at canopy level. Finally, in September 2011 a third campaign was performed with the aim of further characterizing and improving estimates of BVOC fluxes from mixed Mediterranean forests dominated by a mixed holm oak and stone pine forest, using for the first time a proton transfer reaction–time-of-flight–mass spectrometer (PTR-TOF-MS).¹⁶ In contrast to the standard quadrupole PTR-MS, which can only measure one m/z ratio at a discrete time, thus being inadequate to quantify fluxes of more than a handful of compounds simultaneously, PTR-TOF-MS allowed simultaneous measurements (10 Hz) of fluxes of all BVOCs at the canopy level by Eddy Covariance.^{17–20,50}

In this work, we reviewed BEFs from previous campaigns in Castelporziano and calculated new BEFs from the campaign based on PTR-TOF-MS analysis. The new BEFs were used to parametrize the model of emissions of gases and aerosols from nature (MEGAN v2.1¹). The global application of MEGAN generates emission estimates of isoprene, monoterpenes and other reactive BVOCs into the atmosphere. In this study, MEGAN was coupled with CLMv4.0,²¹ a global model used by the coupled Community Earth System Model (CESM v1.0²²), capable of predicting physical and chemical characteristics of the atmosphere at different spatial resolutions^{21,22}

In particular, our goals were to verify (i) whether emission parametrization based on a global average of all tree species, reasonably also applies to Mediterranean forests and (ii) whether changes in BVOC emissions predicted by the model refined by our new data set can produce alterations in the

chemical and physical properties of the lower troposphere in the Mediterranean area.

■ MATERIAL AND METHODS

Field Measurements. Fluxes of BVOCs were measured inside the presidential Estate of Castelporziano, a 6000 ha reserve preserving natural Mediterranean ecosystems located between the city of Rome and the Tyrrhenian Sea coast of central Italy. Site details and BEF calculation methods concerning previous campaigns have been described previously.^{2,4,13} Our recent field campaign was carried out in the mixed oak and pine forest between September and October 2011. The experimental site (41.744N, 12.411E) named “Castello” is primarily dominated by *Pinus pinea* (stone pine), *Quercus ilex* (holm oak), and *Quercus suber* (cork oak).

A PTR-TOF-MS (model 8000, Ionicon Analytik GmbH, Innsbruck, Austria) and an ozone sensor (2-B technology model 205) were housed in a small, air conditioned container, next to a 30 m tall telecommunication tower. Separate inlets for each instrument were mounted on top of the tower a few cm below a 3D sonic anemometer (Young model 81000 VRE). Air was drawn through a 1/4" PFA-Teflon inlet tube to the instruments at flow rates of 18 and 5 SLM to the PTR-TOF-MS and the ozone sensor, respectively. The inlet tube inside the container and the drift tube of the PTR-TOF-MS were heated to 50 °C to avoid condensation. No significant line artifacts of the measured BVOCs have been observed during inlet tube tests of the PFA-Teflon material used for this study.²³ To protect the inlet line and the instruments from dust and particles, a 250 nm Teflon particle filter was mounted in front of the inlet tube.

The PTR-TOF-MS was operated in the H_3O^+ mode, with an E/N in the drift tube of 130 Td (E being the electric field strength and N the gas number density; 1 Td = 10^{-17} V cm²). The inlet tube inside the container and the drift tube were heated to 50 °C to avoid condensation. Integrated mass spectra up to $m/z = 280$ were stored at a frequency of 10 Hz in order

Table 1. Upper Panel: Results from Correlations (R^2 and Slope Calculated from Linear Regression ($p < 0001$)) between Measured Fluxes and Modeled Using MEGAN (G06) Coupled with a Canopy Model (CM) or without the Inclusion of the Canopy Model^a; Lower Panel: Coefficients Used in MEGAN to Calculate Activity Factors^b

	isoprene	monoterpenes	methanol	acetone	acetaldehyde
	R^2 - slope	R^2 - slope	R^2 - slope	R^2 - slope	R^2 - slope
G06 + CM	0.55–0.84	0.70–1.08	0.87–0.43	0.26–0.67	0.70–1.08
G06	0.54–0.41	0.68–0.52	0.43–0.46	0.27–0.33	0.68–0.52
G95 L+T	0.51–0.81	0.61–0.96	0.85–0.45	0.25–0.64	0.61–0.96
G95 T	0.32–0.59	0.34–0.64	0.67–0.33	0.14–0.45	0.63–0.64
coefficients in MEGAN algorithm		standard values	measured	measured	
	CT1	95.0000	95.0000	95.0001	
	CT2	230.0000	230.0000	230.0000	
	d1	0.0040	0.0047	0.0013	
	d2	0.0005	0.0007	0.0002	
	d3	0.0468	0.0472	0.0591	
	d4	2.0340	2.0340	2.0340	
	d5	0.0500	0.0500	0.1418	
	d6	313.0000	313.0000	313.0002	
	d7	0.6000	0.6000	0.5950	
	P0	200.0000	200.0000	200.0000	
	T0	297.0000	297.0000	296.9997	

^aCorrelation with the previous model algorithms (G95) based on light and temperature dependences (L+T) or just temperature dependences (T) are also shown. ^bThe first column shows the standard values used in MEGAN, the following columns show parameters calculated in this study.

to correlate them with the 10 Hz sonic wind data. The data postprocessing procedure, including the method for mass scale calibration, is described in detail by Muller et al.¹⁷

The instrumental background was determined at least twice per day by measuring ambient air purified by a home-built catalytic converter based on a palladium–platinum catalyst heated to 350 °C. Sensitivity measurements were performed several times during the campaign using a gas standard (Apel-Riemer Inc., Denver, CO) including methanol (1.07 ppm), acetone (1.11 ppm), isoprene (1.02 ppm), and α -pinene (0.92 ppm) with an uncertainty of $\pm 5\%$. The gas standard was dynamically diluted with purified ambient air into 1–10 ppb ranges for calibration measurements. Based on these calibrations we estimated an accuracy of the volume mixing ratio determination of the calibrated BVOCs of 11% or better. For compounds that were not included in the gas standard (acetaldehyde, acetic acid, and formic acid) we used the sensitivity factors derived from calibration standards obtained in the laboratory under a similar instrumental set up.

Half-hour fluxes were calculated using the maximum or minimum of the covariance of smoothed BVOC concentration and vertical wind speed in a given lag time window.^{18,24} A three-axis coordinate rotation of the wind data was performed according to Wilczak et al.²⁵ Clear peaks in the covariance function were found for the sum of monoterpenes and the lag times found here were used for identifying fluxes of other compounds with less clear covariance. The lag time varied through the course of the day due to a temperature dependent efficiency of the inlet line pump. In addition, a lag time of 4 s was experimentally determined by spiking acetone in the inlet on top of the tower and recording the signal with the PTR-TOF-MS. All fluxes were visually inspected and only half hour fluxes with a clear maximum or minimum are reported here.

Flux uncertainty was calculated by taking the noise between lag time ranges of –190 to –150 s and 150 and 190 s and multiplying the noise by 1.96 to get a 95% confidence interval for each flux measurement.^{26,27} Quality assurance of the fluxes was performed by removing data that failed the criteria for

turbulence (friction velocity below 0.15 m s⁻¹) or stationarity (when the stationarity test, calculated on 5 min subperiods, for the various BVOC fluxes exceeded 60% as defined by Foken and Wichura²⁸). In total, also including instrument failures, we gap-filled about 60% of the data set, mainly during the night hours. Gap-filled data obtained by interpolation were only used for producing a better graphical representation of daily to weekly dynamics of fluxes, whereas for statistical analysis, correlations were based only on measured data.

Model Algorithm Used in MEGAN. Emission fluxes (F_{BVOC}) are calculated as described in Guenther et al.¹ using algorithms parametrized with environmental parameters (PAR, temperature, and soil moisture) and BEF.

$$F_{\text{BVOC}} = \text{BEF} \cdot \gamma \quad (1)$$

where BEF is an emission factor which represents the emission of a compound into the canopy at standard conditions, γ is an emission activity factor that accounts for emission changes due to deviations from standard conditions. γ was calculated according to eq 2:

$$\gamma = \gamma_{\text{PT}} \cdot \gamma_{\text{age}} \cdot \gamma_{\text{SM}} \cdot \text{LAI} \cdot \text{CE} \quad (2)$$

where γ_{PT} describes the variation due to light and temperature; γ_{age} makes adjustments for effects of the leaf age (1 in our case with mature foliage); γ_{SM} accounts for direct changes due to changes in soil moisture; LAI is the leaf area index (4.77 calculated for this study); CE (=0.57) for the MEGAN canopy environment model is a factor that sets the emission activity to unity at standard conditions. To accurately estimate irradiance and leaf temperatures, we used a multilayer canopy energy balance model,²⁹ based on Goudriaan and van Laar³⁰ and Leuning.³¹

Similarly to Misztal et al.,³² we rearranged in one equation the activity factors γ_{P} and γ_{T} shown in Guenther et al.¹ (eq 3):

Table 2. Main BVOC Measured in the Three PFT at Castelporziano, Italy^a

	PFT1 BEF (ug m ⁻² h ⁻¹)		PFT7 BEF (ug m ⁻² h ⁻¹)		PFT10 BEF (ug m ⁻² h ⁻¹)	
	measured	original	measured	original	measured	original
isoprene		600	612	10000	141.99	4000
total monoterpenes	2082.01	1386	1746.70	936	2008.23	1041
myrcene	55.17	70	66.62	30	115.74	50
sabinene		70	113.25	50	424.39	70
limonene	436.36	100	115.64	80	57.87	100
3-carene		160		30		100
trans-b-ocimene	404.26	70	26.05	120	57.87	150
beta-pinene		300	372.47	130	443.68	150
a-pinene	99.31	500	342.09	400	636.58	300
1,8-cineol	42.13	1.98	336.18	8.55		7.4
b-phellandrene		28.8	10.47	8.55		18.4
g-terpinolene		9.9	8.34	8.55		9.2
terpinolene		12.06	4.08	8.55		11
linalool	867.70	10.8	4.91	20.7		22.2
4-terpineol		0.54	12.19	1.05		1.2
a+g-terpineol	86.27	3.06	33.13	5.1		5.6
camphene		44.64	182.23	27		37.2
cis-b-ocimene		3.96	65.08	6.9	192.90	7.4
cis-linalool oxide	27.08	0.54		1.05		1.2
trans-b-caryophyllene		80	27.95	40		50
methanol		800	91.22	800		800
acetone		240	156.90	240		240
acetaldehyde		200	125.27	200		200
acetic acid		30	347.43	30		30
formic acid		30	14.38	30		30

^aOriginal data used in the global model MEGAN are also shown. The total of measured monoterpenes results higher (<4%) than the sum of individual monoterpene species, since the table only shows those species accounted in MEGAN.

$$\gamma_{PT} = b_3 \cdot \exp[b_2 \cdot (P_{24} - P_0)] \cdot (P_{24})^{0.6} \cdot \frac{[b_1 - b_2 \cdot \ln(P_{240})] \cdot \text{PAR}}{\sqrt{1 + [b_1 - b_2 \cdot \ln(P_{240})]^2 \cdot \text{PAR}^2}} \cdot b_5 \cdot \exp[b_6 \cdot (T_{24} - 297)] \cdot b_5 \cdot \exp[b_6 \cdot (T_{24} - 297)] \cdot \exp[b_6 \cdot (T_{240} - 297)] \cdot \frac{C_{T2} \cdot \exp\left[C_{T1} \cdot \left(\frac{1}{T_{opt}}\right) - \left(\frac{1}{T}\right) \cdot \frac{1}{0.00831}\right]}{C_{T2} - C_{T1} \cdot \left[1 - \exp\left(C_{T2} \cdot \left(\frac{1}{T_{opt}}\right) - \left(\frac{1}{T}\right) \cdot \frac{1}{0.00831}\right)\right]} \quad (3)$$

Where the first equation line represents γ_p , and the second equation line represents γ_T . This allowed solving the equation for unknown constant terms using a Solver function in Excel. The terms are listed in Table 1. For the calculation of the average leaf level PAR of the past 24 h (P_{24}) and past 240 h (P_{240}), and for the average leaf temperature over the past 24 (T_{24}) and 240 (T_{240}) h please refer to the original formulation.¹

CESM Global Model Application. MEGAN is designed for both global and regional emission modeling.¹ The global application of MEGAN generates emission estimates to understand the impacts on atmospheric chemistry when coupled with the CAM-Chem³⁵ in CESM 1.0 release of CLM v4.0, which is a global model capable of predicting physical and chemical characteristics of the atmosphere at different spatial resolutions.^{21,22} In the global application, MEGAN uses 16 plant functional types (PFT, each one with an

associated BEF, calculated through a meta-analysis of studies performed at leaf and canopy level.¹ The environmental inputs (i.e., solar radiation, air temperature) used by MEGAN are those estimated with CESM. Anthropogenic emissions are based on the MACCity inventory,³⁶ with the Asian emissions replaced with the SEAC4RS inventory.³⁷ Fire emissions are estimated using the Fire Inventory from NCAR (FINN) version 1.³⁸

In this study, the model was run at a 2-degree spatial resolution, which included a large portion of central Italy, where Castelporziano is located. The major PFTs used in MEGAN for this region are 1, "Needleleaf Evergreen Temperate Tree"; 7, "Broadleaf Deciduous Temperate Tree"; and 10, "Broadleaf Deciduous Temperate Shrub", which corresponded to a stone pine forest, mixed oak and pine forest, and Mediterranean macchia, respectively. The percent of woodland area coverage by the PFTs 1, 7, 10 in the 2-degree pixel which includes central Italy and Castelporziano were 26%, 14.8%, and 3.5%, respectively, for a total of 44.3%.

BEFs for PFT1 were obtained by reviewing the literature³ in which needle-level emissions of BVOCs using adsorbent cartridges and GC-MS analysis were performed in Castelporziano during the BEMA campaign. Canopy-scale emissions were calculated by multiplying by Leaf Area Index (LAI of 1.9 m² (leaf) m⁻² (ground)) calculated for typical stone pine forests by Ciancio et al.³³

BEFs for PFT7 were based on observations from the 3-week field campaign performed in 2011. Measured fluxes were used in eq 1 and BEFs were obtained by resolving the same equation. The activity factors (γ) were calculated assuming σ and $\gamma_{age} = 1$, and calculating γ_{PT} using solar radiation (W m⁻²)

and air temperature ($^{\circ}\text{C}$) measured at the experimental site. For BEF calculation, we filtered the daytime values of BEF for the central hours of the day (11 AM to 2 PM), and BEFs were obtained by the median of these data. The PTR-TOF-MS allowed measurement of the main compounds reported in Table 2. A vegetation survey (details in³⁴) allowed calculation of the % coverage and biomass allocation of each plant species in the tower footprint, mainly dominated by *Quercus suber*, *Quercus ilex*, *Pinus pinea*. Since PTR-TOF-MS measurements provide the sum of monoterpenes measured at m/z 137.134, we used results from previous analysis of speciated monoterpenes^{2,3} to partition them between the different monoterpene species used in MEGAN (Table 2). For the calculation of γ_{PT} , the canopy model was parametrized with the vegetation parameters calculated for Castelporziano using the vegetation survey.

BEFs for PFT10 were obtained from Davison et al.,¹³ calculated in Castelporziano at canopy level using Eddy Covariance with PTR-MS during the VOCBAS-ACCENT campaign. Also in this case, the total monoterpene fluxes were speciated using detailed analysis on BVOC emissions of the tower footprint reported in Fares et al.² The Guenther model proposed in 1995¹¹ was used for the BEF calculation, which could lead to small changes in BEFs without using a canopy model. However, the PFT10 only represented 3.5% of the plant cover in the 2-degree grid unit under investigation.

Although the model was run globally, comparisons between field observation and model outputs were focused only on the grid unit where Castelporziano is located, approximately covering all of central Italy, including the large conurbation of Rome. In order to compare model output in the grid and the measured data, we scaled the results from the model cell including the experimental site to PFT7. This up-scaling was performed by extracting from the overall contribution the individual contribution from PFT7 in terms of BEFs, weighted for the percentage of occupancy of vegetation type corresponding to PFT7. Three different simulations were run, reproducing different scenarios: the first simulation was run using original BEFs as in the basic parametrization of the global model (Table 2). A second run was performed including the BEFs measured for PFTs 1, 7, 10. The simulation calculated all feedbacks on the physical parameters of the atmosphere induced by changes in the air chemistry due to changes in BVOC emission scenarios. The third run was performed with a 30% increase in the BEF for isoprene with the intent to verify whether isoprene-driven ozone production leads to an increase in air temperature.

RESULTS AND DISCUSSION

Measured BEFs. BEFs from PFT1, which included mainly stone pine, were estimated from data collected at needle levels during the BEMA campaign.³ Upscaling from needles to canopy was performed by multiplying the foliar emission rate by LAI. Stone pine forests in central Italy have negligible understory vegetation, typical “umbrella” canopies and very wide spacing, therefore we consider this simple upscaling procedure acceptable. Isoprene emission was negligible in this PFT, while total emission of monoterpenes was $2082 \mu\text{g m}^{-2} \text{h}^{-1}$, with predominance of linalool, limonene, and trans- β -ocimene (Table 2).

Concerning PFT7, we associated this plant ecosystem to the mixed forest investigated during the 2007 field campaign using the Eddy Covariance technique, which provided measurements at canopy level. Calculation of BEF at canopy level has become

possible thanks to flux measurements by micrometeorological techniques.^{12,15,19} Canopy BEF is preferentially used to parametrize emission models, because it does not require upscaling from leaf to canopy.²⁹ Most trees and shrubs of the mixed Mediterranean forest were shown to be minor isoprene emitters from gas exchange studies at the leaf level.^{2,3} Our measurements confirmed that monoterpenes dominated biogenic emissions (total BEF of $1747 \mu\text{g m}^{-2} \text{h}^{-1}$), while isoprene emission were 1 order of magnitude lower (Figure 1). PTR-TOF-MS operating in H_3O^+ mode detects isoprene at the same m/z as the fragment of methyl-butanol (m/z 69.070),³⁹ a compound emitted from pines in western North America,⁴⁰ whereas methyl-butanol was not found in Mediterranean stone pines.³ Moreover, no significant methyl-butanol signal at the protonated mass m/z 87.081 was found, suggesting no emission of this compound by Mediterranean vegetation. PTR-TOF-MS also allowed calculation of BEF for the main oxygenated BVOC including acetaldehyde, acetone and methanol, with emissions of 125, 157, 91 $\mu\text{g m}^{-2} \text{h}^{-1}$, respectively (Table 2).

PFT10 in our study was associated with the shrubland ecosystem typical of the sand dunes of Mediterranean coasts. Eddy Covariance measurements showed that coastal plant species emitted high levels of BVOC, with fluxes ranging from 370 to 440 $\mu\text{g m}^{-2} \text{h}^{-1}$ for methanol, 180–360 $\mu\text{g m}^{-2} \text{h}^{-1}$ for acetaldehyde, 180–450 $\mu\text{g m}^{-2} \text{h}^{-1}$ for acetone, 71–290 $\mu\text{g m}^{-2} \text{h}^{-1}$ for isoprene, and 240–860 $\mu\text{g m}^{-2} \text{h}^{-1}$ for monoterpenes.¹³ In this study, we only used BEFs for isoprenoids (142 and 2008 $\mu\text{g m}^{-2} \text{h}^{-1}$ for sum of isoprene and monoterpenes, respectively, Table 2), since a clear dependence on light or just temperature was not found for oxygenated BVOC, therefore making it uncertain to calculate BEFs based on light and temperature (hereon called G95 L + T,¹¹) or temperature only algorithm (G95 T).

Canopy Model Performances. Modeled fluxes using MEGAN (hereon called G06) for a mixed oak and pine canopy model were compared with measured fluxes (Figure 1). G06 model was also run without accounting for the canopy model but fluxes were calculated only using the emission algorithms with L+T dependencies, in order to test whether the canopy model can increase accuracy of prediction by comparison with measured fluxes.

Figure 1 shows that G06 better predicts fluxes including the canopy model as compared to G06 without the canopy model application. We observed, however, that modeled fluxes predict well isoprene emissions but underestimate emissions of monoterpenes during the first week of measurements, when temperatures during the day hours were 2–3 $^{\circ}\text{C}$ higher than the following weeks, and slightly overestimate emissions during the remaining mostly cooler weeks (Figure 1). This suggests that even during such a short period of time, BEFs may have changed, in agreement with previous findings in Mediterranean climates, which showed seasonal changes of BEFs in an orange orchard²⁴ and in a holm oak and pine forest.⁴¹ Therefore, we tested the G06 model using two different BEFs (not shown) calculated for warm and cold periods. Results returned a correlation slope with measured fluxes closer to 1 for isoprene and monoterpenes, with R^2 of 0.9 and 0.8, respectively. This suggests that seasonality factors should be taken into account in order to reduce errors in model parametrization, but more long-term studies are necessary to collect observations over periods long enough to extrapolate such BEF. Meteorological conditions may complicate the estimation of BEF when footprints change. This was observed in our campaign when

the wind direction changed from East to South during the central hours of the day (e.g., DOY 261, Figure 1), thus deviating from the prevailing wind direction (driven by East land breeze during the night, and by South sea breeze during the day). Footprint changes, especially in our patchy mixed forest may therefore represent a major contributor to uncertainty.

Results of statistics of the model predictions are reported in Table 1, showing slope coefficients of the correlation analysis between measured fluxes and G06 of 0.84 with canopy model, and 0.41 without canopy model. A third run was performed using the previous G95 model,¹¹ which uses L+T dependencies, and a fourth run was performed using the G95 model and the T algorithm, with a fixed beta value of 0.09. Among the four models, the G06 with canopy model showed the highest correlations and slope coefficient when compared with measured fluxes (Table 1) especially for monoterpenes and isoprene. Statistics for oxygenated BVOCs (methanol, acetaldehyde, and acetone) did not produce high correlation coefficients. However, the slope of the correlation was higher when using the G06 with canopy model for these chemical species as well. The reason for the lower correlation coefficients for oxygenated BVOCs may be due to their low fluxes, with spiky values slightly above or below zero. We cannot exclude however, that the algorithm proposed for isoprenoids does not perfectly predict emission of oxygenated compounds, for which fluxes can also be stress related and have bidirectional behavior.^{2,48–50}

With the intent to verify if activity factors used in MEGAN are properly applied to the ecosystem under investigation, we iteratively calculated the coefficients in eq 3 by comparing the model with observations (Table 1). Only for isoprene and monoterpenes, the newly solved coefficients produced a slightly better correlation, while for the other compounds, given their lower emission rates, no statistical improvement was found. We conclude that the coefficients used in the original parametrization of MEGAN are tenable.

Global model performance. Three months (July–August–September 2011) of BVOC fluxes have been simulated at hourly time resolution using MEGAN v. 2.1, at a spatial resolution of 2-degrees using the online earth system model (CESM) that includes a coupled chemical transport model (CAM-Chem). In order to compare measured and modeled fluxes, we removed the effects from PFT1, PFT10, and other PTFs related to nonwooded areas, in the grid including Castelporziano Estate. BVOC fluxes representing the whole grid was down-scaled to the PFT7-only contribution using the percentage of land cover and the BEF weight in the whole grid. Figure 2 shows hourly averages (DOY 255 to DOY 272) of measured and modeled fluxes of the main BVOCs studied: isoprene, monoterpenes, acetone, and methanol. Without downscaling to PFT7 contribution, fluxes are in some cases overestimated (isoprene and methanol) or underestimated (monoterpenes and acetone) in comparison with measured fluxes. This is because the contribution from the other PFTs may vary depending on individual BEF, and the occupancy of the three PFTs in the area under investigation is only 44%.

The most evident result is that the use of BEF previously adopted for isoprene, produced an overestimation of isoprene flux (above $2000 \mu\text{g m}^{-2} \text{h}^{-1}$), which is about 2 orders of magnitude higher than the measured flux. Castelporziano Estate proved to be a low isoprene emitting forest, as also reported in previous studies highlighting instead that Mediterranean coast

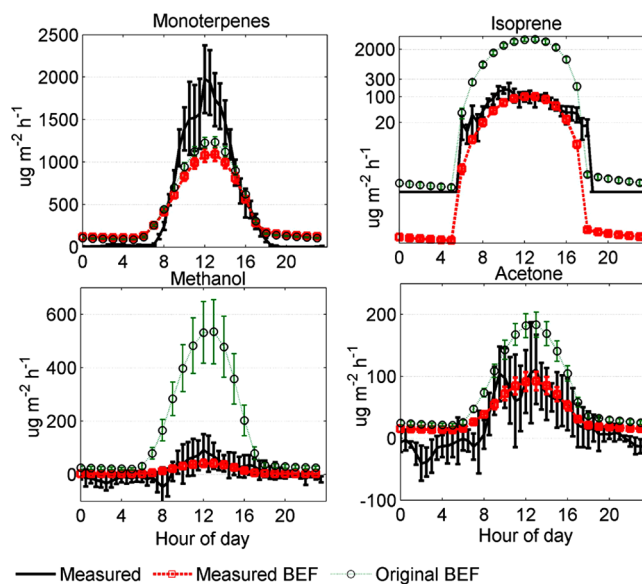


Figure 2. Hourly average (DOY 255 to DOY 280) of measured and gap-filled BVOC fluxes in the mixed Oak Forest of Castelporziano and modeled with new and previously adopted BEF for the sum of monoterpenes, isoprene, methanol, and acetone. Y-axis in the Isoprene box is in logarithmic scale to better visualize the hourly trends in different order of magnitude. Modeled results are proposed for the entire 2-degrees grid spatial resolution, and also scaled to PFT 7.

areas in Italy are dominated by monoterpene emissions.^{2–4} When using the calculated BEF, a good agreement between measured and modeled isoprene fluxes was reached ($R^2 = 0.6$ and slope = 0.85 for PFT7). This finding highlights a strong need to incorporate additional PFTs, with representative BEFs, in the database used for global predictions of BVOC emission, in particular for isoprene.

Consequences for Atmospheric Chemistry. An accurate estimate of isoprene emission is important since isoprene affects the chemical and physical properties of the atmosphere. Past research showed that high loads of isoprene in the atmosphere can trigger photochemical reactions leading to ozone formation,⁵ due to its high ozone-forming potential.^{42,43} Richards et al.⁴⁴ used a chemical transport model (TOMCAT) to predict ozone formation in Mediterranean regions and the model sensitivity was tested under variable emissions of ozone precursors. Results showed that ozone formation in the lower troposphere was highly sensitive to BVOC emission changes, with isoprene representing the major isoprenoid involved in ozone formation.

Ground-level ozone was also measured in Castelporziano, and concentrations were compared with the model output. Predicted levels were often above 15 ppb higher compared with field data (Figure 3). This is not surprising since the CESM model ozone prediction is for a 2-degree grid cell, thus including biogenic and anthropogenic emissions from central Italy, while our measuring station in Castelporziano may not be representative of the average atmospheric chemistry for central Italy. Castelporziano is located downwind of the Rome urban area and is very close to anthropogenic NO_x emission sources, therefore fast reactions between ozone and NO_x may result in local ozone depletion, although NO_x can have a high ozone forming potential at the regional scales as discussed in Richards et al.⁴⁴ In order to compare model results with an additional observation site, we also included in our analysis measured data

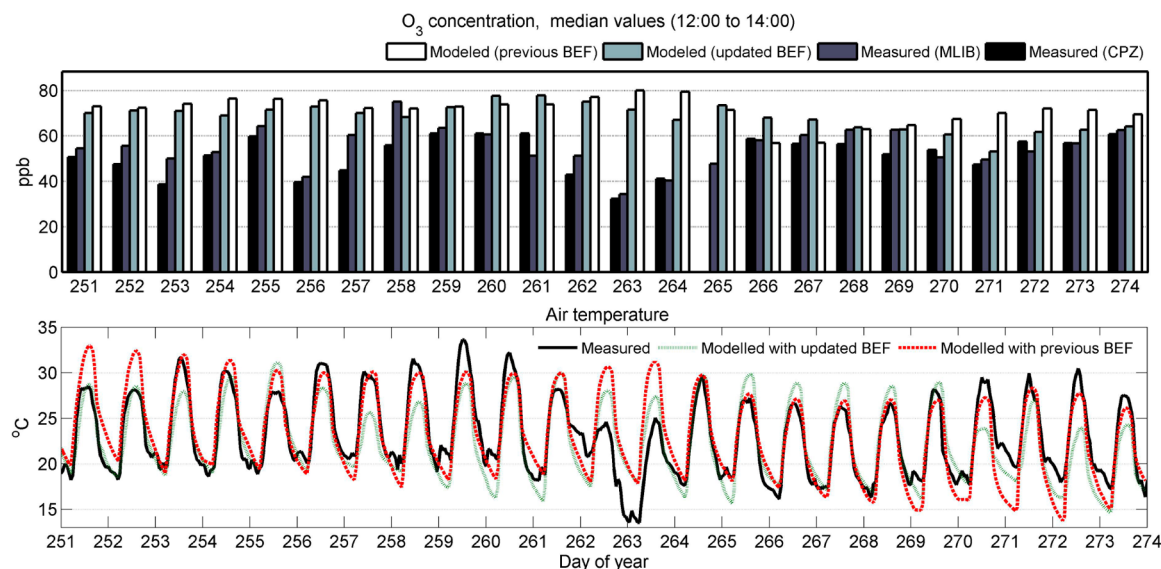


Figure 3. Measured and modeled air temperature, and ozone concentrations (median values in the day hours between 12 PM and 2 PM, standard errors contained in $\pm 5\%$) using previous and newly calculated BEF. Measured ozone concentrations in Montelibretti (MLIB), north of Rome, EMEP experimental site, and Castelporziano (CPZ) are also shown.

from an EMEP (Co-operative program for monitoring and evaluation of the long-range transmission of air pollutants in Europe) station located in Montelibretti, north of Rome. At this location, during the central hours of the day, the most recurrent wind circulation is characterized by cleaner air masses from mountain areas north of Rome (see details in 2). Therefore, differences in ozone concentrations even above 10 ppb, were observed between Castelporziano and Montelibretti (e.g., DOY 252–253), since ozone is more efficiently removed from the lower layer of the troposphere by the reaction with NO in Castelporziano and the air masses reaching the Estate during the day result in partially depletion of this gas. However, the EMEP data are also consistently lower than ozone predicted with CESM, thus confirming that ozone concentrations are very variable in the region. Richards et al.⁴⁴ showed a better agreement between modeled and measured ozone concentrations at the EMEP station. However, their estimate is based on monthly means, and a direct comparison is not possible. During our study, local meteorology (e.g., cloudy days like in DOY 263) could be responsible for larger divergences between modeled and measured ozone concentrations, especially when air temperature decreased and CESM could not predict this meteorological variability. As reported by Gariazzo et al.⁴⁵ who used the FARM model to explain ozone formation in the area of Rome under sea-land breeze regime, conditions of high mid-day ozone concentrations (above 95 ppb) are reached only after a prolonged period of high pressure, as previously observed by Kalabokas et al.⁴⁶ and Gerosa et al.⁴⁷ Our measuring period was characterized by unstable conditions in the transition from dry-hot summer weather to a more humid and moderately cooler autumn weather; therefore the atmospheric conditions were not suitable for large ozone production.

The new BEF parametrization had an impact on air temperature, since CESM considers feedbacks from different emission changes due to changes in radiative forcing of constituents emitted or formed in the atmosphere, like ozone (Figure 3) and organic aerosol. In agreement with our study, Richards et al.⁴⁴ found that decreases in BVOC emissions lead

to a significant radiative effect (-33.3 mW m^{-2}), confirming that BVOC emissions, and isoprene in particular, can be an important temperature driver. In our model simulation, temperature predictions using the original BEF parametrizations showed better agreement with measured temperatures, especially when modeled ozone concentrations using original BEF were consistently higher than ozone concentrations modeled adopting the new parametrization (e.g., DOY 270–272). This may suggest that the model is too sensitive to the radiative effect of BVOC emission. As changes of BVOCs also affect organic aerosols, the latter could also be responsible for the observed feedback on temperature.

In order to test whether the ozone formation responds linearly to temperature changes induced by changes in isoprene emission, we compared temperature and ozone concentrations predicted by the two model runs, first with the measured BEF and successively with BEF in which we deliberately increased isoprene BEF by 30%, leaving unchanged anthropogenic emissions (Figure 4). These model outputs are expressed as a difference with ozone concentrations measured in Castelporziano, and correlations with differences in modeled and observed surface temperatures are also shown. Correlations were similar (slopes = 0.26 and 0.28 for the two model runs, respectively), since an increase in ozone concentration induced by increased isoprene emission is proportional to the increase in air temperature, thus suggesting that ozone increase is proportional to isoprene emission.

Monoterpene fluxes were significantly underestimated by the models ($1000 \mu\text{g m}^{-2} \text{ h}^{-1}$ vs $2000 \mu\text{g m}^{-2} \text{ h}^{-1}$ measured during the central hours of the day, Figure 2). The model might have been unable to catch the complexity of the mixture of monoterpene species occurring in PFT7, or uncertainties in down-scaling cell emissions to individual contribution from PFT7 might have been larger. Moreover, air temperature was predicted to be lower in the model run with the measured BEF. A decrease in the air temperature in the model prediction in response to low isoprene emissions may therefore explain the decrease in monoterpene emissions, given their exponential dependence on temperature.

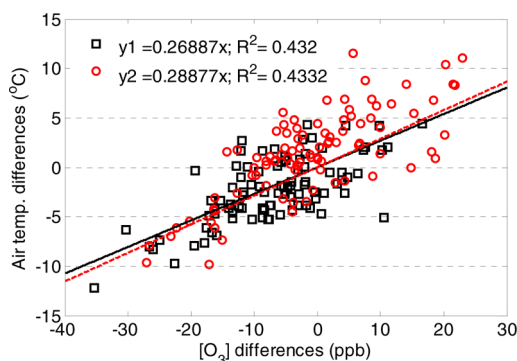


Figure 4. Linear correlation between the ozone and temperature differences. For each variable, the difference is calculated by subtracting the modeled value to the measured one in Castelporziano. Two modeled values were used: the first was obtained using BEF measured in Castelporziano (squares), the second was obtained using BEF measured in Castelporziano, with isoprene increased by 30% (circles).

Methanol and acetone were the other important BVOC fluxes measured in Castelporziano, although the magnitude of these fluxes was lower than the sum of monoterpene flux, and rarely exceeded $150 \mu\text{g m}^{-2} \text{h}^{-1}$. Slopes between measured and modeled fluxes with the original and the new BEF equaled 1.35 and 0.87, respectively. Modeled fluxes with measured BEF fit measured fluxes, whereas previous calculation using original BEF produced a large overestimation of methanol fluxes. Negative fluxes of methanol and acetone in Figure 4 indicate deposition occurring in the night hours. The interpretation of oxygenated BVOC fluxes is complicated, and a compensation point between in-canopy production and atmospheric deposition, with bidirectional fluxes occurring during day and night, is suggested. We cannot exclude however, interferences by isomers of acetone such as propanal, although emission of this compound was shown to be minor (less than 10%) relative to acetone.⁴⁸ The existence of these bidirectional fluxes is a topic that has been addressed only in recent times,^{49,50} and deserves more careful investigation.

We conclude that current algorithms used to predict BVOC emissions perform best when a canopy energy balance model is used. We also found that emission parametrization based on a global average of all tree species reasonably also applies to Mediterranean forests, and that the sensitivity of the model to variations in BVOC emission capacity of plants is high, and that these reactive compounds can play a major role in controlling tropospheric concentration of secondary pollutants like ozone and ultimately modify the chemical and physical properties of the lower troposphere.

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Notes

The authors declare no competing financial interest.

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