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MODELLING OF BIOGENIC VOLATILE ORGANIC COMPOUNDS EMISSIONS OVER ITALY

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Abstract: Biogenic Volatile Organic Compounds (BVOC) emitted from terrestrial vegetation account for about 90 % of the total atmospheric VOC emission and are of great importance for their role in ozone-forming reactions. BVOC are also precursors of secondary organic aerosols (BSOA) that absorb and scatter the atmospheric radiation, affect precipitations by acting as cloud condensation nuclei and affect human health. For these reasons, it is important to develop models able to estimate such emissions accurately. BVOC emissions depend on plant species distributions, emissions potentials and seasonal behaviour. This work presents a high-spatial (~1 km^2) BVOC emission model based on an accurate recognition of plants over the Italian territory together with their measured basal emission potentials. The CORINE Land Cover (CLC) level IV dataset was used to identify the areas covered by agriculture, vegetation and forests. MODIS-based LAI data were used to derive the emissions' seasonality for crops and deciduous trees (growing and the leaf-on seasons). BVOC emissions estimated by the developed model were compared with those provided by MEGAN model evidencing significant differences, particularly for isoprene. Such emissions were then used to fed a Chemical Transport Model (CTM) applied over the Vesuvius area, where different BVOC vertical profiles were measured by tethered balloon soundings. The comparison between observed and predicted BVOC concentrations evidenced the capability of the developed model to estimate the biogenic emissions and highlighted the necessity of an accurate inventory of the plants present in the investigated area.

Key words: *Biogenic VOC emissions, tethered balloon, PTRMS, emission models*

INTRODUCTION

BVOC are organic trace gases (isoprenoids, alkanes, alkenes, carbonyls, alcohols, esters) released in the atmosphere by above- and below-ground plant organs. There are different factors determining BVOC emissions: vegetation type and distribution of plant species covering the land surface (e.g. coniferous, deciduous and broadleaved evergreen trees); photosynthetically active photon flux density (PPFD) reaching the leaf surface; leaf temperature; soil moisture; seasonal phenological variations of plants physiology. Once emitted into the atmosphere, BVOC react with anthropogenic pollutants leading to the formation of tropospheric ozone, other photochemical oxidants and the so-called biogenic secondary organic aerosols (BSOA). The correct estimation of BVOC emissions from the vegetation is therefore relevant to simulate properly the tropospheric pollutants by means of CTMs. This work presents the results obtained by the application of a CTM fed with biogenic emissions estimated respectively by MEGAN model (Guenther *et al.*, 2006) and a plant-specific emission model based on laboratory and field observations and an accurate recognition of plant trees over the Italian territory (Kemper *et al.*, 2014). The simulated ozone and BVOC concentrations were then compared with the observations collected during the QuASAR (Qualità dell'Aria, Studi Ambientali e Ricerca) experimental field campaign (July 14-16, 2015), performed over the Vesuvius area (Naples, Southern Italy) within the AriaSaNa project (http://www.ariasana.org/). The simulations were performed by a modelling system based on the CTM FARM (Silibello *et al.*, 2008) that was applied to the Vesuvius target area considering an horizontal resolution of 1 km (**Figure 1**).

FIELD MEASUREMENTS

A commercial tethered balloon filled with 9 m^3 of helium was used to lift the inlet of a Teflon sampling line connected to a proton-transfer-reaction mass spectrometer with a quadrupole mass analyser (PTRMS) to altitudes up to 100 m above the site of measurements, the Vesuvius Observatory (614 m a.s.l.). An electric winch was employed to raise and lower the balloon. Ambient air was pulled through the inlet at various altitudes at a flow rate of approximately 10 L min^{-1}. Three measurements per day were performed during the campaign (July 14-16, 2015). Real time surveys performed by means of PTRMS allowed estimating different BVOC compounds.

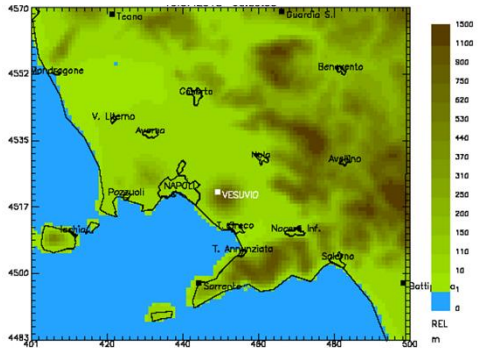


Figure 1. Vesuvius target area.

PLANT-SPECIFIC EMISSION MODEL

The biogenic emission model is based on the CORINE Land Cover (CLC) level IV for the year 2006 and a survey of the main tree species in Italy. The inventory was prepared following the approach described in Pacheco *et al.* (2014), by associating to each CLC subclass the different tree species/vegetation types according to the data collected by the Italian regional forestry departments. The emission model distinguishes between synthesis emission, dependent on both light and temperature (E_{L+T}), and pool emission, dependent on temperature only (E_T). Isoprene and oxygenated volatile organic compounds (OVOC) were treated as pure synthesis emission, monoterpenes included both synthesis (MTS) and pool (MTP) emission; sesquiterpenes (SQT) were treated as pure pool emissions. The following formulas were used to derive the maximum synthesis and pool emission rates:

$$E_{L+T,\max} = BEF_{\max} C_L C_T \quad (1)$$

$$E_{T,\max} = BEF_{\max} \exp\left[-\beta\left(T - T_S\right)\right] \quad (2)$$

where C_L and C_T are activity factors accounting for light and temperature dependencies, β a diffusion term ranging between 0.07 and 0.9 and generally assumed to be 0.09, T=leaf temperature (°K) and T_S=303 °K. We used the algorithms developed by Guenther (1997) for C_L and C_T. Basal emission factors (BEF, µg g $(DW)^{-1}$ h^{-1}) are the key parameters and express the capacity of plants to emit isoprenoids under so called "basal conditions" (air temperature of 30°C and PPFD of 1000 µmol m^{-2} s^{-1}). In this work we used, for the different species, the BEF values measured at different sites across Italy. BEF change through the year; therefore, a phenology correction factor *p* was introduced into the model with values varying between 0 (during months with no emission) and 1 (during months with full emission). **Figure 2** shows monthly curves of the *p* factor for broad-leaved species, based on experimental data collected over Italy. The seasonality correction factor for needle-leaved plants was calculated as follows (Karl *et al.*, 2009):

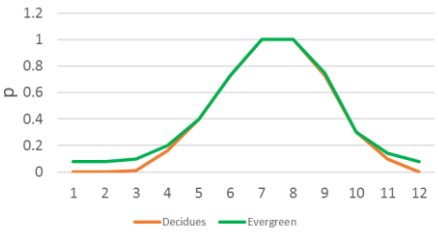


Figure 2. Phenology correction factor *p* applied to broad-leaved species.

$$p = 1 - \rho\left\{1 - \exp\left[-\left(M - M_0\right)^2 / \tau\right]\right\} \quad (3)$$

where *M* is the month of the year (from May to October for deciduous species), M_0 the month with the maximum BEF (=7, Central Europe 40-50°N), τ the period (in months) of growth of the chosen species (=6, Central Europe 40-50°N) and $\rho=(BEF_{max}-BEF_{min})/BEF_{max}$. For deciduous needle-leaved plants $BEF_{min}=0$ and consequently $p=exp[-(M-M_0)^2/\tau$. Once the phenology correction factor *p* was computed the seasonality of emissions was derived from the leaf coverage per unit ground area, expressed by the leaf area index (LAI). MODIS LAI data, with 1 km horizontal resolution, were used to provide information regarding the evolution and structure of seasonal vegetation characteristics. Since the MODIS LAI in each grid cell is the sum of the LAI contributions from each vegetation type in that cell, the LAI associated to the vegetation phenology type *k* is given by:

$$LAI_{i,j,k} = f_{i,j,k}\, p_k LAI_{i,j}^{MODIS} / \sum_{k=1}^{N} f_{i,j,k}\, p_k \qquad (4)$$

where p_k and $f_{i,j,k}$ are the phenology correction factor and area fraction of the vegetation type k respectively in the cell (i,j) (Karl *et al.*, 2009). The seasonality of emissions from each vegetation type was considered by using the seasonality factor C_s together with the specific vegetation type LAI_k as follows:

$$C_{s,k} = 0.49 LAI_k / \sqrt{1 + 0.2 LAI_k^2} \qquad (5)$$

According to Lenz *et al.* (2002) the different emissive characteristics of the leaves under direct sunlight or shaded were accounted for by introducing a correction factor R_c based on data obtained by Lenz e*t al.* (1997) at Casteporziano site, central Italy. For pool emissions, we adopted a value of R_c equal to 0.68 based on Mediterranean pines, while for synthesis emissions we used the algorithm derived from deciduous plants data. The algorithm assumes that 50% of the biomass has an emission rate equal to BEF_{max} (contribution of the illuminated area) plus a value equal to a 25% of the remaining BEF_{max}, corresponding to the contribution of the shaded part, leading to R_c value of 0.625. Finally, we included the emissions from dead biomass accumulated on the soil that were predicted by "T" algorithm, since it is decoupled from above-ground photosynthetic process and continues also after leaf shading. To include this contribution, we considered an additional contribution to canopy emissions equal to 10% (unpublished results from BEMA campaign) of BEF for species whose emissions depended only on temperature and equal to 0 in the other case. The real emission rates (E_{real}) [µg m^{-2} h^{-1}] can be expressed through the following equation:

$$E_{real} = E_{max} \cdot C_S \cdot R_c \cdot (1 + C_E) \cdot D_B \qquad (6)$$

where C_S, R_c and C_E are the correction factors that consider the seasonal distribution of the emissions, the "canopy effect" and the contribution of the litter, and D_B is the amount of foliar biomass density for unit ground area (g (DW leaves) m^{-2}(ground)).

SIMULATIONS RESULTS

Figure 3 shows the comparison between averaged isoprene and monoterpenes emissions rates [µg m^{-2} s^{-1}] during the period July 14-16, 2015 estimated by the plant emission model and MEGAN.

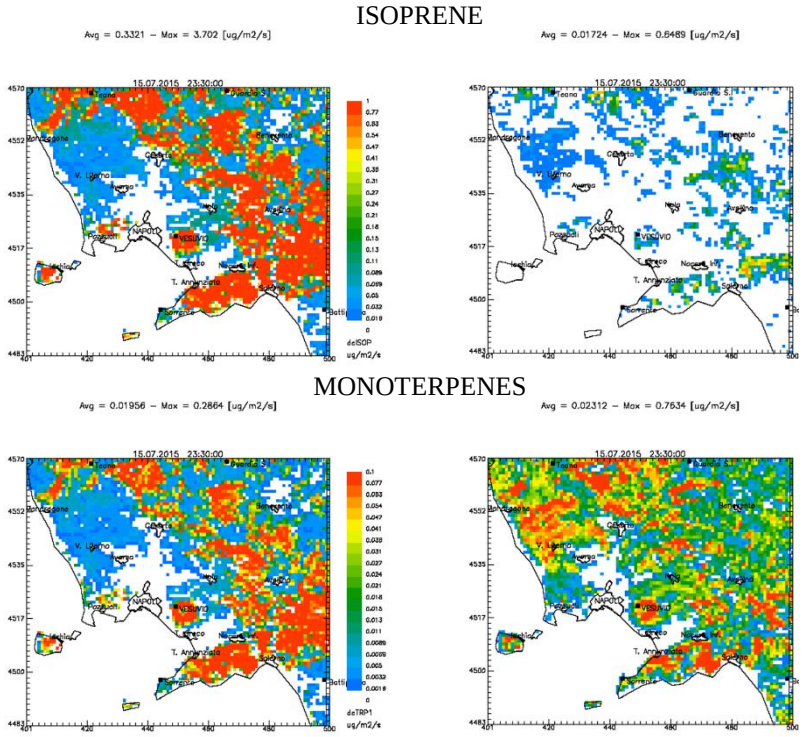


Figure 3. Comparison between averaged biogenic isoprene and monoterpenes emissions rates [µg m^{-2} s^{-1}] using MEGAN (left) and the developed model (right).

Significant differences on both the spatial distribution and the intensity of BVOC emissions are clearly visible in the figure, thus highlighting the relevance of using the spatial distribution of different trees species instead of Plant Functional Types (MEGAN). The availability of BVOC vertical profiles collected during the QuASAR experimental field campaign (July 14-16, 2015) permits to compare the observed levels with those computed by FARM using the biogenic emissions estimated by the two models and, consequently, to evaluate their performances. In the following **Figure 4** is presented, for some BVOCs, the comparison between observed and predicted vertical profiles during the second day of the experimental campaign. The analysis of the figure evidence: a significant overestimation of isoprene using the emissions provided by MEGAN, similar predicted monoterpenes levels (with higher levels using MEGAN), a better agreement between observed and predicted biogenic secondary organic compounds (MVK and methacrolein) using the emissions provided by the plant emission model and an underestimation of methanol observed levels.

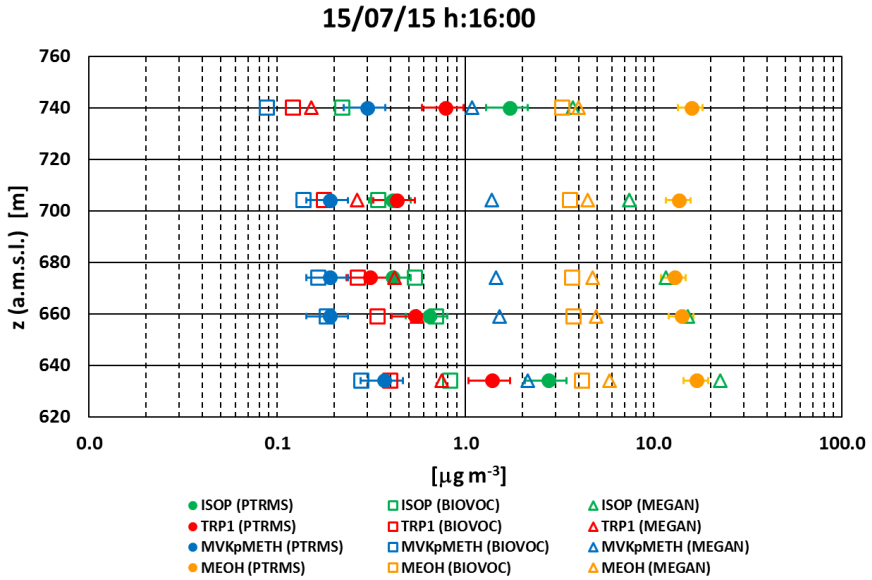


Figure 4. Observed (PTRMS) and predicted isoprene (ISOP), monoterpenes (TRP1), methanol (MEOH) and the sum of MVK and methacrolein (MVKpMETH) vertical profiles using the plant emission model (BIOVOC) and MEGAN.

Since it was expected that differences in the vegetation inventories would lead to differences in the estimated BVOC emissions and consequently in their predicted levels, a further simulation was performed using data from the "Tree species maps for European forests" (http://www.efi.int). As an example, the spatial distribution of *Quercus petraea* and *Quercus robur*, recognized as the main tree species in Italy, from the CLC database and from the "Tree species maps for European forests" are presented in the **Figure 5**, evidencing differences in the coverage of these species.

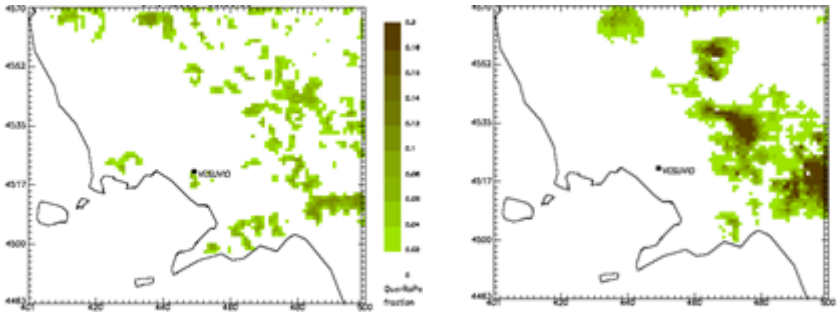
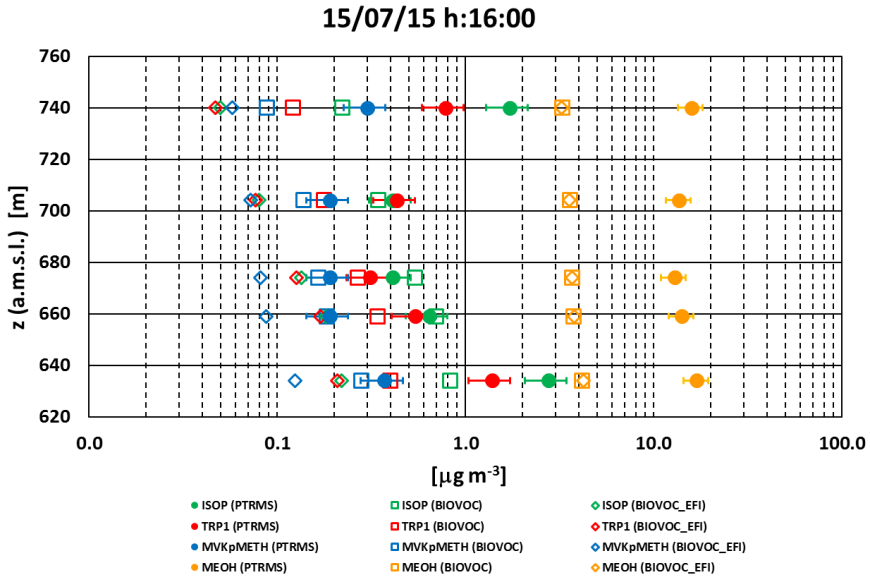


Figure 5. Fraction covered by *Quercus petraea* and *Quercus robur* from the elaboration of CLC database (left) and from the "Tree species maps for European forests" (right).

The comparison between observed and predicted BVOCs vertical profiles using the plant emission model fed with the two vegetation inventories is presented in **Figure 6** that evidences a better agreement using the vegetation inventory obtained from the CLC dataset. The results obtained in this work confirmed the importance of using detailed vegetation inventories and, if available, measured basal emission factors.



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