# Estimating the biogenic non-methane hydrocarbon emissions over Attica.

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**Abstract**

Biogenic emissions affect the urban air quality as they are ozone and SOA precursors and should be taken into account when applying photochemical pollution models. The present study presents an estimation of the magnitude of Non-Methane Volatile Organic Compounds emissions (NMVOCs) emitted by vegetation over Attica. The methodology is based on computation performed with the aid of a Geographic Information System (GIS) and theoretical equations in order to develop anemission inventory on a 6x6km$^2$ spatial resolution and in a temporal resolution of 1hr covering the Greater Athens Area for one year period. For this purpose, a variety of input data was used: improved satellite land-use data, land-use specific emission potentials, foliar biomass densities, temperature and solar radiation data. Hourly, daily and annual isoprene, monoterpenes and other volatile organic compounds (OVOCs) were estimated. Results delineate an annual cycle with increasing values from March to April, while maximum emissions were observed from July to August, followed by a decrease from October to December.

**Keywords:** Biogenic emissions, Athens, Geographic Information System (GIS).

## 1. Introduction

A vast variety and significant quantities of NMVOCs are produced and emitted into the atmosphere by vegetation (Seinfeld and Pandis, 1998). As a matter of fact, globally, biogenic sources of volatile organic compounds are estimated to exceed those from anthropogenic sources by a factor of ten to one (Hough and Johnson, 1991). A great number of VOCs are emitted from vegetation with isoprene ($C_5H_8$) and monoterpenes ($C_{10}H_x$) being the most abundant species (Singh and Zimmerman, 1992). The calculation of their fluxes is an important input in air quality models, since they are highly reactive in the troposphere (Atkinson, 1990) by affecting regional photochemical processes. They react with the hydroxyl radical, ozone and the nitrate radical, resulting in the formation of carbon monoxide and organic species (including secondary aerosols) that can enhance concentrations of ozone and other oxidants in environments rich in nitrogen oxides (Naik etal., 2004). On a global cycle, Biogenic Volatile Organic Compounds (BVOCs) contribute to the global carbon cycle and have a key role in the global climate (Guenther *et al*., 1995). Furthermore, most of them are oxidised to carbon dioxide ($CO_2$) into the atmosphere and determine the growth rate of atmospheric methane concentrations (Guenther *et al.*, 1995). Presently in Greece there does not exist such a database even though it is known that biogenics emissions play a significant part in the formation of photochemical pollution especially during the warm season. Moreover, this region, like other Mediterranean areas, has a complex vegetal biodiversity which is quite different from the usual northern latitude or US vegetation, (2) it receives high fluxes of solar radiation in the summertime and is dominated by high temperatures, (3) ozone exceedances are often very pronounced. The present work aims to develop a computational system for estimating BVOCs emissions based on GIS technology over Attica, an area that includes the GAA. It covers the year 2016 and has the possibility to be regularly updated to include more years.

## 2. Methodology

### *2.1 Mathematical Model*

In the present study, the mathematical model for estimating isoprene, monoterpenes and OVOCs emissions in Attica was incorporated into the GIS. The mathematical model that had been used for all types of vegetation, describing the emissions flux on an hourly basis is that of Guenther *et al*. (1996):

$$Flux\,(\mu g\, m^{-2}\, yr^{-1}) = \int (\varepsilon.\, D.\, \gamma.\, dt) \qquad (1)$$

where ε is the average emission potential ($\mu g\, g^{-1} h^{-1}$) for any particular species, D is the foliar biomass density ($g\, dry\, weight\;\; foliage\, m^{-2}$) and γ is a unit less environmental correction factor representing the effects of short- term (hourly) temperature and solar radiation changes on emissions. For the estimation of isoprene emissions, Guenther *et al*. (1991, 1993) showed that, to a very good approximation, the short-term (hourly) variations in emissions could be described by the product of light-dependant factor, $C_L$, and a temperature dependant factor $C_T$ .Thus, the so called ISOG algorithm (EMEP/ EEA, 2016):

$$\gamma_{iso} = C_L . C_T \quad (2)$$

The light factor, $C_L$ is given by:

$$C_{(L_{iso})} = \frac{(a.C_{L1}.L)}{\sqrt{1+a^2 L^2}} \quad (3)$$

where a=0.0027 and $C_{L1} = 1.066$ are empirical constants, and L is the PAR flux $(\mu mol\ photons (400-700\, nm) m^{-2} s^{-1})$ .

Temperature dependance $C_{(T_{iso})}$ is described by:

$$C_{(T_{iso})} = \frac{[\exp(C_{T1}(T-T_s)/RT_sT)]}{[1+\exp(C_{T2}(T-T_M)/RT_sT)]} \quad (4)$$

where R is the gas constant (= 8.314 $J\,K^{-1} mol^{-1}$), and $C_{T1}$ (=95000 $J\,mol^{-1}$), $C_{T2}$ (=230000 $J\,mol^{-1}$), and $T_M$ (=314 K) are empirical coefficients based upon measurements of three plant species: eucalyptus, aspen, and velvet bean, but which seem to be valid for a variety of different plant species (Guenther *et al*., 1993, Guenther, 1997) and $T_s$ (=303 K) is the standard temperature.

For the estimation of monoterpenes emissions, the environmental correction factor from most plants are parameterised using the following equation (Guenther *et al*., 1993):

$$\gamma_{mts} = \exp(\beta.(T-T_s)) \quad (5)$$

where β (= $0.09K^{-1}$) is an empirical coefficient based on non-linear regression analysis of numerous measurements present in the literature. This algorithm is referred as MTS (EMEP/ EEA, 2016). Since the environmental conditions controlling emissions of OVOCs are not entirely understood than isoprene and monoterpenes and given the lack of other information, OVOCs emissions are considered temperature dependent and the use of equation (5) is recommended for the estimation of their emissions (Guenther *et al*., 1994):

$$\gamma_{OVOC} = \gamma_{mts} \quad (6)$$

*2.2 Computational Model*

In order to produce the NMVOCs emission inventory on a 6x6 $km^2$ spatial and a 1hr temporal resolution covering one year, the GIS software (ArcView v10) was used in order to combine a variety of input data: improved satellite land-use data, land-use specific emission potentials, foliar biomass densities, temperature and solar radiation data. Initially, the area under study was Attica. For the calculation of the hourly biogenic emissions, detailed meteorological data for the time period of a whole year (2016) were used. After calculating the hourly emission fluxes, daily and monthly emission values were also estimated. The land use/ land cover (LULC) data used in the present study was provided by the United States Geological Survey (USGS) Global LULC version 2.0 Database derived from the 1 km Advanced Very High Resolution Radiometer (AVHRR) data spanning April 1992- March 1993. The USGS classification system includes 24 land cover categories, only 10 of which are found in the area under study (Fig.1). The different land use classes emitting BVOC are characterised by one ecosystem type or a combination of two of them. The area was divided into cells using a spatial resolution of 6x6 $km^2$ with Lambert Conic Conformal projection. Each cell was checked separately and correction of the LULC category was made if necessary. During the inventory process the methodology used was that of USGS Geological Survey Professional Paper 964. According to this paper, the land use category adapted to each cell when multiple uses of land were recognized was the one that had the most coverage. The only exception was the urban and built-up category which took advantage over others (Fameli *et al*., 2013). The National Observatory of Athens (www.meteo.gr) provided hourly temperature values recorded from 33 meteorological stations for 2016. A typical temperature diurnal variation was reproduced by calculating the average hourly temperature values from all the recorded values of each month of the year. This process was repeated for every station among the area under study. Hourly temperature maps were constructed using the technique of the inverse distance interpolation (IDW), increasing the spatial resolution of the data and providing a continuous temperature field covering the area under study.

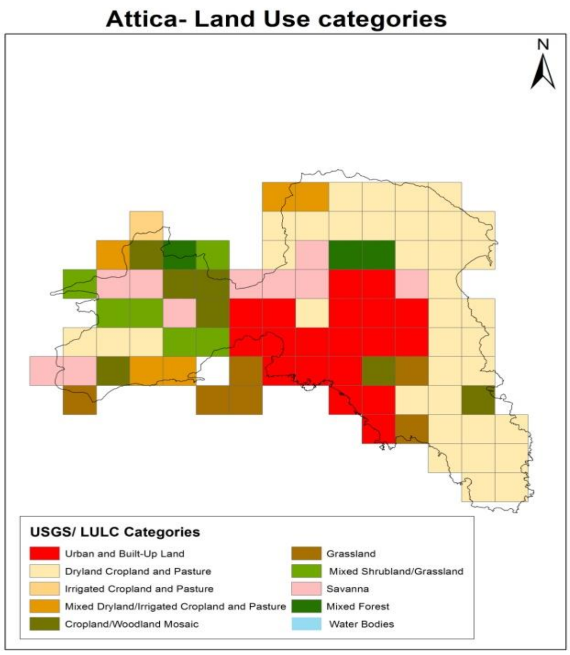


**Fig. 1.** Attica with the land use categories attributed at each cell.

In order to estimate the solar radiation data, a new research project for the development of SOLar Energy Applications (SOLEA, www.solea.gr) was used (Taylor *et al*., 2015). SOLEA is based on solar irradiance spectra produced via a synergy of neural networks and radiative transfer simulations. The Photosynthetically Active Radiation (PAR) was calculated for every month of 2016 having $0.05^0$ latitude by $0.05^0$ longitude spatial resolution and 1hr temporal resolution. The use of land-use specific emission potentials is essential for the estimation of isoprene, monoterpenes and OVOCs and foliar biomass densities for every month covering the whole year. The main references used for the selection of these values were from the recent study of Steinbrecher *et al*. (2009) under the NatAir program (Impoving and Applying Methods for the Calculation of Natural and Biogenic Emissions and Assessment of Impacts on Air Quality) for the region of Europe and the neighboring ones. According to this study, foliar biomass densities and emission potentials are assigned to commonly observed European vegetation species. When a land-use class was characterised by a combination of different vegetation species, it was assumed that the monthly average foliar biomass density is use class and n is the number of vegetation types within the land use class (Symeonidis *et al*., 2007).

## 3. Results and Discussion

Isoprene, monoterpenes and OVOCs emissions over Attica were estimated using a GIS system for the year of 2016. The temperature and light dependency of the biogenic emissions determine their magnitude. This leads to an increase of BVOC emissions during the daytime, with observed maximum values in the midday as well as during summer. For that reason, a winter month (January) and a summer month (June) were chosen to be presented in the present study. More precisely, isoprene emissions during winter do not exceed 0.453 kg $km^{-2}$ $day^{-1}$ (Fig. 2). As we can observe, this maximum value comes from mixed forest because of their high emission potential and foliar biomass density that characterizes this land use category. During summer, the maximum value appearing at the same land use category, reaches 26.7kgk$m^{-2}$ $day^{-1}$ (Fig. 3). The monoterpenes emissions over Attica are higher during January than the isoprenes ones, with a maximum value of 2.66 kgk$m^{-2}$da$y^{-1}$ (Fig. 4) above mixed forests. The maximum monoterpenes emissions in June are about 25.9 kg $km^{-2}$ $d^{-1}$ (Fig. 5). Regarding the OVOCs emission rates estimated, during January, the maximum value observed is about 1.53 kg $km^{-2}$ $d^{-1}$ and during June is about 25.9 kg $km^{-2}$ $d^{-1}$ (not shown here). Briefly, the total monthly biogenic emissions are estimated to be 79,229 kg (50% OVOCs, 45% monoterpenes and 5% isoprenes) for January and 732706 kg (60% monoterpenes, 38% isoprene and 2% OVOCs) for June. The results delineate an annual cycle, with minimum values during winter and maximum during summer.

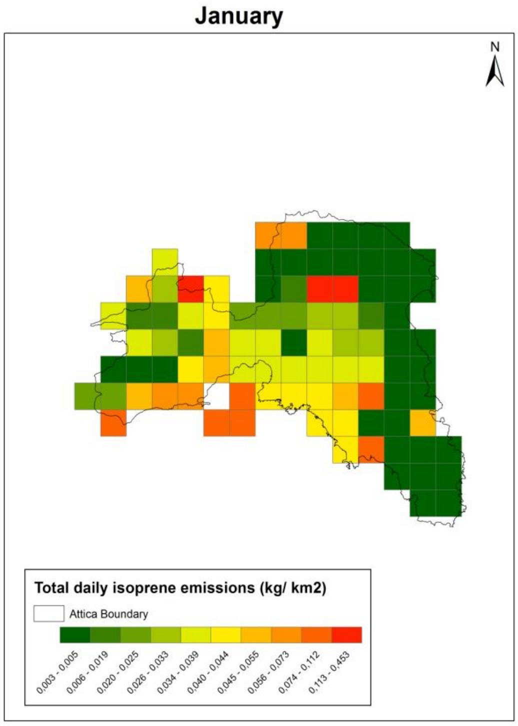


**Figure 2.** Total daily isoprene emissions over Attica in January.

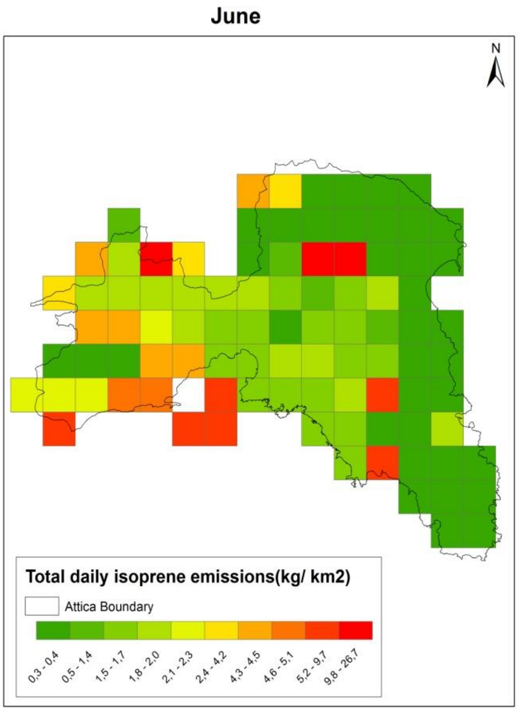


**Figure 3.** Total daily isoprene emissions over Attica in June.

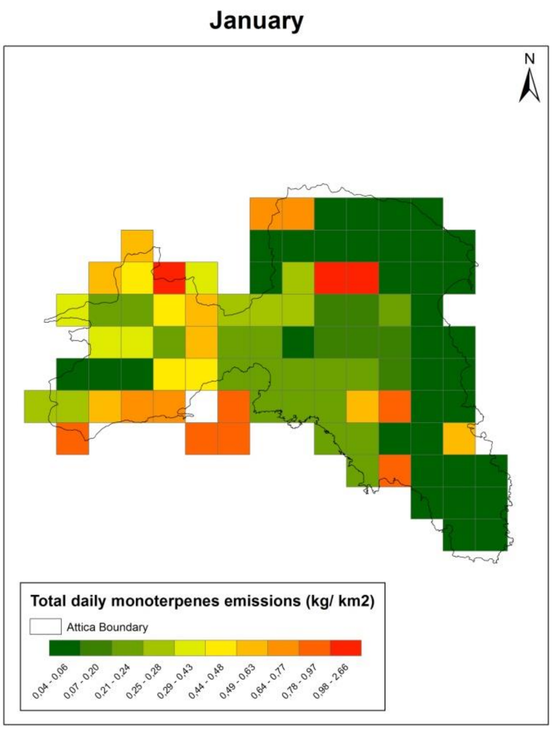


**Figure 4.** Spatial distribution of total daily monoterpenes Emissions in January.

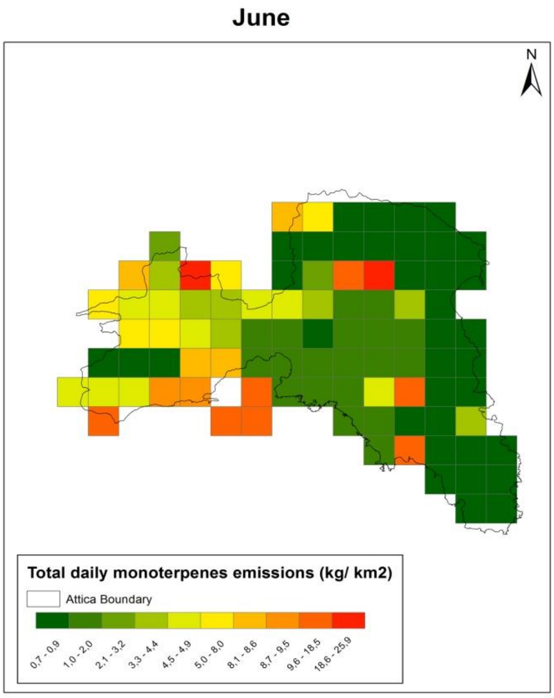


**Figure 5.** Spatial distribution of total daily monoterpenes Emissions in June.

## 4. Concluding remarks

The effort to develop the Greece and Attica biogenics emissions database has been presented. Preliminary results indicate that within Attica, the areas producing the highest quantities of isoprene and monoterpene are located at the western part. Moreover, higher quanitites are emitted during the intense solar radiation period. Further work envisaged includes expansion of the database to cover Greece on a 6x6km$^2$ resolution and Attica on a 2x2km$^2$ equal to the mean value of the foliar biomass densities of all vegetation types within the land use class (Symeonidis *et al*.,2007). In order to describe the seasonal variation of the foliar biomass densities, it was necessary to use correction factors which vary between the different vegetation species. The references used for the selection of the corrective factors were from the study of Simeonidis *et al*. (2009). Finally, the specific emission potentials for the land use classes that are a combination of different vegetation types were calculated using the formula:

$$\varepsilon = \frac{\sum_{i=1}^{i=n} (\varepsilon_i D_i / n)}{\sum_{i=1}^{i=n} (D_i / n)} \qquad (8)$$

where $\varepsilon_i$ and $D_i$ are the emission potentials and the foliar biomass densities of each vegetation type within the land

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