Estimation of biogenic emissions of non-methane volatile organic compounds from Catalonia

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Abstract

The magnitude, and the superficial and temporal distribution of non-methane volatile organic compounds (NMVOC) emitted by vegetation in Catalonia for the year 2000 have been estimated, as a first step to using a chemical transport model (CTM). Vegetation represents an important source of isoprene, monoterpenes and other volatile organic compounds (OVOC) whose interactions and reactions in lower troposphere are important constituents involved in photochemical pollution episodes.

This estimation was developed using a high-resolution land-use map (squared cells of 1 km²) that differentiates twenty-two categories. Air temperature and solar radiation for the year 2000 were collected from different meteorological surface stations. We have used a standard biogenic emissions mathematical model built into a geographic information system (GIS) software. In comparison with other estimations made before, this uses new information, mainly related to some recent emission factors for typical Mediterranean species; and better knowledge of the composition of Catalonia’s forest cover; implying therefore a qualitative uncertainty improvement. Results indicate an annual cycle with increasing values in March - April and the highest emissions in July - August followed by a decrease in October – November. Annual biogenic NMVOC emission reaches 55.7 kt, being monoterpenes the most abundant (29.2 kt), followed by OVOC (16.0 kt) and isoprene (10.2 kt), which represent 53, 29 and 18 percent of total emissions, respectively.
1 Introduction

Vegetation is an important source of biogenic non-methane volatile organic compounds (NMVOC). Interactions and reactions of these compounds in the lower troposphere are important elements for photochemical pollution episodes. Also, their annual emission estimation is useful and necessary for comparison with NMVOC emitted by other sources, such as traffic and industrial activities, like basic information to manage air quality and other environmental issues.

In Catalonia (Spain), located in the NE of Iberian peninsula, more than 1260 cases of exceedances in the legislative hourly ozone concentration threshold for people information (180 µg m\(^{-3}\)) were recorded in the period 1991 - 2000, and almost 80% of these happened into the period June – August.

Like other Mediterranean areas, this region has a complex vegetal biodiversity; and in summer time it receives high fluxes of solar radiation. Under these conditions, NO\(_x\) and NMVOC emissions exacerbate ozone formation.

This kind of pollution can be understood by mathematical modelling. As a previous step to using a chemical transport model (CTM), it is necessary to know the magnitude, superficial and temporal distribution of NMVOC emitted by vegetation. For this purpose one specific ozone pollution episode presented on August 15th 2000 was selected, when the highest annual concentration in the Alt Camp region (273 µg m\(^{-3}\)) was measured.

The most recent approach relating to the estimation of biogenic NMVOC emissions from Catalonia was presented by Gómez and Baldasano (1999), who worked with a land-use map for the year 1992, using climatological hourly data for air temperature and solar radiation; and emission factors established for each land-use category, such as the average of the emission factors of the vegetal species associated for each of these land-use categories. The association of vegetal species was established by literature information.

In recent years, the quality of this base information has improved mainly in two aspects:

- Availability of quantitative information of forest composition
- Availability of new local emission factors for some of vegetal species

This new information and meteorological data for the year 2000, enable a good base for hourly estimation of biogenic NMVOC emission required for modelling the pollution episode formerly mentioned.

2 Methodology

2.1 Mathematical model

We have used the model of Guenther et al. (1993) for the estimation of hourly, daily, monthly and annual biogenic NMVOC emissions, grouping them in three categories attending to their typical lifetime: isoprene (1-2 h lifetime), monoterpenes (0.5–3 h) and other biogenic volatile organic compounds (OBVOC)(reactives < 1 day, other > 1 day)
Emission factors are expressed for the standard conditions:

- Isoprene: air temperature = 30 °C, photosynthetically active radiation (PAR) 1 000 μmol m⁻² s⁻¹
- Monoterpenes and OBVOC: air temperature = 30 °C

Also, before the model description, the following general variables of space \( k \) and time \( t \), are defined:

- \( k \): space unit (definition of the grid size, 1 km²)
- \( t \): time unit

### 2.1.1 Isoprene

Hourly isoprene emissions were estimated using the equation (1):

\[
E_{\text{iso}}(k, t) = E_{\text{iso}}(k, \text{hourly}) = \frac{\text{EF}_{j}^{\text{iso}} \cdot \text{ECF}(T, P) \cdot \text{BF}_{j} \cdot \text{Area}_{k}}{1000}
\]  

(1)

**Parameters:**

- \( j \): land-use category (1, 2, ......., 22)

**Terms:**

- \( E_{\text{iso}}(k, \text{hourly}) \): hourly isoprene emission from the \( k \)th cell (kg h⁻¹)

**Data:**

- \( \text{EF}_{j}^{\text{iso}} \): standard emission factor associated to the \( j \) land-use category (μg g⁻¹ h⁻¹)
- \( \text{ECF}(T, P) \): environmental correction factor. It is established for hourly average air temperature and PAR (unit less)
- \( \text{BF}_{j} \): biomass factor assigned to the \( j \) land-use category (g m⁻²)
- \( \text{Area}_{k} \): area of each grid cell (1 km²)

The environmental correction factor is calculated using the equation (2):

\[
\text{ECF}(T, P) = C_{\text{T}} \cdot C_{\text{p}}
\]

(2)

where,

- \( C_{\text{T}} \): correction factor by air temperature
- \( C_{\text{p}} \): correction factor by PAR

These factors are described in the original paper (Guenther et al., 1993). Daily emissions were established adding up the respective hourly values. The same procedure is used for monthly and annual periods.

Figure 1 shows the behaviour of \( C_{\text{T}} \) and \( C_{\text{p}} \). \( C_{\text{T}} \) is almost 0 for a air temperature of 0 °C and increases to almost 1.9 at 40 °C and then goes down. \( C_{\text{p}} \) is zero for PAR of 0 μmol m⁻² s⁻¹ (there are no isoprene emissions during nighttime) and it increases with an asymptotic trend to 1.1 over 1000 μmol m⁻² s⁻¹. Both of them are 1 in standard conditions.
2.1.2 Monoterpenes

Hourly emissions were estimated using an analogous equation as showed for isoprene. However, the environmental correction factor $M(T)$ is a function only of air temperature (description in Guenther et al., 1993).

Figure 2 shows the behaviour of $M(T)$, which is almost 0 for an air temperature of 0 °C, and increases until almost 2.5 for 40 °C and it continues rising for higher temperatures.

2.1.3 Other volatile organic compounds

OBVOC emissions were estimated by a similar equation to the one used for monoterpenes.

2.2 Database information

The model and database were implemented into a geographical information system (GIS) software.

2.2.1 Land-use map

We used the digital land-use map of the Ministry of the Environment of the Catalonia’s Government (MECG) for the year 1997. Originally it has a resolution in cells of 30 m by side and differences 22 land-use categories. It has been adjusted for cells of 1 km by side, assigning one land-use category by cell.
This adjusted land-use map covers about 32000 km², being the most important categories by their superficial coverage, the following:

- Shrub lands (category 15), 26 %
- Coniferous forest (category 18), 19 %
- Non-irrigated herbaceous crops (category 9), 15 %
- Non-irrigated fruit trees (category 11), 7 %
- Sclerophyllous forest (category 16), 7 %
- Irrigated herbaceous crops (category 10), 6 %
- Deciduous forest (category 17), 5 %

Figure 3 shows Catalonia’s location and the geographical distribution of these land-use categories.

![Map of Catalonia with land-use categories]

Figure 3: Catalonia’s location and its main vegetation land-use categories

### 2.2.2 Meteorological data

We used hourly air temperature records from 81 meteorological stations for the year 2000 provided by Catalonia’s Meteorological Service. Hourly global solar
radiation records were obtained from 6 stations from the Solar Radiation’s Network of the Catalan Institute of Energy.

2.2.3 Emission factors
Emission factors for each land-use category were deduced, taking into account its coverage of vegetal species. For forest categories and shrub lands, the main source of information was the Ecological and Forest Inventory of Catalonia, developed by the Centre for Ecological Research and Forestry Applications.

Table 1 shows the vegetal species associated for land-use categories whose percent coverage are at least 15 %, and also depicts their respective weights to define the emission factors. After an extensive revision, emission factors for each vegetal species were chosen from the literature, giving priority to those ones established inside Catalonia or in the Mediterranean zone. This task is fully described in Parra (2002).

2.2.4 Biomass factors
We used the biomass factors reported in Gómez (1998), where different values for coniferous, deciduous and sclerophyllous forests, and only one for the other land-use categories are presented at a regional level. Table 2 summarizes monoterpenes emission factors deduced by land-use category.

Table 1. Vegetal species by land-use category and weights for emission factors calculation.

<table>
<thead>
<tr>
<th>Code category</th>
<th>Description</th>
<th>Coverage (%)</th>
<th>Vegetal species associated</th>
<th>Foliar type</th>
<th>Weight (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>Shrub lands</td>
<td>26.1</td>
<td>Arbutus unedo</td>
<td>Perenne</td>
<td>8.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Buxus sempervirens</td>
<td>Perenne</td>
<td>8.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Erica arborea</td>
<td>Perenne</td>
<td>8.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Erica multiflora</td>
<td>Perenne</td>
<td>8.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Hedera helix</td>
<td>Perenne</td>
<td>8.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Juniperus communis</td>
<td>Perenne</td>
<td>8.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Pistacia lentiscus</td>
<td>Perenne</td>
<td>8.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Quercus cocifera</td>
<td>Perenne</td>
<td>8.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Quercus ilex</td>
<td>Perenne</td>
<td>8.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Rosmarinus officinalis</td>
<td>Perenne</td>
<td>8.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Rubus ulmifolius</td>
<td>Perenne</td>
<td>8.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Thymus vulgaris</td>
<td>Perenne</td>
<td>8.3</td>
</tr>
<tr>
<td>18</td>
<td>Coniferous forest</td>
<td>19.0</td>
<td>Pinus halepensis</td>
<td>Perenne</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Pinus sylvestris</td>
<td>Perenne</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Pinus pinea</td>
<td>Perenne</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Pinus nigra</td>
<td>Perenne</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Pinus uncinata</td>
<td>Perenne</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Quercus humilis</td>
<td>Deciduous</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Abies Alba</td>
<td>Perenne</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Pinus pinaster</td>
<td>Perenne</td>
<td>1</td>
</tr>
<tr>
<td>9</td>
<td>Non-irrigated</td>
<td>15.0</td>
<td>Hordeum vulgari (barley)</td>
<td></td>
<td>51</td>
</tr>
<tr>
<td></td>
<td>herbaceous crops</td>
<td></td>
<td>Triticum aestivum (wheat)</td>
<td></td>
<td>35</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Medicago sativa (alfalfa)</td>
<td></td>
<td>14</td>
</tr>
</tbody>
</table>
Table 2. Monoterpenes emission factors by land-use category (µg g⁻¹ h⁻¹).

<table>
<thead>
<tr>
<th>Description</th>
<th>Winter</th>
<th>Spring</th>
<th>Summer</th>
<th>Autumn</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Jan/Feb/Mar</td>
<td>Apr/May</td>
<td>Jun</td>
<td>Jul/Aug/Sep</td>
</tr>
<tr>
<td>Urban areas</td>
<td>1.34/1.34/1.34</td>
<td>1.34/1.34</td>
<td>1.95/1.95</td>
<td>1.95/1.95</td>
</tr>
<tr>
<td>Non-irrigated herbaceous crops</td>
<td>0.03/0.03/0.03</td>
<td>0.03/0.03/0.03</td>
<td>0.03/0.03/0.03</td>
<td>0.03/0.03/0.03</td>
</tr>
<tr>
<td>Irrigated herbaceous crops</td>
<td>0.05/0.05/0.05</td>
<td>0.05/0.05/0.05</td>
<td>0.05/0.05/0.05</td>
<td>0.05/0.05/0.05</td>
</tr>
<tr>
<td>Non-irrigated fruit trees</td>
<td>0.00/0.00/0.00</td>
<td>0.00/0.00/0.00</td>
<td>0.00/0.00/0.00</td>
<td>0.00/0.00/0.00</td>
</tr>
<tr>
<td>Irrigated fruit trees</td>
<td>0.00/0.00/0.00</td>
<td>0.00/0.00/0.00</td>
<td>0.00/0.00/0.00</td>
<td>0.00/0.00/0.00</td>
</tr>
<tr>
<td>Vineyards</td>
<td>0.00/0.00/0.00</td>
<td>0.00/0.00/0.00</td>
<td>0.00/0.00/0.00</td>
<td>0.00/0.00/0.00</td>
</tr>
<tr>
<td>Shrub lands</td>
<td>1.64/1.64/1.64</td>
<td>2.97/2.97/2.97</td>
<td>2.97/2.97/2.97</td>
<td>2.02/2.02/2.02</td>
</tr>
<tr>
<td>Sclerophyllous forest</td>
<td>3.43/3.43/3.43</td>
<td>7.11/7.11/7.11</td>
<td>7.11/7.11/7.11</td>
<td>5.05/5.05/5.05</td>
</tr>
<tr>
<td>Coniferous forest</td>
<td>4.43/4.43/4.43</td>
<td>7.13/7.13/7.13</td>
<td>7.13/7.13/7.13</td>
<td>5.95/5.95/5.95</td>
</tr>
<tr>
<td>Wetlands</td>
<td>0.05/0.05/0.05</td>
<td>0.05/0.05/0.05</td>
<td>0.05/0.05/0.05</td>
<td>0.05/0.05/0.05</td>
</tr>
</tbody>
</table>

3 Results

Figure 3 shows the monthly evolution of emissions, and Figure 4 depicts the geographical distribution of annual emissions. For the year 2000, total emissions reached 55.4 kt, corresponding to 10.2 kt of isoprene (18 %), 29.2 kt of monoterpenes (53 %) and 16 kt of OBVOC (29 %).

In autumn and winter, monthly emissions of isoprene were between 37 and 455 t month⁻¹, and in the period from May to September, they amounted to values between 1072 and 2612 t month⁻¹. During July, August and September, about 60 % of annual isoprene emissions were produced, but this percentage is lower for monoterpenes and OBVOC (40 and 46 %, respectively).

Results depicted in Figure 3 show the annual cycle with increasing values in March - April and the highest emissions in June - August (higher air temperature and solar radiation) followed by a decrease in October – November.

The highest annual emission (see Figure 5) came from coniferous forest (4.1 kt of isoprene + 14.9 kt of monoterpenes and 2.7 kt of OBVOC = 21.7 kt total NMVOC), followed by shrub lands (4.5 kt of isoprene + 9.6 kt of monoterpenes and 5.1 kt of OBVOC = 19.2 kt total NMVOC) and sclerophyllous forest (0.5 kt of isoprene + 3.1 kt of monoterpenes and 1.8 kt of OBVOC = 5.4 kt total NMVOC).

Figure 6 shows the hourly emissions for August 15th 2000. Isoprene emissions are presented only during daytime and their highest levels reach 13.2 t h⁻¹ at midday hours. Monoterpenes and OBVOC are emitted throughout the whole day, the fluxes being lower in the first hours (4.3 t h⁻¹ for monoterpenes, 2.6 t h⁻¹ for OBVOC) and higher at midday hours (14.3 t h⁻¹ for monoterpenes, 8.2 t h⁻¹ for OBVOC).
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Figure 3: Monthly biogenic emissions of volatile organic compounds in Catalonia for the year 2000

Figure 4: Geographical distribution of biogenic emissions of volatile organic compounds in Catalonia for the year 2000
Figure 5: Biogenic NMVOC emissions in Catalonia for the 2000 by land-use categories

Figure 6: Hourly biogenic emissions of volatile organic compounds in Catalonia for August 15th 2000

4 Discussion

We described a model for the estimation of biogenic NMVOC emitted in Catalonia for the year 2000, using high temporal (hourly) and superficial resolution (cells of 1 km²). This model includes updated information of vegetal composition of land-use categories and local available emission factors.

In the annual cycle, isoprene was emitted mainly by shrub lands (44 %) and coniferous forest (40 %). Monoterpenes were emitted mainly by coniferous forest (50 %) and shrub lands (33 %). OBVOC came mainly from shrub lands (32 %), coniferous forest (17 %) and non-irrigated herbaceous crops (16 %). Daily and annual cycles showed their agreement with the emission behaviour expected, in relation with influence of air temperature and solar radiation.
July’s NMVOC emission (see Figure 6) is lower than June’s and August’s because some species (Quercus ilicx, Pinus halcensis and Erica arborcna) were assigned lower monoterpenes emission factors for summer in relation with spring values. It was made to include the effect of summer drought stress on the emission behaviour of these species.

Considering the complexity of vegetal biodiversity in Catalonia, the use of emission factors by land-use categories is a pragmatic and useful approach, in comparison with direct use of emission factors at the level of specific vegetal species. In forest categories, the weights for emission factors calculation of each land-use category was established with surface coverage of species, but for shrub lands (one of the most important source of biogenic NMVOC), the quality of available information is lower and was only possible to identify the most important vegetal species by their presence (no weights were established)

Availability of local emission factors is still very scarce, especially for isoprene. Therefore a priority field of research is their establishment for Catalonian and Mediterranean species jointly with a better knowledge of the composition of shrub lands. Nowadays the use of more developed emission models, as used for other regions (Guenther et al., 2000), could be premature.

Although we used the standard model (which include the influences of air temperature and PAR, the two best-understood abiotic factors), emissions of biogenic NMVOC are the result of a complex net of interactions which include many internal (genetic and biochemical) and external (abiotic – air temperature, PAR, water availability, wind, ozone, and biotic – animal, plant and micro organisms interactions) factors (Peñuelas and Llusia, 2001), which produce large spatial and temporal variability, especially for local and short-term scale.

5 References


