### ESTIMATION OF BIOGENIC VOC EMISSIONS FROM ECOSYSTEMS IN THE CZECH REPUBLIC

#### Katerina Zemankova and Josef Brechler

### Department of Meteorology and Environment Protection, Faculty of Mathematics and Physiscs, Charles University in Prague, Czech Republic

**Abstract**: Characteristics of biogenic VOC (Volatile Organic Compounds) as well as methodology of BVOC (Biogenic VOC) emission estimation are presented in this article. It has been shown in previous studies (e.g. Simpson et al, 1995) that contribution of volatile organic compounds (VOC) emitted from biogenic sources to total amount of VOC in the atmosphere can be significant. Especially while modeling photochemical processes over forested areas biogenic sources should not be neglected. Emissions of volatile organic compounds – isoprene and monoterpenes from forest ecosystems in the area of Czech Republic were estimated. Results were compared with antropogenic emission data in different regions of the Czech Republic. It has been shown that the amounts of biogenic VOC emissions are presented as well.

Key words: biogenic emissions, volatile organic compounds, model, anthropogenic emissions.

# **1. INTRODUCTION**

Large quantities of volatile organic compounds (VOC) are emitted into the atmosphere from natural sources such as marine and fresh water, soil and sediments, microbiological decomposition of organic material, while the most important emitter is vegetation, especially forests (Guenther et al., 1995). A group of biogenic VOC (BVOC) is relatively wide including isoprene, terpenes and number of oxygenated compounds (Seinfeld and Pandis, 1998). However, according to many emission inventory studies, species emitted from vegetation in highest concentrations are isoprene ( $C_5H_8$ ) and monoterpenes ( $C_{10}H_{16}$ ) (e.g. Simpson et al., 1995).

The purpose and processes of VOC production in plants are subjects of research and are not yet well understood, although some ecophysiological functions have been described. There is evidence that plants emit monoterpenes to defeat themselves against pathogens and parasites or herbivore. On the other hand isoprene formation inside the plant foliage may serve to prevent light or heat damage (Kesselemier and Staudt, 1999).

Concentration of BVOC in the atmosphere ranges from few ppt to several ppb and their chemical lifetime varies between minutes to hours (Kesselemier and Staudt, 1999). Such short time of presence in the atmosphere corresponds to high reactivity and therefore importance of these gaseous compounds in controlling the chemical capacity of the atmosphere. While reacting with hydroxyl radical (OH), nitrogen oxides (NO<sub>x</sub>) and ozone (O<sub>3</sub>), BVOC play a significant role in photochemistry of the atmosphere since they affect concentrations of low level ozone (Fiala, Zavodsky, 2003). Further consequence of interaction between VOC and ambient air is the formation of secondary aerosol particles, a component of  $PM_{10}$ . Both ozone and  $PM_{10}$  are known to have negative effect on human health.

Emissions of BVOC from vegetation vary with plant species, plant conditions (e.g. developmental stage, injuries or damage) and plant environment. Due to dependence on geographical position and on environmental factors, mainly ambient temperature, light intensity, air pollution, etc., biogenic emissions exhibit significant diurnal and seasonal variation (Kesselemier and Staudt, 1999). Guenther et al., 1993, have shown that emissions of isoprene increase linearly with increasing photosynthetically active radiation (PAR) until saturation at higher values of PAR and increase exponentially with increasing leaf temperature with maximum around 35°C which is followed by emission decrease due to inactivation of isoprene forming enzyme. While isoprene volatilization from vegetation seems to be controlled by temperature as well as light, monoterpene emissions appear to depend on temperature only.

Since BVOC play an important role in atmospheric chemistry its proper estimation for the purpose of atmospheric photochemical modelling seem to be necessary. Also when compared to anthropogenic VOC emissions, the contribution of natural sources may be extensive. Unfortunately the estimations of biogenic emissions are subject to a considerable uncertainty. Simpson et al., 1995 estimate uncertainty of their results as high as a factor of 5 at some regions in Europe. The uncertainties in emissions are estimated to be the greatest during beginning and ending of the growing season (Guenther, 1997). Their sources are mainly plant emission factors and insufficient ecosystem description in the modelling area.

The methodologies of BVOC estimation as well as application of the method on the area of Czech Republic are described in the following section. In the section below several results of temporal and spatial distribution of VOC emissions from forest ecosystems are shown and discussed.

# 2. METHODOLOGY

In our study we applied model of biogenic VOC emissions proposed by Guenther et al., 1995. Emission flux F (µgm<sup>-2</sup>h<sup>-1</sup>) of each chemical compound for each ecosystem is calculated as

$$F = \varepsilon \cdot D \cdot \gamma \tag{1}$$

where  $\varepsilon$  is an ecosystem dependent emission factor (µg.m<sup>-2</sup>.h<sup>-1</sup> at PAR flux of 1000 µmolm<sup>-2</sup>s<sup>-1</sup> and leaf temperature of 303.15 K), *D* is foliar density (g dry matter per m<sup>2</sup>) and  $\gamma$  is a dimensionless correction factor that accounts for the influence of PAR and leaf temperature. Emission factor  $\varepsilon$  and foliar density *D* are ecosystem dependent while correction factor  $\gamma$  depends on environmental conditions only.

In case of isoprene, correction factor  $\gamma$  is a product of two coefficients,  $C_T$  which stands for temperature dependence and  $C_L$  for sunlight dependence. Unlike the original formula, approximation of leaf temperature with ambient air temperature has been used in this study. Environmental coefficients  $C_L$  and  $C_T$  are defined as

$$C_{T} = \frac{\exp \frac{C_{T1}(T_{A} - T_{S})}{RT_{A}T_{C}}}{1 + \exp \frac{C_{T2}(T_{A} - T_{M})}{RT_{S}T_{A}}}$$
(2)

$$C_L = \frac{\alpha . C_{L1} . L}{\sqrt{1 + \alpha^2 . L^2}} \tag{3}$$

Elements  $C_{TI}$  (= 95000 Jmol<sup>-1</sup>),  $C_{T2}$  (= 230000 Jmol<sup>-1</sup>),  $T_M$  (= 314 K) in Equation 2 are empirical coefficients, R is ideal gas constant (= 8.314 J K<sup>-1</sup>mol<sup>-1</sup>),  $T_A$  is temperature of ambient air and  $T_S$  is standard temperature of 303.15 K. Parameter L in Equation 3 stands for the amount of photosynthetically active radiation (PAR),  $\alpha$ (=0.0027) and  $C_{LI}$  (=1.066) are empirical coefficients.

Correction factor  $\gamma$  for monoterpene emissions is only temperature dependent and is defined as

$$\gamma = \exp(\beta (T_A - T_S)) \tag{4}$$

where  $\beta(K^{-1})$  is empirical coefficient (= 0.09 K<sup>-1</sup>),  $T_A$  and  $T_S$  is ambient and standard temperature respectively.

Crucial for proper estimation of VOC emissions from natural sources is the description of ecosystem coverage in the model domain. In the case of our study we used Corine landcover 2000 (EEA, 2007) in the resolution of 1x1 km grid. Since tree species are the main BVOC emitters, only forest landcover categories (i.e. deciduous, coniferous, mixed forest) were taken into account. In order to properly assign an emission factor of particular chemical compound to each landcover category, it was desirable to have information about the tree species composition in each ecosystem. Data of the main forest constituents in each of fourteen administrative regions of Czech Republic were available from the database of the Forest management Institute, Brandys nad Labem. Tree species prevailing in Czech Republic are spruce, pine, larch, fir, oak, beech, birch, hornbeam, maple, ash, alder, linden and black locust, and their proportional distribution within each administrative region were used in the calculations.

Aggregating data of emission factor and foliar density for each tree species, distribution of the tree species within land cover category and portion of the grid box surface covered by particular land cover category, emission factor for each grid box has been received. Since foliar density varies with seasons, values for deciduous tree species were assigned their maximum from May to September, decreased by half in April and October and were equal to zero from January to March as well as from November to December. Foliar densities of coniferous trees remained the same throughout whole year.

Since the data of photosynthetically active radiation were not available it has been assumed that the value of PAR approximately equals to double of global radiation (Gonzalez, 2002). Hourly meteorological data of surface temperature (K) and global radiation (W.m<sup>-2</sup>) for year 2000 were obtained from the regional climate model RegCM (Cecilia project, 1.1.6.3.I.3.2.).

# **3. RESULTS**

Biogenic emissions of isoprene and monoterpene were estimated for each 1x1 km grid box of the area of Czech Republic. The sum of emissions from whole domain showing the month to month variation is presented on Figure 1. Isoprene emissions decrease to zero in winter season due to loss of foliage of deciduous trees since these species, especially oaks, are dominant isoprene emitters, and due to decrease of temperature and sun light as well.

Monoterpene emissions remain at significant concentrations for the whole year long since these compounds are emitted mainly by conifers. The decrease in emissions due to lower temperatures in winter seasons is also visible.

Total annual biogenic emissions from each region of the domain were compared with the emission inventory of anthropogenic sources on Figure 2. The inventory is provided by Czech Hydrometeorological Institute and divides anthropogenic emissions into two groups: REZZO 1-4 and REZZO 1-3. The first group REZZO 1-4 covers emissions from major stationary sources, area sources (including domestic heating) and mobile sources. The last ones

mentioned are not accounted for in the second group REZZO 1-3. Location of particular administrative region is shown on Figure 3.



Figure 1. Monthly BVOC emissions of isoprene and monoterpene.





Figure 2. Comparison of VOC emissions from biogenic and antropogenic sources.

Figure 3. Scheme of administrative regions in the Czech Republic.

Spatial distributions of isoprene and monoterpene total annual emissions are presented on Figure 4. One can see that isoprene sources are located mainly in the south-eastern region where with a high percentage of oak trees. On the other hand monoterpene emitters are more of less uniformly distributed over the whole area. The total annual emission released from whole domain is approximately 12 kt for isoprene and 70 kt of monoterpenes.



Figure 4. Spatial distribution of annual emissions of isoprene and monoterpenes.

Differences in the quantity of emitted compound between winter and summer seasons are captured on Figure 5 and Figure 6. The isoprene emissions rise from almost negligible concentrations in winter season to values of order of tons in summer whereas monoterpene emissions remain considerably high along whole year.







Figure 6. Monthly sums of estimated biogenic emissions of monoterpenes in winter (January) and summer (July) seasons.

# 4. CONCLUSIONS

Presented results show that estimated emissions of isoprene and monoterpenes from forest ecosystems in the Czech Republic are not inconsiderable but, on the contrary, they are comparable to anthropogenic emissions of VOC. For the area of Czech Republic, total amount of VOC emitted from anthropogenic sources with and without inclusion of mobile sources are approximately 178 kt and 39 kt respectively, while emissions of isoprene and monoterpenes from forest ecosystems are estimated to be as high as 82 kt. Therefore in the photochemical modelling of processes in the atmosphere, where volatile organic compounds are important components in the tropospheric ozone forming reactions, natural sources should be accounted for. Further research in applaying the biogenic emission data into a photochemical model is needed.

# REFERENCES

- Atkinson, R., Arey J., 2003: Gas-phase tropospheric chemistry of biogenic volatile organic compounds: a review, *Atmospheric Environment*, **37**, No. 2, 197-219.
- EEA, 2007: European Environment Agency, Corine Land Cover 2000 (CLC2000) 250- version 9/2007:
- http://dataservice.eea.europa.eu/dataservice/metadetails.asp?id=1008
- Fiala, J. and D. Zavodsky, 2003: Chemical Aspects of Polluted Air Tropospheric Ozone. *Apendix of Atmosphere Protection Journal*, Part 2., Prague.
- Gonzalez, J.A., and J. Calbo, 2002: Modelled and measured ratio of PAR to global radiation under cloudless skies. *Agricultural and Forest Meteorology*, **110**, Issue 4, 319-325.
- Guenther, A.B., Zimmerman, P.R., Harley, P.C., Monson, R.K., and Fall, R., 1993: Isoprene and monoterpene rate variability: model evaluations and sensitivity analyses. *J. Geophys. Res.*, **98**, 12609-12617.
- Guenther, A., Hewitt N., Erickson D., Fall R., Geron Ch., Graedel T., Harley P., Klinger L., Lerdau M., McKay W. A., Pierce T., Scholes B., Steinbrecher R., Tallamraju R., Taylor J., Zimmerman P., 1995: Global model of natural organic compound emissions. J. Geophys. Res., 100, 8873-8892.
- Guenther, A., 1997: Seasonal and spatial variations in natural volatile organic compound emissions. *Ecological Applications*, **7**(1), 34-45.
- Kesselmeier, J. and M. Staudt, 1999: Biogenic volatile organic compounds (VOC): An overview on emission, physiology and ecology, *Journal of Atmos. Chem.*, **33**, 23–88.
- Seinfeld, J. H. and S.N. Pandis, 1998: Atmospheric Chemistry and Physics, John Wiley & Sons, Inc., USA.

Simpson, D., Guenther A., Hewit C.N. and Steinbrecher R., 1995: Biogenic emissions in Europe. 1. estimates and uncertainties. *J. Geophys. Res.-Atmospheres*, **100** (D11), 22875-22890.