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BIOGENIC EMISSIONS OF VOLATILE ORGANIC COMPOUNDS FROM TURKEY

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ABSTRACT

This study shows the results of the first to our knowledge detailed biogenic emission inventory of volatile organic compounds (VOCs) for the whole of Turkey. Of the thousands of VOCs present in the atmosphere, the emission inventory was prepared for isoprene and monoterpenes, which are known to be the most important biogenic VOCs considering their role in photochemical reactions and the formation of ozone. The other VOCs were also calculated but the results for this category have very great uncertainty and should be taken only informative. The basis for the calculations was a land cover dataset depending mainly on satellite data. The emission results were found to be higher than some earlier global studies, especially for isoprene.

Key Words: Biogenic emissions, volatile organic compounds, Turkey, isoprene, monoterpenes

1. INTRODUCTION

Photochemical smog, focusing mostly on tropospheric ozone, has been an important subject of air quality studies especially from the last quarter of the past century. Because of several factors like computational limitations, relatively poor explanation of the chemical mechanisms and the natural interest in urban sources of pollution, the earlier studies focused on the anthropogenic emissions of precursors of photochemical smog components. In the following years, with the help of the developing models and better explanation of the chemical mechanisms, the extent of the studies became greater and the contribution of biogenic emissions of VOCs is being considered in most recent and current studies (Biswas et al., 2001). Because of the great number of VOCs emitted, most studies are limited to the contribution of the emissions of isoprene and monoterpenes, which are known to have the most important role in photochemical reactions.

Considering the relatively new interest in ozone modeling in Turkey and the fact that the current studies are realized by considering the contribution of anthropogenic emissions only, the estimation of biogenic emissions of VOCs from Turkey was realized in this study. To our knowledge, this is the first national biogenic VOC emission inventory for Turkey.

2. METHODOLOGY

Considering the known effect of the biogenic volatile organic compounds (VOCs) in the formation of ozone, an inventory of biogenic VOCs for the whole area of Turkey has been prepared with a resolution of 1 km x 1 km.

Because of the known effect of solar radiation and temperature on the emissions of the biogenic VOCs (Guenther et al., 1993), it is important to consider the variation of these parameters on monthly and hourly basis and the inventory should be prepared accordingly. Hence, the inventory was prepared for each hour of a typical day of each month of the year. As in many other similar studies worldwide, the emission inventory was prepared for three main groups of compounds; isoprene, monoterpenes and "other VOCs".

The level of uncertainties for the group called "other VOCs" is too high and the results should be considered only informative. Therefore, the results of other VOC emission estimates are not included here. These calculations are carried out only for having a general idea of the level of emissions and for most of the species the default emission factor of 1.5 μg C m^{-2} h^{-1} has been used. Since a large number of VOC species are included in this group, the problem of uncertainty in the emission factors of this group is likely to continue for quite some time.

Although the mechanisms of emissions from vegetation and their importance and role in the metabolism of the plants are still not exactly well known, the important role of isoprene and monoterpenes in photochemical reactions is well known and there has been quite a number of studies in order to precisely determine the emission factors for different species. The members of the same family of plants can exhibit different emissions depending on the region in which it is found in the world. In the literature, there are no such studies carried out in Turkey. Therefore, the emission factors accepted in the scientific literature were used for the calculations, sticking to EMEP-CORINAIR emission factors when they were available.

The model developed by Guenther et al. (1995) formulizes the foliar emissions of VOCs as:

$$F = D\,\varepsilon\,\gamma \quad (1)$$

F: Foliar emissions (μg-C m^{-2} h^{-1})
D: Foliar density (g m^{-2} : dry weight of leaves per unit area of land)
ε: Emission Factor (μg g^{-1} h^{-1}) (Since the emissions are dependent on temperature and solar radiation, the published emission factors are normalized to a reference state, most frequently the reference PAR being 1000 μmol m^{-2} s^{-1} and the reference leaf temperature being 303.15 K)
γ: A correction factor for the emissions (rising from the difference of real PAR and leaf temperature values to the reference values for which the emission factor has been given)

The sources of the inputs to the biogenic emissions model and the way of handling these inputs are explained in the following part.

Land Cover Data: The source of the land cover information used in this study was the Seasonal Land Cover Characterization dataset provided by USGS (http-1). These data are distributed by the Land Processes Distributed Active Archive Center (LP DAAC), located at the U.S. Geological Survey's EROS Data Center (http://LPDAAC.usgs.gov). This dataset has been prepared from the interpretation of satellite data and is updated by local contributions where possible. Of the 253 total different land cover classes included in the dataset, 138 were found to exist within the land of Turkey.

Temperature: In order to have a general picture of the biogenic VOC emissions, the climatic dataset "IPCC Data Distribution Centre Climate Baseline Download" was chosen (http-2). The dataset contains the minimum and maximum temperatures of each month averaged between the years 1981-1990 with a resolution of 0.5°. Temperature values for every hour of the day was assigned by an assumption of a linear daily change between the minimum and maximum temperatures obtained from the dataset. The temperatures defined at certain points of the world were transformed to continuous raster datasets by interpolation methods embedded in the GIS system.

PAR (Photosynthetically Active Radiation): The PAR values which control the emissions of isoprene, and in some cases monoterpenes, were estimated by the use of the TUV model developed by The National Center for Atmospheric Research (NCAR)- Atmospheric Chemistry Division (ACD) (http-3). The PAR values at given locations were interpolated by the GIS software in order to have a continuous spatial data.

The TUV model was run in order to estimate the visible range net solar radiation. According to CORINAIR documents, the PAR value is approximately half of the values of the visible range solar radiation (EEA, 2004). In this study, the ratio of the photosynthetic photon flux density (which is a measure of PAR) to the solar broadband irradiance was taken to be 1.990 μE/J as advised by Gonzalez and Calbo (2002) and the PAR values were assigned accordingly.

Of the essential inputs to the TUV model are the geographical coordinates of the point for which the radiation amount will be estimated and its elevation from sea level. Elevation values, together with their geographical coordinates were obtained from the dataset "The Global Land One-km Base Elevation (GLOBE) Project" that has a resolution of 0.0083333° (approximately 1 km) available from the website http://www.ngdc.noaa.gov (http-4).

The estimations for PAR were realized with the assumption of clear skies. Although this assumption leads to some mistakes especially for winter months, the scope of being able to estimate the total emission potential from biogenic sources together with the fact that the bulk of the isoprene emissions occur during summer months and that the sensitivity of biogenic emissions to radiation decreases significantly after certain values of PAR (EEA, 2004) may lead to the idea that the error rising from this assumption can be expected to be relatively small (Symeonidis et al., 1999).

Emission factors: The two main references during the selection of the emission factors were EMEP CORINAIR emission factors (EEA, 2004) and the emission factors assigned by Guenther et al. (1995) for the ecosystem types compiled by Olson (1992). The factors given by Guenther et al. (1995) are generally for more general classes while CORINAIR documents list factors for commonly observed types of species, stating factors for European species where available. This made the CORINAIR documents the more preferable reference in the selection of emission factors. The other references used were the studies by Guenther et al. (1994), Levis et al. (2003), Lamb et al. (1993) and Parra (2004).

Foliar density: For foliar densities (sometimes referred to as biomasses also), the values given by CORINAIR were used where possible.

There are temporal changes in foliar densities of deciduous trees and agricultural products, resulting from climatic changes and agricultural activity. Adopting the assumption used by Symeonidis et al. (1999), the deciduous tress were assumed to possess the maximum foliar densities given in the literature from May until September while the foliar densities are reduced to half of these values during October, November and April and are zero during other months of the year. For the temporal changes related to agricultural products, the assumptions were based on communications with experts.

Since the land cover dataset used contain mostly classes of a mixed type (i.e. classes containing deciduous and evergreen species together, or containing isoprene and monoterpene emitters together), the dataset of foliar densities and emission factors were prepared in order to have foliar density and emission factor values separately for all 12 months and again separately for isoprene, monoterpenes and other VOCs (leading to a dataset of 138 rows by 36 columns of foliar densities and 36 columns of emission factors). Table 1 shows the land cover classes from the used land cover data set (SLCR (Seasonal Land Cover Region) version 2.0) that occur most frequently within the land of Turkey, the percentage of their spatial coverage to the whole area, foliar densities (biomasses) and emission factors of isoprene, monoterpenes and other VOCs for the months of June and July as examples of low and high emission conditions.

Correction factor for emissions (γ): Since the emission factors are given at a reference PAR and leaf temperature, a correction factor is included in the calculations in order to estimate the emissions for the actual PAR and leaf temperature values (EEA, 2004). All isoprene emissions are dependent on both solar radiation and temperature and the correction factor includes both the PAR and temperature as a variable. The emissions of most monoterpenes, on the other hand, are controlled only by temperature and the correction factor includes only temperature as a variable. Some of the monoterpene emissions, however, have been found to be controlled by both solar radiation and temperature. For vegetation classes related with such monoterpene emissions, the same algorithm with isoprene emissions was used and hence the correction factor calculation is the same. Generally, monoterpene emissions that are controlled both by radiation and temperature arise from some evergreen oak species and evergreen shrub-like species.

Table 1. Biomasses (foliar densities) and emission factors for isoprene, monoterpenes and other VOC's for January and July for the most frequently observed land cover classes

SLCR 2.0 LABEL	%	JAN-BIO (ISOP)	JUL-BIO (ISOP)	JAN-BIO (MT)	JUL-BIO (MT)	JAN-BIO (OVOC)	JUL-BIO (OVOC)	JAN-EF (ISOP)	JUL-EF (ISOP)	JAN-EF (MT)	JUL-EF (MT)	JAN-EF (OVOC)	JUL-EF (OVOC)
Cropland (Small Grains) with Grassland	6.50	0	0	100	200	100	200	0.000	0.000	0.100	0.100	1.500	1.500
Grassland with Winter Wheat	6.47	0	0	100	200	100	200	0.000	0.000	0.100	0.100	1.500	1.500
Short Grassland	6.27	0	0	200	400	200	400	0.000	0.000	0.100	0.100	1.500	1.500
Cropland (Wheat, Orchards)	6.21	0	180	0	180	0	180	0.000	0.150	0.000	0.490	0.000	1.370
Cropland/Shrubland Mosaic	5.73	409	818	409	818	409	818	1.540	1.541	0.225	0.225	1.500	1.500
Short Grassland/Oak Woodland/Cropland	5.51	223	552	289	685	289	685	0.090	11.674	0.123	0.135	1.500	1.500
Oak Woodland/Grassland	5.46	0	160	100	360	100	360	0.000	60.000	0.100	0.140	1.500	1.500
Grassland/Cropland (Corn, Wheat) Mosaic	4.85	0	0	67	133	67	670	0.000	0.000	0.100	0.100	1.500	1.500
Cropland/Woodland Mosaic	4.22	334	885	552	1103	552	1103	0.090	7.932	0.394	0.394	1.500	1.500
Sparse Short Grassland	3.57	0	0	200	400	200	400	0.000	0.000	0.100	0.100	1.500	1.500
Short Montane Grassland	3.21	0	0	200	400	200	400	0.000	0.000	0.100	0.100	1.500	1.500
Cropland (Small Grains, Sugar Beets, Orchards)/Pasture	2.49	0	424	50	524	50	524	0.000	0.103	0.100	0.186	1.500	1.478
Deciduous Broadleaf Forest	2.40	0	300	0	300	0	300	0.000	24.000	0.000	0.800	0.000	1.500
Oak Woodland	2.35	0	320	0	320	0	320	0.000	60.000	0.000	0.200	0.000	1.500
Cropland (Winter Wheat, Small Grains)	2.24	0	0	0	0	0	0	0.000	0.000	0.000	0.000	0.000	0.000
Grassland/Cropland (Small Grains) Mosaic	2.06	0	0	100	200	100	200	0.000	0.000	0.100	0.100	1.500	1.500
Inland Water	1.77	0	0	0	0	0	0	0.000	0.000	0.000	0.000	0.000	0.000
Sparsely Vegetated Shrubland/Grassland	1.74	75	150	175	350	175	350	8.000	8.000	0.340	0.340	1.500	1.500
Woodland/Cropland Mosaic	1.57	334	885	552	1103	552	1103	0.090	7.932	0.394	0.394	1.500	1.500
Cropland and Pasture (Wheat, Orchards, Vineyards) with Woodland	1.54	0	533	109	641	109	641	0.000	6.623	0.800	0.392	1.500	1.482
Small Grains (Barley, Wheat) with Grassland	1.51	0	0	67	133	67	133	0.000	0.000	0.100	0.100	1.500	1.500
Cropland (Wheat, Barley, Corn)	1.48	0	0	0	0	0	537	0.000	0.000	0.000	0.000	1.500	1.500
Woodland (Pine, Oak, Gum)	1.42	125	232	358	465	358	465	8.000	31.942	2.163	1.713	1.500	1.500
Grassland/Irrigated Cropland	1.40	334	668	434	868	434	868	0.090	0.090	0.123	0.123	1.500	1.500
Oak Woodland/Cropland (Small Grains, Orchards)/Pasture	1.21	0	170	50	270	50	270	0.000	28.315	0.100	0.260	1.500	1.457
Larch Forest/Woodland	1.11	0	218	218	585	218	585	0.000	32.000	0.800	0.979	1.500	1.500
Short Grass and Sparse Shrub	1.03	75	150	175	350	175	350	8.000	8.000	0.340	0.340	1.500	1.500

BIO: Biomass (foliar density) (g m^{-2}) **EF**: Emission factor (μg-C g^{-1} h^{-1})
JAN: January **JUL**: July **ISOP**: Isoprene **MT**: Monoterpenes **OVOC**: Other VOCs

3. RESULTS

The emission inventory for isoprene, monoterpenes and other VOCs from vegetation of Turkey has been prepared on hourly basis for a typical day of every month of the year. Both during the calculations and the presentation of the results on maps, GIS has been used intensively. As observed in Figure 1, which shows the yearly total emissions of isoprene, the emissions of isoprene is quite low (even zero in certain parts, depending on the vegetation cover) in central Turkey where green canopy is sparse, while it is much higher in the Black Sea region where dense green forests are found and in the Aegean, Marmara and Southeastern Anatolia where irrigated agriculture is practiced. In Figure 2, which shows the yearly total monoterpene emissions, the high emission regions observed for isoprene in the Black Sea and Marmara regions are not observed any more, while the monoterpene emissions are higher for the Aegean and Mediterranean regions, the canopy of which are generally maquis which is known to have higher monoterpene emissions.

Because of different values and assumptions used in different studies, the results of studies carried out for the same area can vary significantly from each other. When the results of this study are compared with the results of the study of Simpson et al (1995), it is seen that the results of this study are generally higher than those of the earlier study of Simpson et al (1995). As can be seen in the mentioned study of Simpson et al (1995), there can be significant differences in the results depending on the method used for modeling (In Simpson et al. (1995), emissions are estimated with differnet methodologies, the results of which range from 200 to 400 kilotons per year). In the mentioned study, the highest total observed emission of isoprene (total of emissions from April to September) is around 400 kilotons while in this study, emissions up to 1090 kilotons are observed for the same period . Such differences can be a result of:

- The vegetation classes used in Simpson et al. (1995) are much more general groups, while in this study, the classes used are much more detailed.
- In the years that passed between the two studies, there have been important changes in the generally accepted emission factors as a result of new and more detailed studies. Especially the emissions of isoprene from oak populations have turned out to be even more than they were known earlier and the isoprene emission factors have been revised.
- There is a difference between the resolutions of the two studies. The former study is a global model study and has a much coarser resolution while the resolution in this study is a fine resolution of 1km x 1km.

When the total emissions of isoprene are calculated, the value found is 1131 kilotons per year, a value slightly larger than the value of 1090 which is the emissions from April to September. This is expectable because of the dependence of isoprene emissions on solar radiation and the foliar density and also because of the fact that the isoprene is emitted mainly by deciduous trees.

It can be said that the monoterpene emission estimations are more comparable with the EMEP CORINAIR estimates. In the EMEP CORINAIR emission inventory guide, biogenic emissions are listed only for those from forests for each country. The

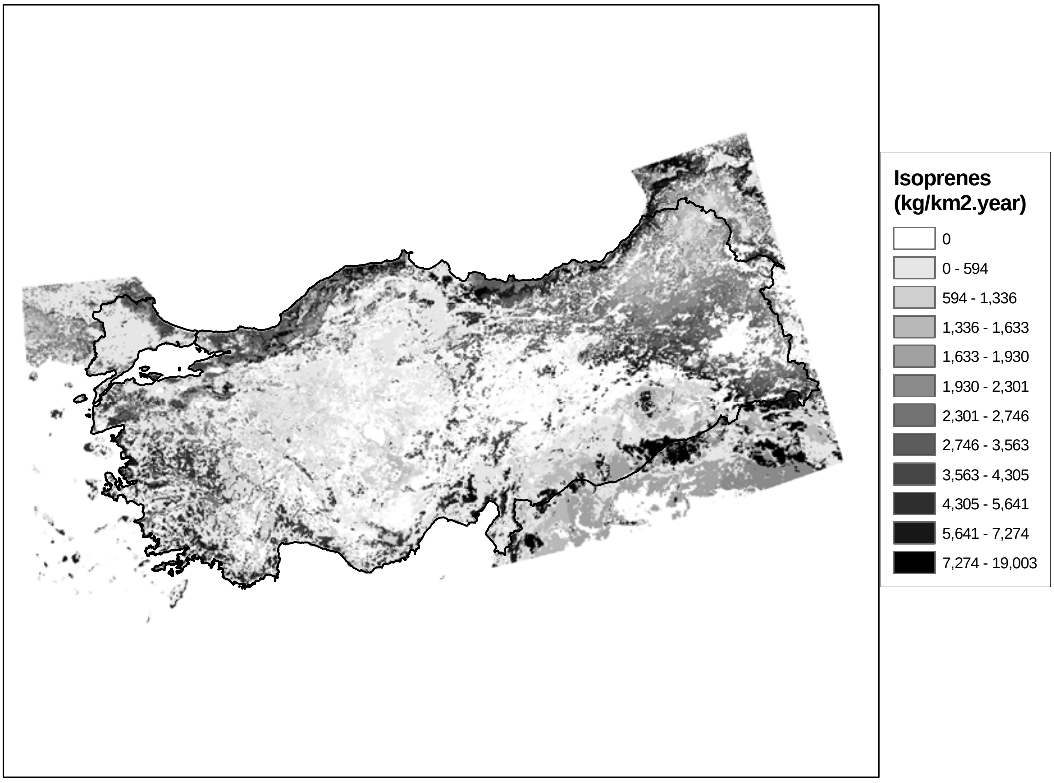

Figure 1. Yearly emissions of isoprene (kg/km^2.year)

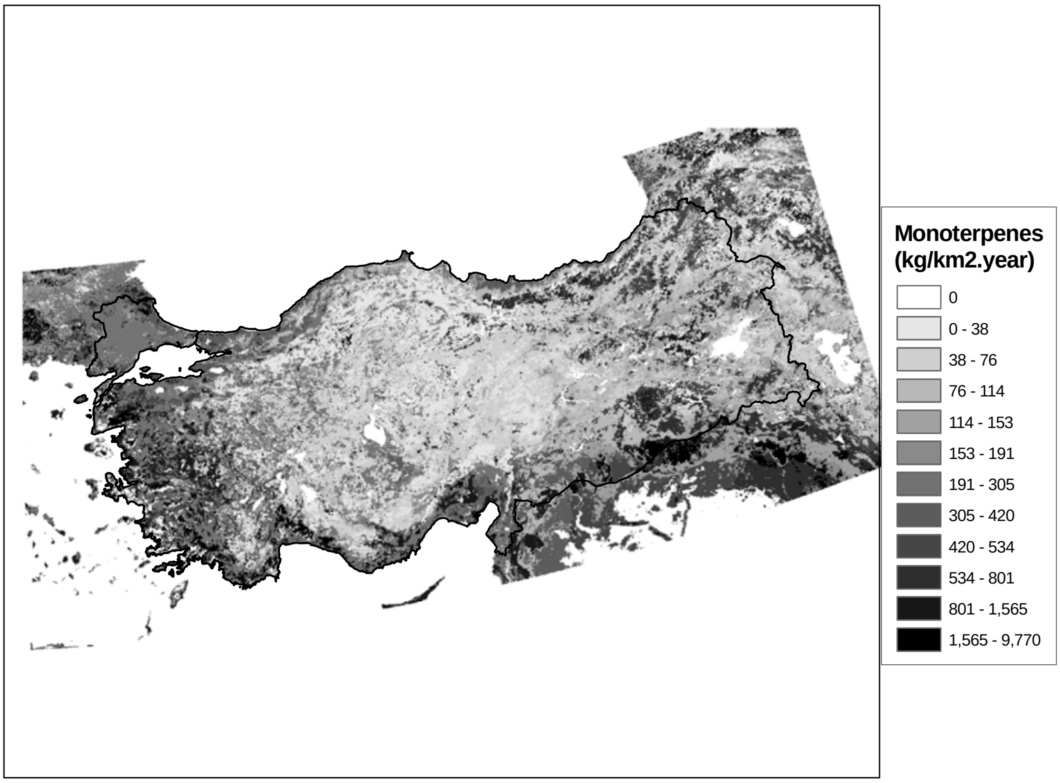

Figure 2. Yearly emissions of monoterpenes (kg/km^2.year)

total monoterpenes emissions of 224 kilotons per year estimated in this study seems to be in better agreement with the value of 175 kilotons per year given by CORINAIR, which is the emission value from forests. The isoprene emissions' estimation of CORINAIR from forests is only 213 kilotons per year, a value rather below the total emissions estimate of this study which is 1131 kilotons per year.

The advantage of the current study was the use of more specifically defined vegetation classes, allowing to assign more specific emission factors. The satellite-based data which gives this opportunity, however, comes with its disadvantage also as any other remote sensing dependent study, which may always have misinterpretations. The future study should revise these results by using real observations of vegetation classes, when a national land cover database is available.

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http-2) http://ipcc-ddc.cru.uea.ac.uk/asres/baseline/climate_download.html (The IPCC Data Distribution Centre Climate Baseline Download)

http-3) http://www.acd.ucar.edu/TUV/ (Tropospheric Ultraviolet & Visible Radiation Model)

http-4) http://www.ngdc.noaa.gov/seg/topo/globe.shtml (The Global Land One-km Base Elevation (GLOBE) Project)

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