Preparation of a National Inventory of Biogenic Volatile Organic Compound (BVOC) Emissions in Turkey

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***Abstract*—** The primary source of biogenic volatile organic compounds (BVOCs) is the vegetation. Plants emit BVOCs as a result of their photosynthetic activities. BVOCs in the atmosphere plays role in ozone and secondary organic aerosol formation in the presence of sunlight. As a result of these photochemical reactions, BVOCs indirectly deteriorate air quality and affect human health. This study aims to inventory BVOC emissions in Turkey. In a recent study, emission factors of isoprene, monoterpenes, sesquiterpenes, and oxygenated VOCs from thirty eight commonly grown tree species in the forested areas of Turkey were determined using a dynamic-enclosure sampling method followed by thermal desorption (TD)-gas chromatography/mass spectrometry (GC/MS) analysis. These emission factors were used to estimate the BVOC emissions. A spatially and temporally resolved national BVOC emission inventory for Turkey was prepared based on a geographical information system (GIS), and national forest inventory data. Emissions were distributed to a forested area of 21.6 million ha including coniferous and broad-leaved species. This is the first comprehensive BVOC inventory prepared for Turkey including specific emission factors. The inventory will serve as a database for further modeling studies.

***Keywords*—** Biogenic volatile organic compounds, emission factor, emission inventory, Turkey.

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I. Introduction

A SUBSTANTIAL source of biogenic volatile organic compounds (BVOCs) is the vegetation. BVOCs emitted from plants act as defense substances against environmental stress [1] and also play a significant role in the photochemical processes and contribute to tropospheric ozone and secondary aerosol formation in the presence of nitrogen oxides (NO_x) and sunlight [2-4].

Several studies on determination of BVOC emissions are being performed in regional and global scales. Guenther et al. (1995) [2] estimated that the global BVOC emissions from plants are 1 150 x10^6 tones/year accounting for more than 90% of global VOC emissions. BVOCs include isoprene, terpenes (monoterpenes and sesquiterpenes) and oxygenated VOCs. Isoprene and monoterpenes are the most abundant BVOC species in the atmosphere. The annual global BVOC flux is composed of 44% isoprene and 11% monoterpenes [5].

Quantity of isoprene emissions from vegetation depend on temperature, solar radiation, leaf age and foliar density [6, 7]. Isoprene emission is mostly emitted by broad-leaved trees. Seasonal isoprene emission inventories are available in the literature [8, 9]. On the other hand, monoterpenes are typically emitted by conifers [10]. Their emissions are believed to be temperature dependent only [11]. The other BVOC compounds include sesquiterpens, oxygenated sesquiterpenes and other oxygenated VOCs. These compounds are emitted from defense tissues, during plant growth, from cut and drying vegetation, and from blossoms [5].

BVOCs vary with meteorological conditions, plant species, plant conditions (e.g. physical condition, age, stress) and environment. Biogenic emissions show distinct temporal and spatial variations arising from their dependence on geographic and climatic differences such as ambient temperature and light intensity [12-14].

The main aim of recent studies is to develop a capacity for investigating of BVOC emissions in a regional or global scale. Many BVOC emission inventories were established and

spatial and temporal distributions of BVOC emissions were estimated. Accurate prediction of biogenic emissions relies on accurate characterizations of land cover, surface temperature, soil temperature, and photosynthetically active radiation (PAR).

In a recent study [15], emission factors from thirty eight commonly grown tree species in the forested areas of Turkey were determined using a dynamic-enclosure sampling method followed by thermal desorption (TD)-gas chromatography/ mass spectrometry (GC/MS) analysis. Using species based emission factors produced from this study, a national BVOCs emission inventory was prepared. This study aims inventorying of BVOC emissions in the forested areas of Turkey. This is the first comprehensive BVOCs emission inventory prepared for Turkey based on a geographic information system (GIS) technology.

II. MATERIALS AND METHODS

A. Characteristics of Study Area and Forest Resources

Turkey is located between latitudes of 35–42˚N and longitudes of 25–45˚E. Turkey has a unique geographic position, lying partly in Asia and partly in Europe and it is surrounded by three seas. The Mediterranean climate is predominant in the southern and western parts of Turkey. A continental climate with hot and dry summers accompanied by rain in the spring and fall and snow in the winter prevails in central parts. The Black Sea region has a distinct climate type with mild temperatures and precipitation almost uniformly distributed throughout the year. Mediterranean climate having cool and rainy winters, and hot and moderately dry summers, dominates a significant section of the country. However, the topography of the country ensures that winters are often much colder than common in Mediterranean climates [16].

Forests in Turkey are generally located on mountainous areas. Deciduous forests are prevalent and relatively uninterrupted at moderate elevations along northern Turkey. Coniferous forests, depending on the species and locations, are found at varying altitudes from sea level to the timber line. Forest formations of the country include species belonging to different floristic regions, namely Irano-Turanion, Mediterranean and Euro-Siberian [17].

Turkey is a country with a land mass of 78 million ha, of which 21.6 million ha is forested, representing about 27.6% of the country's total land area that has increased approximately 1.5 million ha at recent 40 years. Coniferous forests occupy the greatest area (66%). Among them pines (*Pinus brutia* (27%); *Pinus nigra* (22%); *Pinus sylvestris* (7%)) occupy 56%, four of common firs (*Abies nordmanniana, Abies cilicica, Abies equi-trojani, Abies nord. sbsp. Born.*) occupy 3% and the other coniferous species occupy 7%. Broad-leaved forests are mainly formed by oak including 18 species, beech (*Fagus orientalis*) and the other broad-leaved species which occupy 24, 9 and 1% of the tree-covered area, respectively [17]. The distribution of the species of trees in Turkey is shown in Fig. 1.

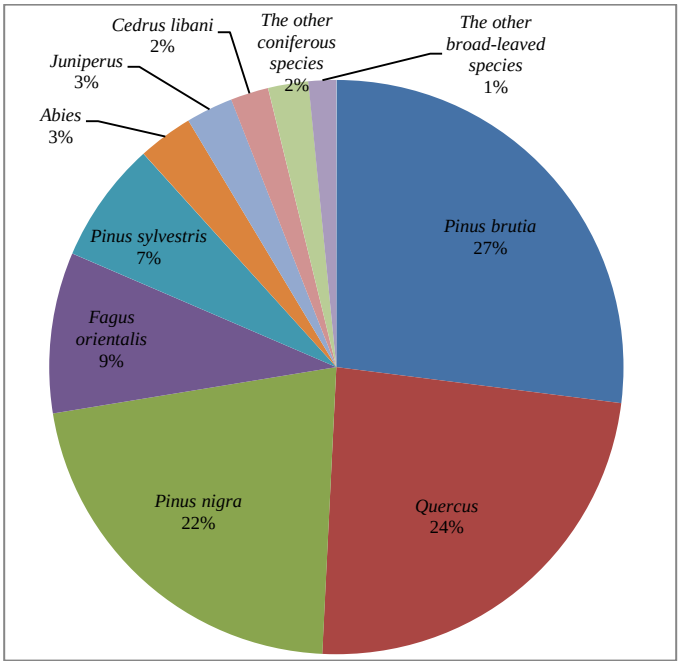

Fig. 1 Distribution of the tree species in Turkey

The digital forest resources map updated by General Directorate of Forestry (GDF) for the year 2012 was used in this study. In order to create a more accurate forest database for estimating reasonable BVOC emissions a new GIS based forest database was created. Only 8 species (3 pines, oak, beech, fir, juniper and cedar) cover 96% of the all forested areas in Turkey.

In Turkey, approximately 24% of all forested areas are covered by 18 oak species and 5 of them (*Quercus petraea, Quercus cerris, Quercus vulcanica, Quercus aucheri and Quercus macr. sbsp. Sysp.*) were investigated in the database [17]. *Quercus cerris* and *Quercus petraea* involve over 50% of the all oaks [18].

B. Calculation of BVOC Emissions

The primary BVOC emitter is leaves [2], so only BVOC emissions from leaves were taken into consideration in this study. BVOC emissions were grouped into five major groups: isoprene, monoterpenes, sesquiterpens, oxygenated sesquiterpenes and other oxygenated VOCs including 65 compounds (isoprene, 21 monoterpenes, 15 sequiterpenes, 3 oxygenated sesquiterpenes, and 25 oxygenated VOCs).

Emission factors for each individual tree species (Table I) were used from a recent study [15]. All factors used were normalized to 30 ˚C and 1000 µmol/m^2 s of PAR.

BVOC emissions of tree species were estimated by using the method developed by Guenther et al. (1993) [19] as in Equation (1).

$$E = \varepsilon D A t \quad (1)$$

TABLE I
EMISSION FACTORS (μg/g h) FOR BVOC GROUPS OF BROAD-LEAVED AND CONIFEROUS TREES (NORMALIZED TO 1000 μmol/m^2 s PAR AND 30°C TEMPERATURE)

	Emission Factors (μg/g h)					
	Isoprene	**MT[a]**	**SQ[b]**	**OS[c]**	**OC[d]**	**Total**
Broad Leaved Trees						
Fagus orientalis	0.047	0.020	0.003	0.00156	0.023	0.095
Quercus petraea	9.63	0.012	0.007	0.00169	0.037	9.69
Quercus cerris	0.079	0.020	0.005	0.01035	0.042	0.157
Quercus vulcanica	9.79	0.063	0.022	0.00008	0.060	9.93
Quercus aucheri	0.028	0.879	0.006	0.00014	0.033	0.946
Quercus macr. sbsp. *Sysp.*	19.2	0.070	0.067	0.00032	0.090	19.4
Carpinus orientalis	0.102	0.009	0.006	n.d	0.034	0.150
Carpinus betulus	0.060	0.061	0.013	0.0005	0.136	0.270
Alnus glutinosa	0.018	0.133	0.003	n.d	0.054	0.209
Populus tremula	22.4	0.235	0.015	0.00074	0.034	22.7
Populus deltoides	4.72	0.070	0.022	0.00021	0.022	4.83
Castanea sativa	0.378	14.4	0.033	0.00027	0.281	15.1
Fraxinus excelsior	0.011	0.011	0.0007	0.00002	0.014	0.038
Fraxinus ornus	0.014	0.005	0.006	0.00003	0.008	0.033
Tilia argentea	0.077	0.483	0.005	0.00037	0.089	0.655
Eucalyptus camaldulensis	5.14	0.169	0.078	0.00091	0.414	5.80
Acacia cyanophylla	0.196	0.099	0.014	0.00070	0.042	0.351
Robinia pseudo-acacia	12.4	0.075	0.013	0.00354	0.041	12.5
Platanus orientalis	27.0	0.027	0.029	0.00040	0.102	27.1
Liqiudambar orientalis	15.0	1.31	0.061	n.d	0.164	16.5
Coniferous Trees						
Pinus brutia	0.022	10.6	0.166	0.00630	1.48	12.3
Pinus nigra	0.051	3.48	0.017	0.00017	0.344	3.89
Pinus sylvestris	0.183	1.57	0.027	0.00043	0.734	2.51
Pinus halepensis	0.046	3.81	0.049	0.00575	0.590	4.50
Pinus pinaster	0.015	0.583	0.022	0.00224	0.171	0.793
Pinus radiata	0.108	0.329	0.007	0.00068	0.361	0.805
Pinus pinea	0.084	1.11	0.006	0.00171	2.20	3.40
Picea orientalis	2.37	3.90	0.098	0.00014	0.439	6.81
Cedrus libani	0.010	0.526	0.045	0.00008	0.363	0.945
Juniperus excelsa	0.025	2.03	0.032	n.d	0.105	2.20
Juniperus phoenicea	0.005	0.611	0.019	0.00012	0.059	0.695
Juniperus oxycedrus	0.010	0.502	0.047	0.00054	0.057	0.616
Juniperus foetidissima	0.028	0.398	0.005	0.00003	0.037	0.468
Cupressus sempervirens	0.049	0.403	0.039	0.00064	0.278	0.769
Abies nordmanniana	2.26	0.329	0.089	0.00008	0.190	2.87
Abies cilicica	14.1	1.16	0.074	0.00011	0.135	15.5
Abies equi-trojani	1.35	1.66	0.009	0.00024	0.554	3.57
Abies nord. sbsp. *Born.*	1.50	2.30	0.036	0.00012	0.502	4.34

n.d.:not detected, [a] Monoterpenes, [b] Sesquiterpenes, [c] Oxygenated sesquiterpenes, [d] Oxygenated compounds

Where • (μg/g.h) is the emission factor, D (g/m^2) is the foliar biomass density, ³ is the environmental correction factor for isoprene and monoterpenes, t (h/yıl) is sunny hours (or vegetation time for deciduous trees) during the year, A (m^2) is the area of tree species and E (kg/year) is the annual total BVOC emissions.

The environmental correction factors, ³ are empirical functions to correct the basal emission rates to a given leaf temperature T and PAR L. The environmental correction factor was calculated for isoprene using Equation (2).

$$^3{}_{iso} = C_L\, C_T \quad (2)$$

Where C_T is the correction factor for temperature and C_L is the correction factor for PAR. These factors are defined by Equations (3) and (4).

$$C_L = \frac{\alpha C_{L1} L}{\sqrt{(1+\alpha^2 L^2)}} \quad (3)$$

$$C_T = \frac{exp C_{T1}(T - T_S)/\, RT_S T}{1 + exp C_{T2}(T - T_M)/\, RT_S T} \quad (4)$$

Where ± (0.0027), C_{L1} (1.066), C_{T1} (95 000 J/mol), C_{T2} (230 000 J/mol) and T_M (314 K), are empirical coefficients; L is the PAR flux (μmol/m^2 s), T_S is the standard reference

temperature (303 K), R (8.314 J/K mol) is the universal gas constant and T (˚C) is the foliar biomass temperature.

The environmental correction factor for temperature is calculated for monoterpenes as in Equation (5).

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

Where ² (0.09/K) is an empirical coefficient.

The equation used for monoterpenes was also used for estimating the other BVOC emissions.

By using the forest database, the amount of leaf biomass in the forested areas of Turkey was calculated. The volume of biomass per unit area (m^3 biomass/m^2 area) taken from the forest database was converted to the weight of biomass per unit area (kg/m^2). The density data (kg/m^3) according to tree species were taken from a study [20].

BVOCs emissions were calculated using standard daily light hours per month depending on area's latitude. The average monthly light hours data for 50 years were retrieved from the Turkish State Meteorological Service (TSMS) database [21].

III. RESULTS

The annual total BVOC emissions over the study area were estimated at 674 ktonnes. The contributions of monoterpenes, isoprene, sequiterpenes, oxygenated sesquiterpenes and oxygenated VOCs to total BVOC emissions were of 72.2%, 15.2%, 1.3%, 0.1%, and 11.2%, respectively.

Fig. 2 shows the spatial distribution of annual total BVOC emissions in Turkey. Maximum isoprene emission was 26.1 tones/km^2. Higher isoprene emissions were calculated in north-west part of Turkey and associated mainly with broad-leaved species. The highest monoterpenes emission was 26.5 tones/km^2. Higher monoterpenes emissions were calculated at the southwest coast of Turkey dominated by coniferous trees.

Isoprene emissions varied from 1.5 ktonnes/month in December to 18.5 ktonnes/month in July. Monoterpenes emissions varied from 20.2 ktonnes/month in December to 64.4 ktonnes/month in July. The emission ranges for sequiterpenes, oxygenated sesquiterpenes and oxygenated VOCs were 0.4-1.2; 0.01-0.06 and 3.1-10.2 ktonnes/month, respectively. The seasonal variation of total biogenic emissions shows that the highest emissions values were in summer months due to higher ambient air temperature and solar radiation and larger vegetation period.

Various BVOC emission inventories have been recently prepared for several European countries [22-26]. Oderbolz et al. (2013) [24] estimated the total annual European emissions as 3 571–5 328 ktonnes/year consisting of 2 964–4 124 ktonnes monoterpenes, 1 450–2 650 ktonnes isoprene and 150–257 ktonnes sesquiterpenes per year. In the same study total BVOC emissions in Turkey was predicted as 884 ktonnes/year (391 ktonnes/year for isoprene, 480 ktonnes/year for monoterpenes and 13 ktonnes/year for sesquiterpenes) that was higher than the total emissions estimated in the present study (674 ktonnes/year). The difference may be in part due to the different emission factors used in these two studies. The emission estimates of the present study are more realistic since they are based on recently measured specific emission factors by field samplings for Turkey.

Symeonidis et al. (2008) [10] estimated isoprene and monoterpene emissions for Greece as 181 and 422 ktonnes/year, respectively. These results showed similarities with the values determined in this study since Greece and Turkey are the geographically located in the same temperature zone. Another study [22] estimated the total BVOC emissions as 440.6 ktonnes for 1992 in Poland where the forested areas cover 8.7 million ha in the country. Isoprene emissions were also estimated as 86.6 ktonnes/year.

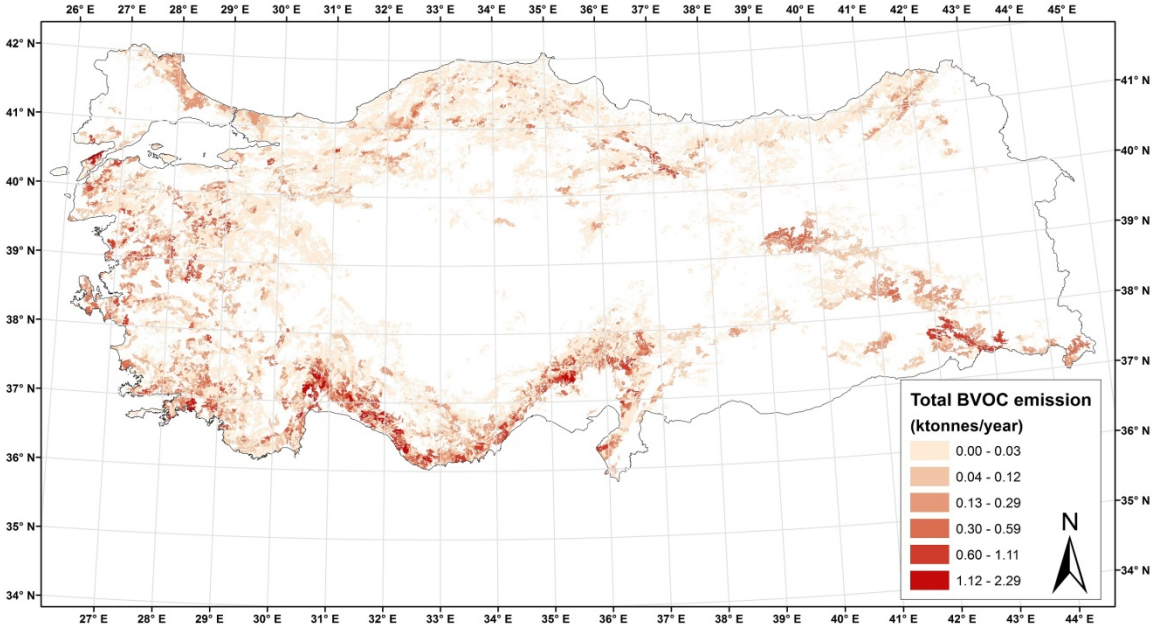

Fig. 2 Distribution of total BVOC emissions in Turkey.

In summary, a spatially and temporally resolved national BVOC emission inventory for Turkey was prepared based on a GIS (ArcGIS 10.1) and the national forest inventory data. This is the first comprehensive BVOC emission inventory prepared for Turkey including specific emission factors. The inventory will also serve as a database for further modeling studies.

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