

DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

**PREPARATION OF A GIS BASED EMISSION
INVENTORY OF BIOGENIC VOLATILE
ORGANIC COMPOUNDS (BVOC) IN TURKEY**

by
Hüsnü KOCA

January, 2015
İZMİR

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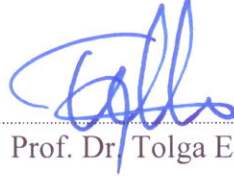
**A Thesis Submitted to the
Graduate School of Natural and Applied Sciences of Dokuz Eylül University
In Partial Fulfillment of the Requirements for the Degree of Master of
Science in the Department of Geographic Information Systems**

**by
Hüsnü KOCA**

**January, 2015
İZMİR**

M.Sc THESIS EXAMINATION RESULT FORM

We have read the thesis entitled “**PREPARATION OF A GIS BASED EMISSION INVENTORY OF BIOGENIC VOLATILE ORGANIC COMPOUNDS (BVOC) IN TURKEY**” completed by **HÜSNÜ KOCA** under supervision of **PROF. DR. TOLGA ELBİR** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.



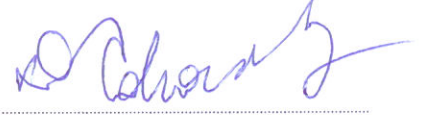
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PREPARATION OF A GIS BASED EMISSION INVENTORY OF BIOGENIC VOLATILE ORGANIC COMPOUNDS (BVOC) IN TURKEY

ABSTRACT

The main source of biogenic volatile organic compounds (BVOCs) is the terrestrial vegetation. Plants synthesize BVOCs in substantial amounts during respiration and photosynthesis and emit to the atmosphere. BVOCs emitted from plants play a significant role in the photochemical processes and contribute to tropospheric ozone and secondary organic aerosol (SOA) formation in the presence of nitrogen oxides (NO_x) and sunlight. As a result of these photochemical reactions, BVOCs indirectly deteriorate air quality and affect human health. The main aim of this study is to inventory BVOC emissions in Turkey. In recent studies, emission rates of isoprene, monoterpenes, sesquiterpenes, and oxygenated VOCs from thirty one commonly grown tree species and seven endemic tree species in the forested areas of Turkey were determined using a dynamic-enclosure sampling method in the field followed by thermal desorption (TD) gas chromatography-mass spectrometry (GC-MS) analysis in the laboratory. Using specific emission rates of tree species obtained from these previous studies, a spatially and temporally resolved national emission inventory of BVOC emissions in the forested areas of Turkey was prepared within the scope of this study. Emissions were distributed to a forested area of about twenty two million ha including coniferous and broadleaved species. This study provides the first detailed spatially high resolution based BVOC emissions inventory in Turkey. The inventory will serve as a database for further modeling studies.

Keywords: Biogenic volatile organic compounds (BVOC), emission factor, emission inventory, Turkey.

TÜRKİYEDEKİ BİYOJENİK UÇUCU ORGANİK BİLEŞİKLERİN CBS TABANLI EMİSYON ENVANTERİNİN HAZIRLANMASI

ÖZ

Biyojenik kökenli uçucu organik bileşiklerin (BVOC) doğadaki en önemli kaynağı ormanlık alanlardır. Bitkiler gerçekleştirdikleri fotosentetik aktiviteler ve solunum sonucunda temel fotosentez ürünleri ile birlikte önemli miktarlarda uçucu organik bileşikler de atmosfere verirler. Bu bileşikler; başta isopren, terpenler (monoterpenler ve sesquiterpenler) ve oksijenli uçucu organik bileşiklerdir. BVOC'ler, atmosferde fotokimyasal reaksiyonlarla ozon ve diğer oksidantların oluşumunda rol oynarlar. Bu fotokimyasal reaksiyonların sonucunda dolaylı olarak hava kalitesinin bozulmasına ve insan sağlığının olumsuz etkilenmesine sebep olurlar. Bu çalışma kapsamında ülke geneli BVOC emisyonlarının hesaplanması hedeflenmiştir. Envanterin hazırlanmasında; dinamik test odası yöntemiyle, arazi çalışmaları sonucunda ülkemiz ormanlarında en yaygın görülen otuz bir ağaç türü ve yedi endemik tür için örneklemeler yapılmış ve sonrasında gaz kromatografisi-kütle spektrometresi ile analizlenmesi sonucu hesaplanan emisyon faktörleri kullanılmıştır. Ülke geneli ibrelili ve geniş yapraklı ağaçların bulunduğu yaklaşık yirmi iki milyon hektarlık ormanlık alan orman envanteri verileri yardımıyla coğrafi bilgi sistemi yazılımlarıyla proses edilerek konumsal dağılımları ulusal ölçekte hazırlanmıştır. Bu çalışma ilk kez ülkemize ait üretilen özel emisyon faktörleri kullanılarak hazırlanan detaylı ulusal bir BVOC emisyon envanteri olması sebebiyle önemlidir. Ayrıca bu envanter çalışması sonraki model çalışmalarına da temel teşkil edecektir.

Anahtar kelimeler: Biyojenik uçucu organik bileşikler (BVOC), emisyon faktörü, emisyon envanteri, Türkiye.

CONTENTS

	Page
THESIS EXAMINATION RESULT FORM	ii
ACKNOWLEDGMENTS	iii
ABSTRACT	iv
ÖZ	v
LIST OF FIGURES	vii
LIST OF TABLES	x
 CHAPTER ONE - INTRODUCTION	 1
1.1 Introduction	1
 CHAPTER TWO – LITERATURE REVIEW	 5
2.1 Definition and Sources of Biogenic Volatile Organic Compounds (BVOCs)..	5
2.2 BVOC Emission Measurement Methods	6
2.3 Previous Studies	7
 CHAPTER THREE – MATERIALS AND METHODS.....	 12
3.1 Study Area	12
3.2 Determination of BVOC Emission Rates.....	22
3.3 Standard BVOC Emission Rates	23
3.4 Calculation of Annual BVOC Emissions.....	29
 CHAPTER FOUR – RESULTS AND DISCUSSION	 35
4.1 Inventory of BVOC Emissions.....	35
 CHAPTER FIVE – CONCLUSIONS AND RECOMMENDATIONS.....	 75
5.1 Conclusions and Recommendations.....	75
 REFERENCES.....	 77

LIST OF FIGURES

	Page
Figure 3.1 Spatial distribution of the forests in Turkey	15
Figure 3.2 Spatial distribution of major tree species in Turkey	17
Figure 3.3 The mean sunshine durations on the basis of province in Turkey for January and July	32
Figure 3.4 PAR values on the basis of province in Turkey for January and July.....	33
Figure 3.5 The mean temperatures on the basis of province in Turkey for January and July	34
Figure 4.1 Spatial distribution of province based total BVOC emissions in Turkey in 2012.....	37
Figure 4.2 Spatial distribution of total BVOC emission for the regional directorates of forestry in Turkey in 2012	38
Figure 4.3 Spatial distribution of total BVOC emission for the forest sub-district directorates in Turkey in 2012	39
Figure 4.4 Spatial distribution of monoterpene emissions in the provinces of Turkey in 2012.....	40
Figure 4.5 Spatial distributions of monoterpene emissions for the regional directorates of forestry in Turkey in 2012.....	41
Figure 4.6 Spatial distributions of monoterpene emissions for the forest sub-district directorates in Turkey in 2012	42
Figure 4.7 Spatial distributions of isoprene emissions in the province of Turkey in 2012.....	43
Figure 4.8 Spatial distributions of isoprene emissions for the regional directorates of forestry in Turkey in 2012.....	44
Figure 4.9 Spatial distribution of isoprene emission for the forest sub-district directorates in Turkey in 2012	45
Figure 4.10 Spatial distribution of oxygenated compounds emissions in the provinces of Turkey in 2012	46

Figure 4.11 Spatial distributions of oxygenated compounds emissions for the regional directorates of forestry in Turkey in 2012	47
Figure 4.12 Spatial distribution of oxygenated compound emission for the forest sub-district directorates in Turkey in 2012	48
Figure 4.13 Spatial distribution of oxygenated sesquiterpenes emissions in the provinces of Turkey in 2012	49
Figure 4.14 Spatial distributions of oxygenated sesquiterpene emissions for the regional directorates of forestry in Turkey in 2012	50
Figure 4.15 Spatial distribution of oxygenated sesquiterpene emission for the forest sub-district directorates in Turkey in 2012	51
Figure 4.16 Spatial distribution of sesquiterpenes emissions in the provinces of Turkey in 2012	52
Figure 4.17 Spatial distribution of sesquiterpene emission for the regional directorates of forestry in Turkey in 2012	53
Figure 4.18 Spatial distribution of sesquiterpene emission for the forest sub-district directorates in Turkey in 2012	54
Figure 4.19 Compositions of BVOC emission groups for the regions of Turkey	56
Figure 4.20 Distribution of monthly total BVOC emissions	59
Figure 4.21 Percentages of the most prominent compounds for each BVOC group.	60
Figure 4.22 Spatial distribution of the total BVOC emissions in the EMEP 50x50 km ² grid system in 2012	62
Figure 4.23 Spatial distribution of monoterpene emissions in the EMEP 50x50 km ² grid system in 2012	63
Figure 4.24 Spatial distribution of oxygenated compounds emission in the EMEP 50x50 km ² grid system in 2012	64
Figure 4.25 Spatial distribution of sesquiterpenes emission in the EMEP 50x50 km ² grid system in 2012	65
Figure 4.26 Spatial distribution of oxygenated sesquiterpenes emission in the EMEP 50x50 km ² grid system in 2012	66
Figure 4.27 Spatial distribution of isoprene emission in the EMEP 50x50 km ² grid system in 2012	67

Figure 4.28 Spatial distribution of the total BVOC emission in the EMEP 0.1°x0.1° grid system in 2012	69
Figure 4.29 Spatial distribution of monoterpenes emission in the EMEP 0.1°x0.1° grid system in 2012	70
Figure 4.30 Spatial distribution of isoprene emission in the EMEP 0.1°x0.1° grid system in 2012.....	71
Figure 4.31 Spatial distribution of oxygenated compounds emission in the EMEP 0.1°x0.1° grid system in 2012	72
Figure 4.32 Spatial distribution of oxygenated sesquiterpenes emission in the EMEP 0.1°x0.1° grid system in 2012	73
Figure 4.33 Spatial distribution of sesquiterpenes emission in the EMEP 0.1°x0.1° grid system in 2012	74

LIST OF TABLES

	Page
Table 3.1 Monthly mean temperatures for each region in Turkey during 1960-2012	13
Table 3.2 Forest areas in Turkey between 1972-2012 (10^6 hectares).....	14
Table 3.3 Growing stocks in the forests of Turkey between 1972-2012 (10^6 m ³).....	14
Table 3.4 Forest areas and growing stocks based on tree species in Turkey in 2012	18
Table 3.5 Tree species and sampled tree numbers in 2012 within the scope of FEMP program.....	19
Table 3.6 The list of the tree species studied within the scope of this study	21
Table 3.7 Studied BVOCs into five groups	24
Table 3.8 Normalized emission rates for coniferous tree species based on dry foliage weight	25
Table 3.9 Normalized emission rates for broad leaved tree species based on dry foliage weight	26
Table 3.10 Normalized emission rates for coniferous tree species based on foliage area.....	27
Table 3.11 Normalized emission rates for broad leaved tree species based on foliage area.....	28
Table 3.12 The dry stem wood densities of each tree species and the calculated $BCEF_f$ parameters	31
Table 4.1 Regional distribution of BVOC emissions in Turkey (t yr ⁻¹).....	55
Table 4.2 BVOC emissions based on tree species (t yr ⁻¹).....	58

CHAPTER ONE

INTRODUCTION

1.1 Introduction

All of the plants in the earth are in interaction with the atmosphere continuously during their natural biological activities. A lot of organic compounds are emitted by those plants since the gases (generally carbon dioxide and oxygen) are mainly originated from some metabolic activities like respiration, photosynthesis, etc. (Laothawornkitkul, Taylor, Paul, & Hewitt, 2009). Those compounds are defined as “Biogenic Volatile Organic Compounds (BVOCs)” in the literature. In recent years, BVOCs have been intensively studied in the literature (Guenther et al., 1995; Hewitt, Karl, Langford, Owen, & Possell, 2011; Penuelas & Staudt, 2010; Street, Owen, Duckham, Boissard, & Hewitt, 1997; Yassaa, Meklati, & Cecinato, 2000). These studies indicate that plants synthesize BVOCs in significant amounts during respiration and photosynthesis and emit to the atmosphere (Dudareva, Negre, Nagegowda, & Orlova, 2006; Kesselmeier & Staudt, 1999; Matsui, 2006).

BVOCs are synthesized by plants through various complex enzymatic reactions and bio-chemical pathways (Dudareva et al., 2006; Kesselmeier & Staudt, 1999; Laothawornkitkul et al., 2009). Some of the BVOCs commonly known as plant hormones are synthesized by plants for communication with other organisms or between different tissues of the same plant (Penuelas & Staudt, 2010). Moreover, BVOCs are also known as defense compounds against to pathogens, herbivores and environmental factors (Farmer & Ryan, 1990; Kegge & Pierik, 2010; Langenheim, 1994; Lerdau, Guenther, & Monson, 1997; Yuan, Himanen, Holopainen, Chen, & Stewart, 2009). There are several factors affecting the emission of BVOCs that are both biological (species, genetics, growth stage, etc.) and environmental (habitat, climate, stress sources etc.) factors (Dudareva et al., 2003; Fall, 1999; Hermsmeier, Schittko, & Baldwin, 2001; Mithofer, Wanner, & Boland, 2005; Ortega & Helmig, 2008).

Isoprene, terpenes (monoterpenes, and sesquiterpenes) and several oxygenated compounds (alcohols, aldehydes, ketones) are known as the most common BVOCs having a large variety of physicochemical characteristics. Especially isoprene, the most dominant BVOC emitted to the atmosphere, responds to both light and temperature because its formation pathway is primarily in the leaf chloroplast, and strictly related to photosynthesis. Besides, it is released immediately after production (Lichtenthaler, Schwender, Disch, & Rohmer, 1997). Monoterpenes are 10-carbon isoprenoids whose emissions are dependent on temperature and, in some cases, on light as well (Fares et al., 2011; Kesselmeier & Staudt, 1999; Lamb, Guenther, Gay, & Westberg, 1987). In the literature, light dependency for some terpene storing and non-storing species emitting large amount of monoterpenes has been established (Bertin et al., 1997; Keenan, Niinemets, Sabate, Gracia, & Penuelas, 2009; Llusia & Penuelas, 1999; Owen, Harley, Guenther, & Hewitt, 2002; Staudt et al., 1997). Monoterpene emissions from many plants have been described as temperature-dependent because their emissions are mainly the result of volatilization from storage organs (Kesselmeier & Staudt, 1999; Niinemets et al., 2002). Sesquiterpenes are another important group of BVOCs whose emissions depend primarily on temperature, but they are formed by a different biosynthetic pathway than isoprene and monoterpenes. These hydrocarbons, containing 15 carbon atoms, have been previously considered to account for a small percentage of global BVOC emissions (Guenther et al., 1995), but recent results indicate that their total emission rates are close to monoterpenes (Ormeno et al., 2010).

BVOCs emitted from plants 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 (Bonn & Moortgat, 2003; Fares et al., 2011; Joutsensaari et al., 2005; Simpson, 1995). They can change the oxidation capacity of the atmosphere due to their high reactivity. Particularly it is known that isoprene is more reactive than many anthropogenic VOCs (Andreae & Crutzen, 1997; Fehsenfeld, 1992; Fuentes et al., 2000; Roselle, 1994; Simpson, 1995). These kinds of compounds have potential for changing physical characteristics and chemical

compositions of the atmosphere directly (Andreae & Crutzen, 1997; Fehsenfeld, 1992; Fuentes et al., 2000; Roselle, 1994).

Estimation of BVOC emissions is a multi-disciplinary research topic, that involves knowledge in botanical science, scientific computing, atmospheric science, and geography (Leung, Wong, Cheung, & Guenther, 2010). Global and regional BVOC emission inventories have been recently prepared in the literature (Curtis, Helmig, Baroch, Daly, & Davis, 2014; Pacheco, Fares, & Ciccioli, 2014; Schurgers, Hickler, Miller, & Arneth, 2009; Warneke et al., 2010; Zemankova & Brechler, 2010). Guenther et al. (1995) estimated that the global BVOC emissions from plants are $1150 \times 10^6 \text{ t C yr}^{-1}$ accounting for more than 90% of global VOC emissions. The study indicated that 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 (Guenther et al., 1995; Guenther et al., 2000). In recent years, determination of regional biogenic emissions emitted from plants have been becoming an interested issue on air pollution control strategies and atmospheric modeling studies (Brilli et al., 2013; Llusia, Penuelas, Alessio, & Ogaya, 2011; Noe, Huve, Niinemets, & Copolovici, 2012; Pacheco et al., 2014; Pokorska et al., 2012a; Sharkey, 2012). In Turkey, anthropogenic air pollutant sources such as industry, traffic, residential heating, etc. were studied in several emissions inventories up to now (Alyuz & Alp, 2014; Elbir & Muezzinoglu, 2004; Deniz & Durmusoglu, 2008; Kara, Mangir, & Bayram, 2014; Muezzinoglu, Elbir, & Bayram, 1998; Ozden, Dogeroglu & Kara, 2008), but natural sources were not included in these inventories due to the lack of national data.

Turkey is a country with a land mass of 78 million ha, of which 21.7 million ha is forest, representing about 27.6% of the country's total land area (General Directorate of Forestry [GDF], 2012). Therefore, specifying the BVOC emission rates from the trees in the Turkish forests is crucial. In recent studies, emission rates from thirty one commonly grown tree species (Aydin et al., 2014) and seven endemic tree species (Yaman et al., 2015) in the forest areas of Turkey were determined using a dynamic-enclosure sampling method in the field followed by thermal desorption (TD)-gas

chromatography/mass spectrometry (GC/MS) analysis in the laboratory. Using specific emission rates of tree species obtained from these previous studies, a comprehensive emission inventory of BVOC emissions in the forest areas of Turkey was prepared within the scope of this study. This study provides the first detailed temporally and spatially high resolution based BVOC emissions inventory in Turkey.

CHAPTER TWO

LITERATURE REVIEW

2.1 Definition and Sources of Biogenic Volatile Organic Compounds (BVOCs)

BVOCs are generally based on biochemical reactions and metabolic processes in biosphere. They mainly include the isoprenoids (isoprene and monoterpenes) as well as alkanes, alkenes, carbonyls, alcohols, esters, ethers, and acids (Kesselmeier & Staudt, 1999). BVOCs are synthesized via several complex biochemical processes. Plants synthesize BVOCs in their various cellular organelles, but then they are stored in specialized secretory structures, thus the plant's metabolic processes are protected from their toxic effects (Dudareva et al., 2006; Laothawornkitkul et al., 2009; Matsui, 2006; Xiang, Milc, Pecchioni, & Chen, 2007). The previous studies indicated that emissions emitted from flower and fruit trees have the widest variety of BVOCs, while emissions from leaves and needles of trees have much fixed types of BVOCs (Laothawornkitkul et al., 2009).

There are a lot of identified BVOCs releases from various plant types in the literature, but there are only several important BVOCs that are critical in terms of atmospheric chemistry on a global scale. Isoprene, terpenes (monoterpenes, and sesquiterpenes) and oxygenated compounds (alcohols, aldehydes, and ketones) are the most common BVOCs as commonly addressed in previous studies (Llusia, Penuelas, Seco, & Filella, 2012; Pokorska et al., 2012b; A. P. Singh, R. Singh, Mina, M. P. Singh, & Varshney, 2011). Isoprene and monoterpenes have particularly higher importance with more considerable emission levels into the atmosphere (Guenther et al., 2006; Helmig, Daly, Milford, & Guenther, 2013; Penuelas & Staudt, 2010). However, sesquiterpenes are important precursors for formation of secondary organic aerosols while estimation of their emission rates is difficult due to their reactivity and low vapor pressures (Bonn & Moortgat, 2003).

BVOCs vary with meteorological conditions, types of plant species, plant characteristics (e.g. physical condition, age, stress) and environmental conditions

(Calfapietra et al., 2013). Biogenic emissions show temporal and spatial variations arising from their dependence on geographic and climatic differences such as ambient temperature and light intensity (Bertin et al., 1997; Calfapietra et al., 2013; Curtis et al., 2014; Guenther, Zimmerman, Harley, Monson, & Fall, 1993; Harley, Guenther, & Zimmerman, 1995; Tingey, Manning, Grothaus, & Burns, 1980).

2.2 BVOC Emission Measurement Methods

In the literature, there is no standardized measurement technique for determination of BVOC emissions. Leaf/needle, branch, canopy or ecosystem level measurements with various methods and equipments have been conducted to determine the biogenic emissions over the world (Baghi, Helmig, Guenther, Duhl, & Daly, 2012; Guenther et al., 1996; Holzke, Hoffmann, Jaeger, Koppmann, & Zimmer, 2006; Matsunaga et al., 2013; Singaas & Sharkey, 2000). Vegetative emission profile of an interested region is mostly obtained by using the species-specific emission factors of the dominating plant species native to the region. They are determined with leaf/needle or branch level measurements either on-site or in laboratory (Komenda, Parusel, Wedel, & Koppmann, 2001; Ortega & Helmig, 2008; Padhy & Varshney, 2005). However, a common method named “dynamic enclosure” is the most frequently used method in the literature (Geron & Arnts, 2010; Joó et al., 2010; Kim, 2001; Matsunaga et al., 2013; Owen et al., 1997; Pokorska et al., 2012a; Wilske et al., 2007).

In the dynamic enclosure method, a leaf/needle, a branch or a whole plant is enclosed in a transparent chamber. The main requirements for an enclosure system are to maintain inside-chamber conditions (e.g. temperature, CO₂ concentration, humidity, light intensity) similar to ambient air. Air circulation is an essential requirement for enclosure systems to prevent unsteady CO₂ concentrations and excessively increasing the inside-air temperatures. Despite the main principal of the enclosure method is invariable, most researchers have constructed their own apparatus and modified the methods unique to their laboratories (Aydin et al., 2014; Harley, Guenther, & Zimmerman, 1995; Ortega & Helmig, 2008; Yaman et al.,

2015). However, a common equation is used for calculation of BVOC amounts emitted from leaves/needles. The emission rate from a dynamic enclosure is calculated by:

$$\varepsilon = \frac{(C_{out} - C_{in})Qt}{m t} \quad (2.1)$$

where, C_{out} and C_{in} are the outlet and inlet concentrations of the compound of interest ($\mu\text{g L}^{-1}$), Q is the flow rate of the enclosure purge air (L min^{-1}), t is the sampling period (h) and m is the dried mass (g) of leaves or needles enclosed. Calculation of the emission rate depends directly on the difference in the concentrations between the outlet and inlet air. The procedure is specially simplified if the inlet air is scrubbed and the BVOC concentrations can be considered negligible.

2.3 Previous Studies

Estimations of BVOC emissions are very complex because there are several environmental parameters affecting those emissions. The effects of several factors such as temperature and photosynthetically-active radiation (PAR) are relatively well known (Dindorf et al., 2006; Graus et al., 2004; Llusia et al., 2012; Monson et al., 2007). In recent years, several parameters such as the period of growing season, types of vegetation species, biomass densities, temperature and PAR values have been studied as critical factors for preparation of emission inventories. In the literature, the emissions can be obtained by manual operations (Pacheco et al., 2014) or remote sensing/satellite images technologies (Feldman et al., 2010; Nichol & Wong, 2011; Wong et al., 2013).

All methodologies for determination of BVOC emissions essentially involve multiplying an emission rate of a type of vegetation by the amount of vegetation in a region. Two major approaches for this operation are available in the literature; (1) performing these calculations based on a genera or preferably specific species, i.e. Turkish red pine, European silver fir, sugar maple, etc. (Curtis et al., 2014; Oderbolz et al., 2013; Simon, Luchetta, & Torres, 2001) or (2) performing the calculations for

general ecosystem types (deciduous or coniferous, shrub land, grass, agricultural land, etc.) (Aleksandropoulou, Torseth, & Lazaridis, 2011; J. Y. Zheng, Z. Y. Zheng, Yu, & Zhong, 2010).

Inventorying of BVOC emissions from the forest areas is crucial input for air quality dispersion models. BVOC emission inventories are widely for modeling of tropospheric ozone and secondary organic aerosol (SOA) formation (Andreae & Crutzen, 1997; Fuentes et al., 2000). Preparation of these emission inventories require major efforts for determination of species-specific emissions factors of different vegetation species. The emissions are usually determined with on-site leaf/needle or branch level measurement.

Emission rates at different environmental conditions should be normalized to standard conditions to compare with different rates published in the literature. The emission rates were generally normalized to standard conditions (30°C and 1000 $\mu\text{mol m}^{-2} \text{s}^{-1}$ PAR) to eliminate variability of environmental conditions. It is crucial to derive species specific normalized emission rates for preparing an emission inventory in a region.

First estimation of total BVOC emissions on the global scale was reported as 175 Tg C yr^{-1} by Went (1960). There were some assumptions in this study like that the period of active vegetation was 100 days per year and the area of plant cover in the overall world was $14 \times 10^7 \text{ km}^2$. Rasmussen & Went (1965) indicated the total BVOC emissions as 200-400 Tg C yr^{-1} for the global scale in subsequent years. The values estimated within the scope of these incomprehensive initial studies even show that biogenic emissions are very important for atmospheric chemistry. Nowadays, it is possible to find many studies about the BVOC emissions released from vegetation that are determined for global or regional scales (Chang, Yu, Chen, & Lin, 2009; Oderbolz et al., 2013; Tsui, Guenther, Yip, & Chen, 2009; Waked, Afif, & Seigneur, 2012; Warneke et al., 2010; Zemankova & Brechler, 2010). A recent study reported that total annual BVOC emissions are 1150 Tg C yr^{-1} in global scale in 1995 (Guenther et al., 1995). Furthermore Lathiere, Hauglustaine, De Noblet-

Ducoudre, Krinner, and Folberth (2005) investigated the total BVOC emissions in different scenarios based on an interactive global BVOC and dynamic vegetation model. The results indicated that the total global BVOC emissions were estimated to be 702 Tg C yr⁻¹ at the preindustrial period (1850s), 725 Tg C yr⁻¹ in 1990s and 1251 Tg C yr⁻¹ at the future (2100).

Several BVOC emission inventories for different spatial scales were studied in the literature. For example; BVOC emission inventories have been prepared on country scales for Hong Kong (Tsui, Guenther, Yip, & Chen, 2009), France (Simon, Dumergues, Ponche, & Torres, 2006), Greece (Symeonidis et al., 2008), China (Tie, Li, Ying, Guenther, & Madronich, 2006), Poland (Isidorov, Jaroszynska, Sacharewicz, & Piroznikow, 1999) and Taiwan (Chang, Yu, Chen, & Lin, 2009). BVOC emissions in some countries were more than anthropogenic VOC emissions. It had been reported that the ratio of emissions of BVOCs to total VOC emissions were 60% in Ukraine, 45% in Spain (Simpson et al., 1999) and more than 50% in America (Guenther, 1997). Some researchers have also prepared BVOC emission inventories on the global scale (Guenther et al., 1995; Lathière et al., 2005). These studies indicated that 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 (Guenther et al., 1995; Guenther et al., 2000). In another study, Lathiere et al. (2006) also estimated approximately similar results with Guenther et al. (1995) for the emissions of isoprene and monoterpenes. A lot of studies were aimed to determine only local isoprene and monoterpene emissions (Dominguez-Taylor, Ruiz-Suarez, Rosas-Perez, Hernandez-Solis, & Steinbrecher, 2007; Guenther et al., 1993; He, Murray, & Lyons, 2000; Wong et al., 2013) while there are a few studies for the other groups of BVOCs such as sesquiterpenes and oxygenated VOCs in the literature (Faubert et al., 2011; Lathiere et al., 2006; Oderbolz et al., 2013).

Emission inventory studies can be considered as the data processing stages after on-site BVOC measurements in a region. Several emission estimation models are widely used for BVOCs in the literature. In United States, the EPA BEIS3.0

(Environmental Protection Agency Biogenic Emissions Inventory System 3) is the most commonly used biogenic emissions model that includes many BVOC components such as isoprene, monoterpenes and other species (Sakulyanontvittaya et al. 2008). The latest two versions; BEIS3.12 and BEIS3.13 include a 1 km vegetation database that resolves forest canopy coverage by tree species, and emission factors for isoprene, 14 monoterpenes and methanol. Additionally, Chang, Chen, and Huang (2005) customized BEIS2.0 to The Taiwan Biogenic Emission Inventory System (TBEIS) with following some fittings on the empirical coefficients used in the BEIS2.0. Additionally, GloBEIS (The Global Biogenic Emission Inventory System) is a BEIS based model which developed by Guenther et al. (1999) and then used to compute annual emissions of isoprene, monoterpenes, and other VOCs from North America (Guenther et al., 2000). Symeonidis et al. (2008) developed a system for estimating biogenic non-methane VOCs emissions based on the GloBEIS model and used this tool to estimate the biogenic emissions from the Balkan Peninsula in Europe. Song et al. (2008) compared the modeled results from GloBEIS with observed isoprene concentrations from ground and aircraft measurements in southeast Texas and found good agreement for diurnal isoprene patterns.

Another model is called MEGAN (Model of Emissions of Gases and Aerosols from Nature) which is a modeling system for estimating the net emissions of gases and aerosols from terrestrial ecosystems into the atmosphere (Guenther et al., 2006). It is driven by land cover, weather and atmospheric chemical composition. MEGAN is a global-scale model with a base spatial resolution of $\sim 1 \text{ km}^2$ that can be used for both regional and global modeling studies (Guenther et al., 2006). MEGAN has been updated to MEGAN2.1 recently (Guenther et al., 2012). MEGAN2.1 includes emission rates of 147 individual compounds in the 19 categories (i.e. isoprene, monoterpenes, sesquiterpenes, other VOCs etc.). MEGAN has been applied to many studies including the estimation of emissions and OH reaction potential of BVOCs from a mixed northern hard-wood forest. MEGAN has been used to estimate both branch-level emissions of individual tree species and whole-canopy fluxes of isoprene, monoterpenes, and sesquiterpenes at specific locations (Ortega et al., 2007) and regional to global scale studies (Heald et al., 2009). Recently,

Sakulyanontvittaya et al. (2008) used MEGAN model to estimate emissions of BVOCs in the United States with a focus on monoterpenes and sesquiterpenes in particular. Some emission factors were provided in this publication based on recent laboratory measurements. When MEGAN was compared with the BEIS3.0, MEGAN was found to estimate higher isoprene emissions but lower monoterpene emissions for the period between July 2001 and January 2002 (Sakulyanontvittaya et al., 2008).

In Turkey, only a few BVOC emission inventories have been prepared recently (Can & Yay, 2014; Symeonidis et al., 2008; Yay, 2007). In the mentioned studies, a land cover dataset depending mainly on satellite data, namely the “Global Land Cover Characteristics Database” was used to estimate BVOC emissions from Turkey. In these studies the vegetation classes and emission rates were studied as much more general. Can and Yay (2014) calculated the BVOC emissions based on Amanos Forest and its surrounding during four months.

CHAPTER THREE

MATERIAL AND METHOD

3.1 Study Area

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 (Aegean, Marmara and Black Sea). The country is situated in large Mediterranean geographical location where climatic conditions are quite temperate, diverse nature of the landscape, and the existence in particular of the mountains that run parallel to the coasts, result in significant differences in climatic conditions from one region to the other. 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 (Atalay, Efe, & Ozturk, 2014; Sekercioglu et al., 2011). In winter season, mean temperature in the country is usually below 5°C and most of the rainfall occurs in this season. Annual precipitation in the Aegean and Mediterranean regions varies from 580 to 1300 mm. The Black Sea region receives the greatest amount of rainfall (2200 mm). Long term annual average precipitation of Turkey is about 640 mm. In Turkey, there are great temperature differences between day-night and winter-summer. Turkey's long term mean temperature is about 13°C (Sensoy, Demircan, Ulupinar, & Balta, 2008). The long term mean temperature for each region in Turkey is given in Table 3.1.

Table 3.1 Monthly mean temperatures for each region in Turkey during 1960-2012 (Turkish State Meteorological Service [TSMS], 2013)

	Mediterranean	Aegean	Black Sea	Marmara	Central Anatolia	Eastern Anatolia	Southeastern Anatolia
January	6.9	4.7	3.1	4.9	-0.6	-5.1	3.4
February	8.0	5.7	3.9	5.6	0.8	-3.7	4.8
March	11.2	8.7	6.6	7.9	5.2	2.0	9.0
April	15.3	13.1	11.1	12.5	10.6	8.9	14.1
May	19.8	18.1	15.4	17.3	15.2	14.3	19.7
June	24.1	22.8	19.3	21.7	19.4	19.2	25.8
July	27.0	25.6	22.0	24.0	22.6	23.4	29.9
August	27.1	25.2	21.9	23.7	22.2	23.2	29.4
September	23.8	21.0	18.4	19.9	17.7	18.3	24.8
October	18.8	15.7	14.0	15.3	12.1	11.6	18.0
November	12.7	10.4	9.0	10.7	6.0	4.3	10.6
December	8.5	6.6	5.3	7.1	1.7	-1.9	5.4
ANNUAL	16.9	14.8	12.5	14.2	11.1	9.5	16.2

Turkey is a country with a land mass of 78 million ha, of which 21.7 million ha is forest, representing about 27.6% of the country's total land area that has increased approximately 1.5 million ha at recent 40 years (Table 3.2) (GDF, 2012). 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. Spatial distribution of the forests in Turkey is shown in Figure 3.1.

Approximately sixty six percent of the forests in Turkey are composed of coniferous species, while the rest consists of broad-leaved species. Almost half of the forests covered by only broad leaved trees are managed as coppice forests. Although Turkey's forests cover 28% of surface area of the country, almost half of these forest areas include canopy cover values of less than 10%, and these areas are classified as

degraded (Table 3.2). Forest areas in Turkey have been increased in the last years (Tables 3.3). When tree growing stock was $976.3 \times 10^6 \text{ m}^3$ in 1972, approximately that value reached to $1500 \times 10^6 \text{ m}^3$ in 2012.

Table 3.2 Forest areas in Turkey between 1972-2012 (10^6 hectares) (GDF, 2012)

Forest Classification	Vegetation type	1972	2005	2010	2012
Productive Forest	Coniferous	4.5	7.0	7.3	7.5
	Deciduous	1.6	1.8	2.3	2.7
	Coppice	2.6	1.6	1.4	1.2
	Total	8.8	10.6	11.2	11.5
Degraded Forest	Coniferous	3.9	5.6	5.7	5.6
	Deciduous	0.8	0.8	1.1	1.3
	Coppice	6.5	4.0	3.4	3.1
	Total	11.3	10.5	10.3	10.1
Total		20.2	21.2	21.5	21.6

Table 3.3 Growing stocks in the forests of Turkey between 1972-2012 (10^6 m^3) (GDF, 2012)

Forest Classification	Vegetation type	1972	2005	2010	2012
Productive Forest	Coniferous	548.7	827.1	910.7	941.7
	Deciduous	210.0	310.3	377.5	423.4
	Coppice	117.7	71.5	59.0	52.3
	Total	876.4	1208.9	1347.4	1417.4
Degraded Forest	Coniferous	44.4	51.0	49.3	47.3
	Deciduous	9.9	12.6	12.2	11.9
	Coppice	45.5	23.6	19.4	17.6
	Total	99.8	87.36	81.05	76.9
Total		976.3	1296.3	1428.5	1494.4

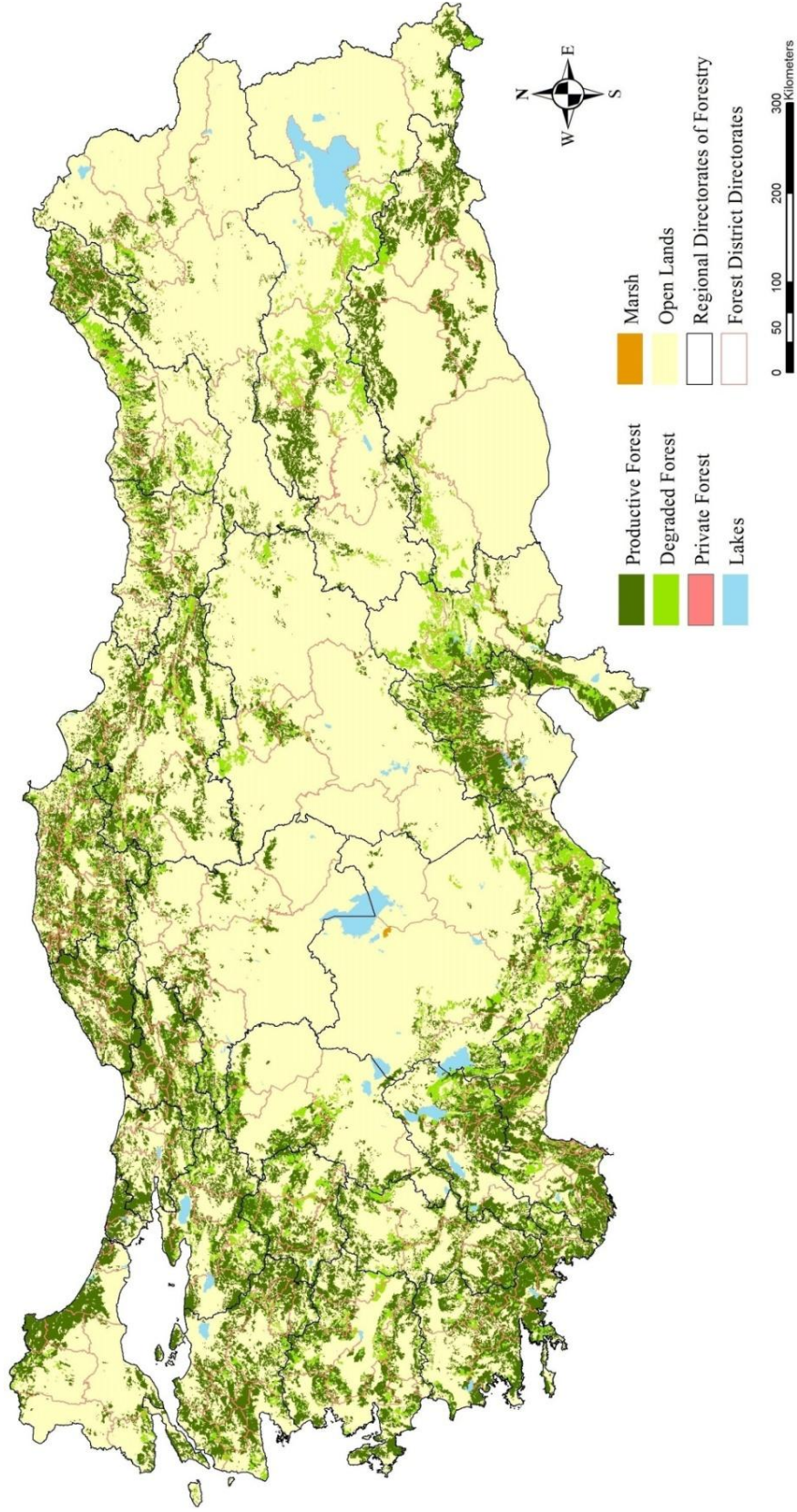


Figure 3.1 Spatial distribution of the forests in Turkey (GDF, 2012)

Turkish forests have rich biological diversity including many coniferous and broad-leaved tree species. Ministry of Forestry and Water Affairs – General Directorate of Forestry (GDF) regularly inventory the data of forest areas, growing stock capacity and increment ratios on annual basis in Turkey. The final forest inventory in Turkey was prepared by GDF for the year of 2012. This inventory consisted of 39 different tree species (Table 3.4). Another database related to the tree species in Turkey is a national monitoring program called “Forest Ecosystem Monitoring Programme (FEMP)” (Tolunay et al., 2013). In this program, a field-based monitoring system based on a 16x16 km grid network covering the whole country’s forests started in 2006. Within the scope of the program, 13602 trees categorized in 61 different tree types were studied in selected sampling areas in 2012. The information about the sampled trees is given in Table 3.5.

Coniferous forests cover the largest area (66%). Among them pines (Turkish red pine (27%); black pine (22%); Scots pine (7%)) cover 56% of all forests. Turkish red pine covering 5.85 million hectares has the biggest areas in Turkey. However, four of common firs (Nordmann fir, Troy fir, Cilician fir, and Uludag fir) cover 3% and the other coniferous species cover 7% of total forest areas. Broad-leaved forests (44%) are mainly formed by oaks including eighteen species, beech (oriental beech) and the other broad-leaved species which cover 24, 9 and 1% of the tree-covered area, respectively. Spatial distribution of major tree species is given in Figure 3.2.

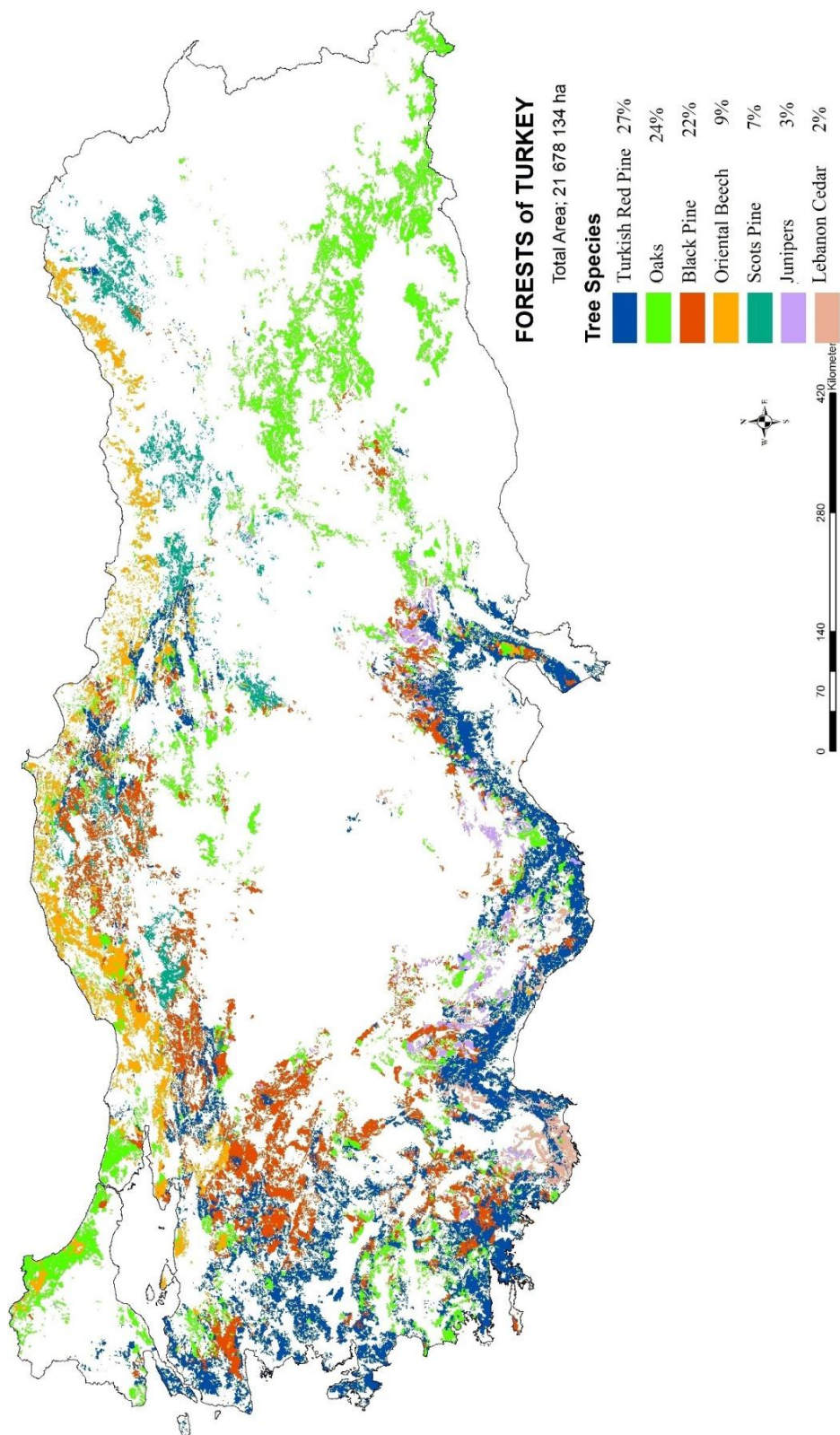


Figure 3.2 Spatial distribution of major tree species in Turkey (GDF, 2012)

Table 3.4 Forest areas and growing stocks based on tree species in Turkey in 2012 (GDF, 2012)

	Tree species	Area (ha)	Growing stock (m³)
CONIFEROUS	Turkish Red Pine	5,854,673	287,866,092
	Black Pine	4,693,060	344,805,505
	Scots Pine	1,479,648	136,757,147
	Firs	670,390	118,340,520
	Oriental Spruce	334,472	62,610,870
	Lebanon Cedar	463,521	27,944,133
	Junipers	575,315	8,594,547
	Stone Pine	89,028	1,878,900
	Mediterranean Cypress	1,470	19,170
	Aleppo Pine	715	17,257
	Maritime Pine	63,668	5,698,095
	Radiata Pine	58	7,120
	Other	145	7,427
	Total	14,226,161	994,546,781
BROAD-LEAVED	Oriental Beech	1,961,660	343,896,424
	Oaks	5,152,562	129,719,530
	Hornbeams	19,962	1,718,131
	Alder	141,119	11,268,978
	Poplars	6,547	140,356
	Sweet Chestnut	111,044	9,445,725
	Ashes	9,444	1,395,596
	Limes	11,523	1,000,543
	Oriental Plane	692	122,801
	River Red Gum	2,528	158,863
	Oriental Sweetgum	499	131,621
	Western Australian Golden Wattle	2,352	52,322
	Black Locust	65	4,484
	Other	31,981	852,694
	Total	7,451,973	499,908,069
TOTAL		21,678,135	1,494,454,850

Table 3.5 Tree species and sampled tree numbers in 2012 within the scope of FEMP program (Tolunay et al., 2013)

Tree species	Sampled tree numbers	%	Tree species	Sampled tree numbers	%
<i>Fagus orientalis</i>	981	7.21	<i>Prunus dulcis</i>	1	0.01
<i>Quercus cerris</i>	1045	7.68	<i>Pyrus communis</i>	9	0.07
<i>Quercus petraea</i>	596	4.38	<i>Salix alba</i>	10	0.07
<i>Quercus pubescens</i>	366	2.69	<i>Salix caprea</i>	5	0.04
<i>Quercus infectoria</i>	256	1.88	<i>Sorbus torminalis</i>	17	0.12
<i>Quercus robur</i>	209	1.54	<i>Tilia platyphyllos</i>	9	0.07
<i>Quercus coccifera</i>	150	1.10	<i>Ulmus glabra</i>	6	0.04
<i>Quercus frainetto</i>	117	0.86	<i>Arbutus unedo</i>	1	0.01
<i>Carpinus orientalis</i>	177	1.30	<i>Arbutus andrachne</i>	17	0.12
<i>Carpinus betulus</i>	129	0.95	<i>Ceratonia siliqua</i>	1	0.01
<i>Castanea sativa</i>	115	0.85	<i>Laurus nobilis</i>	3	0.02
<i>Quercus ilex</i>	14	0.10	<i>Phillyrea latifolia</i>	29	0.21
<i>Quercus macrolepis</i>	38	0.28	<i>Pistacia lentiscus</i>	4	0.03
<i>Quercus hartwissiana</i>	25	0.18	<i>Pistacia terebinthus</i>	32	0.24
<i>Quercus libani</i>	53	0.39	<i>Crataegus monogyna</i>	11	0.08
<i>Quercus brantii</i>	11	0.08	Other broad leaved sp.	209	1.54
<i>Quercus ithaburensis</i>	7	0.05	<i>Pinus brutia</i>	3253	23.92
<i>Acer campestre</i>	18	0.13	<i>Pinus nigra</i>	2485	18.27
<i>Acer platanoides</i>	18	0.13	<i>Pinus sylvestris</i>	800	5.88
<i>Acer pseudoplatanus</i>	3	0.02	<i>Juniperus excels</i>	783	5.76
<i>Alnus glutinosa</i>	72	0.53	<i>Abies nordmanniana</i>	260	1.91
<i>Corylus avellana</i>	14	0.10	<i>Cedrus libani</i>	180	1.32
<i>Fraxinus angustifolia</i>	12	0.09	<i>Picea orientalis</i>	134	0.99
<i>Fraxinus excelsior</i>	8	0.06	<i>Abies cilicica</i>	109	0.80
<i>Fraxinus ornus</i>	1	0.01	<i>Juniperus foetidissima</i>	125	0.92
<i>Juglans regia</i>	3	0.02	<i>Juniperus oxycedrus</i>	108	0.79
<i>Olea europaea</i>	39	0.29	<i>Juniperus communis</i>	32	0.24
<i>Ostrya carpinifolia</i>	27	0.20	<i>Cupressus sempervirens</i>	1	0.01
<i>Platanus orientalis</i>	27	0.20	<i>Pinus pinaster</i>	14	0.10
<i>Populus nigra</i>	8	0.06	<i>Pinus pinea</i>	30	0.22
<i>Populus tremula</i>	94	0.69	Other coniferous sp.	288	2.12
<i>Prunus avium</i>	3	0.02	Total	13,602	100

Thirty eight tree species that cover the 99.85% of national forest areas in Turkey were studied for determination of BVOC emissions in the previous studies (Aydin et al., 2014; Yaman et al., 2015). The remained species like Douglas fir (*Pseudotsuga menziesii*), Teada pine (*Pinus teada*), etc. are not typical tree species covering very small areas in Turkish, and therefore, they were not included in this study.

Eighteen coniferous and twenty broad-leaved trees were studied in this study. The list of the studied species is given in Table 3.6. Pine and spruce are always green and coniferous trees, and they are subgroup of *Pinaceae* family. In case junipers and Mediterranean cypress are the members of *Cupressaceae* family. Radiata pine and maritime pine are exotic species in Turkey, but they were included in this study. Due to their high growth rate, these species are widely used for afforestation facilities in Turkey. Several endemic species such as Troy fir, Uludag fir, oriental sweetgum, bozpirnal oak, Ispir oak and vulcanic oak were also studied in the study. Oaks, oriental beech and sweet chestnut are the members of *Fagaceae* family. River red gum, black locust and Western Australian golden wattle are not natural species of our country (Yaltirik, 1988a). Although river red gum, Western Australian golden wattle and bozpirnal oak are broad leaved species, they do not lose their leaves in winter season.

Table 3.6 The list of the tree species studied within the scope of this study

Coniferous Trees (Ever-green species)			Broad-leaved Trees (Deciduous species)		
Genus	Species	Binomial Name (Latin)	Genus	Species	Binomial Name (Latin)
Pine	Turkish Red Pine	<i>Pinus brutia ten.</i>	Oak	Sessile Oak	<i>Quercus petraea</i>
	Black Pine	<i>Pinus nigra</i>		Turkey Oak	<i>Quercus cerris</i>
	Scots Pine	<i>Pinus sylvestris</i>		Vulcanic Oak	<i>Quercus vulcanica*</i>
	Stone Pine	<i>Pinus pinea</i>		Ispir Oak	<i>Quercus macr. subsp. syspir.*</i>
	Maritime Pine	<i>Pinus pinaster</i>		Boz Pirnal Oak	<i>Quercus aucheri*</i>
	Radiata Pine	<i>Pinus radiata</i>	Poplar	Eastern Cottonwood	<i>Populus deltoids</i>
	Aleppo Pine	<i>Pinus halepensis</i>		European Aspen	<i>Populus tremula</i>
Juniper	Greek Juniper	<i>Juniperus excels</i>	Acacia	Western Australian Golden Wattle	<i>Acacia cyanophylla**</i>
	Prickly Juniper	<i>Juniperus oxycedrus</i>		Black Locust	<i>Robinia pseudo-acacia</i>
	Phoenicean Juniper	<i>Juniperus phoenicea</i>	Hornbeam	Oriental Hornbeam	<i>Carpinus orientalis</i>
	Foetid Juniper	<i>Juniperus foetidissima</i>		European Hornbeam	<i>Carpinus betulus</i>
Fir	Nordmann Fir	<i>Abies nordmanniana</i>	Ash	European Ash	<i>Fraxinus excelsior</i>
	Troy Fir	<i>Abies equi-trojani*</i>		South European Flowering Ash	<i>Fraxinus ornus</i>
	Cilician Fir	<i>Abies cilic. subsp. isaur.*</i>	Plane	Oriental Plane	<i>Platanus orientalis</i>
	Uludag Fir	<i>Abies nord. subsp. born.*</i>	Eucalyptus	River Red Gum	<i>Eucalyptus camaldulensis**</i>
Cedar	Lebanon Cedar	<i>Cedrus libani</i>	Beech	Oriental Beech	<i>Fagus orientalis</i>
Cypress	Mediterranean Cypress	<i>Cupressus sempervirens L.</i>	Sweetgum	Oriental Sweetgum	<i>Liquidambar orientalis*</i>
			Alder	European Alder	<i>Alnus glutinosa</i>
Spruce	Oriental Spruce	<i>Picea orientalis</i>	Lime	Silver Lime	<i>Tilia argentea</i>
			Chestnut	Sweet Chestnut	<i>Castanea sativa</i>

*Endemic species

**Ever-green species

3.2 Determination of BVOC Emission Rates

Monoterpene emissions were calculated based on the ambient air temperature using the following equation (Guenther et al., 1993):

$$\varepsilon_{mtp} = \varepsilon_{mtps} \gamma_{mtp} \quad (3.1)$$

$$\gamma_{mtp} = \exp \beta (T - T_s) \quad (3.2)$$

where, ε_{mtp} is emission rate for monoterpenes, ε_{mtps} is normalized emission rate under standard conditions (30°C), T is the ambient temperature (K), T_s is the temperature at normal conditions (303 K), β is the empirical constant (0.1 K⁻¹ for monoterpenes and oxygenated BVOCs and 0.17 K⁻¹ for sesquiterpenes and oxygenated sesquiterpenes) and γ_{mtp} is the correction factor.

Guenther et al. (1993) have developed another algorithm to calculate isoprene rates that are dependent with temperature and light intensity. Isoprene emission rates at any temperature and PAR were determined by multiplying measured emission rate (ε_s) with temperature (C_T) and light (C_L) correction factors.

$$\varepsilon_{iso} = \varepsilon_{isos} \gamma_{iso} \quad (3.3)$$

$$\gamma_{iso} = C_L C_T \quad (3.4)$$

where, ε_{iso} is the emission factor for isoprene, ε_{isos} is the emission factor under standard conditions, C_T and C_L are the temperature and light related coefficients, respectively, and γ_{iso} is the correction factor.

Light (C_L) (Guenther et al., 1993) and temperature (C_T) (Dominguez-Taylor et al., 2007) based correction factors were formulated as:

$$C_L = \frac{\alpha C_{L1} L}{\sqrt{(1 + \alpha^2 L^2)}} \quad (3.5)$$

where, C_{L1} (1.066) and α (0.0027) are the empirical constants, L is the PAR value ($\mu\text{mol m}^{-2} \text{s}^{-1}$).

$$C_T = \frac{\exp C_{T1}(T - T_S)/RT_S T}{1 + \exp C_{T2}(T - T_M)/RT_S T} \quad (3.6)$$

where, T is the ambient temperature (K), R is the ideal gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), T_S is the temperature under standard conditions (303 K), T_M (314 K), C_{T1} (95000 J mol^{-1}) and C_{T2} ($230000 \text{ J mol}^{-1}$) are the empirical constants.

The emission rates measured at different environmental conditions were calculated and corrected under standard conditions [i.e., monoterpenes and other BVOCs were normalized using the Equations (3.1), (3.2), and isoprene was calculated using equations (3.3), (3.4), (3.5), and (3.6)].

3.3 Standard BVOC Emission Rates

BVOC emission inventory was prepared by using emission rates of tree species for 65 different BVOCs analyzed in previous studies (Aydin et al., 2014; Yaman et al., 2015). Table 3.7 shows the list of these compounds in detail. Tables 3.8-3.9 summarize the reported average normalized emission rates of 65 BVOCs based on dry foliage weight for 38 tree species in Turkey. Normalized emission rates based on foliage area into five basic BVOC groups (isoprene, monoterpenes, sesquiterpenes, oxygenated sesquiterpenes and oxygenated compounds) were also given in Tables 3.10-3.11.

Table 3.7 Studied BVOCs into five groups

CAS No	Compounds	CAS No	Compounds
	Isoprene		Oxygenated Compounds
78-79-5	Isoprene	78-93-3	2-Butanone
	Monoterpenes	534-22-5	Furan, 2-methyl-
508-32-7	Tricyclene	115-18-4	2-Methyl-3-buten-2-ol
80-56-8	Alpha-Pinene	4170-30-3	Crotonaldehyde
471-84-1	Alpha-Fenchene	5780-40-5	Butyl aldoxime, 3-methyl-, syn-
79-92-5	Camphene	470-67-7	Isocineole
3387-41-5	Sabinene	104-93-8	p-Methylanisole
127-91-3	Beta-Pinene	470-82-6	Eucalyptol
123-35-3	Beta-Myrcene	111-87-5	1-Octanol
99-83-2	l-Phellandrene	18479-58-8	Dihydromyrcenol
13466-78-9	Delta 3-Carene	586-81-2	Gamma-Terpineol
99-86-5	Alpha-Terpinene	1195-79-5	L-Fenchone
535-77-3	m-Cymene	15186-51-3	Rosefuran
138-86-3	Limonene	78-69-3	Tetrahydrolinalool
555-10-2	Beta-Phellandrene	78-70-6	Linalool L
08-10-6874	cis-Ocimene	1632-73-1	D-Fenchyl alcohol
3779-61-1	trans-beta-Ocimene	41702-60-7	2-Methyl-6-methylene-1,7-octadien-3-one
99-85-4	Gamma-Terpinene	1728-46-7	2-tert-Butylcyclohexanone
586-62-9	Terpinolene	7322-63-6	trans-Dihydro-b-terpineol
673-84-7	Alloocimene	76-22-2	Camphor
460-01-5	2,6-Dimethyl-1,3,5,7-octatetraene, E	10385-78-1	Isoborneol
99-87-6	p-isopropyl toluene (p-Cymene)	34413-88-2	d-Pinocarvone
51911-82-1	(E)-4,8-Dimethyl-1,3,7-nonatriene	13491-79-7	2-(1,1-dimethylethyl)-cyclohexanol
	Sesquiterpenes	562-74-3	4-Terpineol
3856-25-5	Copaene	98-55-5	Alpha-Terpineol
13744-15-5	Beta-cubebene		Oxygenated Sesquiterpenes
1135-66-6	Isolongifolene	93-15-2	Methyl Eugenol
469-61-4	Alpha-cedrene	77171-55-2	(-)-Spathulenol
87-44-5	trans-Caryophyllene	489-86-1	Guaiol
6753-98-6	Alpha-humulene		
18794-84-8	Beta-farnesene		
23986-74-5	Germacrene-D		
17699-05-7	Alpha-Bergamotene		
502-61-4	E,E-Alpha-Farnesene		
17066-67-0	Beta-selinene		
10208-80-7	Alpha-murolene		
39029-41-9	Gamma-cadinene		
24406-05-1	Alpha-cadinene		
17627-44-0	Cis-Alpha-Bisabolene		

Table 3.8 Normalized emission rates for coniferous tree species based on dry foliage weight

	Emission Rates ($\mu\text{g g}^{-1} \text{h}^{-1}$)				
	Isoprene	Monoterpenes	Sesquiterpenes	Oxygenated Sesquiterpenes	Oxygenated Compounds
Turkish Red Pine*	0.022±0.019	10.6±4.6	0.16±0.13	0.0061±0.0087	1.48±1.36
Black Pine*	0.051±0.024	3.83±3.50	0.072±0.097	0.00037±0.00023	0.38±0.29
Scots Pine*	0.18±0.01	1.53±0.68	0.023±0.019	0.00039±0.00023	0.71±0.32
Stone Pine*	0.084±0.062	1.24±0.95	0.0087±0.0064	0.0022±0.0015	2.49±1.57
Aleppo Pine*	0.046±0.047	3.53±1.72	0.034±0.051	0.0032±0.058	0.66±0.26
Maritime Pine*	0.015±0.0068	0.59±0.27	0.018±0.017	0.0010±0.0015	0.18±0.14
Radiata Pine*	0.11±0.10	0.33±0.26	0.0059±0.0039	0.00062±0.00034	0.35±0.25
Nordmann Fir*	2.26±1.4	0.32±0.21	0.076±0.075	0.00010±0.00013	0.19±0.11
Troy Fir**	1.34±1.11	1.58±1.58	0.0064±0.0055	0.00016±0.00019	0.53±0.44
Cilician Fir**	14.1±10.5	1.15±0.76	0.067±0.05	0.0001±0.0001	0.13±0.11
Uludag Fir**	1.50±1.39	2.27±1.26	0.032±0.038	0.00011±0.00007	0.49±0.20
Greek Juniper*	0.025±0.024	1.93±1.05	0.021±0.012	-	0.099±0.044
Prickly Juniper*	0.0099±0.0098	0.46±0.16	0.026±0.031	0.00028±0.00029	0.052±0.043
Phoenicean Juniper*	0.0054±0.0042	0.55±0.39	0.0081±0.0082	0.00005±0.00005	0.052±0.025
Foetid Juniper*	0.028±0.0045	0.40±0.26	0.0065±0.0053	0.00004±0.00004	0.037±0.016
Lebanon Cedar*	0.010±0.0082	0.48±0.45	0.028±0.037	0.00004±0.00006	0.34±0.36
Mediterranean Cypress*	0.049±0.062	0.34±0.24	0.0092±0.0104	0.00024±0.00016	0.18±0.12
Oriental Spruce*	2.37±1.79	3.69±1.69	0.069±0.067	0.0001±0.00008	0.43±0.23
					6.5±3.77

*Aydin et al. (2014)

**Yaman et al. (2015)

Table 3.9 Normalized emission rates for broad leaved tree species based on dry foliage weight

	Emission Rates ($\mu\text{g g}^{-1} \text{h}^{-1}$)					
	Isoprene	Monoterpenes	Sesquiterpenes	Oxygenated Sesquiterpenes	Oxygenated Compounds	TOTAL
Sessile Oak*	9.63 $\pm$ 7.83	0.013 $\pm$ 0.004	0.009 $\pm$ 0.0044	0.0032 $\pm$ 0.0011	0.039 $\pm$ 0.011	9.70 $\pm$ 7.85
Turkey Oak*	0.079 $\pm$ 0.078	0.021 $\pm$ 0.006	0.008 $\pm$ 0.0058	0.016 $\pm$ 0.014	0.044 $\pm$ 0.028	0.17 $\pm$ 0.13
Vulcanic Oak**	9.79 $\pm$ 7.57	0.055 $\pm$ 0.062	0.02 $\pm$ 0.02	0.000064 $\pm$ 0.00086	0.059 $\pm$ 0.040	8.29 $\pm$ 7.95
Ispir Oak**	19.2 $\pm$ 19.0	0.1 $\pm$ 0.06	0.08 $\pm$ 0.097	0.00019 $\pm$ 0.00022	0.091 $\pm$ 0.060	19.4 $\pm$ 19.0
BozPirnal Oak**	0.028 $\pm$ 0.026	0.78 $\pm$ 0.63	0.0022 $\pm$ 0.0023	0.000051 $\pm$ 0.000083	0.029 $\pm$ 0.019	0.84 $\pm$ 0.62
Eastern Cottonwood*	4.72 $\pm$ 5.26	0.067 $\pm$ 0.044	0.017 $\pm$ 0.016	0.00011 $\pm$ 0.0001	0.021 $\pm$ 0.009	4.82 $\pm$ 5.33
European Aspen*	22.4 $\pm$ 11.2	0.22 $\pm$ 0.18	0.014 $\pm$ 0.012	0.000146 $\pm$ 0.00021	0.028 $\pm$ 0.011	22.7 $\pm$ 11.4
Western Australian Golden Wattle*	0.20 $\pm$ 0.20	0.088 $\pm$ 0.172	0.0056 $\pm$ 0.0055	0.00029 $\pm$ 0.00018	0.037 $\pm$ 0.025	0.33 $\pm$ 0.40
Black Locust*	12.4 $\pm$ 11.1	0.071 $\pm$ 0.029	0.0089 $\pm$ 0.0037	0.0022 $\pm$ 0.0028	0.038 $\pm$ 0.029	12.5 $\pm$ 11.2
Oriental Hornbeam*	0.060 $\pm$ 0.050	0.065 $\pm$ 0.081	0.017 $\pm$ 0.011	0.0011 $\pm$ 0.0026	0.14 $\pm$ 0.13	0.29 $\pm$ 0.27
European Hornbeam*	0.10 $\pm$ 0.11	0.0093 $\pm$ 0.0032	0.011 $\pm$ 0.006	-	0.036 $\pm$ 0.018	0.16 $\pm$ 0.14
European Ash*	0.011 $\pm$ 0.0049	0.012 $\pm$ 0.011	0.0011 $\pm$ 0.0003	0.00002 $\pm$ 0.00003	0.015 $\pm$ 0.007	0.039 $\pm$ 0.023
South European Flowering Ash*	0.014 $\pm$ 0.016	0.0047 $\pm$ 0.0026	0.0042 $\pm$ 0.0034	0.00002 $\pm$ 0.00002	0.0074 $\pm$ 0.0041	0.03 $\pm$ 0.026
Oriental Plane*	27.0 $\pm$ 25.3	0.025 $\pm$ 0.006	0.018 $\pm$ 0.016	0.00056 $\pm$ 0.00046	0.096 $\pm$ 0.052	27.1 $\pm$ 25.4
Oriental Sweetgum**	15.0 $\pm$ 15.2	1.12 $\pm$ 0.82	0.018 $\pm$ 0.011	-	0.14 $\pm$ 0.045	16.3 $\pm$ 15.6
River Red Gum*	5.14 $\pm$ 4.04	0.18 $\pm$ 0.18	0.090 $\pm$ 0.107	0.0011 $\pm$ 0.0007	0.43 $\pm$ 0.55	5.84 $\pm$ 4.89
Silver Lime*	0.077 $\pm$ 0.081	0.51 $\pm$ 0.22	0.0067 $\pm$ 0.0052	0.00061 $\pm$ 0.00064	0.096 $\pm$ 0.088	0.69 $\pm$ 0.40
Sweet Chestnut*	0.38 $\pm$ 0.5	14.2 $\pm$ 7.5	0.026 $\pm$ 0.026	0.00049 $\pm$ 0.00044	0.28 $\pm$ 0.10	14.9 $\pm$ 8.10
Oriental Beech*	0.047 $\pm$ 0.044	0.021 $\pm$ 0.013	0.0028 $\pm$ 0.0024	0.0022 $\pm$ 0.0024	0.016 $\pm$ 0.01	0.09 $\pm$ 0.071
European Alder*	0.018 $\pm$ 0.015	0.13 $\pm$ 0.14	0.0044 $\pm$ 0.002	-	0.056 $\pm$ 0.038	0.21 $\pm$ 0.20

*Aydin et al. (2014)

**Yaman et al. (2015)

Table 3.10 Normalized emission rates for coniferous tree species based on foliage area

	Emission Rates ($\mu\text{g m}^{-2} \text{h}^{-1}$)				
	Isoprene	Monoterpenes	Sesquiterpenes	Oxygenated Sesquiterpenes	Oxygenated Compounds
Turkish Red Pine*	7.86±7.06	3754±1537	60.2±50.3	2.30±3.34	541±516
Black Pine*	25.2±4.81	1714±1595	32.3±44.7	0.17±0.11	162±113
Scots Pine*	58.2±32.4	481±204	7.77±6.55	0.12±0.08	229±117
Stone Pine*	28.1±21.6	418±323	2.87±2.07	0.75±0.49	828±519
Aleppo Pine*	14.3±14.6	1155±646	10.9±15.9	1.13±2.15	182±41
Maritime Pine*	8.00±4.03	315±163	9.60±9.11	0.54±0.78	68.9±34.0
Radiata Pine*	30.9±30.8	93.5±76.7	1.70±1.17	0.18±0.11	100±74
Nordmann Fir*	821±512	118±81	27.1±26.7	0.034±0.044	71±43.1
Troy Fir**	395±279	554±629	2.2±1.7	0.049±0.056	178±142
Cilician Fir**	5472±3559	461±286	27.2±19.4	0.044±0.045	52.8±43.6
Uludag Fir**	567±552	892±621	12.3±15.3	0.039±0.025	178±83
Greek Juniper*	13.1±12.1	1026±528	11±5.9	-	53.4±24.0
Prickly Juniper*	4.30±4.22	271±153	12.1±14.8	0.13±0.13	23.0±18.2
Phoenicean Juniper*	4.33±3.61	426±305	6.11±6.08	0.036±0.04	41.1±20.3
Foetid Juniper*	15.9±2.53	222±141	3.48±2.65	0.019±0.021	20.9±9.1
Lebanon Cedar*	4.75±3.71	235±231	12.1±15.7	0.021±0.029	161±175
Mediterranean Cypress*	22.1±32.2	121±80	3.58±3.91	0.10±0.07	66.7±42.0
Oriental Spruce*	911±703	1384±614	26.8±26.2	0.038±0.030	204±82
					2525±1426

*Aydin et al. (2014)

**Yaman et al. (2015)

Table 3.11 Normalized emission rates for broad leaved tree species based on foliage area

	Emission Rates ($\mu\text{g m}^{-2} \text{h}^{-1}$)				
	Isoprene	Monoterpenes	Sesquiterpenes	Oxygenated Sesquiterpenes	Oxygenated Compounds
Sessile Oak*	1056±812	1.38±0.40	1.07±0.44	0.36±0.12	4.53±1.70
Turkey Oak*	6.60±6.68	1.79±0.64	0.63±0.46	1.32±1.13	3.79±2.58
Vulcanic Oak**	1193±927	6.74±7.63	2.37±2.41	0.0075±0.01	7.22±5.03
Ispir Oak**	2745±2623	10.95±5.44	12.04±14.29	0.030±0.033	15.8±7.25
BozPimal Oak**	7.06±6.22	206±164	0.58±0.59	0.013±0.021	7.62±4.97
Eastern Cottonwood*	491±542	6.52±4.90	1.80±1.68	0.012±0.013	2.33±1.17
European Aspen*	2114±963	21.6±16.2	1.41±1.02	0.046±0.022	2.68±0.87
Western Australian Golden Wattle*	36.5±37.6	17.8±36.0	1.0±0.98	0.051±0.030	6.74±4.53
Black Locust*	857±752	5.05±2.22	0.63±0.28	0.16±0.20	2.73±2.12
Oriental Hornbeam*	4.15±3.24	4.26±4.90	1.16±0.72	0.068±0.159	9.59±8.18
European Hornbeam*	8.34±9.58	0.94±0.34	1.00±0.66	-	2.21±0.88
European Ash*	1.17±0.38	1.50±1.31	0.11±0.030	0.0029±0.0039	1.64±0.98
South European Flowering Ash*	1.32±1.37	0.45±0.24	0.40±0.33	0.0020±0.0023	0.72±0.38
Oriental Plane*	2310±2325	2.10±0.77	1.59±1.59	0.047±0.041	6.27±3.21
Oriental Sweetgum**	1240±1248	88.6±67.9	1.61±0.98	-	11.8±3.8
River Red Gum*	831±704	31.6±34.3	7.40±8.96	0.18±0.12	68.5±87.3
Silver Lime*	7.00±7.38	46.8±19.0	0.65±0.45	0.056±0.057	8.73±7.90
Sweet Chestnut*	39.7±51.5	1255±791	2.83±2.72	0.055±0.047	26.0±9.3
Oriental Beech*	3.94±3.90	1.59±0.83	0.21±0.16	0.18±0.20	1.29±0.79
European Alder**	1.81±1.56	11.2±11.3	0.47±0.16	-	5.26±3.64
					18.7±16.7

*Aydin et al. (2014)

**Yaman et al. (2015)

3.4 Calculation of Annual BVOC Emissions

Emission calculations were based on a commonly used method in the literature (European Environment Agency [EEA], 2009). According to this method; annual emissions of isoprene, monoterpenes, sesquiterpenes, oxygenated sesquiterpenes and other oxygenated compounds are calculated using Equations 3.7 and 3.8:

$$\text{Emission}_{\text{isoprene}}(\text{kg/year}) = \sum_{v=v_1}^{v_2} \varepsilon A D \gamma_{\text{iso}} N_d(v) N_L(v) \quad (3.7)$$

where; v_1 and v_2 are the beginning and the end of the growing season for a particular vegetation type, ε is the normalized emission rate ($\mu\text{g g}^{-1} \text{h}^{-1}$), A is the area covered by the existing tree species (m^2), D is the foliage density (kg m^{-2}), γ_{iso} , is the correction factor for isopren, N_d is the number of days in a month that the vegetation continues (d m^{-1}) and N_L is the number of light hours per day (h d^{-1}) in the growing season.

Emissions of monoterpene and the other BVOCs are also described by this equation. For the yearly emissions of monoterpenes and the other BVOCs there is no light dependency and the determination is performed for 24 hours per day. In the literature, there are a large number of studies related to preparing of emission inventories with the same assumption (Monson, Lerdau, Sharkey, Schimel, & Fall, 1995; Staudt et al., 1997).

$$\text{Emission}_{\text{MTs-OVOC}}(\text{kg/year}) = \sum_{v=v_1}^{v_2} \varepsilon A D \gamma_{\text{mtp}} N_d(v) 24 \quad (3.8)$$

Similarly, for other types of BVOC (sesquiterpenes, oxygenated sesquiterpenes and other oxygenated compounds), it is recommended to use Equation 3.8 for the calculations of annual emissions (EEA, 2009).

Turkish forest inventory is predominantly derived from the works based on forest management plans, field studies and remote sensing methods used by GDF. In this study; the forest inventory in 2012 was obtained directly from GDF. This inventory contains the data of the tree species, the amount of growing stock (m^3) and the forest condition (coppice-cover). Spatial distribution of emissions was studied by a geographic information system software (ARCGIS 10.0). In the presence of the forest inventory, the information regarding tree species was only based on genus; however there was no information on subspecies. For example; oaks that constitute 24% of the Turkey's forests have 18 subspecies (T.C. Ministry of Forest and Water Affairs, 2013). In the forest inventory, the area having any types of these oaks spread is defined with a general code as "oak". A similar approach was applied to firs, junipers, ashes, hornbeams and poplars that involve more than one subspecies.

For calculation of the regional emissions, the dry foliage weight per unit area in the forest has to be determined. Calculation of the foliage mass in the forests of Turkey was made as following:

$$Y_a = S_a BCEF_f \quad (3.9)$$

where; Y represents foliage weight (t), S represents the growing stock (m^3), $BCEF_f$ represents the biomass conversion and expansion factor that converts the growing stock into the foliage weight ($t\ m^{-3}$), and a represents the tree species.

The mass of the different tree components (stem, branch, leaf, and root) in a forest area must be determined through various regression equations. However, these equations are usually used for the local studies. Working in larger areas or using national forest inventory data, the conversion of growing stock value into mass requires certain factors (biomass expansion and conversion factors) (Intergovernmental Panel on Climate Change [IPCC], 2006).

$$BCEF_i = \frac{B_i}{S} \quad (3.10)$$

where; $BCEF_i$ represents tree weight expansion and the conversion factor ($t\ m^{-3}$), B represents tree weight (t), S represents the amount of growing stock (m^3), i represents the components of tree species.

In Equation 3.9, $BCEF_f$ parameters were used for the estimation of leaf/needle mass through volume of stem over bark. These values are given in Table 3.12.

Table 3.12 The dry stem wood densities of each tree species and the calculated $BCEF_f$ parameters (Tolunay et al., 2013)

Coniferous Trees	Wood Density ($t\ m^{-3}$)	$BCEF_f$	Broad leaved trees	Wood Density ($t\ m^{-3}$)	$BCEF_f$
Turkish Red Pine	0.478	0.094	Oriental Beech	0.530	0.048
Black Pine	0.470	0.011	Oaks	0.570	0.080
Scots Pine	0.426	0.085	Hornbeams	0.630	0.145
Firs	0.350	0.121	European Alder	0.407	0.030
Oriental Spruce	0.358	0.052	Poplars	0.350	0.059
Lebanon Cedar	0.430	0.080	Sweet Chestnut	0.480	0.020
Junipers	0.460	0.062	Ashes	0.562	0.059
Stone Pine	0.470	0.062	Silver Lime	0.550	0.059
Mediterranean Cypress	0.431	0.062	Oriental Plane	0.550	0.059
Aleppo Pine	0.480	0.062	River Red Gum	0.550	0.059
Maritime Pine	0.440	0.062	Oriental Sweetgum	0.468	0.059
Radiata Pine	0.380	0.062	Western Australian Golden Wattle	0.550	0.059
Other	0.431	0.062	Black Locust	0.680	0.091
			Other	0.550	0.059

On the next stage, the total leaf mass in the forests was calculated by multiplying the growing stock value according to the species and $BCEF_f$ parameter.

Determinations of spatial and temporal distribution of the emissions require several meteorological data such as monthly average temperature, daily solar radiation and mean daily sunshine duration. Required data was obtained from Turkish State Meteorological Service (TSMS). The town/city based observations from the synoptic stations (372 stations for temperature, 241 stations for sunshine duration, 187 stations for solar radiation for the period of 1960-2012 were used in the

study (TSMS, 2013). Variation of temperature, sunshine duration and PAR values for January and July, in which the lowest and highest values were observed, is given in Figures 3.3-3.5. It was assumed that the vegetation period starts when the average temperature is over 10°C (Cepel, 1988). This value was determined by considering the vegetation periods of the species that defoliates.

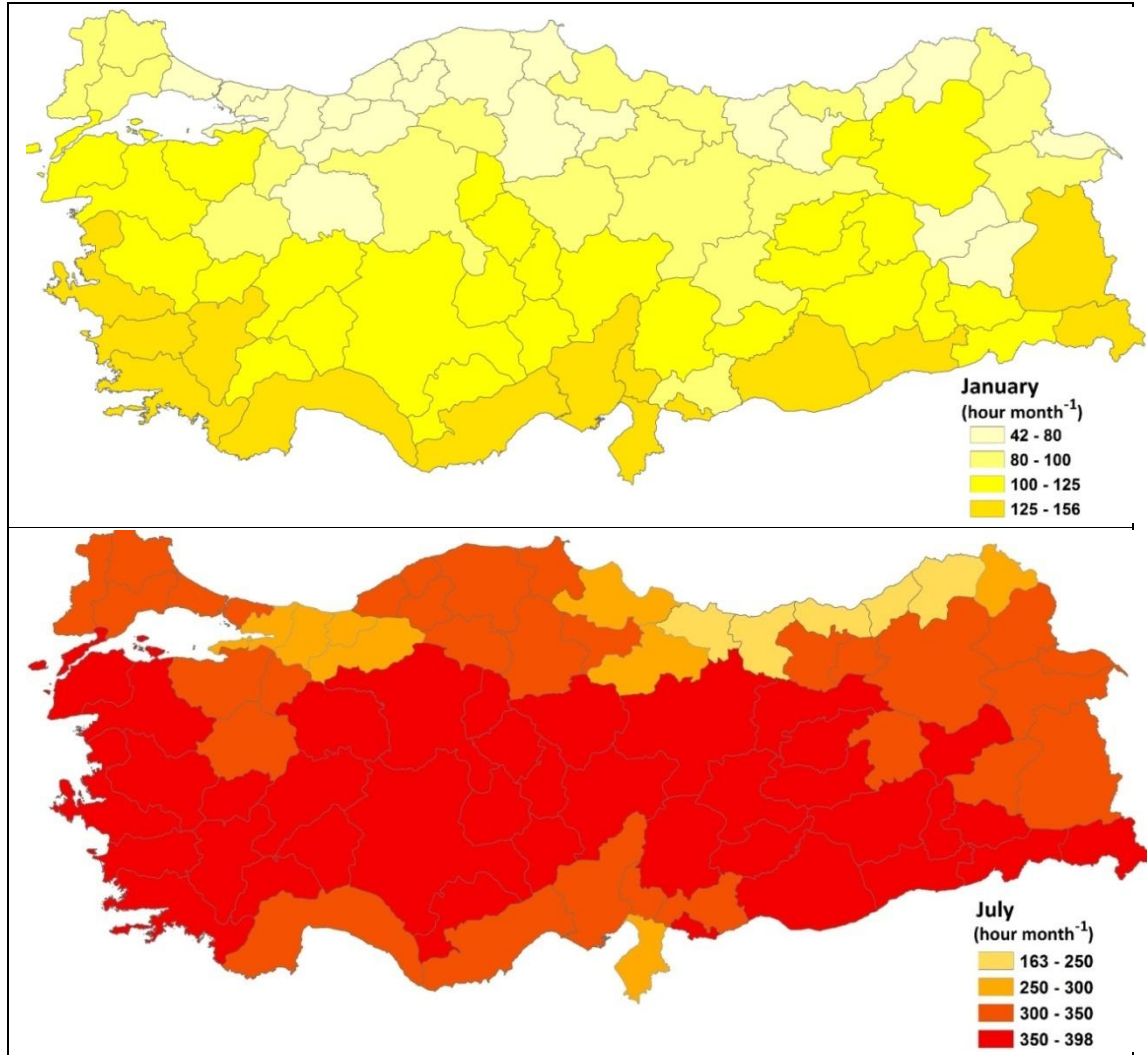


Figure 3.3 The mean sunshine durations on the basis of province in Turkey for January and July

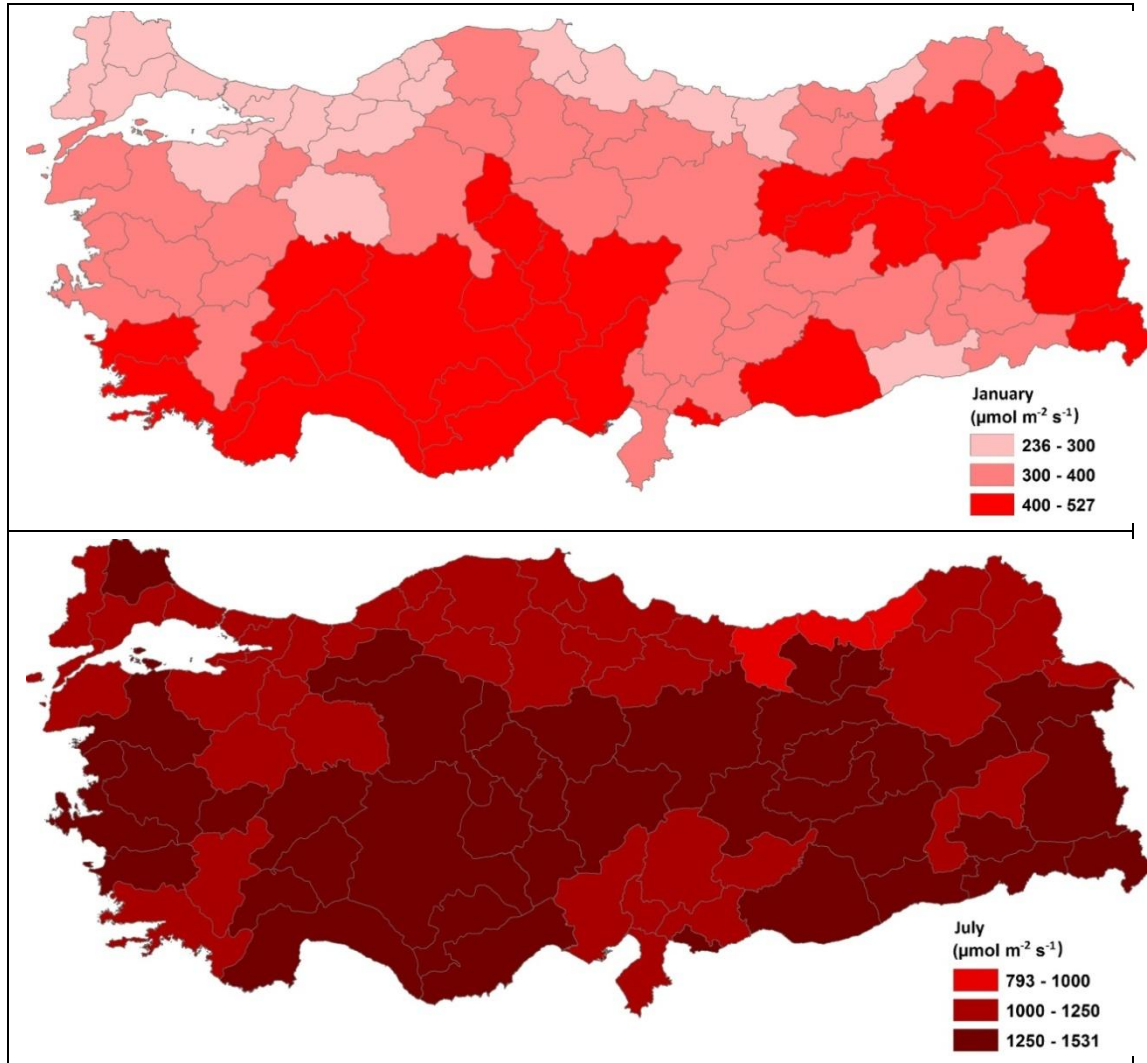


Figure 3.4 PAR values on the basis of province in Turkey for January and July

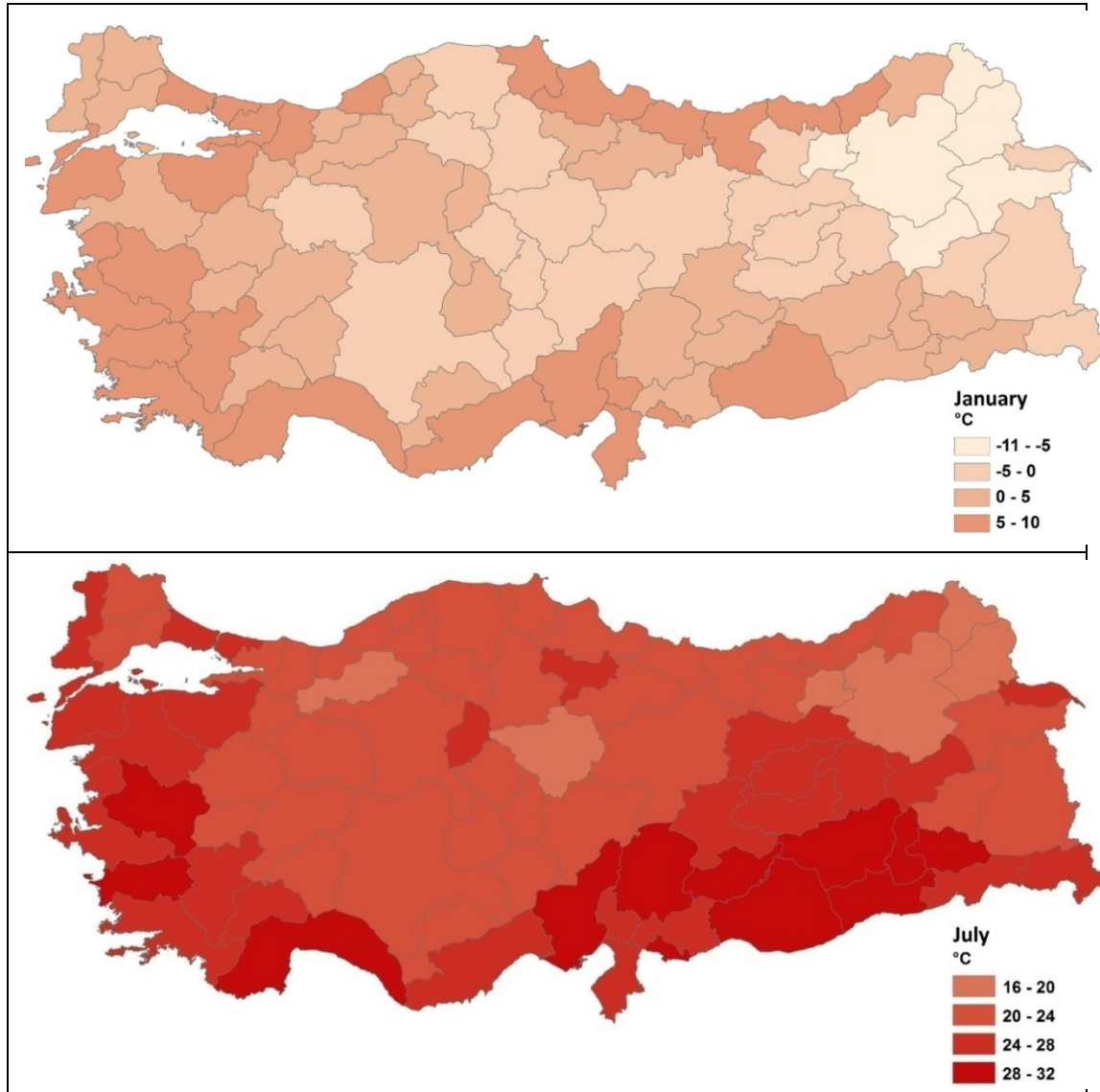


Figure 3.5 The mean temperatures on the basis of province in Turkey for January and July

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Inventory of BVOC Emissions

The national forest inventory, observed meteorological data and recent measurements of emission rates for tree species in Turkey were used to estimate the amount of BVOC emissions in this study. The results showed that the total BVOC emissions in 2012 was estimated as 637.7 kt in Turkey. Monoterpene emissions consist of 81.7% (520.1 kt) of the total emissions. These ratios for isoprene, sesquiterpenes, oxygenated compounds, and oxygenated sesquiterpenes were found as 4.9% (31.3 kt), 0.85% (5.4 kt), 12.5% (79.9 kt) and 0.05% (0.3 kt), respectively. As indicated in the literature, isoprene was mostly emitted by broad leaved trees while coniferous species dominantly emitted monoterpene. Coniferous species especially pine species spread over all of Turkey and emit high monoterpenes emissions. Monoterpene emissions were found as the dominant emissions similarly in several studies (Oderbolz et al., 2013; Simon et al., 2006; Steinbrecher et al., 2009; Symeonidis et al., 2008). Although isoprene emissions had substantial amounts in some regions where broad leaved species spread on large areas (Bao et al., 2008; Chang et al., 2012).

Calculations were done based on the boundaries of provinces, regional directorate of forestry and forest sub-districts directorate. The spatial distribution of total annual BVOC emissions based on the boundaries of the provinces of the country and forest sub-district directorate are shown in Figures 4.1-4.3. The highest emissions were found along the Mediterranean coastline. The highest emission (129.6 kt yr⁻¹) was observed in the province of Antalya where the dominant and ever-green species, i.e. Turkish red pine are available (Figure 4.1). The highest emission calculated on the basis of forest sub-district directorate (5.9 kt yr⁻¹) was observed in Kemer (Figure 4.3). The trees in this region have large amounts of growing stocks that means large amounts of foliage weight. Additionally the mean temperature in south and southeastern parts of Turkey is warmer than the other regions. For this reason the

highest emissions were observed in this region. The highest emissions of other BVOC groups except isoprene were observed in the forest areas of this region like the distribution of total BVOC emissions. Higher isoprene emissions were observed in the northwest and the south-southeast regions of the country. Because broad leaved species especially oak species spread large areas in these regions. The highest isoprene emission (1 kt yr^{-1}) was observed in Ibradi region under Antalya Forest Regional Directorate's responsibility (Figure 4.9). There were productive Cilician fir forests in Ibradi. The highest isoprene emissions were observed as 2.8 and 2.5 kt yr^{-1} in the provinces of Antalya and Kirklareli, respectively. Several regions such as Igdir, Agri and Nevsehir had almost no forest areas in the country and they have less than 10 t BVOC emissions per year. The spatial distribution maps of BVOC emission groups on the basis of province, regional directorate of forestry and forest sub-district directorates are shown in Figures 4.4-4.18.

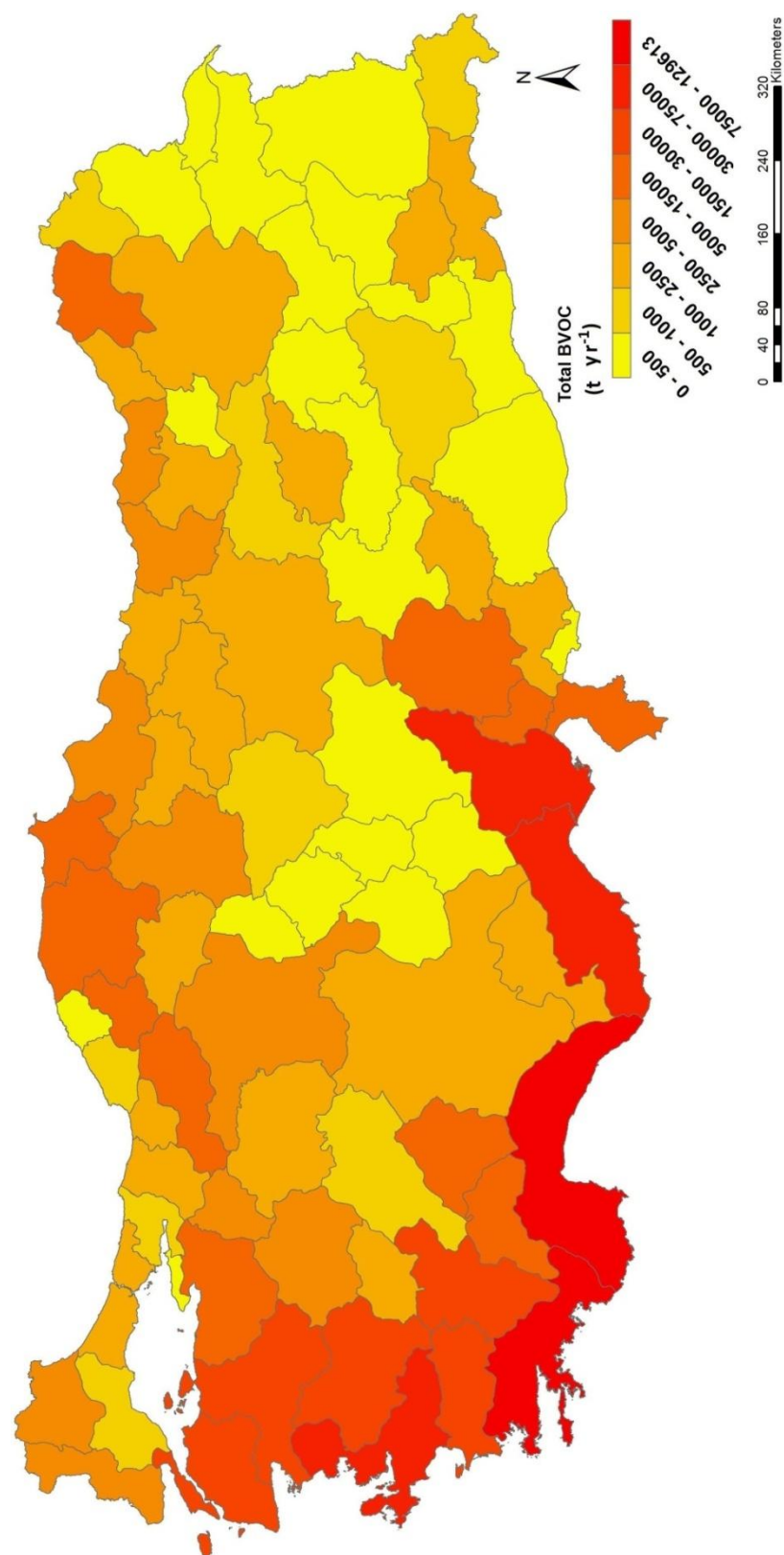


Figure 4.1 Spatial distribution of province based total BVOC emissions in Turkey in 2012.

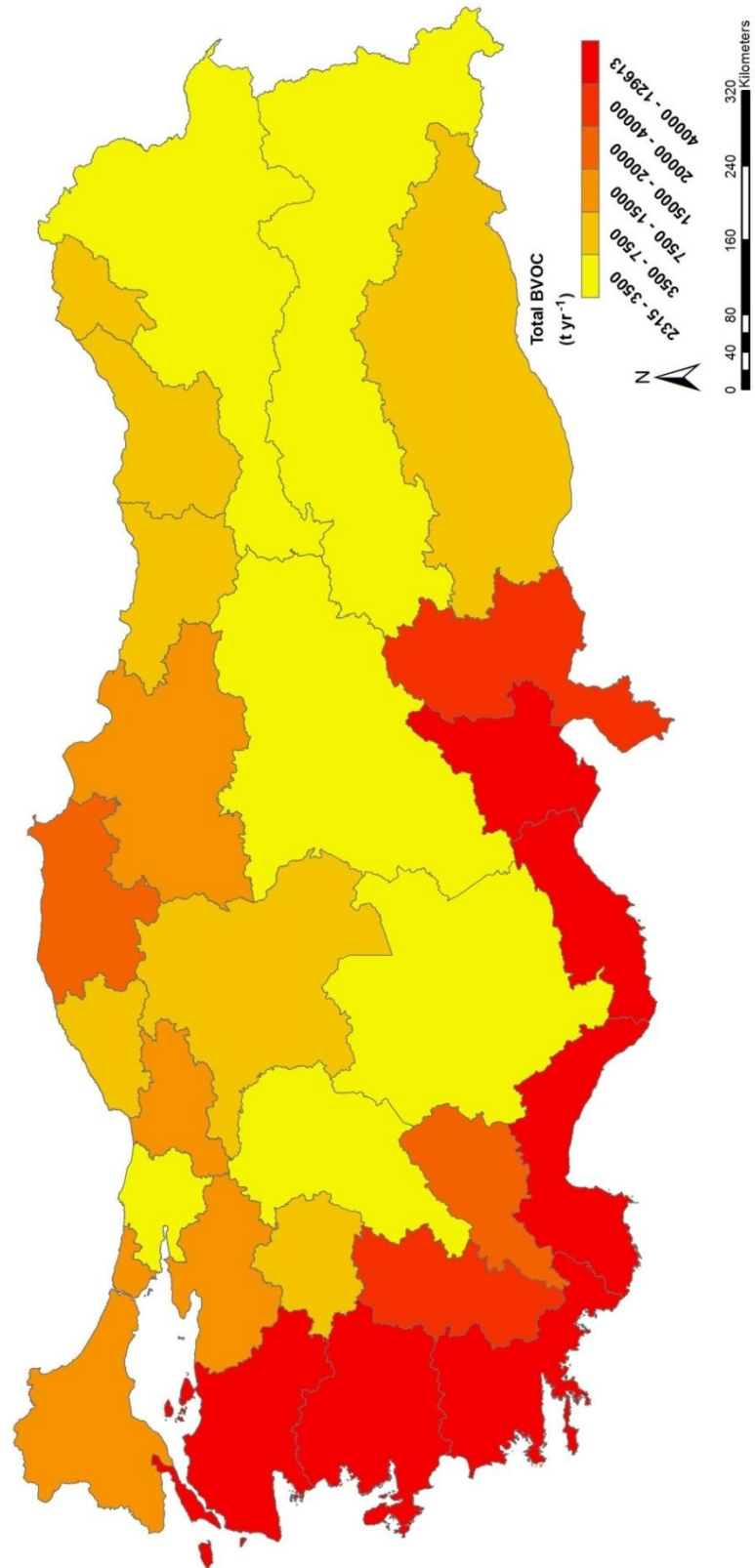


Figure 4.2 Spatial distribution of total BVOC emission for the regional directorates of forestry in Turkey in 2012.

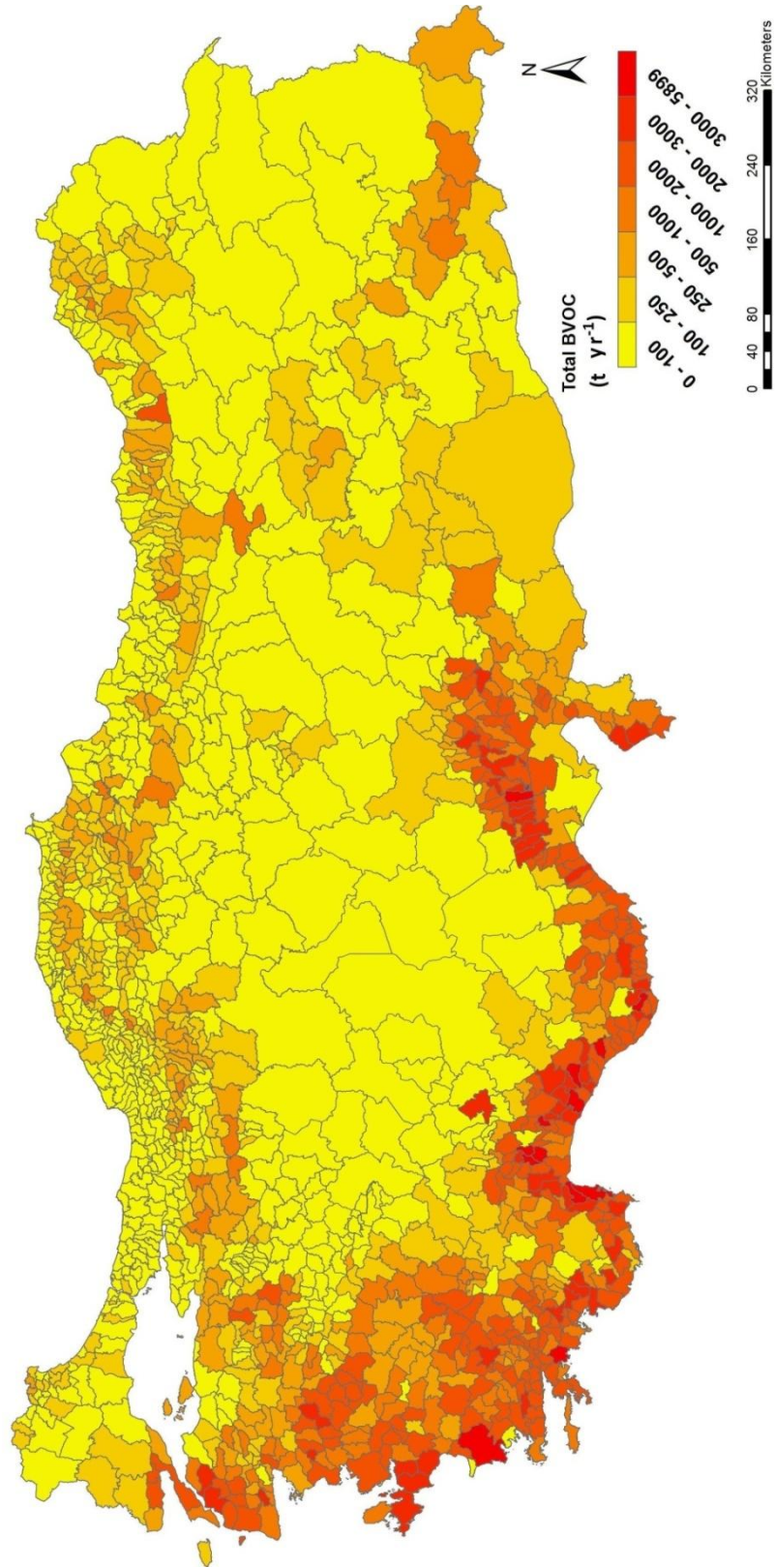


Figure 4.3 Spatial distribution of total BVOC emission for the forest sub-district directorates in Turkey in 2012.

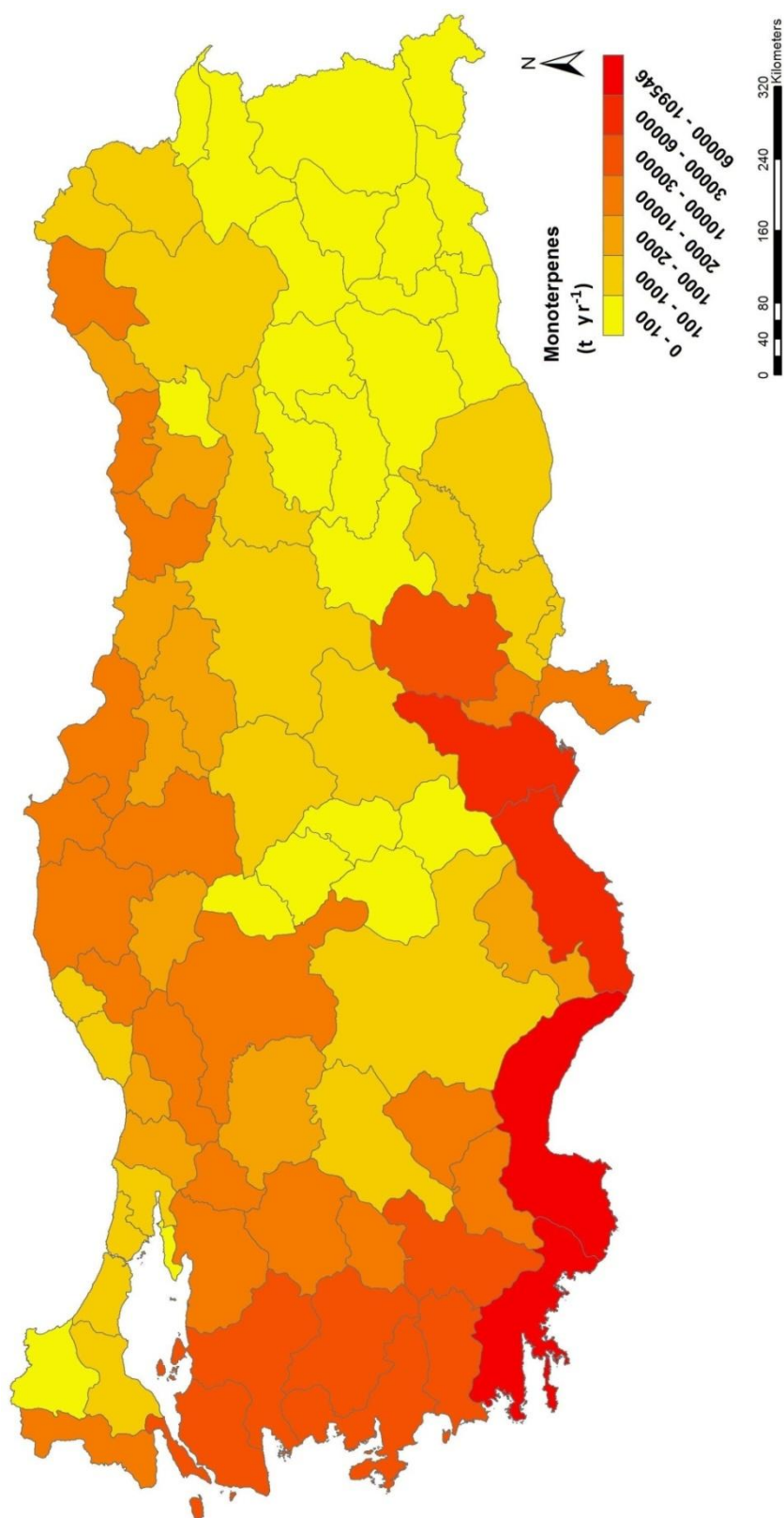


Figure 4.4 Spatial distribution of monoterpene emissions in the provinces of Turkey in 2012.

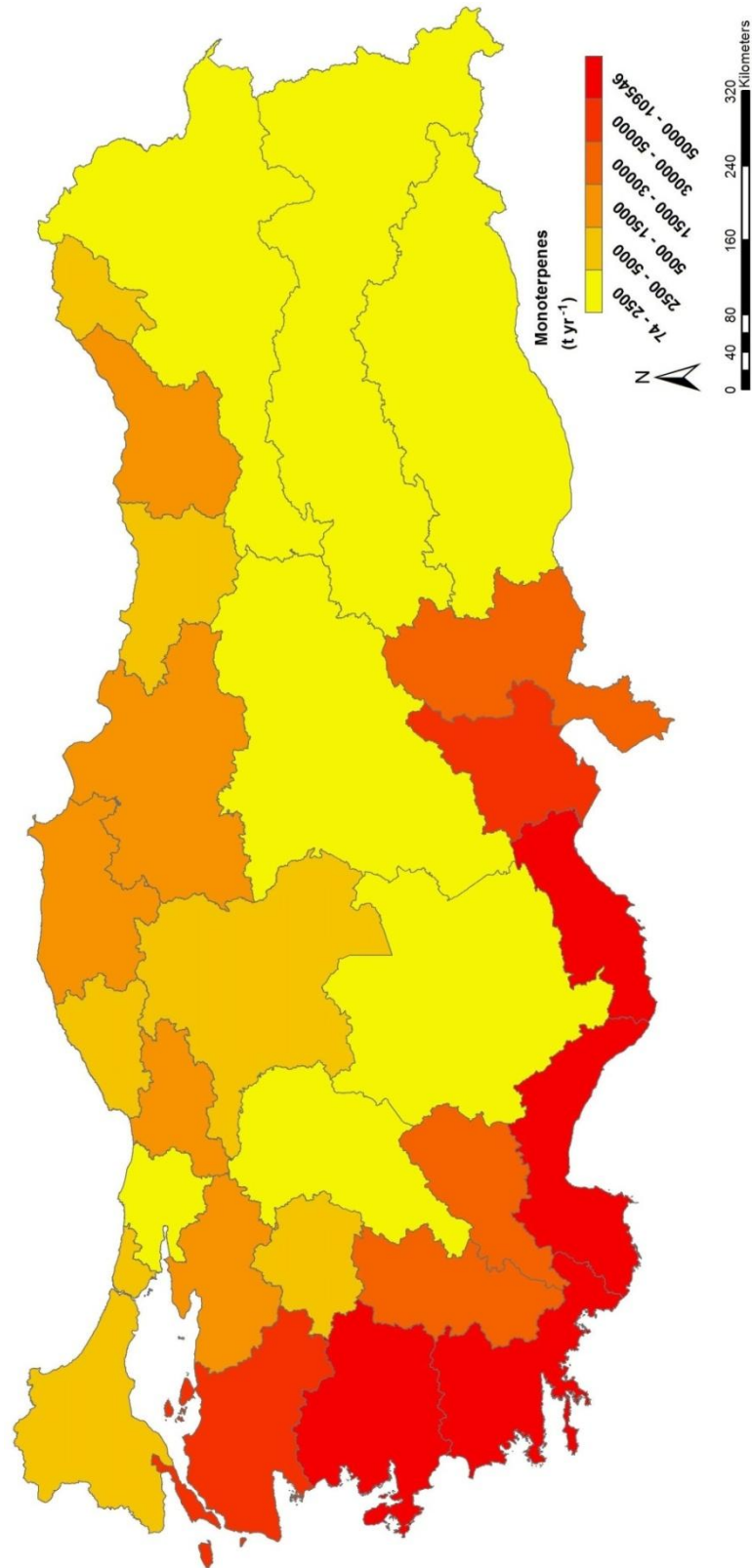


Figure 4.5 Spatial distributions of monoterpene emissions for the regional directorates of forestry in Turkey in 2012.

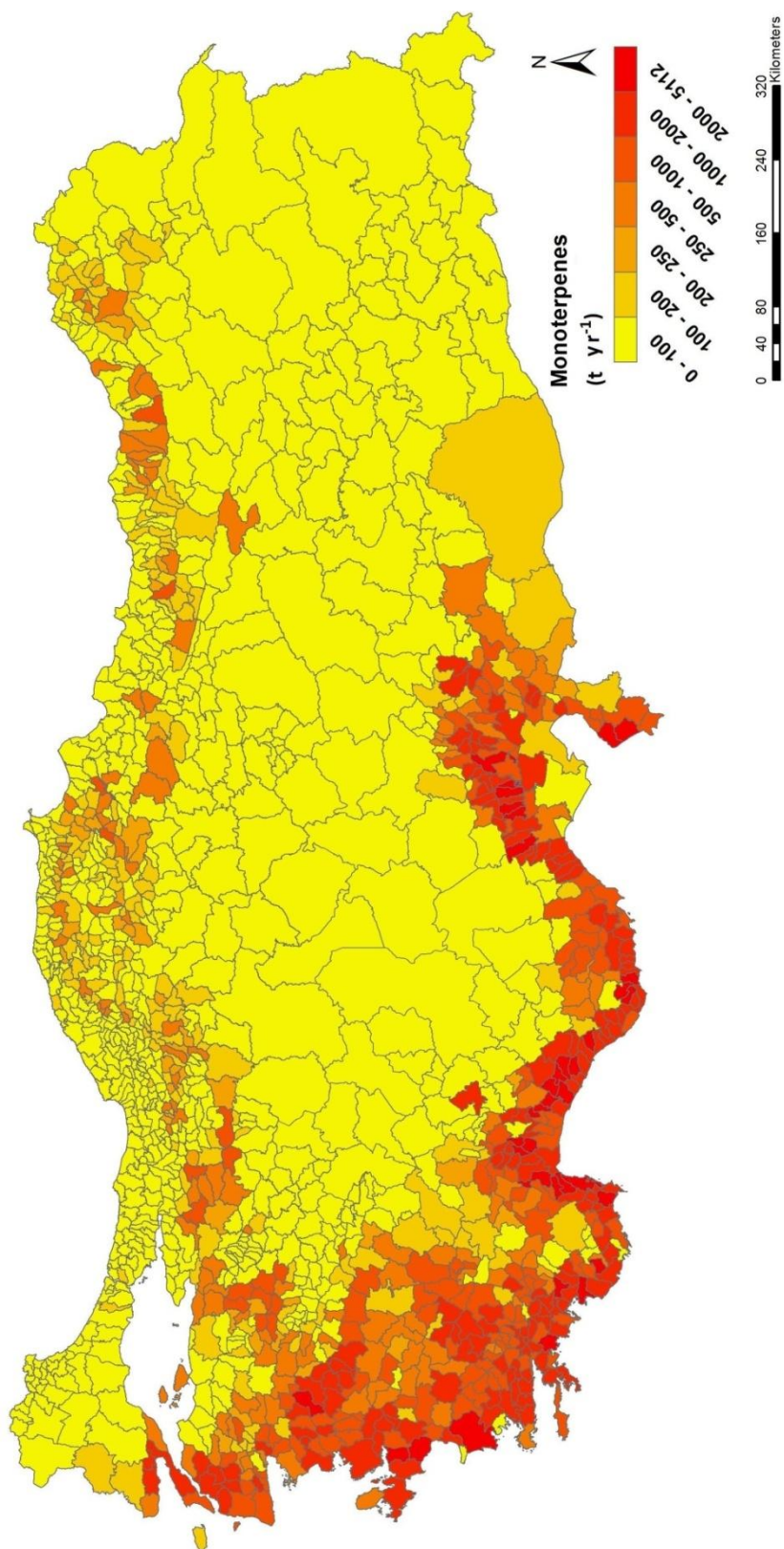


Figure 4.6 Spatial distributions of monoterpene emissions for the forest sub-district directorates in Turkey in 2012.

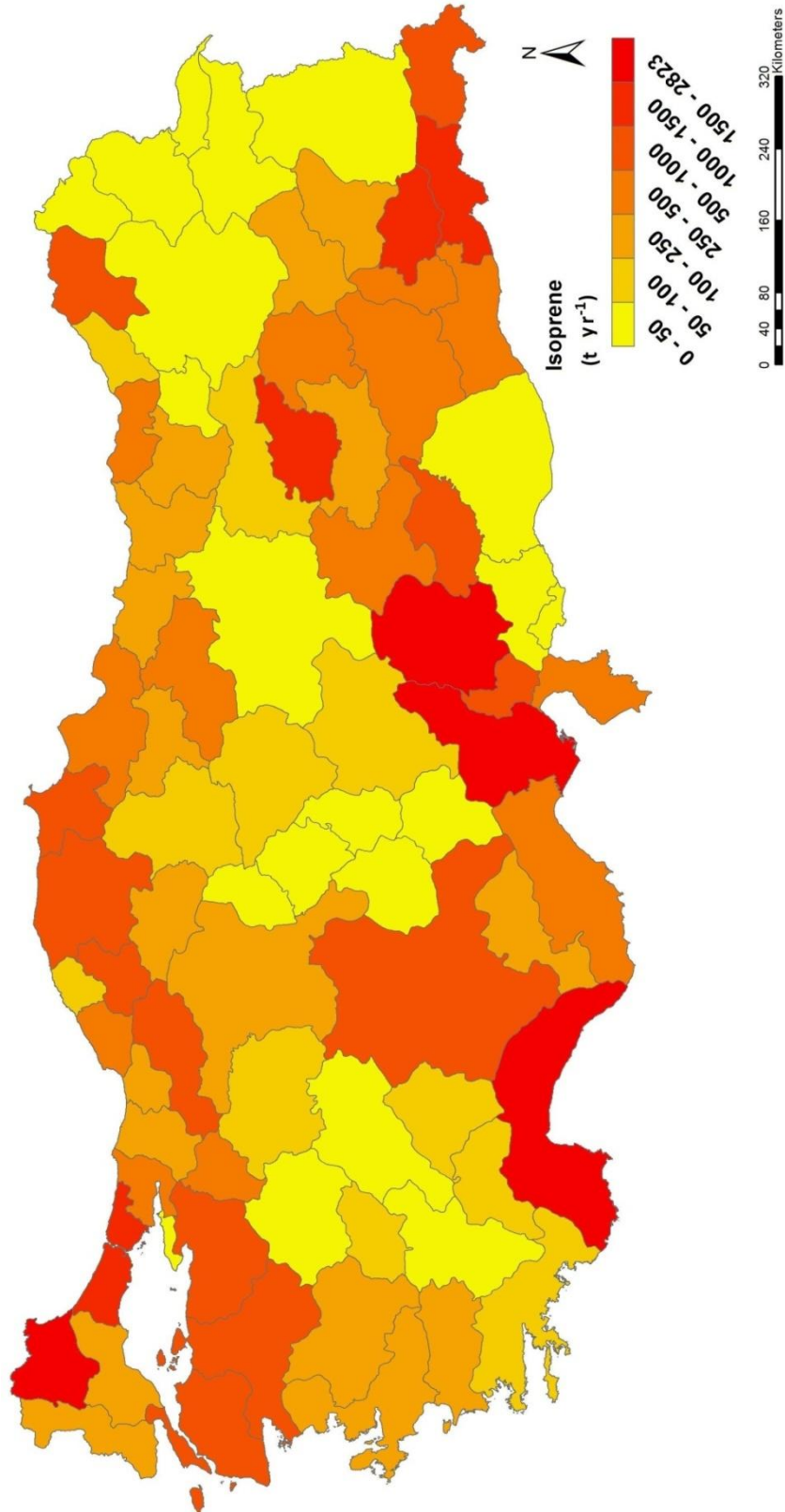


Figure 4.7 Spatial distributions of isoprene emissions in the province of Turkey in 2012.

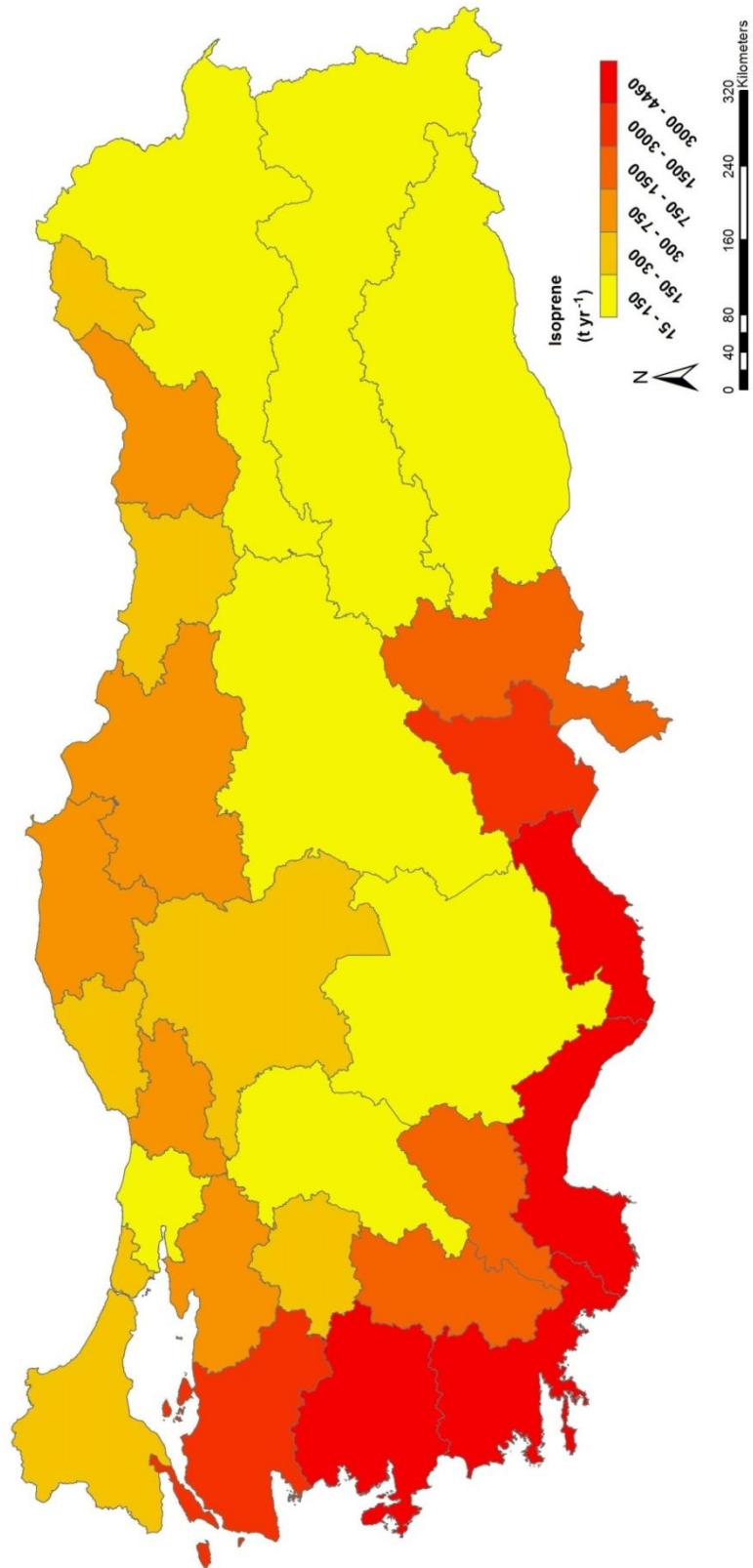


Figure 4.8 Spatial distributions of isoprene emissions for the regional directorates of forestry in Turkey in 2012.

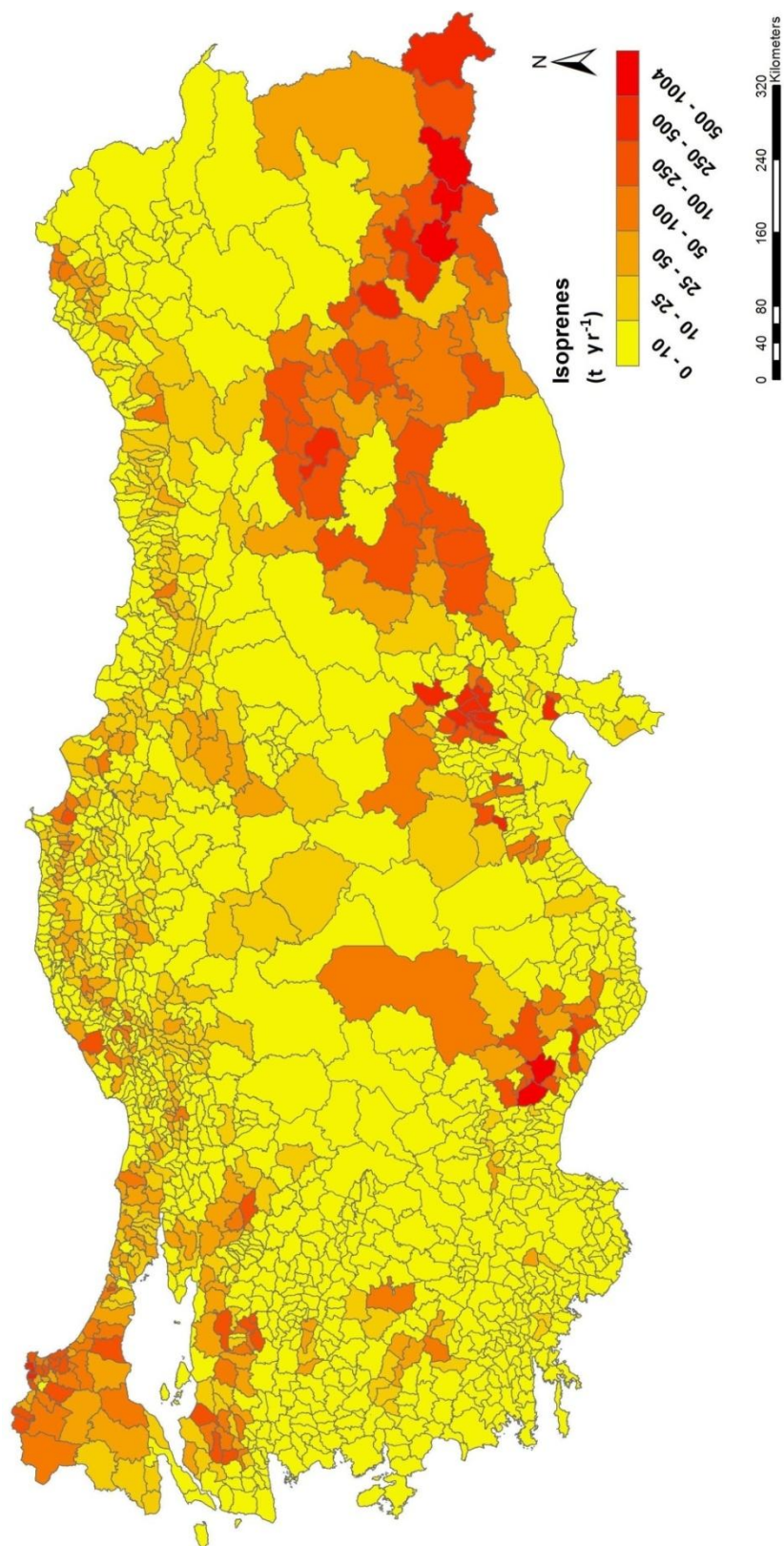


Figure 4.9 Spatial distribution of isoprene emission for the forest sub-district directorates in Turkey in 2012.

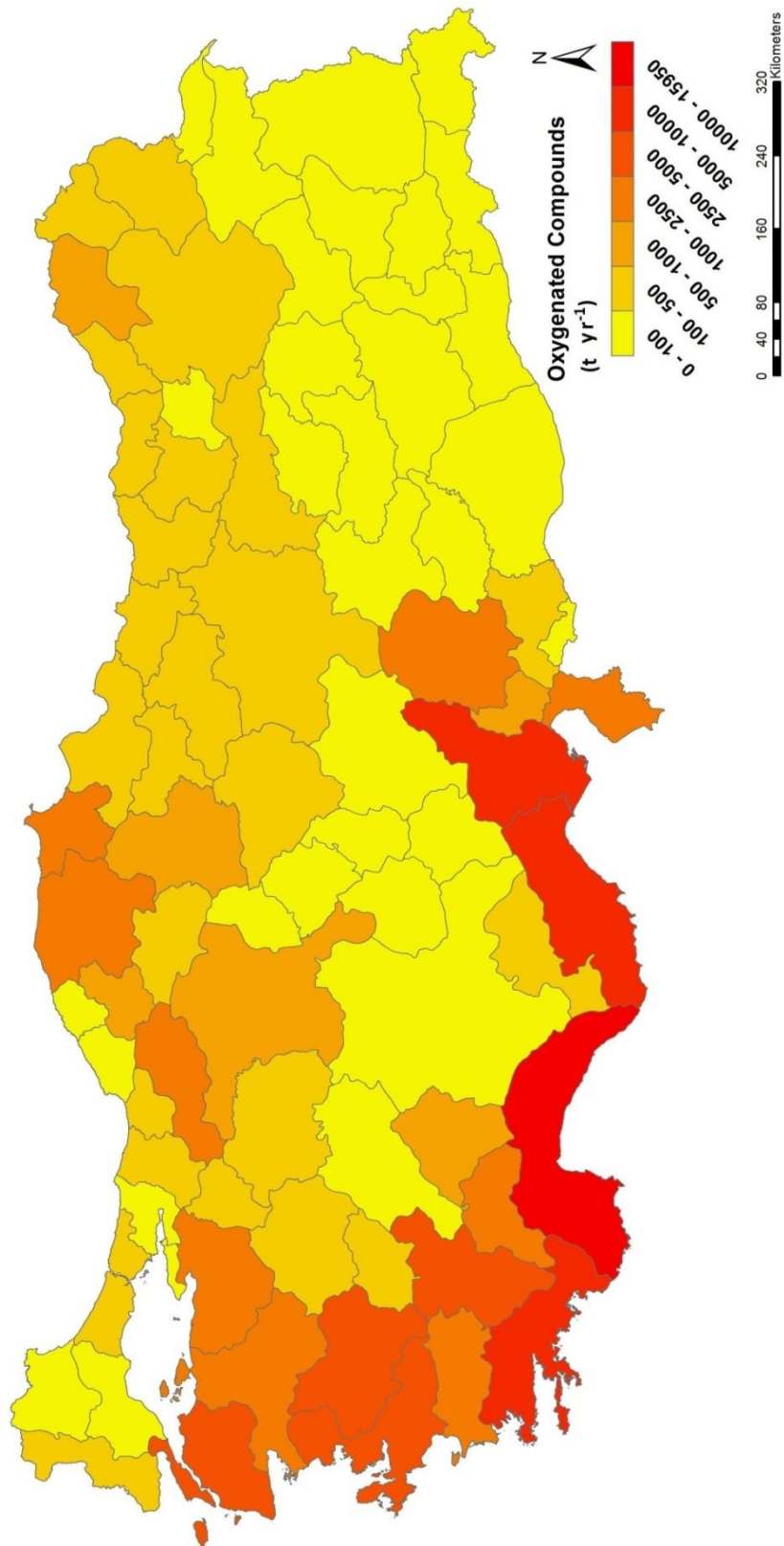


Figure 4.10 Spatial distribution of oxygenated compounds emissions in the provinces of Turkey in 2012.

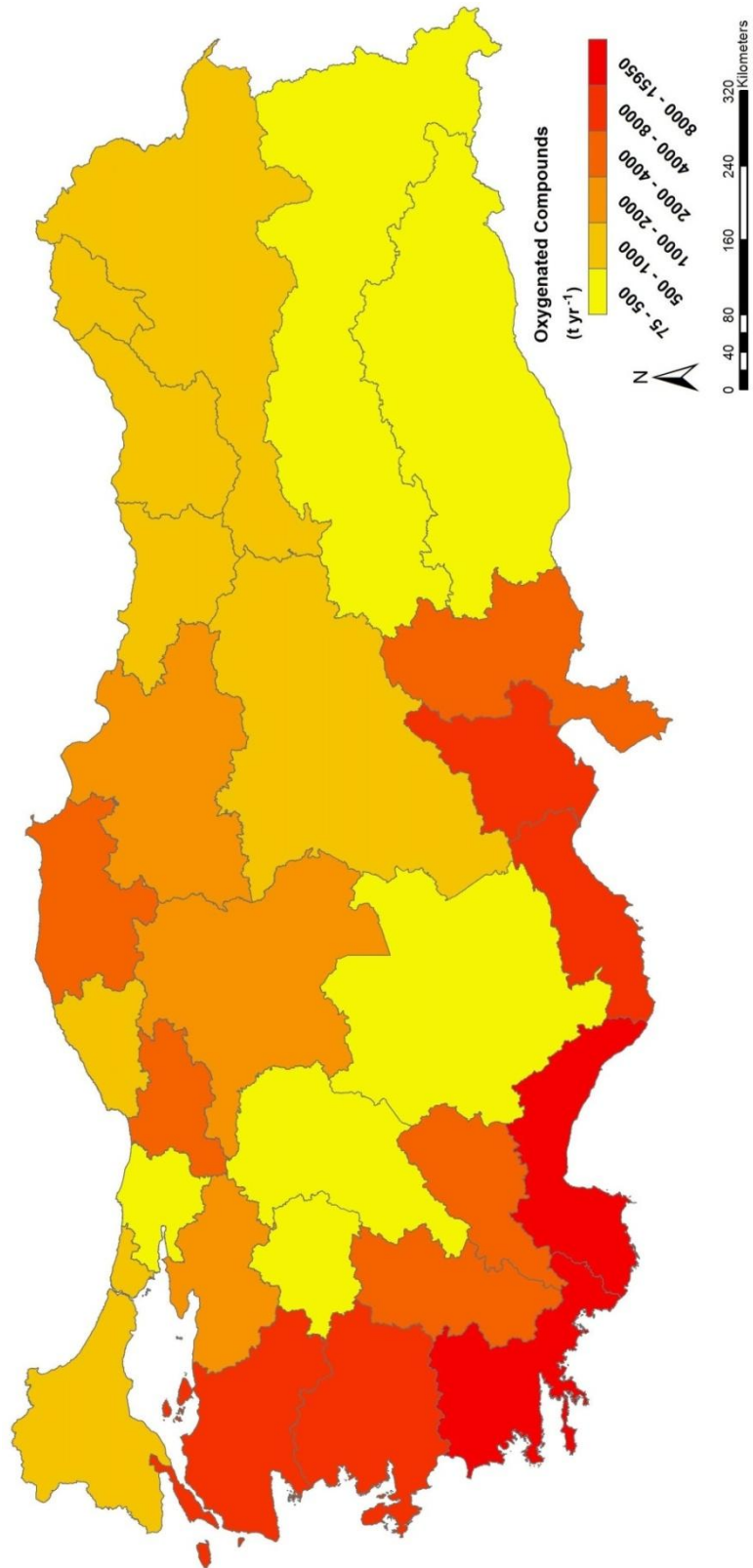


Figure 4.11 Spatial distributions of oxygenated compounds emissions for the regional directorates of forestry in Turkey in 2012.

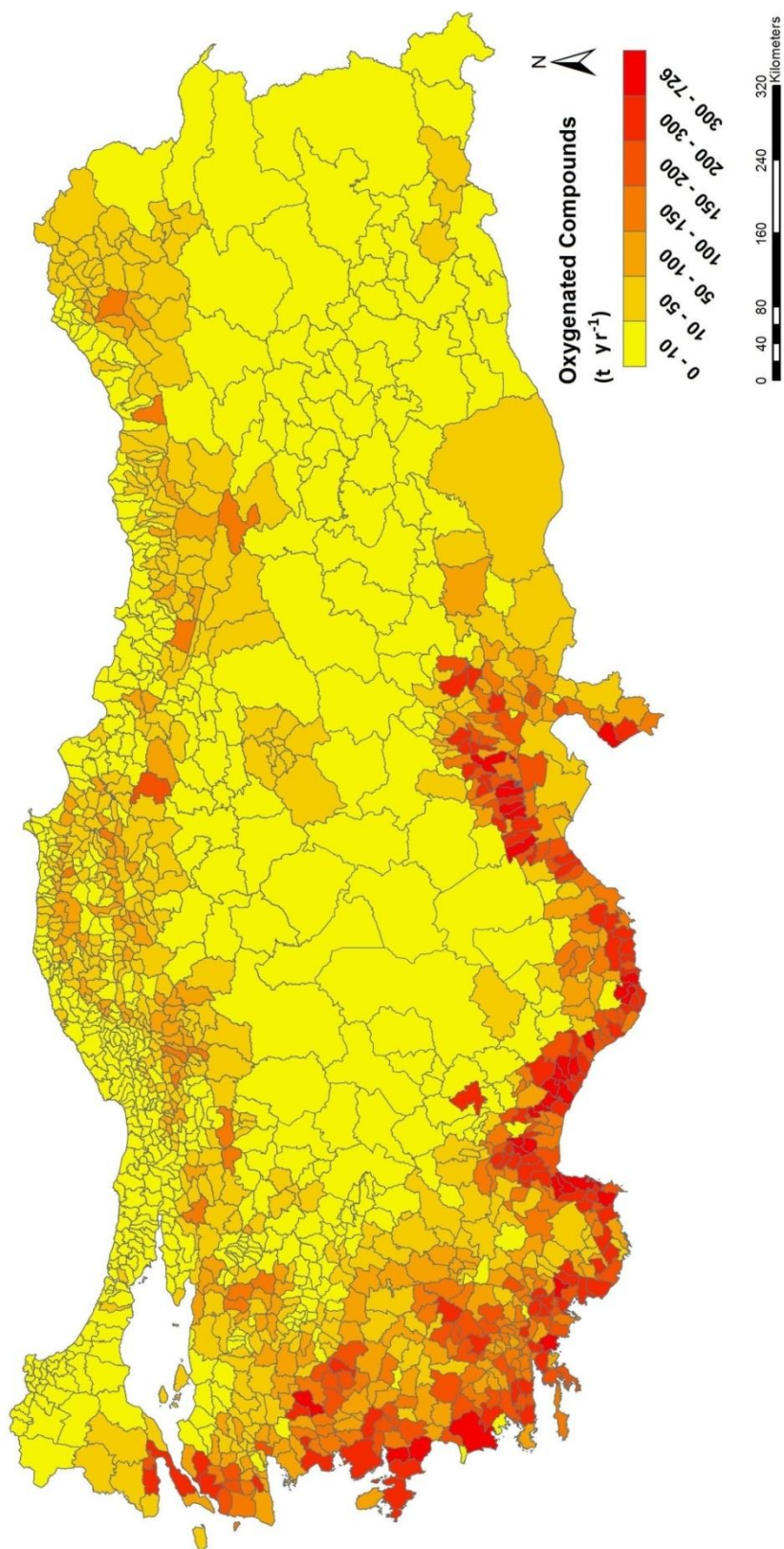


Figure 4.12 Spatial distribution of oxygenated compound emission for the forest sub-district directorates in Turkey in 2012.

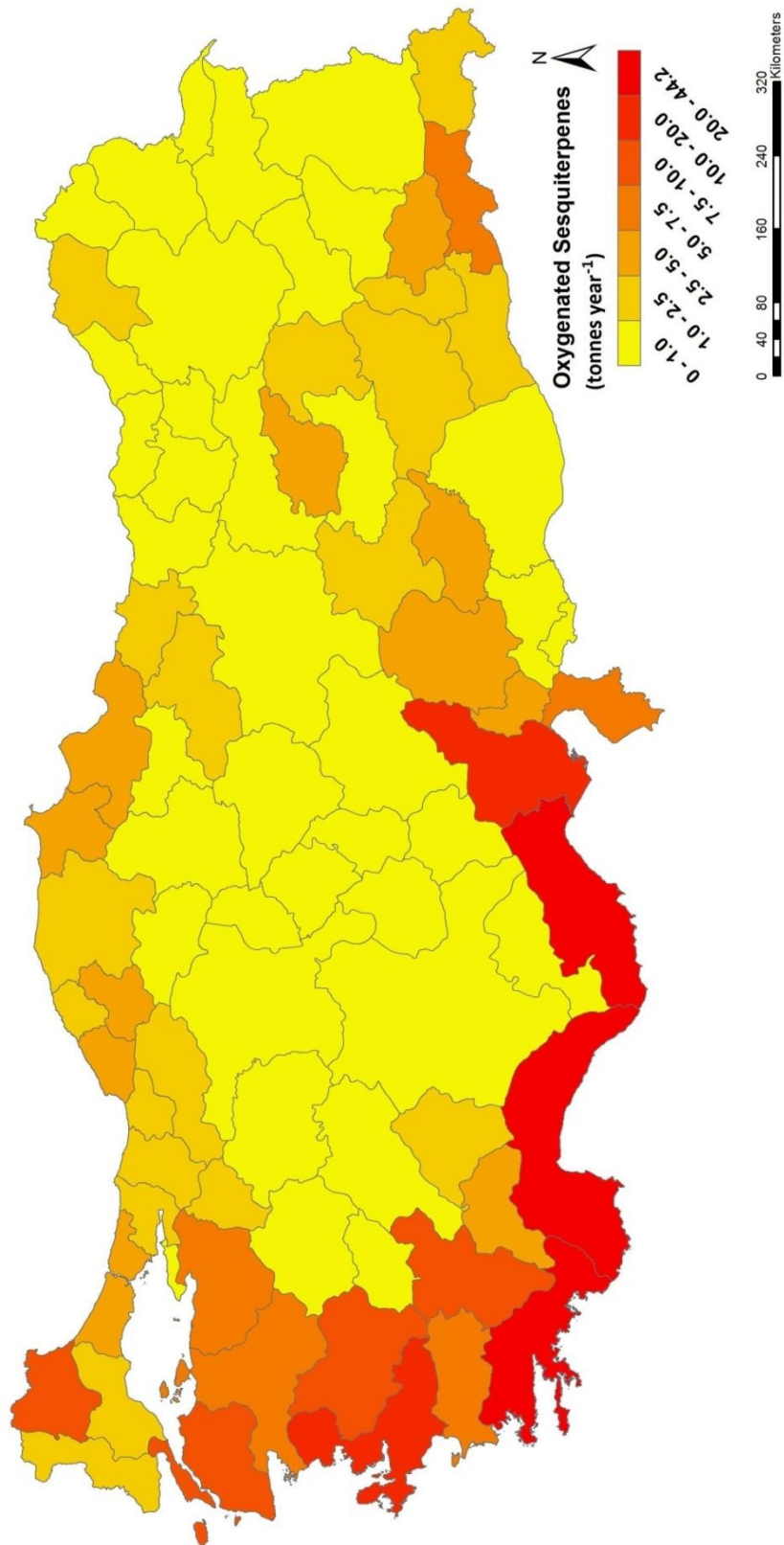


Figure 4.13 Spatial distribution of oxygenated sesquiterpenes emissions in the provinces of Turkey in 2012.

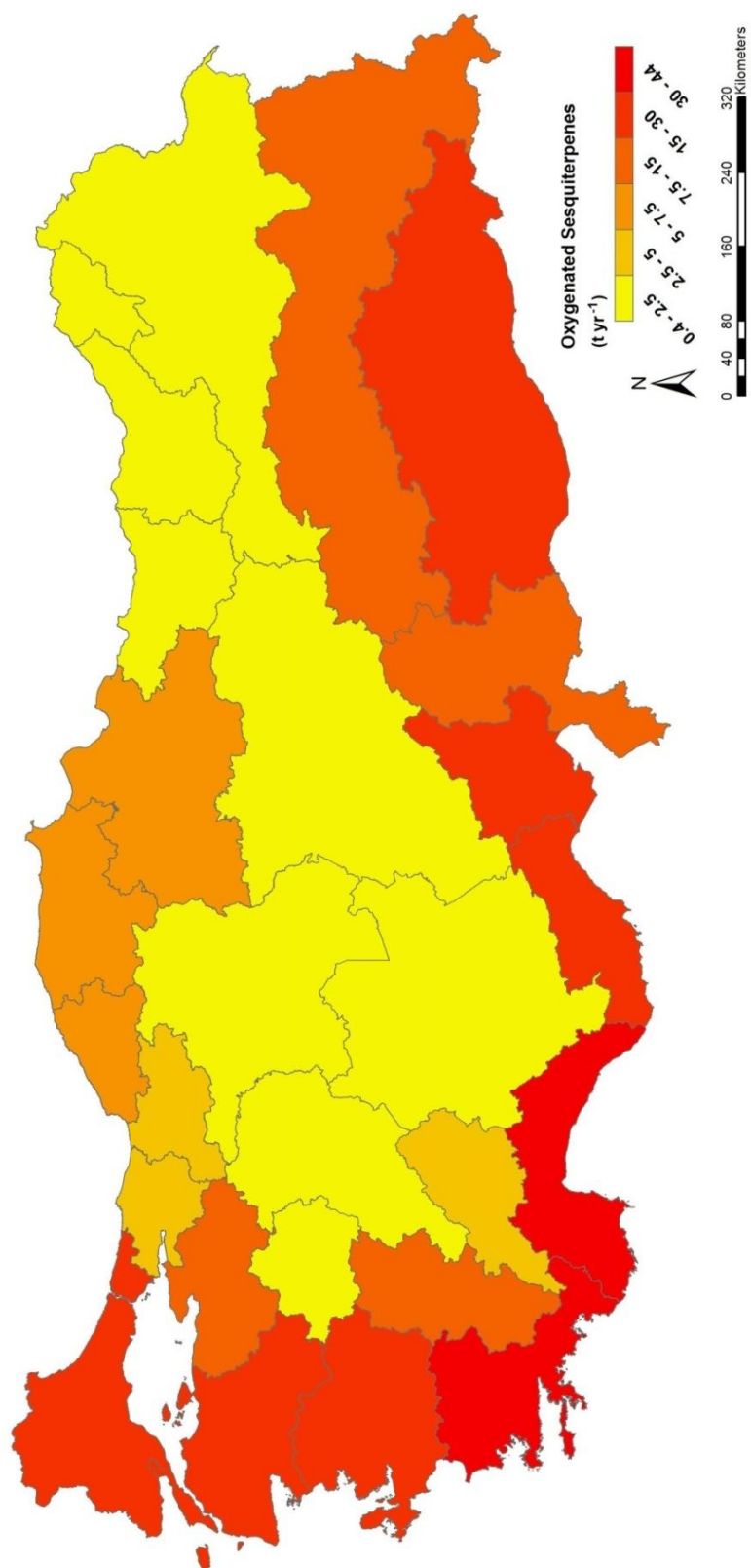


Figure 4.14 Spatial distributions of oxygenated sesquiterpene emissions for the regional directorates of forestry in Turkey in 2012.

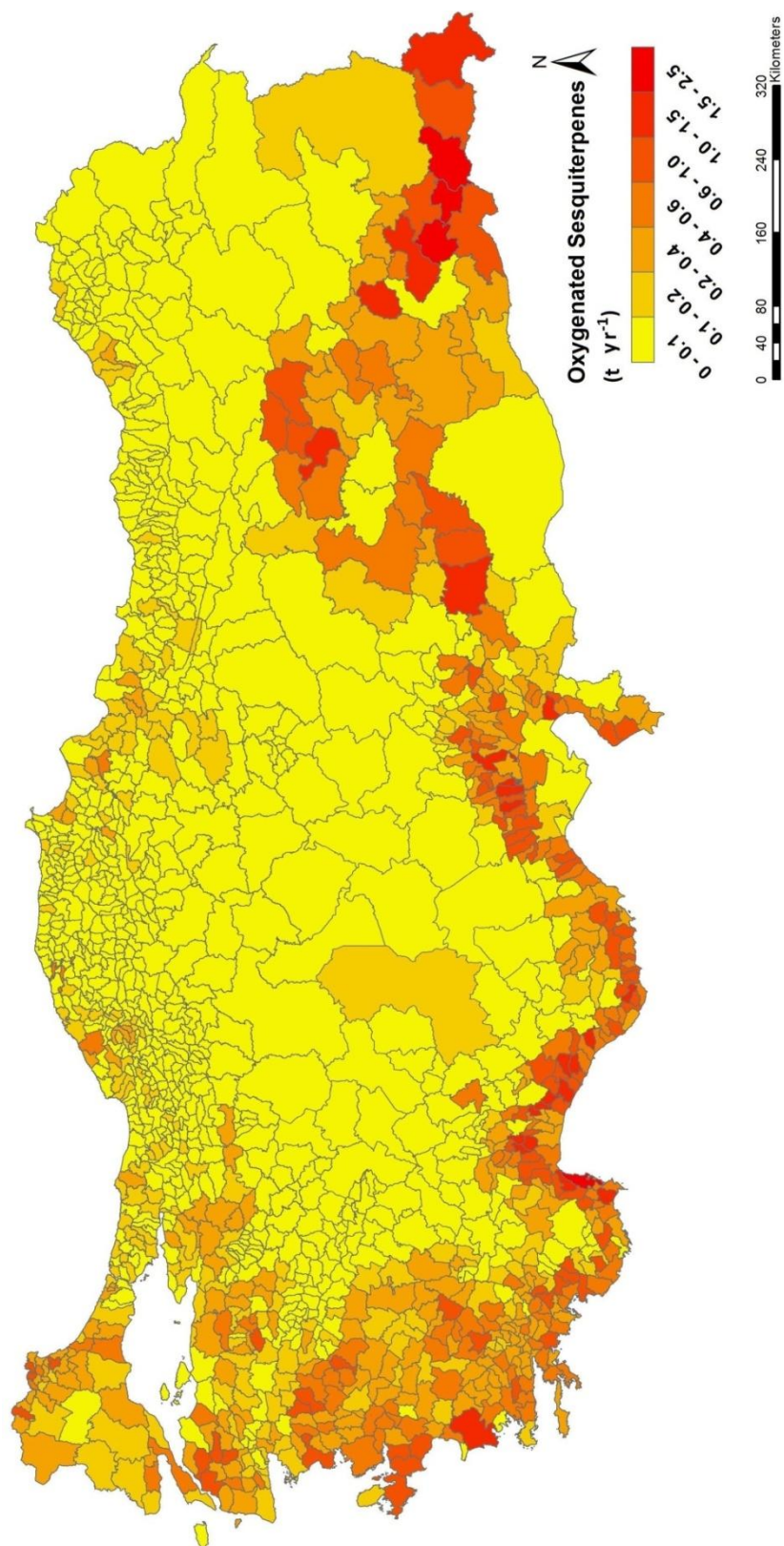


Figure 4.15 Spatial distribution of oxygenated sesquiterpene emission for the forest sub-district directorates in Turkey in 2012.

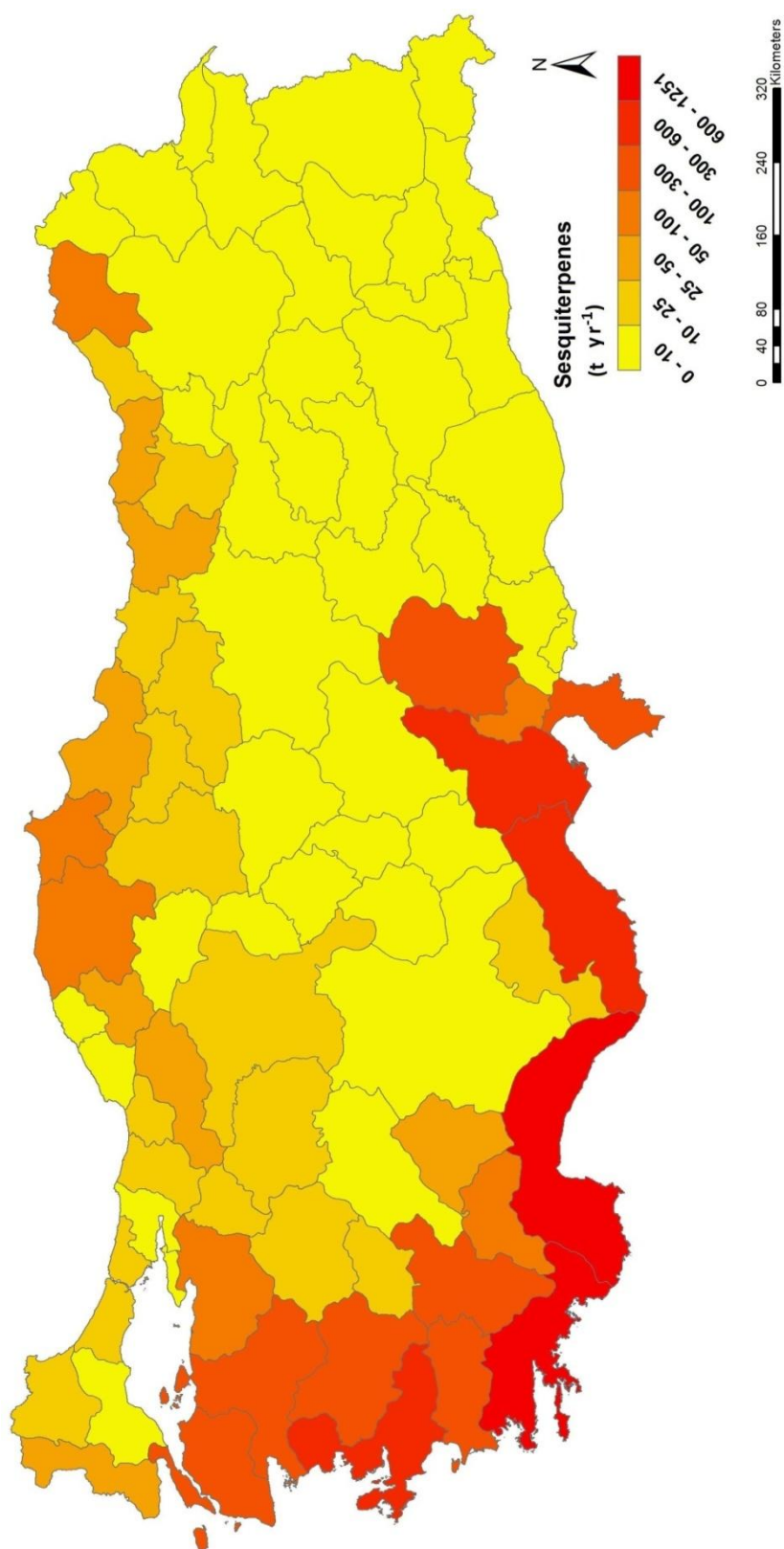


Figure 4.16 Spatial distribution of sesquiterpenes emissions in the provinces of Turkey in 2012.

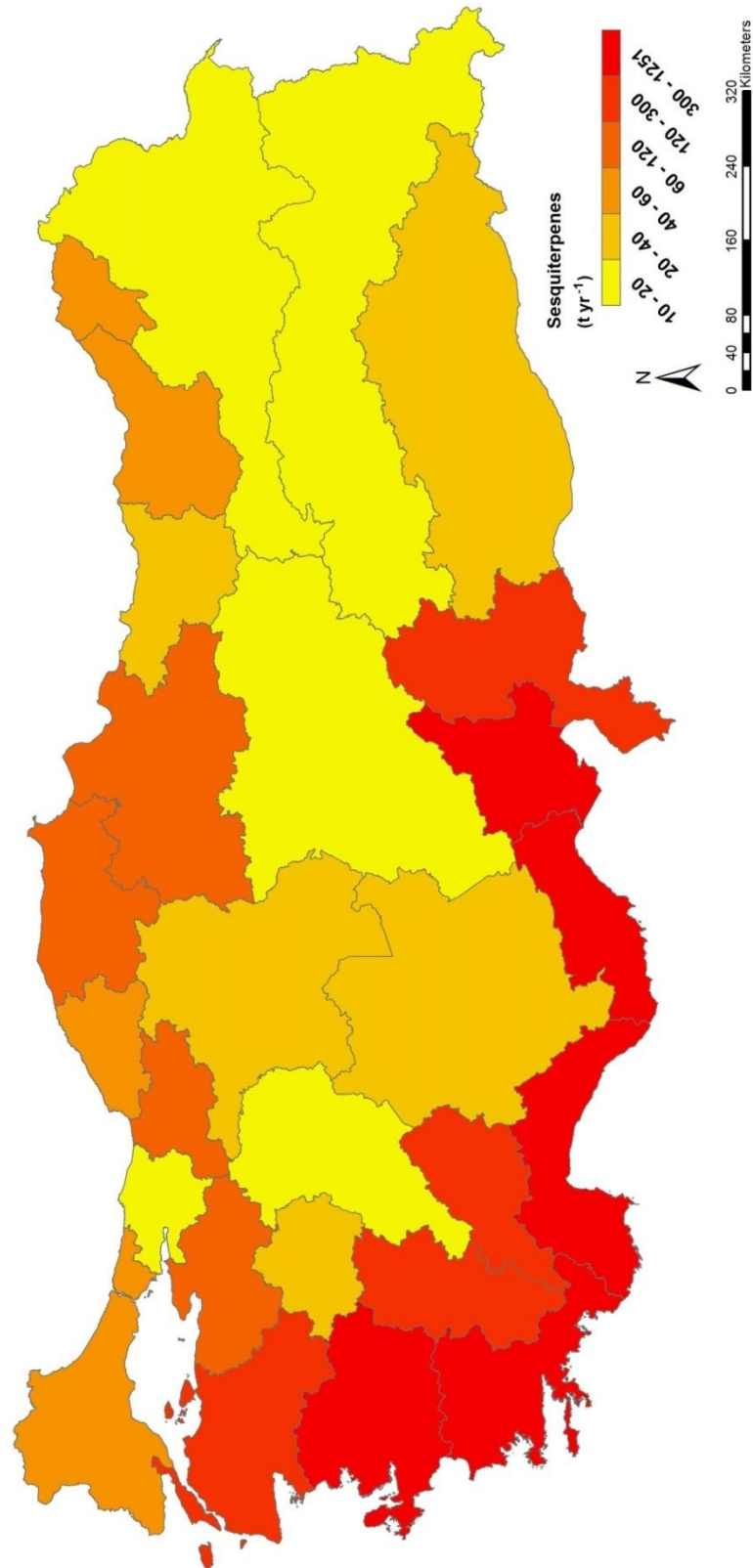


Figure 4.17 Spatial distribution of sesquiterpene emission for the regional directorates of forestry in Turkey in 2012.

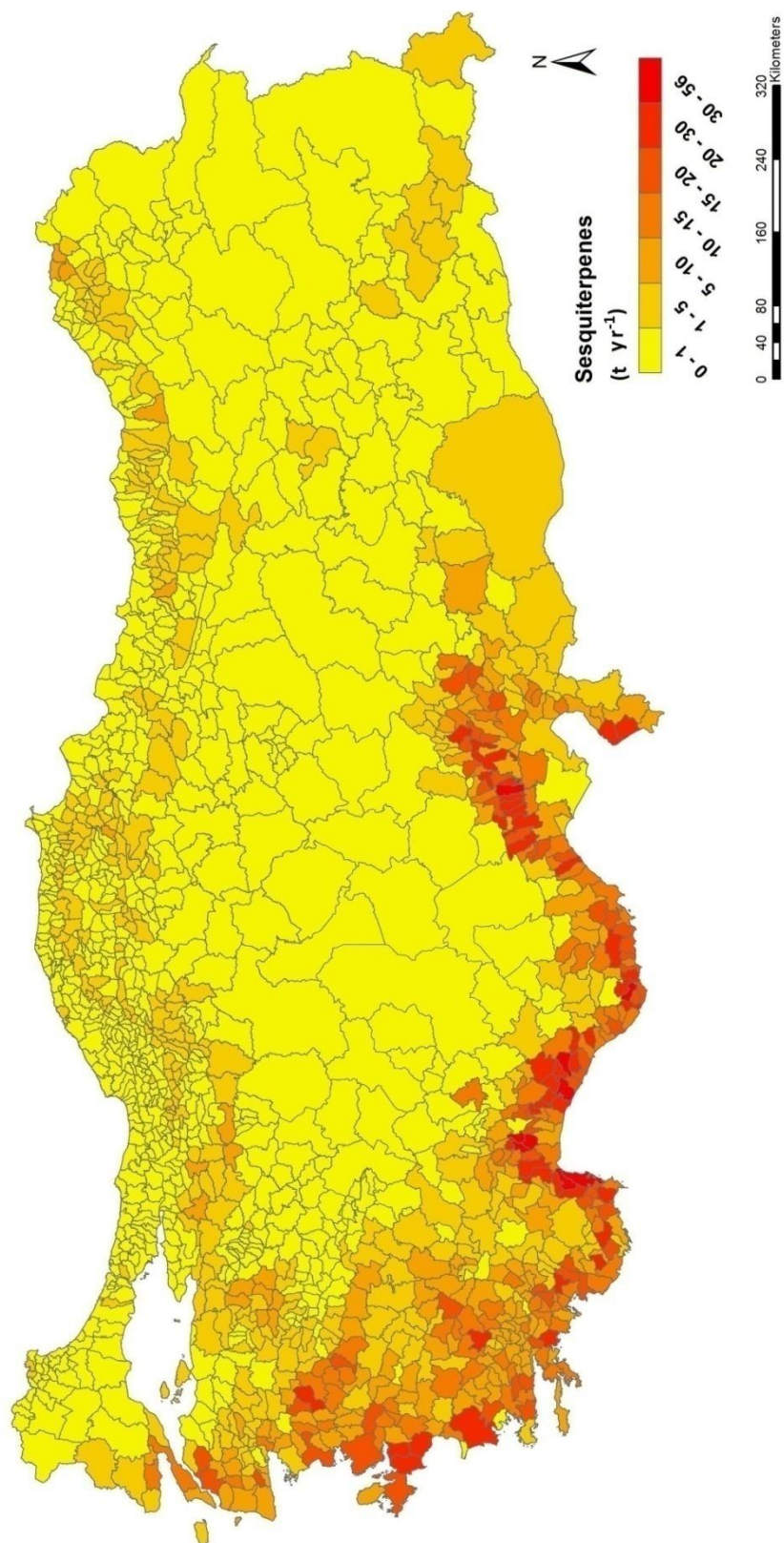


Figure 4.18 Spatial distribution of sesquiterpene emission for the forest sub-district directorates in Turkey in 2012.

After Mediterranean region, highest emissions were calculated in Aegean and Black Sea regions, respectively. The regional distributions of the total BVOC emissions were found different for BVOC groups. The presence of coniferous species in all regions except East and Southeast Anatolia regions cause that the dominant group was monoterpenes. Oaks species and Cilician fir species were characteristically strong isoprene emitters. Therefore, the highest isoprene emissions were observed in Marmara region especially about Kırklareli-Igneada and in Toros Mountains in the Mediterranean region. Sesquiterpenes and oxygenated VOCs were also similar with the spatial distribution of monoterpene emissions. Highest oxygenated sesquiterpenes were observed in the fir forests in the Mediterranean coast, Aegean region, and the north of Trakya and around Bolu. Table 4.1 summarizes the BVOC emissions based on geographic regions and Figure 4.19 illustrates the compositions of BVOC emission groups.

Table 4.1 Regional distribution of BVOC emissions in Turkey (t yr⁻¹)

Geographic Region	Isoprene	Monoterpenes	Oxygenated Compounds	Sesquiterpenes	Oxygenated Sesquiterpenes	TOTAL
Mediterranean	8,271	247,045	35,613	2,793	101	293,823
Aegean	729	162,675	23,137	1,623	62	188,225
Black Sea	6,046	48,628	10,450	426	28	65,578
Marmara	7,435	49,468	7,299	461	45	64,708
Central Anatolia	1,305	9,318	2,159	77	3	12,862
Eastern Anatolia	2,971	1,920	870	23	10	5,794
Southeastern Anatolia	4,499	1,786	348	43	18	6,694
TOTAL	31,256	520,841	79,876	5,446	268	637,686

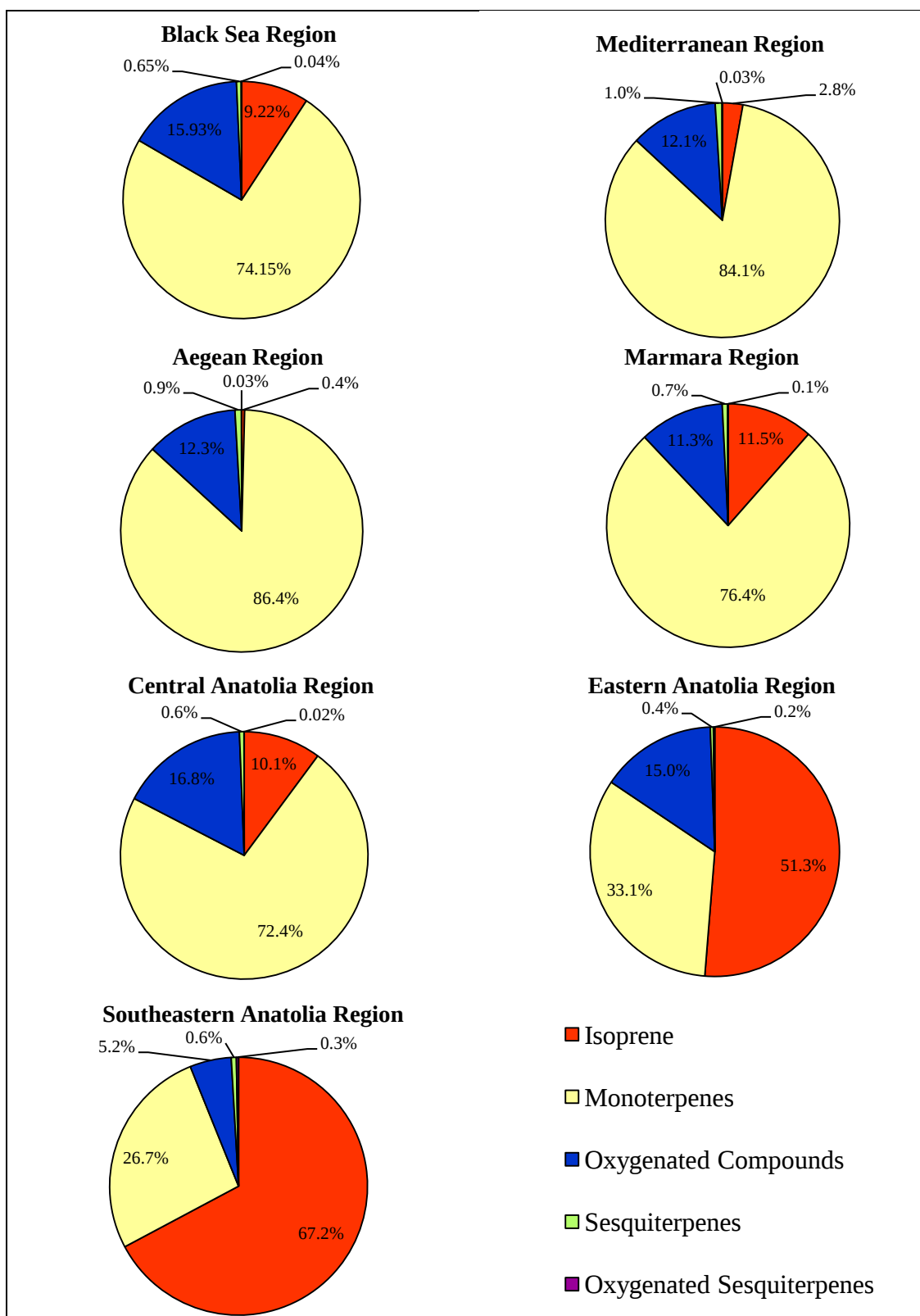


Figure 4.19 Compositions of BVOC emission groups for the regions of Turkey.

The forest areas are dominated by coniferous tree species and they are known as strong monoterpenes emitters. Therefore, monoterpene emissions dominated the total BVOC emissions in Turkey. Turkish red pine which has the largest spreading specie covered 5.9 million ha area in Turkey constituted about 82.6% of the total BVOC emissions, followed by Uludag fir constituted about 3.5%. Oak species despite having 5.1 million ha area contribute only 3.1% to the total annual BVOC emissions. Considering the spatial distribution of BVOC emissions, only one tree species (Turkish red pine) becomes prominent and specifies the emission distribution pattern.

Oak species emitted to the atmosphere in significant amounts of isoprene and contributed 60.3% to the total isoprene emissions. In addition, oaks and Turkish red pine emitted 90% of oxygenated sesquiterpenes emissions in total. However, the other tree species were also observed to be effective in some BVOC groups. For example, Cilician fir that is an endemic coniferous species emitted 25% of the isoprene emissions alone. Another endemic tree species, Uludag fir had significant BVOC emissions (22 kt yr^{-1}) as a strong monoterpene emitter. Since coniferous species are the largest spreading and evergreen species, they emit BVOCs constantly during the year. The BVOC emissions based on tree species are given in Table 4.2.

Calculations of national BVOC emissions were repeated by using normalized emission rates based on foliage areas along emission rates based on dry foliage weight. The main aim was to compare the inventories and to check the accuracy of the results. According to the results, total annual BVOC emissions that were calculated on the basis of foliage area ($637.65 \text{ kt yr}^{-1}$) and on the basis of dry foliage weight ($637.69 \text{ kt yr}^{-1}$). The results obtained by both methods showed great similarities. Additionally compositions of BVOC emissions groups for both of inventories were identical. Furthermore the spatial distributions of BVOC emissions also showed similarities.

Table 4.2 BVOC emissions based on tree species (t yr⁻¹)

Tree Species	Isoprene	Monoterpenes	Oxygenated Compounds	Oxygenated Sesquiterpenes	Sesquiterpenes	TOTAL
Turkish Red Pine	262	456,876	64,654	174	4,645	526,610
Uludag Fir	2,331	16,012	3,574	0.37	130	22,048
Scots Pine	318	13,832	5,942	1.25	80.7	20,175
Oaks	18,856	242	525	69	90	19,781
Black Pine	53.4	15,206	1,509	0.85	156	16,926
Oriental Spruce	846	10,228	1,147	0.12	90.1	12,312
Cilician Fir	7,855	2,166	253	0.18	84.5	10,358
Lebanon Cedar	10.2	1,707	1,109	0.18	81.5	2,908
Sweet Chestnut	13.3	2,272	50.7	0.047	2.65	2,339
Junipers	4.63	1,015	64	0.074	12.9	1,097
Nordmann Fir	358	406	230	0.046	32.2	1,026
Oriental Beech	175	335	308	20.4	28.6	867
Stone Pine	4.2	185	366	0.26	0.98	556
Maritime Pine	1.34	230	72	0.21	4.59	308
Oriental Plane	55.2	0.21	0.91	0.0021	0.088	56.4
Oriental Sweetgum	43.2	11.2	1.35	0	0.17	56
Silver Lime	1.38	44.1	9.59	0.025	0.39	55.5
European Alder	0.76	34.5	17.2	0	0.73	53.1
Hornbeams	5.02	13.9	27	0.42	2.48	48.9
River Red Gum	29.7	3.24	7.72	0.015	1.57	42.2
Poplars	28.6	1.47	0.2	0.0011	0.043	30.3
Troy Fir	2.82	12.4	3.98	0.0007	0.035	19.3
Aleppo Pine	0.019	4.79	1.11	0.0029	0.032	5.94
Ashes	0.34	0.45	0.94	0.0013	0.22	1.95
Western Australian Golden Wattle	0.35	1.03	0.37	0.0011	0.032	1.78
Black Locust	1.54	0.043	0.024	0.00088	0.003	1.61
Mediterranean Cypress	0.03	0.65	0.36	0.00029	0.012	1.05
Radiata Pine	0.0082	0.14	0.17	0.00011	0.0012	0.31

The highest emissions were observed in summer due to the growing season of the plants. The highest total BVOC emission was 120.4 kt per month in July due to higher ambient air temperature and solar radiation. The minimum total BVOC

emission was 15.2 kt m^{-1} in February. Monthly changes of monoterpenes and isoprene emissions indicated the different pattern in accordance with monthly changes of total BVOC emissions. The monoterpenes emissions were 13.1 kt m^{-1} in February and increase by a factor of 7.3 in July (95.6 kt m^{-1}). Isoprene emissions ranged from 0.06 kt in February to 8.7 kt in July and the increase ratio for isoprene was about 144 times. The main reason for this increase is that isoprene emission was mainly emitted from the broad-leaved trees which are deciduous in winter due to losing their emission effectiveness in this period. Moreover, isoprene emission is directly related to temperature and PAR. However, monoterpenes and other BVOCs are only related to temperature and they are emitted to atmosphere from evergreen trees during 24 hours of the day. Accordingly, in summer when temperature is high, sunlight is strong and the foliage biomass is the largest, the BVOC emissions are the maximum levels. The calculated monthly total BVOC emissions were shown in Figure 4.20.

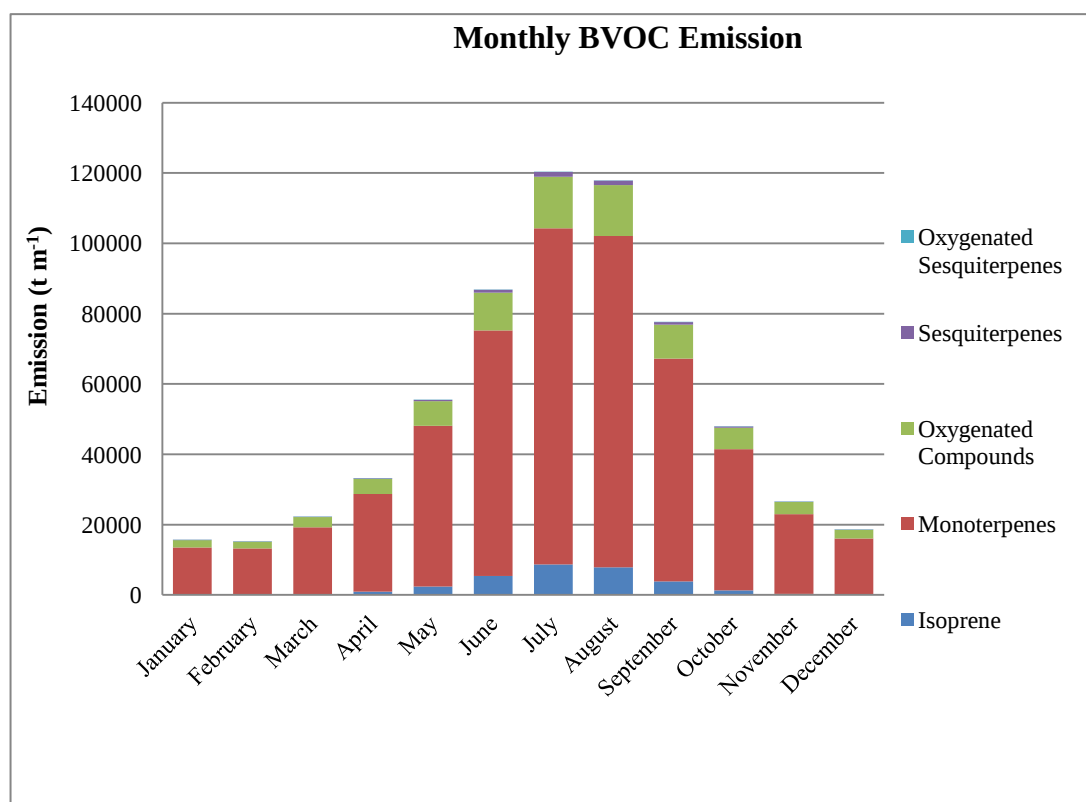


Figure 4.20 Distribution of monthly total BVOC emissions.

Monoterpene emissions mainly consist of beta-pinene (38.4%). This compound is the first rank in the group with the 200.2 kt yr⁻¹ emissions. Eucalyptol provided the largest contribution (40%) in the oxygenated VOC group and that is the first rank in this group with the 32.1 kt yr⁻¹ emissions. The most dominant compound is trans-caryophyllene (68.4%-3.8 kt yr⁻¹) in sesquiterpenes groups. Compounds which put the most contribution for each BVOC groups and contribution rates are given in Figure 4.21.

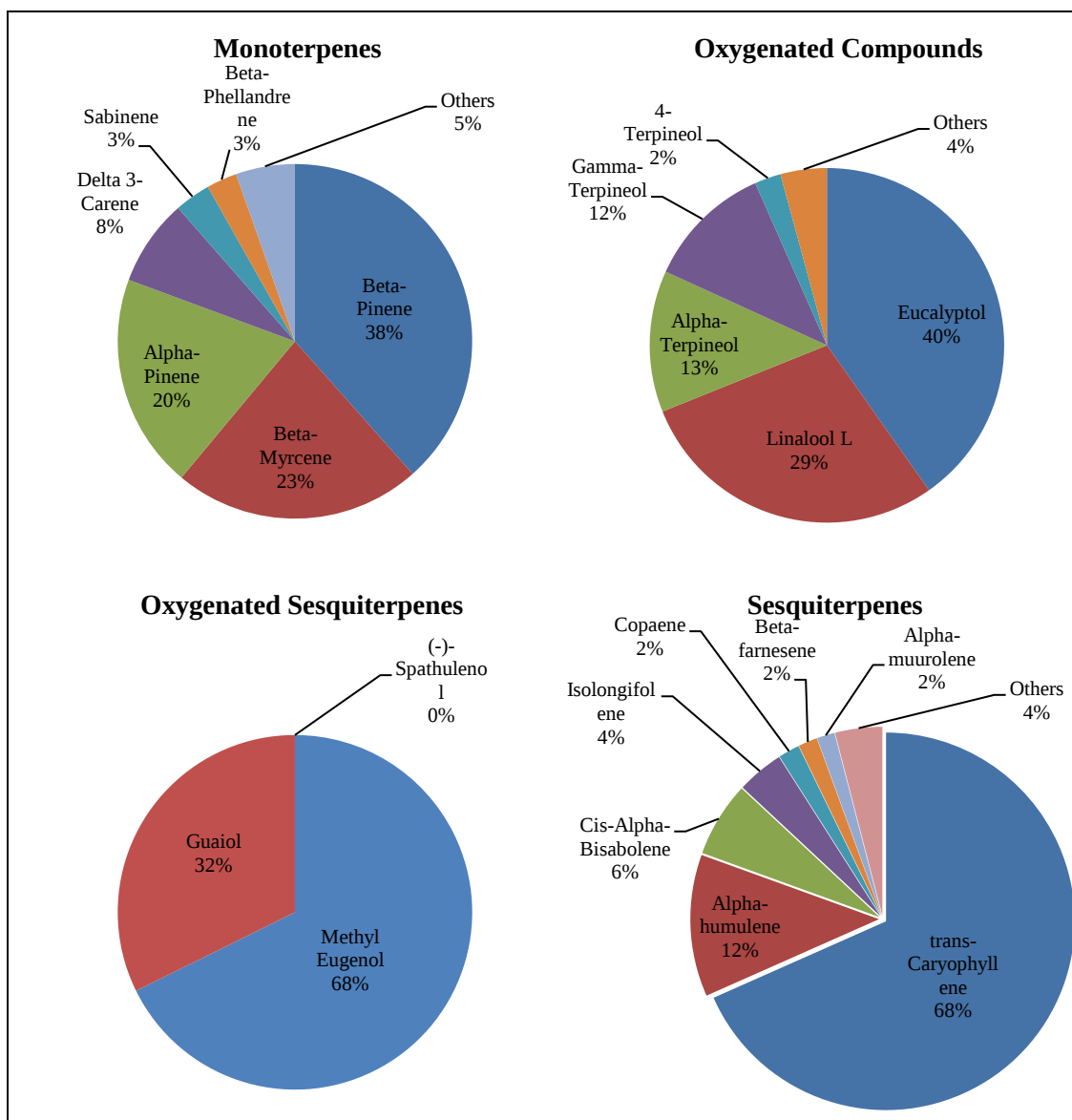


Figure 4.21 Percentages of the most prominent compounds for each BVOC group.

Several BVOC emission inventories were prepared in Europe (Isidorov et al., 1999; Oderbolz et al., 2013; Poupkou et al., 2010). Oderbolz et al. (2013) determined the total annual BVOC emissions for Europe between 8147 and 12359 kt yr⁻¹ within three different scenarios. These scenarios were specified through using three completely different land-cover data. According to land-cover data prepared by Skjoth et al. (2008); total isoprene, monoterpenes, sesquiterpenes and cumulative BVOC emissions were determined as 2650, 4124, 257, and 5328 kt yr⁻¹, respectively. The results of the present study indicated that emissions from forest areas of Turkey were 10,7% of those emitted by forests of Europe. Oderbolz et al. (2013) determined this ratio as 10.9, 9.2, 6.5, and 4.9% for Spain, Ukraine, France and Italy respectively. However, the inventory of the present study based on species-specific emission rates of each tree species that covers whole the forest areas of Turkey. Oderbolz et al. (2013) also determined that monoterpenes covered the largest part of the total BVOC emissions that similarly observed in the present study.

Emission rates are important inputs of air quality modeling studies. They were included as the natural air pollutant sources and calculated in the EMEP grids as 50x50 km² for regional photochemical modeling studies in Europe (Simpson et al., 1999; Skjoth et al., 2008; Symeonidis et al., 2008). Up to now, Turkey was not either included in such studies or included with some assumptions like Oderbolz et al. (2013)'s methods bringing many errors due to insufficient data. Spatial distributions of BVOCs were also calculated based on the EMEP grids as 50x50 km², to provide integration of results with the literature and future regional modeling studies. The highest value was calculated as 19.1 kt yr⁻¹ in these grids (Figure 4.22). The highest values of all the other groups except isoprene were observed in the same grid [for monoterpenes: 16.6 kt yr⁻¹, oxygenated VOCs: 2.4 kt yr⁻¹, sesquiterpenes 174 t yr⁻¹ and oxygenated sesquiterpenes 6.5 t yr⁻¹ (Figure 4.23-4.26)]. The highest isoprene emission value was also observed as 1.3 kt yr⁻¹ in another grid (Figure 4.27).

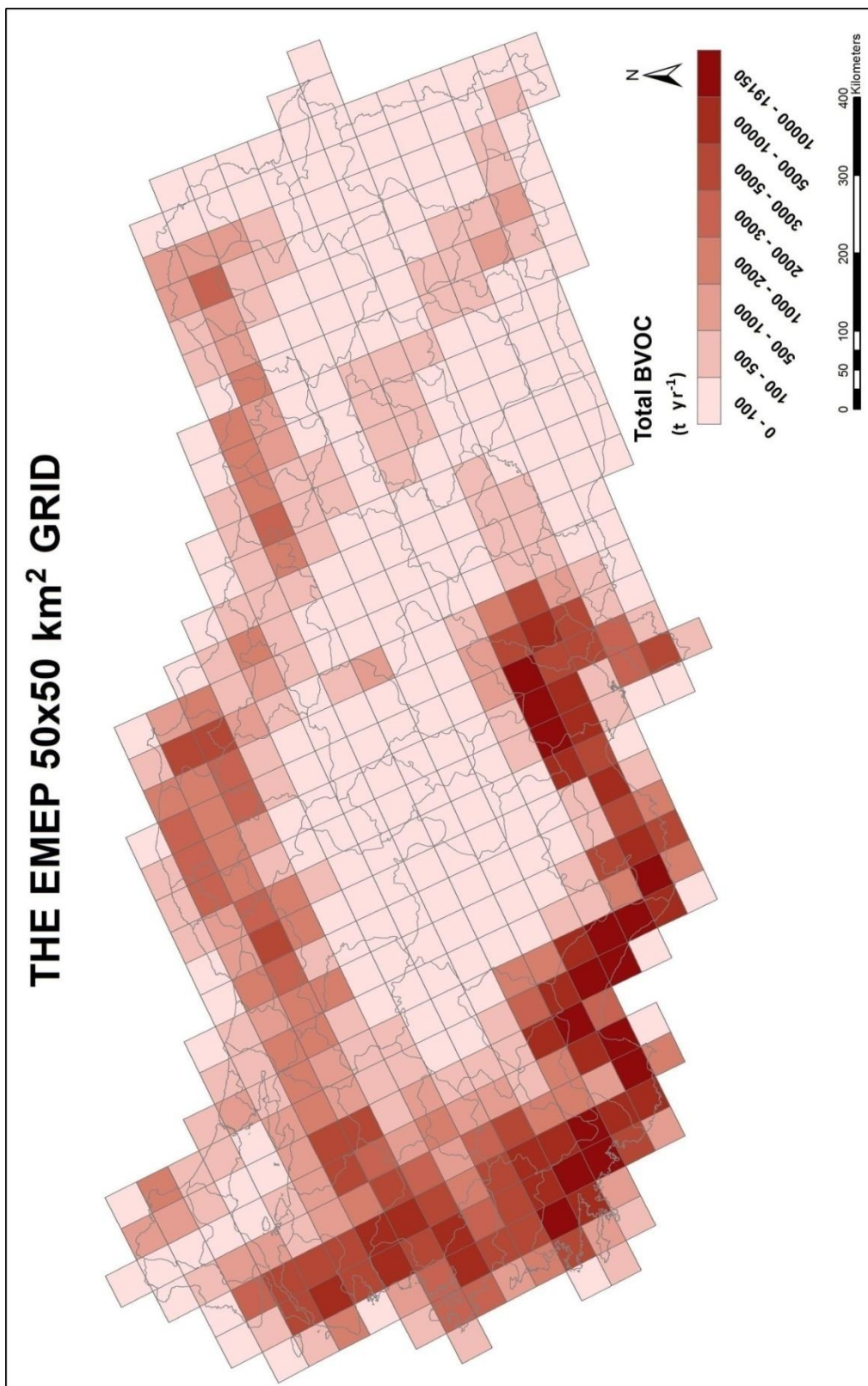


Figure 4.22 Spatial distribution of the total BVOC emissions in the EMEP 50x50 km² grid system in 2012.

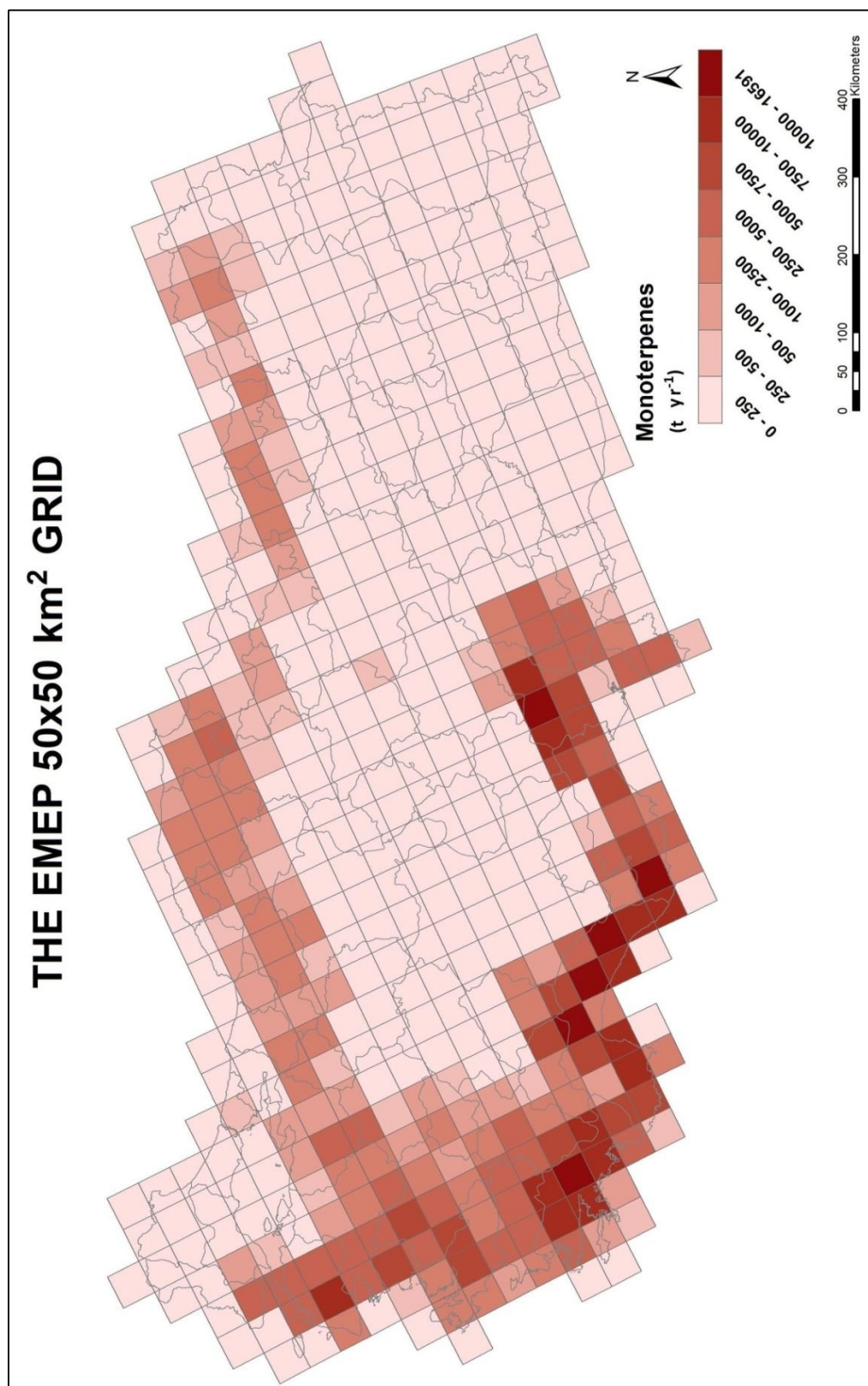


Figure 4.23 Spatial distribution of monoterpane emissions in the EMEP 50x50 km² grid system in 2012.

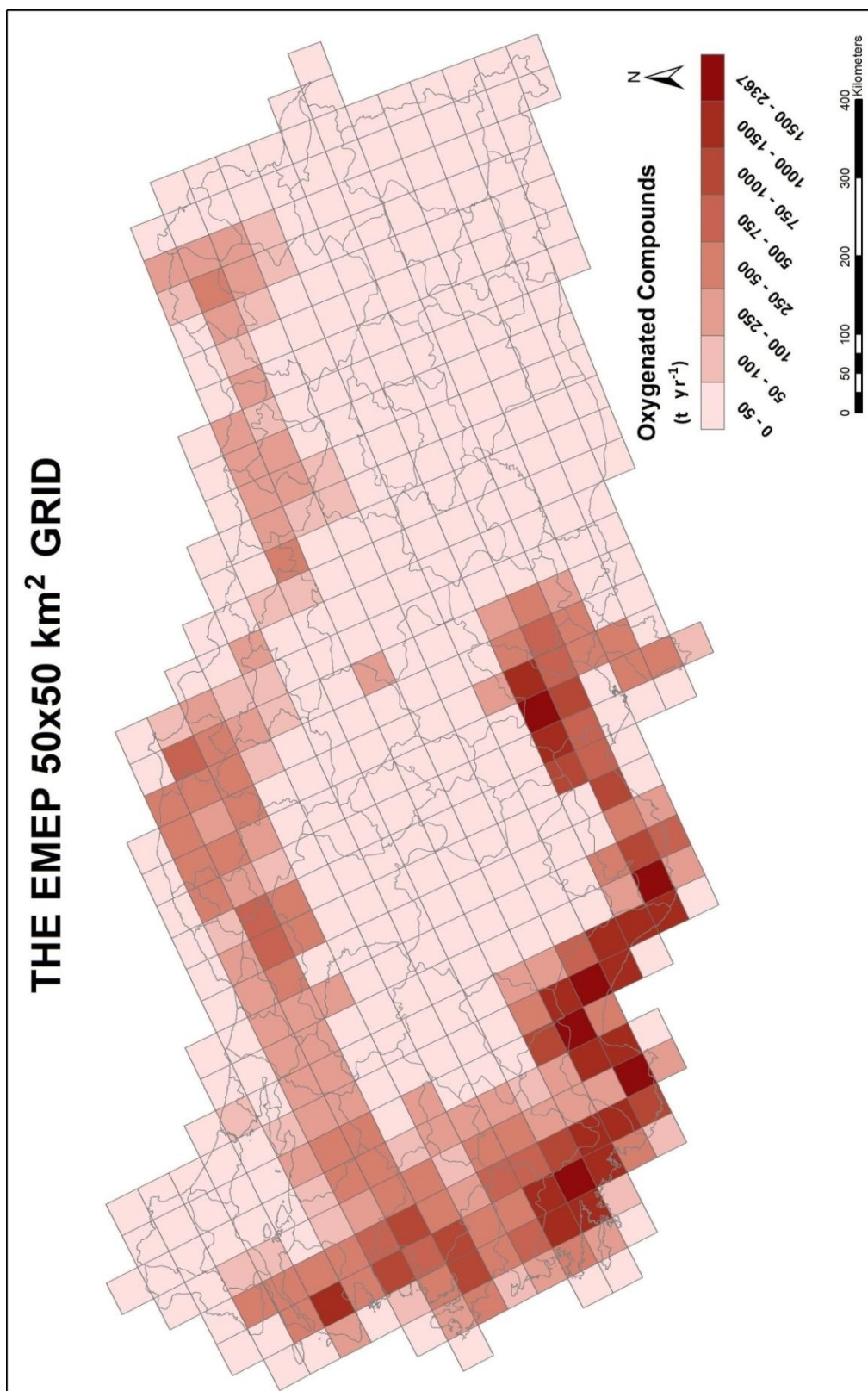


Figure 4.24 Spatial distribution of oxygenated compounds emission in the EMEP 50x50 km² grid system in 2012.

THE EMEP 50x50 km² GRID

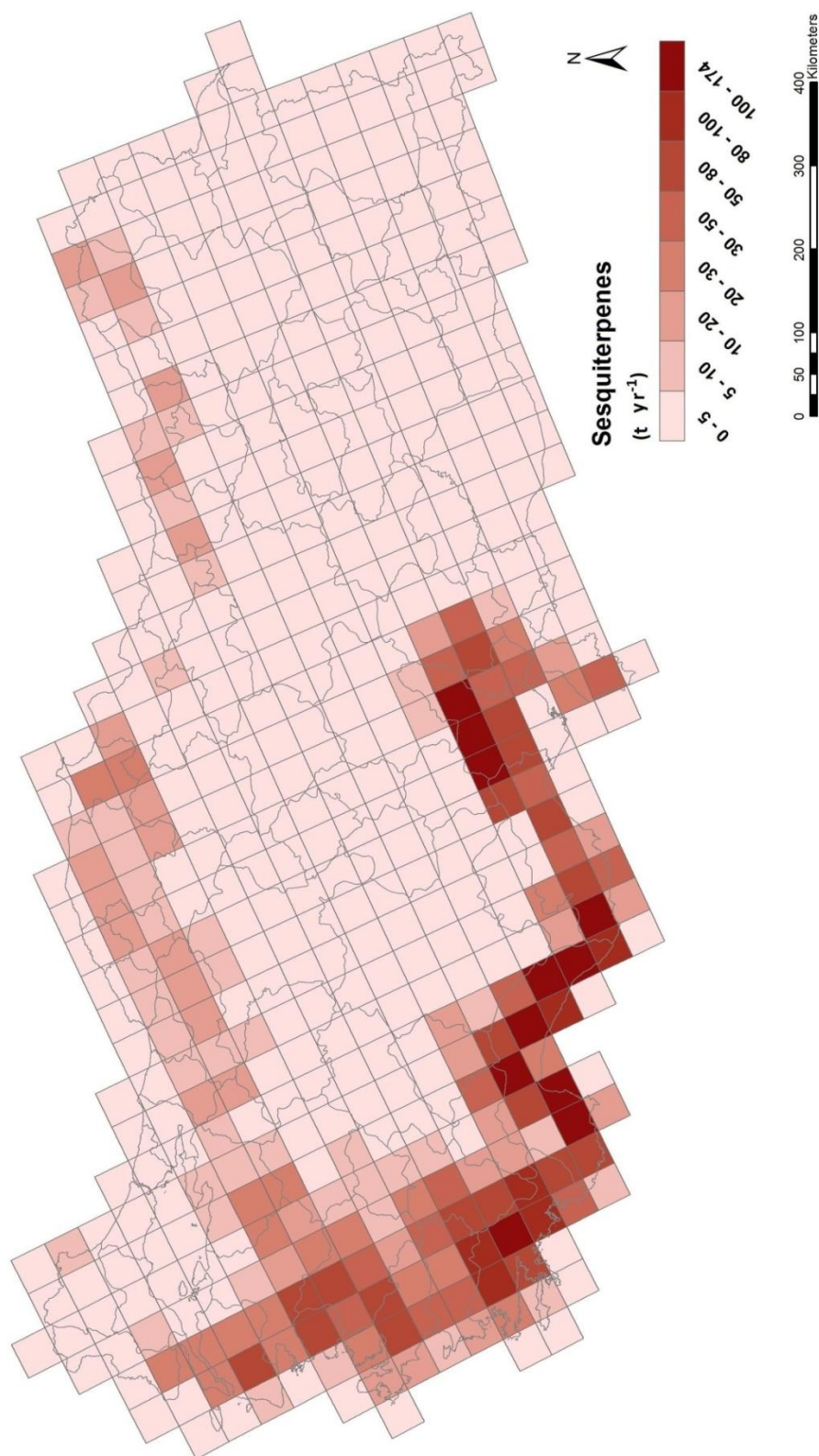


Figure 4.25 Spatial distribution of sesquiterpenes emission in the EMEP 50x50 km² grid system in 2012.

THE EMEP 50x50 km² GRID

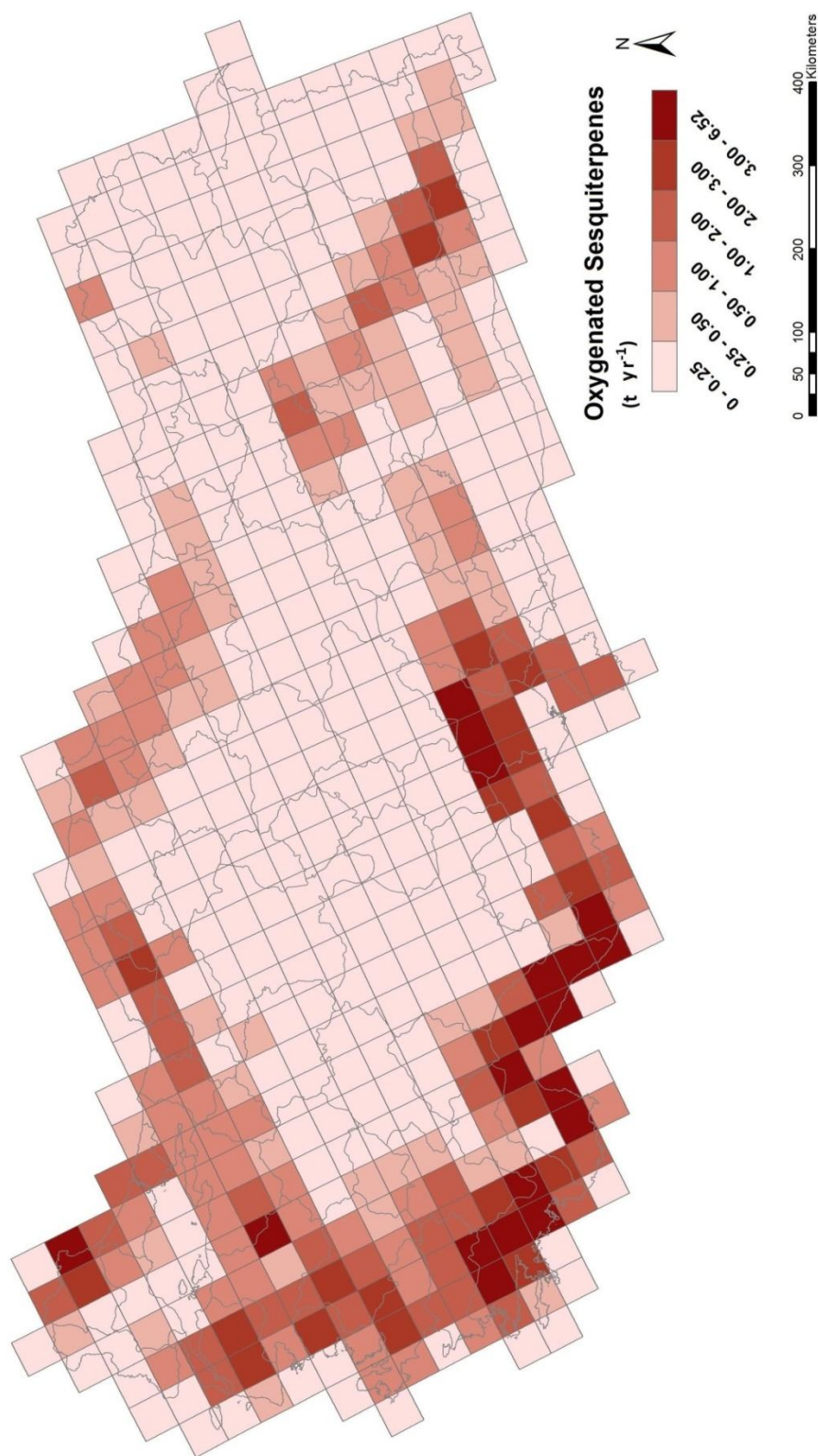


Figure 4.26 Spatial distribution of oxygenated sesquiterpenes emission in the EMEP 50x50 km² grid system in 2012.

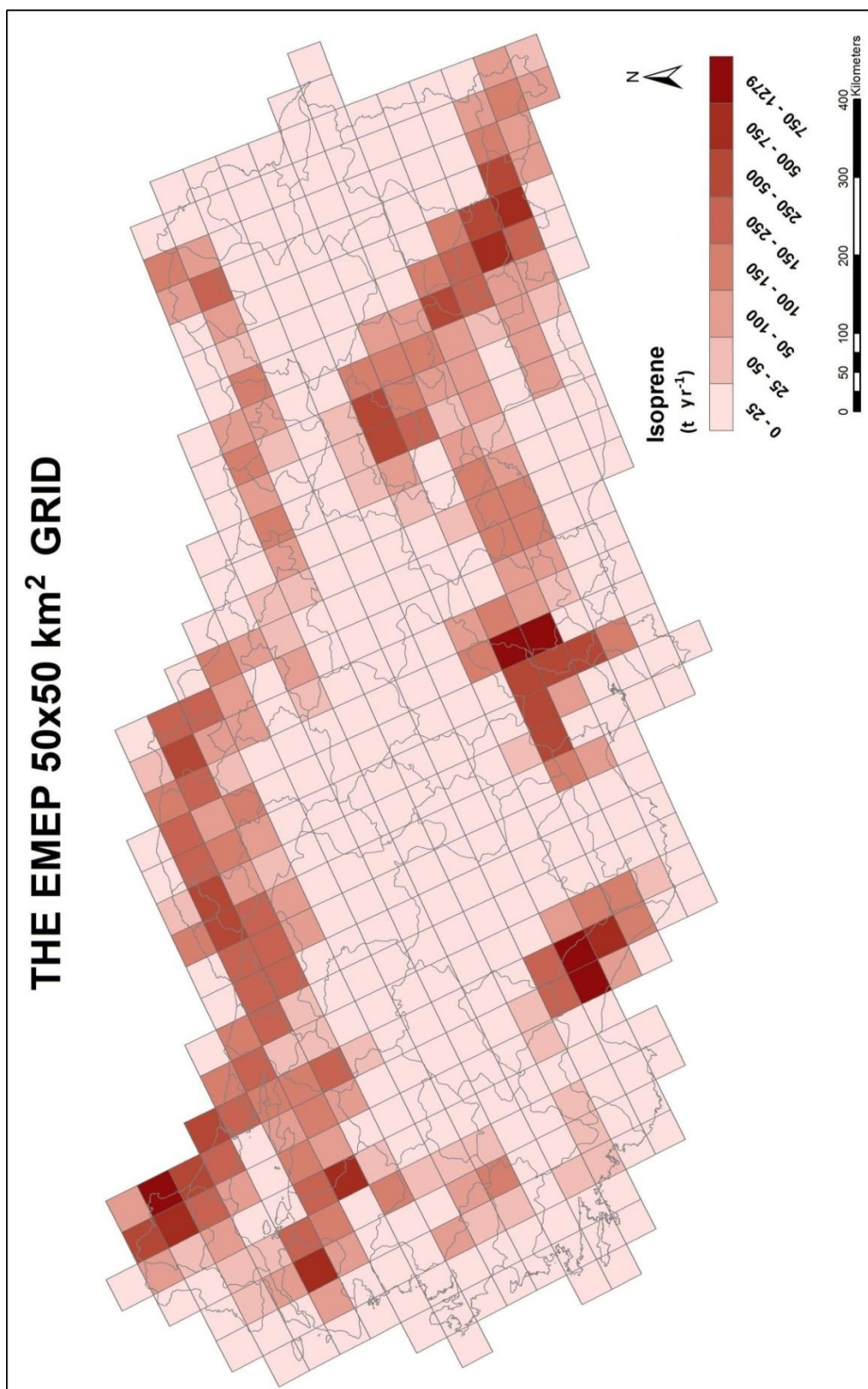


Figure 4.27 Spatial distribution of isoprene emission in the EMEP 50x50 km² grid system in 2012.

At the 36th session of the EMEP Steering Body the EMEP suggested to increase spatial resolution of reported emissions from 50x50 km resolution grid to 0.1°x0.1° long-lat in a geographic coordinate system (WGS84). The new domain will cover the geographic area between 30°N-82°N latitude and 30°W-90°E longitude (Centre on Emission Inventory and Projections [CEIP], 2013). And this suggestion should obtain more accurate results for inventories. The calculations for emission inventory were revised by using 0.1x0.1 degree grid system. Consequently emissions were recalculated as total annual inputs per 0.1°x0.1° grid. Spatial distributions of each emission groups for the EMEP 0.1°x0.1° grid system were shown in Figures 4.28-4.33.

Many atmospheric emission inventories of anthropogenic sources include the transport, energy production, industrial, etc. were developed for Turkey. However natural sources were not included in the emission inventories due to lack of data. The BVOC emission inventory that was prepared within the present study was compared with the VOC inventory of anthropogenic sources in Turkey. The both sources indicated the same contribution to the total VOC emissions. The total amount of VOC emission emitted from anthropogenic sources in 2011 that was reported in 2013 by The Ministry of Environment and Urbanization was calculated as 728 kt yr⁻¹ (Cetinturk Gurtepe & Koksall, 2013). The calculated total amount of annual BVOC emissions in the present study was relatively abreast (638 kt yr⁻¹). BVOC emissions in some countries were more than anthropogenic VOC emissions in literatures. It was reported that the contribution of emissions of BVOC to total VOC emissions are 60% in Ukraine, 45% in Spain (Simpson et al., 1999) and more than 50% in America (Guenther, 1997).

THE EMEP GRID (0.1° x 0.1° longitude/latitude)

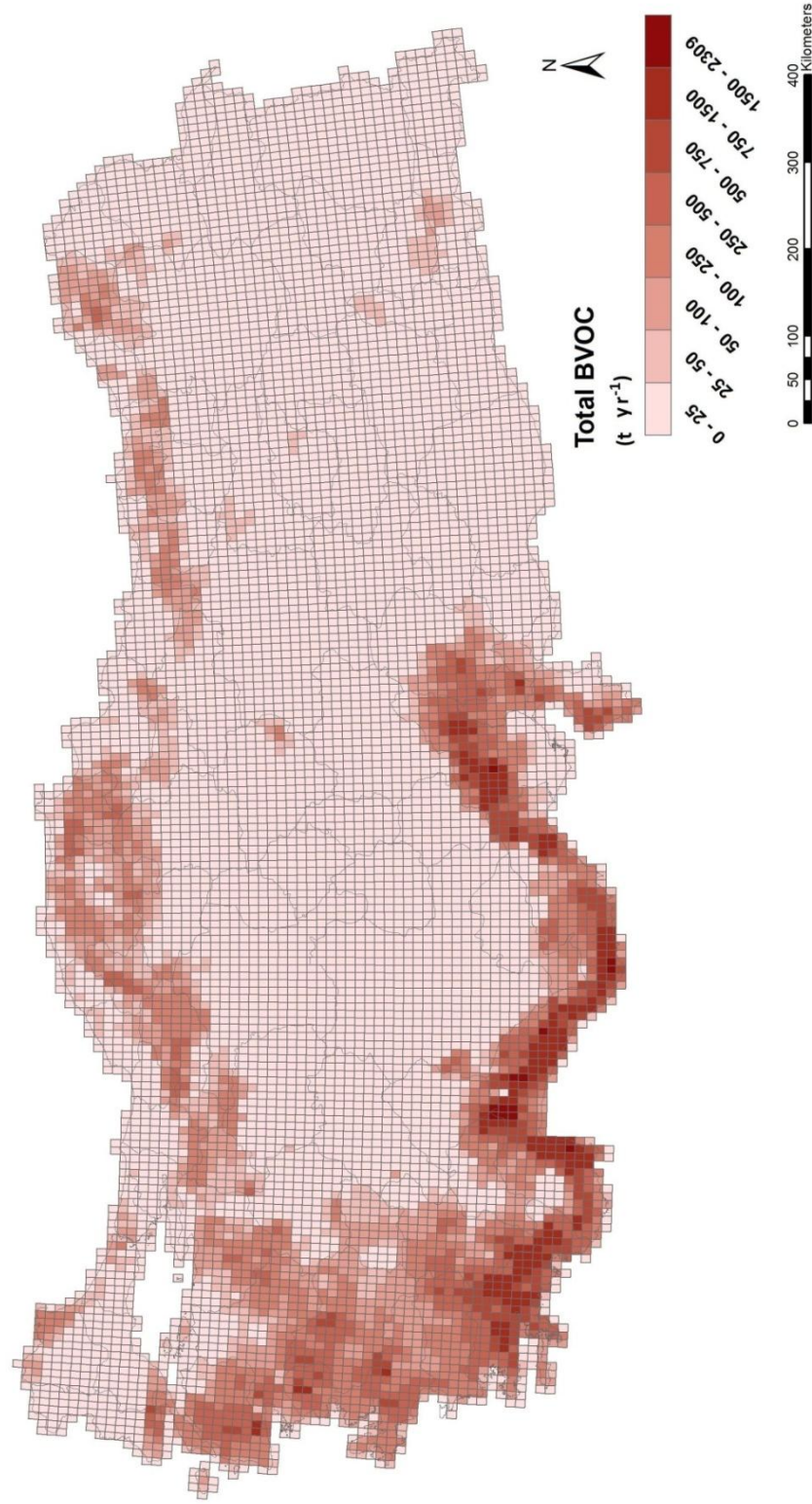


Figure 4.28 Spatial distribution of the total BVOC emission in the EMEP 0.1°x0.1° grid system in 2012.

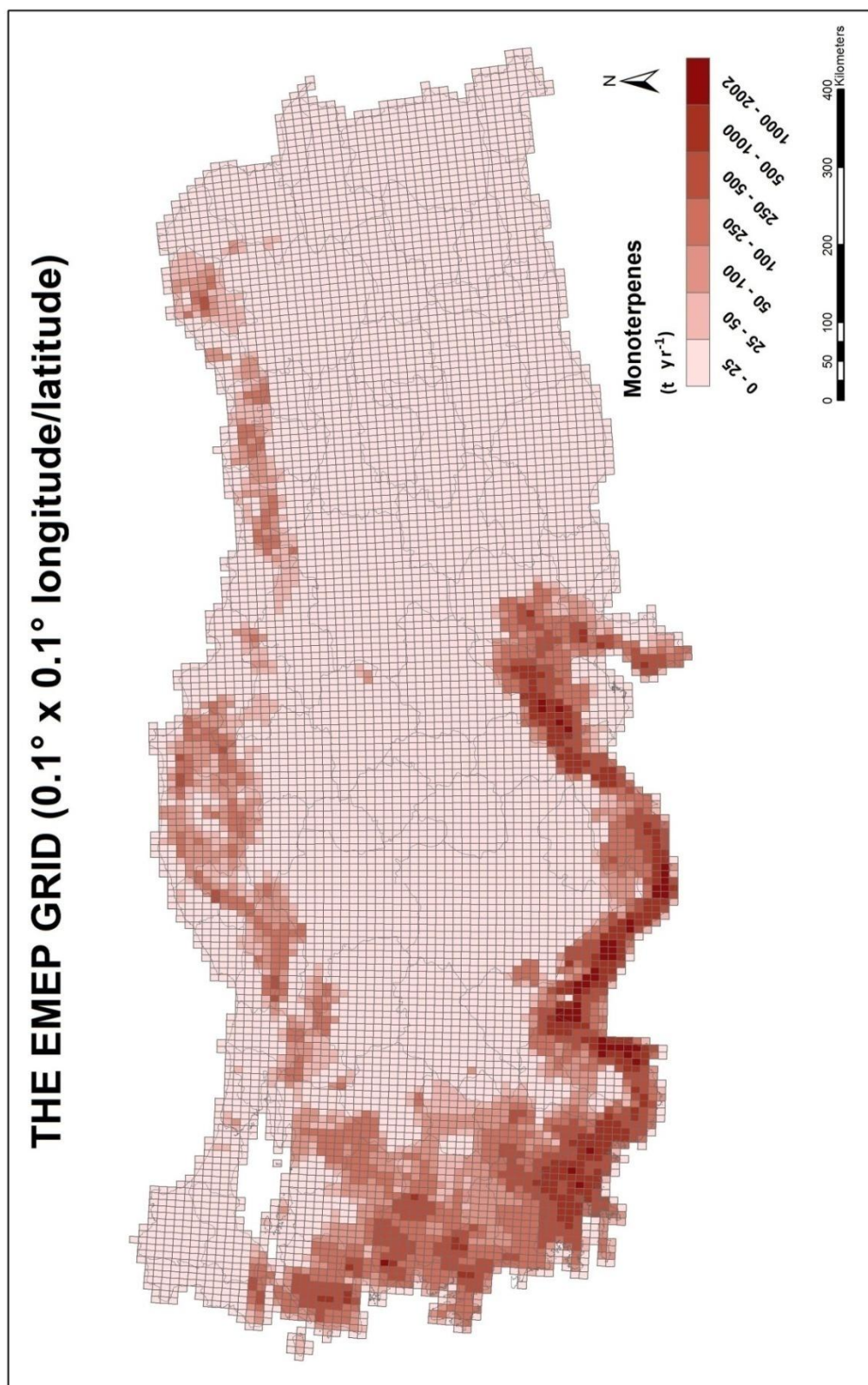


Figure 4.29 Spatial distribution of monoterpenes emission in the EMEP 0.1°x0.1° grid system in 2012.

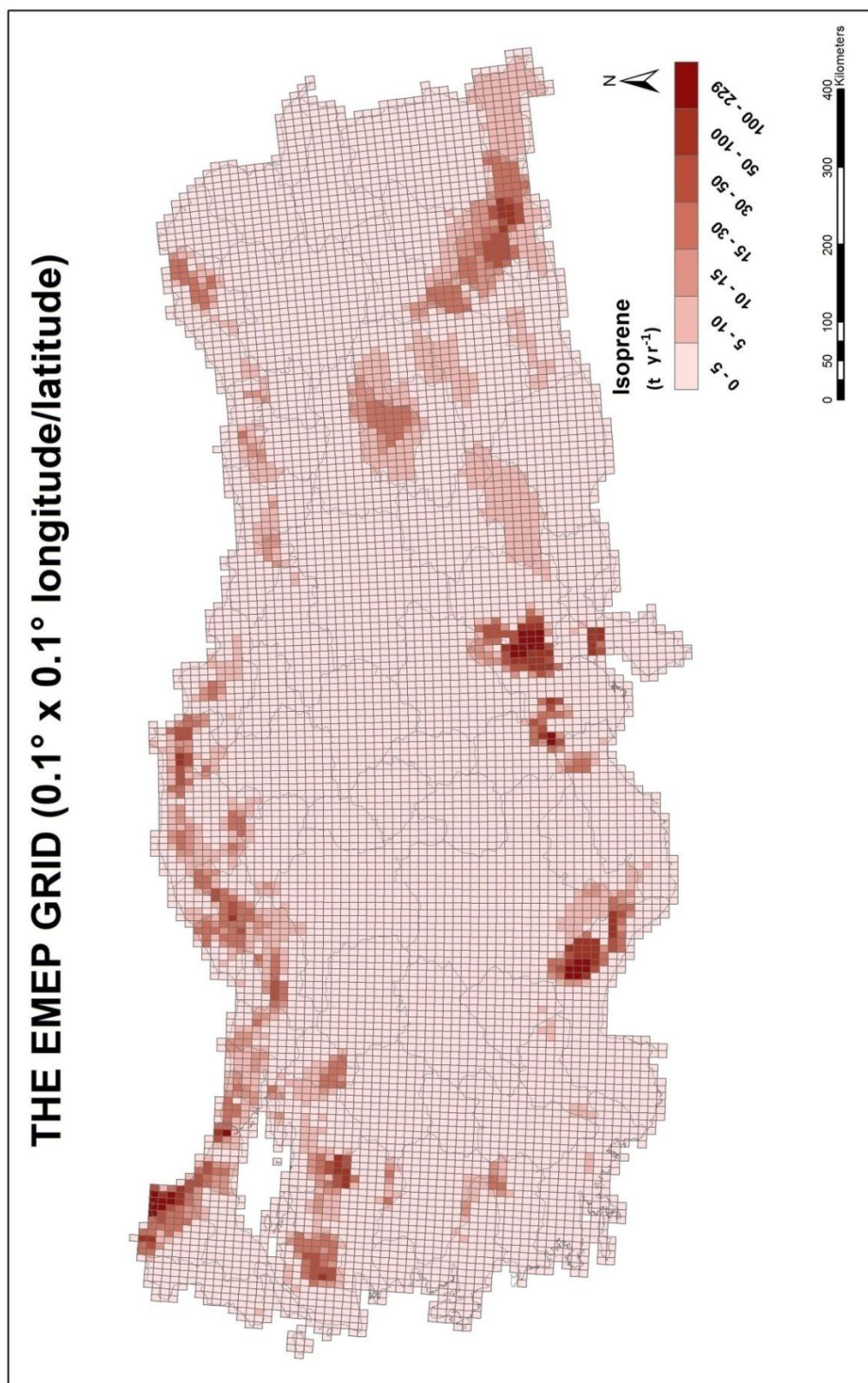


Figure 4.30 Spatial distribution of isoprene emission in the EMEP 0.1°x0.1° grid system in 2012.

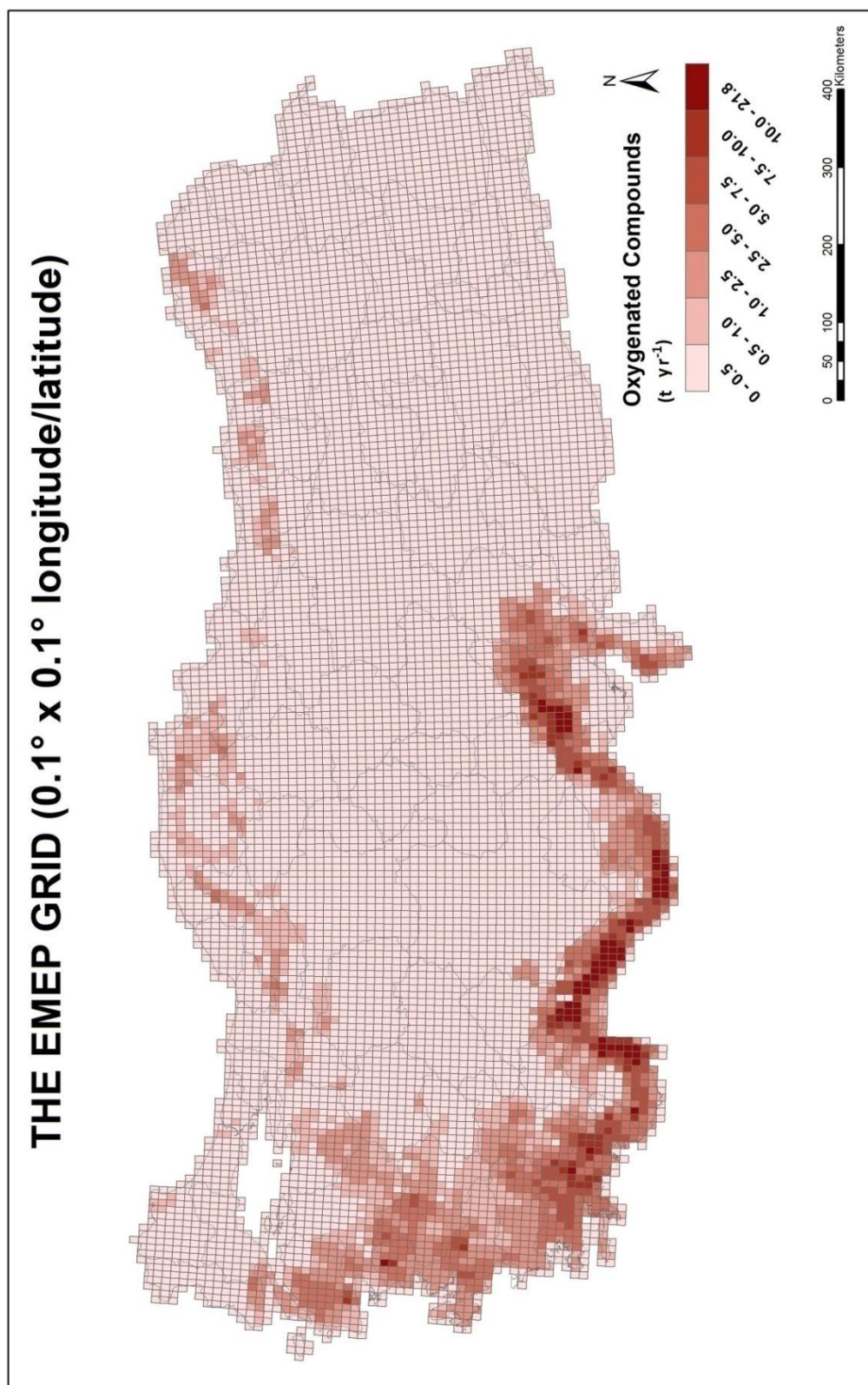


Figure 4.31 Spatial distribution of oxygenated compounds emission in the EMEP 0.1°x0.1° grid system in 2012.

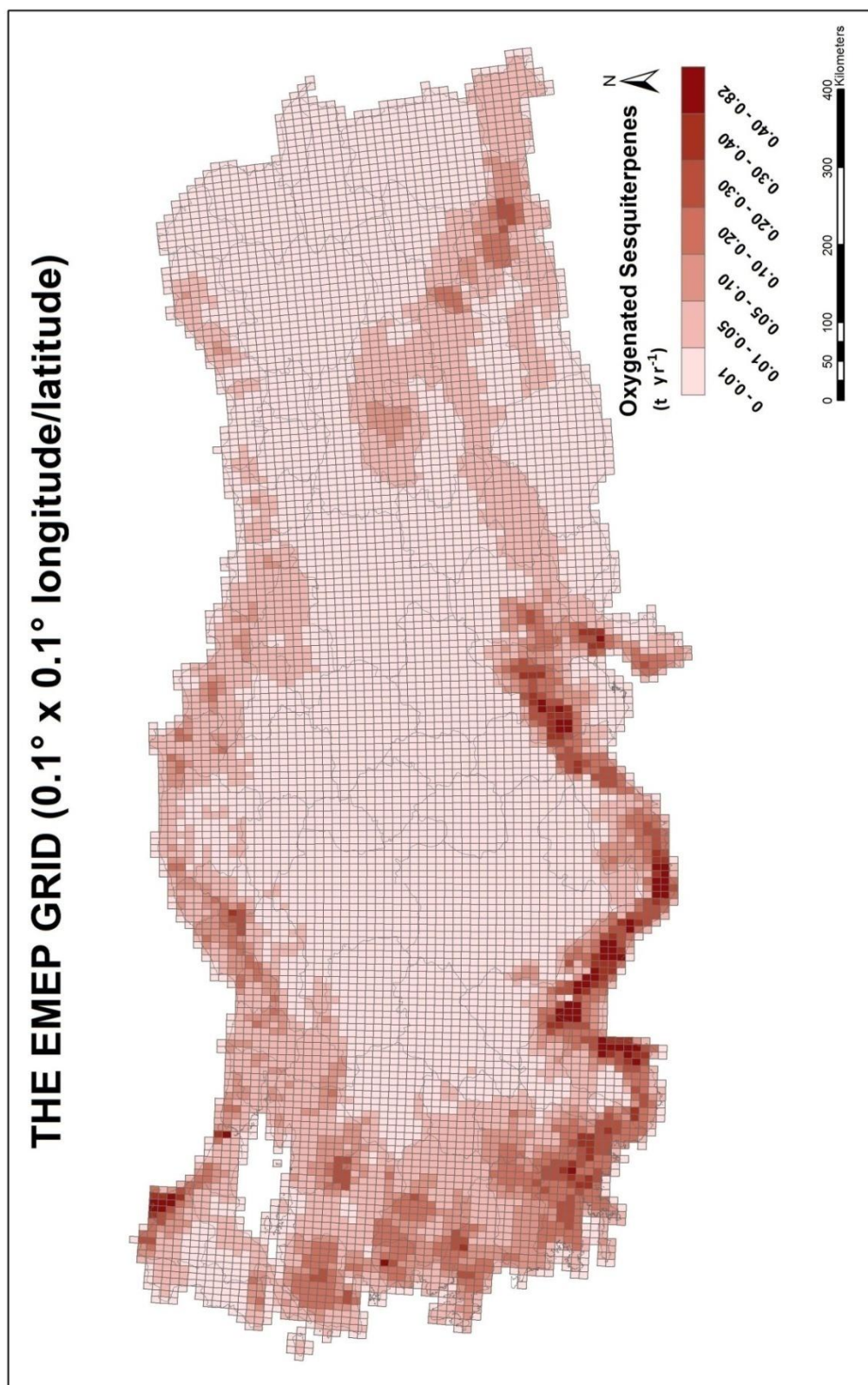


Figure 4.32 Spatial distribution of oxygenated sesquiterpenes emission in the EMEP 0.1°x0.1° grid system in 2012.

THE EMEP GRID (0.1° x 0.1° longitude/latitude)

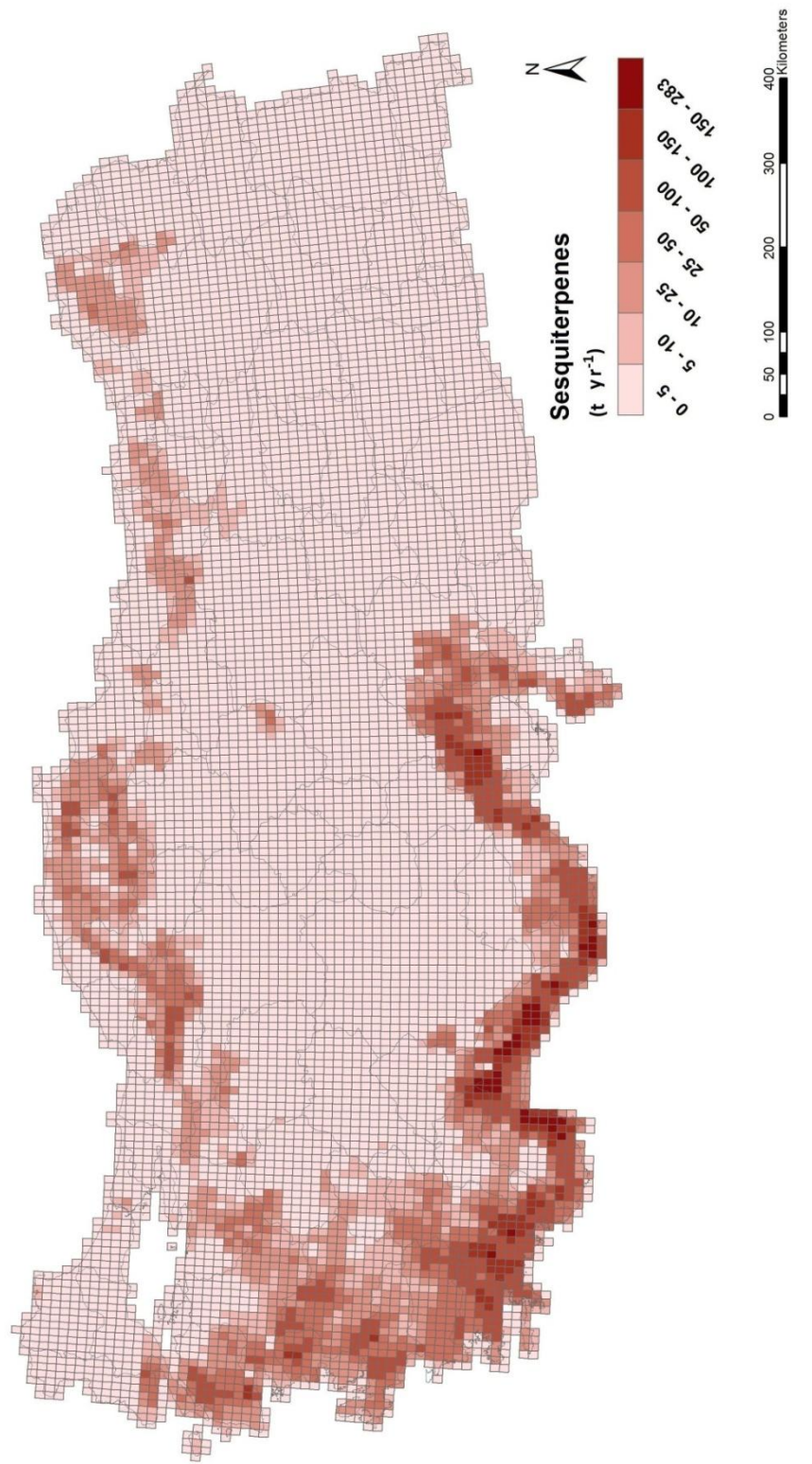


Figure 4.33 Spatial distribution of sesquiterpenes emission in the EMEP 0.1°x0.1° grid system in 2012.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions and Recommendations

This study aims preparation of a comprehensive emission inventory of BVOC emissions in the forest areas of Turkey. Forest inventory, meteorological data and recent measurements of emission rates for tree species in Turkey were used to estimate the amount of BVOC emissions. A spatially and temporally resolved BVOC emission inventory was compiled using long period averages of meteorological data. The total BVOC emissions for the year of 2012 were calculated as 637.7 kt, of which monoterpenes contributes 81.7% (520.1 kt), isoprene 4.9% (31.3 kt), sesquiterpenes 0.85% (5.4 kt), oxygenated compounds 12.5% (79.9 kt) and oxygenated sesquiterpenes 0.05% (0.3 kt). The higher emissions were observed in the southern part of the country and especially in the Mediterranean coastline region due to the distribution of the vegetation, climate and strong solar radiation. Other highest emissions were also calculated in Aegean and Black Sea regions.

Turkish red pine which was an ever-green coniferous tree emitted the highest emission (527 kt yr^{-1} ; 82.6%) to the atmosphere. Uludag fir covers only an area of about 285,000 ha, which is 1.3% of the forest area in Turkey, but it is predicted to produce trees of the genus oaks clearly dominate the isoprene emissions (60.3%) because they are both common species and have high emission factors.

The annual cycle of total BVOC emissions indicates higher values during summer months due to high temperature and solar radiation. The results showed that in summer especially in July the highest emission (120 kt m^{-1}) occurred and the lowest emission (15 kt m^{-1}) occurred in winter (February).

In Turkey, air pollutant sources with anthropogenic origin as industry, traffic, residential heating, etc. were studied in several emissions inventories, but natural sources were not included in these inventories due to lack of national data. This study

presents a first detailed BVOCs emission inventory in Turkey. BVOC emissions are considerable levels as high as anthropogenic emissions. However, in most regions, the BVOC emissions were approximately 50% of the anthropogenic emissions. The total amount of VOCs emitted anthropogenic sources in Turkey based on the inventory prepared in 2011 was approximately 728 kt yr⁻¹, while BVOC emissions from forest areas in the present study were determined as 678 kt yr⁻¹.

The study has several suggestions for further researches; since the study focused on only common tree species in forest areas. There is a need to broaden the scope of this study by including other vegetation types such as crops, grasslands, shrub land, pasture, etc. in Turkey. In future urban ecosystem planning, new planting of species with low BVOC emissions with large canopy layers should be considered.

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