**T.R.**
**BOLU ABANT İZZET BAYSAL UNIVERSITY**
**INSTITUTE OF GRADUATE STUDIES**

# INVESTIGATION OF SPATIAL AND SEASONAL VARIATIONS OF ANTROPOGENIC AND BIOGENIC VOLATILE ORGANIC CARBONS (VOCS) DETERMINED BY THERMAL DESORPTION GC-MS TECHNIQUE AND CONTRIBUTION OF BIOGENIC VOCS TO OZONE CONCENTRATIONS AT HIGH ALTITUDE SEMI-RURAL SITE

**DOCTOR OF PHILOSOPHY**

**MELİKE DÖRTER**

**BOLU, APRIL - 2021**

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**ACADEMIC SUPERVISOR**
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# APPROVAL OF THE THESIS

**INVESTIGATION OF SPATIAL AND SEASONAL VARIATIONS OF ANTROPOGENIC AND BIOGENIC VOLATILE ORGANIC CARBONS (VOCS) DETERMINED BY THERMAL DESORPTION GC-MS TECHNIQUE AND CONTRIBUTION OF BIOGENIC VOCS TO OZONE CONCENTRATIONS AT HIGH ALTITUDE SEMI-RURAL SITE** submitted by **Melike DÖRTER** and defended before the Examining Committe Members listed below in partial fulfillment of the requirements for the degree of **Doctor of Philosophy** in **Department of Chemistry, Institute of Graduate Studies of Bolu Abant Izzet Baysal University in 27.04.2021** by

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# ETHICAL DECLARATION

In this thesis dissertation that was properly prepared according to the Thesis Writing Rules of Bolu Abant İzzet Baysal University of the Institute of Graduates Studies, I hereby declare that;

- All data, information, and documents presented in the thesis were obtained in accordance with the academic and ethical rules,
- All data, documents, assessments, and results were presented in accordance with the scientific ethical and moral rules,
- All works that were benefitted in the thesis were appropriately cited,
- No alteration was made in the data used,
- Study presented in this thesis is original,

Otherwise, I declare that I accept the loss of all my rights in case any contradiction that may arise against me.

_____

**Melike DÖRTER**

# ABSTRACT

**INVESTIGATION OF SPATIAL AND SEASONAL VARIATIONS OF ANTHROPOGENIC AND BIOGENIC VOLATILE ORGANIC CARBONS (VOCS) DETERMINED BY THERMAL DESORPTION GC-MS TECHNIQUE AND CONTRIBUTION OF BIOGENIC VOCS TO OZONE CONCENTRATIONS AT HIGH ALTITUDE SEMI-RURAL SITE**
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**INSTITUTE OF GRADUATE STUDIES**
**BOLU ABANT IZZET BAYSAL UNIVERSITY**
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**BOLU, APRIL 2021**
**(xvi + 183 page)**

The ambient air contains a group of pollutants called volatile organic compounds. Some of them have been the subject of most of the research due to their negative effects on the environment and health. In this study, it was aimed to collect and evaluate a total of 70 volatile organic compounds (biogenic and anthropogenic origin) in Bolu atmosphere. Passive and active sampling techniques were performed. The passive sampling was carried out at 47 sampling points during the winter (28 January 2017 - 12 February 2017) and 63 sampling points in the summer (7 July 2017 - 23 July 2017). At our station in the university campus, 68 compounds for every month between April - November 2017; January 2018 and 70 compounds for every month between April - August 2018 were collected with active sampling in daily and 6-hour periods. Analyses were performed using a thermal desorption gas chromatography-mass spectroscopy system. The results have been compared with similar studies around the world. It is valuable to be able to identify the mechanisms, atmospheric roles and sources of these compounds as well as determine their atmospheric concentrations. For this purpose, the time-dependent changes of the compounds, their relations with meteorological factors and the correlations between each other were examined. Especially, the ozone formation potential of volatile organic compounds and the effective factors in the formation have been investigated. Pollutant distribution maps were plotted and thus, source regions were determined for each compound. Source apportionment was carried out with Positive Matrix Factorization. The studies had shown that biogenic sources were the predominant source for volatile organic compounds in the region.

**KEYWORDS:** Volatile Organic Compounds, Ozone Formation Potential, Passive and Active Sampling, Pollution Distribution Map, Positive Matrix Factorization

# ÖZET


**YÜKSEK RAKIMLI YARI-KIRSAL BİR ALANDATERMAL DESORPSİYONLU GC-MS TEKNİĞİ İLE BELİRLENEN ANTROPOJENİK VE BİYOJENİK UÇUCU ORGANİK KARBONLARIN (UOB'LER) ALANSAL VE MEVSİMSEL DEĞİŞİMLERİNİN VE BİYOJENİK UOB'LERİN OZON KONSANTRASYONLARINA KATKISININ İNCELENMESİ**
**DOKTORA TEZİ**
**MELİKE DÖRTER**
**BOLU ABANT İZZET BAYSAL ÜNİVERSİTESİ**
**LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ**
**KİMYA ANABİLİM DALI**
**(TEZ DANIŞMANI: PROF. DR. SERPİL YENİSOY KARAKAŞ)**
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Atmosfer, uçucu organik bileşikler olarak adlandırılan bir grup kirletici içermektedir. Bu bileşikler arasından önde gelen bazıları çevre ve sağlık üzerine olumsuz etkileri nedeniyle çoğu çalışmada araştırma konusu olmuştur. Bu çalışmada, toplam 70 adet uçucu organik bileşiğin (biyojenik ve/veya antropojenik kökenli) Bolu atmosferinde toplanması ve değerlendirilmesi amaçlanmıştır. Pasif ve aktif örnekleme teknikleri uygulanmıştır. Pasif örnekleme çalışması kışın (28 Ocak 2017-12 Şubat 2017) 47 örnekleme noktasında ve yazın (7 Temmuz 2017-23 Temmuz 2017) 63 örnekleme noktasında gerçekleştirilmiştir. Aktif örnekleme tekniği ise üniversite kampüsündeki istasyonda, Nisan- Kasım 2017 arasındaki her ay için 68 adet bileşik; Ocak 2018 ve Nisan- Ağustos 2018 arasındaki her ay için 70 adet bileşik, günlük ve 6 saatlik periyotlarda toplanmıştır. Analizler termal desorpsiyonlu gaz kromotografisi kütle spektroskopisi sistemi kullanılarak yapılmıştır. Sonuçlar dünyadaki benzer çalışmalar ile kıyaslanmıştır. Bu bileşiklerin atmosferik derişimlerini tespit etmek kadar mekanizmalarını, atmosferik rollerini ve kaynaklarını tespit edebilmek de değerlidir. Bu amaçla, bileşiklerin zamana bağlı değişimleri, meteorolojik faktörler ile ilişkileri ve birbirleri arasındaki korelasyonlar incelenmiştir. Özellikle, uçucu organik bileşiklerin ozon oluşturma potansiyeli ve etkin faktörler araştırılmıştır. Kirletici dağılım haritaları oluşturulmuş ve böylece her bir bileşik için kaynak bölgeler belirlenmiştir. Kaynak paylaşımı çalışmaları ise Pozitif Matriks Faktorizasyonu ile yürütülmüştür. Çalışmalar bölgedeki en baskın uçucu organik bileşik kaynağının biyojenik kaynaklar olduğunu göstermiştir.



**ANAHTAR KELİMELER:** Uçucu Organik Bileşikler, Ozon Oluşturma Potansiyeli, Pasif ve Aktif Örnekleme, Kirlilik Dağılım Haritası, Pozitif Matriks Faktorizasyonu

# TABLE OF CONTENTS

# LIST OF FIGURES

**Page**

# LIST OF TABLES

**Page**

# LIST OF ABBREVIATIONS AND SYMBOLS

**BVOCs** : Biogenic Volatile Organic Compounds

**CFCs** : Chlorofluorocarbons

**CMB** : Chemical Mass Balance

**CV** : Coefficient of Variation

**ECD** : Electron Capture Detector

**FID** : Flame Ionization Detector

**GIS** : Geographical Information Systems

**HAPs** : Harmful Air Pollutants

**KI** : Potassium Iodide

**MACR** : Methacrolein

**MDL** : Method Detection Limit

**MIR** : Maximum Incremental Reactivity

**MLOQ** : Method Limit of Quantification

**MS** : Mass Spectrometry

**MVK** : Methyl Vinyl Ketone

**$NaNO_2$** : Sodium Nitrite

**$Na_2CO_3$** : Sodium Carbonate

**$NH_3$** : Ammonia

**NOx** : Nitrogen Oxides

**$O_2$** : Molecular Oxygen

**$O_3$** : Ozone

**$O^3P$** : Monatomic Oxygen

**OFP** : Ozone Formation Potential

**PAHs** : Polycyclic Aromatic Hydrocarbons

**PCA/APCS** : Principal Component Analysis/Absolute Principal Component Scores

**PM** : Particulate Matter

**PMF** : Positive Matrix Factorization

**QA / QC** : Quality Control and Quality Assurance

**RSD%** : Percentage Relative Standard Deviation

**SIM** : Selected Ion Monitoring

**S/N** : Signal to Noise Ratio

**$SO_2$** **:** Sulphur Dioxide

**T/B** **:** Toluene-to-Benzene Ratio

**TD-GC-MS** **:** Thermal Desorption-Gas Chromatography-Mass Spectroscopy

**TCD** **:** Thermal Conductivity Detector

**TEX** **:** Toluene, Ethylbenzene and Xylenes

**TWA** **:** Time-Weighted Average

**UR** **:** Uptake Rate

**US EPA** **:** The United States Environmental Protection Agency

**VOC** **:** Volatile Organic Compound

**X/E** **:** Xylene-to-Ethylbenzene Ratio

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# 1. INTRODUCTION

The atmosphere plays a key role in the sustainability of life on earth. It enabled the formation of an ozone shield against solar ultraviolet radiation. The atmosphere is a source of carbon dioxide for photosynthesis, nitrogen for nitrogen-binding bacteria and ammonia-producing industrial plants and of course oxygen for respiration of living organisms [1]. It is made up of approximately 78 % nitrogen, 21 % oxygen, 0.9 % argon, 0.04 % carbon dioxide and small amounts of other gases. The gases are also generated by natural sources such as forest fires, volcanic eruptions, sea salt, dust storms, lightning and biogenic emissions. In addition, some human activities have become part of life with modernization. They interrupt natural ratios in the environment. Deforestation, transportation, fossil fuel burning, industrial activities, waste disposal and solvent production and usage are some examples of anthropogenic activities [2]. Such anthropogenic activities have significantly changed the atmosphere, especially in terms of its composition of minor constituents and trace gases. It is called air pollution when foreign substances in the air reach an above-normal amount and density.

Today, increasing air pollution disrupts the global balance, which has serious consequences for life on Earth. Global warming can be evaluated in this context. Elevated levels of greenhouse gases (especially carbon dioxide, methane and ozone) in the atmosphere may cause global warming. Atmospheric concentrations of these gases have increased since 1760 when industrialization emerged. The global rise in carbon dioxide levels is mainly due to fossil fuel burning and deforestation [3], while that of methane is related to the usage of natural gas [4]. Ozone, on the other hand, is one of the photochemical smog elements that are formed because of chemical reactions between nitrogen oxides (NOx) and volatile organic compounds (VOCs) in the presence of sunlight [5]. These gases produce a “green-house effect” by increasing the atmospheric absorption of incoming solar radiant energy [6]. The term radiative forcing is used to describe the decrease in infrared radiation penetrating out of the atmosphere per unit increase in gas level in the atmosphere. Carbon dioxide is estimated to have the highest (+1.66 [1.49 to 1.83] W $m^{-2}$) contribution to the global radiative forcing, followed by methane (0.48 [0.43 to 0.53] W $m^{-2}$) and ozone (0.35 [0.25 to 0.65] W $m^{-2}$) [6]. Differently, sulfur dioxide (principally from fossil-fuel usage) and nitrogen oxides

(mainly from vehicular emissions) undergo atmospheric oxidation to form sulphuric and nitric acid. High atmospheric concentrations of these acid-forming gases lead to increased acidity in the atmosphere and thus acid rain which is a regional phenomenon [7]. Threats to the ozone layer in the stratosphere are another global subject. The large anthropogenic emissions of chlorofluorocarbons (CFCs) and halocarbons are determined as mainly responsible for the ozone layer depletion. While the production and use of these substances are almost completely banned, emphasis is placed on the ozone destruction potential of the $N_2O$ for the 21$^{st}$ century [8]. $N_2O$ gas is emitted from both natural sources (such as an ocean, tropical forests) and anthropogenic sources (such as industrial processes, fossil fuel combustion and biomass burning), and about 10% of the released gas turns into nitric oxide. Nitric oxide is a compound that contributes greatly to the depletion of stratospheric ozone [8].

In addition to its environmental effects, air pollution is responsible for the loss of life and property. According to data from 2015, air pollution was responsible for 24% of ischemic heart disease deaths, 23% of lung cancer deaths, 21% of stroke deaths and 19% of cardiovascular deaths [9]. It is known that exposure to air pollution causes different health problems such as respiratory diseases, cardiovascular diseases, mental problems, cancer and infertility depending on factors such as pollutants, individual features, dose and exposure time [10-13]. Also, poor air quality has a role in the development and severity of virus-borne diseases. Studies on the new coronavirus disease, namely COVID-19, which emerged in Wuhan, China in December 2019 and spread all over the world in a short time, prove this. Exposure to fine particulate matter ($PM_{2.5}$), particles with a diameter of 10 micrometers or less ($PM_{10}$), CO, $NO_2$ and $O_3$ pollutants were found to be significantly positively associated with COVID-19 infection [14, 15]. Moreover, the economical consequences of air pollution are directly related to financial loss due to additional medical expenditures, loss in productivity, expenditures for damaged buildings and crop yield losses [16].

Thus, every step taken to prevent air pollution will serve the continuity of life in the world, economic growth, protection of human health and lessen the spread of epidemics. Effective pollution control strategies contain the establishment and enforcement of standards about air quality. In Turkey, the Air Quality

Assessment and Management Regulations include air quality targets (limit values), assessments and improvement strategies [17].

At this point, detection of atmospheric concentrations of pollutants, finding out their atmospheric fates and identification of possible sources is vital to establish pollution control. There are too many pollutants including nitrogen oxides ($NO_x$), volatile organic compounds (VOCs), sulphur dioxide ($SO_2$), ozone ($O_3$), polycyclic aromatic hydrocarbons (PAHs) and ammonia ($NH_3$). In this study, a large range of VOCs (totally 70) have been investigated in terms of their atmospheric concentrations, spatial distributions, temporal (intraday, interday and seasonal) variations, ozone formation potentials and source apportionment.

## 1.1 Volatile Organic Compounds

Volatile organic compounds (VOCs) are a very broad class containing a variety of chemicals. The definition of VOCs made by the EPA [18] is "Volatile organic compound (VOC) means any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates and ammonium carbonate, which participates in atmospheric photochemical reactions, except those designated by EPA as having negligible photochemical reactivity".

VOCs are an important pollutant group that can be found widely in rural, urban or industrial areas due to their wide range of sources and favorable properties (boiling point, molecular weight, volatility, solubility, etc.). VOCs are organic compounds consisting mostly of carbon and hydrogen. Some may additionally contain halogen, oxygen or sulfur atoms in their structures. They can have different structural forms, including straight or branched chain (aliphatic), cyclic (aromatic and cyclic), halogenated or oxygenated (alcohols, ketones, aldehydes, ethers, and esters) compounds. In Figure 1.1 the chemical structures of VOCs considered within the scope of this thesis study are presented.

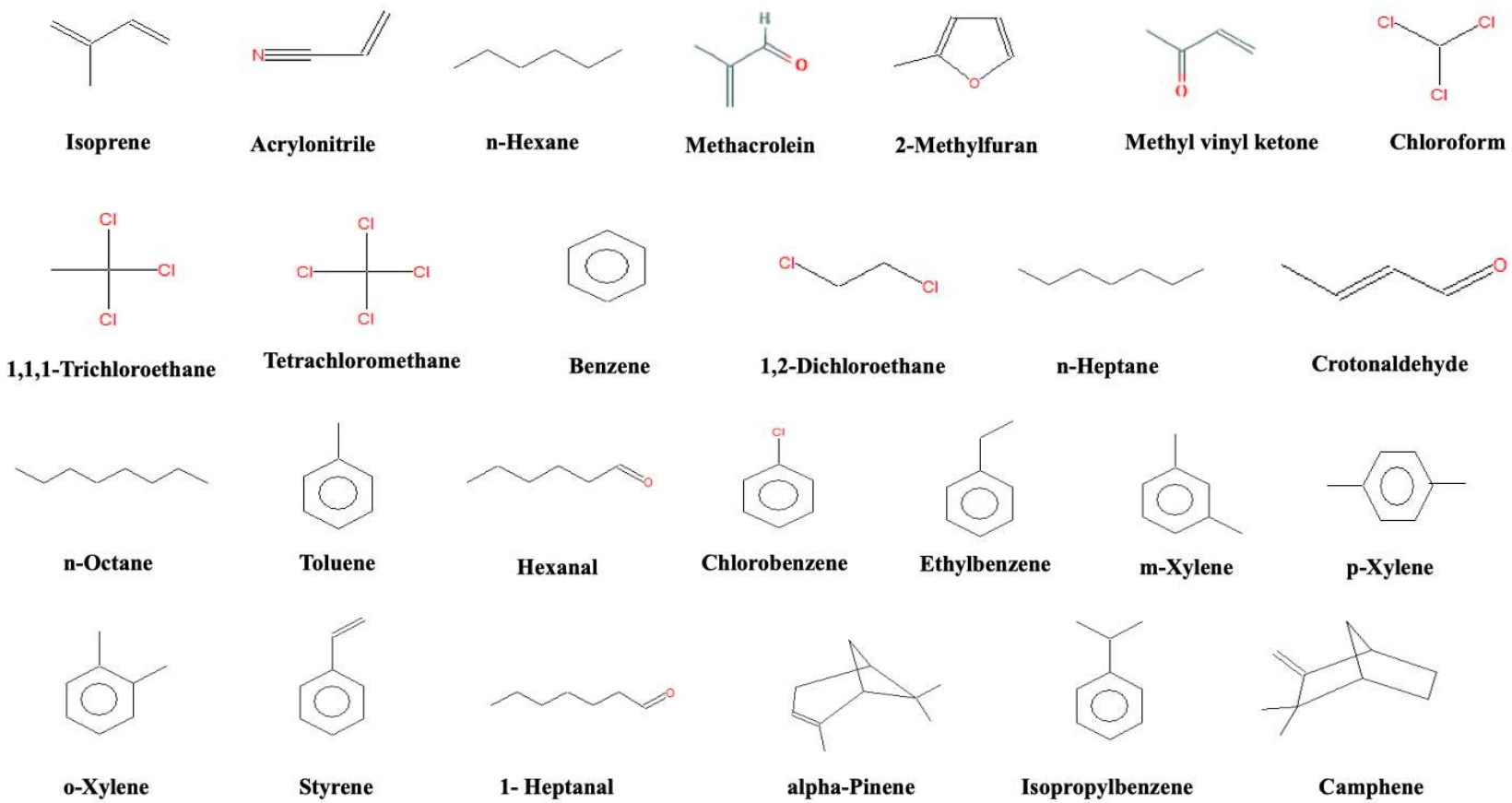


**Figure 1.1**. Chemical structures of VOCs studied in this thesis [19].

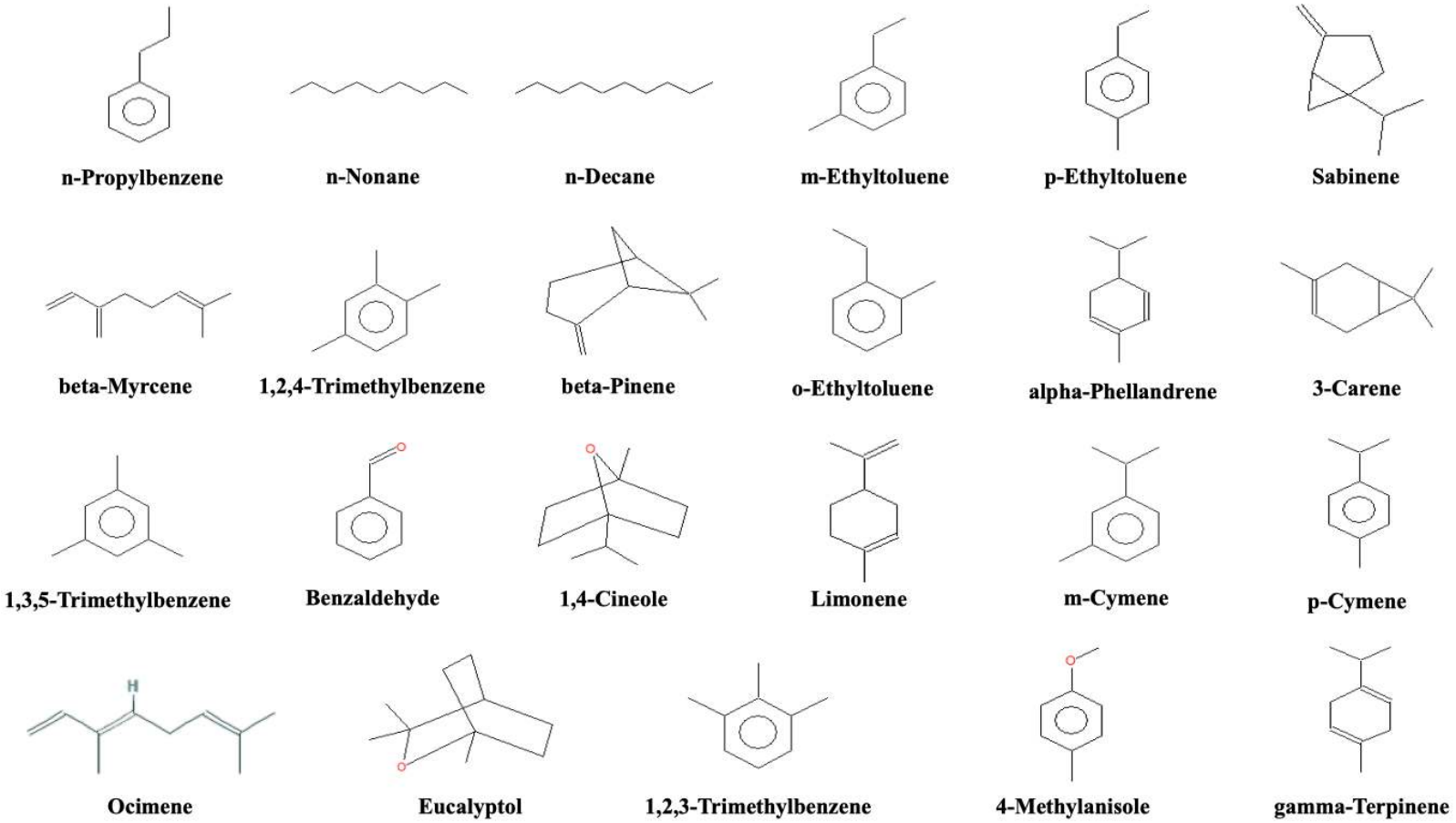


**Figure 1.1 (continued)** Chemical structures of VOCs studied in this thesis [19].

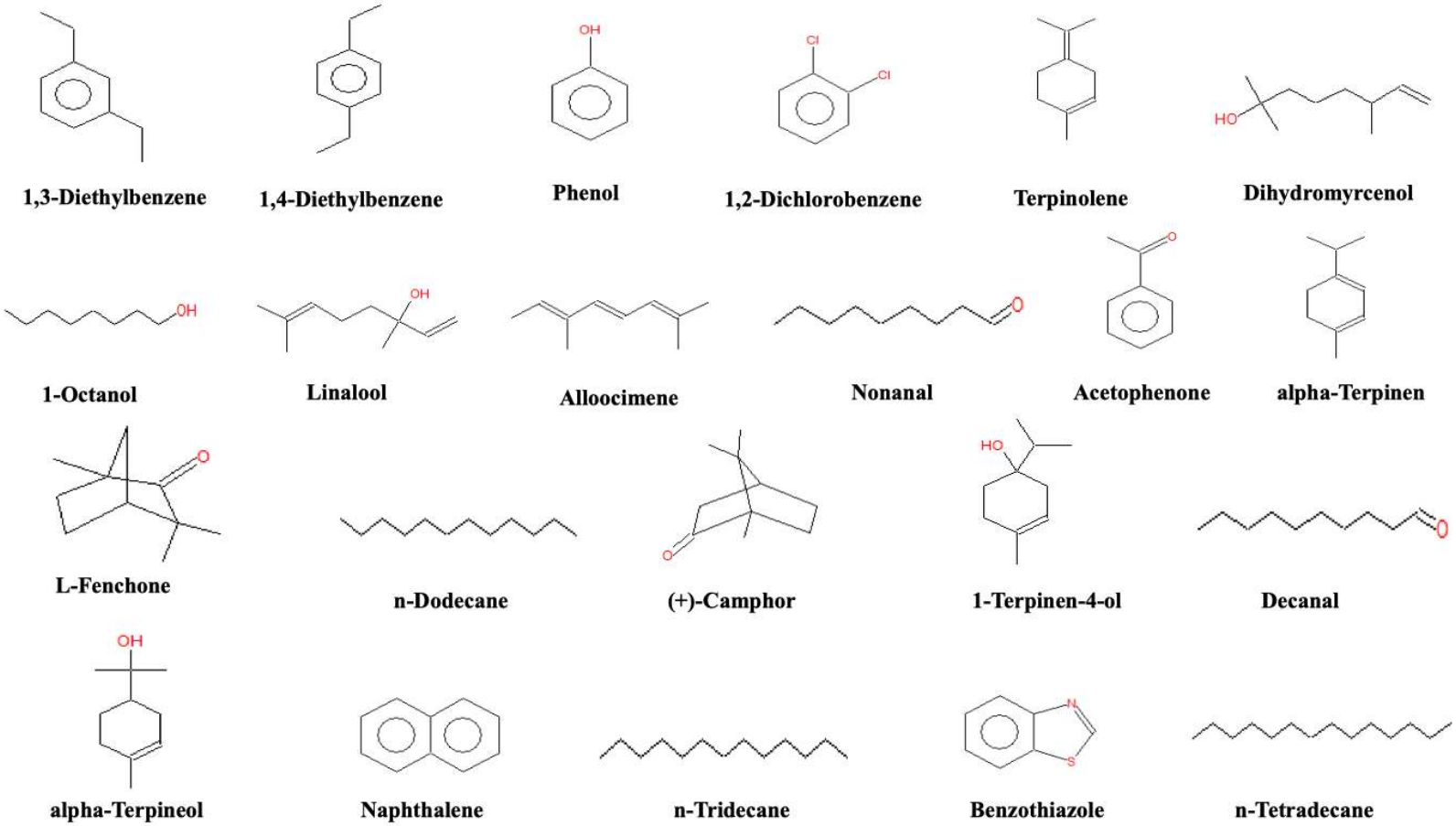


**Figure 1.1 (continued)** Chemical structures of VOCs studied in this thesis [19].

The lower the boiling point of a compound, the more likely it is to spread into the air. VOCs are volatile due to their low boiling points and therefore high vapor pressures. They are completely in the vapor phase at room temperature and have a vapor pressure above 10 Pa at 25 ° C. Boiling points range from 50 to 100 ° C to 240 to 260 ° C [20]. Table 1.1 includes some characteristics of VOCs considered within the scope of this thesis.

**Table 1.1.** Some chemical properties of VOCs studied in this thesis [21].

| VOC | Chemical Formula | Molecular Weight (g $mol^{-1}$) | Boiling Point (℃) | Melting Point (℃) | Vapor Pressure (mmHg) at 25 ℃ |
|---|---|---|---|---|---|
| **Isoprene** | $C_5H_8$ | 68.12 | 34.07 | -145.95 | 550 |
| **Acrylonitrile** | $C_3H_3N$ | 53.06 | 77.2 | -83.51 | 109 |
| **n-Hexane** | $C_6H_{14}$ | 86.18 | 68.73 | -95.35 | 153 |
| **Methacrolein** | $C_4H_6O$ | 70.09 | 68.4 | -81 | 155 |
| **2-Methylfuran** | $C_5H_6O$ | 82.10 | 65.0 | -87.5 | 156 |
| **Methyl vinyl ketone** | $C_4H_6O$ | 70.09 | 81.4 | -7 | 152 |
| **Chloroform** | $CHCl_3$ | 119.38 | 61.12 | -63.47 | 197 |
| **1,1,1-Trichloroethane** | $C_2H_3Cl_3$ | 133.40 | 74.0 | -30 | 124 |
| **Tetrachloromethane** | $CCl_4$ | 153.82 | 76.7 | -22.2 | 115 |
| **Benzene** | $C_6H_6$ | 78.11 | 80.08 | 5.56 | 94.8 |
| **1,2-Dichloroethane** | $C_2H_4Cl_2$ | 98.96 | 83.4 | -35.6 | 78.9 |
| **n-Heptane** | $C_7H_{16}$ | 100.20 | 98.38 | -90.55 | 46.0 |
| **Crotonaldehyde** | $C_4H_6O$ | 70.09 | 102.2 | -69 | 30 |
| **n-Octane** | $C_8H_{18}$ | 114.23 | 125.62 | -56.73 | 14.1 |
| **Toluene** | $C_7H_8$ | 92.14 | 110.6 | -94.9 | 28.4 |
| **Hexanal** | $C_6H_{12}O$ | 100.16 | 129.6 | -58.2 | 11.3 |
| **Chlorobenzene** | $C_6H_5Cl$ | 112.56 | 131.6 | -45.2 | 12.0 |
| **Ethylbenzene** | $C_8H_{10}$ | 106.16 | 136.2 | -94.95 | 9.6 |
| **m+p Xylene** | $C_8H_{10}$ | 106.16 | 139.1 | -47.85 | 8.29 |
| **o-Xylene** | $C_8H_{10}$ | 106.16 | 144.5 | -25.16 | 6.65 |
| **Styrene** | $C_8H_8$ | 104.15 | 145.3 | -30.65 | 6.40 |
| **1- Heptanal** | $C_7H_{14}O$ | 114.18 | 152.8 | -43.3 | 3.52 |
| **Alpha-pinene** | $C_{10}H_{16}$ | 136.24 | 156 | -62.5 | 4.75 |
| **Isopropylbenzene** | $C_9H_{12}$ | 120.19 | 152.4 | -96.0 | 4.5 |
| **Camphene** | $C_{10}H_{16}$ | 136.23 | 161 | 52 | 2.5 |
| **n-Propylbenzene** | $C_9H_{12}$ | 120.19 | 159.2 | -99.5 | 3.42 |
| **n-Nonane** | $C_9H_{20}$ | 129.26 | 150.47 | -53.47 | 4.45 |
| **n-Decane** | $C_{10}H_{22}$ | 142.28 | 174.1 | -29.7 | 1.43 |
| **m-Ethyltoluene** | $C_9H_{12}$ | 120.19 | 161.3 | -95.5 | 3.04 |
| **p-Ethyltoluene** | $C_9H_{13}$ | 120.19 | 162.0 | -62.3 | 3.00 |

n: No data

**Table 1.1 (continued)** Some chemical properties of VOCs studied in this thesis [21].

| VOC | Chemical Formula | Molecular Weight (g $mol^{-1}$) | Boiling Point (℃) | Melting Point (℃) | Vapor Pressure (mmHg) at 25 ℃ |
|---|---|---|---|---|---|
| **Sabinene** | $C_{10}H_{16}$ | 136.23 | 163.4 | n | n |
| **beta-Myrcene** | $C_{10}H_{16}$ | 136.24 | 167 | < -10 | 2.09 |
| **1,2,4-Trimethylbenzene** | $C_9H_{12}$ | 120.19 | 168.89 | -43.77 | 2.10 |
| **beta-Pinene** | $C_{10}H_{16}$ | 136.24 | 166 | -61.5 | 2.93 |
| **o-Ethyltoluene** | $C_9H_{12}$ | 120.19 | 165.2 | n | 2.61 |
| **alpha-Phellandrene** | $C_{10}H_{16}$ | 136.23 | 172.0 | n | 1.40 |
| **3-Carene** | $C_{10}H_{16}$ | 136.23 | 170.0 | < 25 | n |
| **1,3,5-Trimethylbenzene** | $C_9H_{12}$ | 120.19 | 164.7 | -44.8 | 2.48 |
| **Benzaldehyde** | $C_7H_6O$ | 106.12 | 178.7 | -57.12 | 1.27 |
| **1,4-Cineole** | $C_{10}H_{18}O$ | 154.26 | 173.5 | 1.0 | 1.93 |
| **Limonene** | $C_{10}H_{16}$ | 136.24 | 176.0 | -95.5 | 1.55 |
| **m-Cymene** | $C_{10}H_{14}$ | 134.22 | 175 | -63.8 | 1.72 |
| **p-Cymene** | $C_{10}H_{14}$ | 134.22 | 177.10 | -68.9 | 1.50 |
| **Ocimene** | $C_{10}H_{16}$ | 136.23 | n | n | 2.68 |
| **Eucalyptol** | $C_{10}H_{18}O$ | 154.25 | 176.0 | 1.5 | 1.90 |
| **1,2,3-Trimethylbenzene** | $C_9H_{12}$ | 120.19 | 176.12 | -25.4 | 1.69 |
| **4-Methylanisole** | $C_8H_{10}O$ | 122.17 | 175.5 | -32 | 1.14 |
| **gamma-Terpinene** | $C_{10}H_{16}$ | 136.23 | 183.0 | -10.0 | 1.09 |
| **1,3-Diethylbenzene** | $C_{10}H_{14}$ | 134.22 | 181.1 | -83.9 | 1.20 |
| **1,4-Diethylbenzene** | $C_{10}H_{14}$ | 134.22 | 183.7 | -42.83 | 1.03 |
| **Phenol** | $C_6H_6O$ | 94.11 | 181.75 | 40.91 | 0.35 |
| **1,2-Dichlorobenzene** | $C_6H_4Cl_2$ | 147.00 | 180.1 | -16.7 | 1.36 |
| **Terpinolene** | $C_{10}H_{16}$ | 136.23 | 187 | < 25 | 0.74 |
| **Dihydromyrcenol** | $C_{10}H_{20}O$ | 156.26 | n | n | n |
| **1-Octanol** | $C_8H_{18}O$ | 130.23 | 194.7 | -14.7 | 0.08 |
| **Linalool** | $C_{10}H_{18}O$ | 154.25 | 198 | < 25 | 0.16 |
| **Alloocimene** | $C_{10}H_{16}$ | 136.23 | n | n | n |
| **Nonanal** | $C_9H_{18}O$ | 142.24 | 195 | -19.3 | 0.37 |
| **Acetophenone** | $C_8H_8O$ | 120.15 | 202.1 | 19.4 | 0.40 |
| **alpha-Terpinen** | $C_{10}H_{16}$ | 136.23 | 175.0 | < 25 | n |
| **L-Fenchone** | $C_{10}H_{16}O$ | 152.23 | n | n | n |
| **n-Dodecane** | $C_{12}H_{26}$ | 170.33 | 216.3 | -9.55 | 0.14 |
| **(+)-Camphor** | $C_{10}H_{16}O$ | 152.23 | 209 | 179 | 0.65 |
| **1-Terpinen-4-ol** | $C_{10}H_{18}O$ | 154.28 | 209 | n | 0.04 |
| **Decanal** | $C_{10}H_{20}O$ | 156.27 | 212 | -3.9 | 0.10 |
| **alpha-Terpineol** | $C_{10}H_{18}O$ | 154.25 | 219 | 37 | 0.04 |
| **Naphthalene** | $C_{10}H_8$ | 128.17 | 217.9 | 80.2 | 0.08 |
| **n-Tridecane** | $C_{13}H_{28}$ | 184.36 | 235.4 | -5.35 | 0.038 |
| **Benzothiazole** | $C_7H_5NS$ | 135.19 | 231 | 2.0 | 0.014 |
| **n-Tetradecane** | $C_{14}H_30$ | 198.39 | 253.5 | 5.8 | 0.015 |

n: No data

## 1.2 Sources of Volatile Organic Compounds

Volatile organic compounds can be emitted directly from their sources or can be formed in the atmosphere as the product of the chemical reactions of some other compounds [22].

Primary sources are often categorized as natural and anthropogenic sources. Forest fires are an important natural source for oxygenated VOCs such as methanol, formaldehyde, acetaldehyde and acetone. Oxygenated VOCs which have the highest contribution to total VOC generated directly or indirectly from a forest fire, are followed by aliphatics (ethane, ethane, propane and propene), aromatics (benzene and toluene), isoprene and terpenes [23-25]. Volcanic eruptions can be considered as another natural source for VOCs. It was stated that volcanic emissions in the Lusi volcano contain benzene and toluene [26]. Biosynthetic activities of plants result in emissions of VOCs which are commonly referred to as biogenic volatile organic compounds (BVOCs). Some of them have several functions in growth, reproduction, communication and defense which are vital processes in the life cycle of plants [27]. Forests with extensive vegetation are the main source of BVOCs. Biogenic VOCs include isoprene, terpenes (monoterpenes, sesquiterpenes, diterpenes, triterpenes, tetraterpenes and polyterpenes) as well as some species from alkanes, alkenes, aldehydes, ketones, alcohols, esters and acids [28]. Isoprene containing 5 carbons in its structure is a member of a hemiterpene group. The number of C-5 units is also considered in defining the groups of terpenes. For example, compounds containing 10 carbons, 15 carbons, 20 carbons, 30 carbons, 40 carbons and more than 45 carbons in their structures are defined as monoterpene, sesquiterpene, diterpene, triterpene, tetraterpene and polyterpene, respectively [29]. BVOC emissions (isoprene and monoterpenes) are temperature dependent. Isoprene emission additionally depends on light because its synthesis and release are related to photosynthesis [30]. On the other hand, with few exceptions, the emission of many monoterpenes has been identified as light-independent. Their emissions are mainly based on the volatilization out of the storage organs [31].

Isoprene and monoterpenes are the dominant biogenic compounds in the atmosphere; therefore, they are of great importance [29]. Significant amounts of isoprene are emitted by broad-leaved trees including Oriental Plane, Sessile Oak, Black Locust, European Aspen, Eastern Cottonwood and also coniferous trees such as Nordmann Fir and Oriental Spruce [32]. Monoterpenes are a broad class that

includes compounds such as alloocimene, alpha-fenchene, alpha-pinene, alpha-terpinene, beta-pinene, beta-myrcene, camphene, m-cymene, p-cymene, delta 3-carene, gamma-terpinene, limonene, ocimene, phellandrene, sabinene, terpinolene. High monoterpene emissions are generally provided by coniferous trees. Black Pine, Greek Juniper, Phoenician Juniper, Prickly Juniper, and Radiata Pine emit high percentages of alpha-pinene [32]. Beta-pinene (for Turkish Red Pine), beta-myrcene (for Scots Pine), delta-3-carene (for Oriental Spruce, Mediterranean Cypress and Nordmann Fir) and ocimene (for Aleppo Pine and Stone Pine) are other widespread monoterpenes [32]. However, some broad-leaved trees including Sweet Chestnut, European Alder and Silver Lime also release important amounts of monoterpenes, especially sabinene [32]. Following isoprenoids, carbonyls are another dominant group. The biogenic carbonyls contain formaldehyde, acetaldehyde, propanal, acetone, butanal, i-butanal, butenal, i-butenal, butanone-2, crotonaldehyde, pentanone-2, 2-methyl-2-pentenal, hexanal, (E)-2-hexenal, (Z)-3-hexenal, octanone-3, nonanal, benzaldehyde, citronellal, 6,6-dimethyl-bicyclo[3.1.1]-heptane, 2-carboxaldehyde, methyl-isopropyl-ketone, methyl-vinyl-ketone [29]. Vegetation (directly or indirectly) and microbial processes are indicated as natural sources of hexanal, heptanal, nonanal and decanal [33]. Plants that are effective in the emission of aldehydes (crotonaldehyde, hexanal, heptanal, nonanal and decanal) are Oak, Hornbeam, Beech, Ash, Juniper, Pine, grain and grass [29, 32, 34].

Although biogenic VOC emissions are estimated as more significant than anthropogenic ones on a global scale, at the local level the situation is the opposite [35]. Vehicular emissions, fossil fuel burning, industrial activities and solvent usage are the main anthropogenic sources for VOC emissions. In urban regions, ambient VOCs mainly originate from vehicle emissions [36, 37]. Ethylene, benzene, toluene, ethylbenzene, m,p-xylene and o-xylene are the compounds related to vehicular emissions [38]. Vehicle types (gasoline-powered and diesel vehicles) may create differences in the chemical composition of VOCs emitted into the atmosphere. It was stated that the major difference between the emissions from gasoline vehicles and diesel vehicles is that the latter mostly emits VOC species containing 10 or more carbon in their formula (such as n-decane, n-undecane and n-dodecane) unlike gasoline vehicles [37]. In domestic heating, burning anthracite (mainly emits benzene, naphthalene, ethylene, toluene) and bituminous coal

(primarily emits acetylene, ethylene, propane, propylene) are also important VOC sources for residential areas [37]. Solvent evaporation is an anthropogenic source for aromatics and halogenates [39] as well as n-hexane and 2-methylpentane [38]. The variety of industrial facilities in the region also affects the ambient VOC composition. It was stated that toluene, chloroform, 1,2-dichloroethane and 1,1,2-trichloroethane were the dominant VOCs found around the petrochemical complex in Izmir, Turkey [40]. On the other hand, paint factories were defined as an important source for ambient benzene, toluene, ethylbenzene and xylenes [41, 42].

Photochemical reactions of VOCs with reactive species ($NO_3$ and OH radicals) in the atmosphere result in the formation of secondary VOCs [43, 44]. To illustrate, methacrolein (MACR) and methyl vinyl ketone (MVK) are major products generated from the reactions of isoprene with OH, $O_3$ and NOx [45, 46].

The mechanism for the formation of methyl vinyl ketone from the OH radical-initiated reaction of isoprene was given in (1.1) and it is followed by the reactions of the first radical (reactions from (1.2) to (1.5)) and second radical (reactions from (1.6) to (1.9)) [46].

$$OH + \mathbf{CH_2{=}CHC(CH_3){=}CH_2} \rightarrow CH_2{=}CH\dot{C}(CH_3)CH_2OH + CH_2{=}CHCOH(CH_3)\dot{C}H_2 \quad (1.1)$$

$$CH_2{=}CH\dot{C}(CH_3)CH_2OH + O_2 \rightarrow CH_2{=}CHC(O\dot{O})(CH_3)CH_2OH \quad (1.2)$$

$$CH_2{=}CHC(O\dot{O})(CH_3)CH_2OH + NO \rightarrow CH_2{=}CHC(\dot{O})(CH_3)CH_2OH + NO_2 \quad (1.3)$$

$$CH_2{=}CHC(\dot{O})(CH_3)CH_2OH \rightarrow \mathbf{CH_3COCH{=}CH_2} + \dot{C}H_2OH \quad (1.4)$$

$$\dot{C}H_2OH + O_2 \rightarrow HCHO + HO_2 \quad (1.5)$$

$$CH_2{=}CHCOH(CH_3)\dot{C}H_2 + O_2 \rightarrow CH_2{=}CHCOH(CH_3)CH_2O\dot{O} \quad (1.6)$$

$$CH_2{=}CHCOH(CH_3)CH_2O\dot{O} + NO \rightarrow CH_2{=}CHCOH(CH_3)CH_2\dot{O} + NO_2 \quad (1.7)$$

$$CH_2{=}CHCOH(CH_3)CH_2\dot{O} \rightarrow HCHO + CH_3\dot{C}OHCH{=}CH_2 \quad (1.8)$$

$$CH_3\dot{C}OHCH{=}CH_2 + O_2 \rightarrow \mathbf{CH_3COCH{=}CH_2} + HO_2 \quad (1.9)$$

The mechanism for the formation of methacrolein starting from the OH radical-initiated reaction of isoprene was given in (1.10) and it is followed by the reactions of the first radical (reactions from (1.11) to (1.14)) and second radical (reactions from (1.15) to (1.18)) [46].

$$OH + \mathbf{CH_2{=}CHC(CH_3){=}CH_2} \rightarrow HOCH_2\dot{C}HC(CH_3){=}CH_2 + \dot{C}H_2CHOHC(CH_3){=}CH_2 \quad (1.10)$$

$$HOCH_2\dot{C}HC(CH_3){=}CH_2 + O_2 \rightarrow HOCH_2CH(O\dot{O})C(CH_3){=}CH_2 \quad (1.11)$$

$$HOCH_2CH(O\dot{O})C(CH_3){=}CH_2 + NO \rightarrow HOCH_2H(\dot{O})C(CH_3){=}CH_2 + NO_2 \quad (1.12)$$

$HOCH_2CH(\dot{O})C(CH_3)=CH_2 \rightarrow \dot{C}H_2OH + \mathbf{CH_2=C(CH_3)CHO}$ (1.13)

$\dot{C}H_2OH + O_2 \rightarrow HCHO + HO_2$ (1.14)

$\dot{C}H_2CHOHC(CH_3)=CH_2 + O_2 \rightarrow \dot{O}OCH_2CHOHC(CH_3)=CH_2$ (1.15)

$\dot{O}OCH_2CHOHC(CH_3)=CH_2 + NO \rightarrow \dot{O}CH_2CHOHC(CH_3)=CH_2 + NO_2$ (1.16)

$\dot{O}CH_2CHOHC(CH_3)=CH_2 \rightarrow HCHO + CH_2=C(CH_3)\dot{C}HOH$ (1.17)

$CH_2=C(CH_3)\dot{C}HOH + O_2 \rightarrow \mathbf{CH_2=C(CH_3)CHO} + HO_2$ (1.18)

Moreover, methyl vinyl ketone (Figure 1.2) and methacrolein (Figure 1.3) give OH-initiated oxidation reactions which yield compounds including glycolaldehyde, methylglyoxal and hydroxyacetone. The mechanism also shows that isoprene and its oxidation products have an important role in tropospheric ozone formation through oxidation of NO into $NO_2$ [47].

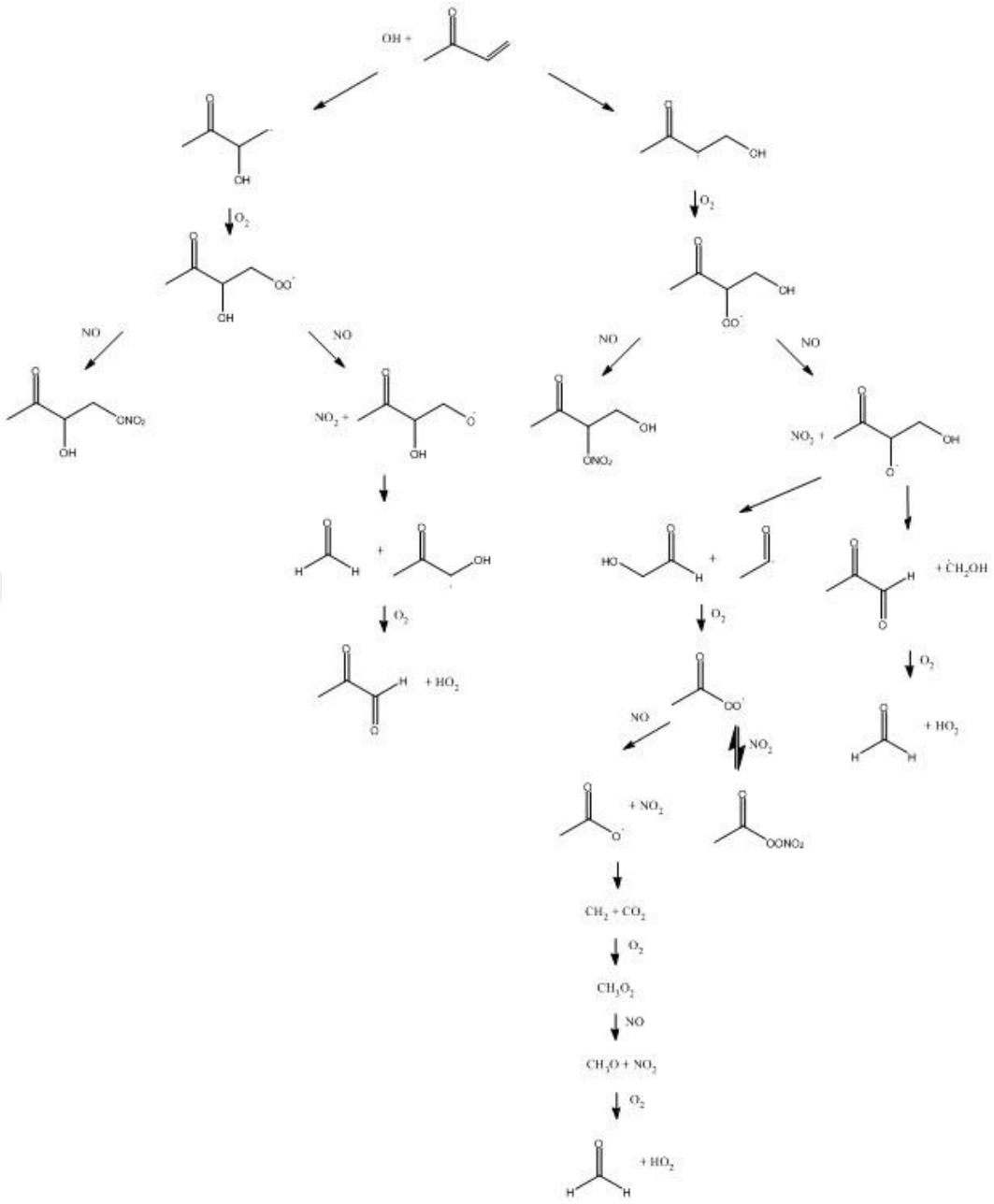


**Figure 1.2**. Mechanism for the oxidation of methyl vinyl ketone (adapted from [47]).

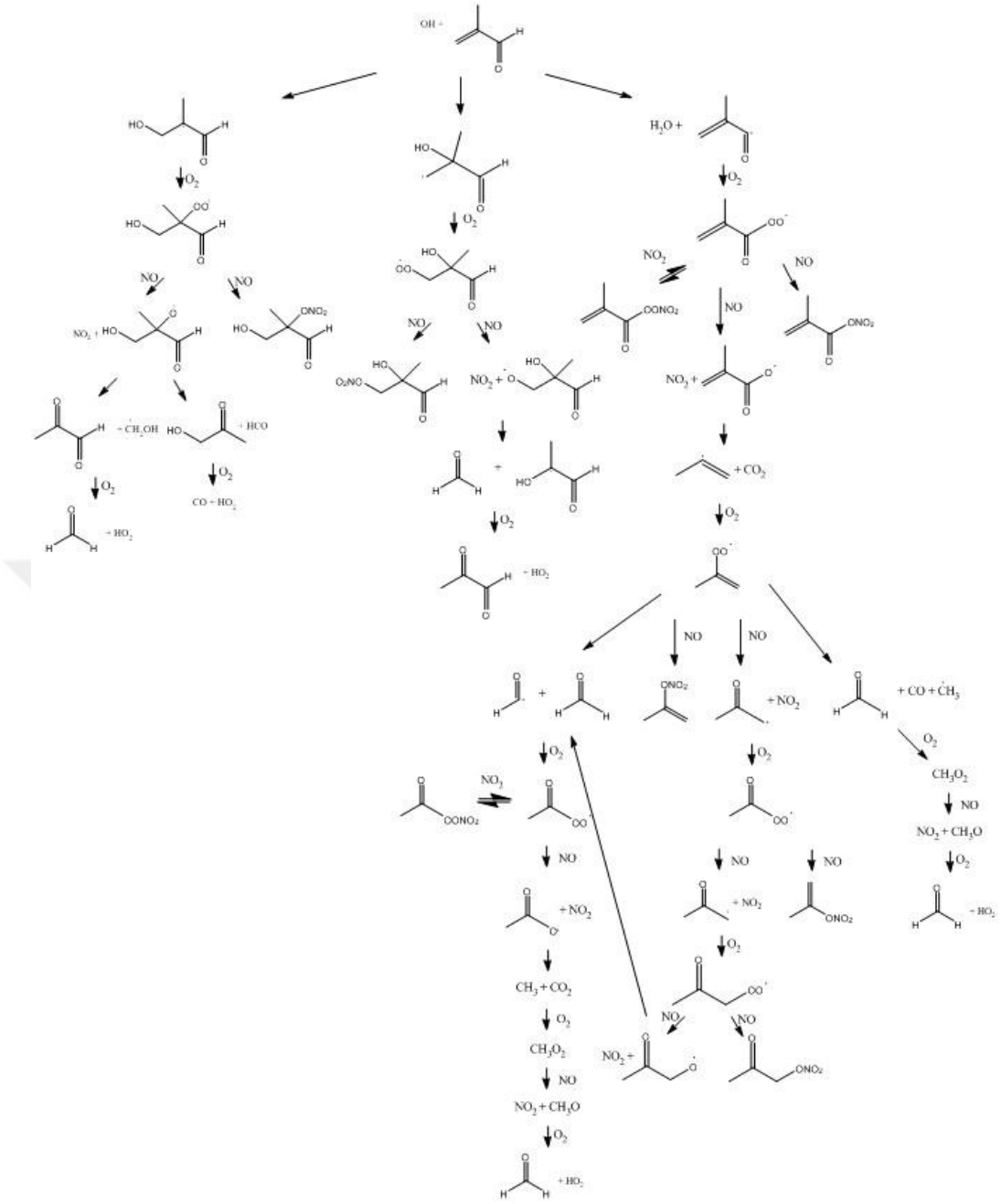

**Figure 1.3**. Mechanism for the oxidation of methacrolein (adapted from [47]).

## 1.3 Removal Pathways of Volatile Organic Compounds

Volatile organic compounds are removed from the atmosphere by several physical processes. These processes contain wet deposition, dry deposition, uptake by plants and photochemical reactions [1].

The deposition is one of the major mechanisms for the removal of atmospheric pollutants including gases and particulate matter. It can occur in two different routes, namely dry deposition and wet deposition. Dry deposition mainly results from the scavenging of pollutants from the atmosphere by sedimentation

under gravity. It was suggested that the dry deposition has minor importance [48]. The other deposition pathway, wet deposition, is the process whereby pollutants are dissolved and washed out through mechanisms such as rain, snow or fog [49]. The scavenging potential of wet precipitation is not as effective as photochemical reactions for VOCs [35]. That distinction has been associated with the chemical properties of VOCs such as hydrophobicity, volatility and high reactivity [35].

In section 1.2, it was mentioned that some VOCs are emitted by a variety of plants. However, another role of plants is to take part in atmospheric purification by absorbing pollutants from the atmosphere [1]. It was indicated that the main atmospheric removal mechanism for VOCs was the uptake by the plant and followed by the OH-initiated oxidation reactions [50]. It has been also stated that the uptake by plants is directly related to the lipophilicity of compounds and with the surface area of the plant leaves [51].

The major removal pathway for atmospheric VOCs is oxidation reactions. Secondary pollutants including hydrocarbons, NOx and ozone arise from oxidation reactions of VOCs. The following sub-section gives a review of the production and loss mechanisms of ozone, an important actor of atmospheric chemistry due to its serious influences on the ecosystem.

### 1.3.1 Tropospheric Ozone Formation

The troposphere contains many pollutants, some of which are ozone precursors. Nitrogen oxides (NOx = NO + $NO_2$), which are mostly caused by vehicle emissions and are thus concentrated in the city atmosphere, are important ozone precursors. In the troposphere, the photodissociation of $NO_2$ below 430 nm created the highly active-monatomic oxygen ($O^3P$). The combination reactions between monatomic oxygen ($O^3P$) and molecular oxygen ($O_2$) result in ozone formation. The M involved in the reactions is another molecule (usually $N_2$ or $O_2$) that removes the excess energy released by the oxygen atom or an aerosol surface that allows this reaction to occur.

$$NO_2 + hv \rightarrow NO + O(^3P) \quad (1.19)$$

$$O(^3P) + O_2 + M \rightarrow O_3 + M \quad (1.20)$$

Ozone oxidizes nitric oxide to nitrogen dioxide or forms OH radicals [52].

$$O_3 + NO \rightarrow NO_2 + O_2 \quad (1.21)$$

$$O_3 + hv \rightarrow O_2 + O\bullet \quad (1.22)$$

$$O\bullet + H_2O \rightarrow 2OH\bullet \quad (1.23)$$

Moreover, the tropospheric oxidants such as $HO_2$ and $RO_2$ efficiently oxidize NO to $NO_2$ which then produces ozone. The pathway which is called as NOx cycle has an important role in the accumulation of ozone [53].

$$HO_2 + NO \rightarrow OH + NO_2 \quad (1.24)$$

$$RO_2 + NO \rightarrow RO + NO_2 \quad (1.25)$$

The other reaction series between (1.26) and (1.29) which are defined as ROx cycle, supply $HO_2$ and $RO_2$ to oxidize two molecules of NO to $NO_2$. It is also followed by the NOx cycle which produces ozone [53]. The entire photochemical ozone formation mechanism is summarized in Figure 1.4.

$$OH + VOC + O_2 \rightarrow RO_2 + H_2O \quad (1.26)$$

$$RO_2 + NO \rightarrow RO + NO_2 \quad (1.27)$$

$$RO + O_2 \rightarrow HO_2 + carbonyl \quad (1.28)$$

$$HO_2 + NO \rightarrow OH + NO_2 \quad (1.29)$$

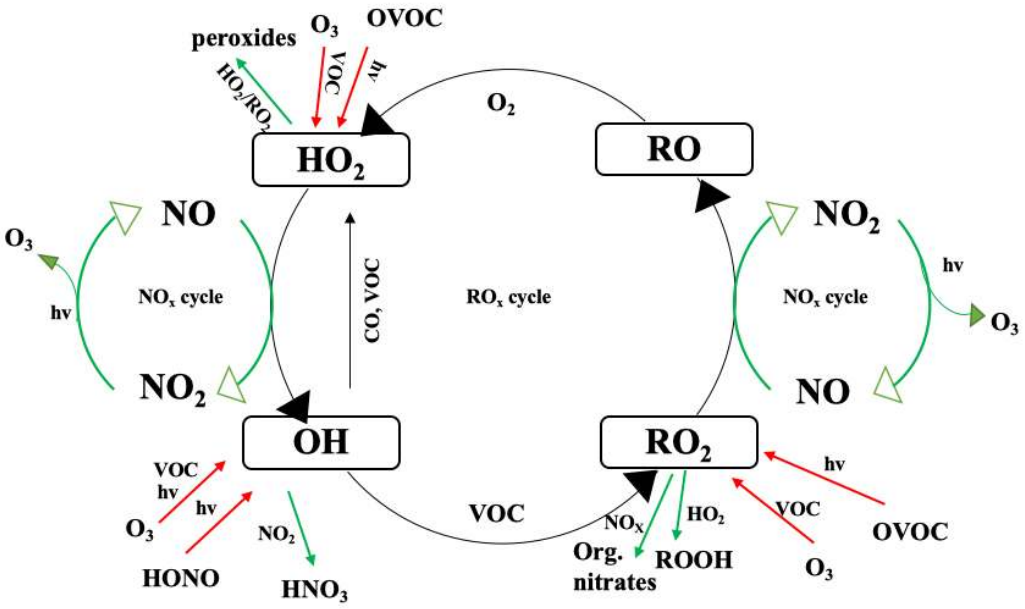


**Figure 1.4.** The photochemical ozone formation mechanism (adapted from [53]).

In brief, the photochemical reactions between VOCs and NOx in the presence of sunlight produce ozone. The ratio between VOCs and NOx and the VOCs composition has a great influence on the formation amount of ozone [52]. If VOCs/NOx ratio is high, NOx cycle is weaker and thus, becomes the limiting factor in ozone production (NOx-limited ozone formation regime). Conversely, when

VOCs/NOx ratio is lower, ozone production is limited by the ROx cycle (VOC-limited ozone formation regime). It was designated the ranges of VOCs/NOx ratios as VOC-limited zone (VOC/NOx <4), optimum ozone production zone (15 > VOC/NOx > 4) and NOx-limited zone (VOC/NOx > 15) [54].

## 1.4 Effects of Volatile Organic Compounds

The United States Environmental Protection Agency (US EPA) has identified a total of 187 compounds as harmful air pollutants (HAPs) due to serious health effects (such as cancer, infertility, and birth defects) or adverse environmental effects. Acetophenone, acrylonitrile, benzene, carbon tetrachloride, chlorobenzene, chloroform, ethyl benzene, 1,2-dichloroethane, hexane, 1,1,1-trichloroethane, naphthalene, phenol, styrene, toluene, o-xylenes, m-xylenes and p-xylenes are the volatile organic compounds among HAPs and they were also included in this study.

### 1.4.1 Effects on Human Health

The health effects of VOCs change greatly based on the compound, exposure level and exposure time. Moreover, the chemical character of VOC such as molecular size, lipophilicity and volatility has a significant influence on the exposure potential [55].

The health effects of VOCs, which are given in the HAPs list, were examined in this section. Acetophenone is classified in Group D by EPA, not classifiable as causing human carcinogenicity [56]. Its non-cancerogenic effects on humans are reported as skin irritation and corneal injury. Acute exposure to acrylonitrile produces mucous membrane irritation, dizziness, headaches and nausea. EPA has classified acrylonitrile as a probable human carcinogen (Group B1) [56]. Acute exposure to benzene results in drowsiness, dizziness, headaches, irritation of the eye, skin, and respiratory tract. Serious disorders such as anemia, leukemia and infertility have been determined in humans chronically exposed to benzene. EPA has classified benzene as a known human carcinogen (Group A) for all routes of exposure [56]. Acute exposure to carbon tetrachloride causes headache, weakness and nausea. However, acute exposures to higher levels or chronic exposure cause liver and kidney damage in humans. Based on animal experiments, carbon tetrachloride exposures have been found to increase the risk of liver cancer.

Carbon tetrachloride has been classified as a probable human carcinogen (Group B2) [56]. Chlorobenzene, on the other hand, is a VOC in the D risk group consisting of components that do not carry cancer risk [56]. Chronic exposure of humans to chlorobenzene affects the central nervous system. Symptoms are usually numbness, hyperesthesia and muscle spasms. For chloroform, chronic exposure leads to some effects such as hepatitis, jaundice, depression and irritability. Chloroform which has been found to increase kidney and liver tumors in animals is classified as a probable human carcinogen (Group B2) by EPA [56]. Acute exposure to ethylbenzene in humans causes throat irritation, chest constriction, eye irritation and dizziness. In addition, ethylbenzene is in the D group in terms of cancer risk. Inhalation of concentrated 1,2-Dichloroethane can produce effects on the nervous system, liver, and kidneys. EPA has classified 1,2-Dichloroethane as a probable human carcinogen (Group B2) [56]. Acute exposure to hexane is associated with dizziness, nausea, and headache whereas chronic exposure causes muscular weakness, blurred vision, headache and fatigue. Since there is no information on the carcinogenic effects of hexane on humans or animals, EPA has classified hexane in Group D, not classifiable as a carcinogen [56]. Effects related to acute exposure to methyl chloroform are dizziness, nausea, diarrhea, loss of consciousness, and decreased blood pressure in humans. Methyl chloroform is also in the D group in terms of cancer risk [56]. Exposure to naphthalene through inhalation, ingestion, and skin contact can cause hemolytic anemia, liver damage, cataracts and neurological damage. Naphthalene has been classified as a possible human carcinogen (Group C) [56]. Phenol irritates the skin, eyes, and mucous membranes in humans. Also, chronic exposure to phenol in humans can lead to weight loss, diarrhea, vertigo, and salivation. Phenol has been classified in Group D by EPA [56]. Styrene exposure in humans can cause headaches, fatigue, depression and hearing loss. EPA has not given any carcinogen classification to styrene [56]. Similarly, EPA has not concluded about the carcinogenic potential of toluene [56]. Toluene exposure which especially affects the central nervous system, leads to nausea, fatigue, dizziness, and headache. Acute exposure to xylenes in humans influences gastrointestinal and neurological systems. Chronic exposure to xylenes has an impact on the central nervous system (headache, dizziness and incoordination). Xylenes have been classified as a Group D, not classifiable as to human carcinogenicity [56].

### 1.4.2 Effects on Ecosystem

The ecological effects of VOCs mostly depend on their role in photochemical pollution. In the presence of sunlight and sufficient NOx, VOCs produce photochemical smog which includes particulate matter (PM), ozone and other organic species [1]. Particulate matters, which are effective in reducing the visibility in photochemical smog, are formed by the polymerization reactions of small molecules in the smog. Because of ecological consequences, ozone can be estimated as the most important photochemical product of VOCs. Tropospheric ozone is the third most important greenhouse gas after then carbon dioxide and methane. The gas increases the atmospheric absorption of outgoing radiation, so its elevated atmospheric levels lead to global warming [6]. Moreover, ozone is known to cause leaf damage, reduction in photosynthesis and crop yield losses [57]. The commonly used index for vegetation, AOT40, is defined as the accumulation of hourly mean ozone concentrations above 40 ppb during daylight hours. It was derived the critical levels of a 3-month AOT40 of 3 ppm h and a 3.5-month AOT40 of 6 ppm h for wheat and tomato, respectively [58]. Some crops including wheat, pulses, cotton and tomato were indicated as ozone sensitive. Some are even so sensitive to the effects of ozone that they can be considered a biological indicator of the photochemical smog. On the other hand, potato, oilseed rape and maize are moderately ozone-sensitive crops [58]. Tree species also differ in sensitivity to ozone. Deciduous broadleaf species were remarkably more susceptible than evergreen broadleaf and coniferous species [59]. Ground level ozone is a strong oxidant gas having detrimental effects also on materials such as rubber [1].

## 1.5 Sampling Methods of Volatile Organic Compounds

Ambient air sampling is the collection of a known volume of samples to measure the amounts of various compounds in the air. Atmospheric VOCs can be determined with sampling techniques such as active sampling, passive sampling, online automatic analyzers and chemisorption [60]. It was stated that the following parameters should be considered to choose the most appropriate sampling method for the study [61]:

- Components to be sampled,
- Sampling environment (indoor, outdoor, workplace or personal sampling),

- Number of sampling points,
- Sampling time,
- Sampling conditions (meteorological, physical, etc.)
- Sampling and analysis methods to be used,
- Quality control and reliability of sampling and analysis methods.

Active sampling and passive sampling techniques have been mostly used in the detection of VOCs [62-70].

### 1.5.1 Active Sampling

Active sampling is based on the collection of samples on adsorbents packed in an appropriate sampler with the use of a sampling pump. Sampling rate and sampling duration are important parameters in active sampling. In determining these parameters, factors such as sorbent type, sorbent amount and ambient conditions (contaminant amount, reactivity) should be considered. For accurate and reliable sampling, the pump needs to be calibrated to a determined flow rate before sampling.

The sampled air volume is calculated by multiplying the pump flow rate (mL $min^{-1}$) and the sampling time. Dividing the amount (ng) reached because of the analysis by the sampled air volume (L) gives the atmospheric concentration of the compound.

$$C = \left[\frac{m}{Q \times t}\right] \times 10^3 \qquad (1.30)$$

C: pollutant concentration in air (μg $m^{-3}$)

m: pollutant mass at the open end of the sampler (ng)

Q: pump flow rate (mL $min^{-1}$)

t: sampling time (min)

Active sampling is ideal for short-term sampling. In addition, it allows air samples to be collected at high volumes. In this method, there is much more effective pre-enrichment. However, it can be said that the most advantageous feature of active sampling is the use of more than one adsorbent in series, making it easier to hold a wide range of samples. One of the disadvantages of active sampling is that it requires large and expensive equipment. Due to the high cost, the difficulty of transportation and the need for electrical power, the sampling points

remain limited. Also, samplers used in active sampling are more complex compared to passive samplers. Regular maintenance/calibration of the equipment is required for a reliable active sampling study [61].

### 1.5.2 Passive Sampling

Passive sampling is the process of collecting compounds in the vapor or gas phase from the atmosphere at a rate controlled by molecular diffusion. Figure 1.5 illustrates the principle of passive sampling of any compound.

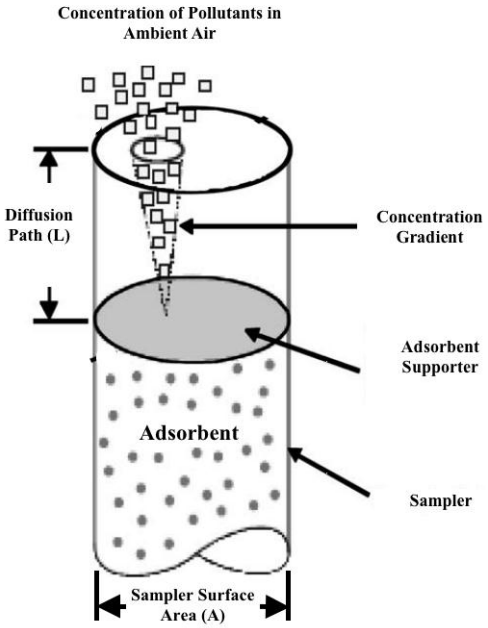


**Figure 1.5**. Scheme of the passive sampling method [60].

This process, based on molecular diffusion, is expressed by Fick's first law [71].

$$C = \left[\frac{m \times L}{D \times A \times t}\right] \times 10^3 \qquad (1.31)$$

C: the pollutant concentration in air (μg $m^{-3}$)

m: pollutant mass at the open end of the sampler (ng)

L: diffusion path (cm)

D: diffusion coefficient ($cm^2$ $s^{-1}$)

A: sampler surface area ($cm^2$)

t: sampling time (s)

The diffusion coefficient (*D*) in the equation (1.31) is calculated separately for each compound by equation (1.32) [71].

$$D_i = 10^{-3} x \frac{T^{1,75} x \left[\left(\frac{1}{m_{air}}\right)+\left(\frac{1}{m_i}\right)\right]^{\frac{1}{2}}}{P \times \left[V^{1/3}{}_{air}+V^{1/3}{}_{i}\right]^2} \quad (1.32)$$

$D_i$: the diffusion coefficient of the compound ($cm^2\ sn^{-1}$)

T: absolute temperature (298 K)

$m_{air}$: average molar mass of air (28.97 g $mol^{-1}$)

$m_i$: molar mass of compound (g $mol^{-1}$)

P: gas phase pressure (1 atm)

$V_{air}$: average molar volume of gases in air (~20.1 $cm^3\ mol^{-1}$)

$V_i$: molar volume of compound ($cm^3\ mol^{-1}$)

The equation (1.33) is used to adjust the diffusion coefficient to the average temperature during the sampling period [71].

$$D_T = D_{298} \times (T)^{1,75} \times (298.15)^{-1,75} \quad (1.33)$$

Passive sampling is suitable for a variety of environments including indoor, outdoor, workplace and personal sampling. However, the most important advantage of this technique is that it allows working at multiple sampling points simultaneously. The relatively low cost of passive samplers creates such an opportunity for researchers. On the other hand, passive samplers are simple and easy to use. The fact that they do not require electricity and any complex equipment enables sampling to be performed easily, practically and without limitation in field selection. Moreover, time-weighted average (TWA) concentrations are obtained with high accuracy in the passive sampling technique [72]. The sampling time should especially be considered in the choice of technique. Long-term sampling has low sensitivity in determining instantaneous concentration changes. In addition, less efficiency of the pre-enrichment process, unsuitability for automation and high performance dependency on variable environmental conditions (such as temperature, humidity, wind speed, and direction) are the major disadvantages of

the technique [72, 73]. However, it is stated that the accuracy of passive sampling is equal to conventional techniques [74, 75].

## 1.6 Analysis Methods of Volatile Organic Compounds: Thermal Desorption-Gas Chromatography-Mass Spectroscopy

A wide variety of compounds can be included in air samples collected using active or passive methods. It is very important to work with high precision analysis methods that can distinguish target compounds and measure low concentrations. The thermal desorption-gas chromatography-mass spectroscopy (TD-GC-MS) system is an advantageous analysis method that is frequently preferred in VOC analysis (Figure 1.6).

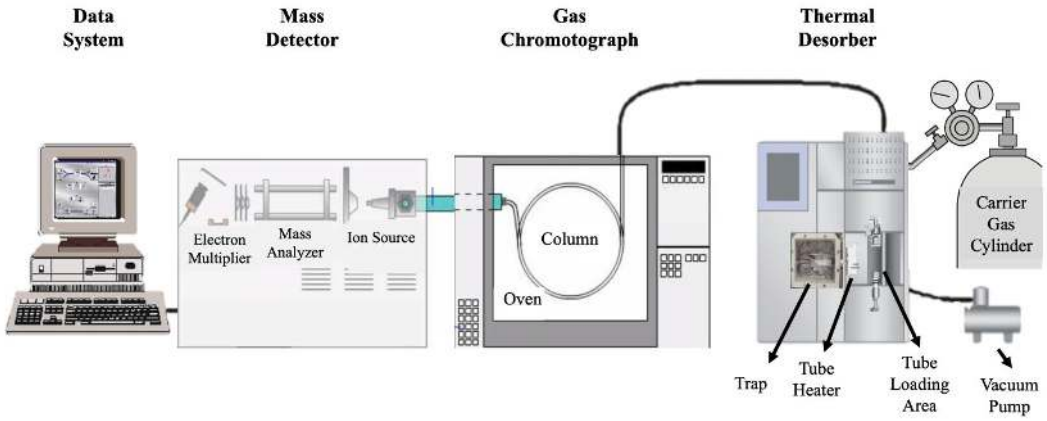


**Figure 1.6**. Scheme of the TD-GC-MS system [61, 76].

Thermal desorption (TD) is a GC preconcentration device that is used to analyze VOCs in a wide variety of samples. The technique extracts volatiles by heating the sample in a flow of inert gas (high purity helium gas). The volatiles are concentrated on a low thermal mass, electrically cooled cold trap. In the end, the analytes are transferred to the gas chromatographic column through a heated transfer line. Thermal desorption maximizes sensitivity for trace-level compounds and minimizes interferences. It is ideal for the measurement of VOCs at the ppb level or below. Another advantage of the technique is that there is no need for solvent-based sample preparation. It also prevents sample loss thanks to full automation in sample preparation, desorption/extraction, pre-concentration and injection.

"Chromatography is a technique in which the components of a mixture are separated based on differences in the rates at which they are carried through a fixed or stationary phase by a gaseous or liquid mobile phase" [77]. It is an extremely effective method used for the qualitative and quantitative analysis of chemical compounds in complex mixtures. Chromatographic separations are based on differences in the migration rates of the components as a mixture is passed through the column constituting the stationary phase by the flow of the mobile phase. The chromatographic methods where the mobile phase is gas (or vapor) are called gas chromatography. After the thermal desorption process, vapor phase analytes are delivered to the chromatographic column [77]. In gas chromatography, the components are separated based on being partitioned between a mobile phase (inert gas) and a stationary phase (liquid or solid) held in a column. The mobile phase does not interact with molecules of the analyte. The only function of the mobile phase is to carry the analytes.

A typical gas chromatography device consists of six parts (Figure 1.7). These are:

- Carrier gas system
- Sample injection system
- Column
- Column oven
- Detection system
- Data system

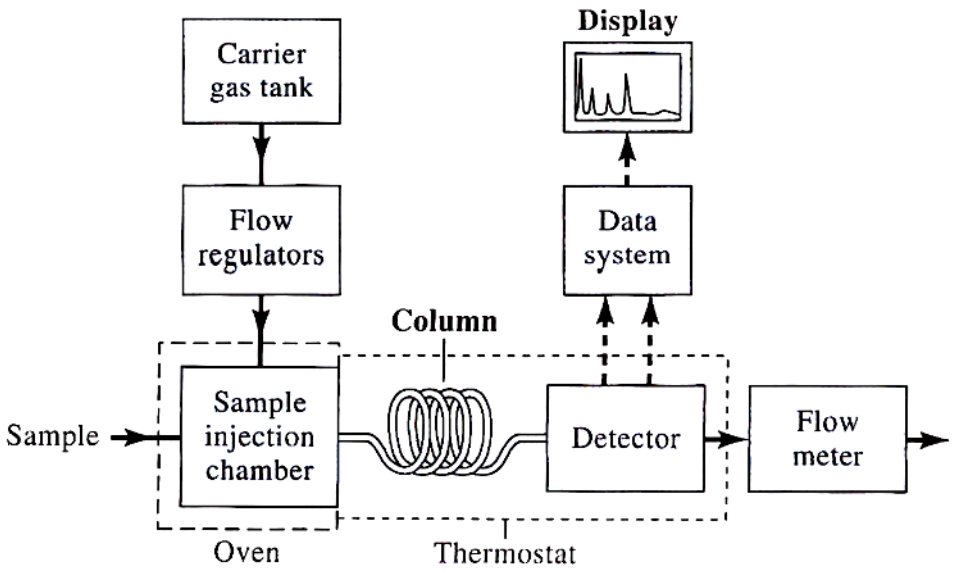


**Figure 1.7**. Block diagram of a gas chromatograph [77].

The mobile phase which is also called carrier gas must be chemically inert. Helium, neon, argon and nitrogen are inert gases mostly used in gas chromatography. They are kept in pressurized cylinders coupled with pressure regulators, gauges and flow meters. The carrier gas drags the substances in the sample injected into the system through the column [77]. Chromatographic columns have lengths varied from less than 2 m to 50 m or more. They are made up of stainless steel, fused silica, glass or Teflon. The optimum temperature of the column is based on the boiling point of the sample and the degree of separation required. Some of the columns suitable for VOC analysis are; Rtx-VMS, Rtx-VRX, Rtx-VGC, DB-624, DB-VRX, HP-624 and HP-VOC columns [61].

The ideal detector should have high sensitivity, high selectivity, reliability, good reproducibility, linearity, wide temperature range (between 298 K to 673 K), short response time, non-destructivity for the sample and ease of use [77]. Mass spectrometry (MS), flame ionization detector (FID), electron capture detector (ECD), thermal conductivity detector (TCD) are the detectors used in gas chromatography. The mass spectrometer is a favorite detector for gas chromatography. A Block diagram of a mass spectrometer is given in Figure 1.8. In the mass spectrometer, sample molecules primarily enter the ionization source where they are converted to ions and are often fragmented. The ions then pass into an analyzer. In the analyzer, they are separated according to their mass-to-charge

values. The separated ions reach to ion detector and turn into an electrical signal which is plotted by the data system.

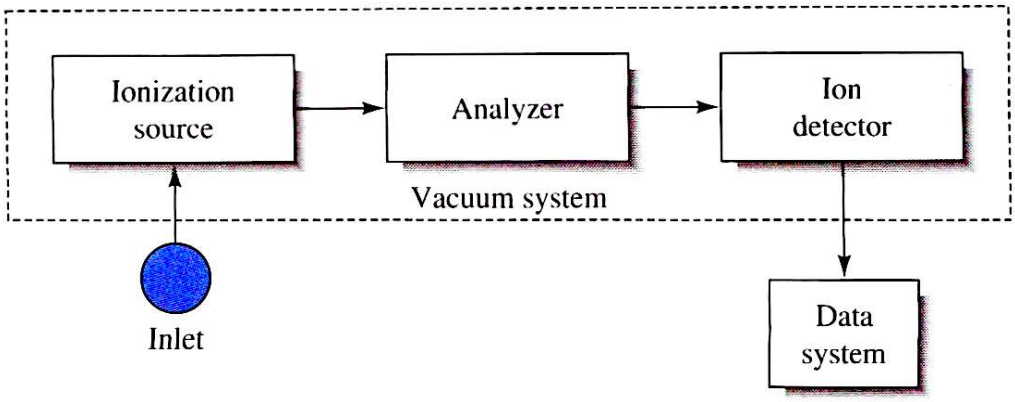


**Figure 1.8**. Block diagram of a mass spectrometer [77].

Two types of signals are obtained in the detector, the mass spectrum of each substance and the chromatogram that includes all substances. A mass spectrum is used for qualitative analysis. Moreover, the position of the peak on the time axis of the chromatogram allows to the identification of the components of the sample. On the other hand, in the chromatogram, the areas under the peaks or peak height provide a quantitative analysis of the components [77].

# 2. AIM AND SCOPE OF THE STUDY

VOCs directly or indirectly create negative effects on both the ecosystem and human health. It has become a necessity to monitor the atmospheric concentrations, distributions and even fates (production and removal patterns) of these compounds, which are important in terms of their behavior in the atmosphere. However, it can not be considered that the amount or variety of pollutants in the ambient air remains constant. Many new technologies produced or developed today will affect air quality at different rates. For this reason, even if there are studies for monitoring air quality, their continuity should be maintained by improving them. In the literature, there are still unresolved mechanisms of VOC formation and depletion. As a result, air pollution studies provide an opportunity to examine changes in air quality, identify regional dominant pollutants and their possible sources and make effective legal regulations against them.

Most of the previous studies remain limited to certain anthropogenic VOCs. In this thesis, a wide variety of VOCs (with biogenic and anthropogenic origins) have been studied, it is very important to obtain new information about VOCs in the environment. In addition, there is no study on ambient VOC determination in Bolu atmosphere, which has a rich variety of sources for VOCs. Our study is also a first in this aspect. The main purpose of passive sampling studies is to determine VOC distributions in the Bolu plateau. In addition, it is predicted that the technique based on many sampling points will be highly representative for the city. Active sampling studies aim to determine the intraday and inter-day trends of VOCs.

The other purposes that make up this thesis are;

- to determine VOC composition in the Bolu atmosphere,
- to determine the spatial distribution of VOCs around Bolu plateau,
- to compare the VOC levels of Bolu with that of other areas in the literature,
- to specify intra-day, inter-day and seasonal variations of VOCs,
- to find possible sources and source regions of VOCs,
- to examine the contribution of VOCs to ozone formation.

# 3. MATERIAL AND METHODS

## 3.1 Sampling Site

The study was performed in the city of Bolu which is in the Western Black Sea Region of Turkey between 30º32' and 32º36' east longitudes; and 40º06' and 41º01' north latitudes. Bolu is surrounded by Düzce, Zonguldak, Eskişehir, Ankara, Karabük, Çankırı, Sakarya and Bilecik. The map showing the location of Bolu is given in Figure 3.1. Bolu has 9 districts namely Dörtdivan, Mengen, Mudurnu, Gerede, Göynük, Kıbrıscık, Seben, Yeniçağa and the city center. The population of the Bolu in 2018 was determined as 311.810 [78].

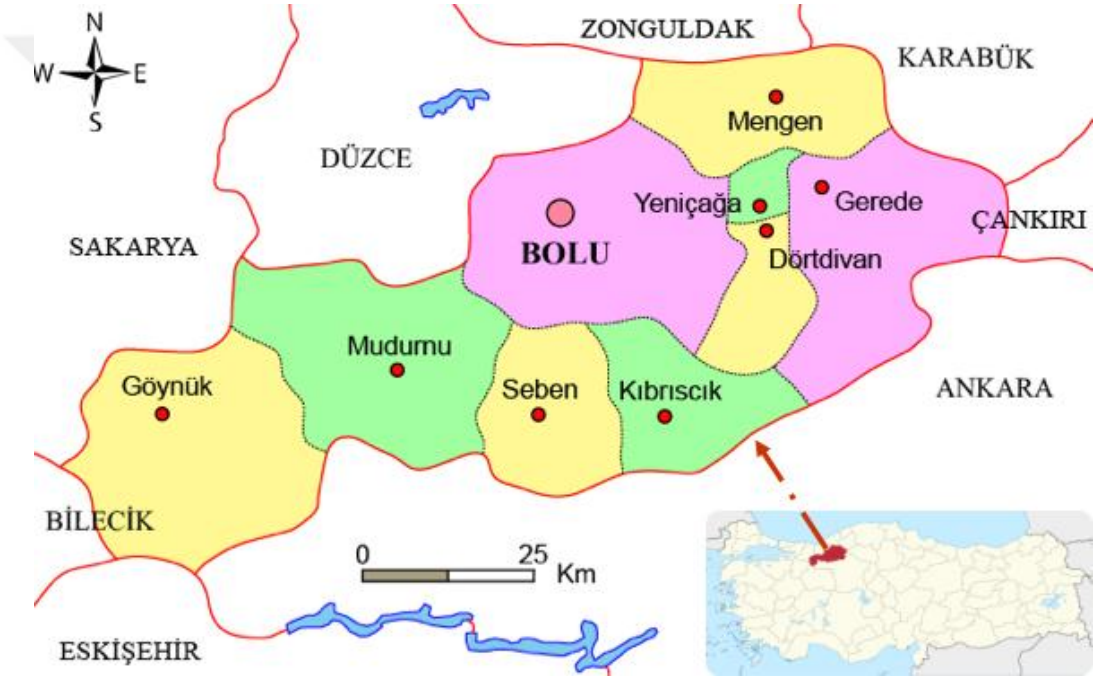


**Figure 3.1**. The location of Bolu.

The total area of Bolu is 8323.39 km$^2$ and approximately 65% of the total area of the city is composed of forests [78]. The most dominant tree species are Fir, Hornbeam, Juniper, Oak, Oriental Beech and Scots Pine (Figure 3.2).

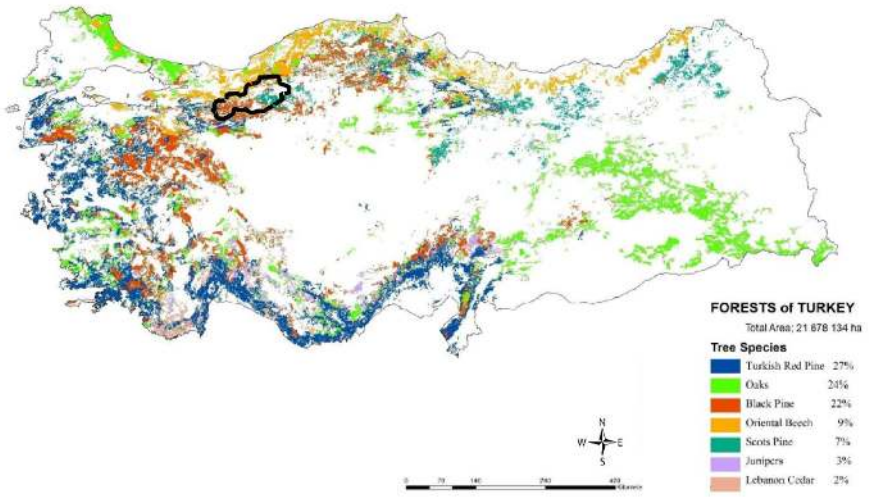


**Figure 3.2**. Distribution of tree species in Bolu [79].

Over the past 89 years, the mean annual precipitation was 388.1 mm, and the mean annual temperature was 12.0 °C [80]. In the northern parts of Bolu, in a narrow area, the Western Black Sea climate is observed. Towards the south, the effect of the Black Sea climate begins to diminish, and the effect of the Central Anatolia climate is felt. The Central Anatolian climate effect is effective in the southern parts of Bolu [78]. In addition, differences in topographic elevation are also an important climate factor in the region. Bolu city center is in a wide valley surrounded by mountains (Figure 3.3). Mountains around the city center limit air circulation. In addition, temperature inversions during cold months make the pollution situations worse. The average altitude of the province is 1000 m while that of the city center is 725 m.

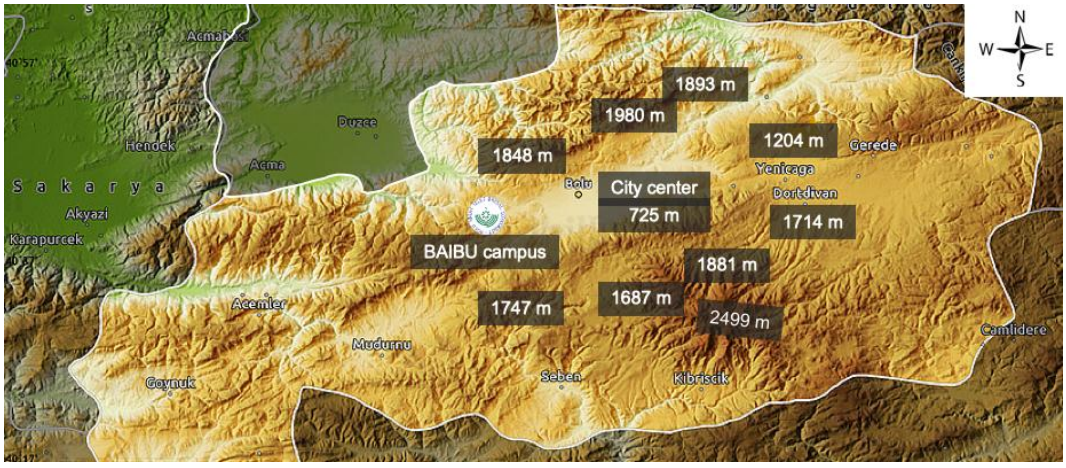


**Figure 3.3**. The bowl-like topography of Bolu city center.

Bolu is in the middle of Turkey's two metropolitan cities, namely Istanbul and Ankara. Two major highways (D-100 and TEM) are located in Bolu. Important industrial sectors operating in the city center of Bolu are cement, poultry, woodworking, metal and glass. The city has also potentials in winter tourism, hunting tourism, health tourism, sports tourism, highland tourism and meeting and seminar tourism [78].

## 3.2 Sampling Campaigns

Two sampling techniques (active sampling and passive sampling) were performed within the scope of the thesis. Sampling points for both methods are illustrated in Figure 3.4. Active sampling studies were carried out in the station set up in Bolu Abant Izzet Baysal University (BAIBU) Gölköy campus. This site has an altitude of 874 meters and coordinates of 40 42 51.8 N latitude- 31 31 02.2 E longitude. It is approximately 3 km far from the major highways (D-100 and TEM) and 12 km far from the city center. At our station on the university campus, 68 VOCs for every month between April - November 2017; January 2018 and 70 VOCs for every month between April - August 2018 were collected with an active sampling in daily and 6-hour periods. Along the Bolu plateau, the passive sampling was performed at 47 sampling points in winter (28 January 2017-12 February 2017) and 63 sampling points in summer (7 July 2017-23 July 2017). In the wintertime, sampling could not be performed in some of the points due to hard winter conditions. The characteristics and geography of the region were taken into account in determining the passive sampling points.

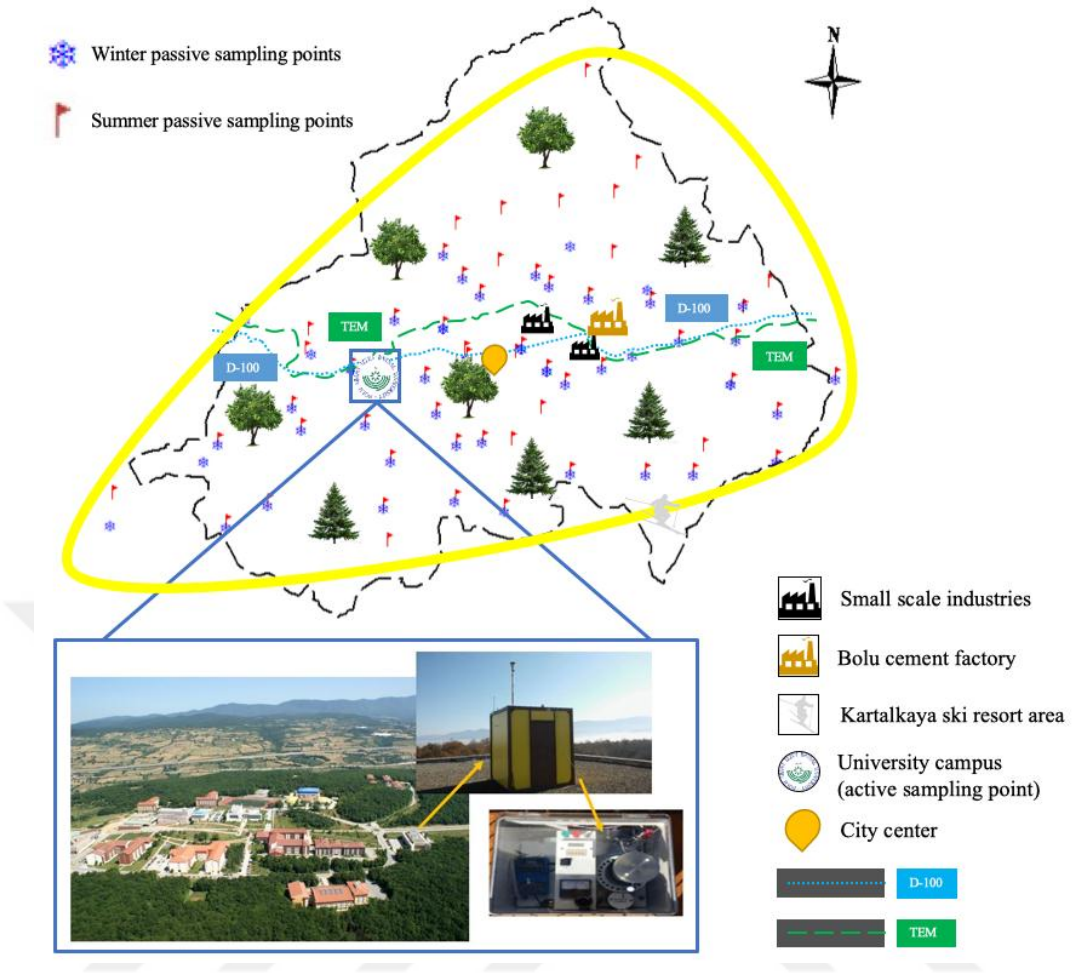


**Figure 3.4.** The locations of active and passive sampling campaigns.

## 3.3 The Compounds under Consideration

A total of 70 volatile organic compounds were considered in the present study (Table 3.1). Based on the literature, they were classified as anthropogenic and biogenic [29, 32, 34, 63, 81].

**Table 3.1.** The VOCs under consideration.

| Anthropogenic VOC | Anthropogenic VOC | Biogenic VOC |
|---|---|---|
| Isoprene [CAS:78-79-5] * | Phenol [CAS:108-95-2] | 2-Methylfuran [CAS:534-22-5] |
| Acrylonitrile [CAS:107-13-1] | Benzaldehyde [CAS:100-52-7] | alpha-Pinene [CAS:80-56-8] |
| n-Hexane [CAS:110-54-3] | 1,4-Cineole [CAS:470-67-7] | Hexanal [CAS:66-25-1] |
| Methacrolein [CAS:78-85-3] ** | 1,2,3-Trimethylbenzene [CAS:526-73-8] | Crotonaldehyde [CAS:123-73-9] |
| Methylvinylketone [CAS:78-94-4] ** | 1,2-Diethylbenzene [CAS:135-01-3] | alpha-Phellandrene [CAS:99-83-2] |
| Chloroform [CAS:67-66-3] | Acetophenone [CAS:98-86-2] | Sabinene [CAS:3387-41-5] |
| 1,1,1-Trichloroethane [CAS:71-55-6] | 1,4-Diethylbenzene [CAS:105-05-5] | 4-Methylanisole [CAS:104-93-8] |
| Tetrachloromethane [CAS:56-23-5] | 1,3,5-Trimethylbenzene [CAS:108-67-8] | gamma-Terpinene [CAS:99-85-4] |
| Benzene [CAS:71-43-2] | Nonanal [CAS:124-19-6] * | Camphene [CAS:79-92-5] |
| 1,2-Dichloroethane [CAS:107-06-2] | 1,2-Dichlorobenzene [CAS:95-50-1] | Dihydromyrcenol [CAS:18479-58-8] |
| n-Heptane [CAS:142-82-5] | n-Dodecane [CAS:112-40-3] | Limonene [CAS:138-86-3] |
| n-Octane [CAS:111-65-9] | Decanal [CAS:112-31-2] * | m-Cymene [CAS:535-77-3] |
| Toluene [CAS:108-88-3] | Naphthalene [CAS:91-20-3] | p-Cymene [CAS:99-87-6] |
| Chlorobenzene [CAS:108-90-7] | n-Tridecane [CAS:629-50-5] | Ocimene [CAS:13877-91-3] |
| Ethylbenzene [CAS:100-41-4] | Benzothiazole [CAS:95-16-9] | Eucalyptol [CAS:470-82-6] |
| m+p Xylene [CAS:108-38-3] [CAS:106-42-3] | n-Tetradecane [CAS:629-59-4] | 1-Terpinen-4-ol [CAS:8000-41-7] |
| o-Xylene [CAS:95-47-6] | | beta-Pinene [CAS:127-91-3] |
| Styrene [CAS:100-42-5] | | Terpinolene [CAS:586-62-9] |
| 1- Heptanal [CAS:111-71-7] * | | beta-Myrcene [CAS:123-35-3] |
| Isopropylbenzene [CAS:98-82-8] | | 3-Carene [CAS:13466-78-9] |
| n-Propylbenzene [CAS:103-65-1] | | 1-Octanol [CAS:111-87-5] |
| n-Nonane [CAS:111-84-2] | | Linalool [CAS:78-70-6] |
| n-Decane [CAS:124-18-5] | | Alloocimene [CAS:673-84-7] |
| m-Ethyltoluene [CAS:620-14-4] | | alpha-Terpinen [CAS:99-86-5] |
| p-Ethyltoluene [CAS:622-96-8] | | L-Fenchone [CAS:7787-20-4] |
| 1,2,4-Trimethylbenzene [CAS:95-63-6] | | alpha-Terpineol [CAS:10482-56-1] |
| o-Ethyltoluene [CAS:611-14-3] | | (+)-Camphor [CAS:464-49-3] |

*VOCs that have both anthropogenic and biogenic origin

** VOCs that sampled during the period of May-August 2018

## 3.4 Pre-sampling Studies

Volatile organic compounds were collected into Tenax-TA sampling tubes (Perkin Elmer, USA). Tenax-TA tubes have a length of 89 mm, an outer diameter of 6.4 mm, an inner diameter of 5 mm and a diffusion path length of 15 mm. It contains Tenax-TA sorbent in 35/60 sieve size. This sorbent type is the most suitable hydrophobic sorbent type for thermal desorption [82].

Before each sampling, Tenax-TA sampling tubes (Perkin Elmer, USA) were cleaned and conditioned using a thermal desorber. Conditioning was carried out at 320 °C for 60 minutes under helium (99.999 % purity). They were stored in screw-capped falcon tubes with a pack including a silica gel and activated carbon (Figure 3.5). While a silica gel was used against a humidity problem, activated carbon was preferred to prevent a possible contamination problem.

**Figure 3.5.** Falcon tube including Tenax-TA sampling tube and a pack of silica gel and activated carbon (photo taken in the laboratory).

## 3.5 Sampling Techniques

### 3.5.1 Active Sampling

An STS-25 sequential automatic sampler (Perkin Elmer, USA) was used in the active sampling (Figure 3.6). The flow rate of the vacuum pump (Gilian, LFS 1130) connected to the STS-25 sampler was adjusted to 250 mL $min^{-1}$.

Since May 2017, potassium iodide had been used as an ozone scavenger in the sampling. Potassium iodide (KI) solution was obtained by dissolving 20 g KI in 15 mL deionized water. Glass fiber filters were soaked in KI solution. After impregnating the filters, they were dried in an oven at 40 ° C for 45 minutes. To

prevent oxidation, the KI solution was freshly prepared and the bottle was covered with aluminum foil to avoid exposure to light. The system in which KI filters are integrated into the STS-25 device is shown in Figure 3.6. The sharp and higher signals were obtained in the samples collected by using a potassium iodide impregnated filter.

The optimization studies revealed that the intra-day active sampling period should be a minimum of 6 hours to detect almost all of the compounds. Hence, 24-hour sampling for 8 days and 6-hour sampling for 2 days were carried out for each month. At the end of the sampling, the samples were transported to the laboratory in the falcon tubes and stored in the deep freezer at -18 ° C until analysis.

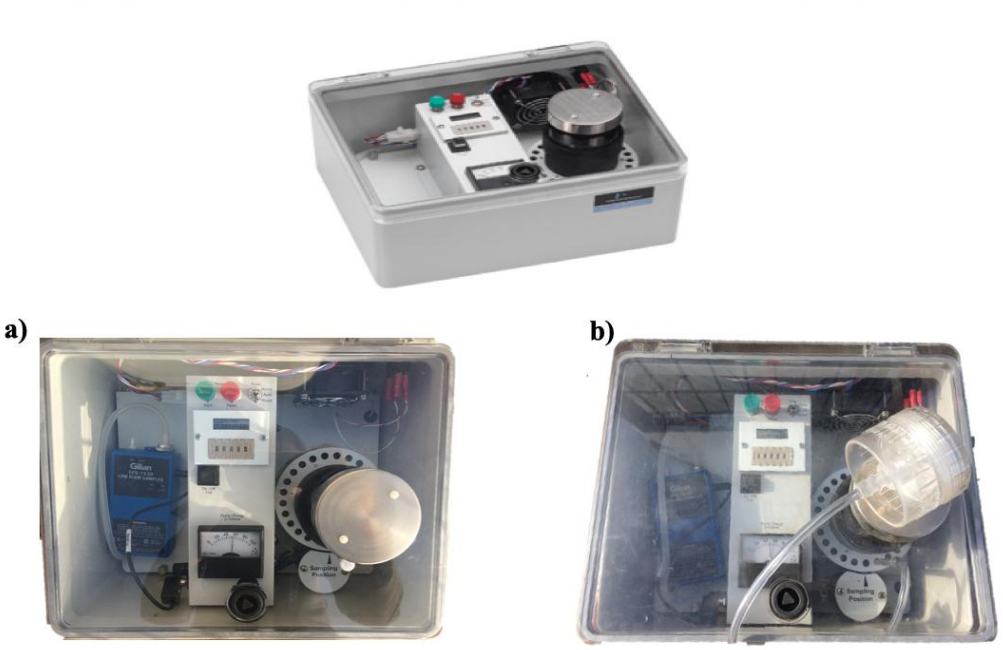


**Figure 3.6.** STS-25 device a) without KI filter (b) with KI filter used in active sampling of VOCs (photo taken in the field).

Simultaneous monitoring was also performed with Environnement 42M ozone analyzer and Davis WeatherLink meteorology station in the station in BAIBU Gölköy campus. Average meteorological data for the active sampling periods are given in Table 3.2.

**Table 3.2.** Average meteorological data for the active sampling period.

| | Average Temperature (°C) | Average daily Minimum / Maximum Temperature (°C) | Average Solar Radiation (W $m^{-2}$ ) | Average Wind Speed (m $sec^{-1}$) | Average Daily Maximum Wind Speed (m $sec^{-1}$) | Average Ozone Conc. (µg $m^{-3}$) |
|---|---|---|---|---|---|---|
| **April 2017** | 6.1 | 1.9 (22.04.17) / 13 (17.04.17) | 168 | 1.7 | 2.4 (20.04.17) | 32.6 |
| **May 2017** | 10.1 | 7.1 (21.05.17) / 14.4 (25.05.17) | 187 | 1.9 | 3.2 (18.05.17) | 30.3 |
| **June 2017** | 15.9 | 13.4 (09.06.17) / 18.6 (07.06.17) | 249 | 1.6 | 2.3 (09.06.17) | 28.1 |
| **July 2017** | 18.8 | 17.8 (19.07.17) / 20.1 (13.07.17) | 275 | 2.4 | 2.9 (17.07.17) | 30.4 |
| **August 2017** | 19.2 | 17.3 (15.08.17) / 20.5 (20.08.17) | 264 | 2.3 | 2.7 (15.08.17) | 26.2 |
| **September 2017** | - | - | - | - | - | 28.2 |
| **October 2017** | 10.2 | 6.6 (29.10.17) / 13.6 (23.10.17) | 111 | 1.3 | 2.2 (28.10.17) | 21.4 |
| **November 2017** | 3.7 | -1.4 (21.11.17) / 10.0 (27.11.17) | 56 | 0.7 | 1.9 (20.11.17) | 19.6 |
| **January 2018** | -1.2 | -6.2 (25.01.18) / 3.7 (30.01.18) | 101 | 1.5 | 2.7 (22.01.18) | 21.9 |
| **April 2018** | 11.8 | 5.8 (20.04.18) / 15.4 (26.04.18) | 266 | 1.7 | 2.1 (27.04.18) | - |
| **May 2018** | 15.4 | 13.5 (30.05.18) / 16.9 (22.05.18) | 204 | 1.6 | 2.1 (22.05.18) | - |
| **June 2018** | 16.9 | 15.0 (17.06.18) / 18.1 (19.06.18) | 226 | 1.4 | 2.0 (23.06.18) | 28.1 |
| **July 2018** | 18.6 | 15.6 (16.07.18) / 21.9 (23.07.18) | 257 | 1.5 | 1.9 (21.07.18) | 30.2 |
| **August 2018** | 18.9 | 16.3 (12.08.18) / 20.3 (06.08.18) | 244 | 1.3 | 1.8 (06.08.18) | 27.2 |

### 3.5.2 Passive Sampling

Passive sampling is a method based on molecular diffusion. At the sampling points, the Tenax-TA tubes were placed vertically with the open end downward in their aluminum shelters which were fixed to tree branches or poles approximately 2-2.5 m high from the ground (Figure 3.7). Diffusion caps were also installed at the open ends of the tubes to protect the sorbent bed from factors such as excessive wind, dust and insects during the 15-day sampling period. At the end of the sampling, the diffusion caps were removed and the covers of the tubes were

installed. The samples were transported to the laboratory in the falcon tubes and stored in the deep freezer at -18 ° C until analysis.

**Figure 3.7.** Tenax-TA passive sampler connected to the shelter in a sampling area (photo taken in the field).

Within the scope of the TÜBİTAK project, which also includes the thesis subject, ozone samples were collected simultaneously with VOCs at the same sampling points. Ozone was collected on passive samplers made of Delrin material developed by Eskişehir Technical University Environmental Engineering Department Air Pollution Research group. Whatman GF / A glass fiber filter papers coated with 1% $NaNO_2$ (sodium nitrite) + 2% $Na_2CO_3$ (sodium carbonate) + 2% glycerin solution were placed in the samplers to retain ozone. Ozone analyzes were performed on Dionex ICS 1100 Series Ion Chromatography. In this thesis, ozone data were used to examine the relationship between ozone and its precursor VOCs. Meteorological data used in the passive sampling studies were obtained from Bolu Provincial Meteorology Directorate. The weather station is located at 742 meters altitude at 40 ° 42′′ North latitude and 31 ° 36′ East longitude. Average meteorological data for the summer and winter sampling periods are presented in Table 3.3.

**Table 3.3.** Average meteorological data for the passive sampling period.

| | Average Temperature (°C) | Minimum / Maximum Temperature (°C) | Average Solar Radiation (W $m^{-2}$ ) | Average Wind Speed (m $sec^{-1}$) | Maximum Wind Speed (m $sec^{-1}$) | Average Ozone (µg $m^{-3}$) |
|---|---|---|---|---|---|---|
| **Winter sampling** | -0.19 | -14 / 13.3 | 123 | 1.15 | 7.6 | 64.2 |
| **Summer sampling** | 19.9 | 10.5 / 32.3 | 387 | 1.63 | 10 | 46.4 |

## 3.6 Analysis

Figure 3.8 shows the integrated Thermal Desorption (Perkin Elmer, USA) and Gas Chromatography-Mass Spectrometer (Shimadzu, Japan) system used to analyze VOC samples. In the system, the VOCs adsorbed into Tenax-TA were thermally desorbed by thermal desorption (TD) and sent to Gas Chromatography Mass Spectrometer (GC-MS).

**Figure 3.8.** TD-GC-MS system used in VOC analysis (photo taken in Environmental Analysis Laboratory in the Chemistry Department of BAIBU).

The RTX-624 column used to analyze VOCs has a length of 60.0 m, a diameter of 0.25 mm and a thickness of 1.40 µm. Operating conditions for Thermal Desorber and GC-MS during the analysis are given in Table 3.4.

**Table 3.4.** TD-GC-MS operating parameters.

| **GC** | SHIMADZU-QP2010SE |
|---|---|
| **GC column** | RTX-624 60.0 m x 0.25 mm x 1.40 µm |
| **Column oven temperature** | 40 °C |
| **Injection temperature** | 100 °C |
| **Injection mode** | splitless |
| **Sampling time** | 1 min |
| **Carrier gas** | High purity Helium, %99.999 |
| **Pressure** | 155.9 kPa |
| **Total flow** | 50 mL $min^{-1}$ |
| **Column flow** | 1.4 mL $min^{-1}$ |
| **Linear velocity** | 30.2 cm $sec^{-1}$ |
| **Purge flow** | 3 mL $min^{-1}$ |
| **Split ratio** | -1 |
| **Oven temperature program** | 40 °C (5 min), 7.5°C $min^{-1}$ to 180°C, 28°C $min^{-1}$ to 240°C (15 min) |
| **Injection volume** | 1 µL |
| **MS** | |
| **Mass spectrometer** | Elektron impact, 70 eV |
| **Ion source temperature** | 230 °C |
| **Interface temperature** | 240 °C |
| **Solvent cut time** | 1 min |
| **Detector voltage** | 0 kV |
| **GC program time** | 40.81 min. |
| **TD** | |
| **Valve temperature** | 230 °C |
| **Tube temperature** | 250 °C |
| **Transfer temperature** | 250 °C |
| **Ratio** | 40 °C $sec^{-1}$ |
| **High temperature** | 250 °C |
| **Low temperature** | -30 °C |
| **Purge time** | 2 min |
| **Desorb time** | 10 min |
| **Cycle time** | 20 min |
| **Mode** | 2-stage desorb |
| **Split** | Flow |
| **Outlet Split flow** | 30 mL $min^{-1}$ |
| **Column flow** | 1.4 mL $min^{-1}$ |
| **Desorb flow** | 20 mL $min^{-1}$ |
| **Inlet Split flow** | 30 mL $min^{-1}$ |

Selected Ion Monitoring (SIM) mode was preferred in GC-MS to maximize the precision and the sensitivity. VOCs were grouped in 6 different SIM windows. The main and auxiliary ions of the compounds were entered into the detector for the selected time intervals while creating the groups. The time intervals of the groups and the ions of the components in the ranges are given in Table 3.5.

**Table 3.5.** SIM parameters.

| SIM Window | Time (min) | Monitored ions (m/z) |
|---|---|---|
| **1** | 1.00-9.36 | 67, 68, 53 |
| **2** | 9.36-12.27 | 53, 52, 51, 57, 41, 43, 82, 81 |
| **3** | 12.27-15.94 | 83, 85, 47, 97, 99, 61, 117, 119, 121, 78, 77, 52, 62, 64, 49, 43, 71, 41, 70, 39 |
| **4** | 15.94-18.08 | 43, 85, 57, 91, 92, 65 |
| **5** | 18.08-19.44 | 44, 56, 41 |
| **6** | 19.44-35.00 | 112, 77, 114, 91, 106, 65, 43, 57, 105, 104, 103, 78, 70, 44, 93, 92, 120, 79, 121, 75, 41, 69, 119, 111, 71, 68, 67, 134, 81, 122, 107, 136, 94, 66, 146, 148, 59, 55, 56, 95, 128, 127, 129, 135, 108 |

Chromatograms containing 70 targets VOCs were plotted by GC-MS software. The chromatograms belonging to the lowest standard (10 ng) and the first passive sample are shown in Figure 3.9.

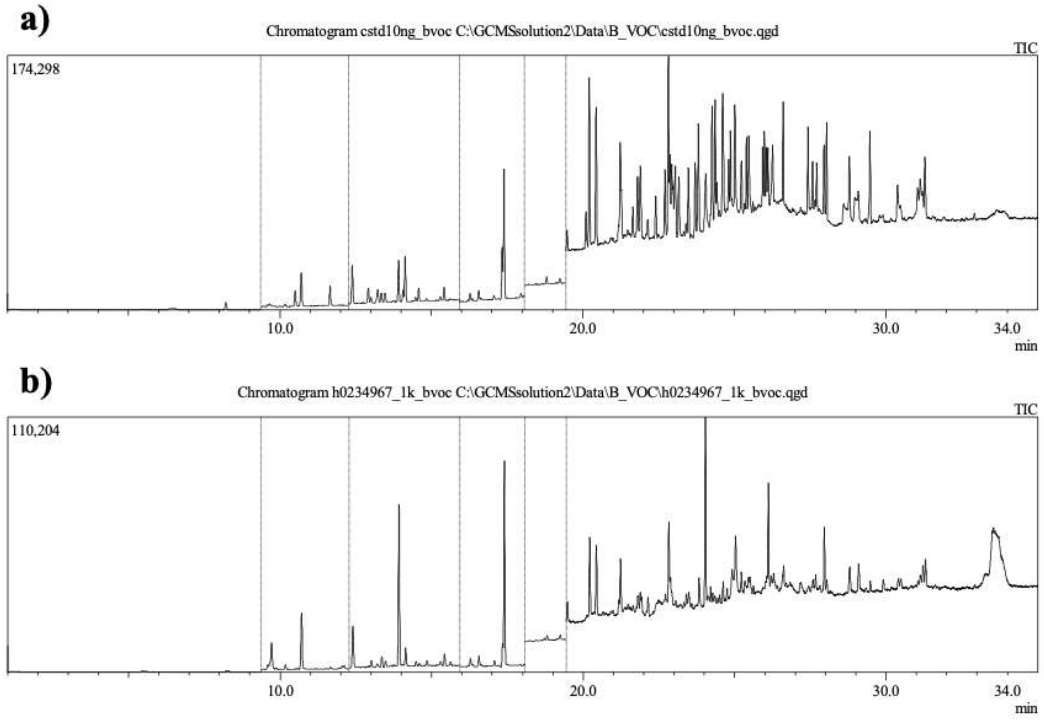


**Figure 3.9.** Chromatograms belonging to (a) the lowest standard and (b) the first passive sample.

For the preparation of the calibration curve, the standards were primarily prepared. 10 ppm intermediate stock was prepared by taking 100 µL of 100 ppm main stock and filling it with 1 mL of methanol. 10 ng, 20 ng and 50 ng standards

were obtained, respectively, by injecting 1 µL, 2 µL and 5 µL of the intermediate stock of 10 ppm into the Tenax tube. 100 ng and 200 ng standards were also obtained by injecting 1 µL and 2 µL of 100 ppm stock into the Tenax tube. Thus, a 5-point (10 ng, 20 ng, 50 ng, 100 ng and 200 ng) calibration curve was drawn. The calibration curve of the nonanal compound is given in Figure 3.10.

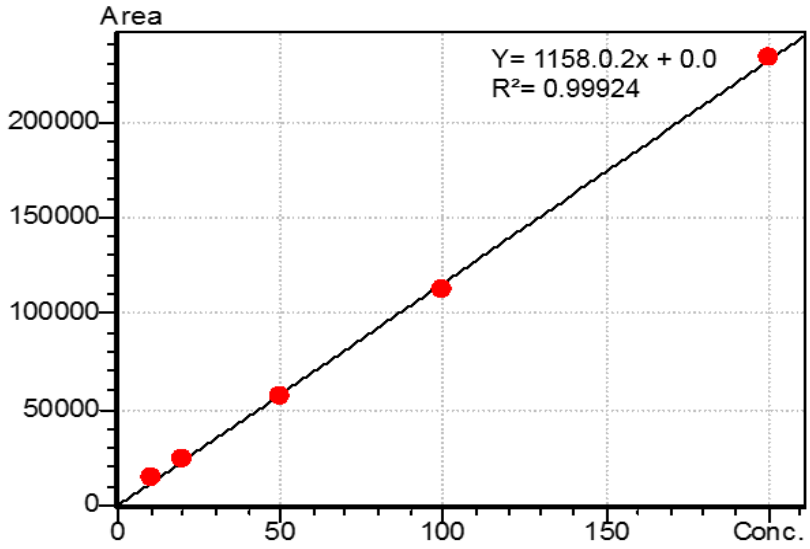


**Figure 3.10.** Calibration curve obtained using TD-GC-MS system - Nonanal.

### 3.7 Calculations of Atmospheric Concentrations

To find out the atmospheric concentration of the compound in active samples, the mass of the compound (ng) was divided to the sampled air volume (L). The sampled air volume was obtained by multiplying the pump flow rate (mL $min^{-1}$) and the sampling time (min) (see equation 1.30).

On the other hand, atmospheric concentrations of passive samples can be determined either theoretically, using Fick's Law (see equation 1.31), or experimentally, using the uptake rate (UR). It is stated that the uptake rate calculation reflects the field conditions better than the theoretical method [60, 83-85]. Since the URs of many VOCs are scarce in the literature, it is planned to calculate the uptake rate of as many VOC compounds as possible. The studies based on the determination of uptake rate for VOCs were given in the following sub-section.

### 3.7.1 Determination of Uptake Rate for VOCs

For the uptake rate calculation, one-week concurrent passive (3 potassium iodide replicate samples and 3 potassium iodide-free replicate samples) and one potassium iodide active sample (24-hour) for five months in 2018 (April-August) were collected to the Tenax-TA sampling tubes at the university station.

#### 3.7.1.1 Experimental Procedure for Uptake Rate Determination

Before the sampling, the Tenax-TA samplers were cleaned and conditioned using the thermal desorber system. The conditioning was carried out at 320 $^{o}$C for 60 minutes under the high purity helium gas.

The conditioned Tenax-TA stainless steel tubes have been stored in the screw-capped falcon tubes including a pack of silica gel and activated carbon until sampling.

The active VOC samples were collected on the Tenax-TA by STS-25 sequential sampler for 24-hour periods whereas the passive samplers were placed vertically with the open end downward in the aluminum shelters. During the sampling of potassium iodide (KI) -free passive samples, the diffusion headers were used to protect the sorbent bed from the effects of excessive wind, dust, and insects. The open ends of the active and passive samplers, in which potassium iodide solution was used, were also equipped with a filter pack. Figure 3.11 illustrates the uptake-rate sampling conditions.

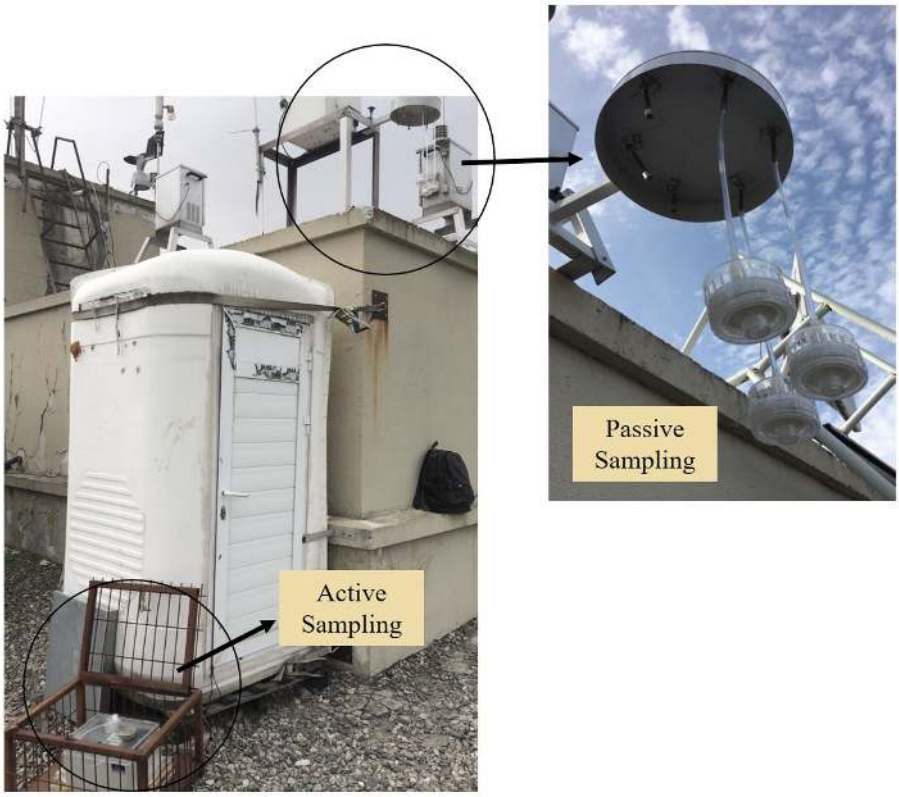


**Figure 3.11.** Sampling station during the uptake rate studies.

At the end of the sampling, the samplers were capped and transported to the laboratory in the falcon tubes. VOCs adsorbed into the Tenax-TA were desorbed thermally by the thermal desorption (TD) system (Perkin Elmer, Turbomatrix 300, USA) and sent to the Gas Chromatography Mass Spectrometer (GC-MS) system (Shimadzu, GCMS-QP2010SE, Japan).

### 3.7.1.2 Theoretical Procedure for Uptake Rate Determination

Atmospheric concentrations of VOCs that were collected by passive sampling were calculated using Fick's first law of diffusion (3.1).

$$Q = \frac{(C \; x \; L)}{(D \; x \; A \; x \; t)} \; x \; 10^3 \qquad (3.1)$$

where $Q$ is the amount of absorbed pollutant ($\mu g \; m^{-3}$), $L$ is the diffusion path (cm), $A$ is the sampler surface area ($cm^2$), $D$ is the diffusion coefficient ($cm^2 \; sec^{-1}$), $C$ is the pollutant concentration at the open end of the sampler (ng) and $t$ is the sampling time (sec). For the Tenax-TA samplers, the diffusion path ($L$) is 1.5 cm,

and the surface area ($A$) is 0.1963 $cm^2$. The diffusion coefficient for 298 K is specific for each compound.

For the calculation of atmospheric concentrations (µg $m^{-3}$) of active sampling VOC results, equation (3.2) was used.

$$A\ (\mu g\ m^{-3}) = \frac{(A\ ng\ x\ \frac{1\ \mu g}{1000\ ng})}{(250\ \frac{cc}{min}\ x(24x60)min\ x\frac{1\ L}{1000\ cc}\ x\ \frac{1\ m3}{1000\ L})} \qquad (3.2)$$

Because the passive sampling period was about seven days and the active samples had to be collected daily, the total of the active sampling results was compared to the results from passive sampling. The results of passive samples with potassium iodide showed a significant difference when compared with other methods and thus were excluded from the evaluation. The difference is thought to be because of the used apparatus or KI impregnated filter changing the length of diffusion. For the verification, the percent error values were calculated between these two methods and the data were discarded accordingly.

The uptake rates on passive samplers (mL $min^{-1}$) were calculated as the ratio of the sorbed mass on the passive sampler (ng) to the exposure time (min) and the average concentration (ng $mL^{-1}$) obtained from the simultaneous active sampling (3.3),

$$UR = \frac{(md - mb)}{c\ x\ t} \qquad (3.3)$$

where *md* is the adsorbed mass of compound (ng) during the exposure time (*t*) (min), *mb* is the mass of compound (ng) on the non-exposed cartridge (a blank) and *c* (ng $mL^{-1}$) is an ambient concentration of the compound.

#### 3.7.1.3 Results for Uptake Rate Determination

Since some VOCs could not be detected in the samples and some data were discarded while making the calculations, the uptake rate result could be obtained for a total of 51 VOCs. The average environmental uptake rates were given in Table 3.6. The URs shown in the table had a very wide range of values (0.03 to 2.33 mL

$min^{-1}$). Due to the differences in the affinity and diffusion rates of the VOCs to the adsorbent, each VOC had its unique UR value.

**Table 3.6.** Calculated average uptake rates of VOCs (mL $min^{-1}$).

| VOC | April | May | June | July | August | All months |
|---|---|---|---|---|---|---|
| **Isoprene** | 2.267 | 1.612 | 2.024 | 1.410 | 1.731 | 1.855 |
| **Acrylonitrile** | | | | | | |
| **n-Hexane** | 0.908 | | 0.866 | | 0.976 | 0.917 |
| **Methachrolein** | | | 0.590 | 0.536 | 0.529 | 0.547 |
| **2-Methylfuran** | | | | 0.080 | 0.095 | 0.084 |
| **Methylvinylketone** | | | 0.368 | 0.373 | 0.451 | 0.400 |
| **Chloroform** | | | 1.749 | | 1.928 | 1.820 |
| **1,1,1-Trichloroethane** | | | | | | |
| **Tetrachloromethane** | | 0.861 | 0.822 | | 0.840 | 0.841 |
| **Benzene** | 1.077 | 1.345 | 1.032 | 1.067 | 1.216 | 1.121 |
| **1,2-Dichloroethane** | 0.520 | 0.480 | | 0.519 | 0.463 | 0.496 |
| **n-Heptane** | 0.087 | 0.084 | 0.039 | 0.078 | 0.062 | 0.070 |
| **Crotonaldehyde** | 0.359 | | | | | 0.359 |
| **n-Octane** | 0.076 | 0.130 | 0.048 | | | 0.084 |
| **Toluene** | | 0.350 | 0.218 | | | 0.271 |
| **Hexanal** | 0.089 | 0.052 | 0.023 | 0.018 | 0.014 | 0.039 |
| **Chlorobenzene** | 0.004 | 0.015 | | 0.090 | 0.061 | 0.043 |
| **Ethylbenzene** | 0.435 | 0.488 | 0.198 | 0.268 | 0.277 | 0.338 |
| **m+p Xylene** | 0.395 | 0.353 | 0.220 | 0.343 | 0.350 | 0.330 |
| **o-Xylene** | 0.414 | 0.299 | 0.176 | 0.479 | 0.455 | 0.361 |
| **Styrene** | 0.143 | 0.109 | 0.079 | 0.054 | 0.087 | 0.094 |
| **1- Heptanal** | 0.180 | 0.162 | 0.101 | | | 0.148 |
| **Alpha-pinene** | 0.193 | 0.158 | 0.190 | 0.291 | | 0.208 |
| **Isopropylbenzene** | | | | 0.221 | | 0.221 |
| **Camphene** | 0.170 | 0.219 | 0.163 | 0.289 | 0.376 | 0.244 |
| **n-Propylbenzene** | 0.365 | 0.286 | 0.161 | 0.269 | 0.240 | 0.264 |
| **n-Nonane** | | | | | | |
| **n-Decane** | | | | | | |
| **m-Ethyltoluene** | | 0.277 | 0.154 | 0.277 | 0.211 | 0.230 |
| **p-Ethyltoluene** | 0.369 | 0.247 | 0.104 | 0.269 | 0.250 | 0.229 |
| **Sabinene** | | | | | | |
| **beta-Myrcene** | | | | | | |
| **1,2,4-Trimethylbenzene** | 0.378 | 0.272 | | 0.151 | 0.166 | 0.237 |
| **beta-Pinene** | 0.162 | 0.147 | 0.155 | 0.343 | | 0.201 |
| **o-Ethyltoluene** | | 0.240 | 0.126 | 0.201 | 0.223 | 0.197 |
| **alpha-Phellandrene** | | | | | | |
| **3-Carene** | | | | 0.082 | | 0.082 |

| | | | | | | |
|---|---|---|---|---|---|---|
| **1,3,5-Trimethylbenzene** | 0.344 | 0.223 | 0.143 | 0.204 | 0.164 | 0.216 |
| **Benzaldehyde** | | 1.473 | 2.252 | 1.348 | 2.122 | 1.799 |
| **1,4-Cineole** | | | | | | |
| **Limonene** | 0.004 | 0.043 | | 0.190 | 0.183 | 0.111 |
| **m-Cymene** | 0.170 | | | 0.328 | | 0.249 |
| **p-Cymene** | 0.046 | 0.109 | 0.064 | 0.089 | 0.171 | 0.096 |
| **Ocimene** | | | | | | |
| **Eucalyptol** | 0.210 | | 0.080 | | | 0.113 |
| **1,2,3-Trimethylbenzene** | 0.334 | 0.201 | 0.169 | 0.183 | 0.140 | 0.205 |
| **4-Methylanisole** | | | | | | |
| **gamma-Terpinene** | | | | | | |
| **1,3-Diethylbenzene** | | | | | | |
| **1,4-Diethylbenzene** | 0.276 | | | 0.252 | 0.252 | 0.261 |
| **Phenol** | | | 0.344 | 0.349 | 0.490 | 0.394 |
| **1,2-Dichlorobenzene** | | | | | | |
| **Terpinolene** | | | | | | |
| **Dihydromyrcenol** | 0.378 | 0.075 | | 0.191 | | 0.255 |
| **1-Octanol** | 0.379 | 0.075 | | 0.186 | | 0.255 |
| **Linalool** | | | | | | |
| **Alloocimene** | | | | | | |
| **Nonanal** | 0.042 | 0.146 | 0.091 | 0.093 | 0.036 | 0.082 |
| **Acetophenone** | | 2.223 | 2.359 | 2.061 | 2.686 | 2.332 |
| **alpha-Terpinen** | | | | | | |
| **L-Fenchone** | | | | | | |
| **n-Dodecane** | | 0.121 | 0.220 | 0.174 | 0.287 | 0.190 |
| **(+)-Camphor** | 0.029 | 0.036 | | 0.025 | | 0.031 |
| **1-Terpinen-4-ol** | | 0.038 | | | | 0.038 |
| **Decanal** | 0.035 | 0.352 | 0.274 | 0.226 | 0.103 | 0.196 |
| **alpha-Terpineol** | | | | | | |
| **Naphthalene** | 0.233 | 0.123 | 0.064 | 0.182 | 0.273 | 0.174 |
| **n-Tridecane** | 0.181 | 0.108 | 0.035 | 0.072 | 0.057 | 0.091 |
| **Benzothiazole** | | | 0.341 | 0.383 | 0.420 | 0.376 |
| **n-Tetradecane** | | 0.147 | 0.069 | 0.054 | 0.057 | 0.076 |

In the literature, the UR values are mostly calculated for BTEX compounds, but there are very few studies examining more VOC compounds. The average URs for the VOCs that were calculated in this study were compared with the corresponding values reported in the literature as given in Table 3.7. It revealed that the calculated uptake rates did not provide very much similarity with those given in the literature.

**Table 3.7.** Comparison of average uptake rates of VOCs (mL $min^{-1}$).

| VOC | AVERAGE URS (mL $min^{-1}$) | | | | |
|---|---|---|---|---|---|
| | This study | [84] | [85] | [86] | [87] |
| **Benzene** | 1.12 | 0.57-0.61 | 0.39 | 0.68 | 0.57 |
| **Toluene** | 0.27 | 0.42-0.49 | 0.44 | 0.62 | 0.51 |
| **Octane** | 0.08 | | 0.45 | | |
| **Ethylbenzene** | 0.34 | 0.51-0.54 | 0.39 | 0.55 | 0.5 |
| **m+p Xylene** | 0.33 | 0.41-0.58 | 0.4 | 0.53 | 0.47 |
| **Styrene** | 0.09 | | 0.37 | | |
| **o Xylene** | 0.36 | 0.41-0.48 | 0.35 | 0.54 | 0.47 |
| **Isopropylbenzene** | 0.22 | | 0.61 | | |
| **n-Propylbenzene** | 0.26 | | 0.4 | | |
| **m Ethyltoluene** | 0.23 | | 0.36 | | |
| **p Ethyltoluene** | 0.23 | | 0.38 | | |
| **1,3,5 Trimethylbenzene** | 0.22 | | 0.36 | | |
| **o Ethyltolene** | 0.20 | | 0.35 | | |
| **1,2,4 Trimethylbenzene** | 0.24 | | 0.41 | | |

Our results were evaluated as inconsistent since similar uptake rates were detected for 8-carbon and 14-carbon compounds. Low precision in the rates decreased the reliability of the results. In this context, the fact that KI was used in the active sampling and not used in the passive sampling study caused uncertainty in the methods. Difficulties in detecting all VOCs and ignoring the temperature parameter in the calculations were the critical disadvantages of the experimental uptake rate calculation. As a result, it was preferred to use the theoretical uptake rates (see equations between 1.31 and 1.33) in the determination of atmospheric concentrations of the passive samples.

## 3.8 Quality Control and Quality Assurance

Environmental sampling studies are consisting of many stages, from choosing the sampling point to calculating atmospheric concentrations of compounds. Errors that occur during any of these stages (failure to store samples without contamination, incorrect transfer of data, etc.), method errors or abnormal environmental conditions (meteorological anomalies, irregular source emissions, etc.) may cause noncorrect or suspicious data. Quality Control and Quality Assurance (QA / QC) procedure should be applied from the beginning of the experimental studies to detect and remove the erroneous data points that may be in

the data set due to various reasons. Within the scope of the quality control (QC) and quality assurance (QA), maximum care was taken at all stages. Findings of the QA / QC procedure applied in this study are explained in the following sub-sections.

### 3.8.1 Detection Limits

A total of 24 blank samples (16 for active sampling and 8 for passive sampling) were used. The blanks were moved to the sampling point under the same conditions as the samples and kept there for 10 seconds with the covers were open. The analysis of the blank samples, which were then moved to the laboratory with the lids closed, was carried out in the same way as the samples.

The method detection limit (MDL) and the method limit of quantification (MLOQ) values of VOCs were determined by multiplying the standard deviation of field blank values with three and ten, respectively. However, if the compound was not detected in the field samples, the standard deviation of the calibration standard with the lowest concentration (10 ng) was used instead of the concentrations of field samples. The MDL and MLOQ values of VOCs were given in Tables 3.8 and 3.9. The values obtained by using the lowest calibration standard values (n:6) are indicated by the symbol (*) in Tables 3.8 and 3.9.

**Table 3.8.** The MDL and MLOQ values (μg $m^{-3}$) of 16 field blanks for active sampling.

| VOC | MDL | MLOQ | VOC | MDL | MLOQ |
|---|---|---|---|---|---|
| **Isoprene** | 0.0002 | 0.0005 | **3-Carene*** | 0.0003 | 0.0010 |
| **Acrylonitrile** | 0.0002 | 0.0007 | **1,3,5-Trimethylbenzene** | 0.0005 | 0.0016 |
| **n-Hexane** | 0.0022 | 0.0074 | **Benzaldehyde** | 0.0021 | 0.0071 |
| **2-Methylfuran** | 0.0001 | 0.0003 | **1,4-Cineole*** | 0.0013 | 0.0044 |
| **Chloroform** | 0.0005 | 0.0015 | **Limonene*** | 0.0004 | 0.0013 |
| **1,1,1-Trichloroethane*** | 0.0017 | 0.0056 | **m-Cymene** | 0.0002 | 0.0006 |
| **Tetrachloromethane*** | 0.0003 | 0.0009 | **p-Cymene** | 0.0000 | 0.0001 |
| **Benzene** | 0.0035 | 0.012 | **Ocimene*** | 0.0006 | 0.002 |
| **1,2-Dichloroethane*** | 0.0036 | 0.012 | **Eucalyptol*** | 0.0002 | 0.0007 |
| **n-Heptane** | 0.0003 | 0.0012 | **1,2,3-Trimethylbenzene** | 0.0001 | 0.0004 |
| **Crotonaldehyde** | 0.0001 | 0.0004 | **4-Methylanisole*** | 0.0007 | 0.0024 |
| **n-Octane** | 0.0001 | 0.0004 | **gamma-Terpinene*** | 0.00003 | 0.0001 |

| | | | | | |
|---|---|---|---|---|---|
| **Toluene** | 0.0017 | 0.0056 | **1,3-Diethylbenzene** | 0.00002 | 0.0001 |
| **Hexanal** | 0.0028 | 0.0092 | **1,4-Diethylbenzene** | 0.0002 | 0.0007 |
| **Chlorobenzene** | 0.0009 | 0.0031 | **Phenol** | 0.0005 | 0.0017 |
| **Ethylbenzene*** | 0.0003 | 0.0008 | **1,2-Dichlorobenzene*** | 0.0003 | 0.0009 |
| **m+p Xylene** | 0.0000 | 0.0001 | **Terpinolene*** | 0.0002 | 0.0007 |
| **o-Xylene** | 0.0001 | 0.0002 | **Dihydromyrcenol*** | 0.0005 | 0.0017 |
| **Styrene** | 0.0001 | 0.0002 | **1-Octanol*** | 0.0018 | 0.0060 |
| **1- Heptanal** | 0.0007 | 0.0024 | **Linalool** | 0.0004 | 0.0015 |
| **Alpha-pinene** | 0.0002 | 0.0007 | **Alloocimene*** | 0.0015 | 0.0051 |
| **Isopropylbenzene** | 0.0001 | 0.0003 | **Nonanal** | 0.0018 | 0.006 |
| **Camphene*** | 0.0009 | 0.0029 | **Acetophenone** | 0.0009 | 0.0031 |
| **n-Propylbenzene** | 0.00001 | 0.00003 | **alpha-Terpinen*** | 0.0003 | 0.0009 |
| **n-Nonane*** | 0.001 | 0.004 | **L-Fenchone*** | 0.00005 | 0.0002 |
| **n-Decane*** | 0.001 | 0.004 | **n-Dodecane** | 0.0001 | 0.0005 |
| **m-Ethyltoluene** | 0.00002 | 0.0001 | **(+)-Camphor*** | 0.0008 | 0.0025 |
| **p-Ethyltoluene** | 0.00001 | 0.00003 | **1-Terpinen-4-ol*** | 0.0006 | 0.0021 |
| **Sabinene*** | 0.0004 | 0.001 | **Decanal** | 0.0008 | 0.0026 |
| **beta-Myrcene*** | 0.0007 | 0.002 | **alpha-Terpineol*** | 0.0004 | 0.0013 |
| **1,2,4-Trimethylbenzene** | 0.0001 | 0.0002 | **Naphthalene** | 0.0002 | 0.0007 |
| **beta-Pinene*** | 0.0002 | 0.0005 | **n-Tridecane** | 0.0001 | 0.0003 |
| **o-Ethyltoluene** | 0.0001 | 0.0004 | **Benzothiazole** | 0.002 | 0.007 |
| **alpha-Phellandrene*** | 0.0006 | 0.0021 | **n-Tetradecane** | 0.0002 | 0.0006 |

**Table 3.9.** The MDL and MLOQ values (μg $m^{-3}$) of 8 field blanks for passive sampling.

| VOC | MDL | MLOQ | VOC | MDL | MLOQ |
|---|---|---|---|---|---|
| **Isoprene** | 0.003 | 0.01 | **3-Carene*** | 0.004 | 0.01 |
| **Acrylonitrile** | 0.001 | 0.005 | **1,3,5-Trimethylbenzene** | 0.003 | 0.008 |
| **n-Hexane** | 0.04 | 0.12 | **Benzaldehyde** | 0.06 | 0.19 |
| **2-Methylfuran** | 0.0003 | 0.001 | **1,4-Cineole*** | 0.06 | 0.19 |
| **Chloroform** | 0.003 | 0.01 | **Limonene** | 0.003 | 0.01 |
| **1,1,1-Trichloroethane** | 0.04 | 0.14 | **m-Cymene** | 0.004 | 0.01 |
| **Tetrachloromethane*** | 0.05 | 0.16 | **p-Cymene** | 0.002 | 0.006 |
| **Benzene** | 0.03 | 0.12 | **Ocimene*** | 0.02 | 0.07 |
| **1,2-Dichloroethane*** | 0.001 | 0.003 | **Eucalyptol*** | 0.02 | 0.07 |
| **n-Heptane** | 0.0004 | 0.001 | **1,2,3-Trimethylbenzene** | 0.002 | 0.008 |

| | | | | | |
|---|---|---|---|---|---|
| **Crotonaldehyde** | 0.002 | 0.01 | **4-Methylanisole*** | 0.04 | 0.13 |
| **n-Octane** | 0.008 | 0.03 | **gamma-Terpinene*** | 0.007 | 0.02 |
| **Toluene** | 0.02 | 0.05 | **1,3-Diethylbenzene** | 0.002 | 0.01 |
| **Hexanal** | 0.01 | 0.03 | **1,4-Diethylbenzene** | 0.001 | 0.004 |
| **Chlorobenzene** | 0.0003 | 0.001 | **Phenol** | 0.005 | 0.02 |
| **Ethylbenzene** | 0.0008 | 0.003 | **1,2-Dichlorobenzene*** | 0.03 | 0.11 |
| **m+p Xylene** | 0.002 | 0.007 | **Terpinolene*** | 0.05 | 0.15 |
| **o-Xylene** | 0.005 | 0.016 | **Dihydromyrcenol** | 0.0003 | 0.001 |
| **Styrene** | 0.0001 | 0.0005 | **1-Octanol** | 0.01 | 0.04 |
| **1- Heptanal*** | 0.002 | 0.01 | **Linalool*** | 0.06 | 0.20 |
| **Alpha-pinene** | 0.001 | 0.003 | **Alloocimene*** | 0.07 | 0.25 |
| **Isopropylbenzene** | 0.000 | 0.001 | **Nonanal*** | 0.03 | 0.08 |
| **Camphene*** | 0.02 | 0.05 | **Acetophenone** | 0.003 | 0.01 |
| **n-Propylbenzene** | 0.001 | 0.004 | **alpha-Terpinen** | 0.04 | 0.15 |
| **n-Nonane*** | 0.001 | 0.004 | **L-Fenchone** | 0.001 | 0.004 |
| **n-Decane*** | 0.005 | 0.018 | **n-Dodecane** | 0.002 | 0.006 |
| **m-Ethyltoluene** | 0.0004 | 0.001 | **(+)-Camphor** | 0.01 | 0.04 |
| **p-Ethyltoluene** | 0.0005 | 0.002 | **1-Terpinen-4-ol*** | 0.01 | 0.04 |
| **Sabinene*** | 0.001 | 0.002 | **Decanal** | 0.02 | 0.06 |
| **beta-Myrcene*** | 0.04 | 0.12 | **alpha-Terpineol** | 0.06 | 0.19 |
| **1,2,4-Trimethylbenzene** | 0.0009 | 0.003 | **Naphthalene** | 0.004 | 0.01 |
| **beta-Pinene*** | 0.003 | 0.01 | **n-Tridecane** | 0.01 | 0.03 |
| **o-Ethyltoluene** | 0.0004 | 0.001 | **Benzothiazole** | 0.02 | 0.06 |
| **alpha-Phellandrene*** | 0.04 | 0.13 | **n-Tetradecane** | 0.008 | 0.03 |

### 3.8.2 Repeatability

Repeatability is an indication of the deviation between the plurality of sampler results placed at the same sampling point, and hence the consistency of the sampler results with each other. In the present study, three parallel VOC samplers were placed at 6 sampling points to examine the repeatability of the samplers. The repeatability value of passive samplers was calculated as a percentage relative standard deviation (RSD %). Percent relative standard deviation values (RSD %) of repeated samples are given in Table 3.10.

In the European Standards [88, 89], which is prepared to determine the procedures for testing the performance of passive samplers, the RSD value for passive sampler repeatability is expected to be <15%. From the VOCs given in

Table 3.10, an RSD % value of >15% was found for only seven compounds (n-hexane, 2-methylfuran, 3-carene, 1,3-diethylbenzene, nonanal, alpha-terpinene and n-tridecane). RSD % values were calculated between 20-25% for the three compounds (n-hexane, 1,3-diethylbenzene and alpha-terpinene), and <20% for the rest of them. Because the number of RSD % values >15% was not too high, there was no problem in terms of repeatability. In addition, other studies in the literature had similarly reported high RSD % values for some of the compounds. It was found that the RSD % values of alpha-pinene and decane were 67 and 34.8, respectively [90]. In addition, RSD % values for ethylbenzene, m + p xylene and o-xylene compounds were indicated as 22.8, 23.5 and 36.2, respectively [91].

**Table 3.10.** Relative standard deviation values (RSD %) for VOCs (n=6).

| VOC | RSD % | VOC | RSD % |
|---|---|---|---|
| **Isoprene** | 8.3 ± 6.0 | **3-Carene** | 16 ± 13 |
| **Acrylonitrile** | 11 ± 7.6 | **1,3,5-Trimethylbenzene** | 6.2 ± 4.6 |
| **n-Hexane** | 25 ± 14 | **Benzaldehyde** | 15 ± 12 |
| **2-Methylfuran** | 17 ± 12 | **1,4-Cineole** | BDL |
| **Chloroform** | 13 ± 6.8 | **Limonene** | 6.0 ± 6.0 |
| **1,1,1-Trichloroethane** | 13 ± 0.6 | **m-Cymene** | 6.7 ± 3.5 |
| **Tetrachloromethane** | 5.2 ± 2.8 | **p-Cymene** | 5.3 ± 5.0 |
| **Benzene** | 6.7 ± 6.0 | **Ocimene** | BDL |
| **1,2-Dichloroethane** | 9.8 ± 6.2 | **Eucalyptol** | BDL |
| **n-Heptane** | 3.6 ± 1.4 | **1,2,3-Trimethylbenzene** | 11 ± 10 |
| **Crotonaldehyde** | 11 ± 7.0 | **4-Methylanisole** | 15 ± 13 |
| **n-Octane** | 5.9 ± 2.7 | **gamma-Terpinene** | BDL |
| **Toluene** | 5.2 ± 3.4 | **1,3-Diethylbenzene** | 20 ± 12 |
| **Hexanal** | 15 ± 12 | **1,4-Diethylbenzene** | 13 ± 9.9 |
| **Chlorobenzene** | 13 ± 7.0 | **Phenol** | 15 ± 14 |
| **Ethylbenzene** | 7.4 ± 4.8 | **1,2-Dichlorobenzene** | BDL |
| **m+p Xylene** | 5.2 ± 3.4 | **Terpinolene** | BDL |
| **o-Xylene** | 5.4 ± 4.4 | **Dihydromyrcenol** | BDL |
| **Styrene** | 15 ± 6.2 | **1-Octanol** | BDL |
| **1- Heptanal** | BDL | **Linalool** | BDL |
| **Alpha-pinene** | 11 ± 12 | **Alloocimene** | BDL |

| | | | |
|---|---|---|---|
| **Isopropylbenzene** | 6.2 ± 8.3 | **Nonanal** | 19 ± 16 |
| **Camphene** | 9.3 ± 3.9 | **Acetophenone** | 13 ± 4.0 |
| **n-Propylbenzene** | 5.8 ± 4.6 | **alpha-Terpinen** | 20 ± 0.42 |
| **n-Nonane** | BDL | **L-Fenchone** | 14 ± 7.1 |
| **n-Decane** | BDL | **n-Dodecane** | 13 ± 8.3 |
| **m-Ethyltoluene** | 6.1 ± 4.2 | **(+)-Camphor** | 9.0 ± 6.0 |
| **p-Ethyltoluene** | 10 ± 11 | **1-Terpinen-4-ol** | BDL |
| **Sabinene** | BDL | **Decanal** | BDL |
| **beta-Myrcene** | BDL | **alpha-Terpineol** | BDL |
| **1,2,4-Trimethylbenzene** | 14 ± 7.1 | **Naphthalene** | 8.2 ± 5.8 |
| **beta-Pinene** | 13 ± 8.5 | **n-Tridecane** | 18 ± 11 |
| **o-Ethyltoluene** | 12 ± 9.3 | **Benzothiazole** | 9.7 ± 7.3 |
| **alpha-Phellandrene** | BDL | **n-Tetradecane** | 11 ± 6.7 |

BDL: Below detection limit

## 3.9 Source Apportionment

To determine the pollution sources, some receptor models including chemical mass balance (CMB), [4, 92, 93], principal component analysis/absolute principal component scores (PCA/APCS) [94-96] and positive matrix factorization (PMF) [40, 97-99] have been applied. In the present study, the source apportionment of VOCs in the ambient air was examined using the PMF receptor model.

### 3.9.1 Positive Matrix Factorization (PMF)

PMF is a multivariate tool used to determine the number of effective sources, the names of sources, and the contribution of compounds to sources. Factor contributions and profiles are obtained by the PMF model that minimizes the target function $Q$ (equation 3.4).

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left[ \frac{x_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj}}{u_{ij}} \right]^2 \quad (3.4)$$

where $X$ is the data matrix of $i$ number of samples and $j$ constituents of species, $g$ is the amount of mass measured at each source, $f$ is the profiles of the

species from each source, $p$ is the number of sources and $u_{ij}$ is the uncertainties [100].

EPA Positive Matrix Factorization (PMF) 5.0 was used to identify the source profile of VOCs. The data file contained the results of concentration and uncertainty. A row of data file consists of concentrations of all compounds in a sample and a column of it consists of the concentration of one compound for each sample.

PMF requires all values and uncertainties to be positive values. Compounds with a detected percentage below 70% in the samples were removed from the data file. If there was a missing value (below %30), it was filled with an MDL/2 value. When the concentration was greater than the MDL, the uncertainty was calculated based on equation 3.5 [100]. However, if the concentration was lower than the MDL, the uncertainty was calculated with ((5/6) * MDL).

$$u = \sqrt{\left((0.1)\ x\ concentration\right)^2 + (0.5\ x\ MDL)^2)} \tag{3.5}$$

Some quality control procedures should have been also applied to the data file which was uploaded to the program. To do this, each compound was categorized based on the signal to noise (S/N) ratios. When the S/N ratio of a compound was less than 0.5, it was categorized as bad. Additionally, compounds having an S/N ratio between 0.5 and 1 were classified as weak. The S/N ratios greater than 1 were accepted as strong. Thus, the compounds classified as bad were excluded, and the contribution of weak ones was reduced by the program.

The concentration-time series served as indicators of the extreme values (very high or very low). These outliers can lead to errors in identifying and interpreting sources of pollution. For this reason, the dates involving extreme values were extracted using the program (Figure 3.12).

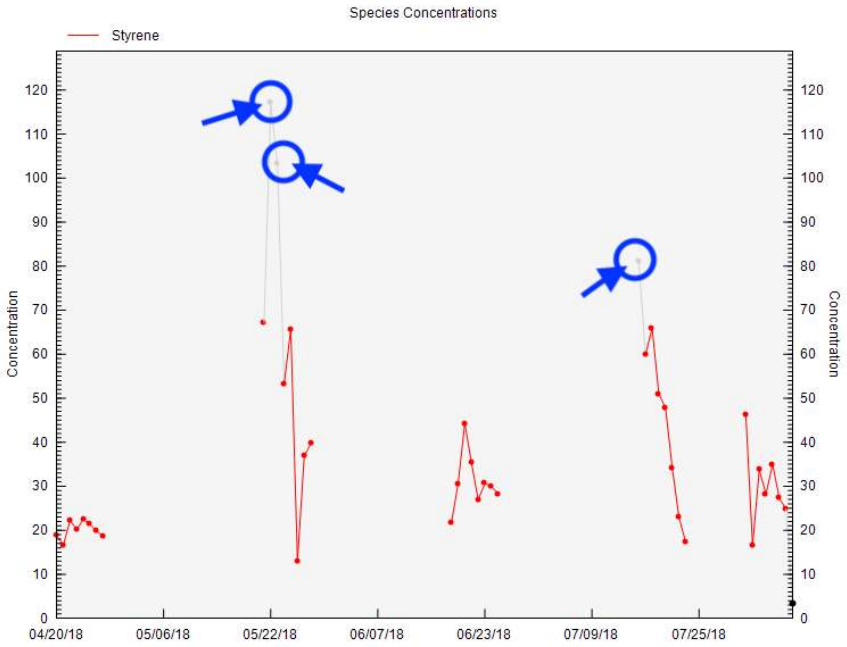


**Figure 3.12.** The concentration-time series of styrene.

The program was run by entering the number of runs and the factor number into the program. The recommended number of studies is 20. Determining the number of factors is one of the most important points of PMF analysis. While too low a few factors may cause the sources to be misidentified, entering this number too high may cause the distribution of the components that make up a real resource [101].

There are two types of Q calculated by the program, $Q_{true}$ and $Q_{robust}$. $Q_{robust}$ must be about 10% lower than the $Q_{true}$. In addition, the ratio between $Q_{robust}$ and $Q_{theoretical}$ must be lower than 1.5. $Q_{theoretical}$ was calculated by the equation (3.6) [101].

$$Q_{theoric} = (n \times m) - p\ x\ (n + m) \tag{3.6}$$

where $n$ is the number of samples $m$ is the number of species (strong and weak) and $p$ is the number of factors. To be $Q_{robust}$ and $Q_{theoretical}$ ratio in the desired range and thus to achieve consistent results, some adjustments (increase the number of factors, decrease the number of species etc.) may be required in PMF data.

One example of the histogram is shown in Figure 3.13, presenting how well the model fits each compound. Residual distributions of each compound should be approximately symmetric within a range of +3 and -3 that indicates a well modeled data set. The data outside the range shown in the Figure 3.13 should not be included in PMF analysis. Therefore, some of the samples are discarded from the PMF data (this date is generally problematic for other species).

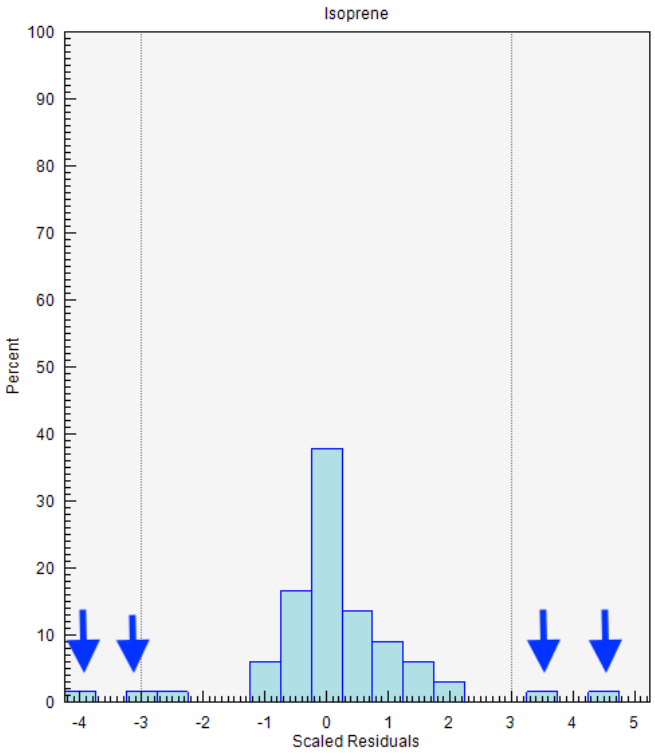


**Figure 3.13.** Residual distributions of isoprene.

Observed/predicted scatter plot also provided useful information to detect non-explained compounds. The low $r^2$ values (less than 0.5) indicate a poor correlation for a compound in the PMF analysis. So, compounds with low $r^2$ values should be excluded.

Finally, compounds occurring in more than two groups of factors should be evaluated with care.

### 3.9.2 Pollution Map: MapInfo

Pollution maps are used to predict the source regions of each pollutant over the study area. In this thesis, pollution maps were created for each VOC detected in both the summer and winter samplings through MapInfo 7.5 program. The coordinates of the sampling points and the corresponding pollutant concentrations were entered into the MapInfo which is Geographical Information Systems (GIS) software. To obtain spatial data in the form of contour, an interpolation technique "triangulation with smoothing" has been applied using the Vertical Mapper V3 of the MapInfo software.

### 3.9.3 Ozone Formation Potential (OFP)

The fact that VOCs have different reactivities and are likely to compete with their reaction partners causes the ozone formation potential of each compound to vary and differ from each other depending on atmospheric conditions [102]. Ozone formation potential (OFP) is used to determine the contribution of compounds to ground level ozone formation. The ozone formation potential (OFP) of individual VOC was examined based on the maximum incremental reactivity (MIR) method [103]. The MIR method was defined by equation (3.7).

$$OFP\ (i) = conc\ (i) \times MIR_{Coefficient}\ (i) \tag{3.7}$$

where *OFP(i)* represents the ozone formation potential of compound *i*, *conc(i)* is a concentration of compound *i* and $MIR_{Coefficient}(i)$ is a constant of compound *i* [103].

# 4. RESULTS AND DISCUSSION

## 4.1 Active Sampling

### 4.1.1 Statistical Evaluation of VOCs

At our station on the university campus, 68 VOCs for every month between April - November 2017 and April 2018 and 70 VOCs for every month between April - August 2018 were collected daily and 6-hour periods. However, 1,1,1-trichloroethane, nonane, decane, alpha-phellandrene, 1,4-cineole, dihydromrycenol, octanol and alloocimene were not detected in the samples. The lack of sources of these compounds rather than their atmospheric lifetimes should be the main reason for their absence. Thus, a total of 62 VOCs could be determined for the active sampling studies.

The statistical parameters produced with daily VOC data for each sampling period are shared in Appendix 1. According to April 2017 sampling data, the highest average concentration belonged to benzaldehyde (0.0454 μg $m^{-3}$), and this compound was followed by hexanal (0.0332 μg $m^{-3}$) and decanal (0.0313 μg $m^{-3}$), respectively. Among the compounds, the species with the lowest ambient concentrations during the April 2017 sampling were 1,2,4-trimehylbenzene (0.0004 μg $m^{-3}$), n-propylbenzene (0.0004 μg $m^{-3}$), p-ethyltoluene (0.0003 μg $m^{-3}$) and p-cymene (0.0002 μg $m^{-3}$). In the April 2017 sampling, most of the VOCs (1,2-dichloroethane, chlorobenzene, camphene, sabinene, beta-mrycene, 3-carene, 1,4-cineole, limonene, m-cymene, ocimene, 4-methylanisole, gamma-terpinene, 1,2-dichlorobenzene, terpinolene, linalool, alpha-terpinen, L-fenchone, camphor, terpinen-4-ol and alpha-terpineol) could not be detected. For the following active sampling studies, as mentioned in the 'Material and Methods' section, KI impregnated filters were used to ensure maximum retention of VOCs trapped in the tubes. As a result, there was a significant increase in the number of observed VOCs in the subsequent samples.

Except for April 2017, the sequence of the compounds was mostly the same in other months. Hexanal was drawn the attention as the compound with the highest average concentration (2.54 μg $m^{-3}$; 4.90 μg $m^{-3}$; 2.71 μg $m^{-3}$; 4.57 μg $m^{-3}$; 5.39 μg $m^{-3}$; 2.81 μg $m^{-3}$; 1.28 μg $m^{-3}$; 0.46 μg $m^{-3}$; 1.07 μg $m^{-3}$; 3.16 μg $m^{-3}$; 3.29 μg $m^{-3}$; 5.68 μg $m^{-3}$; 4.27 μg $m^{-3}$) in all months (May 2017, June 2017, July 2017, August

2017, September 2017, October 2017, November 2017, January, 2018, April 2018, May, 2018, June 2018, July 2018, August 2018). This compound was followed by nonanal, hexane and isoprene. Hexanal concentrations were significantly higher than the ambient concentrations of other compounds. The difference between hexanal and compound with the second highest concentration was about 1.5-15 fold whereas the difference between the remaining compounds was quite low. The higher levels of hexanal denote the stronger influence of plants; especially Oak which is commonly present around the campus. On the other hand, L-fenchone (0.0004 μg $m^{-3}$; 0.001 μg $m^{-3}$; 0.001 μg $m^{-3}$; 0.001 μg $m^{-3}$; 0.001 μg $m^{-3}$; 0.001 μg $m^{-3}$; 0.0005 μg $m^{-3}$; 0.0004 μg $m^{-3}$; 0.001 μg $m^{-3}$; 0.003 μg $m^{-3}$; 0.004 μg $m^{-3}$; 0.006 μg $m^{-3}$; 0.005 μg $m^{-3}$) and 1,3-diethylbenzene (0.0003 μg $m^{-3}$; 0.0004 μg $m^{-3}$; 0.0005 μg $m^{-3}$; 0.0004 μg $m^{-3}$; 0.0004 μg $m^{-3}$; 0.0002 μg $m^{-3}$; 0.0001 μg $m^{-3}$; 0.0002 μg $m^{-3}$; 0.0004 μg $m^{-3}$; 0.0009 μg $m^{-3}$; 0.0007 μg $m^{-3}$; 0.001 μg $m^{-3}$; 0.001 μg $m^{-3}$) were determined as the compounds with the lowest average concentrations in the region during all months.

Another parameter presented in Appendix 1 is the coefficient of variation (CV), which can be used to examine the distribution of compounds depending on the average value. Environmental studies generally show a log-normal distribution and as a result, high coefficients of variation (%) are obtained. High coefficients of variations of dodecane (166 for April 2017), decanal (157 for April 2017), 2-methylfuran (123 for April 2017; 88 for January 2017), tridecane (113 for April 2017), benzothiazole (92 for May 2017), octane (87 for June 2017), hexane (81 for July 2017; 93 for September 2017), chloroform (80 for August 2017; 86 for September 2017), isoprene (81 for November 2017; 85 for May 2018), alpha-pinene (105 for January 2017; 96 for July 2018), isopropylbenzene (99 for January 2017) gamma-terpinene (101 for April 2018) sabinene (135 for June 2018), beta-myrcene (86 for June 2018), beta-pinene (108 for July 2018; 120 for August 2018) and limonene (105 for August 2018) showed that these compounds were released from variable sources or as a result of batch processes. However, for the compounds with CV below 50%, it can be supposed that the distribution is close to normal.

However, it can be stated that VOCs detected during the active sampling period did not reach critical levels in the Bolu atmosphere. Considering that the limit value for benzene is 5 μg $m^{-3}$, the average concentration of benzene was found to be well below the limit value [17].

Figure 4.1 reveals that biogenic VOCs were more dominant than anthropogenic VOCs for most of the months. While the total BVOC percentages in January and April were around 50 %, they reached 80 % in months such as August and September when temperature, solar radiation and the amount of leafy tree species are greater (see Table 3.2). Leafy parts of trees are supposed to play an important role in the amount of VOC emitted into the atmosphere and thus atmospheric levels of biogenic VOCs are related to the number of leaves [104]. Therefore, a steady increase in VOC levels was observed since April, when deciduous trees began to renew their leaves.

Highly contributing biogenic and anthropogenic VOCs had a similar profile each year. Hexanal, decanal, nonanal, heptanal and alpha-pinene were among BVOCs with high concentrations in our sampling region. Common Oak around the campus had high source potential for these compounds. Moreover, benzaldehyde, toluene, benzene, hexane, heptane, octane, phenol, chloroform and chlorobenzene were found to have high contributions. The high levels of these compounds indicating that emission sources such as vehicle traffic and solvent evaporation were the potential sources in the sampling site [41, 97].

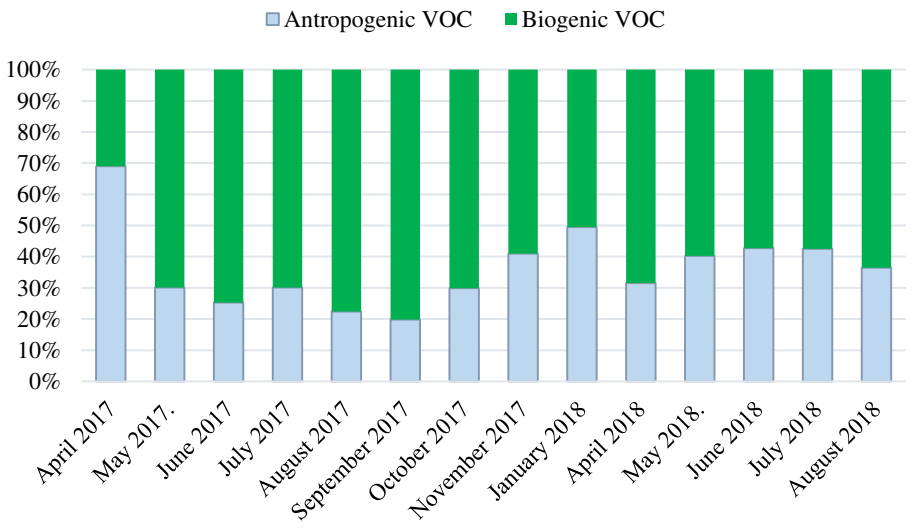


**Figure 4.1.** The percentage of the biogenic and anthropogenic compounds.

### 4.1.2 Temporal Variation

The intraday, inter-day and inter-annual variations of compounds were also examined. Figure 4.2 includes VOCs sampled in the same months (May-August) for two consecutive years. VOC concentrations obtained in 2017 were mostly lower than those in 2018. The proportional difference between the average concentrations of the years was found to be the highest for the compounds, 2-methylfuran (50 fold) and camphor (35 fold). The remarkable difference seen between years is related to meteorological conditions. There were higher values in temperature and solar radiation between May and August 2018 (see Table 3.2). These parameters are directly related to the emissions of both biogenic and solvent-originated compounds which were obtained in higher concentrations during 2018. On the contrary, dodecane, octane and chloroform were recorded at 1.4, 2- and 8-times higher concentrations, respectively, in 2017. For these compounds, it was concluded that the source strength was more dominant than the meteorological variations.

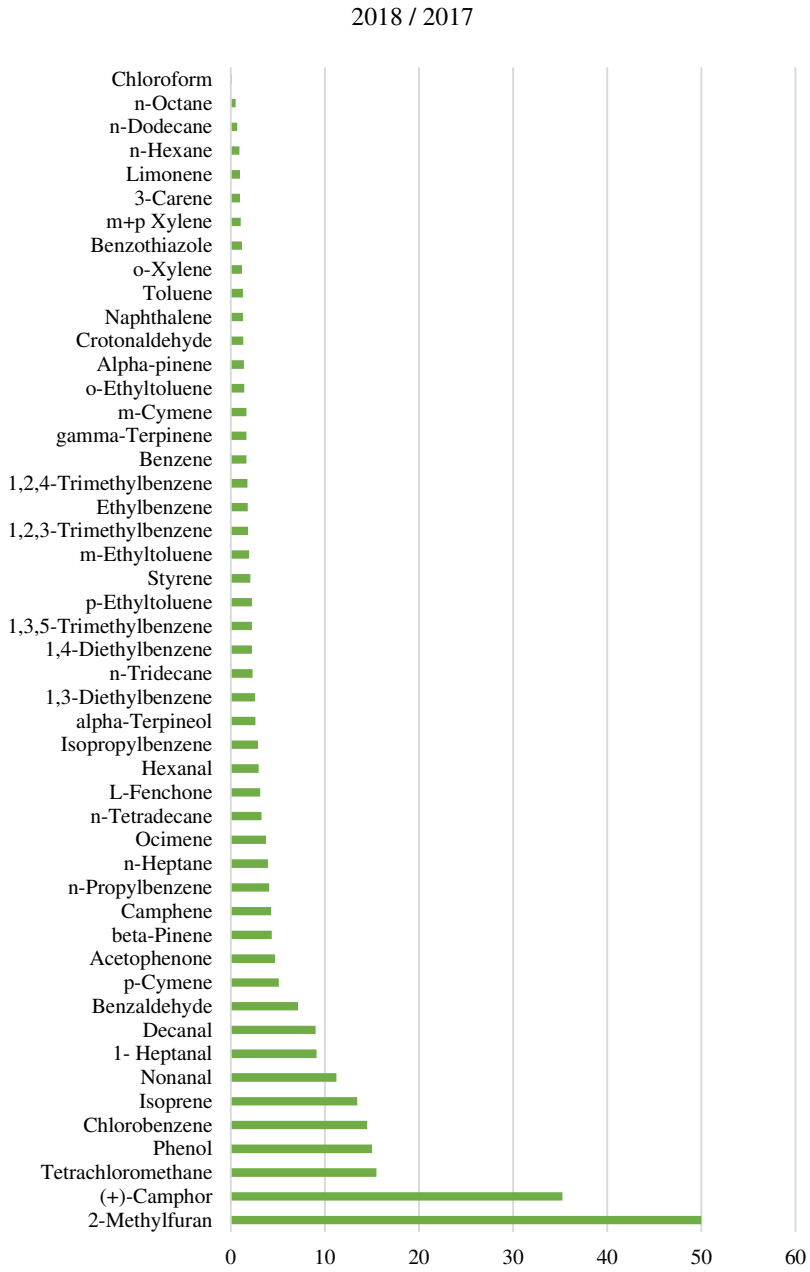


**Figure 4.2.** 2018 to 2017 ratio of detected VOCs.

The graphs were prepared for each VOC to examine intraday, interday and annual VOC changes, but the representative ones are given here and the rest are shared in Appendix 2. Among the dates presented in graphs, the dates 27 May, 28 May, 11 June, 22 July of 2017 and the dates of 16 June, 17 June, 11 August and 12 August 2018 were the weekend days. In addition, although the dates of May 27, May 28 and June 11 in 2017 were on the weekend, the AVOC concentrations might have been affected by the heavy traffic due to the national exams held in the university. Excluding the 2017 sampling period, when the ÖSYM (national) exams

held at the weekend were intense, it was found that weekday AVOC concentrations were generally higher than those on the weekend. On the other hand, a significant decrease was observed in some of VOCs such as toluene and ethylbenzene with the end of the 2017 academic term and the summer vacation. In 2018, no such effect was observed in the same periods.

Intraday distributions of compounds have significant differences between 2017 and 2018. In 2017, most of the compounds of both anthropogenic and biogenic origin were found higher in the daytime (11: 00-17: 00) zone. A daytime zone represents the time interval during which temperature and solar radiation reach their maximum. This situation creates favorable conditions for the emission of biogenic VOCs from plant surfaces, while it is also effective in the remarkable release of anthropogenic VOCs through evaporation. Daytime VOC concentrations were relatively lower in 2018. Even the lowest values of the day for some compounds were obtained between 11:00 and 17:00 hours, increased between 17:00 and 23:00 hours, and then decreased gradually. This trend is considered an indicator of photochemical reactions in the atmosphere.

Alpha-pinene, beta-pinene and camphene showed different trends in their intraday concentrations in each year (Figure 4.3). In 2017, the midday time interval was the zone with higher concentrations of these biogenic. However, it shifted to the morning (05:00 to 11:00) and the night (23:00 to 05:00) in 2018. The fact that monoterpenes can be spread even in the absence of light due to pool (stored) emissions at all time intervals.

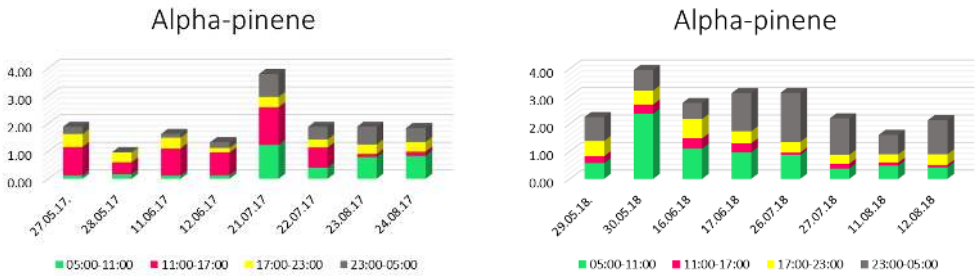


**Figure 4.3.** Intraday, interday and annual variations of alpha-pinene.

Although m-cymene, p-cymene, camphor and 3-carene reached their highest values at midday time intervals in 2017, they had their lowest concentrations in this time in 2018 (Figure 4.4). In addition to their similar annual

trends, day-dependent concentration variations of these two compounds were found to be strikingly similar. All these revealed that these compounds might be under the influence of the same sources.

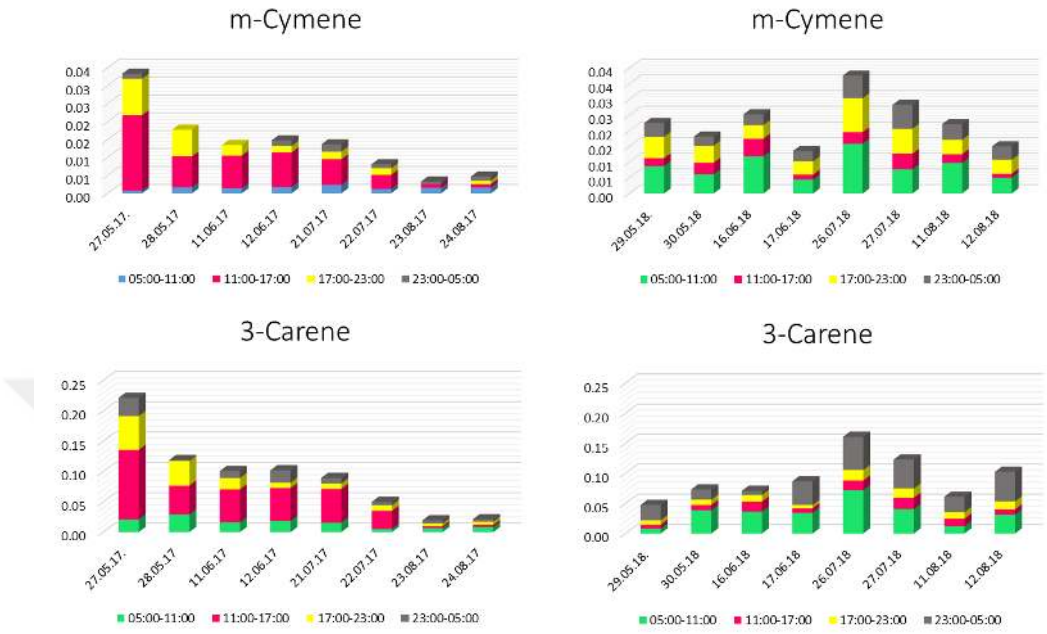


**Figure 4.4.** Intraday, interday and annual variations of m-cymene and 3-carene.

The time-dependent changes of methacrolein, methylvinylketone and 2-methylfuran compounds were found to be similar. Isoprene and its oxidation products (methacrolein, methylvinylketone) were investigated in Figure 4.5. Isoprene was found in higher atmospheric levels during the morning (05:00 to 11:00) and midday (11:00 and 17:00) time intervals which are ideal for isoprene formation due to the strong sunlight. Although, methachrolein and methylvinylketone were almost absent at midday, increased in the evening and gradually decreased from night to morning. The increasing atmospheric values of the compounds just after the midday indicated that they were formed because of photodegradation reactions of isoprene. Apart from this, additional sources (such as vehicular emissions) might have been effective in the atmospheric existence of these compounds.

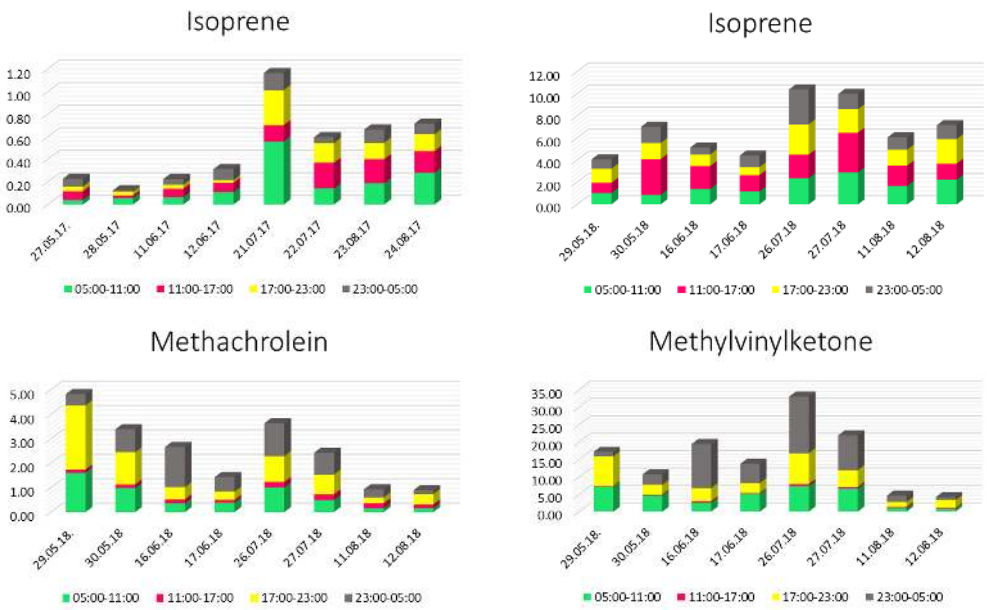


**Figure 4.5.** Intraday, interday and annual variations of isoprene and its oxidation products.

Benzene, toluene, ethylbenzene, xylenes, styrene, isopropylbenzene, n-propylbenzene, ethyltoluenes, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, 1,3-diethylbenzene, 1,4-diethylbenzene, dodecane, tridecane and tetradecane compounds showed similar trends over time. However, the most prominent similarity in the intra-day and between-day variations were detected between toluene, ethylbenzene and xylenes (TEX) compounds (Figure 4.6). There are two maxims on the 27$^{th}$ and 28$^{th}$ of May 2017. The heavy campus traffic between 11:00-17:00 hours when the exam (KPSS, national exam) performed in University campus caused higher concentrations of these traffic originated compounds. In 2018, the higher levels were obtained during rush hours (05:00-11:00) and (17:00-23:00) on weekdays (29 May, 30 May, 26 July and 27 July 2018).

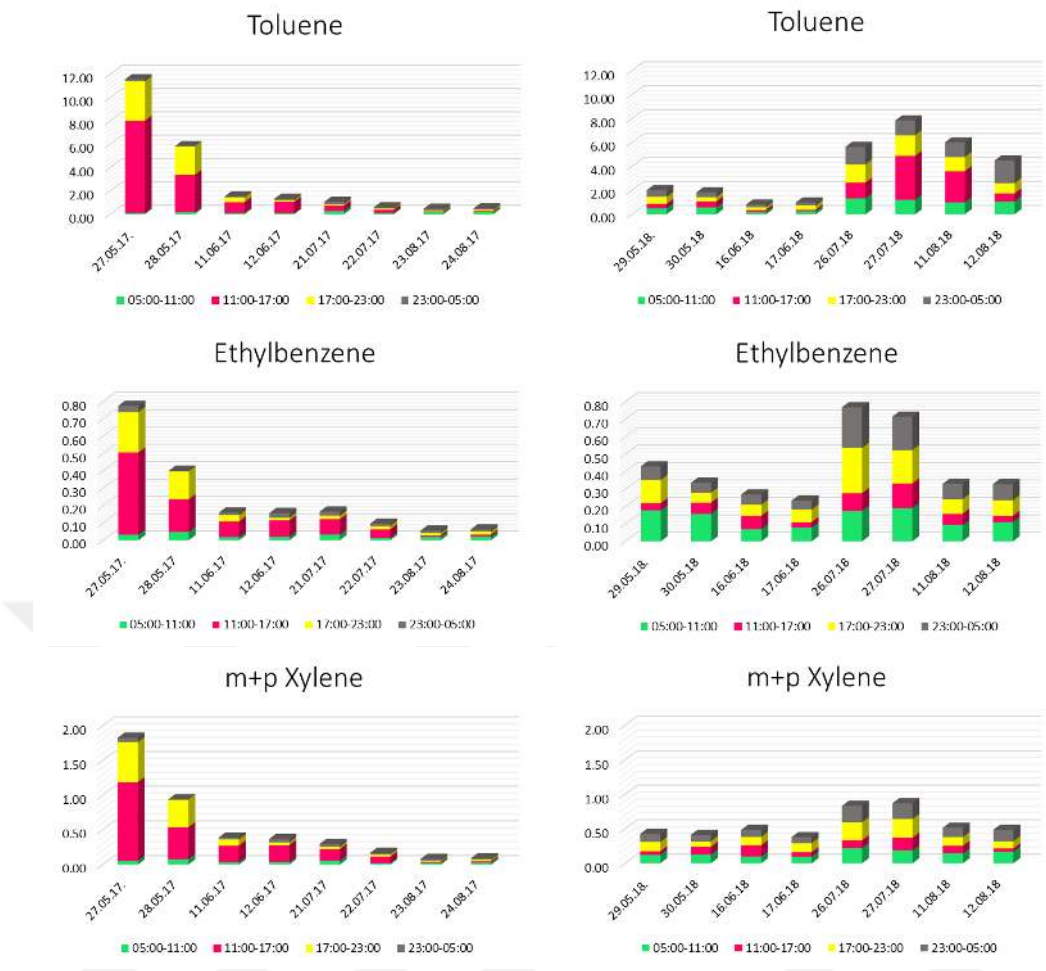


**Figure 4.6.** Intraday, interday and annual variations of toluene, ethylbenzene and m,p xylene.

Octane and heptane showed different trends from TEX compounds (Figure 4.7). They might be under the influence of different sources such as solvent evaporation [105]. Although midday concentrations were higher in May and June 2017, morning and evening concentrations became dominant compared with other time zones. Intraday and interday variations of these compounds were also similar to that of hexanal and crotonaldehyde. Hexanal and crotonaldehyde are compounds with mostly biogenic origin. Although these compounds showed similar temporal changes as octane and heptane, they were not necessarily to be emitted from the same sources. Temperature is an important parameter for the spread of compounds from the sources such as solvent evaporation and biogenic emissions.

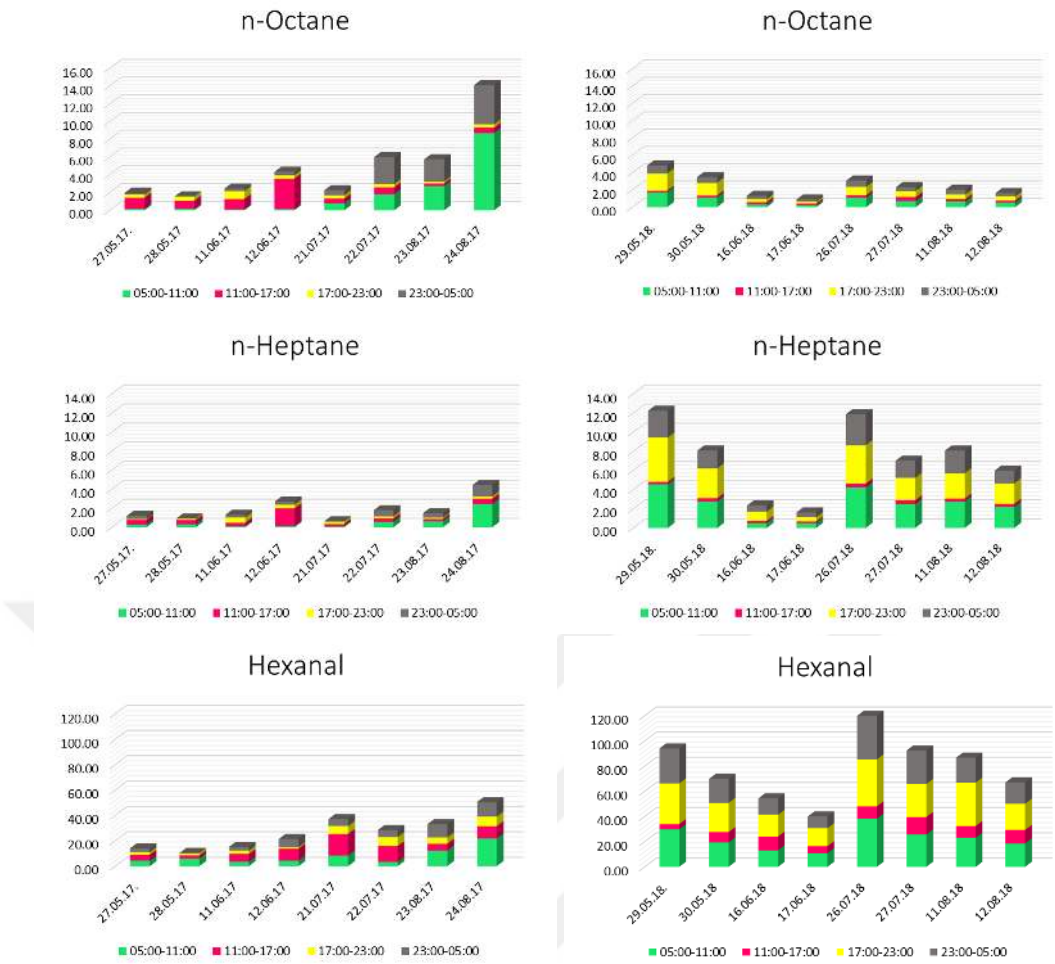


**Figure 4.7.** Intraday, interday and annual variations of octane and heptane.

### 4.1.3 Ozone Formation Potential (OFP)

The OFP results of active sampling campaigns were carried out in three periods April-August 2017, September-November 2017-January 2018 and April-August 2018, at the station located in BAİBÜ Gölköy campus are given in Table 4.1. The highest OFP values were obtained in April-August 2018 period (0.008 µg $m^{-3}$ -7.48 µg $m^{-3}$). Isoprene was the compound with the highest ozone formation potential in September-November 2017-January 2018 (0.73 ± 0.51 µg $m^{-3}$) and April-August 2018 (7.48 ± 8.80 µg $m^{-3}$). Differently, hexane was the compound with the highest OFP values (0.45 ± 0.40 µg $m^{-3}$) in April-August 2017. On the other hand, isopropylbenzene, n-propylbenzene and tridecane had the lowest OFPs.

**Table 4.1.** OFP values (μg $m^{-3}$) of VOCs determined in April-August 2017 (N = 40), September-November 2017 -January 2018 (N = 32) and April-August 2018 (N =40).

| | **April - August 2017 (mean ± sd)** | **September - November 2017 and January 2018 (mean ± sd)** | **April - August 2018 (mean ± sd)** |
|---|---|---|---|
| **Isoprene** | 0.34 ± 0.25 | 0.73 ± 0.51 | 7.48 ± 8.80 |
| **n-Hexane** | 0.45 ± 0.40 | 0.40 ± 0.30 | 0.53 ± 0.36 |
| **Benzene** | 0.03 ± 0.02 | 0.04 ± 0.02 | 0.03 ± 0.01 |
| **n-Heptane** | 0.07 ± 0.07 | 0.05 ± 0.03 | 0.18 ± 0.14 |
| **n-Octane** | 0.04 ± 0.05 | 0.03 ± 0.02 | 0.10 ± 0.06 |
| **Toluene** | 0.19 ± 0.10 | 0.24 ± 0.09 | 1.04 ± 0.55 |
| **Ethylbenzene** | 0.05 ± 0.04 | 0.03 ± 0.01 | 0.14 ± 0.08 |
| **m+p Xylene** | 0.23 ± 0.18 | 0.11 ± 0.06 | 0.57 ± 0.31 |
| **o-Xylene** | 0.18 ± 0.13 | 0.08 ± 0.04 | 0.42 ± 0.23 |
| **Styrene** | 0.06 ± 0.04 | 0.05 ± 0.04 | 0.08 ± 0.05 |
| **alpha-Pinene** | 0.40 ± 0.28 | 0.40 ± 0.32 | 0.69 ± 0.63 |
| **Isopropylbenzene** | 0.006 ± 0.003 | 0.005 ± 0.004 | 0.008 ± 0.005 |
| **n-Propylbenzene** | 0.006 ± 0.004 | 0.005 ± 0.004 | 0.02 ± 0.01 |
| **1,2,4-Trimethylbenzene** | 0.02 ± 0.02 | 0.02 ± 0.01 | 0.07 ± 0.04 |
| **beta-Pinene** | 0.06 ± 0.04 | 0.05 ± 0.03 | 0.24 ± 0.22 |
| **1,3,5-Trimethylbenzene** | 0.13 ± 0.08 | 0.09 ± 0.06 | 0.35 ± 0.20 |
| **1,2,3-Trimethylbenzene** | 0.03 ± 0.02 | 0.02 ± 0.01 | 0.10 ± 0.05 |
| **Phenol** | 0.03 ± 0.02 | 0.02 ± 0.02 | 0.81 ± 0.50 |
| **n-Dodecane** | 0.01 ± 0.009 | 0.007 ± 0.005 | 0.03 ± 0.02 |
| **Naphthalene** | 0.01 ± 0.009 | 0.01 ± 0.008 | 0.07 ± 0.03 |
| **n-Tridecane** | 0.01 ± 0.008 | 0.005 ± 0.005 | 0.05 ± 0.02 |
| **n-Tetradecane** | 0.01 ± 0.007 | 0.009 ± 0.008 | 0.06 ± 0.04 |

The major contributors to ozone formation in the sampling site are given in Figure 4.8. Although the OFP values of VOCs changed among the periods, the top ten compounds were almost the same. The top ten contributors in OFP were isoprene, hexane, alpha-pinene, m,p-xylene, toluene, o-xylene, 1,3,5-trimethylbenzene, heptane, beta-pinene and styrene (phenol for April-August 2018).

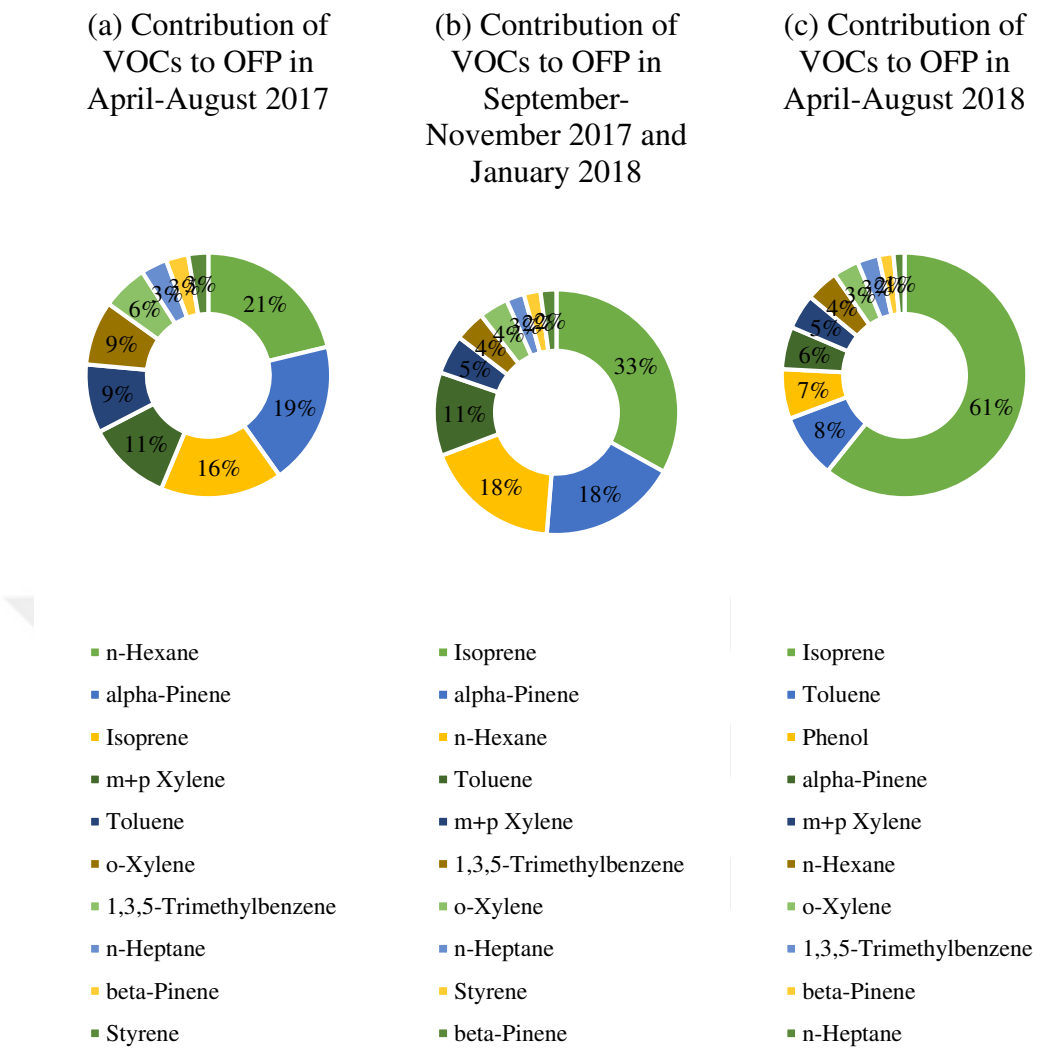


**Figure 4.8.** Top ten OFP species and their contributions to total for (a) April-August 2017 (b) September-November 2017 and January 2018 (c) April-August 2018.

The relationship between atmospheric concentrations of ozone and the total ozone formation potential of VOCs, as well as the corresponding meteorological conditions, is examined in Figure 4.9. Because there is no meteorological data for September, it was not included in Figure 4.9. Under higher temperature, solar radiation and OFP, higher ozone levels were found between April and August 2018 period. It is also remarkable that ozone levels were significantly lower in October-November 2017-January 2018 period when the temperature and solar radiation were lower. Increasing temperature and solar radiation created favorable conditions for VOCs to be released from their sources and to undergo ozone formation reactions in the atmosphere. However, the atmospheric concentration of ozone in

the April-August 2017 period was determined to be almost the same as the April-August 2018 period, which had the highest total OFP value. Although the total OFP value was lower during April-August 2017, ozone concentrations were not the lower as expected, associated with wind speed and long-distance transport. In the period of April-August 2017, the transfer of the ozone-containing air mass to the region was considered to be an effective factor, as the wind speed was relatively higher. The lower ratio of ethylbenzene to xylene also supported the aged airflow reaching the sampling site. This will be explained in the following section in detail.

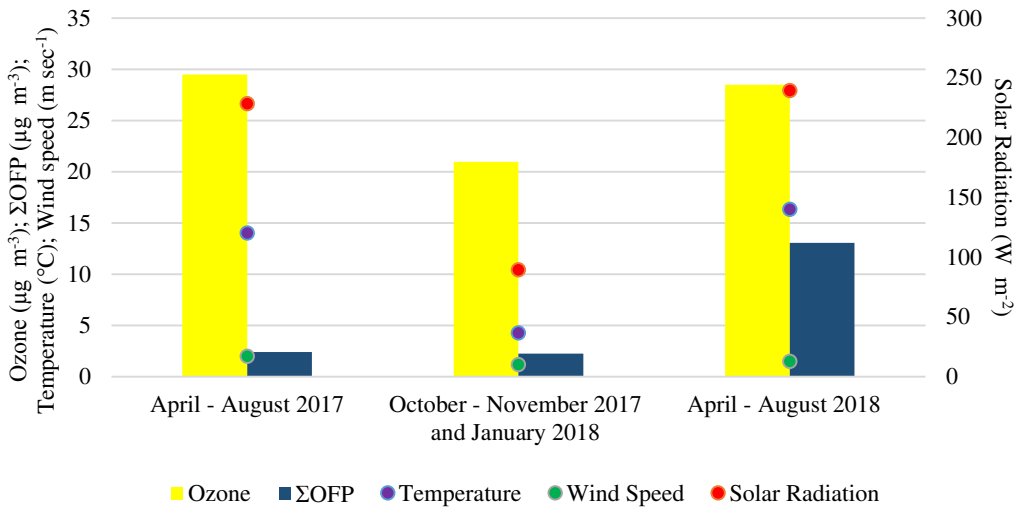


**Figure 4.9.** The relation of atmospheric ozone concentrations with OFP and meteorological parameters.

### 4.1.4 Source Apportionment

#### 4.1.4.1 VOC Ratios

Vehicular emissions are mostly responsible for the release of benzene and toluene into the atmosphere. However, vehicle traffic is not the only source for toluene, it can also be emitted from non-traffic sources. Based on this, the toluene-to- benzene (T/B) ratio is used to get information about whether traffic sources or non-traffic sources are more efficient. If the T/B ratio is in the range between 1.5 and 3, it indicates a strong contribution of traffic sources [106]. Higher T/ B ratio indicates that non-traffic sources are more efficient [107].

The average T/B ratio of the whole active sampling period was found as 2.88 ±3.51. This value is very close to the upper limit value representing traffic

emissions. When we examine the T/B ratios by separating the data according to years, a significant variation in the source profile was determined. In the period including April-August 2017, T/B ratios varied between 0.41 and 4.18 with an average value of 1.05 ±0.65. This indicated that VOCs were mostly emitted by vehicle emissions. In the September-November 2017 and January 2018 period, T/B ratios averaged 0.93 ±0.27, representing vehicle emissions. However, a much higher average T/B ratio (6.28 ±4.03) was determined in April and August 2018. It changed between 0.84 and 16. The fact that this value is above 3 indicates that there was a non-traffic source for toluene. Besides toluene, which acts as an indicator for non-traffic sources, there should be also other VOCs emitted from these non-traffic sources.

Another VOC ratio, xylene-to-ethylbenzene (X/E), is used as an indicator to determine the aged air mass. Degradation rates of m,p xylene and ethylbenzene, whose rate of emissions are assumed to be constant, differ significantly [107]. Therefore, the more reactive m,p xylene (lifetime for m,p xylene is 11.8 hours) is depleted faster than ethylbenzene (lifetime for ethylbenzene is 1.6 days) as the air mass moves, resulting in a decrease in the xylene-to-ethylbenzene (X/E) ratio. This ratio in the source samples is 3.5 ± 0.5 [108]. Air masses with a low X/E ratio are characterized as being aged. The average X/E ratios were found as 1.66 ±0.21 for April-August 2017, 1.45 ±0.12 for September-November 2017 and January 2018, 1.49 ±0.15 for April and August 2018 and 1.54 ±0.19 for the whole active sampling period. There was an aged air flow transferred from distant sources to the sampling station, especially in 2018.

#### 4.1.4.2 Positive Matrix Factorization (PMF): April-August 2017 and January 2018 Active Sampling Period

PMF analysis was firstly applied on the VOC data including the concentrations of April-August 2017 and January 2018 of active sampling. $Q_{robust}$ and $Q_{true}$ values were found to be 1020 and 1029. As a result, VOC sources were explained with six factors (Figure 4.10).

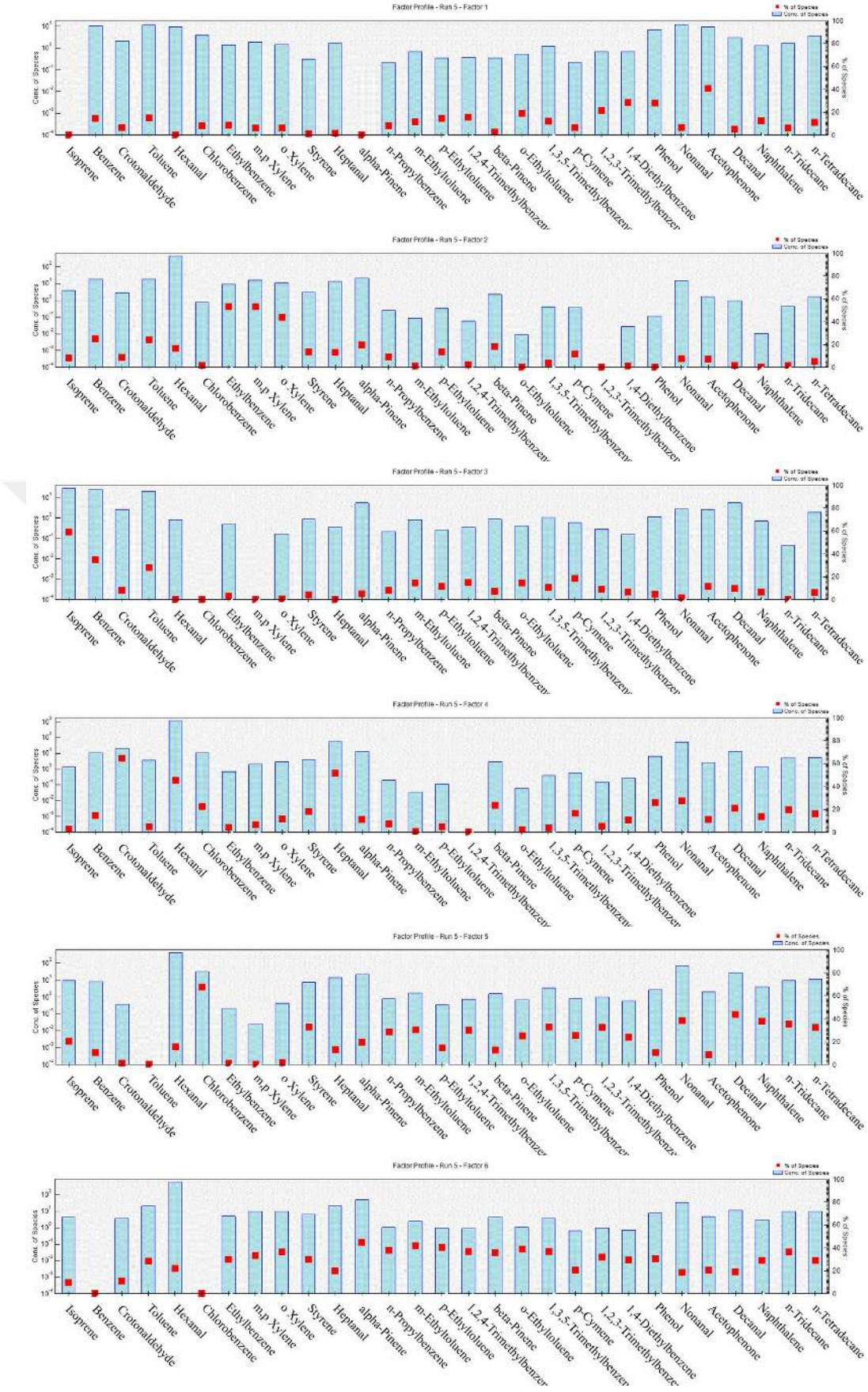


**Figure 4.10.** Factor profiles.

The chemical profiles of the compounds and the literature information are used to identify each factor. Potential sources of VOCs were determined as solvent evaporation, gasoline-powered vehicle emissions, fossil fuel (domestic heating), biogenic emissions (hornbeam/grass/oak/beech), diesel/domestic activities and forested city atmosphere (Table 4.2). The contribution of sources to the total was 2.5%, 16%, 2.9%, 38.6%, 17.6% and 22.4%, respectively (Figure 4.11).

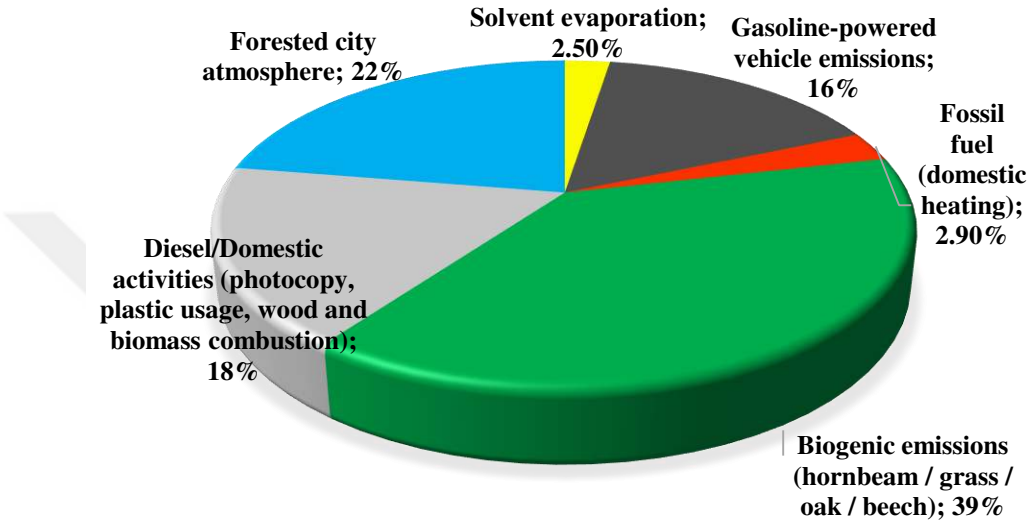


**Figure 4.11.** Source contributions to the VOC concentrations.

**Table 4.2.** PMF results of VOCs determined in April-August 2017 and January 2018 active sampling study ($N_{Total}$ = 44; the compounds explained at least 20% in the factor were given).

| Factors | VOCs | Source |
|---|---|---|
| **Factor 1** | acetophenone, 1,4-diethylbenzene, phenol, 1,2,3-triethylbenzene | Solvent evaporation |
| **Factor 2** | ethylbenzene, xylenes, benzene, toluene | Gasoline-powered vehicle emissions |
| **Factor 3** | isoprene, benzene, toluene | Fossil fuel (domestic heating) |
| **Factor 4** | crotonaldehyde, heptanal, hexanal, nonanal, phenol, beta-pinene, chlorobenzene, decanal | Biogenic emissions (hornbeam/grass / oak beech) |

| | | |
|---|---|---|
| **Factor 5** | chlorobenzene, decanal, nonanal, napthalene, tridecane, styrene, 1,3,5-trimethylbenzene, tetradecane, 1,2,3-trimethylbenzene, m-ethyltoluene, 1,2,4-trimethylbenzene, n-propylbenzene, p-cymene, o-ethyltoluene, 1,4-diethylbenzene, isoprene | Diesel/Domestic activities (photocopy, plastic usage, wood and biomass combustion) |
| **Factor 6** | alpha-pinene, ethyltoluene, n-propylbenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, tridecane, xylene, beta-pinene, 1,2,3-trimethylbenzene, phenol, ethylbenzene, styrene, 1,4-diethylbenzene, tetradecane, napthalene, toluene, hexanal, p-cymene, acetophenone, heptanal | Forested city atmosphere |

In the first factor, highly explained VOCs were acetophenone, 1,4-diethylbenzene, phenol and 1,2,3-triethylbenzene. Based on the daily G-score variations (Figure 4.12), the highest G-score was obtained on August 20, 2017. Solvents used in the campus laboratories and even perfumes and other chemicals spread to the atmosphere were effective pollution sources [109].

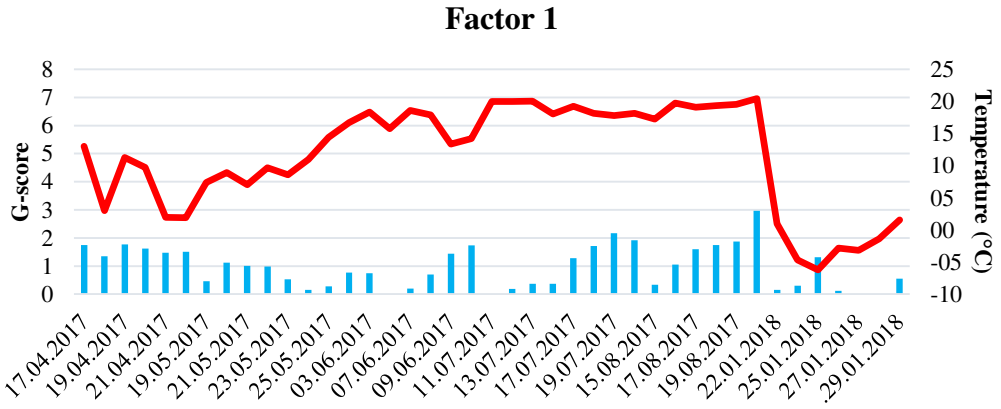


**Figure 4.12.** PMF results of factor 1 (G-score daily and temperature dependent changes).

Gasoline exhaust trace compounds ethylbenzene, m+p-xylene, o-xylene, benzene and toluene compounds constituted the second factor [63, 110]. The highest G-score value of the factor was determined on May 19, 2017 (Figure 4.13). This was also supported by the fact that the values in the spring semester were higher than the summer period and the interim holiday period. In the sampling period, the T/B ratio was found as 1.01 ±0.61. This showed the significant influence

of traffic emissions. Moreover, X/E ratios (1.61 ±0.24) which were below 3.5 revealed that in addition to the campus traffic, D-100 and TEM highways affected the sampling point. Traffic emissions were identified as the second factor.

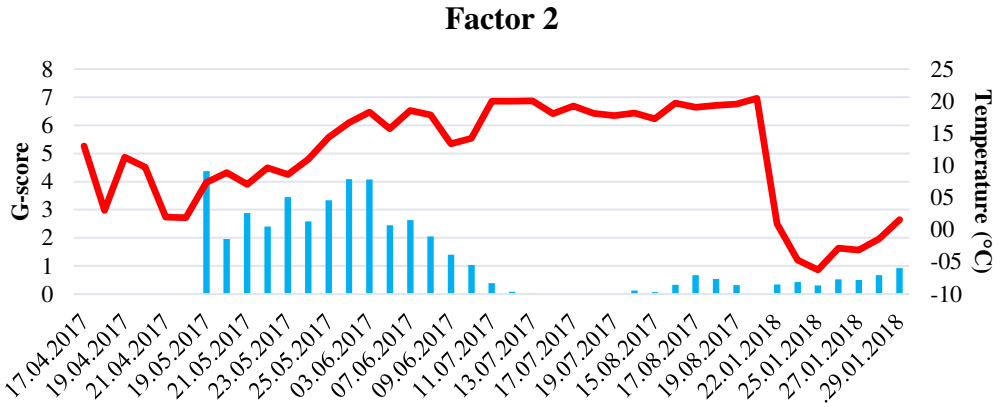


**Figure 4.13.** PMF results of factor 2 (G-score daily and temperature dependent changes).

Factor 3 was identified as a fossil fuel (domestic heating) factor. It was stated that benzene and toluene which had high percentages in the factor are caused by coal combustion [37]. The contribution of domestic heating factor increased in January while temperature decreased (Figure 4.14). The highest G-score was found on 29$^{th}$ January 2018.

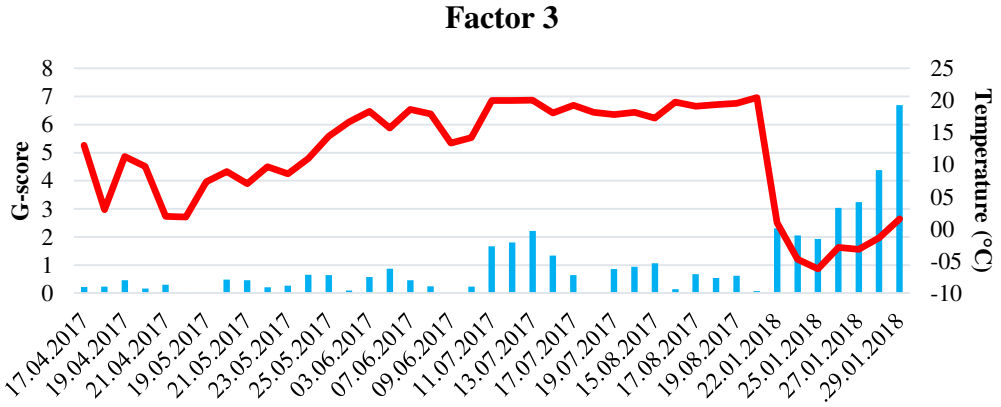


**Figure 4.14.** PMF results of factor 3 (G-score daily and temperature dependent changes).

Factor 4 explained the high proportion of compounds such as crotonaldehyde, heptanal, hexanal, nonanal and beta-pinene. This represented

biogenic emissions. The highest G-scores were detected on the 8th of June 2017 (Figure 4.15). The change in temperature levels had an effective role in the release of these biogenic. Tree species such as Hornbeam and Oak which are dominant around the sampling station, are good emitters of aldehydes.

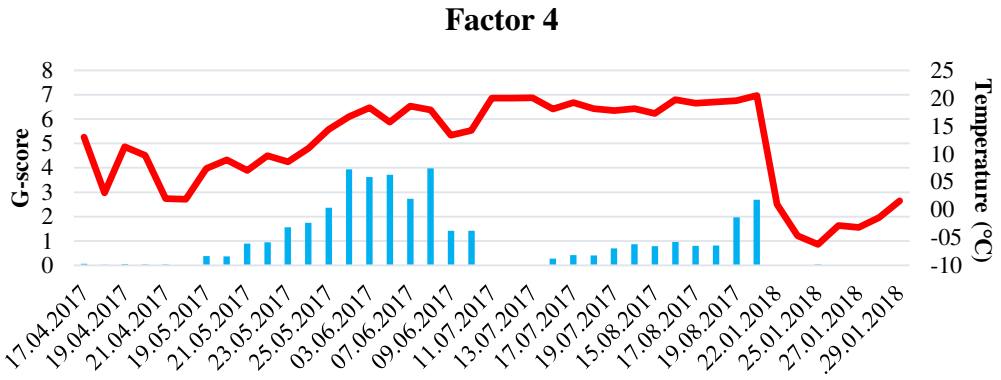


**Figure 4.15.** PMF results of factor 4 (G-score daily and temperature dependent changes).

Factor 5 included VOCs that were generally emitted from diesel and/or domestic activities (photocopy, plastic usage, wood and biomass combustion) [40, 63]. The highly explained VOCs were chlorobenzene, decanal, nonanal, napthalene, tridecane, styrene, 1,3,5-trimethylbenzene, tetradecane, 1,2,3-trimethylbenzene, m-ethyltoluene, 1,2,4-trimethylbenzene, n-propylbenzene, p-cymene, o-ethyltoluene, 1,4-diethylbenzene and isoprene. The highest G-score value was obtained on 17th August 2017 (Figure 4.16).

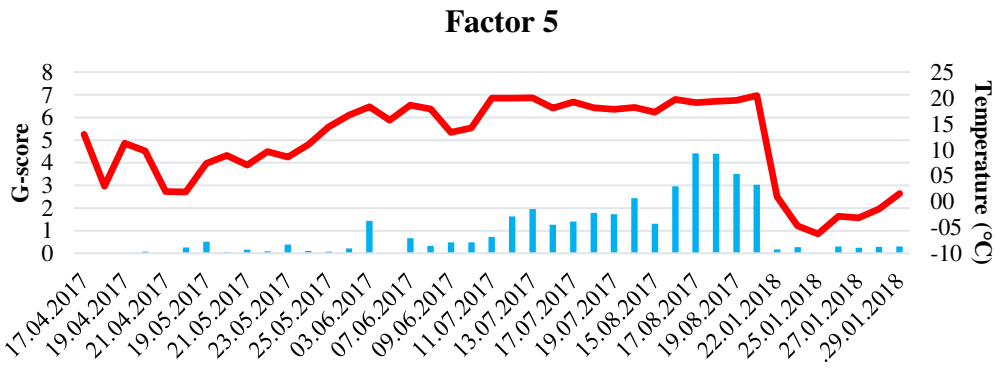


**Figure 4.16.** PMF results of factor 5 (G-score daily and temperature dependent changes).

VOCs describing the forested city atmosphere were grouped under factor 6. Based on G-score results, the highest value was obtained on 11th July 2017 (Figure 4.17). The factor contained the compounds such as alpha-pinene, ethyltoluene, n-propylbenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, tridecane, xylene, beta-pinene, 1,2,3-trimethylbenzene, phenol, ethylbenzene, styrene, 1,4-diethylbenzene, tetradecane, naphthalene, toluene, hexanal, p-cymene, acetophenone and heptanal.

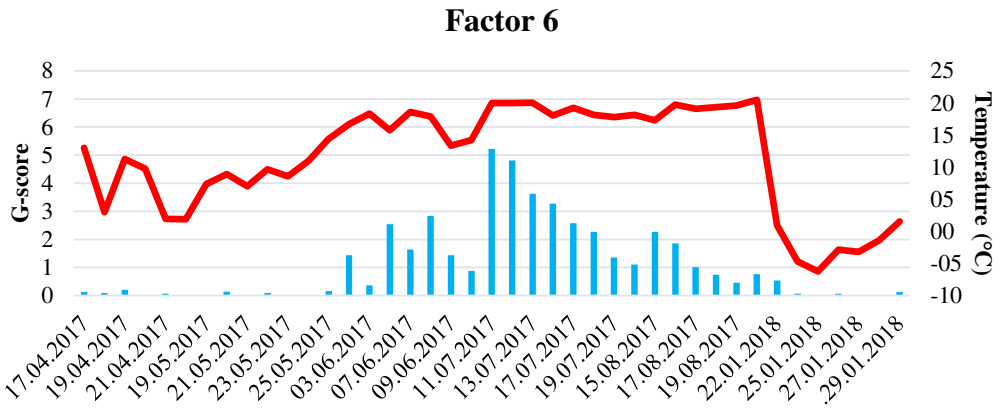


**Figure 4.17.** PMF results of factor 6 (G-score daily and temperature dependent changes).

### 4.1.4.3 Positive Matrix Factorization (PMF): April-August 2018 Active Sampling Period

PMF analysis was applied to the VOC data including the concentrations of April-August 2018 of active sampling. $Q_{robust}$ and $Q_{true}$ values were 1161.3 and 1166.3. As a result, VOC sources were explained with six factors (Figure 4.18).

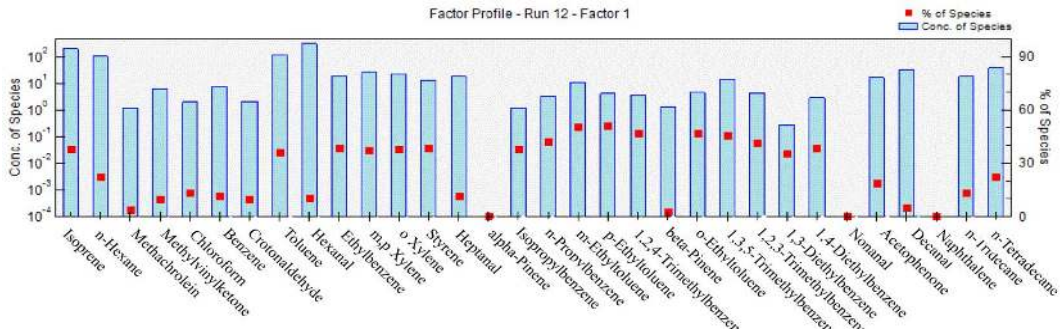


**Figure 4.18.** Factor profiles.

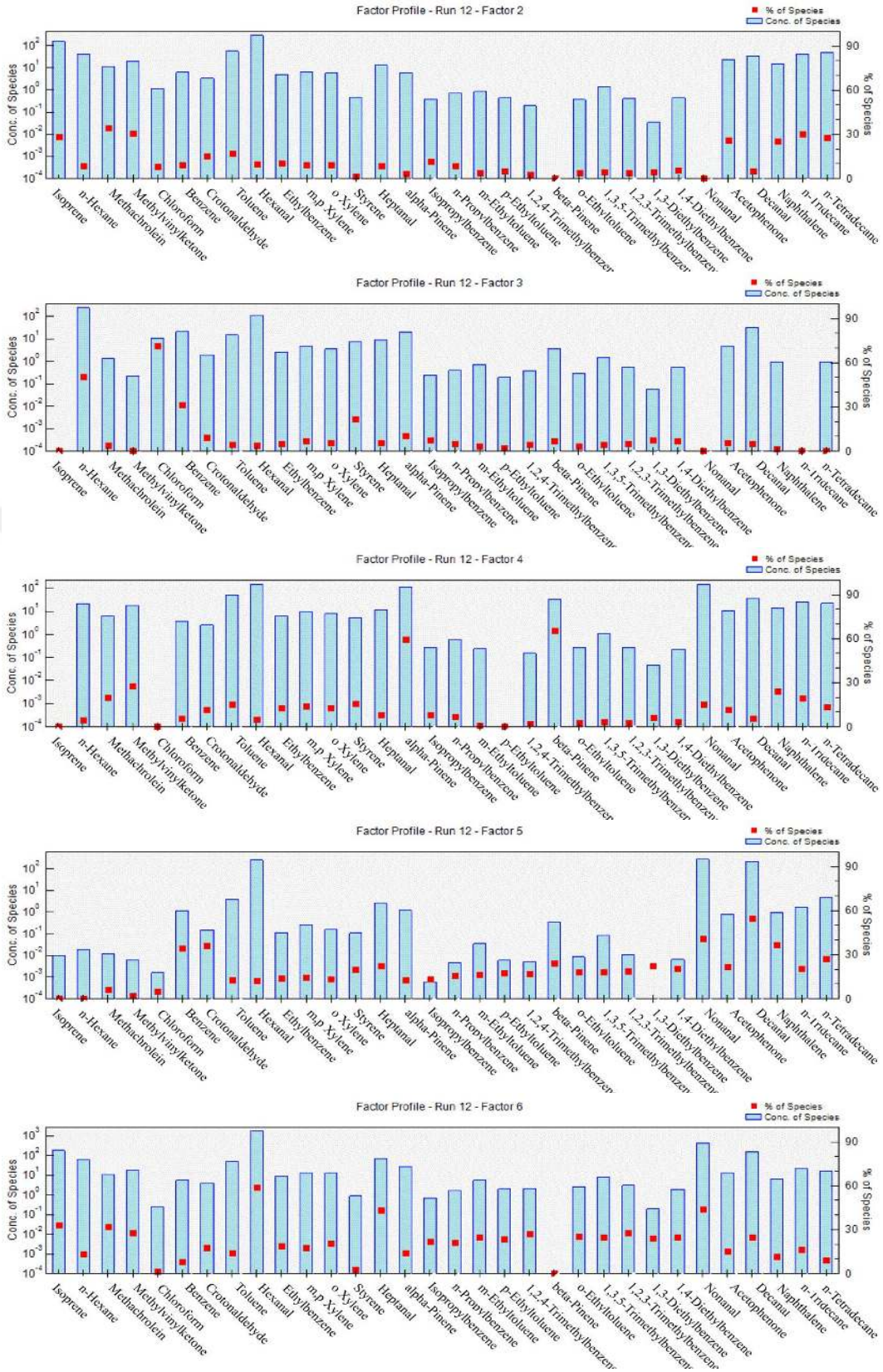


**Figure 4.18 (continued)** Factor profiles.

The potential sources of VOCs were determined as solvent evaporation 1/vehicle emission, secondary photochemical formation/background, solvent

evaporation 2, biogenic emissions (hornbeam/pine/juniper), wood-coal-biomass burning and biogenic emissions (oak/pine/juniper/grain/grass) (Table 4.3). The contribution of sources to the total was 14%, 11%, 6.8%, 9.6%, 20% and 39%, respectively (Figure 4.19).

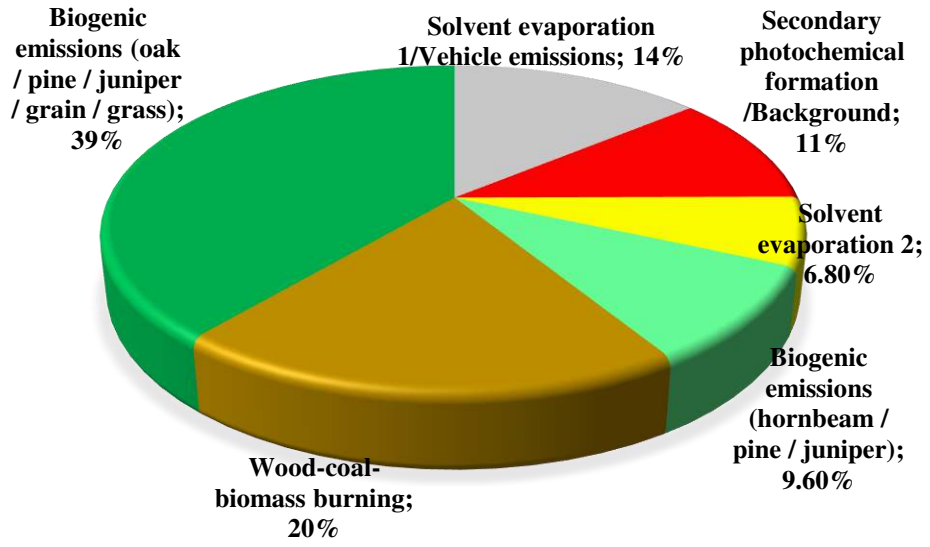


**Figure 4.19.** Source contributions to the VOC concentrations.

**Table 4.3.** PMF results of VOCs determined in April-August 2018 active sampling study ($N_{Total}$ = 27; the compounds explained at least 20% in the factor were given).

| Factors | VOCs | Source |
|---|---|---|
| **Factor 1** | isoprene, toluene, ethylbenzene, xylenes, styrene, ısopropylbenzene, n-propylbenzene, ethyltoluenes, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, 1,2,3-trimethylbenzene, 1,3-diethylbenzene, 1,4-diethylbenzene, | Solvent evaporation 1 /Vehicle emissions |
| **Factor 2** | methachrolein, methylvinylketone, isoprene, acetophenone, naphthalene, tridecane, tetradecane | Secondary photochemical formation /Background |
| **Factor 3** | chloroform, hexane, benzene, styrene | Solvent evaporation 2 |

| | | |
|---|---|---|
| **Factor 4** | alpha-pinene, beta-pinene | Biogenic emissions (hornbeam / pine / juniper) |
| **Factor 5** | decanal, nonanal, crotonaldehyde, benzene, naphthalene | Wood-coal-biomass burning |
| **Factor 6** | hexanal, nonanal, heptanal | Biogenic emissions (oak / pine / juniper / grain / grass) |

Factor 1 was explained by solvent related species such as toluene, styrene, ethylbenzene, m+p-xylene, o-xylene, n-propylbenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene and 1,2,3-trimethylbenzene [64, 99, 110]. The highest G-score value of the factor was determined on July 18, 2018 (Figure 4.19). On the other hand, toluene, ethylbenzene, m + p-xylene and o-xylene compounds can also be emitted from vehicle emissions [63, 111]. The factor profile also included solvent-derived compounds such as styrene. In addition, the G-score values were found to be higher in the summer holiday period than in the spring semester when campus traffic is expected to be heavy (Figure 4.20). The first factor was identified as solvent evaporation 1/vehicle emission.

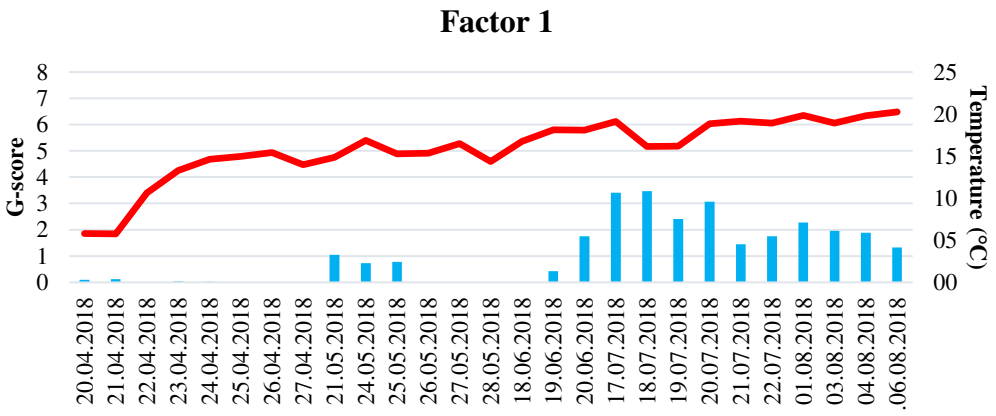


**Figure 4.20.** PMF results of factor 1 (G-score daily and temperature dependent changes).

Methachrolein and methylvinylketone have been highly contributing compounds to the second factor. The compounds are the main products from the

photochemical reaction of isoprene [112, 113]. In addition to oxidation products, the presence of primary compounds such as isoprene, acetophenone, naphthalene, tridecane and tetradecane showed that the background also contributed to the factor. Thus, factor 2 was attributed as secondary photochemical formation and background. The highest G-score was observed on 20 July 2018 (Figure 4.21). In general, the highest contribution to the factor occurred on the dates when the temperature was high, which indicated the effect of photochemical oxidation reactions in this factor.

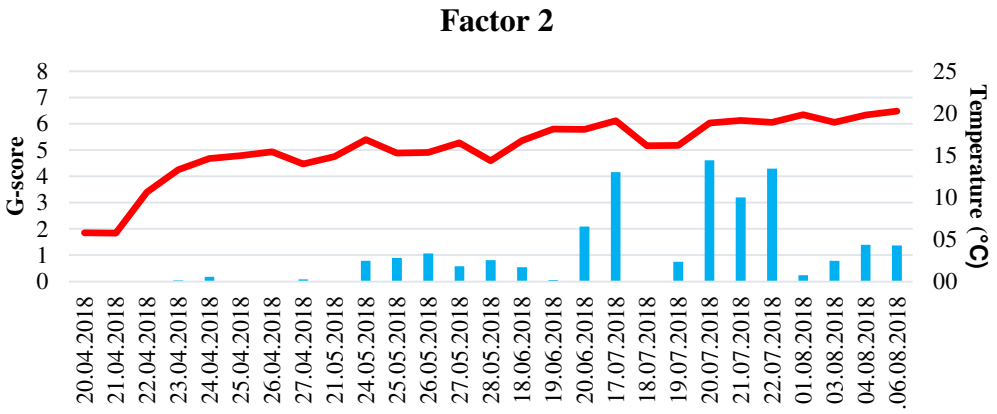


**Figure 4.21.** PMF results of factor 2 (G-score daily and temperature dependent changes).

The high proportion of compounds such as chloroform, hexane, benzene and styrene were examined in factor 3. The high loadings of aromatics and halogenates are related to solvent evaporation [39]. Solvents used in campus laboratories were seen as potentially important sources. According to the daily G-score variations, the highest G-score was observed on May 21, 2018 in Figure 4.22. In addition to temperature, solvent usage periods should be affecting the contribution to the factor. Therefore, factor 3 was attributed to solvent evaporation.

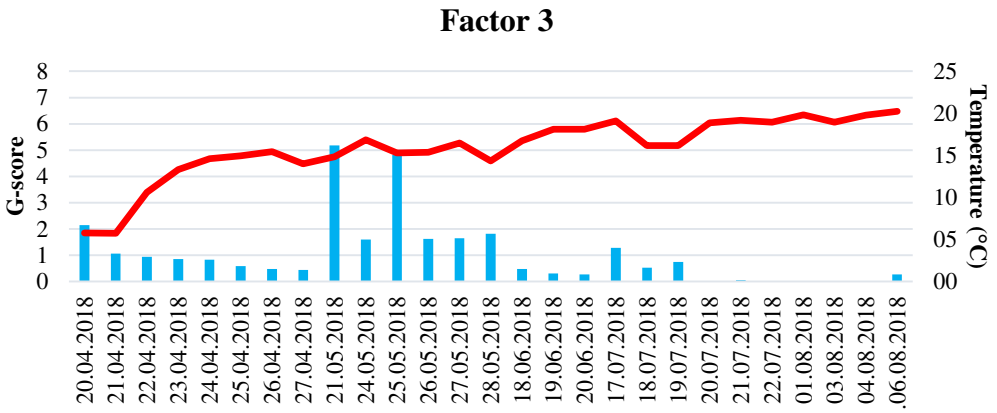


**Figure 4.22.** PMF results of factor 3 (G-score daily and temperature dependent changes).

Factor 4 was highly contributed by alpha-pinene and beta-pinene. The pinenes were mostly emitted by tree species such as Hornbeam, Pine and Juniper [32]. The higher G-scores were found between May and July (Figure 4.23). Increased temperatures played an active role in the release of biogenic VOCs in warmer months. Thus, factor 4 was identified as biogenic (hornbeam/pine / juniper).

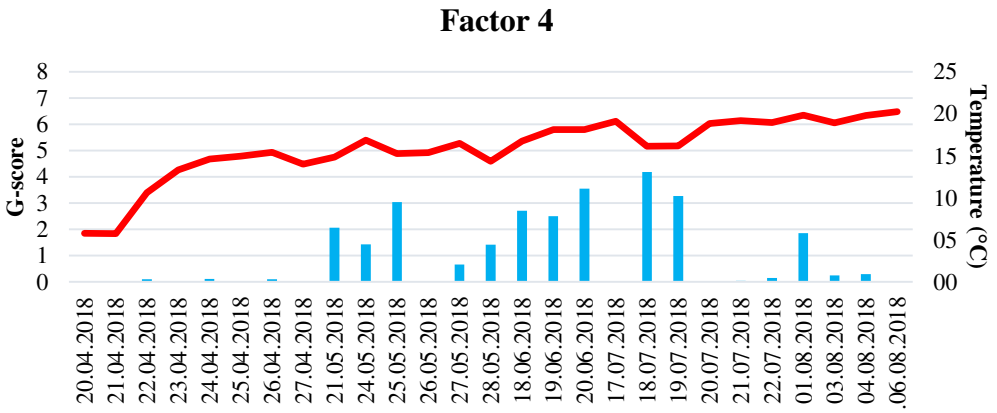


**Figure 4.23.** PMF results of factor 4 (G-score daily and temperature dependent changes).

Factor 5 was distinguished by high levels of decanal, nonanal, crotonaldehyde, benzene and naphthalene. Aldehydes (decanal, nonanal and crotonaldehyde) are compounds having biogenic origin. The processes such as wood combustion and biomass burning also lead to their emission from the surface [114, 115]. They were determined as the emission product from wood pellets of

scots pine [116]. Also, benzene and naphthalene are other highly contributed compounds in this factor. It was expressed that biomass and coal burnings are important emission sources for benzene and naphthalene [37]. The highest G-score value was determined on 27 April 2018 (Figure 4.24). In Bolu generally up to June, the people living in villages use wood-coal for the domestic heating due to low temperature at night time.

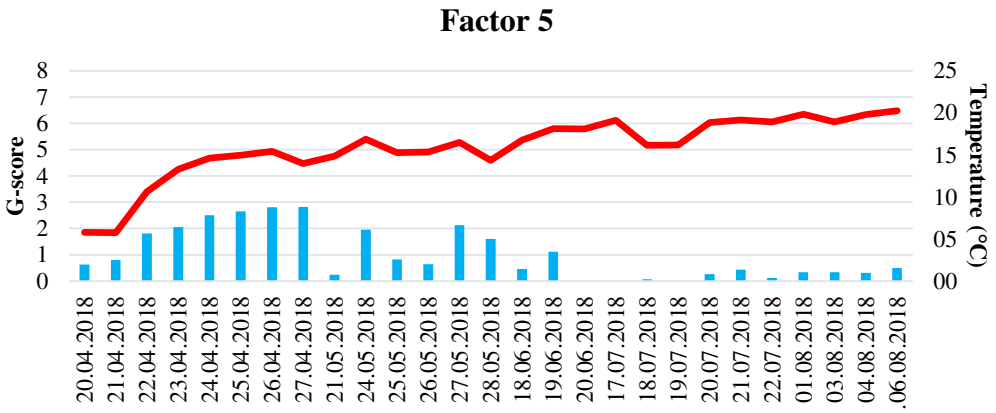


**Figure 4.24.** PMF results of factor 5 (G-score daily and temperature dependent changes).

The predominant species found in factor 6 were hexanal, nonanal and heptanal. These aldehydes are produced from the ozonolysis of plant lipids [117]. Plants that are effective in the emission of these compounds were determined as tree species of Oak, Pine, Juniper; grain and grass [29, 34]. According to G-score results, the highest value was found on 04 August 2018 (Figure 4.25). It is seen that the contribution of biogenic compounds to the factor increased with temperature. Therefore, factor 6 was identified as biogenic emissions (oak/pine/juniper/grain/grass).

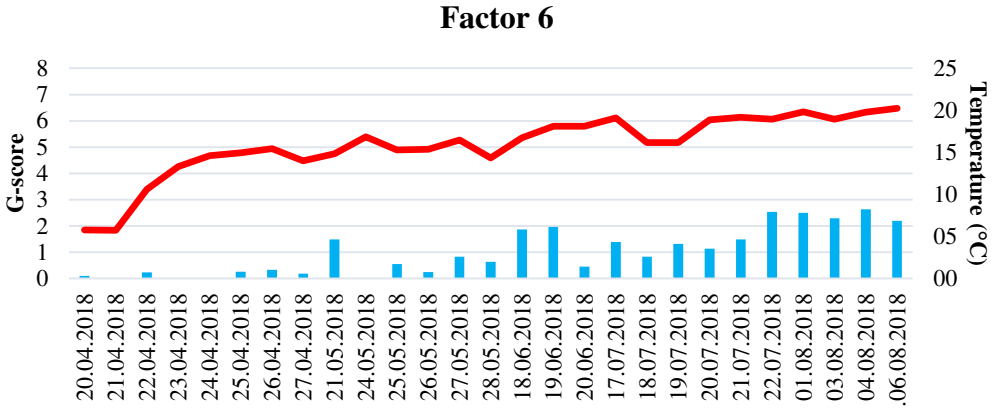


**Figure 4.25.** PMF results of factor 6 (G-score daily and temperature dependent changes).

#### 4.1.4.4 Positive Matrix Factorization (PMF): 2017- 2018 Active Sampling Period

Finally, in PMF analysis, a more comprehensive set of VOC data was used by combining the concentrations of the years of 2017 and 2018 of active sampling. $Q_{robust}$ and $Q_{true}$ values were found to be 2833.2 and 2856.6. As a result, VOC sources were explained with six factors (Figure 4.26).

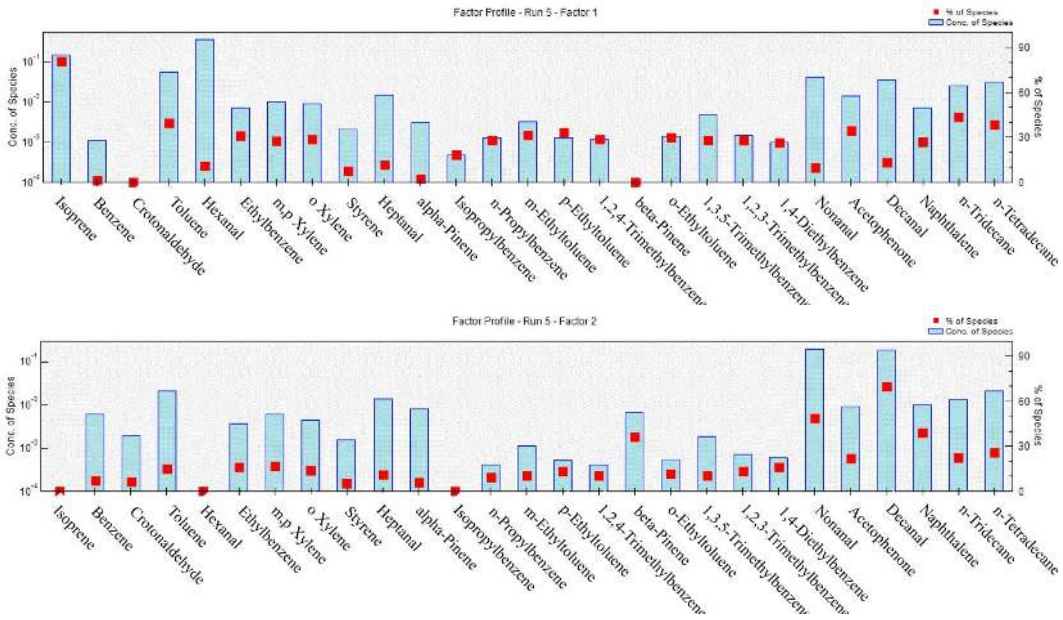


**Figure 4.26.** Factor profiles.

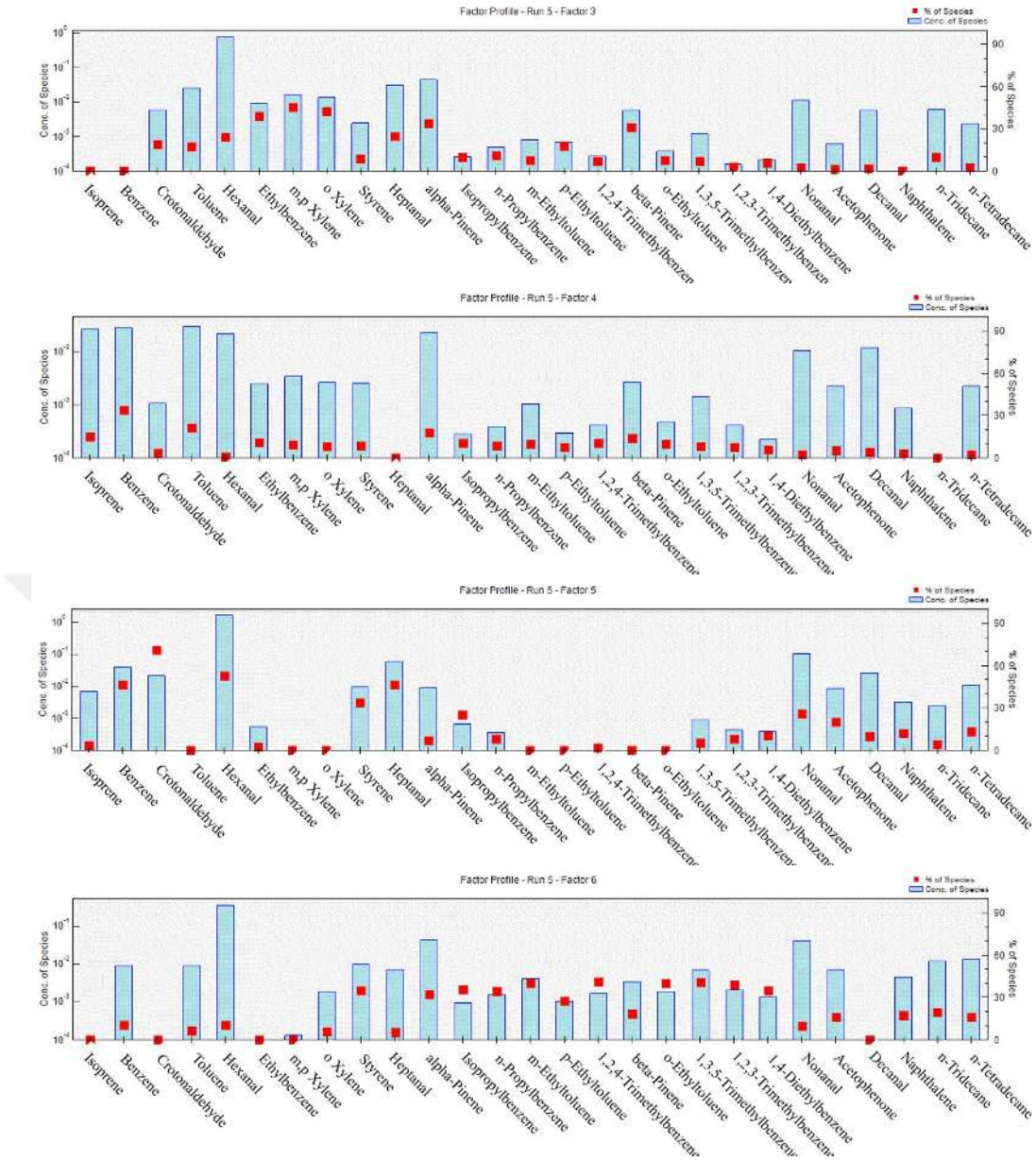


**Figure 4.26 (continued)** Factor profiles.

Potential sources of VOCs were determined as solvent evaporation/vehicle emission, wood-coal-biomass burning, forested city atmosphere, fossil fuel burning (domestic heating), biogenic emissions (oak/pine/juniper/grain/grass) and mixed source (Table 4.4). Contribution of sources to the total was 16%, 10%, 19%, 3.6%, 40% and 11%, respectively (Figure 4.27).

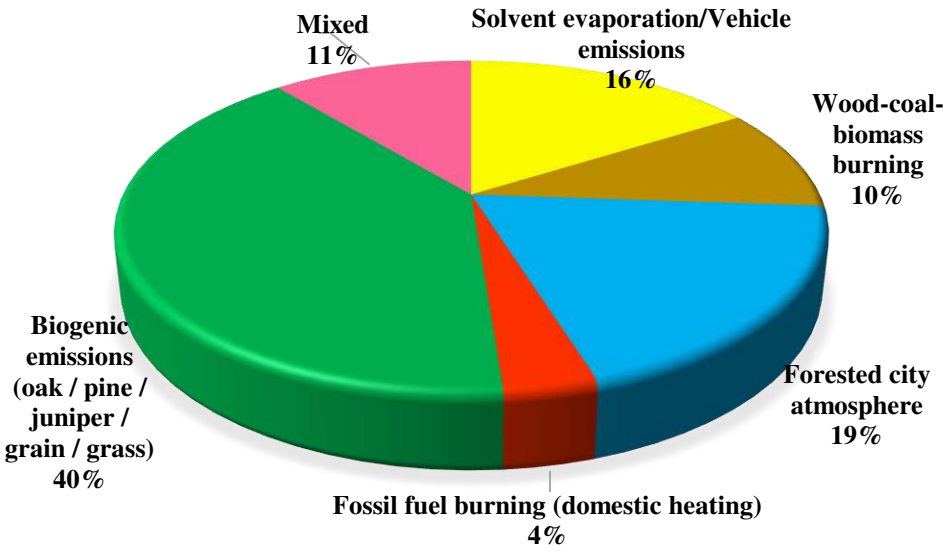


**Figure 4.27.** Source contributions to the VOC concentrations.

**Table 4.4.** PMF results of VOCs determined in full (2017- 2018) active sampling study ($N_{Total}$ = 66; the compounds explained at least 20% in the factor were given).

| Factors | VOCs | Source |
|---|---|---|
| **Factor 1** | isoprene, toluene, ethylbenzene, xylenes, n-propylbenzene, ethyltoluenes, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, 1,2,3-trimethylbenzene, 1,4-diethylbenzene, acetophenone, naphthalene, tridecane, tetradecane | Solvent evaporation/Vehicle emissions |
| **Factor 2** | Decanal, nonanal, beta-pinene, naphthalene | Wood-coal-biomass burning |
| **Factor 3** | Ethylbenzene, xylenes, alpha-pinene, beta-pinene | Forested city atmosphere |
| **Factor 4** | Benzene, toluene | Fossil fuel burning (domestic heating) |

| | | |
|---|---|---|
| **Factor 5** | Crotonaldehyde, hexanal, heptanal, nonanal, benzene, styrene | Biogenic emissions (oak/pine/juniper/ grain/grass) |
| **Factor 6** | Styrene, alpha-pinene, isopropylbenzene, propylbenzene, ethyltoluenes, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, 1,2,3-trimethylbenzene, 1,4-diethylbenzene | Mixed source |

Factor 1 was characterized by high loadings of solvent related species such as toluene, ethylbenzene, m+p-xylene, o-xylene, n-propylbenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene and 1,2,3-trimethylbenzene [99, 110]. Moreover, toluene, ethylbenzene, m + p-xylene and o-xylene compounds can also be emitted from vehicle emissions [63, 111]. It is seen that June and July 2018 made a high contribution to the factor (Figure 4.28). However, no such contribution was found in 2017, when the temperature was at a similar level. This situation shows that the factor is not only temperature-dependent, but also the change in the usage of solvents in each year. Considering the G-score data, factor 1 can be explained as solvent evaporation/vehicle emissions.

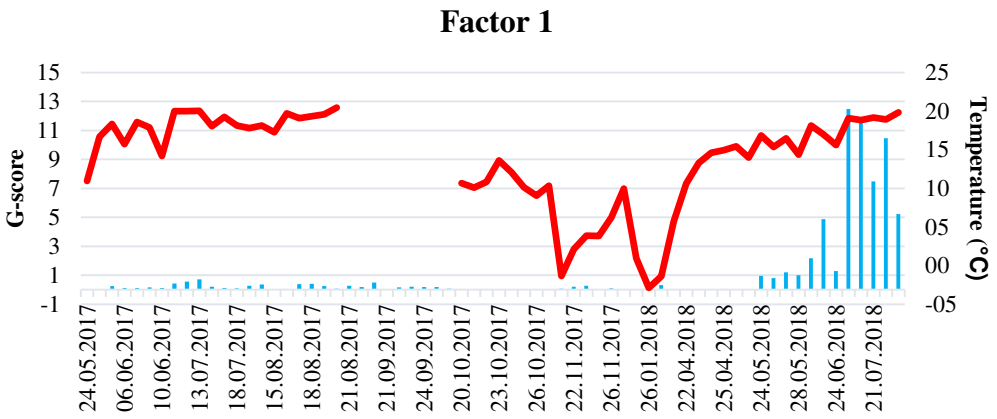


**Figure 4.28.** PMF results of factor 1 (G-score daily and temperature dependent changes).

A high proportion of compounds such as decanal, nonanal, beta-pinene and naphthalene were found in factor 2. Except for naphthalene, the other compounds exist on the surface of plants. The processes such as wood combustion and biomass

burning also lead to their release into the atmosphere [114-116]. Naphthalene is also an emission product of biomass and coal burning [37]. The highest G-score value was determined on April 27, 2018, when the temperature was not too low (15 $^{o}$C) (Figure 4.29). So, the biomass and wood burning explained factor 2.

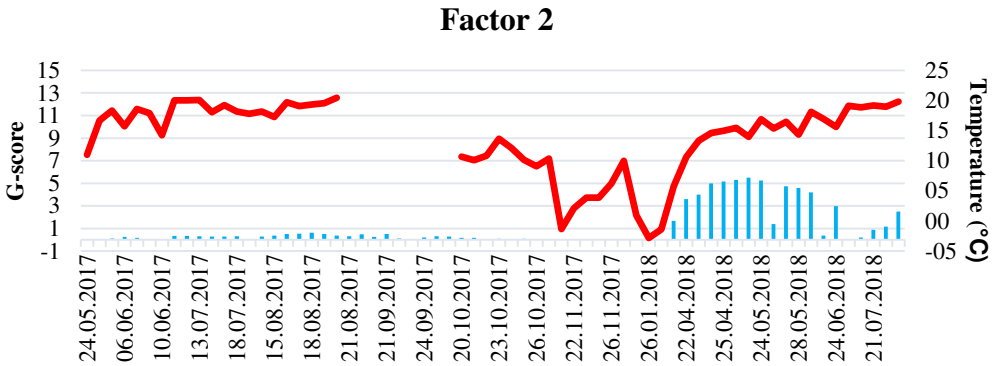


**Figure 4.29.** PMF results of factor 2 (G-score daily and temperature dependent changes).

Factor 3 was distinguished by high levels of ethylbenzene, xylenes, alpha-pinene and beta-pinene. Ethylbenzene and xylenes have a variety of sources such as solvent evaporation, vehicular emission, coal burning and biomass burning [37]. This factor also explained the pinenes which are mostly emitted by tree species such as Hornbeam, Pine and Juniper [32]. These tree species are especially found all around the campus. It is seen that the contribution to the factor was made in every period of the year and it increased especially in May and June (Figure 4.30). Therefore, factor 3 was attributed to the forested city atmosphere.

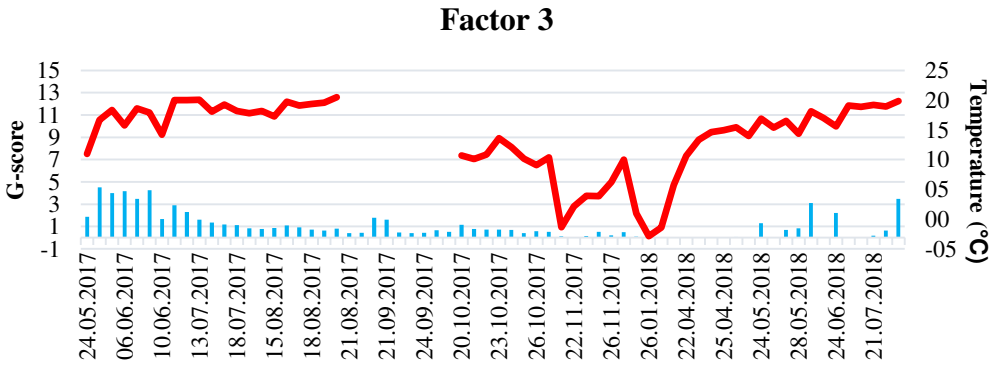


**Figure 4.30.** PMF results of factor 3 (G-score daily and temperature dependent changes).

Factor 4 was highly contributed by benzene and toluene. These compounds are emitted by coal combustion [37]. Significantly, the G-score values were found to be high in November and January when the temperature is low (Figure 4.31). In light of all these, factor 4 was identified as fossil fuel burning (domestic heating).

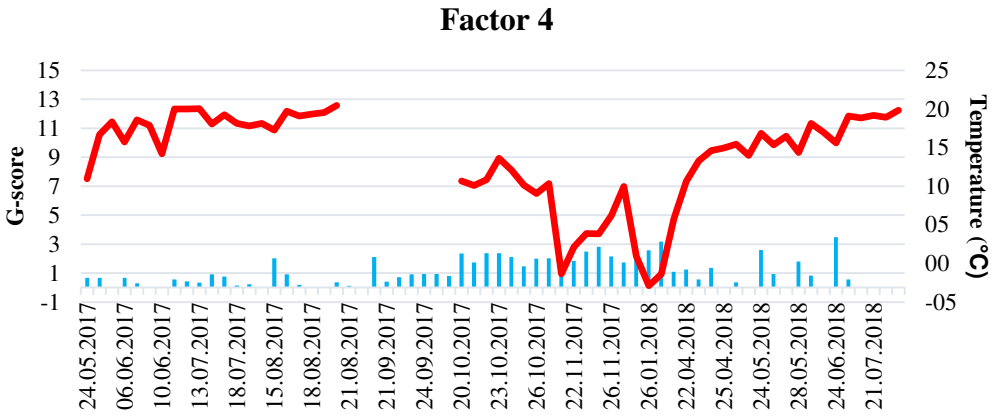


**Figure 4.31.** PMF results of factor 4 (G-score daily and temperature dependent changes).

VOCs reflect the biogenic emissions from tree species such as Oak, Pine, Juniper; grain and grass were gathered under factor 5 [29, 34]. According to G-score results, the highest value was found on 20 September 2017 (Figure 4.32). Therefore, the factor 5 was called as biogenic emissions (oak/pine/juniper/grain/ grass).

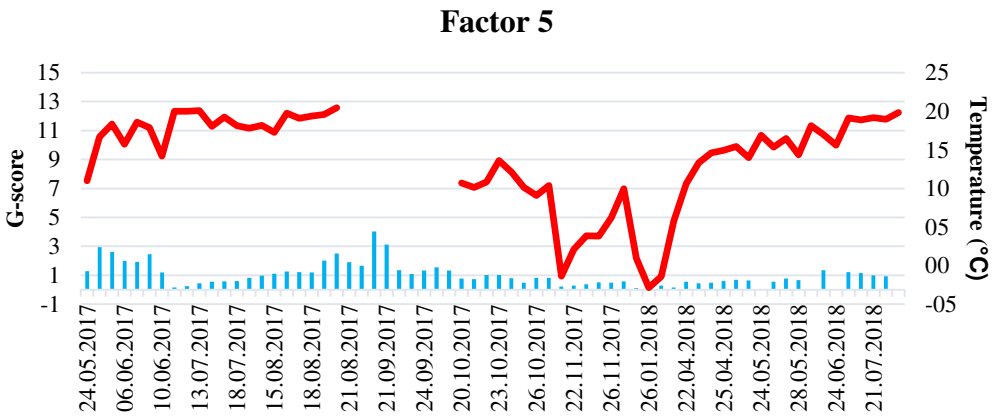


**Figure 4.32.** PMF results of factor 5 (G-score daily and temperature dependent changes).

Factor 6 contains the high loadings of compounds such as styrene, alpha-pinene, isopropylbenzene, propylbenzene, ethyltoluenes, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, 1,2,3-trimethylbenzene. It is the effect of both biogenic and anthropogenic (evaporative-combustion related) compounds, so it was called a mixed source (Figure 4.33).

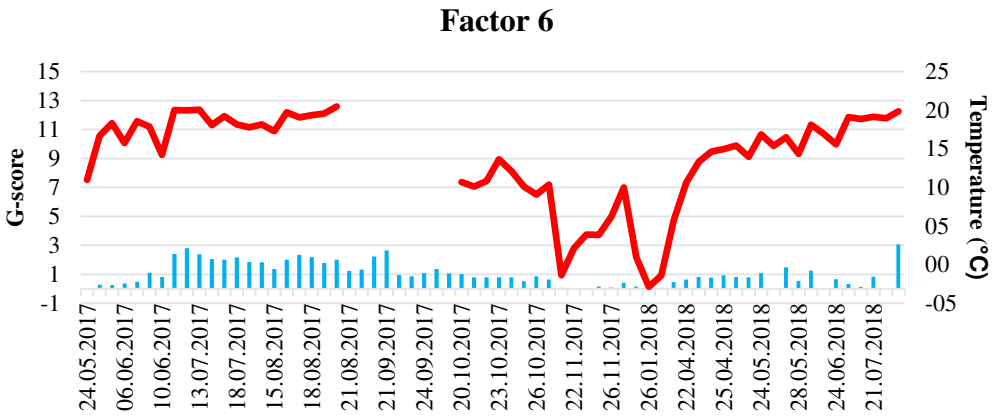


**Figure 4.33.** PMF results of factor 6 (G-score daily and temperature dependent changes).

### 4.1.5 Comparision of Active VOC Results with Literature

The comparison of the present study with other studies based on the active sampling of VOCs is given in Table 4.5. The VOC concentrations of this study are lower (~2–900 times) than those expressed for urban and semi-urban regions. Compared to Lamas de Olo [118] which is the mountainside-rural area, same (p-cymene) and higher results (~2–9 fold) for some VOCs (isoprene, benzene, o-xylene, hexane, toluene, ethylbenzene, limonene, and alpha-pinene) and lower results (~2–8 fold) for m,p xylene, beta-pinene, and 3-carene were detected. Another study performed in a rural-mountainous area of Spain [119] reported comparable concentrations of benzene, hexane and toluene. If we compare the biogenic VOC concentrations in these two studies, higher concentrations of crotonaldehyde and alpha-pinene were obtained in Spain (7 and 2-fold respectively), and the hexanal concentration was found approximately 4 times below that found in the present study.

**Table 4.5.** Comparative analysis of active sampling VOC results (μg $m^{-3}$).

| Compound | Beijing, China [70] (semi-urban) | Coruna, Spain [120] (urban) | Pinheiros, Brazil [121] (urban) | Lamas de Olo, Portugal [118] (mountaneous rural) | Ankara, Turkey [110] (semi-urban) | Cabaneros National Park, Spain [119] (mountaneous rural-oak trees) | Bolu, Turkey (semi-urban, forested) |
|---|---|---|---|---|---|---|---|
| | November 2014 | November – December 2000 | June 2005 | June-July 2006 | January-June 2008 | August-November 2010, February-August 2011 | April-November 2017, January, April-August 2018 |
| **Isoprene** | | 0.68 ± 0.40 | | 0.13 | | | 0.33 ± 0.68 |
| **Crotonaldehyde** | | | | | | 0.21±0.93 | 0.03± 0.02 |
| **Hexanal** | | | | | | 0.79±1.33 | 3.01± 2.24 |
| **Alpha-pinene** | | 1.07 ± 1.87 | | 0.06 | | 0.35±0.61 | 0.15 ± 0.14 |
| **Beta-Pinene** | | 0.39 ± 0.32 | | 0.11 | | | 0.03 ± 0.03 |
| **3-Carene** | | 0.53 ± 0.83 | | 0.18 | | | 0.01 ± 0.01 |
| **Limonene** | | 0.34 ± 0.26 | | 0.02 | | | 0.06 ± 0.10 |
| **p-Cymene** | | | | 0.01 | | | 0.01 ± 0.01 |
| **n-Hexane** | 1.0 ± 0.9 | | 7.8 ± 3.1 | 0.05 | | 0.34± 0.49 | 0.47 ± 0.36 |
| **Tetrachloromethane** | | 2.19 ± 1.99 | | | | | 0.08 ± 0.07 |
| **Benzene** | 3.0 ± 2.9 | 2.69 ± 2.26 | 5.2 ± 1.0 | 0.05 | 2.18 ± 2.25 | 0.07±0.47 | 0.08 ± 0.04 |
| **Heptane** | | 1.13 ± 0.83 | 4.0 ± 0.9 | | | | 0.13 ± 0.14 |
| **n-Octane** | | 1.11 ± 0.91 | 1.8 ± 0.3 | | 0.15 ± 0.17 | | 0.10 ± 0.09 |
| **Toluene** | 3.8 ± 3.4 | 17.3 ± 17.1 | 20 ± 4.4 | 0.1 | 7.89 ± 9.64 | 0.07±0.51 | 0.19 ± 0.19 |
| **Chlorobenzene** | | 0.08 ± 0.03 | | | | | 0.18 ± 0.21 |
| **Ethylbenzene** | 1.7 ± 1.7 | 2.37 ± 1.73 | 6.4 ± 1.9 | 0.01 | 0.85 ± 0.91 | | 0.03 ± 0.03 |
| **m+p Xylene** | 1.3 ± 1.2 | 3.64 ± 3.48 | 9.0 ± 1.8 | 0.06 | 2.21 ± 2.50 | | 0.04 ± 0.04 |
| **o-Xylene** | 0.9 ± 1.0 | 2.00 ± 1.71 | 2.6 ± 0.4 | 0.01 | 0.41 ± 0.47 | | 0.04 ± 0.03 |
| **Styrene** | | 0.58 ± 0.38 | 2.9 ± 0.5 | | 0.41 ± 2.48 | | 0.03 ± 0.02 |
| **Isopropylbenzene** | | 0.17 ± 0.20 | | | 0.06 ± 0.19 | | 0.003 ± 0.002 |
| **n-Propylbenzene** | | 0.35 ± 0.27 | | | 0.04 ± 0.07 | | 0.005 ± 0.004 |
| **m-Ethyltoluene** | 0.3 ± 0.2 | | | | 0.22 ± 0.27 | | 0.01 ± 0.005 |
| **p-Ethyltoluene** | | 0.31 ± 0.44 | | | | | 0.005 ± 0.005 |
| **1,2,4-Trimethylbenzene** | | 3.17 ± 2.16 | 4.5 ± 0.5 | | 0.27 ± 0.35 | | 0.005 ± 0.004 |
| **o-Ethyltoluene** | 0.3 ± 0.2 | | | | 0.13 ± 0.22 | | 0.006 ± 0.005 |
| **1,3,5-Trimethylbenzene** | | 0.67 ± 0.51 | 1.2 ± 0.3 | | 0.17 ± 0.40 | | 0.02 ± 0.02 |
| **1,2,3-Trimethylbenzene** | | 0.51 ± 0.24 | | | | | 0.006 ± 0.006 |

## 4.2 Passive Sampling

### 4.2.1 The Results of Winter Passive Sampling

#### 4.2.1.1 Statistical Evaluation of VOCs

In the Bolu plateau, passive sampling was performed at 47 sampling points in winter (28 January 2017-12 February 2017). It was aimed to examine a total of 68 VOCs in the samples. However, 1,1,1-trichloroethane, nonane, decane, sabinene, beta-myrcene, alpha-phellandrene, 1,4-cineole, ocimene, eucalyptol, 4-methyl anisole, gamma-terpinene, 1,2-dichlorobenzene, terpinolene, octanol, linalool, alloocimene, alpha-terpinene, l-fenchone, terpinene-4-ol and alpha-terpineol were found to be below their LOD values. The majority of undetected compounds have a biogenic origin. The fact that the tree species responsible for the emission of the compounds were not found in the sampling area or did not release enough in winter conditions may be the reasons behind the failure to detect these compounds. Thus, a total of 48 VOCs could be determined in the winter sampling.

The statistical data are given in Table 4.6. Anthropogenic VOCs with the highest concentrations were benzaldehyde (3.64 μg $m^{-3}$), toluene (2.38 μg $m^{-3}$), benzene (1.75 μg $m^{-3}$) and acetophenone (1.44 μg $m^{-3}$) whereas hexanal (0.56 μg $m^{-3}$), nonanal (0.35 μg $m^{-3}$), decanal (0.26 μg $m^{-3}$) and alpha-pinene (0.21 μg $m^{-3}$) were the dominant biogenic VOCs. It was observed that beta-pinene, alpha-pinene, styrene, acrylonitrile, dihydromrycenol, 3-carene, 2-methylfuran, and decanal had higher standard deviation than other components and therefore had high CV values. Thus, it was concluded that these components had variable sources or source strengths in spatial distribution.

Among the identified VOCs, benzene is one of the primary pollutants that adversely affect human health and causes cancer. According to the Regulation on Air Quality Assessment and Management [122], the average annual benzene concentration in the atmosphere should not exceed 5 μg $m^{-3}$. This limit value was not exceeded in winter passive sampling but a very close value to the limit (4.55 μg $m^{-3}$) was obtained in the city center.

**Table 4.6.** Descriptive statistical parameters for VOCs in winter passive sampling (μg $m^{-3}$).

| Compound | Number of samples (N) | Arithmetic Mean | Median | Geometric Mean | Standard Deviation | Variation coefficient (CV) | Min - Max |
|---|---|---|---|---|---|---|---|
| Isoprene | 59 | 0.10 | 0.08 | 0.08 | 0.06 | 58 | 0.01-0.25 |
| Acrylonitrile | 57 | 0.02 | 0.02 | 0.02 | 0.03 | **128** | 0.01-0.21 |
| n-Hexane | 59 | 1.15 | 0.64 | 0.87 | 1.00 | 87 | 0.39-4.00 |
| 2-Methylfuran | 59 | 0.04 | 0.02 | 0.03 | 0.05 | **107** | 0.005-0.19 |
| Chloroform | 59 | 0.07 | 0.06 | 0.06 | 0.03 | 38 | 0.01-0.20 |
| Tetrachloromethane | 58 | 0.37 | 0.36 | 0.37 | 0.05 | 12 | 0.32-0.57 |
| Benzene | 59 | 1.75 | 1.36 | 1.48 | 1.06 | 60 | 0.20-4.55 |
| 1.2-Dichloroethane | 58 | 0.04 | 0.04 | 0.04 | 0.01 | 17 | 0.03-0.06 |
| n-Heptane | 59 | 0.51 | 0.41 | 0.46 | 0.29 | 57 | 0.34-1.53 |
| Crotonaldehyde | 57 | 0.06 | 0.05 | 0.05 | 0.03 | 50 | 0.02-0.16 |
| n-Octane | 59 | 0.66 | 0.51 | 0.60 | 0.41 | 62 | 0.44-2.02 |
| Toluene | 59 | 2.38 | 2.08 | 2.12 | 1.27 | 53 | 1.13-6.63 |
| Hexanal | 59 | 0.56 | 0.50 | 0.50 | 0.26 | 46 | 0.07-1.57 |
| Chlorobenzene | 55 | 0.01 | 0.01 | 0.01 | 0.01 | 67 | 0.004-0.03 |
| Ethylbenzene | 59 | 0.42 | 0.34 | 0.37 | 0.23 | 56 | 0.22-1.22 |
| m+p Xylene | 59 | 0.43 | 0.33 | 0.37 | 0.28 | 65 | 0.19-1.31 |
| o-Xylene | 59 | 0.77 | 0.58 | 0.68 | 0.49 | 64 | 0.46-2.56 |
| Styrene | 59 | 0.02 | 0.01 | 0.01 | 0.03 | **135** | 0.001-0.12 |
| 1- Heptanal | 18 | 0.13 | 0.12 | 0.13 | 0.06 | 41 | 0.08-0.31 |
| Alpha-pinene | 59 | 0.21 | 0.10 | 0.11 | 0.32 | **151** | 0.003-2.24 |
| Isopropylbenzene | 59 | 0.06 | 0.04 | 0.05 | 0.04 | 66 | 0.03-0.19 |
| Camphene | 29 | 0.08 | 0.06 | 0.07 | 0.04 | 54 | 0.05-0.24 |
| n-Propylbenzene | 59 | 0.11 | 0.09 | 0.10 | 0.07 | 63 | 0.05-0.38 |
| m-Ethyltoluene | 59 | 0.26 | 0.20 | 0.22 | 0.16 | 64 | 0.09-0.79 |
| p-Ethyltoluene | 59 | 0.10 | 0.08 | 0.09 | 0.06 | 62 | 0.04-0.28 |
| 1.2.4-Trimethylbenzene | 59 | 0.09 | 0.07 | 0.08 | 0.06 | 64 | 0.04-0.26 |
| beta-Pinene | 50 | 0.04 | 0.03 | 0.03 | 0.06 | **149** | 0.01-0.41 |
| o-Ethyltoluene | 59 | 0.20 | 0.15 | 0.17 | 0.13 | 64 | 0.07-0.64 |
| 3-Carene | 9 | 0.03 | 0.02 | 0.02 | 0.02 | **88** | 0.01-0.08 |
| 1.3.5-Trimethylbenzene | 59 | 0.38 | 0.28 | 0.33 | 0.26 | 67 | 0.12-1.22 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Benzaldehyde | 59 | 3.64 | 3.27 | 3.24 | 1.94 | 53 | 0.30-11.2 |
| Limonene | 29 | 0.02 | 0.01 | 0.01 | 0.03 | **141** | 0.002-0.11 |
| m-Cymene | 59 | 0.04 | 0.03 | 0.04 | 0.03 | 71 | 0.01-0.14 |
| p-Cymene | 59 | 0.03 | 0.02 | 0.03 | 0.01 | 51 | 0.01-0.07 |
| 1.2.3-Trimethylbenzene | 59 | 0.17 | 0.12 | 0.15 | 0.11 | 67 | 0.04-0.56 |
| 1.3-Diethylbenzene | 54 | 0.02 | 0.02 | 0.02 | 0.01 | 66 | 0.01-0.06 |
| 1.4-Diethylbenzene | 59 | 0.19 | 0.15 | 0.17 | 0.13 | 69 | 0.04-0.65 |
| Phenol | 59 | 1.11 | 0.85 | 0.86 | 0.88 | 79 | 0.06-4.77 |
| Dihydromyrcenol | 59 | 0.01 | 0.01 | 0.01 | 0.02 | **118** | 0.003-0.08 |
| Nonanal | 50 | 0.35 | 0.25 | 0.27 | 0.25 | 71 | 0.09-0.95 |
| Acetophenone | 59 | 1.44 | 1.34 | 1.26 | 0.61 | 42 | 0.01-3.79 |
| n-Dodecane | 59 | 0.24 | 0.19 | 0.22 | 0.14 | 60 | 0.05-0.78 |
| (+)-Camphor | 41 | 0.06 | 0.05 | 0.06 | 0.03 | 47 | 0.04-0.19 |
| Decanal | 45 | 0.28 | 0.16 | 0.20 | 0.25 | **91** | 0.06-0.97 |
| Naphthalene | 59 | 0.39 | 0.25 | 0.26 | 0.34 | **87** | 0.02-1.26 |
| n-Tridecane | 59 | 0.16 | 0.14 | 0.15 | 0.06 | 40 | 0.04-0.33 |
| Benzothiazole | 59 | 0.79 | 0.73 | 0.76 | 0.26 | 33 | 0.35-2.43 |
| n-Tetradecane | 59 | 0.18 | 0.16 | 0.17 | 0.05 | 30 | 0.09-0.34 |

#### 4.2.1.2 Spatial Distribution of VOCs

Pollution maps were drawn for each of the identified VOCs using the MapInfo, program. The maps were analyzed by dividing into groups according to their similarities. The winter pollution distribution maps of some of the selected VOCs belonging to each group are shared in this section. Distribution maps of other group members are presented in Appendix 3. The maps of VOCs revealed that the components had significant spatial changes in the city.

The distribution of 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, 1,3-diethylbenzene, 1,4-diethylbenzene, toluene, ethylbenzene, o-xylene, m,p-xylene, o-ethyltoluene, m-ethyltoluene, p-ethyltoluene, heptane, isopropylbenzene, n-propylbenzene, octane, dodecane, tridecane and tetradecane were similar. They were obtained with the highest concentration at sampling point 2 representing the city center (Figure 4.34). In addition, the relatively high concentrations were determined in regions where wood and coal were used for heating purposes (point 17) and exposed to emissions from small facilities and

vehicular traffic (points 63, 35, 45, 47). High concentrations were also found in the Kartalkaya region (point 51) which is an important ski resort area of Bolu. Xylene, ethyltoluene and toluene were found at high levels in regions close to the TEM and D100 highways (points 3, 16, 26, 20).

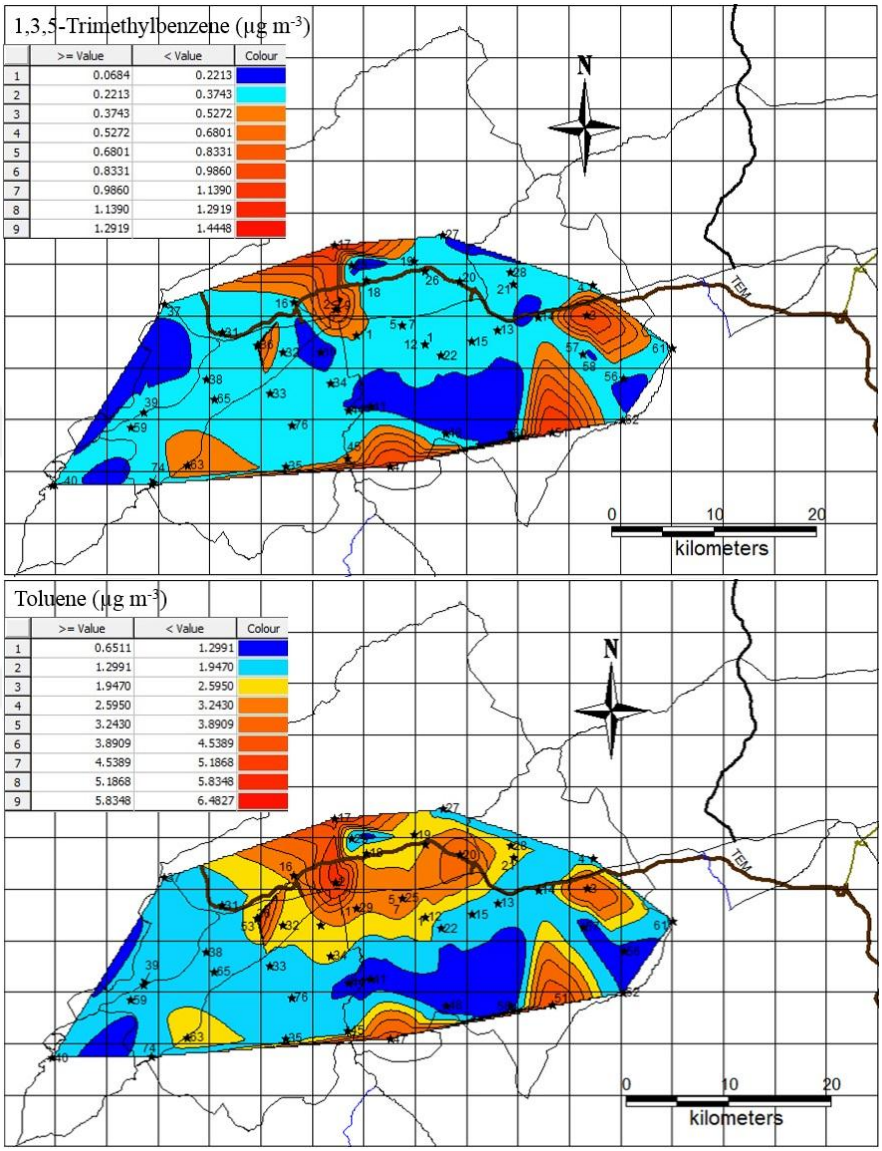


**Figure 4.34.** Pollution level distribution map of 1,3,5-trimethylbenzene and toluene for winter.

Benzene, styrene, hexane, phenol and naphthalene had high concentrations in the city center (point 2), organized industrial zone and areas including various factories (points 1, 5 and 7) (Figure 4.35). A high hexane level was detected in the Kartalkaya region (points 14, 51) which has intense vehicular circulation.

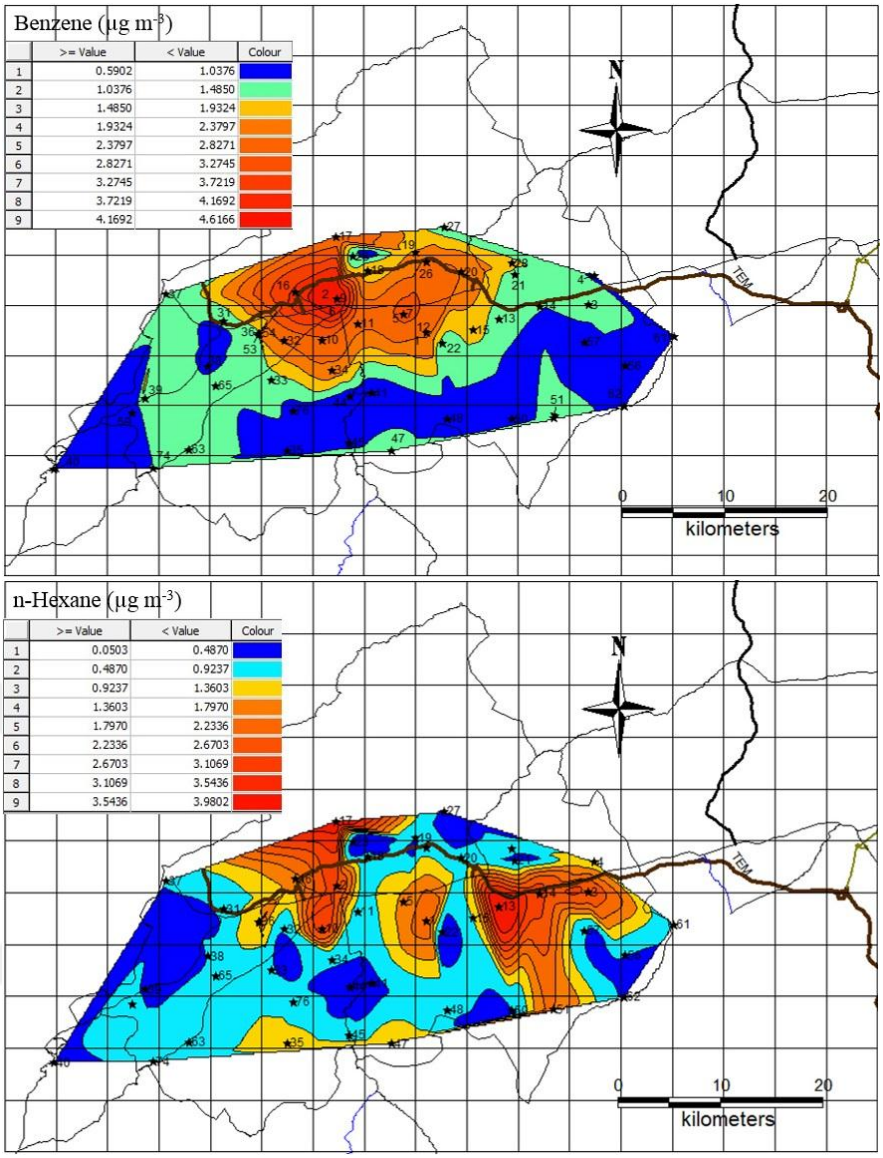


**Figure 4.35.** Pollution level distribution map of benzene and hexane for winter.

The highest concentrations of benzaldehyde, chlorobenzene, tetrachloromethane, 1,2-dichloroethane and chloroform were determined in the university campus (point 36) (Figure 4.36). Solvent released from university labs is considered to be the effective source for these compounds. Also, chloroform was obtained at high levels in the city center and at point 35 where the forest management was located.

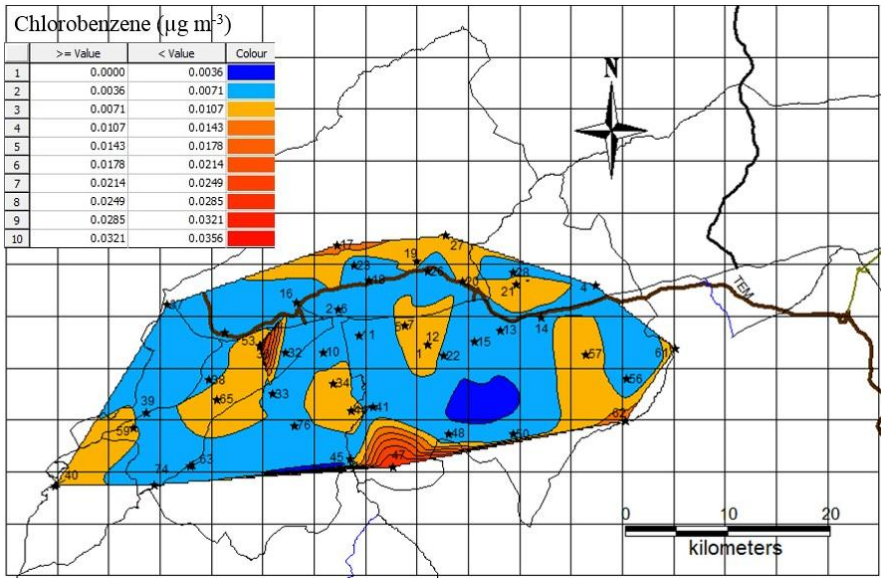


**Figure 4.36.** Pollution level distribution map of chlorobenzene for winter.

When the isoprene pollution distribution map (Figure 4.37) was examined, both biogenic and anthropogenic sources were found to be effective as expected. The highest isoprene concentration was determined in the city center (points 2, 6 and 9) and the rural regions in which Pine species were common (points 45 and 48).

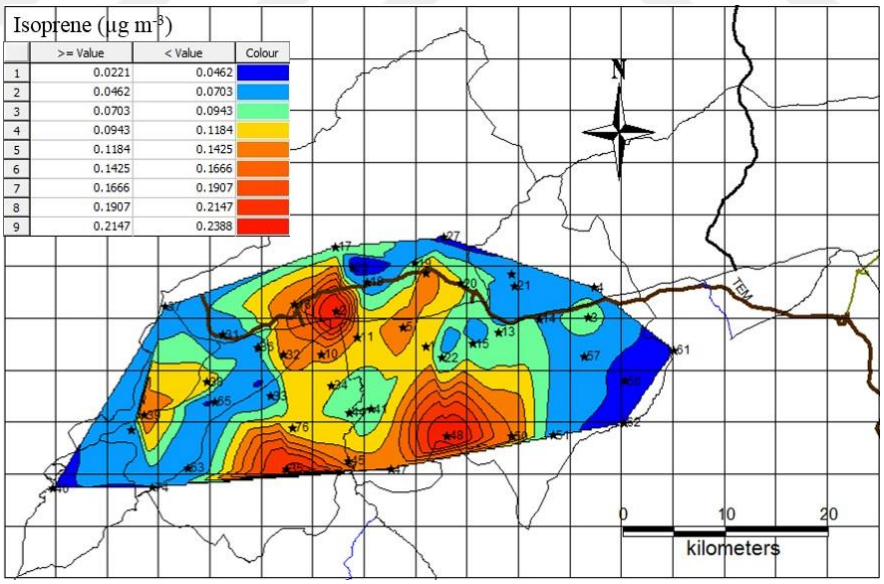


**Figure 4.37.** Pollution level distribution map of isoprene for winter.

Crotonaldehyde and 2-methylfuran are VOCs mostly emitted from Oak, Hornbeam, Beech and Juniper species [32]. As presented in Figure 4.38, their higher concentrations were found to the northwest of Bolu where these species are widespread.

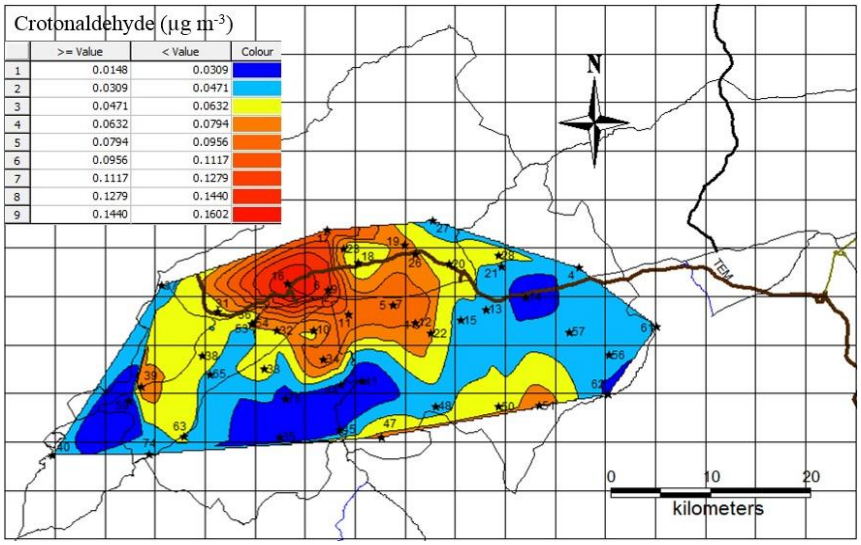


**Figure 4.38.** Pollution level distribution map of crotonaldehyde for winter.

Oak and Hornbeam are tree species that release p-cymene and m-cymene to the atmosphere. The distribution of the compounds coincides with the distribution of these tree species both in the north direction (point 17) and in the south direction (points 47, 51) (Figure 4.39).

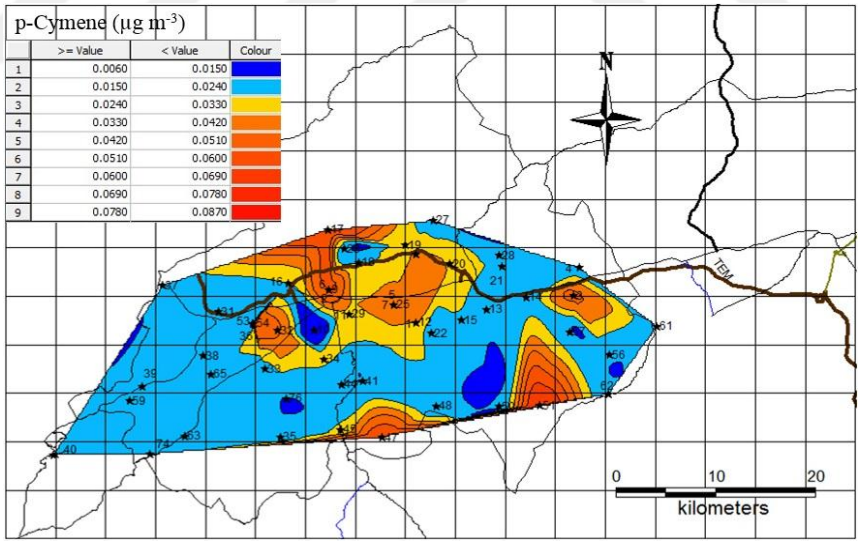


**Figure 4.39.** Pollution level distribution map of p-cymene for winter.

High concentrations of aldehydes including hexanal, nonanal and decanal are found at the university campus (point 36) which is under the influence of emissions from the tree species of Oak, Hornbeam, Beech, Ash, Juniper, Pine and grass (Figure 4.40).

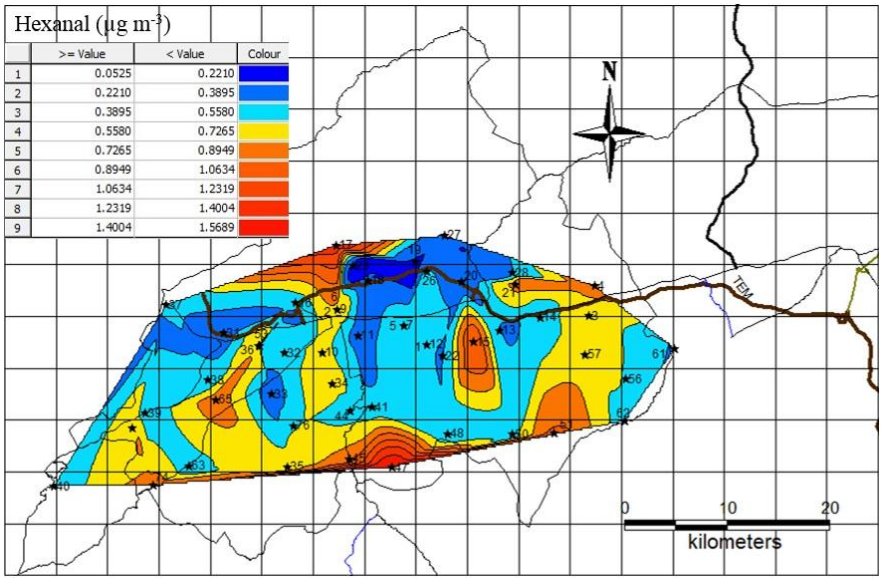


**Figure 4.40.** Pollution level distribution map of hexanal for winter.

Alpha-pinene and beta-pinene were determined in high concentrations at the southern part of the city center of Bolu (Figure 4.41). Pine and Juniper species that exist in these regions are supposed to have major roles in the emission of pinenes.

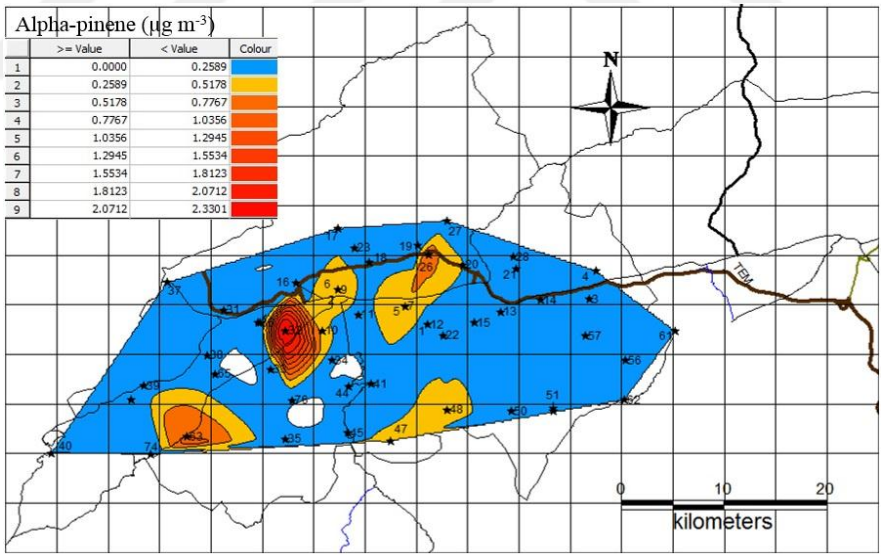


**Figure 4.41.** Pollution level distribution map of alpha-pinene for winter.

Camphene and camphor are supposed to be emitted from Juniper and Pine species, which are especially found in the southern direction of the city center of Bolu (Figure 4.42).

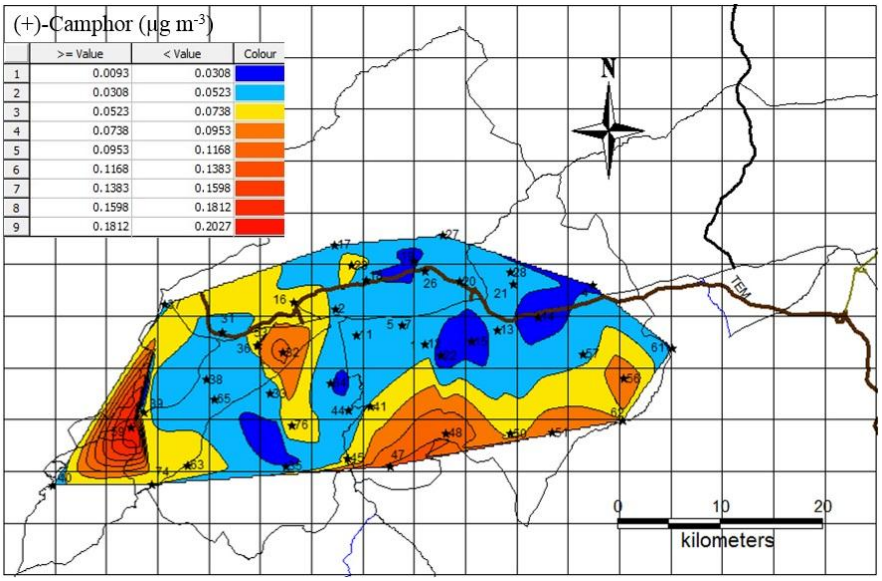


**Figure 4.42.** Pollution level distribution map of camphor for winter.

### 4.2.2 The Results of Summer Passive Sampling

#### 4.2.2.1 Statistical Evaluation of VOCs

In the Bolu plateau, passive sampling was performed at 63 sampling points in summer (7 July 2017-23 July 2017). It was aimed to examine a total of 68 VOCs in the samples. However, 1,1,1-trichloroethane, nonane, decane, beta-myrcene, alpha-phellandrene, 1,4-cineole, m-cymene, ocimene, 4-methyl anisole, gamma-terpinene, 1,3-diethylbenzene, 1,2-dichlorobenzene, terpinolene, octanol, linalool, alloocimene, alpha-terpinene, terpinen-4-ol and alpha-terpineol were below their LOD values. The inability to detect biogenic VOCs can be attributed to the absence of tree species involved in their release. Also, the fact that compounds containing the -chloro group could not be detected suggested that they were not used in industrial activities or laboratories in the sampling area. Thus, a total of 49 VOCs could be determined during the sampling studies.

Summer statistical data is given in Table 4.7. The anthropogenic VOCs with the highest concentrations were benzaldehyde (1.90 µg $m^{-3}$), acetophenone (1.53 µg $m^{-3}$) and isoprene (1.52 µg $m^{-3}$). On the other hand, biogenic VOC with the highest concentration was determined for alpha-pinene (1.00 µg $m^{-3}$). The highest determined benzene concentration (1.28 µg $m^{-3}$) was found to be significantly lower than the limit value (5 µg $m^{-3}$) determined by the Air Quality Assessment and Management Regulation [122]. Diethylbenzene, napthalene, trimethylbenzene,

limonene, n-hexane, n-octane, xylene, styrene, ethyltoluene, n-propylbenzene, sabinene, dihydromrycenol and benzothiazole, which had higher standard deviation and higher CV values than other components, were found to have variable sources or source strengths.

**Table 4.7.** Descriptive statistical parameters for VOCs in summer passive sampling (μg $m^{-3}$).

| Compound | Number of samples (N) | Arithmetic Mean | Median | Geometric Mean | Standard Deviation | Variation coefficient (CV) | Min - Max |
|---|---|---|---|---|---|---|---|
| Isoprene | 63 | 1.52 | 1.05 | 1.21 | 1.17 | 77 | 0.34-7.26 |
| Acrylonitrile | 18 | 0.01 | 0.01 | 0.01 | 0.01 | **90** | 0.01-0.05 |
| n-Hexane | 63 | 0.91 | 0.48 | 0.57 | 1.16 | **128** | 0.16-6.32 |
| 2-Methylfuran | 62 | 0.01 | 0.01 | 0.01 | 0.01 | 56 | 0.002-0.03 |
| Chloroform | 63 | 0.06 | 0.04 | 0.05 | 0.06 | 95 | 0.03-0.35 |
| Tetrachloromethane | 63 | 0.36 | 0.35 | 0.35 | 0.03 | 9.4 | 0.28-0.42 |
| Benzene | 63 | 0.29 | 0.25 | 0.27 | 0.15 | 53 | 0.17-1.28 |
| 1.2-Dichloroethane | 62 | 0.02 | 0.02 | 0.02 | 0.003 | 20 | 0.01-0.03 |
| n-Heptane | 63 | 0.03 | 0.02 | 0.03 | 0.02 | 74 | 0.008-0.14 |
| Crotonaldehyde | 63 | 0.03 | 0.03 | 0.03 | 0.01 | 30 | 0.01-0.06 |
| n-Octane | 42 | 0.06 | 0.05 | 0.05 | 0.06 | **102** | 0.03-0.42 |
| Toluene | 63 | 0.45 | 0.36 | 0.37 | 0.33 | 73 | 0.11-1.68 |
| Hexanal | 63 | 0.28 | 0.27 | 0.27 | 0.08 | 29 | 0.13-0.55 |
| Ethylbenzene | 63 | 0.07 | 0.05 | 0.05 | 0.06 | 88 | 0.01-0.28 |
| m+p Xylene | 63 | 0.12 | 0.06 | 0.07 | 0.13 | **108** | 0.02-0.50 |
| o-Xylene | 63 | 0.09 | 0.05 | 0.06 | 0.09 | **100** | 0.02-0.36 |
| Styrene | 62 | 0.04 | 0.02 | 0.02 | 0.06 | **166** | 0.005-0.47 |
| 1- Heptanal | 63 | 0.07 | 0.06 | 0.07 | 0.02 | 34 | 0.03-0.14 |
| Alpha-pinene | 63 | 1.00 | 0.79 | 0.78 | 0.82 | 82 | 0.19-4.65 |
| Isopropylbenzene | 29 | 0.01 | 0.01 | 0.01 | 0.01 | 96 | 0.001-0.04 |
| Camphene | 51 | 0.12 | 0.10 | 0.10 | 0.06 | 54 | 0.05-0.33 |
| n-Propylbenzene | 49 | 0.01 | 0.01 | 0.01 | 0.02 | **137** | 0.005-0.12 |
| m-Ethyltoluene | 63 | 0.04 | 0.02 | 0.02 | 0.10 | **231** | 0.004-0.60 |
| p-Ethyltoluene | 62 | 0.01 | 0.01 | 0.01 | 0.03 | **199** | 0.002-0.16 |
| Sabinene | 59 | 0.05 | 0.03 | 0.03 | 0.07 | **140** | 0.002-0.37 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 1,2,4-Trimethylbenzene | 45 | 0.02 | 0.01 | 0.01 | 0.06 | **246** | 0.003-0.34 |
| beta-Pinene | 63 | 0.18 | 0.13 | 0.14 | 0.16 | 86 | 0.06-0.92 |
| o-Ethyltoluene | 62 | 0.02 | 0.01 | 0.01 | 0.04 | **209** | 0.002-0.26 |
| 3-Carene | 21 | 0.02 | 0.02 | 0.02 | 0.01 | 54 | 0.01-0.06 |
| 1,3,5-Trimethylbenzene | 60 | 0.08 | 0.03 | 0.03 | 0.21 | **272** | 0.01-1.39 |
| Benzaldehyde | 63 | 1.90 | 1.73 | 1.77 | 0.72 | 38 | 0.84-3.79 |
| Limonene | 21 | 0.04 | 0.02 | 0.03 | 0.07 | **172** | 0.01-0.35 |
| p-Cymene | 63 | 0.02 | 0.01 | 0.01 | 0.01 | 55 | 0.006-0.05 |
| Eucalyptol | 46 | 0.14 | 0.14 | 0.13 | 0.04 | 31 | 0.07-0.24 |
| 1,2,3-Trimethylbenzene | 39 | 0.04 | 0.01 | 0.02 | 0.10 | **240** | 0.01-0.54 |
| 1,4-Diethylbenzene | 46 | 0.06 | 0.01 | 0.01 | 0.24 | **387** | 0.004-1.48 |
| Phenol | 63 | 0.75 | 0.70 | 0.72 | 0.24 | 32 | 0.40-1.70 |
| Dihydromyrcenol | 62 | 0.03 | 0.01 | 0.02 | 0.06 | **181** | 0.003-0.41 |
| Nonanal | 63 | 0.41 | 0.33 | 0.37 | 0.24 | 58 | 0.17-1.43 |
| Acetophenone | 63 | 1.53 | 1.44 | 1.45 | 0.49 | 32 | 0.58-2.66 |
| L-Fenchone | 17 | 0.01 | 0.01 | 0.01 | 0.01 | 55 | 0.004-0.02 |
| n-Dodecane | 63 | 0.33 | 0.17 | 0.20 | 0.54 | **163** | 0.05-3.49 |
| (+)-Camphor | 50 | 0.06 | 0.05 | 0.06 | 0.03 | 50 | 0.04-0.17 |
| Decanal | 63 | 0.57 | 0.38 | 0.42 | 0.71 | **124** | 0.13-4.35 |
| Naphthalene | 63 | 0.08 | 0.03 | 0.04 | 0.25 | **311** | 0.01-1.94 |
| n-Tridecane | 63 | 0.31 | 0.21 | 0.24 | 0.31 | **99** | 0.06-2.04 |
| Benzothiazole | 63 | 0.44 | 0.32 | 0.35 | 0.49 | **112** | 0.12-3.86 |
| n-Tetradecane | 63 | 0.17 | 0.13 | 0.14 | 0.14 | **83** | 0.07-0.90 |

#### 4.2.2.2 Spatial Distribution of VOCs

Pollution maps were also prepared for each VOC which were observed insufficient numbers as a result of the summer sampling period using the MapInfo program. The most significant difference in the VOC distribution maps of the winter and summer seasons was detected in the Kartalkaya region. In Kartalkaya, an important winter tourism center of the city, lower VOC values were measured during the summer sampling period.

The pollution maps were divided into groups according to their similarities in distribution. The summer pollution distribution maps of some of the selected

VOCs belonging to each group were interpreted in this section. Distribution maps of other group members are presented in Appendix 3.

1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene, 1,2,3-trimethylbenzene, m-ethyltoluene, 1,4-diethylbenzene, tetradecane, dodecane and naphthalene similarly had a marked increase in the sampling points (points 1 and 34) close to the TEM highway (Figure 4.43).

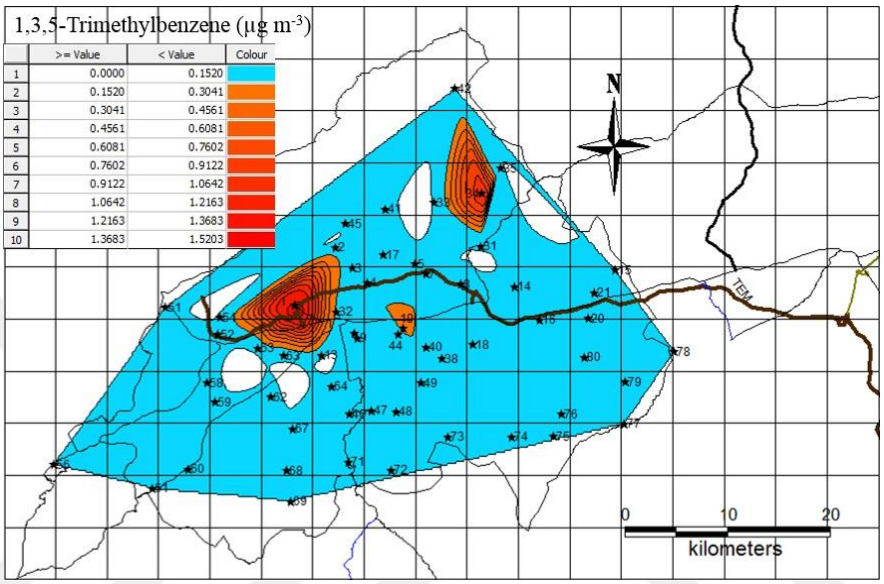


**Figure 4.43.** Pollution level distribution map of 1,3,5-trimethylbenzene for summer.

Xylene, ethylbenzene, toluene, n-propylbenzene, o-ethyltoluene, p-ethyltoluene, heptane, octane and tridecane which are important indicators of traffic emissions had similar trends. The compounds were found in higher concentrations in the city center and along with TEM and D-100 highways (7, 4, 1, 52 and 51 (Bolu mountain)) (Figure 4.44).

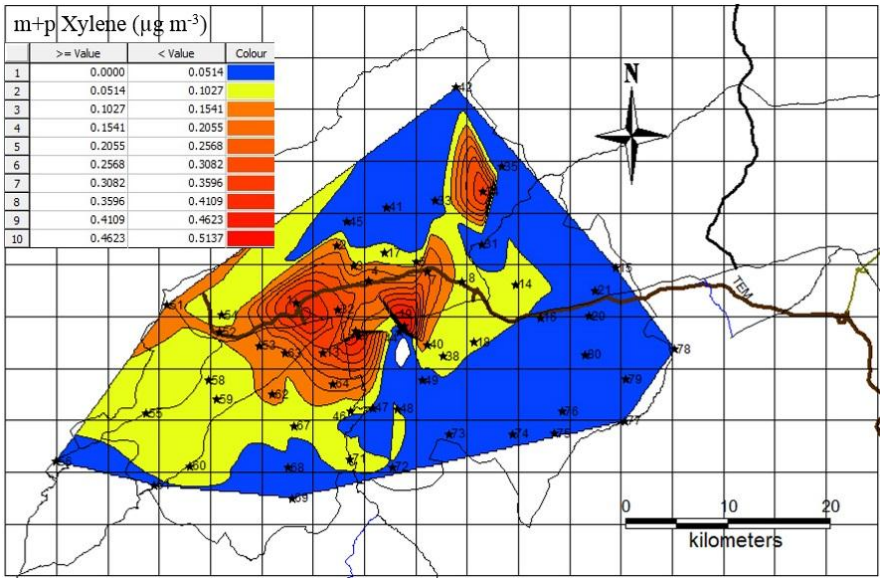


**Figure 4.44.** Pollution level distribution map of m, p xylene for summer.

Benzene, hexane, styrene, benzothiazole and chloroform were obtained in high concentrations in the sampling point 32 representing the city center and some points (79, 48, 53 and 52) (Figure 4.45).

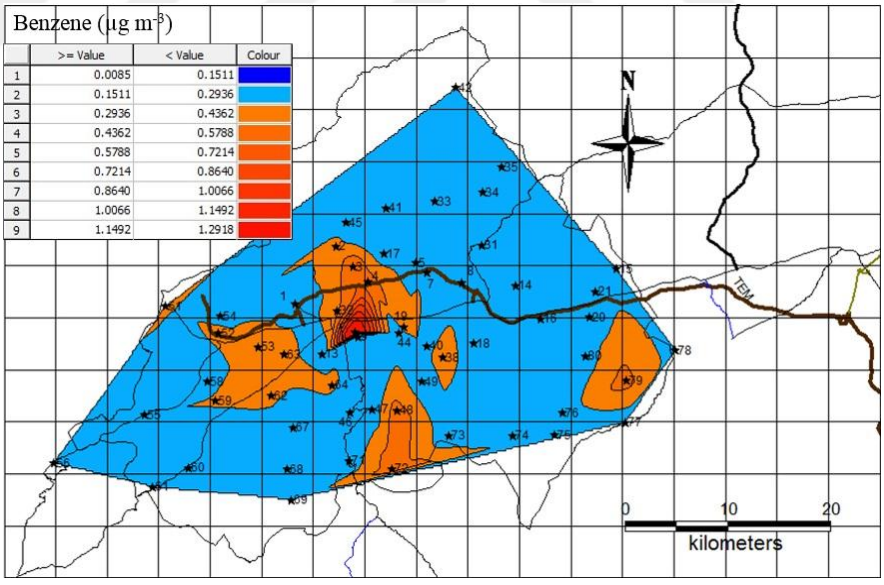


**Figure 4.45.** Pollution level distribution map of benzene for summer.

The university campus (point 53) and Abant had high levels of tetrachloromethane, phenol, benzaldehyde and acetophenone (Figure 4.46).

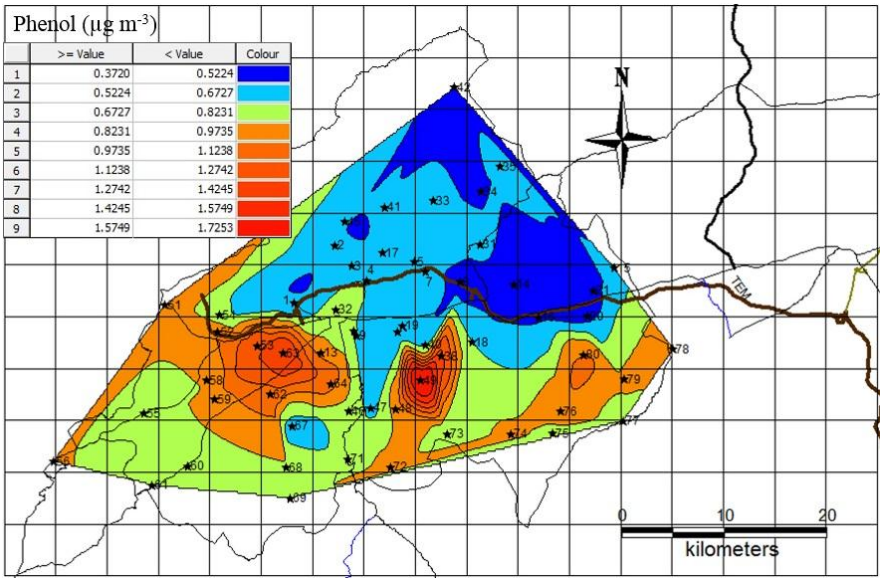


**Figure 4.46.** Pollution level distribution map of phenol for summer.

In summer, the major source of isoprene was biogenic emissions [123]. High levels of isoprene were obtained in the southern part of the city center that is rich in Pine species (Figure 4.47).

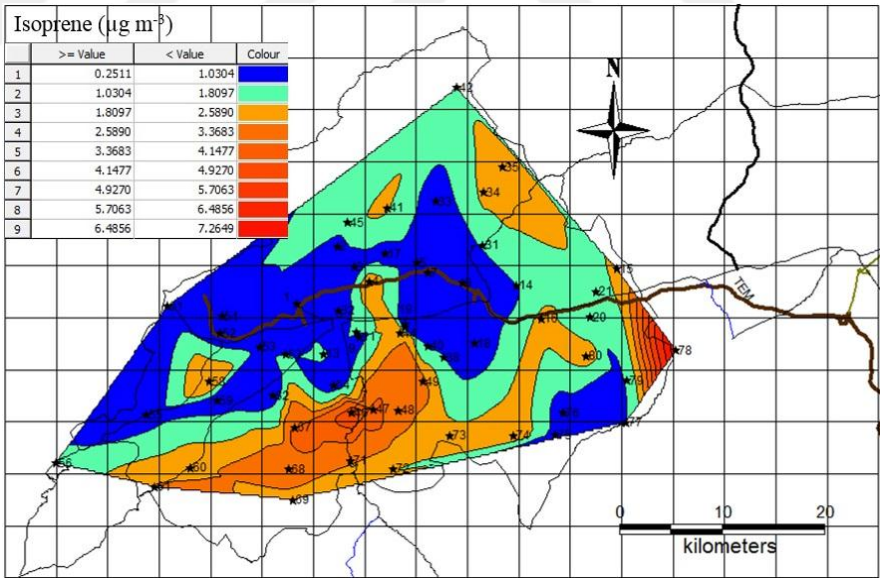


**Figure 4.47.** Pollution level distribution map of isoprene for summer.

Crotonaldehyde, hexanal, heptanal, decanal, 2-methylfuran and sabinene had high concentrations in the northern part of the city center where Beech is the dominant tree species and in villages which represent the emissions of Oak, Hornbeam, grass and grain [32, 34] (Figure 4.48).

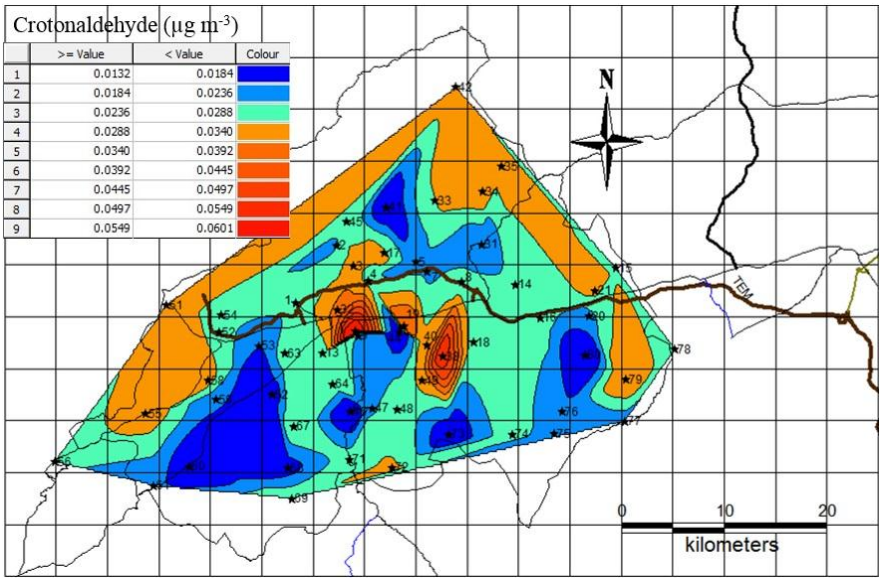


**Figure 4.48.** Pollution level distribution map of crotonaldehyde for summer.

Limonene levels were found to be higher in the city center where Hornbeam and Fir species are dominant (points 19, 12 and 1) and in the southern direction of Bolu reflecting the Juniper emissions (points 71 and 72) (Figure 4.49).

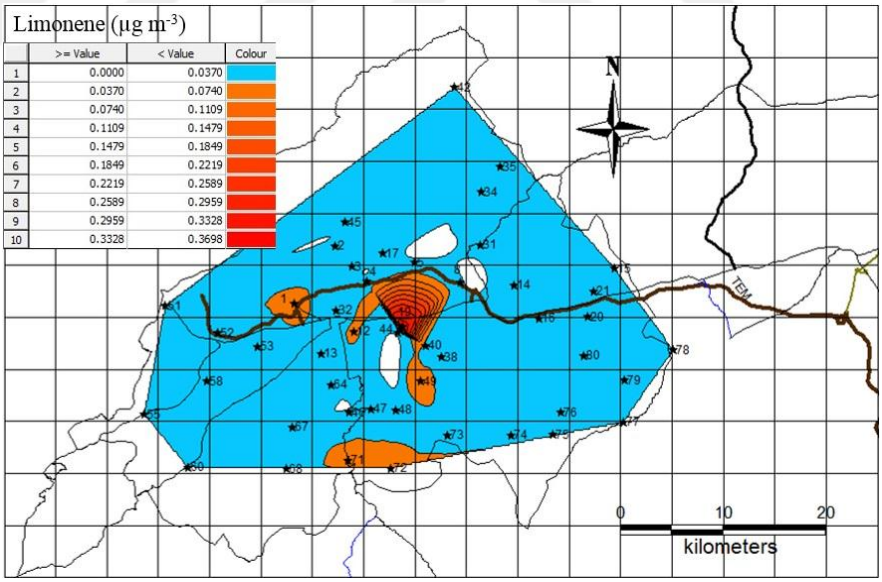


**Figure 4.49.** Pollution level distribution map of limonene for summer.

Pine and Hornbeam species are supposed to be effective in the distribution of alpha-pinene, 3-carene, p-cymene and camphene on the Bolu plateau [32]. Determination of high levels of these compounds in the southern region dominated by Scotch Pine and the inner part of Bolu, where Hornbeam is a common tree, and literature information coincides with each other (Figure 4.50).

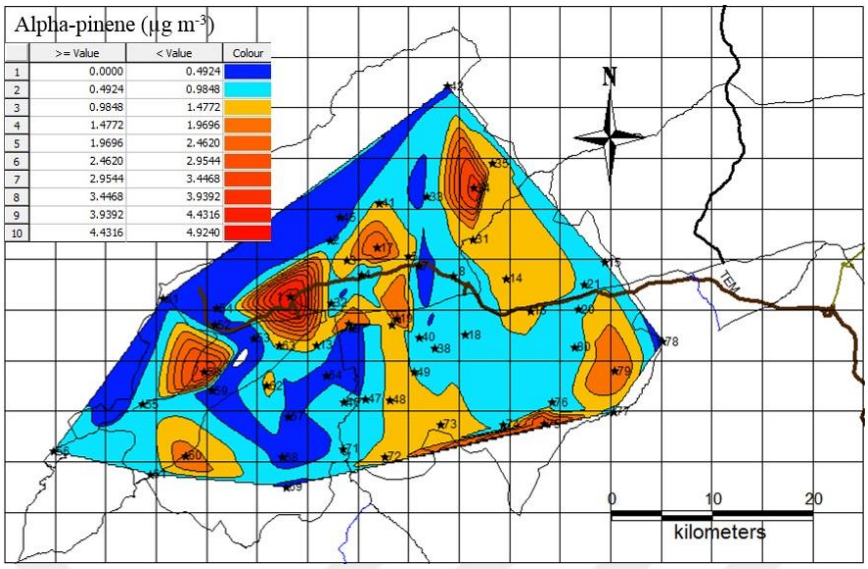


**Figure 4.50.** Pollution level distribution map of alpha-pinene for summer.

Eucalyptol is emitted mostly by Scotch Pine in addition to its high percentage emission by the trees of Black Pine and Fir [32]. This compound was determined in high concentrations in the southern part of Bolu where the Pine species are widespread and in the eastern part where Fir and Pine are dominant (Figure 4.51).

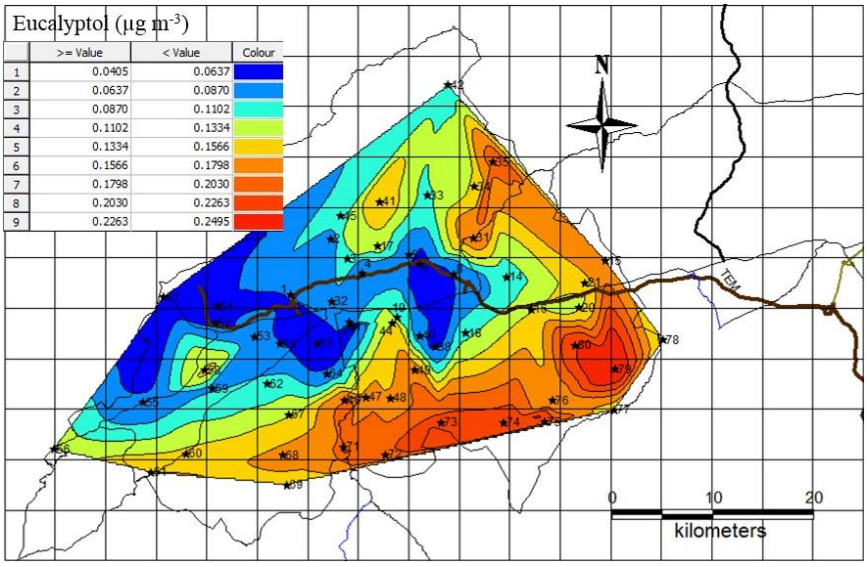


**Figure 4.51.** Pollution level distribution map of eucalyptol for summer.

Beta-pinene, isoprene and camphor are biogenic VOCs mostly emitted from Juniper and Scotch Pine. They were also obtained at high concentrations in the southern part of Bolu (Figure 4.52), where related tree species were common.

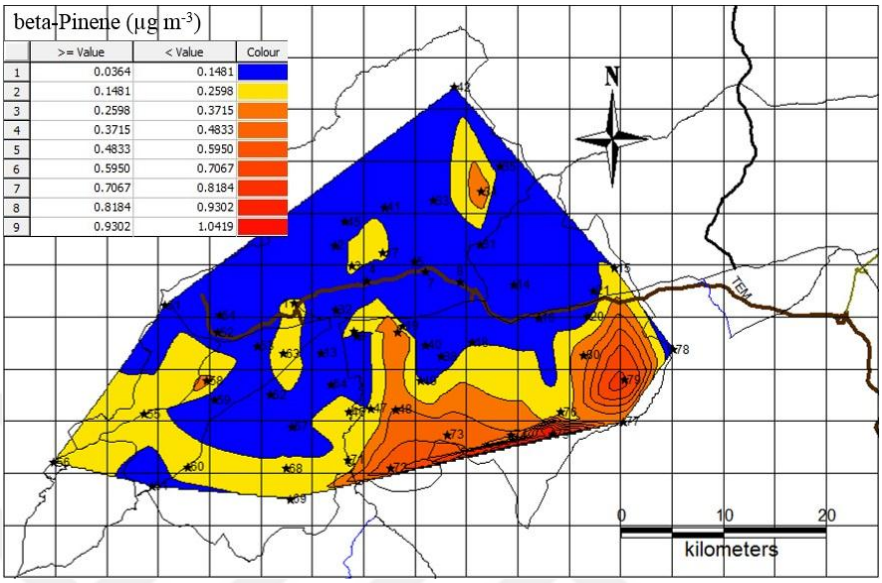


**Figure 4.52.** Pollution level distribution map of beta-pinene for summer.

### 4.2.3 Seasonal Variation

Generally, VOC concentrations were found to be higher in winter than in summer. In the Bolu plateau, decreasing the average mixing height to ~150 m in winter leads to pollutants accumulating in the atmosphere [124]. Moreover, low temperatures (-0.19 °C), low solar radiation (123 watt $m^{-2}$) and low wind speeds (1.15 m $sec^{-1}$) are found to be effective in high VOC concentrations obtained in winter.

As presented in Figure 4.53, some VOC species were at higher concentrations in winter while others were not. As a result, atmospheric concentrations of VOCs are not only dependent on meteorological factors but also the source strength is a determining parameter. Compounds that are particularly dependent on solvent evaporation and biogenic releases are at higher levels in summer than in winter. On the other hand, it is thought that VOCs, which are dominant in winter, is mostly caused by emissions from domestic heating.

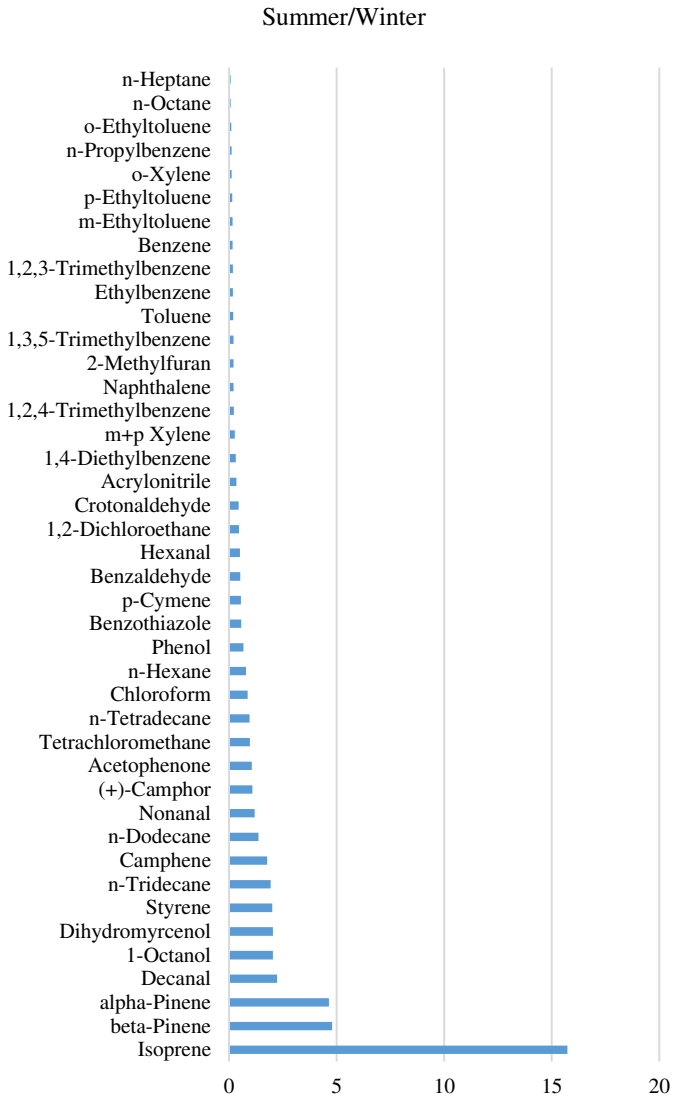


**Figure 4.53.** Winter to summer ratio of detected VOCs.

The contribution of biogenic VOCs to total concentrations was 9% in winter and 31% in summer (Figure 4.54). The increase in biogenic VOC percentage and diversity in summer is remarkable. Increased biogenic VOC percentage can be attributed to the increase in solar radiation (387 watt $m^{-2}$), temperature (19.9 °C) and amount of leafy tree species in summer [30].

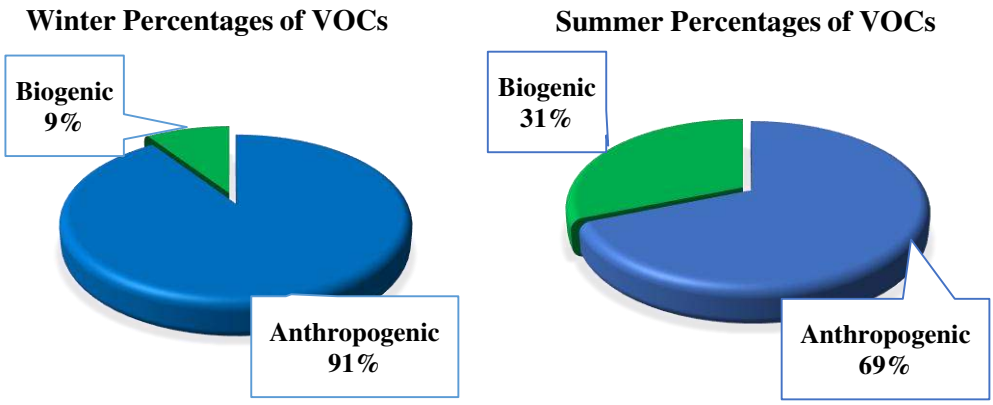


**Figure 4.54.** The percentage of the biogenic and anthropogenic compounds for both seasons.

### 4.2.4 Ozone Formation Potential (OFP)

The ozone formation potential (OFP) of VOCs is calculated based on the maximum incremental reactivity coefficient ($MIR_{coefficient}$) of each compound. The calculated OFPs of measured VOCs are listed in Table 4.8. The OFP values of species and the VOCs with the highest OFP differed in winter and summer.

**Table 4.8.** OFP values (μg $m^{-3}$) of VOCs determined in winter (N = 58) and summer (N = 63) samplings.

| | Winter (mean ± sd) | Summer (mean ± sd) |
|---|---|---|
| **Isoprene** | 0.88 ± 0.50 | 13.81 ± 10.60 |
| **n-Hexane** | 1.14 ± 0.99 | 0.89 ± 1.14 |
| **Benzene** | 0.75 ± 0.44 | 0.12 ± 0.06 |
| **n-Heptane** | 0.41 ± 0.24 | 0.02 ± 0.02 |
| **n-Octane** | 0.40 ± 0.25 | 0.03 ± 0.03 |
| **Toluene** | 6.46 ± 3.42 | 1.22 ± 0.89 |
| **Ethylbenzene** | 1.13 ± 0.63 | 0.19 ± 0.17 |
| **m+p Xylene** | 3.21 ± 2.07 | 0.86 ± 0.93 |
| **o-Xylene** | 5.02 ± 3.23 | 0.56 ± 0.56 |
| **Styrene** | 0.04 ± 0.06 | 0.08 ± 0.14 |
| **Alpha-pinene** | 0.71 ± 1.06 | 3.28 ± 2.69 |
| **n-Propylbenzene** | 0.24 ± 0.15 | 0.03 ± 0.04 |
| **1,2,4-Trimethylbenzene** | 0.82 ± 0.53 | 0.18 ± 0.48 |
| **beta-Pinene** | 0.16 ± 0.26 | 0.79 ± 0.68 |
| **1,3,5-Trimethylbenzene** | 3.84 ± 2.60 | 0.77 ± 2.12 |
| **1,2,3-Trimethylbenzene** | 1.52 ± 1.03 | 0.26 ± 0.73 |
| **Phenol** | 1.26 ± 0.98 | 0.84 ± 0.27 |
| **n-Dodecane** | 0.09 ± 0.06 | 0.12 ± 0.20 |

| | | |
|---|---|---|
| **Naphthalene** | 0.46 ± 0.39 | 0.09 ± 0.29 |
| **n-Tridecane** | 0.06 ± 0.02 | 0.11 ± 0.11 |
| **n-Tetradecane** | 0.06 ± 0.02 | 0.05 ± 0.04 |

The major contributors to ozone formation in the Bolu plateau are given in Figure 4.55. Toluene made the highest contribution (26 %) to the total OFP of measured VOCs in winter. OFP value of toluene was 6.46 ± 3.42 μg $m^{-3}$. It was followed by o-xylene (5.02 ± 3.23 μg $m^{-3}$), 1,3,5-trimethylbenzene (3.84 ± 2.60 μg $m^{-3}$) and m,p xylene (3.21 ± 2.07 μg $m^{-3}$). Moreover, 1,2,3-trimethylbenzene, phenol, hexane, ethylbenzene, isoprene and 1,2,4-trimethylbenzene were key species in ground-level ozone formation in winter. In winter, higher OFP values of vehicle-related and/or solvent-related AVOCs indicating that vehicle emissions and solvent evaporation had a great influence on the formation of ozone. While isoprene contributed low (3%) to ozone formation in winter, it had the highest OFP value (13.81 ± 10.60 μg $m^{-3}$) in summer. The fact that isoprene and alpha-pinene, among the BVOCs, contributed more than half (73%) of the total OFPs showed that biogenic emissions in summer significantly affected ozone formation. Isoprene, alpha-pinene, toluene, hexane, m/p-xylene, phenol, beta-pinene, 1,3,5-trimethylbenzene, o-xylene, and 1,2,3-trimethylbenzene were top ten OFP species in summer.

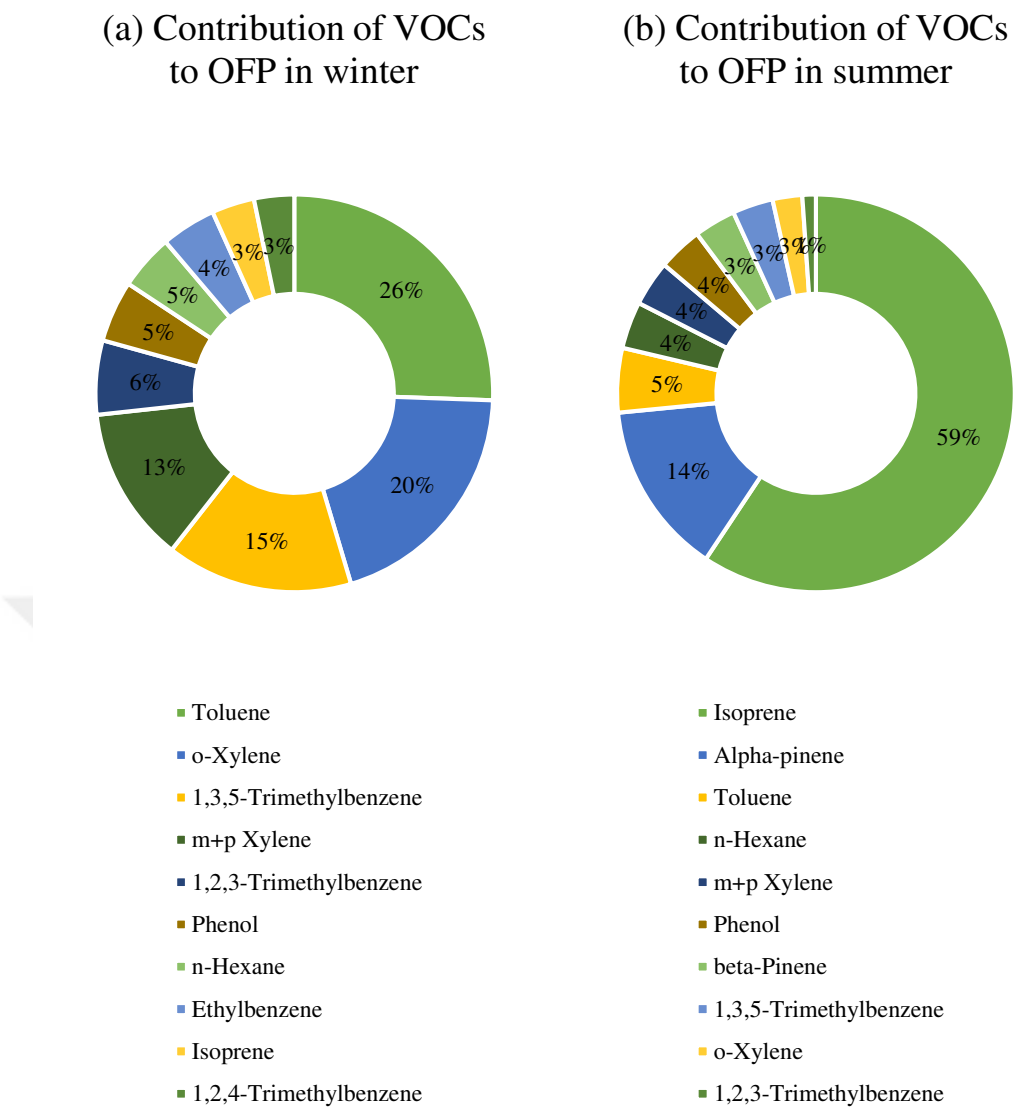


**Figure 4.55.** Top ten OFP species and their contributions to total for (a) winter and (b) summer.

The relationship between atmospheric ozone concentrations, the total ozone formation potential of VOCs and the corresponding meteorological conditions are examined in Figure 4.56 for both seasons. Ozone concentration was found to be higher in winter when the total OFP value of VOCs was higher. However, relatively lower values were expected in the winter period due to low temperature and solar radiation that play an active role in ozone formation. Nevertheless, in winter, in addition to the high OFP values, low mixing height may have enriched the ozone level in Bolu. In summer period sampling, ozone concentrations might have decreased in the long (15 days) waiting time due to high temperature and solar radiation.

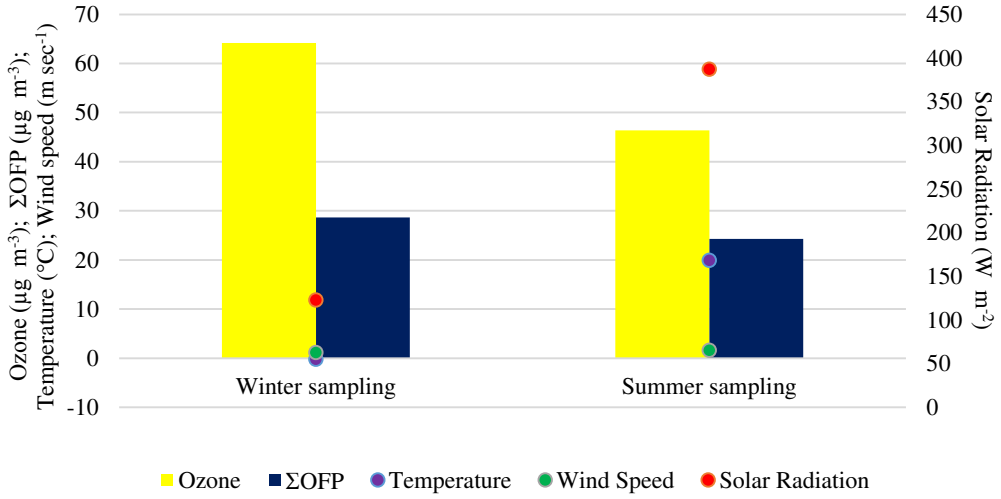


**Figure 4.56.** The relation of atmospheric ozone concentrations with OFP and meteorological parameters.

### 4.2.5 Source Apportionment

#### 4.2.5.1 VOC Ratios

Toluene-to-benzene (T/B) ratio for traffic emissions is in the range between 1.5 and 3, but non-traffic sources increase the ratio [106]. The average T/B ratio of the winter was 1.56 ±0.83 highlighting traffic emissions in the Bolu plateau. Moreover, the distribution of the T/B ratios is given in Figure 4.57. The highest T/B ratio (6.35) was observed at sampling point 30 (Sebenardı) indicating that there is a significant contribution of evaporative sources. On the other hand, lower T/B ratios (0.72 to 2) which are an indicator for traffic sources of toluene were obtained along TEM and D100 highways.

The m,p xylene to ethylbenzene (X/E) ratio is used to indicate the age of the sampled air. In winter, the X/E ratio was between 0.82 and 1.48 with an average value of 1.00 ±0.17. The distribution of X/E ratios given in Figure 4.57 revealed that higher values were obtained in the city center. This showed that the city center was affected by relatively fresh emissions. In addition, typically in rural areas, long-distance transport appeared to be more effective.

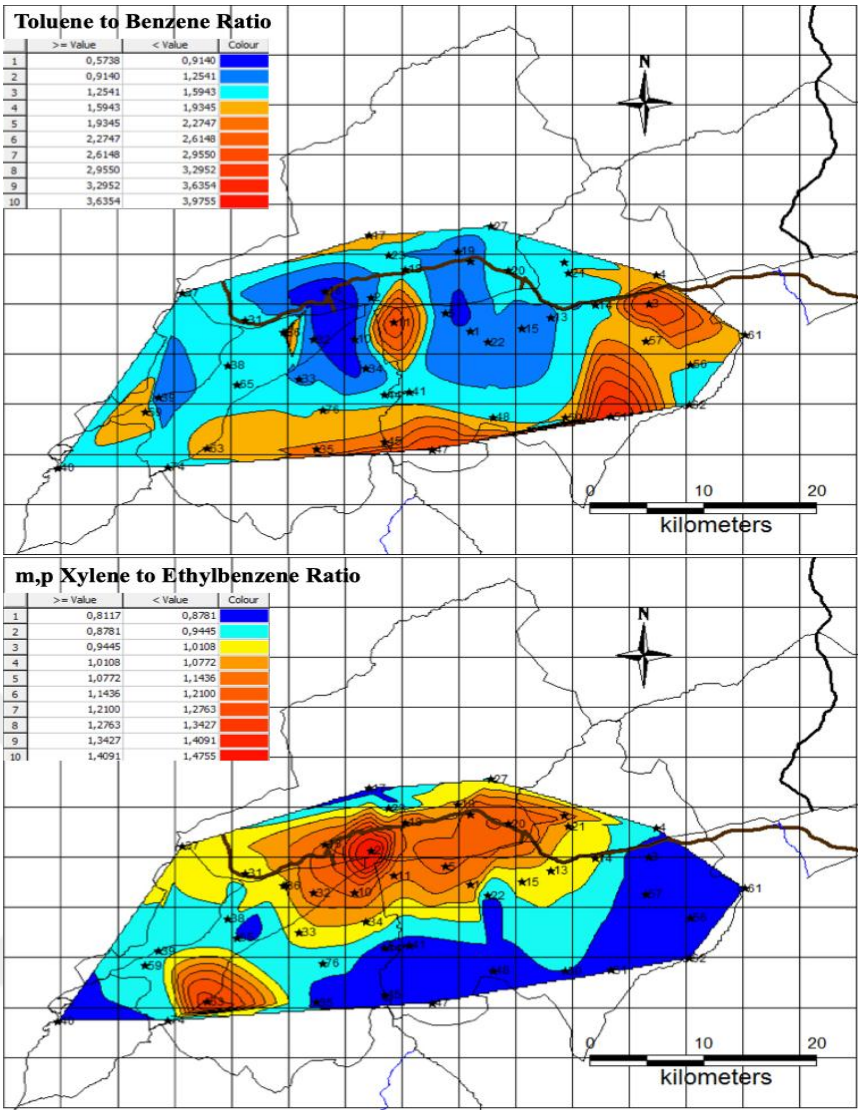


**Figure 4.57.** Distribution maps of T/B and X/E ratios for the winter.

The average T/B ratio of summer (1.5±0.69) was in a range representing traffic emissions. It demonstrates that there is a continuous traffic source in the Bolu plateau. Figure 4.58 represents the distribution of the T/B ratios of summer. The highest ratio (4.10) was obtained in sampling point 19 located in the city center. The distribution of high T/B ratios throughout the city center highlights important non-traffic sources such as evaporation from dyes and/or solvents. Besides, in most points in the city center (except for points 22 and 37) the ratio was found to be below 2.5.

For summer, the m,p xylene to ethylbenzene (X/E) ratio was between 0.14 and 2.33 with an average value of 1.46 ±0.37. The fact that the rates were slightly higher than in the winter (1.00±0.17) could be explained by the enhanced mixing

height in the summer preventing atmospheric accumulation and thus the effect of the relatively fresh emissions. The distribution of X/E ratios is also given in Figure 4.58. The higher values observed around the city center implying that the region was under influence of relatively fresh emissions whereas lower X/E ratios in rural indicate the transport of air mass to the regions from distant sources.

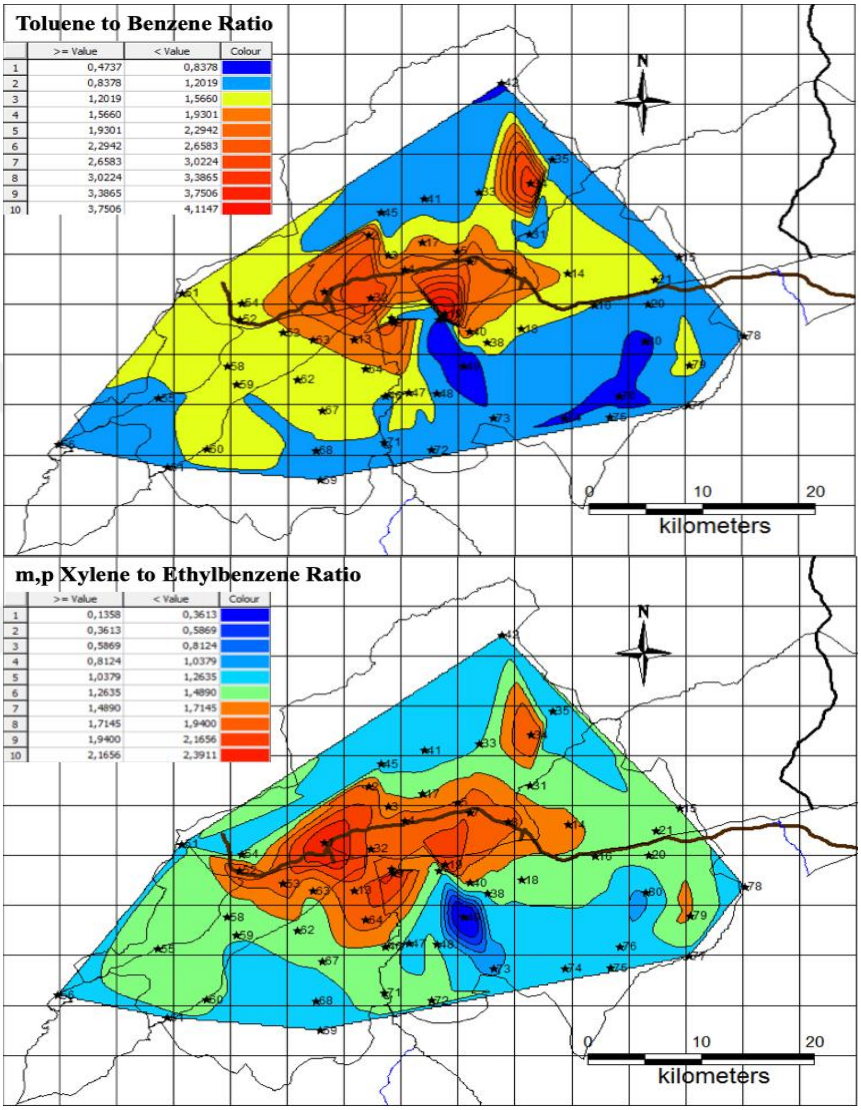


**Figure 4.58.** Distribution maps of T/B and X/E ratios for the summer.

### 4.2.5.2 Positive Matrix Factorization (PMF)

PMF study was primarily conducted separately for summer and winter periods. However, the small number of data used in each analysis led to some complex and indefinite factor solutions. Because a large number of samples should be used to make a realistic definition of resources, a new PMF analysis was performed by combining all data obtained from summer and winter passive

sampling. As a result, the factors were clearly resolved and the factors that could be named based on certain marker VOCs were obtained. $Q_{robust}$ and $Q_{true}$ values were found to be 7090 and 8680. VOC sources were explained with six factors (Figure 4.59).

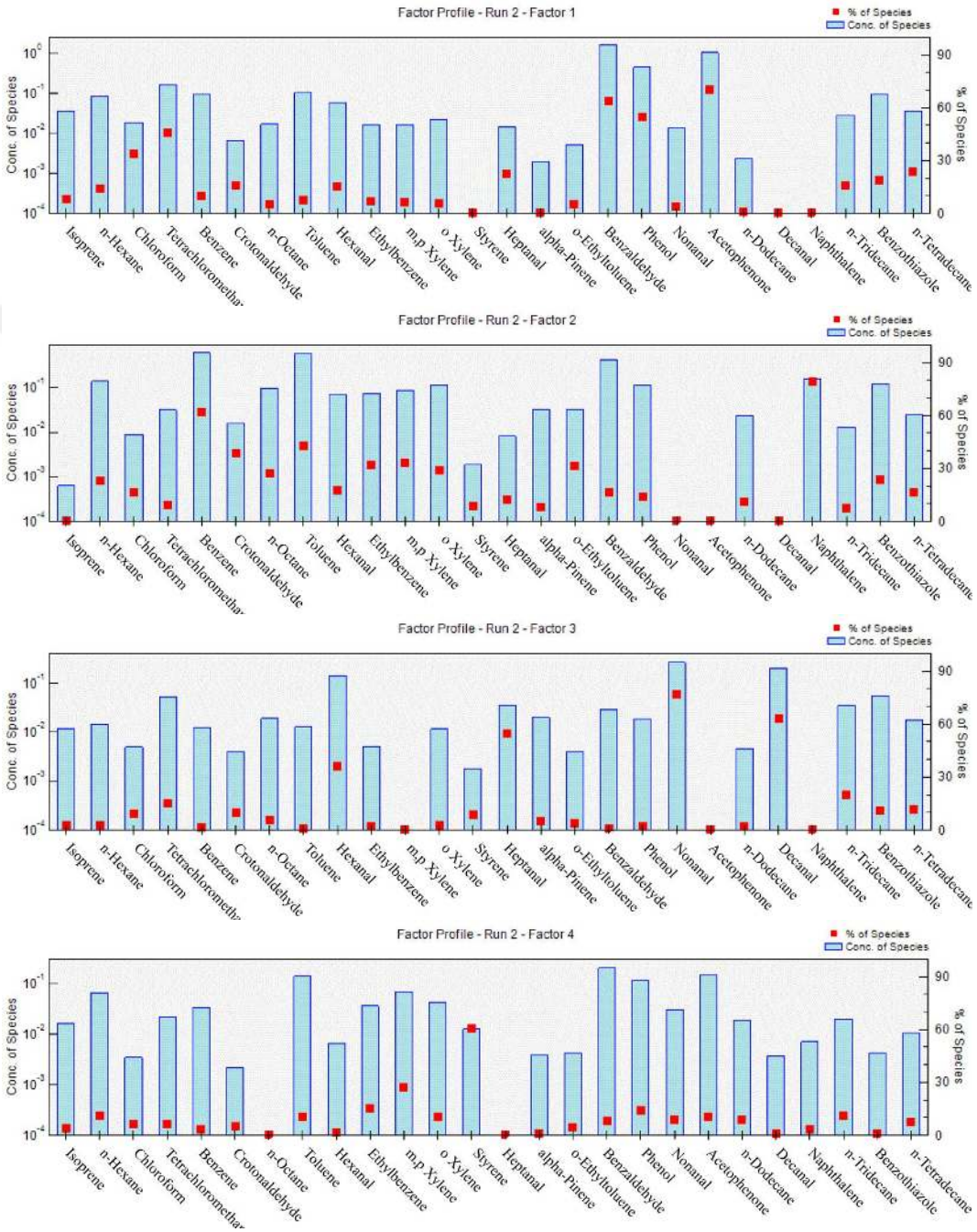


**Figure 4.59.** Factor profiles.

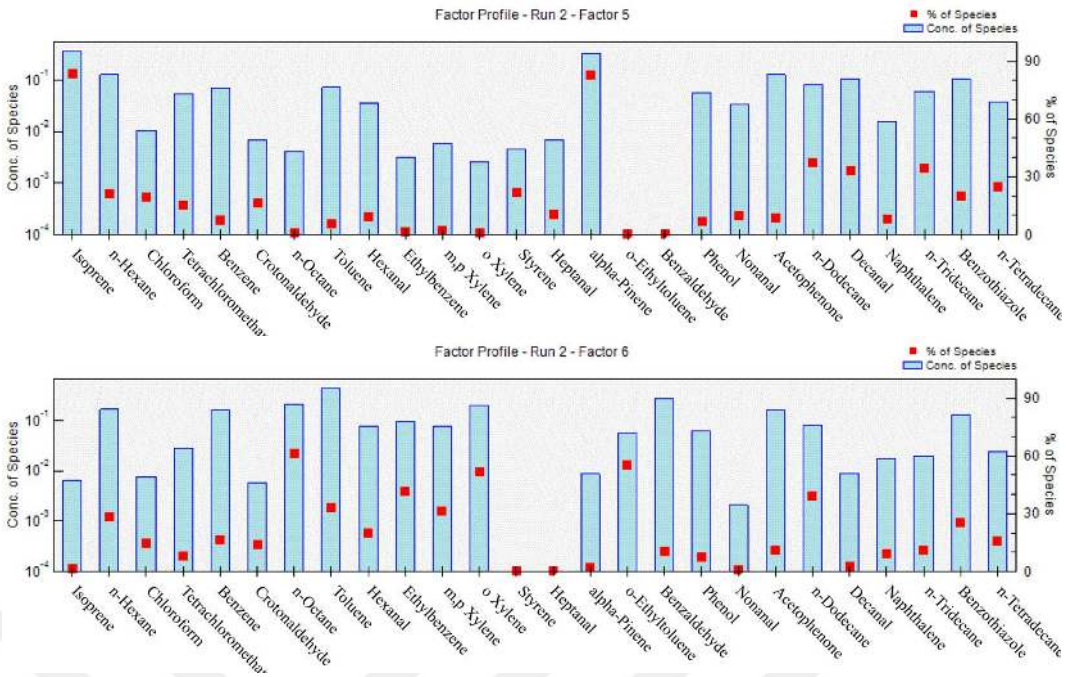


**Figure 4.59 (continued)** Factor profiles.

Potential sources of VOCs were determined as solvent evaporation, wood-coal combustion, biogenic emissions (pine/grain/grass), city atmosphere, biogenic emissions (hornbeam/pine /juniper) and vehicle emissions. Contribution of sources to the total was 31%, 22%, 8.0%, 8.0%, 13% and 18%, respectively (Figure 4.60). The compounds explained at least 20% in the factor are given in Table 4.9.

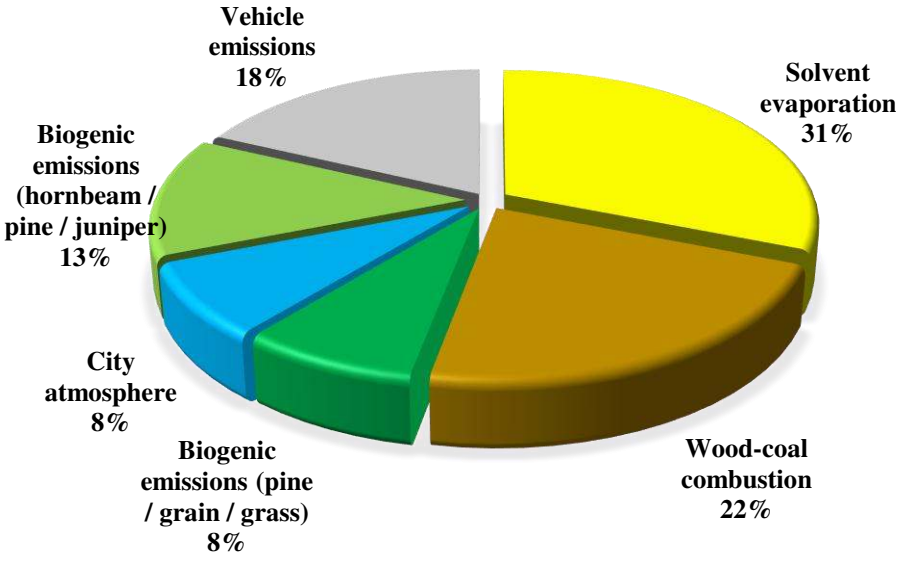


**Figure 4.60.** Source contributions to the VOC concentrations.

**Table 4.9.** PMF results of VOCs determined in passive sampling study (N = 44).

| Factors | VOCs | Source |
|---|---|---|
| **Factor 1** | acetophenone, benzaldehyde, phenol, tetrachloromethane, chloroform, heptanal, tetradecane, benzothiazole | Solvent evaporation |
| **Factor 2** | napthalene, benzene, toluene, crotonaldehyde, ethylbenzene, m,p-xylene, o-xylene, octane, ethyltoluene, benzothiazole, hexane | Wood-coal combustion |
| **Factor 3** | nonanal, decanal, heptanal, hexanal | Biogenic emissions (pine/grain/grass) |
| **Factor 4** | styrene, m,p-xylene | City atmosphere |
| **Factor 5** | alpha-pinene, isoprene, dodecane, decanal, tridecane, tetradecane, benzothiazole, styrene, hexane, chloroform | Biogenic emissions (hornbeam/pine/ juniper) |
| **Factor 6** | octane, o-xylene, o-ethyltoluene, ethylbenzene, dodecane, m,p-xylene, toluene, hexane, benzothiazole | Vehicle emissions |

In the first factor, VOCs with high explained percentages were acetophenone, benzaldehyde, tetrachloromethane, phenol and chloroform. It is known that these compounds are used as solvents in the laboratory/industry and even perfumes and other chemicals spreading to the atmosphere [109]. The G-score values of factor 1 are mapped in Figure 4.61. The highest values were obtained at the sampling points of BAIBU Gölköy Campus.

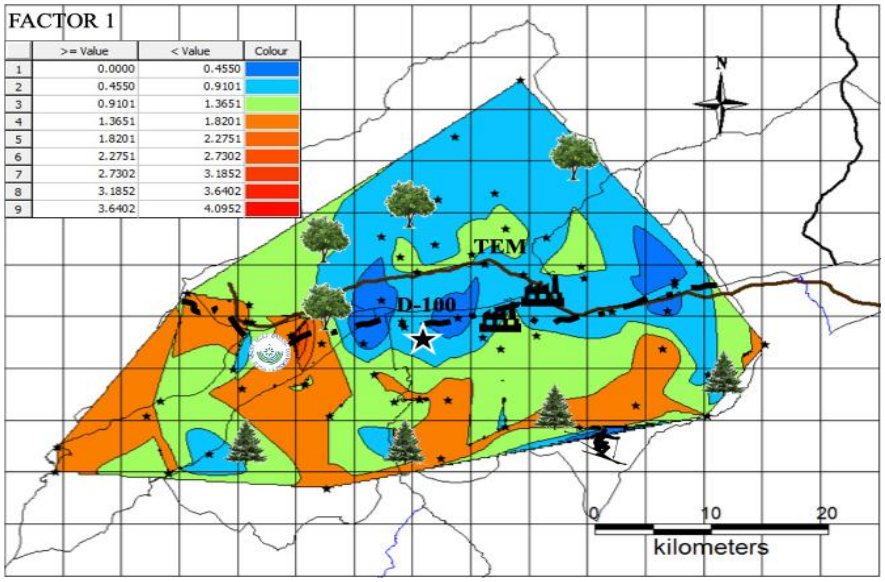


**Figure 4.61.** Passive sampling G-score distribution map of factor 1.

Factor 2 was named as wood-coal combustion factor. The second factor included high concentrations of naphthalene, benzene, toluene, ethylbenzene, crotonaldehyde, m,p-xylene, o-xylene, octane, benzothiazole, ethyltoluene. Naphthalene, benzene, toluene, ethylbenzene, m,p-xylene and o-xylene are compounds in the structure of coal and released as a result of combustion [37]. High G-scores were found in densely populated areas in factor 2 (Figure 4.62).

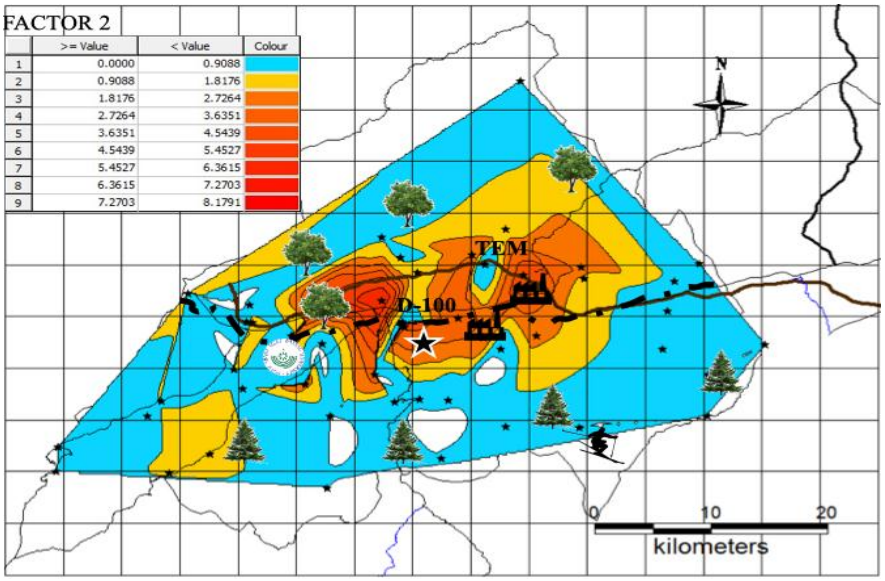


**Figure 4.62.** Passive sampling G-score distribution map of factor 2.

The third factor, which mainly contains decanal, nonanal, hexanal and heptanal compounds, can be called biogenic (pine/grain/grass) emissions. Pine, grass and several plants are known to be effective in the release of aldehydes into the atmosphere [34]. Isoprene has both anthropogenic and biogenic origins. High values in Figure 4.63 were obtained especially in the southern and northern regions of Bolu. Figure 3.2 showed that Pine species that are effective in the release of related compounds are commonly found in the southern regions of the Bolu plateau.

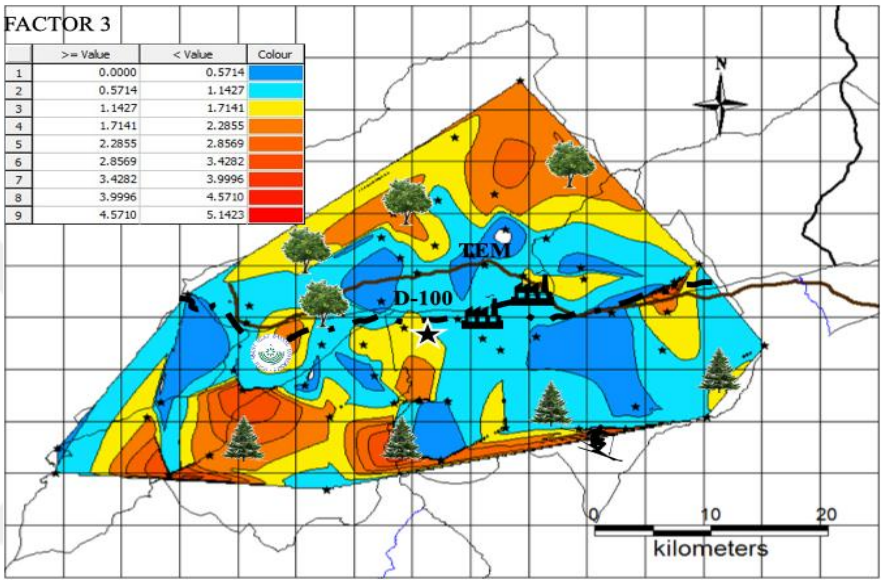


**Figure 4.63.** Passive sampling G-score distribution map of factor 3.

The high percentage of styrene is remarkable in factor 4. This compound is particularly spread through industrial processes in which styrene and its polymers are studied. Moreover, common usage of styrene products in urban areas leads to high styrene concentrations in the city atmosphere [125]. In Figure 4.64, the highest G-score values were obtained in the city center. Hence, factor 4 was called the city atmosphere.

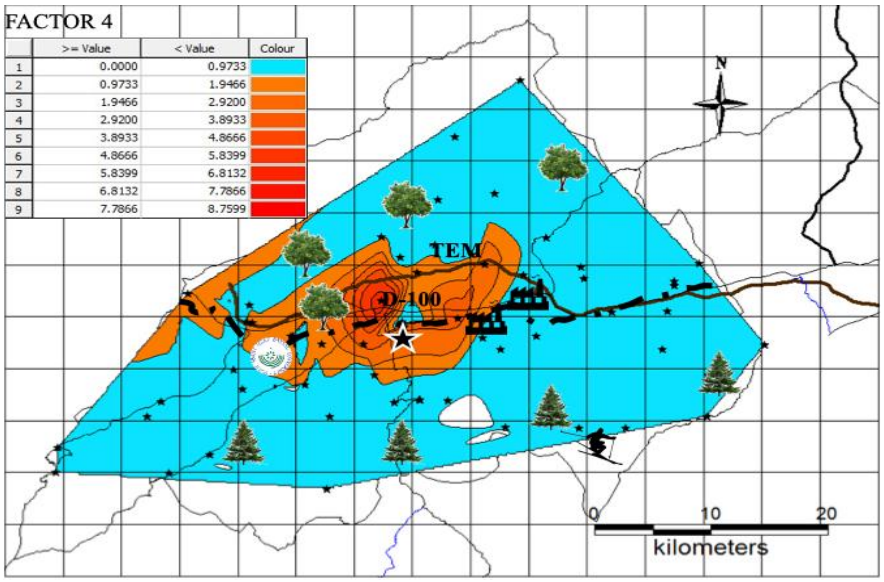


**Figure 4.64.** Passive sampling G-score distribution map of factor 4.

Alpha-pinene and isoprene had higher percentages in factor 5. It was indicated that Pine, Juniper and Fir species released a significant amount of alpha-pinene [32]. Isoprene is mostly emitted from the tree species of Oriental plane, Sessile Oak, Black Locust, European Aspen and Nordmann Fir [32]. Among these tree species, Pine, Hornbeam, Juniper and Fir are widespread in the sampling area. This factor was named as biogenic (hornbeam/pine/juniper). Higher G-score values were obtained in the northern and inland parts of the Bolu plateau in which the related tree species were common (Figure 4.65).

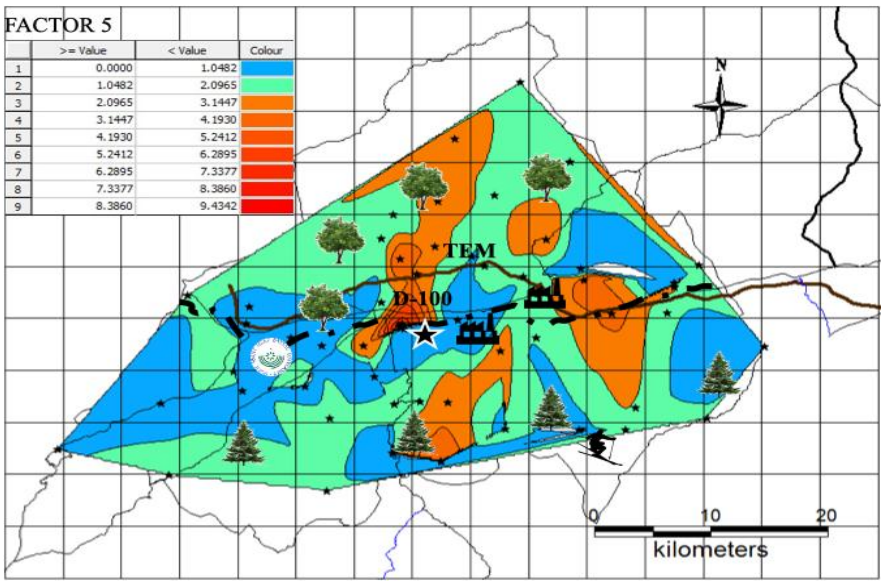


**Figure 4.65.** Passive sampling G-score distribution map of factor 5.

In the last factor, high contributions of compounds including octane, o-xylene, o-ethyltoluene, dodecane, m, p-xylene, toluene, hexane, ethylbenzene and benzothiazole were determined. Ethylbenzene, o-xylene, m, p-xylene, toluene and dodecane are identified as potential tracers for mobile sources [37]. In Figure 4.66, the highest value was observed around the Kartalkaya region.

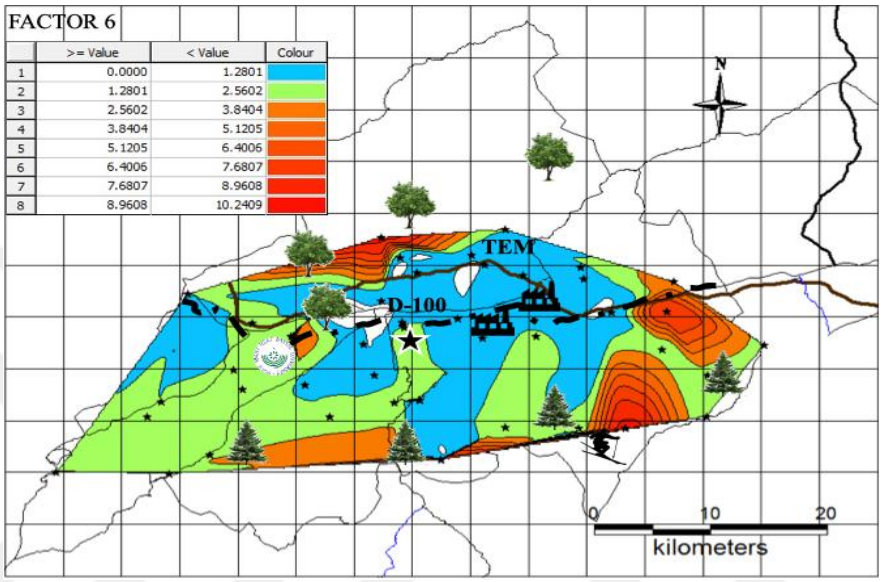


**Figure 4.66.** Passive sampling G-score distribution map of factor 6.

### 4.2.6 Comparison of Passive VOC Results with Literature

The comparison is limited to a small number of VOCs due to the lack of data in the literature. A total of 26 VOCs were examined in the comparison of passive sampling data in Table 4.10. Benzene, which was added to the harmful air pollutants list by US EPA, was obtained in lower concentration in the present study compared to the studies carried out in urban and industrial areas. Also, the concentrations of compounds including toluene, ethylbenzene, m,p xylene and o-xylene were found to be lower in the Bolu atmosphere. All -methyl, −ethyl and -propyl substituted benzene and toluene compounds and dodecane had higher concentrations than the present study in other studies except for the Düzce study [62]. Heptane and octane which are the compounds generally found to be associated with fossil fuel combustion [62], were ~2 to 25 fold lower than the studies performed in industrial and urban areas [40, 121]. Compared to the study conducted in Düzce, which was comparable in terms of industrialization and population, it was

thought that coal consumed for domestic heating in the winter period in Bolu caused higher heptane and octane concentrations. Chloroform and chlorobenzene, whose presence in the atmosphere are based on solvent evaporation, were detected approximately 2-50 times more in the Aliağa industrial zone and capital Ankara, as expected, but surprisingly, the hexane concentration in Bolu was higher than Ankara and Düzce. Isoprene which is a compound having both anthropogenic and biogenic origin, was found lower concentrations in winter in Bolu compared to the study performed in Düzce. However, the concentration of isoprene in the Bolu atmosphere was approximately 10 times higher during the summer period. A higher percentage of forest areas in Bolu (64%) than in Düzce (50%) is thought to be effective in the amount of released biogenic VOC.

**Table 4.10.** Comparative analysis of passive sampling VOC results (μg $m^{-3}$).

| Compound | Düzce, Turkey [62] (urban, industrial, rural) | | Ankara, Turkey [126] (semi-urban) | Aliaga, Turkey [40] (industrial, urban) | Pinheiros, Brazil [121] (urban) | Estarreja, Portugal [127] (industrial) | Bolu, Turkey (urban, semi-urban, rural) | |
|---|---|---|---|---|---|---|---|---|
| | October - November 2014 | August 2017 | May 2010 - February 2011 | July - January 2009 | Spring 2004 - 2005 | June 2012 | January-February 2017 | July 2017 |
| Isoprene | 0.14±0.08 | 0.11±0.01 | | | | | 0.10±0.06 | 1.52±1.17 |
| n-Hexane | 0.68±0.78 | 0.24±0.40 | 0.91±0.72 | | 3.98 | | 1.15±1.00 | 0.91±1.16 |
| Chloroform | | | | 0.4±0.9 | | | 0.07±0.03 | 0.06±0.06 |
| Benzene | 4.64±2.42 | 0.74±0.24 | 2.6±3.3 | 2.7±4.1 | 2.02 | 0.87 | 1.75 ±1.06 | 0.29±0.15 |
| Heptane | 0.37±0.19 | 0.23±0.08 | | 4.6±17.5 | 2.48 | | 0.51 ±0.29 | 0.03±0.02 |
| n-Octane | 0.62± .36 | 0.25±0.14 | 1.3±0.55 | 1.7±8.0 | 1.28 | | 0.66 ±0.41 | 0.06±0.06 |
| Toluene | 6.75±6.39 | 1.32±0.80 | 19±18 | 7.7±26.8 | 15.8 | 3.3 | 2.38 ±1.27 | 0.45±0.33 |
| Chlorobenzene | | | 0.45±0.26 | 0.02± 0.01 | | | 0.01±0.01 | |
| Ethylbenzene | 1.08±1.00 | 0.39±0.66 | 1.3±0.7 | 0.6±1.6 | 3.19 | 0.2 | 0.42±0.23 | 0.07±0.0 6 |
| m+p Xylene | 1.51±1.53 | 0.53±0.69 | 5.9±2.8 | 2.8±5.8 | 6.31 | 0.7 | 0.43±0.28 | 0.12±0.13 |
| o-Xylene | 1.02±1.02 | 0.40±0.49 | 1.0±0.6 | 0.7±1.7 | 2.52 | 0.2 | 0.77±0.49 | 0.09±0.09 |
| Styrene | 0.49±0.74 | 0.17±0.36 | 2.4±3.5 | 0.6±4.4 | 1.39 | | 0.02±0.03 | 0.04±0.06 |
| Alpha-pinene | | | | | | 1.2 | 0.21±0.32 | 1±0.82 |
| Isopropylbenzene | 0.08±0.04 | 0.08±0.02 | 0.15±0.07 | 0.1±0.2 | | | 0.06±0.04 | 0.01±0.01 |
| n-Propylbenzene | 0.20±0.17 | 0.11±0.06 | 3.2±2.2 | 0.1±0.4 | | | 0.11±0.07 | 0.01±0.02 |
| m-Ethyltoluene | 1.14±0.56 | 0.93±0.88 | 1.1±0.7 | 0.4±1.2 | | | 0.26±0.16 | 0.04±0.10 |
| p-Ethyltoluene | 1.21±0.82 | 0.12±0.07 | 0.19±0.08 | 0.2±0.5 | | | 0.10±0.06 | 0.01±0.03 |
| 1,2,4-Trimethylbenzene | 0.38±0.41 | 0.25±0.12 | 0.31±0.12 | 0.2±0.5 | 2.59 | | 0.09±0.06 | 0.02±0.06 |
| Beta-Pinene | | | | | | 0.2 | 0.04±0.06 | 0.18±0.16 |
| o-Ethyltoluene | 0.24±0.13 | 0.18±0.07 | 0.69±0.31 | 0.2±0.5 | | | 0.20±0.13 | 0.02±0.04 |
| 1,3,5-Trimethylbenzene | 0.24±0.30 | 0.52±0.28 | 0.66±0.29 | 0.6±1.6 | 0.85 | | 0.38±0.26 | 0.08±0.21 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Limonene | | | | | | 0.2 | 0.02±0.03 | 0.04±0.07 |
| 1,2,3-Trimethylbenzene | 0.22±0.15 | 0.23±0.15 | 0.66±0.33 | 0.2±0.5 | | | 0.17±0.11 | 0.04±0.10 |
| 1,3-Diethylbenzene | | | | 0.1±0.1 | | | 0.02±0.01 | |
| 1,4-Diethylbenzene | | | | 0.1±0.1 | | | 0.19±0.13 | 0.06±0.24 |
| n-Dodecane | 0.59±1.00 | 0.67±1.21 | 2.0±1.5 | | | | 0.24±0.14 | 0.33±0.54 |

# 5. CONCLUSIONS AND RECOMMENDATIONS

## 5.1 Conclusions

The main purpose of the present study was to examine VOC sources and temporal (annual, seasonal, intraday and interday) variations of VOCs in the Bolu plateau. Two sampling techniques (active sampling and passive sampling) were performed within the scope of the thesis. At our station on the university campus, 68 VOCs for every month between April - November 2017 and January 2018 and 70 VOCs for every month between April - August 2018 were collected with active sampling in daily and 6-hour periods. The passive sampling technique applied simultaneously at multiple sampling points was very effective in determining the pollutant distribution on the plateau. Along the Bolu plateau, the passive sampling was performed at 47 sampling points in winter (28 January 2017-12 February 2017) and 63 sampling points in summer (7 July 2017-23 July 2017).

VOC concentrations in the Bolu atmosphere were generally found to be lower than those expressed for urban and semi-urban areas in active sampling. In addition, it was determined that VOCs did not reach critical levels in all sampling periods. Considering that the limit value for benzene was 5 μg $m^{-3}$, the average concentration of benzene was found to be well below the limit value.

During all sampling periods performed at the active sampling station, hexanal attracted attention as the compound with the highest average concentration. This compound was followed by nonanal, hexane and isoprene. The difference between hexanal and the compound with the second highest concentration was about 1.5-15 fold, while the difference between the remaining compounds was quite small. Higher hexanal levels are thought to indicate strong emissions of Oak, which is commonly found around the campus. Moreover, benzaldehyde, toluene, benzene, hexane, heptane, octane, phenol, isoprene and alpha-pinene were found in higher concentrations.

VOC concentrations detected in 2017 were mostly lower than in 2018. The high temperature and solar radiation observed during the May-August 2018 sampling were particularly effective in the release of volatile organic compounds released from biogenic sources and/or solvent evaporation. On the contrary, dodecane, octane and chloroform, which were at higher levels in 2017, it was

observed that the source strength was more dominant than the meteorological parameters.

In the inter-day evaluation, it was determined that anthropogenic VOCs had higher concentrations during the weekdays. However, the sampling period of 2017, when the ÖSYM exams were held at weekends, was not included in this assessment.

Intraday distributions of compounds differed significantly between 2017 and 2018. In 2017, most compounds of both anthropogenic and biogenic origin were found at higher levels during the daytime hours (11:00 - 17:00) when temperature and solar radiation reached their maximum. In 2018, the levels of some VOCs reached their lowest between 11:00 and 17:00, increased between 17:00 and 23:00 and then decreased gradually. This trend has been accepted as an indicator of photochemical reactions during daytime hours. The increasing atmospheric values of the isoprene oxidation compounds (methachrolein and methylvinylketone) just after midday (17:00 and 23:00) indicated that they were formed as a result of photodegradation reactions of isoprene in 2018.

The ozone formation potential (OFP) has been used to determine the contribution of VOCs to ozone formation at ground level. Under higher temperature, solar radiation and OFP, the highest ozone levels were found in the period April-August 2018 (0.008 $\mu g\ m^{-3}$ - 7.48 $\mu g\ m^{-3}$). Isoprene was the compound with the highest ozone formation potential in September-November 2017 and January 2018 (0.73 ± 0.51 $\mu g\ m^{-3}$) and April-August 2018 (7.48 ± 8.80 $\mu g\ m^{-3}$). Differently, hexane was the compound with the highest OFP (0.45 ± 0.40 $\mu g\ m^{-3}$) in April-August 2017. Isoprene and hexane, which have been identified as the most reactive species, should be taken into account to develop an effective strategy for ozone reduction.

The T/B and X/E ratios were examined to provide a prediction for the source apportionment studies. In the period including April-August 2017, T/B ratios varied between 0.41 and 4.18 with an average value of 1.05 ±0.65. This indicated that VOCs were mostly emitted from vehicle emissions. In the September-November 2017 and January 2018 period, T/B ratios averaged 0.93 ±0.27, representing vehicle emissions. However, the average T/B ratio above 3.0 (6.28 ± 4.03) in April and August 2018 indicated the presence of a non-traffic source for toluene. In addition to toluene, which acts as an indicator for non-traffic sources, the presence of other VOCs emitted from non-traffic sources during this period was thus recognized.

Also, considering the average X/E ratios (1.66 ±0.21 for April-August 2017, 1.45 ±0.12 for September-November 2017 and January 2018 and 1.49 ±0.15 for April and August 2018), it was concluded that there was an old air mass transferred from remote sources to the sampling station.

PMF analysis was used to perform source apportionment on active sampling data. For the April-August 2017-January 2018 period, potential sources of VOCs were determined as solvent evaporation, gasoline-powered vehicle emissions, fossil fuel (domestic heating), biogenic emissions (hornbeam/grass/oak/beech), diesel/domestic activities and forested city atmosphere. When the PMF analysis was applied on the VOC data of April-August 2018, solvent evaporation 1/vehicle emissions, secondary photochemical formation/background, solvent evaporation 2, biogenic emissions (hornbeam/pine/juniper), wood-coal-biomass burning and biogenic emissions (oak/pine/juniper/grain/grass) were identified as potential sources. Finally, for the entire active sampling period, potential sources of VOCs were determined as solvent evaporation/vehicle emissions, wood-coal-biomass burning, forested city atmosphere, fossil fuel burning (domestic heating), biogenic emissions (oak/pine/juniper/grain/grass) and mixed sources.

VOC concentrations in the Bolu plateau were generally lower than those expressed for urban and semi-urban areas in passive sampling. In addition, it was determined that VOCs did not reach critical levels in all sampling periods. Considering that the limit value for benzene was 5 $\mu g\ m^{-3}$, even the highest benzene concentration (4.55 $\mu g\ m^{-3}$) was below the limit value.

In winter, anthropogenic VOCs with high concentrations were benzaldehyde, toluene, benzene and acetophenone whereas benzaldehyde, acetophenone and isoprene were higher in summer in passive sampling. Alpha-pinene, hexanal, nonanal, decanal were the biogenic VOC obtained in higher concentrations in the Bolu plateau for both seasons.

Generally, VOC concentrations were found to be higher in winter than in summer in passive sampling. Variations in meteorological parameters including low mixing height, low temperatures, low solar radiation and low wind speeds were found to be effective in high VOC concentrations obtained in winter. However, not all VOCs decreased at the same level in the summer, and summer concentrations were higher for some VOCs. This draws attention to another parameter, source strength, which determines atmospheric concentrations of VOCs. It was found that

compounds that were particularly dependent on solvent evaporation and biogenic releases were at higher levels in summer than in winter. On the other hand, VOCs, which were dominant in winter, were mostly released from domestic heating.

Pollution maps were drawn for each of the identified VOCs using MapInfo. All -methyl, −ethyl and -propyl substituted benzene and toluene compounds and xylenes were obtained in the higher concentration at the sampling points representing the city center and along TEM and D-100 highways. The higher concentrations of benzene, styrene, hexane, phenol and naphthalene were found in the city center, organized industrial zone and areas including various factories. Solvent-related species such as benzaldehyde, acetophenone, chlorobenzene, tetrachloromethane, 1,2-dichloroethane and chloroform were at higher levels on the university campus. Solvents released from university labs were considered to be the effective source for these compounds. For isoprene, both biogenic and anthropogenic sources were estimated to be effective because the higher isoprene concentrations were determined in the city center and the southern part of the city center. Biogenic VOCs such as crotonaldehyde, 2-methylfuran, p-cymene and m-cymene had higher concentrations at the northern part of Bolu where Oak and Hornbeam are widespread. On the other hand, alpha-pinene and beta-pinene, camphene and camphor were determined in high concentrations at the southern part of Bolu where Pine and Juniper tree species were the dominant ones.

The ozone formation potential (OFP) of VOCs was calculated based on the MIR method. Ozone concentration was found to be higher in winter when the total OFP value of VOCs was higher. Toluene made the highest contribution (26 %) to the total OFP of measured VOCs in winter. Moreover, o-xylene, 1,3,5-trimethylbenzene, m,p xylene, 1,2,3-trimethylbenzene, phenol, hexane, ethylbenzene, isoprene and 1,2,4-trimethylbenzene were the key species in ground-level ozone formation in winter. In winter, higher OFP values of vehicle-related and/or solvent-related AVOCs indicating that vehicle emissions and solvent evaporation had a great influence on the formation of ozone. While isoprene contributed low (3%) to ozone formation in winter, it had the highest OFP value ($13.81 \pm 10.60$ μg $m^{-3}$) in summer. The fact that isoprene and alpha-pinene, among the BVOCs, contributed more than half (73%) of the total OFPs showed that biogenic emissions in summer significantly affected ozone formation. Isoprene, alpha-pinene, toluene, hexane, m/p-xylene, phenol, beta-pinene, 1,3,5-

trimethylbenzene, o-xylene, and 1,2,3-trimethylbenzene were top ten OFP species in summer.

The T/B and X/E ratios provide an idea about possible pollutant sources for passive sampling. The average T/B values both in winter (1.56 ± 0.83) and in summer (1.5 ± 0.69) were found in a range representing traffic emissions. While the average X/E value in winter was 1.00 ± 0.17, it was obtained as 1.46 ± 0.37 in summer. The fact that both values were below the limit indicated the effect of an old air mass in the Bolu atmosphere. Possible pollutant accumulation due to the bowl-like topography of Bolu or the airflow coming from long-distance was the main reason for the lower X/E values. In addition, the relatively higher X/E value in summer could be explained by well mixing of atmospheric pollutants with increasing mixing height and thus the effect of relatively fresh emissions.

For the entire passive sampling period, PMF analysis was performed by combining all data. Potential VOCs sources in the Bolu plateau were identified as solvent evaporation, wood-coal combustion, biogenic emissions (pine/grain/grass), city atmosphere, biogenic emissions (hornbeam/pine/ juniper) and vehicle emissions.

## 5.2 Recommendations for Future Work

1. This study, in which the air quality in Bolu is evaluated depending on a large number of VOCs, should be implemented regularly for other cities.
2. In this study, active sampling was carried out in 6-hour periods per day. This wide time interval lead to the missing points in the evaluation of intraday variation of VOCs. Therefore, there have to be VOC measurements on an hourly basis for a good representation.
3. In this study, PMF analysis was applied to data sets to determine potential sources of VOCs in the Bolu atmosphere. However, in PMF analysis, some factors could not be clearly distinguished and exact sources could not be determined. To determine the source profiles of VOCs, samples need to be collected with chassis dynamometer measurements (for mobile sources), laboratory or industrial facility ambient air measurements (for solvent evaporation) and specific dynamic enclosure systems (for biogenic sources).

4. A health risk assessment study was not applied in this study. Hence, it is recommended to evaluate a health risk assessment study involving as many VOCs as possible.
5. For many of the VOCs in the literature, there are no MIR values to calculate OFP values. However, in this study hexanal are among the highest concentration and its role in the ozone-forming potential is not known. To calculate MIR values, chamber experiments are needed.

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# 7. APPENDICES

## APPENDIX 1 Descriptive statistical parameters for VOCs determined by active sampling

**Table 1.1.** Descriptive statistical parameters for VOCs determined by April 2017 sampling (µg $m^{-3}$).

| Compound | Number of samples (N) | Average | Median | Geometric mean | Standard deviation | Coeff. of variation (CV) | Min-Max |
|---|---|---|---|---|---|---|---|
| **Isoprene** | 8 | 0.0091 | 0.0062 | 0.0072 | 0.0067 | 74 | 0.0023-0.0231 |
| **Acrylonitrile** | 2 | 0.0025 | 0.0025 | 0.0022 | 0.0017 | 69 | 0.0013-0.0037 |
| **n-Hexane** | 8 | 0.0243 | 0.0245 | 0.0231 | 0.0075 | 31 | 0.0110-0.0354 |
| **2-Methylfuran** | 5 | 0.0011 | 0.0005 | 0.0008 | 0.0014 | 123 | 0.0005-0.0036 |
| **Chloroform** | 8 | 0.0030 | 0.0031 | 0.0029 | 0.0006 | 20 | 0.0018-0.0037 |
| **Tetrachloromethane** | 8 | 0.0224 | 0.0246 | 0.0219 | 0.0046 | 21 | 0.0126-0.0262 |
| **Benzene** | 8 | 0.0233 | 0.0211 | 0.0215 | 0.0106 | 45 | 0.0124-0.0449 |
| **n-Heptane** | 7 | 0.0025 | 0.0022 | 0.0024 | 0.0008 | 34 | 0.0016-0.0037 |
| **Crotonaldehyde** | 8 | 0.0016 | 0.0013 | 0.0015 | 0.0007 | 42 | 0.0010-0.0030 |
| **n-Octane** | 8 | 0.0036 | 0.0025 | 0.0031 | 0.0023 | 64 | 0.0019-0.0085 |
| **Toluene** | 8 | 0.0229 | 0.0242 | 0.0215 | 0.0085 | 37 | 0.0122-0.0394 |
| **Hexanal** | 8 | 0.0332 | 0.0320 | 0.0315 | 0.0108 | 33 | 0.0153-0.0479 |
| **Ethylbenzene** | 8 | 0.0022 | 0.0021 | 0.0020 | 0.0011 | 50 | 0.0012-0.0044 |
| **m+p Xylene** | 8 | 0.0029 | 0.0026 | 0.0026 | 0.0014 | 49 | 0.0015-0.0058 |
| **o-Xylene** | 8 | 0.0023 | 0.0022 | 0.0021 | 0.0011 | 47 | 0.0013-0.0046 |
| **Styrene** | 6 | 0.0006 | 0.0005 | 0.0005 | 0.0003 | 53 | 0.0003-0.0010 |
| **1- Heptanal** | 7 | 0.0047 | 0.0047 | 0.0045 | 0.0012 | 27 | 0.0033-0.0067 |
| **Alpha-pinene** | 8 | 0.0035 | 0.0022 | 0.0028 | 0.0026 | 73 | 0.0013-0.0078 |
| **n-Propylbenzene** | 8 | 0.0004 | 0.0003 | 0.0003 | 0.0002 | 45 | 0.0002-0.0007 |
| **m-Ethyltoluene** | 8 | 0.0010 | 0.0009 | 0.0009 | 0.0004 | 39 | 0.0005-0.0017 |
| **p-Ethyltoluene** | 8 | 0.0003 | 0.0004 | 0.0003 | 0.0001 | 44 | 0.0001-0.0005 |
| **1,2,4-Trimethylbenzene** | 7 | 0.0004 | 0.0004 | 0.0004 | 0.0001 | 31 | 0.0003-0.0006 |
| **beta-Pinene** | 5 | 0.0015 | 0.0016 | 0.0013 | 0.0010 | 64 | 0.0006-0.0028 |
| **o-Ethyltoluene** | 6 | 0.0005 | 0.0005 | 0.0005 | 0.0002 | 36 | 0.0004-0.0009 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **1,3,5-Trimethylbenzene** | 2 | 0.0021 | 0.0021 | 0.0021 | 0.0005 | 23 | 0.0018-0.0024 |
| **Benzaldehyde** | 8 | 0.0454 | 0.0451 | 0.0445 | 0.0099 | 22 | 0.0301-0.0619 |
| **p-Cymene** | 7 | 0.0002 | 0.0002 | 0.0002 | 0.0001 | 58 | 0.0001-0.0005 |
| **Eucalyptol** | 2 | 0.0010 | 0.0010 | 0.0010 | 0.0002 | 20 | 0.0009-0.0012 |
| **1,2,3-Trimethylbenzene** | 5 | 0.0006 | 0.0006 | 0.0006 | 0.0002 | 37 | 0.0004-0.0010 |
| **Phenol** | 8 | 0.0196 | 0.0164 | 0.0179 | 0.0094 | 48 | 0.0094-0.0398 |
| **Nonanal** | 8 | 0.0218 | 0.0189 | 0.0197 | 0.0100 | 46 | 0.0092-0.0367 |
| **Acetophenone** | 8 | 0.0183 | 0.0175 | 0.0173 | 0.0065 | 35 | 0.0110-0.0285 |
| **n-Dodecane** | 8 | 0.0063 | 0.0023 | 0.0031 | 0.0105 | 166 | 0.0009-0.0321 |
| **Decanal** | 8 | 0.0313 | 0.0119 | 0.0161 | 0.0492 | 157 | 0.0059-0.1506 |
| **Naphthalene** | 8 | 0.0026 | 0.0021 | 0.0023 | 0.0016 | 62 | 0.0013-0.0064 |
| **n-Tridecane** | 8 | 0.0028 | 0.0018 | 0.0019 | 0.0031 | 113 | 0.0006-0.0102 |
| **Benzothiazole** | 8 | 0.0144 | 0.0149 | 0.0140 | 0.0034 | 23.39 | 0.0069-0.0180 |
| **n-Tetradecane** | 8 | 0.0066 | 0.0070 | 0.0058 | 0.0032 | 48 | 0.0020-0.0118 |

**Table 1.2.** Descriptive statistical parameters for VOCs determined by May 2017 sampling (µg $m^{-3}$).

| Compound | Number of samples (N) | Average | Median | Geometric mean | Standard deviation | Coeff. of variation (CV) | Min-Max |
|---|---|---|---|---|---|---|---|
| **Isoprene** | 8 | 0.0241 | 0.0241 | 0.0232 | 0.0072 | 30 | 0.0164-0.0354 |
| **n-Hexane** | 8 | 0.5268 | 0.4204 | 0.4783 | 0.2995 | 57 | 0.2996-1.2432 |
| **2-Methylfuran** | 8 | 0.0021 | 0.0022 | 0.0021 | 0.0006 | 29 | 0.0013-0.0032 |
| **Chloroform** | 8 | 0.0284 | 0.0251 | 0.0278 | 0.0069 | 24 | 0.0224-0.0429 |
| **Tetrachloromethane** | 8 | 0.0189 | 0.0197 | 0.0174 | 0.0073 | 39 | 0.0066-0.0292 |
| **Benzene** | 8 | 0.1031 | 0.1023 | 0.1022 | 0.0140 | 14 | 0.0854-0.1275 |
| **n-Heptane** | 8 | 0.1779 | 0.1597 | 0.1670 | 0.0785 | 44 | 0.1156-0.3622 |
| **Crotonaldehyde** | 8 | 0.0343 | 0.0322 | 0.0306 | 0.0161 | 47 | 0.0107-0.0629 |
| **n-Octane** | 8 | 0.0406 | 0.0362 | 0.0358 | 0.0207 | 51 | 0.0136-0.0784 |
| **Toluene** | 8 | 0.0695 | 0.0694 | 0.0684 | 0.0132 | 19 | 0.0527-0.0934 |
| **Hexanal** | 8 | 2.5357 | 2.5176 | 2.2839 | 1.0701 | 42 | 0.7564-4.2268 |
| **Chlorobenzene** | 8 | 0.0210 | 0.0218 | 0.0193 | 0.0080 | 38 | 0.0071-0.0307 |
| **Ethylbenzene** | 8 | 0.0287 | 0.0282 | 0.0274 | 0.0088 | 31 | 0.0145-0.0434 |
| **m+p Xylene** | 8 | 0.0480 | 0.0478 | 0.0456 | 0.0151 | 31 | 0.0223-0.0696 |

| | | | | | | |
|---|---|---|---|---|---|---|
| **o-Xylene** | 8 | 0.0346 | 0.0352 | 0.0326 | 0.0112 | 32 | 0.0148-0.0464 |
| **Styrene** | 8 | 0.0147 | 0.0155 | 0.0135 | 0.0056 | 38 | 0.0055-0.0219 |
| **1- Heptanal** | 8 | 0.1032 | 0.0919 | 0.0822 | 0.0623 | 60 | 0.0167-0.1972 |
| **Alpha-pinene** | 8 | 0.0871 | 0.0792 | 0.0848 | 0.0231 | 27 | 0.0665-0.1331 |
| **Isopropylbenzene** | 8 | 0.0013 | 0.0014 | 0.0012 | 0.0005 | 36 | 0.0003-0.0017 |
| **Camphene** | 8 | 0.0042 | 0.0037 | 0.0040 | 0.0013 | 30 | 0.0030-0.0064 |
| **n-Propylbenzene** | 8 | 0.0013 | 0.0013 | 0.0012 | 0.0004 | 33 | 0.0005-0.0019 |
| **m-Ethyltoluene** | 8 | 0.0014 | 0.0014 | 0.0013 | 0.0004 | 30 | 0.0005-0.0018 |
| **p-Ethyltoluene** | 8 | 0.0014 | 0.0014 | 0.0013 | 0.0004 | 32 | 0.0005-0.0019 |
| **Sabinene** | 7 | 0.0044 | 0.0040 | 0.0042 | 0.0015 | 34 | 0.0024-0.0067 |
| **1,2,4-Trimethylbenzene** | 7 | 0.0007 | 0.0007 | 0.0007 | 0.0001 | 16 | 0.0005-0.0008 |
| **beta-Pinene** | 8 | 0.0099 | 0.0096 | 0.0095 | 0.0031 | 31 | 0.0057-0.0142 |
| **o-Ethyltoluene** | 7 | 0.0008 | 0.0009 | 0.0008 | 0.0001 | 17 | 0.0006-0.0010 |
| **3-Carene** | 8 | 0.0184 | 0.0184 | 0.0174 | 0.0061 | 33 | 0.0083-0.0264 |
| **1,3,5-Trimethylbenzene** | 7 | 0.0038 | 0.0038 | 0.0038 | 0.0005 | 12 | 0.0032-0.0045 |
| **Benzaldehyde** | 8 | 0.0463 | 0.0466 | 0.0448 | 0.0115 | 25 | 0.0257-0.0620 |
| **Limonene** | 8 | 0.0122 | 0.0125 | 0.0116 | 0.0039 | 32 | 0.0057-0.0176 |
| **m-Cymene** | 5 | 0.0008 | 0.0008 | 0.0008 | 0.0001 | 17 | 0.0007-0.0010 |
| **p-Cymene** | 8 | 0.0020 | 0.0020 | 0.0019 | 0.0007 | 35 | 0.0008-0.0031 |
| **Ocimene** | 6 | 0.0044 | 0.0040 | 0.0040 | 0.0019 | 43 | 0.0023-0.0069 |
| **1,2,3-Trimethylbenzene** | 7 | 0.0011 | 0.0011 | 0.0011 | 0.0003 | 25 | 0.0008-0.0015 |
| **gamma-Terpinene** | 8 | 0.0009 | 0.0007 | 0.0008 | 0.0003 | 40 | 0.0005-0.0014 |
| **1,3-Diethylbenzene** | 4 | 0.0003 | 0.0003 | 0.0003 | 0.0001 | 24 | 0.0002-0.0004 |
| **1,4-Diethylbenzene** | 7 | 0.0011 | 0.0010 | 0.0011 | 0.0003 | 25 | 0.0007-0.0014 |
| **Phenol** | 8 | 0.0120 | 0.0116 | 0.0116 | 0.0036 | 30 | 0.0064-0.0189 |
| **Nonanal** | 8 | 0.1185 | 0.1184 | 0.1080 | 0.0508 | 43 | 0.0481-0.1969 |
| **Acetophenone** | 8 | 0.0144 | 0.0156 | 0.0140 | 0.0033 | 23 | 0.0076-0.0177 |
| **L-Fenchone** | 7 | 0.0004 | 0.0004 | 0.0004 | 0.0001 | 23 | 0.0002-0.0005 |
| **n-Dodecane** | 8 | 0.0145 | 0.0153 | 0.0136 | 0.0045 | 31 | 0.0049-0.0184 |
| **(+)-Camphor** | 3 | 0.0032 | 0.0030 | 0.0032 | 0.0006 | 19 | 0.0028-0.0039 |
| **Decanal** | 8 | 0.0321 | 0.0304 | 0.0272 | 0.0181 | 57 | 0.0104-0.0573 |
| **alpha-Terpineol** | 8 | 0.0047 | 0.0046 | 0.0042 | 0.0022 | 47 | 0.0017-0.0076 |
| **Naphthalene** | 8 | 0.0036 | 0.0039 | 0.0034 | 0.0012 | 32 | 0.0012-0.0047 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **n-Tridecane** | 8 | 0.0099 | 0.0100 | 0.0092 | 0.0035 | 36 | 0.0041-0.0154 |
| **Benzothiazole** | 8 | 0.0274 | 0.0124 | 0.0176 | 0.0253 | 92 | 0.0068-0.0585 |
| **n-Tetradecane** | 8 | 0.0162 | 0.0170 | 0.0150 | 0.0056 | 35 | 0.0053-0.0254 |

**Table 1.3.** Descriptive statistical parameters for VOCs determined by June 2017 sampling (μg $m^{-3}$).

| Compound | Number of samples (N) | Average | Median | Geometric mean | Standard deviation | Coeff. of variation (CV) | Min-Max |
|---|---|---|---|---|---|---|---|
| **Isoprene** | 8 | 0.0327 | 0.0333 | 0.0293 | 0.0151 | 46 | 0.0125-0.0538 |
| **n-Hexane** | 8 | 0.8290 | 0.7761 | 0.7269 | 0.4404 | 53 | 0.3290-1.5204 |
| **2-Methylfuran** | 8 | 0.0031 | 0.0030 | 0.0029 | 0.0010 | 34 | 0.0010-0.0046 |
| **Chloroform** | 8 | 0.0756 | 0.0709 | 0.0699 | 0.0314 | 42 | 0.0397-0.1314 |
| **Tetrachloromethane** | 8 | 0.0296 | 0.0331 | 0.0258 | 0.0104 | 35 | 0.0046-0.0362 |
| **Benzene** | 8 | 0.0880 | 0.0949 | 0.0809 | 0.0362 | 41 | 0.0365-0.1490 |
| **n-Heptane** | 8 | 0.1405 | 0.0959 | 0.1102 | 0.1026 | 73 | 0.0459-0.2981 |
| **Crotonaldehyde** | 8 | 0.0669 | 0.0697 | 0.0552 | 0.0362 | 54 | 0.0125-0.1058 |
| **n-Octane** | 8 | 0.1330 | 0.0869 | 0.0942 | 0.1154 | 87 | 0.0249-0.3108 |
| **Toluene** | 8 | 0.1011 | 0.0948 | 0.0885 | 0.0432 | 43 | 0.0203-0.1563 |
| **Hexanal** | 8 | 4.8974 | 5.8370 | 4.0179 | 2.3852 | 49 | 0.6680-7.2338 |
| **Chlorobenzene** | 8 | 0.0471 | 0.0463 | 0.0380 | 0.0255 | 54 | 0.0055-0.0948 |
| **Ethylbenzene** | 8 | 0.0296 | 0.0348 | 0.0247 | 0.0143 | 48 | 0.0047-0.0464 |
| **m+p Xylene** | 8 | 0.0556 | 0.0666 | 0.0463 | 0.0263 | 47 | 0.0084-0.0842 |
| **o-Xylene** | 8 | 0.0495 | 0.0584 | 0.0416 | 0.0223 | 45 | 0.0073-0.0721 |
| **Styrene** | 8 | 0.0302 | 0.0356 | 0.0256 | 0.0128 | 43 | 0.0045-0.0423 |
| **1- Heptanal** | 8 | 0.2469 | 0.2580 | 0.2018 | 0.1187 | 48 | 0.0285-0.4194 |
| **Alpha-pinene** | 8 | 0.1720 | 0.2022 | 0.1468 | 0.0824 | 48 | 0.0376-0.2638 |
| **Isopropylbenzene** | 8 | 0.0029 | 0.0030 | 0.0025 | 0.0011 | 38 | 0.0005-0.0040 |
| **Camphene** | 7 | 0.0105 | 0.0108 | 0.0096 | 0.0046 | 44 | 0.0045-0.0189 |
| **n-Propylbenzene** | 8 | 0.0031 | 0.0035 | 0.0026 | 0.0013 | 42 | 0.0005-0.0045 |
| **m-Ethyltoluene** | 8 | 0.0052 | 0.0052 | 0.0045 | 0.0021 | 41 | 0.0008-0.0085 |
| **p-Ethyltoluene** | 8 | 0.0029 | 0.0033 | 0.0025 | 0.0011 | 39 | 0.0005-0.0041 |
| **Sabinene** | 7 | 0.0097 | 0.0117 | 0.0091 | 0.0035 | 36 | 0.0050-0.0143 |
| **1,2,4-Trimethylbenzene** | 8 | 0.0021 | 0.0022 | 0.0019 | 0.0008 | 36 | 0.0004-0.0030 |

| | | | | | | |
|---|---|---|---|---|---|---|
| **beta-Pinene** | 8 | 0.0214 | 0.0254 | 0.0181 | 0.0097 | 45 | 0.0034-0.0299 |
| **o-Ethyltoluene** | 8 | 0.0025 | 0.0026 | 0.0022 | 0.0010 | 40 | 0.0005-0.0041 |
| **3-Carene** | 8 | 0.0276 | 0.0327 | 0.0230 | 0.0129 | 47 | 0.0040-0.0405 |
| **1,3,5-Trimethylbenzene** | 8 | 0.0100 | 0.0107 | 0.0089 | 0.0037 | 37 | 0.0020-0.0149 |
| **Benzaldehyde** | 8 | 0.0738 | 0.0651 | 0.0602 | 0.0466 | 63 | 0.0169-0.1492 |
| **Limonene** | 8 | 0.0205 | 0.0222 | 0.0169 | 0.0101 | 49 | 0.0029-0.0316 |
| **m-Cymene** | 7 | 0.0016 | 0.0017 | 0.0016 | 0.0003 | 18 | 0.0011-0.0020 |
| **p-Cymene** | 8 | 0.0042 | 0.0046 | 0.0036 | 0.0018 | 44 | 0.0007-0.0069 |
| **Ocimene** | 7 | 0.0112 | 0.0122 | 0.0109 | 0.0023 | 21 | 0.0073-0.0139 |
| **1,2,3-Trimethylbenzene** | 8 | 0.0029 | 0.0028 | 0.0026 | 0.0010 | 37 | 0.0007-0.0042 |
| **gamma-Terpinene** | 8 | 0.0015 | 0.0012 | 0.0013 | 0.0011 | 69 | 0.0006-0.0038 |
| **1,3-Diethylbenzene** | 7 | 0.0004 | 0.0004 | 0.0004 | 0.0002 | 42 | 0.0001-0.0007 |
| **1,4-Diethylbenzene** | 8 | 0.0028 | 0.0026 | 0.0025 | 0.0011 | 39 | 0.0007-0.0043 |
| **Phenol** | 8 | 0.0388 | 0.0414 | 0.0342 | 0.0170 | 44 | 0.0089-0.0627 |
| **Nonanal** | 8 | 0.2625 | 0.3060 | 0.2155 | 0.1184 | 45 | 0.0299-0.3898 |
| **Acetophenone** | 8 | 0.0256 | 0.0264 | 0.0242 | 0.0073 | 28 | 0.0094-0.0320 |
| **L-Fenchone** | 7 | 0.0012 | 0.0012 | 0.0012 | 0.0002 | 18 | 0.0009-0.0015 |
| **n-Dodecane** | 8 | 0.0555 | 0.0501 | 0.0502 | 0.0240 | 43 | 0.0161-0.0989 |
| **(+)-Camphor** | 7 | 0.0085 | 0.0083 | 0.0081 | 0.0028 | 33 | 0.0052-0.0132 |
| **Decanal** | 8 | 0.0834 | 0.0933 | 0.0692 | 0.0469 | 56 | 0.0288-0.1383 |
| **alpha-Terpineol** | 7 | 0.0142 | 0.0166 | 0.0135 | 0.0043 | 30 | 0.0077-0.0172 |
| **Naphthalene** | 8 | 0.0109 | 0.0112 | 0.0095 | 0.0046 | 42 | 0.0020-0.0185 |
| **n-Tridecane** | 8 | 0.0362 | 0.0345 | 0.0298 | 0.0196 | 54 | 0.0052-0.0719 |
| **Benzothiazole** | 8 | 0.0321 | 0.0304 | 0.0234 | 0.0236 | 74 | 0.0084-0.0617 |
| **n-Tetradecane** | 8 | 0.0391 | 0.0431 | 0.0356 | 0.0153 | 39 | 0.0120-0.0578 |

**Table 1.4.** Descriptive statistical parameters for VOCs determined by July 2017 sampling (μg $m^{-3}$).

| Compound | Number of samples (N) | Average | Median | Geometric mean | Standard deviation | Coeff. of variation (CV) | Min-Max |
|---|---|---|---|---|---|---|---|
| **Isoprene** | 8 | 0.0680 | 0.0625 | 0.0595 | 0.0360 | 53 | 0.0204-0.1368 |
| **n-Hexane** | 8 | 0.4755 | 0.3437 | 0.3821 | 0.3849 | 81 | 0.1854-1.3478 |
| **2-Methylfuran** | 8 | 0.0042 | 0.0040 | 0.0041 | 0.0006 | 15 | 0.0037-0.0056 |

| | | | | | | |
|---|---|---|---|---|---|---|
| **Chloroform** | 8 | 0.1008 | 0.0842 | 0.0867 | 0.0650 | 64 | 0.0369-0.2452 |
| **Tetrachloromethane** | 8 | 0.0281 | 0.0278 | 0.0280 | 0.0021 | 7 | 0.0253-0.0318 |
| **Benzene** | 8 | 0.0607 | 0.0611 | 0.0597 | 0.0115 | 19 | 0.0427-0.0753 |
| **n-Heptane** | 8 | 0.0369 | 0.0332 | 0.0342 | 0.0157 | 43 | 0.0207-0.0606 |
| **Crotonaldehyde** | 8 | 0.0273 | 0.0253 | 0.0264 | 0.0076 | 28 | 0.0186-0.0391 |
| **n-Octane** | 8 | 0.0606 | 0.0613 | 0.0549 | 0.0281 | 46 | 0.0292-0.1030 |
| **Toluene** | 8 | 0.0936 | 0.0783 | 0.0869 | 0.0418 | 45 | 0.0562-0.1788 |
| **Hexanal** | 8 | 2.7132 | 2.5667 | 2.6682 | 0.5534 | 20 | 2.2004-3.7687 |
| **Chlorobenzene** | 8 | 0.0616 | 0.0597 | 0.0565 | 0.0253 | 41 | 0.0218-0.1074 |
| **Ethylbenzene** | 8 | 0.0181 | 0.0155 | 0.0169 | 0.0074 | 41 | 0.0110-0.0306 |
| **m+p Xylene** | 8 | 0.0335 | 0.0285 | 0.0311 | 0.0140 | 42 | 0.0200-0.0564 |
| **o-Xylene** | 8 | 0.0323 | 0.0290 | 0.0307 | 0.0111 | 34 | 0.0210-0.0491 |
| **Styrene** | 8 | 0.0331 | 0.0289 | 0.0323 | 0.0080 | 24 | 0.0254-0.0454 |
| **1- Heptanal** | 8 | 0.1005 | 0.0976 | 0.0997 | 0.0138 | 14 | 0.0864-0.1236 |
| **Alpha-pinene** | 8 | 0.1873 | 0.1822 | 0.1745 | 0.0754 | 40 | 0.1009-0.3238 |
| **Isopropylbenzene** | 8 | 0.0032 | 0.0031 | 0.0032 | 0.0008 | 24 | 0.0024-0.0044 |
| **Camphene** | 8 | 0.0098 | 0.0101 | 0.0094 | 0.0029 | 30 | 0.0060-0.0152 |
| **n-Propylbenzene** | 8 | 0.0049 | 0.0044 | 0.0048 | 0.0013 | 26 | 0.0036-0.0069 |
| **m-Ethyltoluene** | 8 | 0.0126 | 0.0114 | 0.0123 | 0.0030 | 23 | 0.0097-0.0172 |
| **p-Ethyltoluene** | 8 | 0.0044 | 0.0040 | 0.0042 | 0.0013 | 29 | 0.0028-0.0065 |
| **Sabinene** | 8 | 0.0034 | 0.0033 | 0.0034 | 0.0004 | 13 | 0.0028-0.0041 |
| **beta-Myrcene** | 2 | 0.0034 | 0.0034 | 0.0034 | 0.0005 | 16 | 0.0030-0.0038 |
| **1,2,4-Trimethylbenzene** | 8 | 0.0049 | 0.0046 | 0.0049 | 0.0007 | 15 | 0.0041-0.0061 |
| **beta-Pinene** | 8 | 0.0178 | 0.0179 | 0.0171 | 0.0052 | 29 | 0.0111-0.0257 |
| **o-Ethyltoluene** | 8 | 0.0057 | 0.0053 | 0.0056 | 0.0009 | 16 | 0.0047-0.0071 |
| **3-Carene** | 8 | 0.0096 | 0.0087 | 0.0090 | 0.0034 | 35 | 0.0058-0.0142 |
| **1,3,5-Trimethylbenzene** | 8 | 0.0214 | 0.0199 | 0.0213 | 0.0030 | 14 | 0.0182-0.0267 |
| **Benzaldehyde** | 8 | 0.0782 | 0.0738 | 0.0755 | 0.0220 | 28 | 0.0485-0.1072 |
| **Limonene** | 8 | 0.0193 | 0.0186 | 0.0186 | 0.0051 | 26 | 0.0125-0.0258 |
| **m-Cymene** | 8 | 0.0014 | 0.0013 | 0.0014 | 0.0002 | 18 | 0.0012-0.0018 |
| **p-Cymene** | 8 | 0.0043 | 0.0040 | 0.0043 | 0.0006 | 13 | 0.0038-0.0053 |
| **Ocimene** | 8 | 0.0063 | 0.0060 | 0.0063 | 0.0010 | 15 | 0.0054-0.0082 |
| **Eucalyptol** | 8 | 0.0028 | 0.0029 | 0.0028 | 0.0004 | 14 | 0.0022-0.0034 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **1,2,3-Trimethylbenzene** | 8 | 0.0060 | 0.0059 | 0.0060 | 0.0005 | 8 | 0.0055-0.0069 |
| **gamma-Terpinene** | 8 | 0.0008 | 0.0008 | 0.0007 | 0.0002 | 25 | 0.0004-0.0010 |
| **1,3-Diethylbenzene** | 8 | 0.0005 | 0.0005 | 0.0005 | 0.0001 | 19 | 0.0003-0.0006 |
| **1,4-Diethylbenzene** | 8 | 0.0042 | 0.0041 | 0.0041 | 0.0005 | 11 | 0.0037-0.0050 |
| **Phenol** | 8 | 0.0364 | 0.0341 | 0.0361 | 0.0051 | 14 | 0.0317-0.0447 |
| **Nonanal** | 8 | 0.2297 | 0.2211 | 0.2281 | 0.0294 | 13 | 0.1946-0.2747 |
| **Acetophenone** | 8 | 0.0287 | 0.0277 | 0.0286 | 0.0034 | 12 | 0.0255-0.0338 |
| **L-Fenchone** | 8 | 0.0013 | 0.0013 | 0.0013 | 0.0001 | 7 | 0.0012-0.0014 |
| **n-Dodecane** | 8 | 0.0526 | 0.0506 | 0.0520 | 0.0087 | 17 | 0.0420-0.0669 |
| **(+)-Camphor** | 8 | 0.0073 | 0.0070 | 0.0073 | 0.0009 | 13 | 0.0063-0.0090 |
| **Decanal** | 8 | 0.0919 | 0.0955 | 0.0893 | 0.0204 | 22 | 0.0475-0.1112 |
| **alpha-Terpineol** | 8 | 0.0128 | 0.0121 | 0.0126 | 0.0026 | 20 | 0.0088-0.0165 |
| **Naphthalene** | 8 | 0.0182 | 0.0177 | 0.0181 | 0.0015 | 8 | 0.0167-0.0208 |
| **n-Tridecane** | 8 | 0.0508 | 0.0479 | 0.0501 | 0.0089 | 18 | 0.0414-0.0660 |
| **Benzothiazole** | 8 | 0.0215 | 0.0209 | 0.0205 | 0.0079 | 37 | 0.0149-0.0398 |
| **n-Tetradecane** | 8 | 0.0555 | 0.0506 | 0.0546 | 0.0113 | 20 | 0.0441-0.0747 |

**Table 1.5.** Descriptive statistical parameters for VOCs determined by August 2017 sampling (µg $m^{-3}$).

| Compound | Number of samples (N) | Average | Median | Geometric mean | Standard deviation | Coeff. of variation (CV) | Min-Max |
|---|---|---|---|---|---|---|---|
| **Isoprene** | 8 | 0.0530 | 0.0531 | 0.0510 | 0.0150 | 28 | 0.0335-0.0713 |
| **n-Hexane** | 8 | 0.4332 | 0.3016 | 0.3621 | 0.3112 | 72 | 0.1945-1.1014 |
| **2-Methylfuran** | 8 | 0.0053 | 0.0052 | 0.0051 | 0.0015 | 27 | 0.0036-0.0081 |
| **Chloroform** | 8 | 0.0869 | 0.0647 | 0.0678 | 0.0692 | 80 | 0.0301-0.2309 |
| **Tetrachloromethane** | 8 | 0.0372 | 0.0360 | 0.0369 | 0.0047 | 13 | 0.0317-0.0457 |
| **Benzene** | 8 | 0.1018 | 0.0938 | 0.0978 | 0.0321 | 32 | 0.0702-0.1624 |
| **n-Heptane** | 8 | 0.0821 | 0.0683 | 0.0651 | 0.0608 | 74 | 0.0309-0.2049 |
| **Crotonaldehyde** | 8 | 0.0496 | 0.0423 | 0.0419 | 0.0325 | 66 | 0.0235-0.1176 |
| **n-Octane** | 8 | 0.1323 | 0.1145 | 0.1109 | 0.0851 | 64 | 0.0590-0.2978 |
| **Toluene** | 8 | 0.0667 | 0.0650 | 0.0638 | 0.0207 | 31 | 0.0405-0.0984 |
| **Hexanal** | 8 | 4.5698 | 4.4602 | 4.5218 | 0.7256 | 16 | 3.7139-5.9729 |
| **Chlorobenzene** | 8 | 0.1236 | 0.1321 | 0.1166 | 0.0361 | 29 | 0.0444-0.1553 |

| | | | | | | |
|---|---|---|---|---|---|---|
| **Ethylbenzene** | 8 | 0.0116 | 0.0115 | 0.0112 | 0.0033 | 28 | 0.0071-0.0156 |
| **m+p Xylene** | 8 | 0.0187 | 0.0191 | 0.0179 | 0.0054 | 29 | 0.0110-0.0247 |
| **o-Xylene** | 8 | 0.0189 | 0.0196 | 0.0183 | 0.0047 | 25 | 0.0117-0.0243 |
| **Styrene** | 8 | 0.0423 | 0.0415 | 0.0408 | 0.0115 | 27 | 0.0260-0.0580 |
| **1- Heptanal** | 8 | 0.1466 | 0.1476 | 0.1457 | 0.0166 | 11 | 0.1124-0.1682 |
| **Alpha-pinene** | 8 | 0.1552 | 0.1506 | 0.1491 | 0.0462 | 30 | 0.0878-0.2357 |
| **Isopropylbenzene** | 8 | 0.0034 | 0.0036 | 0.0033 | 0.0007 | 21 | 0.0022-0.0043 |
| **Camphene** | 8 | 0.0089 | 0.0092 | 0.0088 | 0.0011 | 12 | 0.0068-0.0104 |
| **n-Propylbenzene** | 8 | 0.0042 | 0.0041 | 0.0041 | 0.0009 | 22 | 0.0029-0.0056 |
| **m-Ethyltoluene** | 8 | 0.0091 | 0.0093 | 0.0090 | 0.0019 | 21 | 0.0066-0.0120 |
| **p-Ethyltoluene** | 8 | 0.0027 | 0.0029 | 0.0027 | 0.0007 | 24 | 0.0018-0.0036 |
| **Sabinene** | 8 | 0.0030 | 0.0030 | 0.0029 | 0.0006 | 20 | 0.0021-0.0038 |
| **1,2,4-Trimethylbenzene** | 8 | 0.0038 | 0.0039 | 0.0037 | 0.0007 | 19 | 0.0028-0.0049 |
| **beta-Pinene** | 8 | 0.0152 | 0.0154 | 0.0151 | 0.0011 | 7 | 0.0131-0.0166 |
| **o-Ethyltoluene** | 8 | 0.0042 | 0.0044 | 0.0041 | 0.0008 | 18 | 0.0032-0.0054 |
| **3-Carene** | 8 | 0.0046 | 0.0049 | 0.0046 | 0.0009 | 19 | 0.0034-0.0058 |
| **1,3,5-Trimethylbenzene** | 8 | 0.0168 | 0.0176 | 0.0166 | 0.0029 | 17 | 0.0134-0.0209 |
| **Benzaldehyde** | 8 | 0.0693 | 0.0757 | 0.0655 | 0.0218 | 31 | 0.0331-0.0908 |
| **Limonene** | 8 | 0.0148 | 0.0156 | 0.0137 | 0.0055 | 37 | 0.0067-0.0213 |
| **m-Cymene** | 7 | 0.0011 | 0.0011 | 0.0011 | 0.0002 | 17 | 0.0007-0.0013 |
| **p-Cymene** | 8 | 0.0048 | 0.0048 | 0.0047 | 0.0008 | 17 | 0.0036-0.0058 |
| **Ocimene** | 6 | 0.0031 | 0.0030 | 0.0031 | 0.0006 | 18 | 0.0024-0.0039 |
| **Eucalyptol** | 8 | 0.0037 | 0.0033 | 0.0036 | 0.0013 | 34 | 0.0024-0.0063 |
| **1,2,3-Trimethylbenzene** | 8 | 0.0054 | 0.0055 | 0.0054 | 0.0009 | 16 | 0.0041-0.0065 |
| **gamma-Terpinene** | 8 | 0.0005 | 0.0005 | 0.0005 | 0.0002 | 30 | 0.0004-0.0009 |
| **1,3-Diethylbenzene** | 8 | 0.0004 | 0.0004 | 0.0004 | 0.0001 | 19 | 0.0003-0.0006 |
| **1,4-Diethylbenzene** | 8 | 0.0039 | 0.0038 | 0.0039 | 0.0009 | 22 | 0.0028-0.0055 |
| **Phenol** | 8 | 0.0381 | 0.0391 | 0.0377 | 0.0060 | 16 | 0.0286-0.0453 |
| **Nonanal** | 8 | 0.3595 | 0.3594 | 0.3559 | 0.0523 | 15 | 0.2579-0.4152 |
| **Acetophenone** | 8 | 0.0341 | 0.0341 | 0.0338 | 0.0049 | 14 | 0.0280-0.0432 |
| **L-Fenchone** | 8 | 0.0019 | 0.0019 | 0.0019 | 0.0003 | 14 | 0.0016-0.0023 |
| **n-Dodecane** | 8 | 0.0428 | 0.0419 | 0.0406 | 0.0148 | 35 | 0.0232-0.0708 |
| **(+)-Camphor** | 8 | 0.0105 | 0.0107 | 0.0104 | 0.0014 | 13 | 0.0087-0.0121 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Decanal** | 8 | 0.1429 | 0.1442 | 0.1418 | 0.0190 | 13 | 0.1158-0.1669 |
| **alpha-Terpineol** | 8 | 0.0139 | 0.0141 | 0.0137 | 0.0024 | 17 | 0.0109-0.0171 |
| **Naphthalene** | 8 | 0.0206 | 0.0209 | 0.0204 | 0.0032 | 15 | 0.0148-0.0250 |
| **n-Tridecane** | 8 | 0.0461 | 0.0464 | 0.0453 | 0.0090 | 20 | 0.0312-0.0590 |
| **Benzothiazole** | 8 | 0.0313 | 0.0283 | 0.0300 | 0.0119 | 38 | 0.0240-0.0604 |
| **n-Tetradecane** | 8 | 0.0592 | 0.0607 | 0.0581 | 0.0122 | 21 | 0.0454-0.0784 |

**Table 1.6.** Descriptive statistical parameters for VOCs determined by September 2017 sampling (μg $m^{-3}$).

| Compound | Number of samples (N) | Average | Median | Geometric mean | Standard deviation | Coeff. of variation (CV) | Min-Max |
|---|---|---|---|---|---|---|---|
| **Isoprene** | 8 | 0.0790 | 0.0588 | 0.0655 | 0.0563 | 71 | 0.0247-0.1986 |
| **n-Hexane** | 8 | 0.2786 | 0.1605 | 0.2094 | 0.2578 | 93 | 0.1052-0.8540 |
| **2-Methylfuran** | 8 | 0.0057 | 0.0053 | 0.0056 | 0.0011 | 19 | 0.0045-0.0077 |
| **Chloroform** | 8 | 0.2153 | 0.1336 | 0.1702 | 0.1851 | 86 | 0.0815-0.6286 |
| **Tetrachloromethane** | 8 | 0.0424 | 0.0427 | 0.0422 | 0.0038 | 9 | 0.0374-0.0478 |
| **Benzene** | 8 | 0.1083 | 0.0920 | 0.1016 | 0.0445 | 41 | 0.0701-0.1999 |
| **n-Heptane** | 8 | 0.0863 | 0.0638 | 0.0772 | 0.0485 | 56 | 0.0472-0.1861 |
| **Crotonaldehyde** | 8 | 0.0502 | 0.0354 | 0.0431 | 0.0334 | 67 | 0.0253-0.1180 |
| **n-Octane** | 8 | 0.1012 | 0.0847 | 0.0922 | 0.0513 | 51 | 0.0566-0.2077 |
| **Toluene** | 8 | 0.0927 | 0.0794 | 0.0845 | 0.0445 | 48 | 0.0496-0.1725 |
| **Hexanal** | 8 | 5.3883 | 3.2809 | 4.5490 | 3.4600 | 64 | 2.4110-11.190 |
| **Chlorobenzene** | 8 | 0.0833 | 0.0815 | 0.0780 | 0.0314 | 38 | 0.0461-0.1317 |
| **Ethylbenzene** | 8 | 0.0150 | 0.0106 | 0.0133 | 0.0082 | 54 | 0.0080-0.0274 |
| **m+p Xylene** | 8 | 0.0226 | 0.0157 | 0.0200 | 0.0123 | 55 | 0.0127-0.0415 |
| **o-Xylene** | 8 | 0.0200 | 0.0148 | 0.0180 | 0.0099 | 49 | 0.0115-0.0352 |
| **Styrene** | 8 | 0.0453 | 0.0302 | 0.0395 | 0.0260 | 57 | 0.0226-0.0871 |
| **1- Heptanal** | 8 | 0.1720 | 0.1371 | 0.1571 | 0.0801 | 47 | 0.0911-0.3019 |
| **Alpha-pinene** | 8 | 0.1927 | 0.1197 | 0.1590 | 0.1362 | 71 | 0.0848-0.4314 |
| **Isopropylbenzene** | 8 | 0.0041 | 0.0027 | 0.0035 | 0.0024 | 59 | 0.0021-0.0080 |
| **Camphene** | 8 | 0.0097 | 0.0078 | 0.0088 | 0.0047 | 48 | 0.0050-0.0175 |
| **n-Propylbenzene** | 8 | 0.0047 | 0.0036 | 0.0043 | 0.0022 | 48 | 0.0026-0.0082 |
| **m-Ethyltoluene** | 8 | 0.0098 | 0.0075 | 0.0089 | 0.0046 | 47 | 0.0054-0.0174 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **p-Ethyltoluene** | 8 | 0.0032 | 0.0024 | 0.0029 | 0.0016 | 48 | 0.0019-0.0058 |
| **Sabinene** | 7 | 0.0021 | 0.0022 | 0.0020 | 0.0006 | 30 | 0.0013-0.0029 |
| **beta-Myrcene** | 2 | 0.0055 | 0.0055 | 0.0053 | 0.0022 | 40 | 0.0040-0.0071 |
| **1,2,4-Trimethylbenzene** | 8 | 0.0038 | 0.0030 | 0.0035 | 0.0017 | 45 | 0.0021-0.0064 |
| **beta-Pinene** | 8 | 0.0159 | 0.0125 | 0.0143 | 0.0079 | 50 | 0.0082-0.0283 |
| **o-Ethyltoluene** | 8 | 0.0042 | 0.0034 | 0.0039 | 0.0018 | 44 | 0.0024-0.0070 |
| **3-Carene** | 8 | 0.0043 | 0.0032 | 0.0039 | 0.0022 | 52 | 0.0022-0.0076 |
| **1,3,5-Trimethylbenzene** | 8 | 0.0163 | 0.0134 | 0.0152 | 0.0066 | 40 | 0.0096-0.0262 |
| **Benzaldehyde** | 8 | 0.0911 | 0.0514 | 0.0743 | 0.0641 | 70 | 0.0397-0.1885 |
| **Limonene** | 8 | 0.0167 | 0.0105 | 0.0145 | 0.0100 | 60 | 0.0085-0.0312 |
| **m-Cymene** | 6 | 0.0011 | 0.0011 | 0.0010 | 0.0004 | 39 | 0.0007-0.0017 |
| **p-Cymene** | 8 | 0.0047 | 0.0037 | 0.0043 | 0.0021 | 46 | 0.0025-0.0087 |
| **Eucalyptol** | 8 | 0.0048 | 0.0043 | 0.0042 | 0.0024 | 51 | 0.0023-0.0082 |
| **1,2,3-Trimethylbenzene** | 8 | 0.0047 | 0.0041 | 0.0045 | 0.0017 | 37 | 0.0030-0.0071 |
| **gamma-Terpinene** | 7 | 0.0004 | 0.0004 | 0.0004 | 0.0002 | 41 | 0.0002-0.0007 |
| **1,3-Diethylbenzene** | 8 | 0.0004 | 0.0004 | 0.0004 | 0.0001 | 35 | 0.0002-0.0006 |
| **1,4-Diethylbenzene** | 8 | 0.0032 | 0.0027 | 0.0030 | 0.0013 | 40 | 0.0017-0.0050 |
| **Phenol** | 8 | 0.0367 | 0.0308 | 0.0339 | 0.0156 | 43 | 0.0203-0.0614 |
| **Nonanal** | 8 | 0.3618 | 0.3140 | 0.3350 | 0.1530 | 42 | 0.1785-0.6234 |
| **Acetophenone** | 8 | 0.0379 | 0.0329 | 0.0364 | 0.0118 | 31 | 0.0268-0.0532 |
| **L-Fenchone** | 8 | 0.0019 | 0.0016 | 0.0017 | 0.0008 | 42 | 0.0010-0.0031 |
| **n-Dodecane** | 8 | 0.0368 | 0.0317 | 0.0344 | 0.0143 | 39 | 0.0217-0.0573 |
| **(+)-Camphor** | 8 | 0.0100 | 0.0084 | 0.0092 | 0.0043 | 43 | 0.0049-0.0162 |
| **Decanal** | 8 | 0.1262 | 0.1014 | 0.1132 | 0.0659 | 52 | 0.0552-0.2492 |
| **alpha-Terpineol** | 8 | 0.0152 | 0.0128 | 0.0131 | 0.0085 | 55 | 0.0052-0.0262 |
| **Naphthalene** | 8 | 0.0173 | 0.0151 | 0.0162 | 0.0066 | 38 | 0.0106-0.0269 |
| **n-Tridecane** | 8 | 0.0346 | 0.0275 | 0.0315 | 0.0162 | 47 | 0.0186-0.0607 |
| **Benzothiazole** | 8 | 0.0385 | 0.0312 | 0.0343 | 0.0198 | 52 | 0.0191-0.0710 |
| **n-Tetradecane** | 8 | 0.0632 | 0.0506 | 0.0577 | 0.0296 | 47 | 0.0361-0.1124 |

**Table 1.7.** Descriptive statistical parameters for VOCs determined by October 2017 sampling (μg $m^{-3}$).

| Compound | Number of | Average | Median | Geometric mean | Standard deviation | Coeff. of variation (CV) | Min-Max |
|---|---|---|---|---|---|---|---|

| | samples (N) | | | | | |
|---|---|---|---|---|---|---|
| **Isoprene** | 8 | 0.0470 | 0.0480 | 0.0451 | 0.0137 | 29 | 0.0236-0.0715 |
| **n-Hexane** | 8 | 0.5739 | 0.3559 | 0.4710 | 0.4373 | 76 | 0.3118-1.3282 |
| **2-Methylfuran** | 8 | 0.0073 | 0.0075 | 0.0070 | 0.0021 | 28 | 0.0044-0.0101 |
| **Chloroform** | 8 | 0.1589 | 0.1341 | 0.1347 | 0.1132 | 71 | 0.0690-0.4199 |
| **Tetrachloromethane** | 8 | 0.0454 | 0.0454 | 0.0452 | 0.0036 | 8 | 0.0392-0.0517 |
| **Benzene** | 8 | 0.0868 | 0.0911 | 0.0849 | 0.0180 | 21 | 0.0520-0.1089 |
| **n-Heptane** | 8 | 0.0672 | 0.0658 | 0.0639 | 0.0216 | 32 | 0.0341-0.0936 |
| **Crotonaldehyde** | 8 | 0.0241 | 0.0246 | 0.0233 | 0.0062 | 26 | 0.0133-0.0308 |
| **n-Octane** | 8 | 0.0536 | 0.0567 | 0.0519 | 0.0137 | 25 | 0.0314-0.0724 |
| **Toluene** | 8 | 0.0987 | 0.0981 | 0.0957 | 0.0263 | 27 | 0.0638-0.1494 |
| **Hexanal** | 8 | 2.8069 | 2.7947 | 2.6787 | 0.9311 | 33 | 1.5608-4.6505 |
| **Chlorobenzene** | 8 | 0.0501 | 0.0518 | 0.0490 | 0.0102 | 20 | 0.0303-0.0631 |
| **Ethylbenzene** | 8 | 0.0115 | 0.0116 | 0.0112 | 0.0026 | 22 | 0.0078-0.0163 |
| **m+p Xylene** | 8 | 0.0174 | 0.0167 | 0.0171 | 0.0038 | 22 | 0.0123-0.0250 |
| **o-Xylene** | 8 | 0.0147 | 0.0147 | 0.0144 | 0.0032 | 22 | 0.0099-0.0211 |
| **Styrene** | 8 | 0.0236 | 0.0238 | 0.0231 | 0.0051 | 22 | 0.0159-0.0315 |
| **1- Heptanal** | 8 | 0.0735 | 0.0725 | 0.0724 | 0.0131 | 18 | 0.0502-0.0902 |
| **Alpha-pinene** | 8 | 0.1415 | 0.1309 | 0.1328 | 0.0611 | 43 | 0.0812-0.2836 |
| **Isopropylbenzene** | 8 | 0.0019 | 0.0019 | 0.0019 | 0.0005 | 28 | 0.0012-0.0029 |
| **Camphene** | 8 | 0.0089 | 0.0085 | 0.0087 | 0.0020 | 23 | 0.0059-0.0125 |
| **n-Propylbenzene** | 8 | 0.0028 | 0.0028 | 0.0028 | 0.0005 | 18 | 0.0021-0.0035 |
| **m-Ethyltoluene** | 8 | 0.0057 | 0.0058 | 0.0056 | 0.0009 | 16 | 0.0042-0.0068 |
| **p-Ethyltoluene** | 8 | 0.0018 | 0.0018 | 0.0018 | 0.0002 | 11 | 0.0016-0.0020 |
| **1,2,4-Trimethylbenzene** | 8 | 0.0024 | 0.0024 | 0.0023 | 0.0004 | 19 | 0.0016-0.0030 |
| **beta-Pinene** | 8 | 0.0129 | 0.0127 | 0.0126 | 0.0029 | 22 | 0.0085-0.0184 |
| **o-Ethyltoluene** | 8 | 0.0027 | 0.0026 | 0.0026 | 0.0004 | 17 | 0.0019-0.0032 |
| **3-Carene** | 8 | 0.0026 | 0.0027 | 0.0026 | 0.0006 | 21 | 0.0017-0.0036 |
| **1,3,5-Trimethylbenzene** | 8 | 0.0094 | 0.0096 | 0.0093 | 0.0014 | 15 | 0.0068-0.0109 |
| **Benzaldehyde** | 8 | 0.0404 | 0.0386 | 0.0383 | 0.0143 | 35 | 0.0248-0.0656 |
| **Limonene** | 8 | 0.0118 | 0.0115 | 0.0115 | 0.0028 | 24 | 0.0079-0.0165 |
| **m-Cymene** | 4 | 0.0007 | 0.0007 | 0.0007 | 0.0000 | 6 | 0.0007-0.0008 |
| **p-Cymene** | 8 | 0.0025 | 0.0024 | 0.0024 | 0.0004 | 16 | 0.0018-0.0030 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Eucalyptol** | 8 | 0.0030 | 0.0029 | 0.0029 | 0.0005 | 17 | 0.0021-0.0039 |
| **1,2,3-Trimethylbenzene** | 8 | 0.0028 | 0.0028 | 0.0028 | 0.0005 | 17 | 0.0020-0.0035 |
| **gamma-Terpinene** | 7 | 0.0002 | 0.0003 | 0.0002 | 0.0001 | 39 | 0.0001-0.0004 |
| **1,3-Diethylbenzene** | 8 | 0.0002 | 0.0002 | 0.0002 | 0.0001 | 29 | 0.0001-0.0003 |
| **1,4-Diethylbenzene** | 8 | 0.0021 | 0.0020 | 0.0021 | 0.0006 | 28 | 0.0014-0.0033 |
| **Phenol** | 8 | 0.0172 | 0.0175 | 0.0170 | 0.0026 | 15 | 0.0118-0.0197 |
| **Nonanal** | 8 | 0.1655 | 0.1684 | 0.1640 | 0.0239 | 14 | 0.1258-0.2033 |
| **Acetophenone** | 8 | 0.0165 | 0.0168 | 0.0163 | 0.0026 | 16 | 0.0122-0.0209 |
| **L-Fenchone** | 8 | 0.0012 | 0.0011 | 0.0012 | 0.0002 | 16 | 0.0009-0.0015 |
| **n-Dodecane** | 8 | 0.0172 | 0.0168 | 0.0168 | 0.0040 | 23 | 0.0121-0.0248 |
| **(+)-Camphor** | 8 | 0.0053 | 0.0053 | 0.0053 | 0.0007 | 13 | 0.0040-0.0064 |
| **Decanal** | 8 | 0.0619 | 0.0604 | 0.0597 | 0.0170 | 28 | 0.0384-0.0856 |
| **alpha-Terpineol** | 8 | 0.0071 | 0.0070 | 0.0069 | 0.0019 | 27 | 0.0048-0.0100 |
| **Naphthalene** | 8 | 0.0076 | 0.0076 | 0.0075 | 0.0011 | 15 | 0.0056-0.0089 |
| **n-Tridecane** | 8 | 0.0131 | 0.0132 | 0.0129 | 0.0023 | 17 | 0.0088-0.0161 |
| **Benzothiazole** | 8 | 0.0243 | 0.0183 | 0.0208 | 0.0142 | 59 | 0.0093-0.0446 |
| **n-Tetradecane** | 8 | 0.0234 | 0.0240 | 0.0231 | 0.0039 | 16 | 0.0161-0.0282 |

**Table 1.8.** Descriptive statistical parameters for VOCs determined by November 2017 sampling (μg $m^{-3}$).

| Compound | Number of samples (N) | Average | Median | Geometric mean | Standard deviation | Coeff. of variation (CV) | Min-Max |
|---|---|---|---|---|---|---|---|
| **Isoprene** | 8 | 0.0985 | 0.0799 | 0.0811 | 0.0798 | 81 | 0.0421-0.2876 |
| **n-Hexane** | 8 | 0.4762 | 0.4110 | 0.4394 | 0.2070 | 43 | 0.2724-0.7972 |
| **2-Methylfuran** | 8 | 0.0068 | 0.0057 | 0.0059 | 0.0039 | 57 | 0.0032-0.0135 |
| **Chloroform** | 8 | 0.0935 | 0.0795 | 0.0885 | 0.0376 | 40 | 0.0651-0.1795 |
| **Tetrachloromethane** | 8 | 0.0446 | 0.0437 | 0.0444 | 0.0046 | 10 | 0.0379-0.0523 |
| **Benzene** | 8 | 0.0885 | 0.0830 | 0.0814 | 0.0390 | 44 | 0.0455-0.1547 |
| **n-Heptane** | 8 | 0.0563 | 0.0476 | 0.0474 | 0.0336 | 60 | 0.0204-0.1061 |
| **Crotonaldehyde** | 8 | 0.0143 | 0.0109 | 0.0122 | 0.0085 | 60 | 0.0056-0.0263 |
| **n-Octane** | 8 | 0.0382 | 0.0315 | 0.0337 | 0.0201 | 53 | 0.0161-0.0689 |
| **Toluene** | 8 | 0.0718 | 0.0692 | 0.0685 | 0.0220 | 31 | 0.0358-0.1014 |
| **Hexanal** | 8 | 1.2829 | 1.2031 | 1.2231 | 0.4214 | 33 | 0.8079-1.9329 |

| | | | | | | |
|---|---|---|---|---|---|---|
| **Chlorobenzene** | 8 | 0.0211 | 0.0241 | 0.0178 | 0.0113 | 53 | 0.0061-0.0361 |
| **Ethylbenzene** | 8 | 0.0080 | 0.0080 | 0.0077 | 0.0022 | 28 | 0.0045-0.0117 |
| **m+p Xylene** | 8 | 0.0116 | 0.0115 | 0.0112 | 0.0031 | 26 | 0.0067-0.0165 |
| **o-Xylene** | 8 | 0.0094 | 0.0093 | 0.0092 | 0.0024 | 25 | 0.0056-0.0130 |
| **Styrene** | 8 | 0.0120 | 0.0115 | 0.0116 | 0.0031 | 26 | 0.0082-0.0164 |
| **1- Heptanal** | 8 | 0.0275 | 0.0232 | 0.0259 | 0.0105 | 38 | 0.0170-0.0454 |
| **Alpha-pinene** | 8 | 0.0828 | 0.0804 | 0.0783 | 0.0289 | 35 | 0.0471-0.1279 |
| **Isopropylbenzene** | 8 | 0.0010 | 0.0010 | 0.0010 | 0.0002 | 24 | 0.0007-0.0014 |
| **Camphene** | 7 | 0.0062 | 0.0063 | 0.0058 | 0.0024 | 38 | 0.0030-0.0104 |
| **n-Propylbenzene** | 8 | 0.0014 | 0.0014 | 0.0014 | 0.0004 | 27 | 0.0010-0.0020 |
| **m-Ethyltoluene** | 8 | 0.0030 | 0.0028 | 0.0029 | 0.0010 | 33 | 0.0019-0.0047 |
| **p-Ethyltoluene** | 8 | 0.0009 | 0.0008 | 0.0008 | 0.0003 | 35 | 0.0005-0.0013 |
| **1,2,4-Trimethylbenzene** | 8 | 0.0012 | 0.0011 | 0.0011 | 0.0004 | 30 | 0.0007-0.0018 |
| **beta-Pinene** | 8 | 0.0073 | 0.0069 | 0.0067 | 0.0035 | 47 | 0.0036-0.0143 |
| **o-Ethyltoluene** | 8 | 0.0013 | 0.0013 | 0.0012 | 0.0005 | 35 | 0.0007-0.0020 |
| **3-Carene** | 7 | 0.0015 | 0.0014 | 0.0015 | 0.0005 | 30 | 0.0010-0.0024 |
| **1,3,5-Trimethylbenzene** | 8 | 0.0043 | 0.0040 | 0.0041 | 0.0013 | 30 | 0.0028-0.0064 |
| **Benzaldehyde** | 8 | 0.0187 | 0.0195 | 0.0185 | 0.0027 | 14 | 0.0142-0.0223 |
| **Limonene** | 8 | 0.0109 | 0.0108 | 0.0107 | 0.0025 | 23 | 0.0080-0.0153 |
| **p-Cymene** | 8 | 0.0012 | 0.0011 | 0.0012 | 0.0004 | 30 | 0.0008-0.0019 |
| **Eucalyptol** | 6 | 0.0016 | 0.0017 | 0.0016 | 0.0003 | 21 | 0.0012-0.0020 |
| **1,2,3-Trimethylbenzene** | 8 | 0.0013 | 0.0012 | 0.0013 | 0.0003 | 26 | 0.0009-0.0018 |
| **gamma-Terpinene** | 2 | 0.0003 | 0.0003 | 0.0003 | 0.0000 | 4 | 0.0003-0.0003 |
| **1,3-Diethylbenzene** | 7 | 0.0001 | 0.0001 | 0.0001 | 0.0000 | 22 | 0.0001-0.0002 |
| **1,4-Diethylbenzene** | 4 | 0.0009 | 0.0009 | 0.0009 | 0.0002 | 21 | 0.0007-0.0011 |
| **Phenol** | 8 | 0.0079 | 0.0077 | 0.0077 | 0.0018 | 23 | 0.0047-0.0108 |
| **Nonanal** | 8 | 0.0559 | 0.0521 | 0.0526 | 0.0210 | 38 | 0.0329-0.0917 |
| **Acetophenone** | 8 | 0.0101 | 0.0106 | 0.0099 | 0.0024 | 23 | 0.0060-0.0124 |
| **L-Fenchone** | 8 | 0.0005 | 0.0004 | 0.0004 | 0.0002 | 45 | 0.0003-0.0009 |
| **n-Dodecane** | 8 | 0.0077 | 0.0080 | 0.0074 | 0.0020 | 26 | 0.0052-0.0108 |
| **(+)-Camphor** | 3 | 0.0031 | 0.0032 | 0.0031 | 0.0005 | 16 | 0.0026-0.0035 |
| **Decanal** | 8 | 0.0256 | 0.0268 | 0.0226 | 0.0126 | 49 | 0.0115-0.0434 |
| **alpha-Terpineol** | 7 | 0.0031 | 0.0023 | 0.0029 | 0.0014 | 45 | 0.0020-0.0053 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Naphthalene** | 8 | 0.0034 | 0.0034 | 0.0033 | 0.0009 | 27 | 0.0019-0.0047 |
| **n-Tridecane** | 8 | 0.0056 | 0.0052 | 0.0054 | 0.0015 | 27 | 0.0039-0.0081 |
| **Benzothiazole** | 8 | 0.0195 | 0.0149 | 0.0161 | 0.0125 | 64 | 0.0070-0.0375 |
| **n-Tetradecane** | 8 | 0.0133 | 0.0120 | 0.0128 | 0.0038 | 29 | 0.0089-0.0201 |

**Table 1.9.** Descriptive statistical parameters for VOCs determined by January 2018 sampling (μg $m^{-3}$).

| Compound | Number of samples (N) | Average | Median | Geometric mean | Standard deviation | Coeff. of variation (CV) | Min-Max |
|---|---|---|---|---|---|---|---|
| **Isoprene** | 8 | 0.0963 | 0.0843 | 0.0873 | 0.0475 | 49 | 0.0474-0.1807 |
| **Acrylonitrile** | 6 | 0.0014 | 0.0012 | 0.0014 | 0.0005 | 37 | 0.0011-0.0025 |
| **n-Hexane** | 8 | 0.2915 | 0.2007 | 0.2466 | 0.1967 | 67 | 0.1297-0.7052 |
| **2-Methylfuran** | 8 | 0.0346 | 0.0215 | 0.0274 | 0.0304 | 88 | 0.0151-0.1032 |
| **Chloroform** | 7 | 0.0455 | 0.0367 | 0.0393 | 0.0292 | 64 | 0.0160-0.1069 |
| **Tetrachloromethane** | 8 | 0.0653 | 0.0700 | 0.0639 | 0.0137 | 21 | 0.0406-0.0801 |
| **Benzene** | 8 | 0.1200 | 0.1152 | 0.1136 | 0.0414 | 34 | 0.0715-0.1675 |
| **n-Heptane** | 8 | 0.0478 | 0.0394 | 0.0414 | 0.0300 | 63 | 0.0176-0.1133 |
| **Crotonaldehyde** | 8 | 0.0106 | 0.0085 | 0.0091 | 0.0069 | 65 | 0.0049-0.0257 |
| **n-Octane** | 8 | 0.0247 | 0.0241 | 0.0208 | 0.0150 | 60 | 0.0073-0.0537 |
| **Toluene** | 8 | 0.0967 | 0.0895 | 0.0932 | 0.0305 | 32 | 0.0611-0.1652 |
| **Hexanal** | 8 | 0.4625 | 0.3806 | 0.3865 | 0.3236 | 70 | 0.1353-1.1785 |
| **Chlorobenzene** | 8 | 0.0085 | 0.0087 | 0.0081 | 0.0028 | 32 | 0.0042-0.0125 |
| **Ethylbenzene** | 8 | 0.0077 | 0.0066 | 0.0073 | 0.0028 | 36 | 0.0054-0.0140 |
| **m+p Xylene** | 8 | 0.0102 | 0.0096 | 0.0097 | 0.0033 | 33 | 0.0066-0.0170 |
| **o-Xylene** | 8 | 0.0083 | 0.0076 | 0.0080 | 0.0028 | 34 | 0.0057-0.0140 |
| **Styrene** | 8 | 0.0073 | 0.0066 | 0.0069 | 0.0027 | 37 | 0.0031-0.0111 |
| **1- Heptanal** | 8 | 0.0138 | 0.0130 | 0.0127 | 0.0055 | 40 | 0.0056-0.0217 |
| **Alpha-pinene** | 8 | 0.0705 | 0.0435 | 0.0493 | 0.0744 | 106 | 0.0120-0.2460 |
| **Isopropylbenzene** | 8 | 0.0028 | 0.0012 | 0.0020 | 0.0027 | 99 | 0.0011-0.0072 |
| **Camphene** | 5 | 0.0055 | 0.0048 | 0.0051 | 0.0027 | 49 | 0.0035-0.0102 |
| **n-Propylbenzene** | 8 | 0.0013 | 0.0011 | 0.0012 | 0.0005 | 39 | 0.0008-0.0024 |
| **m-Ethyltoluene** | 8 | 0.0040 | 0.0034 | 0.0038 | 0.0017 | 43 | 0.0028-0.0079 |
| **p-Ethyltoluene** | 8 | 0.0013 | 0.0011 | 0.0013 | 0.0006 | 47 | 0.0010-0.0028 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **beta-Myrcene** | 7 | 0.0113 | 0.0109 | 0.0107 | 0.0042 | 37 | 0.0069-0.0196 |
| **1,2,4-Trimethylbenzene** | 8 | 0.0017 | 0.0014 | 0.0016 | 0.0009 | 52 | 0.0011-0.0037 |
| **beta-Pinene** | 8 | 0.0059 | 0.0055 | 0.0051 | 0.0031 | 52 | 0.0013-0.0110 |
| **o-Ethyltoluene** | 8 | 0.0019 | 0.0015 | 0.0017 | 0.0009 | 49 | 0.0012-0.0039 |
| **3-Carene** | 5 | 0.0020 | 0.0022 | 0.0020 | 0.0005 | 25 | 0.0014-0.0026 |
| **1,3,5-Trimethylbenzene** | 8 | 0.0055 | 0.0050 | 0.0053 | 0.0021 | 39 | 0.0038-0.0106 |
| **Benzaldehyde** | 8 | 0.0292 | 0.0291 | 0.0281 | 0.0087 | 30 | 0.0179-0.0471 |
| **Limonene** | 8 | 0.1823 | 0.2081 | 0.1467 | 0.0902 | 49 | 0.0214-0.2834 |
| **m-Cymene** | 6 | 0.0011 | 0.0011 | 0.0011 | 0.0002 | 22 | 0.0008-0.0015 |
| **p-Cymene** | 8 | 0.0025 | 0.0023 | 0.0024 | 0.0010 | 41 | 0.0014-0.0045 |
| **Eucalyptol** | 7 | 0.0016 | 0.0013 | 0.0015 | 0.0009 | 57 | 0.0010-0.0036 |
| **1,2,3-Trimethylbenzene** | 8 | 0.0015 | 0.0014 | 0.0014 | 0.0005 | 36 | 0.0011-0.0028 |
| **gamma-Terpinene** | 8 | 0.0042 | 0.0043 | 0.0034 | 0.0022 | 52 | 0.0005-0.0071 |
| **1,3-Diethylbenzene** | 3 | 0.0002 | 0.0002 | 0.0002 | 0.0000 | 24 | 0.0001-0.0002 |
| **1,4-Diethylbenzene** | 7 | 0.0011 | 0.0010 | 0.0011 | 0.0002 | 22 | 0.0009-0.0016 |
| **Phenol** | 8 | 0.0076 | 0.0068 | 0.0074 | 0.0023 | 31 | 0.0054-0.0114 |
| **Nonanal** | 8 | 0.0410 | 0.0411 | 0.0371 | 0.0162 | 39 | 0.0113-0.0635 |
| **Acetophenone** | 8 | 0.0134 | 0.0108 | 0.0127 | 0.0051 | 38 | 0.0101-0.0241 |
| **alpha-Terpinen** | 4 | 0.0015 | 0.0012 | 0.0014 | 0.0008 | 51 | 0.0011-0.0027 |
| **L-Fenchone** | 7 | 0.0004 | 0.0004 | 0.0004 | 0.0002 | 38 | 0.0003-0.0007 |
| **n-Dodecane** | 8 | 0.0088 | 0.0071 | 0.0079 | 0.0050 | 56 | 0.0045-0.0194 |
| **(+)-Camphor** | 4 | 0.0034 | 0.0034 | 0.0034 | 0.0005 | 14 | 0.0029-0.0040 |
| **Decanal** | 8 | 0.0268 | 0.0279 | 0.0224 | 0.0130 | 48 | 0.0042-0.0460 |
| **alpha-Terpineol** | 7 | 0.0026 | 0.0021 | 0.0025 | 0.0009 | 36 | 0.0020-0.0046 |
| **Naphthalene** | 7 | 0.0040 | 0.0035 | 0.0038 | 0.0015 | 38 | 0.0026-0.0072 |
| **n-Tridecane** | 7 | 0.0036 | 0.0036 | 0.0033 | 0.0014 | 40 | 0.0016-0.0061 |
| **Benzothiazole** | 8 | 0.0286 | 0.0193 | 0.0256 | 0.0161 | 56 | 0.0188-0.0578 |
| **n-Tetradecane** | 8 | 0.0123 | 0.0112 | 0.0117 | 0.0046 | 38 | 0.0078-0.0216 |

**Table 1.10.** Descriptive statistical parameters for VOCs determined by April 2018 sampling (μg $m^{-3}$).

| Compound | Number of samples (N) | Average | Median | Geometric mean | Standard deviation | Coeff. of variation (CV) | Min-Max |
|---|---|---|---|---|---|---|---|

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Isoprene** | 8 | 0.0103 | 0.0099 | 0.0101 | 0.0028 | 27 | 0.0077-0.0164 |
| **n-Hexane** | 8 | 0.2240 | 0.2038 | 0.1986 | 0.1403 | 63 | 0.1163-0.5566 |
| **2-Methylfuran** | 8 | 0.0067 | 0.0071 | 0.0066 | 0.0013 | 19 | 0.0046-0.0080 |
| **Chloroform** | 8 | 0.0123 | 0.0110 | 0.0109 | 0.0075 | 60 | 0.0063-0.0294 |
| **Tetrachloromethane** | 8 | 0.0934 | 0.0909 | 0.0933 | 0.0053 | 6 | 0.0878-0.1016 |
| **Benzene** | 8 | 0.0749 | 0.0679 | 0.0737 | 0.0145 | 19 | 0.0607-0.0971 |
| **n-Heptane** | 8 | 0.0521 | 0.0569 | 0.0438 | 0.0263 | 50 | 0.0098-0.0873 |
| **Crotonaldehyde** | 8 | 0.0195 | 0.0225 | 0.0181 | 0.0068 | 35 | 0.0084-0.0253 |
| **n-Octane** | 8 | 0.0857 | 0.0897 | 0.0709 | 0.0449 | 52 | 0.0142-0.1522 |
| **Toluene** | 8 | 0.1062 | 0.1077 | 0.1008 | 0.0342 | 32 | 0.0541-0.1432 |
| **Hexanal** | 8 | 1.0660 | 0.9803 | 0.9542 | 0.4876 | 46 | 0.3373-1.8357 |
| **Chlorobenzene** | 8 | 0.1851 | 0.2124 | 0.1474 | 0.0964 | 52 | 0.0284-0.2769 |
| **Ethylbenzene** | 8 | 0.0166 | 0.0178 | 0.0160 | 0.0045 | 27 | 0.0084-0.0213 |
| **m+p Xylene** | 8 | 0.0260 | 0.0269 | 0.0251 | 0.0067 | 26 | 0.0140-0.0328 |
| **o-Xylene** | 8 | 0.0202 | 0.0215 | 0.0196 | 0.0049 | 24 | 0.0113-0.0250 |
| **Styrene** | 8 | 0.0200 | 0.0200 | 0.0199 | 0.0020 | 10 | 0.0166-0.0225 |
| **1- Heptanal** | 8 | 0.0855 | 0.0855 | 0.0797 | 0.0308 | 36 | 0.0371-0.1224 |
| **Alpha-pinene** | 8 | 0.0727 | 0.0784 | 0.0704 | 0.0183 | 25 | 0.0433-0.0917 |
| **Isopropylbenzene** | 8 | 0.0011 | 0.0012 | 0.0011 | 0.0002 | 22 | 0.0007-0.0014 |
| **Camphene** | 8 | 0.0116 | 0.0107 | 0.0106 | 0.0051 | 44 | 0.0059-0.0187 |
| **n-Propylbenzene** | 8 | 0.0030 | 0.0033 | 0.0029 | 0.0008 | 25 | 0.0018-0.0038 |
| **m-Ethyltoluene** | 8 | 0.0085 | 0.0091 | 0.0082 | 0.0023 | 27 | 0.0047-0.0110 |
| **p-Ethyltoluene** | 8 | 0.0033 | 0.0035 | 0.0031 | 0.0010 | 31 | 0.0019-0.0045 |
| **Sabinene** | 8 | 0.0029 | 0.0026 | 0.0028 | 0.0009 | 29 | 0.0019-0.0043 |
| **beta-Myrcene** | 6 | 0.0076 | 0.0085 | 0.0066 | 0.0041 | 53 | 0.0028-0.0138 |
| **1,2,4-Trimethylbenzene** | 8 | 0.0032 | 0.0034 | 0.0031 | 0.0008 | 24 | 0.0019-0.0041 |
| **beta-Pinene** | 8 | 0.0317 | 0.0356 | 0.0299 | 0.0101 | 32 | 0.0155-0.0430 |
| **o-Ethyltoluene** | 8 | 0.0040 | 0.0043 | 0.0039 | 0.0012 | 29 | 0.0022-0.0053 |
| **3-Carene** | 8 | 0.0035 | 0.0035 | 0.0034 | 0.0009 | 26 | 0.0018-0.0047 |
| **1,3,5-Trimethylbenzene** | 8 | 0.0138 | 0.0151 | 0.0134 | 0.0033 | 24 | 0.0087-0.0168 |
| **Benzaldehyde** | 8 | 0.1196 | 0.1329 | 0.1152 | 0.0321 | 27 | 0.0643-0.1582 |
| **Limonene** | 8 | 0.3133 | 0.2998 | 0.3011 | 0.0898 | 29 | 0.1661-0.4322 |
| **m-Cymene** | 8 | 0.0028 | 0.0029 | 0.0028 | 0.0004 | 14 | 0.0021-0.0033 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **p-Cymene** | 8 | 0.0179 | 0.0183 | 0.0177 | 0.0026 | 15 | 0.0135-0.0213 |
| **Eucalyptol** | 8 | 0.0150 | 0.0154 | 0.0141 | 0.0051 | 34 | 0.0079-0.0209 |
| **1,2,3-Trimethylbenzene** | 8 | 0.0048 | 0.0054 | 0.0047 | 0.0012 | 24 | 0.0030-0.0059 |
| **4-Methylanisole** | 5 | 0.0032 | 0.0034 | 0.0032 | 0.0003 | 11 | 0.0027-0.0035 |
| **gamma-Terpinene** | 8 | 0.0058 | 0.0032 | 0.0038 | 0.0058 | 101 | 0.0010-0.0159 |
| **1,3-Diethylbenzene** | 8 | 0.0004 | 0.0005 | 0.0004 | 0.0001 | 30 | 0.0002-0.0006 |
| **1,4-Diethylbenzene** | 8 | 0.0038 | 0.0040 | 0.0037 | 0.0008 | 20 | 0.0023-0.0045 |
| **Phenol** | 8 | 0.1804 | 0.2007 | 0.1463 | 0.0989 | 55 | 0.0356-0.3117 |
| **Terpinolene** | 3 | 0.0012 | 0.0011 | 0.0011 | 0.0004 | 36 | 0.0008-0.0016 |
| **Linalool** | 8 | 0.0111 | 0.0110 | 0.0107 | 0.0036 | 32 | 0.0066-0.0177 |
| **Nonanal** | 8 | 0.8529 | 0.9245 | 0.7574 | 0.3679 | 43 | 0.3001-1.2136 |
| **Acetophenone** | 8 | 0.0437 | 0.0486 | 0.0415 | 0.0138 | 32 | 0.0216-0.0605 |
| **L-Fenchone** | 8 | 0.0011 | 0.0011 | 0.0011 | 0.0002 | 20 | 0.0008-0.0015 |
| **n-Dodecane** | 8 | 0.0547 | 0.0633 | 0.0505 | 0.0199 | 36 | 0.0210-0.0783 |
| **(+)-Camphor** | 8 | 0.1608 | 0.1884 | 0.1291 | 0.0855 | 53 | 0.0281-0.2501 |
| **Decanal** | 8 | 0.8017 | 0.8486 | 0.6960 | 0.3832 | 48 | 0.2604-1.2800 |
| **alpha-Terpineol** | 8 | 0.0182 | 0.0209 | 0.0158 | 0.0080 | 44 | 0.0047-0.0258 |
| **Naphthalene** | 8 | 0.0453 | 0.0508 | 0.0390 | 0.0217 | 48 | 0.0121-0.0716 |
| **n-Tridecane** | 8 | 0.0574 | 0.0641 | 0.0489 | 0.0286 | 50 | 0.0157-0.0908 |
| **Benzothiazole** | 8 | 0.0545 | 0.0529 | 0.0514 | 0.0207 | 38 | 0.0324-0.0954 |
| **n-Tetradecane** | 8 | 0.0965 | 0.1139 | 0.0849 | 0.0426 | 44 | 0.0289-0.1350 |

**Table 1.11.** Descriptive statistical parameters for VOCs determined by May 2018 sampling (µg $m^{-3}$).

| Compound | Number of samples (N) | Average | Median | Geometric mean | Standard deviation | Coeff. of variation (CV) | Min-Max |
|---|---|---|---|---|---|---|---|
| **Isoprene** | 8 | 0.5110 | 0.3647 | 0.3821 | 0.4354 | 85 | 0.1640-1.4309 |
| **n-Hexane** | 8 | 0.8201 | 0.6413 | 0.7453 | 0.4048 | 49 | 0.4005-1.4642 |
| **Methachrolein** | 8 | 0.0367 | 0.0333 | 0.0357 | 0.0101 | 27 | 0.0283-0.0590 |
| **2-Methylfuran** | 8 | 0.0135 | 0.0143 | 0.0127 | 0.0043 | 32 | 0.0056-0.0205 |
| **Methylvinylketone** | 8 | 0.0651 | 0.0622 | 0.0627 | 0.0189 | 29 | 0.0431-0.0982 |
| **Chloroform** | 8 | 0.0325 | 0.0240 | 0.0288 | 0.0176 | 54 | 0.0178-0.0606 |
| **Tetrachloromethane** | 8 | 0.2008 | 0.2169 | 0.1923 | 0.0516 | 26 | 0.0839-0.2459 |

| | | | | | | |
|---|---|---|---|---|---|---|
| **Benzene** | 8 | 0.0973 | 0.0983 | 0.0937 | 0.0278 | 29 | 0.0541-0.1452 |
| **1,2-Dichloroethane** | 3 | 0.0136 | 0.0135 | 0.0136 | 0.0003 | 2 | 0.0134-0.0139 |
| **n-Heptane** | 8 | 0.2154 | 0.1677 | 0.1804 | 0.1264 | 59 | 0.0461-0.4174 |
| **Crotonaldehyde** | 8 | 0.0249 | 0.0257 | 0.0242 | 0.0062 | 25 | 0.0136-0.0316 |
| **n-Octane** | 8 | 0.1578 | 0.1222 | 0.1325 | 0.0973 | 62 | 0.0372-0.3517 |
| **Toluene** | 8 | 0.3589 | 0.3886 | 0.3168 | 0.1565 | 44 | 0.0891-0.5251 |
| **Hexanal** | 8 | 3.1618 | 3.2065 | 2.7489 | 1.5390 | 49 | 0.9604-5.5850 |
| **Chlorobenzene** | 8 | 0.3183 | 0.3026 | 0.2673 | 0.1769 | 56 | 0.0915-0.5762 |
| **Ethylbenzene** | 8 | 0.0455 | 0.0520 | 0.0411 | 0.0176 | 39 | 0.0122-0.0618 |
| **m+p Xylene** | 8 | 0.0715 | 0.0813 | 0.0651 | 0.0273 | 38 | 0.0217-0.1046 |
| **o-Xylene** | 8 | 0.0571 | 0.0646 | 0.0514 | 0.0227 | 40 | 0.0154-0.0855 |
| **Styrene** | 8 | 0.0620 | 0.0594 | 0.0520 | 0.0346 | 56 | 0.0129-0.1171 |
| **1- Heptanal** | 8 | 0.1616 | 0.1559 | 0.1493 | 0.0592 | 37 | 0.0548-0.2524 |
| **Alpha-pinene** | 8 | 0.3134 | 0.2582 | 0.2463 | 0.2130 | 68 | 0.0476-0.7092 |
| **Isopropylbenzene** | 8 | 0.0034 | 0.0035 | 0.0030 | 0.0015 | 45 | 0.0009-0.0057 |
| **Camphene** | 8 | 0.0365 | 0.0362 | 0.0275 | 0.0249 | 68 | 0.0032-0.0892 |
| **n-Propylbenzene** | 8 | 0.0075 | 0.0083 | 0.0067 | 0.0028 | 38 | 0.0018-0.0103 |
| **m-Ethyltoluene** | 8 | 0.0165 | 0.0178 | 0.0146 | 0.0068 | 41 | 0.0035-0.0235 |
| **p-Ethyltoluene** | 8 | 0.0062 | 0.0066 | 0.0055 | 0.0027 | 43 | 0.0014-0.0092 |
| **Sabinene** | 8 | 0.0227 | 0.0245 | 0.0211 | 0.0078 | 34 | 0.0081-0.0320 |
| **beta-Myrcene** | 5 | 0.0046 | 0.0041 | 0.0043 | 0.0018 | 40 | 0.0028-0.0066 |
| **1,2,4-Trimethylbenzene** | 8 | 0.0062 | 0.0067 | 0.0056 | 0.0024 | 39 | 0.0014-0.0089 |
| **beta-Pinene** | 8 | 0.0681 | 0.0655 | 0.0551 | 0.0371 | 54 | 0.0078-0.1411 |
| **o-Ethyltoluene** | 8 | 0.0080 | 0.0086 | 0.0070 | 0.0035 | 43 | 0.0017-0.0121 |
| **3-Carene** | 8 | 0.0097 | 0.0094 | 0.0082 | 0.0050 | 51 | 0.0017-0.0194 |
| **1,3,5-Trimethylbenzene** | 8 | 0.0268 | 0.0287 | 0.0240 | 0.0103 | 39 | 0.0064-0.0378 |
| **Benzaldehyde** | 8 | 0.2385 | 0.2431 | 0.2195 | 0.0910 | 38 | 0.0873-0.3501 |
| **Limonene** | 8 | 0.0941 | 0.0815 | 0.0705 | 0.0715 | 76 | 0.0166-0.2292 |
| **m-Cymene** | 7 | 0.0026 | 0.0027 | 0.0025 | 0.0009 | 34 | 0.0016-0.0037 |
| **p-Cymene** | 8 | 0.0148 | 0.0143 | 0.0128 | 0.0069 | 47 | 0.0028-0.0251 |
| **Eucalyptol** | 8 | 0.0328 | 0.0339 | 0.0285 | 0.0149 | 46 | 0.0069-0.0570 |
| **1,2,3-Trimethylbenzene** | 8 | 0.0091 | 0.0096 | 0.0082 | 0.0034 | 38 | 0.0024-0.0125 |
| **gamma-Terpinene** | 7 | 0.0021 | 0.0023 | 0.0019 | 0.0010 | 46 | 0.0008-0.0034 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **1,3-Diethylbenzene** | 8 | 0.0009 | 0.0009 | 0.0008 | 0.0004 | 46 | 0.0003-0.0013 |
| **1,4-Diethylbenzene** | 8 | 0.0069 | 0.0072 | 0.0064 | 0.0025 | 35 | 0.0021-0.0095 |
| **Phenol** | 8 | 0.8189 | 0.8800 | 0.7736 | 0.2600 | 32 | 0.3761-1.1234 |
| **1,2-Dichlorobenzene** | 6 | 0.0019 | 0.0019 | 0.0018 | 0.0003 | 17 | 0.0015-0.0023 |
| **Terpinolene** | 4 | 0.0014 | 0.0014 | 0.0014 | 0.0003 | 20 | 0.0011-0.0017 |
| **Nonanal** | 8 | 1.0457 | 1.0197 | 0.9823 | 0.3461 | 33 | 0.3941-1.6233 |
| **Acetophenone** | 8 | 0.0894 | 0.0995 | 0.0858 | 0.0244 | 27 | 0.0429-0.1199 |
| **L-Fenchone** | 8 | 0.0027 | 0.0030 | 0.0024 | 0.0011 | 40 | 0.0005-0.0039 |
| **n-Dodecane** | 8 | 0.1059 | 0.1066 | 0.0997 | 0.0319 | 30 | 0.0371-0.1418 |
| **(+)-Camphor** | 8 | 0.2011 | 0.2073 | 0.1836 | 0.0737 | 37 | 0.0572-0.2891 |
| **1-Terpinen-4-ol** | 8 | 0.4925 | 0.5018 | 0.4482 | 0.1843 | 37 | 0.1371-0.7148 |
| **Decanal** | 8 | 0.8104 | 0.8112 | 0.7763 | 0.2394 | 30 | 0.3920-1.2546 |
| **alpha-Terpineol** | 8 | 0.0710 | 0.0782 | 0.0648 | 0.0273 | 38 | 0.0256-0.1011 |
| **Naphthalene** | 8 | 0.0731 | 0.0821 | 0.0688 | 0.0221 | 30 | 0.0268-0.0924 |
| **n-Tridecane** | 8 | 0.1317 | 0.1432 | 0.1255 | 0.0384 | 29 | 0.0623-0.1714 |
| **Benzothiazole** | 8 | 0.0600 | 0.0648 | 0.0588 | 0.0125 | 21 | 0.0404-0.0715 |
| **n-Tetradecane** | 8 | 0.1710 | 0.1903 | 0.1618 | 0.0506 | 30 | 0.0694-0.2095 |

**Table 1.12.** Descriptive statistical parameters for VOCs determined by June 2018 sampling (µg $m^{-3}$).

| Compound | Number of samples (N) | Average | Median | Geometric mean | Standard deviation | Coeff. of variation (CV) | Min-Max |
|---|---|---|---|---|---|---|---|
| **Isoprene** | 8 | 0.6072 | 0.4431 | 0.4981 | 0.4461 | 73 | 0.2624-1.4429 |
| **n-Hexane** | 8 | 0.3688 | 0.3515 | 0.3554 | 0.1129 | 31 | 0.2618-0.5970 |
| **Methachrolein** | 8 | 0.0501 | 0.0403 | 0.0472 | 0.0192 | 38 | 0.0335-0.0850 |
| **2-Methylfuran** | 8 | 0.0244 | 0.0242 | 0.0238 | 0.0055 | 23 | 0.0168-0.0310 |
| **Methylvinylketone** | 8 | 0.1500 | 0.1068 | 0.1323 | 0.0829 | 55 | 0.0778-0.2807 |
| **Chloroform** | 8 | 0.0063 | 0.0060 | 0.0061 | 0.0020 | 32 | 0.0036-0.0098 |
| **Tetrachloromethane** | 8 | 0.2086 | 0.2020 | 0.2073 | 0.0252 | 12 | 0.1810-0.2531 |
| **Benzene** | 8 | 0.0674 | 0.0583 | 0.0643 | 0.0246 | 37 | 0.0421-0.1226 |
| **1,2-Dichloroethane** | 2 | 0.0141 | 0.0141 | 0.0140 | 0.0014 | 10 | 0.0130-0.0151 |
| **n-Heptane** | 8 | 0.3089 | 0.1988 | 0.2578 | 0.2017 | 65 | 0.1261-0.6494 |
| **Crotonaldehyde** | 8 | 0.0242 | 0.0237 | 0.0239 | 0.0044 | 18 | 0.0190-0.0312 |

| | | | | | | |
|---|---|---|---|---|---|---|
| **n-Octane** | 8 | 0.2455 | 0.1626 | 0.2090 | 0.1488 | 61 | 0.1110-0.4288 |
| **Toluene** | 8 | 0.4220 | 0.4023 | 0.3988 | 0.1454 | 34 | 0.2174-0.6053 |
| **Hexanal** | 8 | 3.2955 | 3.4569 | 3.0672 | 1.2134 | 37 | 1.3935-4.6980 |
| **Chlorobenzene** | 8 | 0.3650 | 0.3808 | 0.2991 | 0.1895 | 52 | 0.0829-0.5844 |
| **Ethylbenzene** | 8 | 0.0541 | 0.0515 | 0.0525 | 0.0142 | 26 | 0.0336-0.0739 |
| **m+p Xylene** | 8 | 0.0791 | 0.0777 | 0.0766 | 0.0207 | 26 | 0.0506-0.1099 |
| **o-Xylene** | 8 | 0.0663 | 0.0657 | 0.0644 | 0.0166 | 25 | 0.0455-0.0882 |
| **Styrene** | 8 | 0.0309 | 0.0303 | 0.0304 | 0.0066 | 21 | 0.0217-0.0443 |
| **1- Heptanal** | 8 | 0.1534 | 0.1516 | 0.1482 | 0.0417 | 27 | 0.0891-0.2191 |
| **Alpha-pinene** | 8 | 0.3071 | 0.3211 | 0.1773 | 0.2172 | 71 | 0.0081-0.6751 |
| **Isopropylbenzene** | 8 | 0.0031 | 0.0030 | 0.0030 | 0.0007 | 23 | 0.0023-0.0041 |
| **Camphene** | 8 | 0.0445 | 0.0401 | 0.0388 | 0.0257 | 58 | 0.0145-0.0984 |
| **n-Propylbenzene** | 8 | 0.0076 | 0.0077 | 0.0074 | 0.0019 | 25 | 0.0049-0.0096 |
| **m-Ethyltoluene** | 8 | 0.0187 | 0.0186 | 0.0181 | 0.0050 | 27 | 0.0111-0.0252 |
| **p-Ethyltoluene** | 8 | 0.0069 | 0.0068 | 0.0068 | 0.0016 | 24 | 0.0041-0.0088 |
| **Sabinene** | 6 | 0.0268 | 0.0112 | 0.0117 | 0.0364 | 136 | 0.0022-0.0962 |
| **beta-Myrcene** | 5 | 0.0148 | 0.0092 | 0.0104 | 0.0128 | 86 | 0.0039-0.0319 |
| **1,2,4-Trimethylbenzene** | 8 | 0.0070 | 0.0067 | 0.0068 | 0.0019 | 27 | 0.0045-0.0095 |
| **beta-Pinene** | 7 | 0.0984 | 0.0963 | 0.0624 | 0.0567 | 58 | 0.0022-0.1881 |
| **o-Ethyltoluene** | 8 | 0.0087 | 0.0085 | 0.0085 | 0.0022 | 25 | 0.0058-0.0119 |
| **3-Carene** | 8 | 0.0228 | 0.0248 | 0.0207 | 0.0098 | 43 | 0.0083-0.0401 |
| **1,3,5-Trimethylbenzene** | 8 | 0.0288 | 0.0282 | 0.0280 | 0.0073 | 25 | 0.0200-0.0379 |
| **Benzaldehyde** | 8 | 0.1662 | 0.1605 | 0.1609 | 0.0447 | 27 | 0.1031-0.2413 |
| **Limonene** | 7 | 0.0308 | 0.0239 | 0.0281 | 0.0140 | 46 | 0.0170-0.0498 |
| **m-Cymene** | 8 | 0.0021 | 0.0021 | 0.0020 | 0.0008 | 36 | 0.0011-0.0036 |
| **p-Cymene** | 8 | 0.0189 | 0.0169 | 0.0168 | 0.0110 | 58 | 0.0080-0.0442 |
| **Ocimene** | 4 | 0.0069 | 0.0066 | 0.0057 | 0.0044 | 64 | 0.0025-0.0116 |
| **Eucalyptol** | 8 | 0.0707 | 0.0685 | 0.0663 | 0.0275 | 39 | 0.0383-0.1225 |
| **1,2,3-Trimethylbenzene** | 8 | 0.0093 | 0.0089 | 0.0090 | 0.0022 | 23 | 0.0068-0.0123 |
| **gamma-Terpinene** | 7 | 0.0017 | 0.0018 | 0.0016 | 0.0006 | 37 | 0.0007-0.0023 |
| **1,3-Diethylbenzene** | 8 | 0.0007 | 0.0006 | 0.0007 | 0.0003 | 44 | 0.0004-0.0014 |
| **1,4-Diethylbenzene** | 8 | 0.0064 | 0.0064 | 0.0063 | 0.0012 | 19 | 0.0048-0.0084 |
| **Phenol** | 8 | 1.2688 | 1.2754 | 1.2516 | 0.2150 | 17 | 0.8566-1.6344 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Terpinolene** | 2 | 0.0012 | 0.0012 | 0.0012 | 0.0004 | 37 | 0.0009-0.0015 |
| **Nonanal** | 8 | 0.9801 | 0.8617 | 0.9026 | 0.4352 | 44 | 0.4482-1.6818 |
| **Acetophenone** | 8 | 0.0910 | 0.0911 | 0.0895 | 0.0176 | 19 | 0.0601-0.1208 |
| **L-Fenchone** | 8 | 0.0045 | 0.0046 | 0.0043 | 0.0012 | 27 | 0.0025-0.0058 |
| **n-Dodecane** | 8 | 0.0371 | 0.0355 | 0.0341 | 0.0157 | 42 | 0.0185-0.0579 |
| **(+)-Camphor** | 8 | 0.1517 | 0.1404 | 0.1414 | 0.0595 | 39 | 0.0792-0.2409 |
| **1-Terpinen-4-ol** | 8 | 0.3085 | 0.2775 | 0.2673 | 0.1634 | 53 | 0.0980-0.5472 |
| **Decanal** | 8 | 0.4494 | 0.3747 | 0.4222 | 0.1810 | 40 | 0.2612-0.8158 |
| **alpha-Terpineol** | 8 | 0.0639 | 0.0586 | 0.0566 | 0.0326 | 51 | 0.0247-0.1173 |
| **Naphthalene** | 8 | 0.0636 | 0.0643 | 0.0621 | 0.0140 | 22 | 0.0407-0.0807 |
| **n-Tridecane** | 8 | 0.1611 | 0.1627 | 0.1586 | 0.0296 | 18 | 0.1112-0.2035 |
| **Benzothiazole** | 8 | 0.0687 | 0.0653 | 0.0679 | 0.0121 | 18 | 0.0568-0.0937 |
| **n-Tetradecane** | 8 | 0.1528 | 0.1509 | 0.1506 | 0.0272 | 18 | 0.1083-0.1892 |

**Table 1.13.** Descriptive statistical parameters for VOCs determined by July 2018 sampling (μg $m^{-3}$).

| Compound | Number of samples (N) | Average | Median | Geometric mean | Standard deviation | Coeff. of variation (CV) | Min-Max |
|---|---|---|---|---|---|---|---|
| **Isoprene** | 8 | 1.8629 | 1.5252 | 1.5181 | 1.4443 | 78 | 0.7349-5.1375 |
| **n-Hexane** | 8 | 0.8296 | 0.7377 | 0.7466 | 0.3852 | 46 | 0.3029-1.4233 |
| **Methachrolein** | 8 | 0.0584 | 0.0575 | 0.0571 | 0.0129 | 22 | 0.0390-0.0769 |
| **2-Methylfuran** | 8 | 0.0355 | 0.0367 | 0.0346 | 0.0082 | 23 | 0.0226-0.0472 |
| **Methylvinylketone** | 8 | 0.1262 | 0.1231 | 0.1232 | 0.0286 | 23 | 0.0781-0.1633 |
| **Chloroform** | 8 | 0.0146 | 0.0118 | 0.0126 | 0.0093 | 64 | 0.0060-0.0337 |
| **Tetrachloromethane** | 8 | 0.1716 | 0.1690 | 0.1687 | 0.0335 | 20 | 0.1277-0.2262 |
| **Benzene** | 8 | 0.0657 | 0.0533 | 0.0626 | 0.0242 | 37 | 0.0481-0.1154 |
| **n-Heptane** | 8 | 0.3265 | 0.2482 | 0.2723 | 0.2260 | 69 | 0.1415-0.7400 |
| **Crotonaldehyde** | 8 | 0.0267 | 0.0256 | 0.0264 | 0.0047 | 18 | 0.0223-0.0358 |
| **n-Octane** | 8 | 0.1843 | 0.1548 | 0.1632 | 0.1022 | 55 | 0.0815-0.3755 |
| **Toluene** | 8 | 0.6389 | 0.6179 | 0.6325 | 0.1041 | 16 | 0.5507-0.8793 |
| **Hexanal** | 8 | 5.6754 | 5.6239 | 5.4789 | 1.5505 | 27 | 3.3334-7.9912 |
| **Chlorobenzene** | 8 | 0.5934 | 0.5901 | 0.5701 | 0.1748 | 29 | 0.3749-0.8448 |
| **Ethylbenzene** | 8 | 0.0914 | 0.0929 | 0.0893 | 0.0198 | 22 | 0.0532-0.1186 |

| | | | | | | |
|---|---|---|---|---|---|---|
| **m+p Xylene** | 8 | 0.1285 | 0.1369 | 0.1242 | 0.0343 | 27 | 0.0726-0.1886 |
| **o-Xylene** | 8 | 0.1107 | 0.1178 | 0.1085 | 0.0226 | 20 | 0.0697-0.1432 |
| **Styrene** | 8 | 0.0475 | 0.0494 | 0.0425 | 0.0218 | 46 | 0.0173-0.0812 |
| **1- Heptanal** | 8 | 0.2633 | 0.2211 | 0.2494 | 0.0975 | 37 | 0.1786-0.4487 |
| **Alpha-pinene** | 8 | 0.2315 | 0.1055 | 0.1449 | 0.2214 | 96 | 0.0381-0.5921 |
| **Isopropylbenzene** | 8 | 0.0068 | 0.0067 | 0.0066 | 0.0013 | 19 | 0.0045-0.0087 |
| **Camphene** | 8 | 0.0612 | 0.0644 | 0.0558 | 0.0247 | 40 | 0.0208-0.0921 |
| **n-Propylbenzene** | 8 | 0.0163 | 0.0169 | 0.0161 | 0.0025 | 15 | 0.0107-0.0186 |
| **m-Ethyltoluene** | 8 | 0.0444 | 0.0468 | 0.0436 | 0.0089 | 20 | 0.0290-0.0548 |
| **p-Ethyltoluene** | 8 | 0.0174 | 0.0182 | 0.0171 | 0.0033 | 19 | 0.0115-0.0210 |
| **beta-Myrcene** | 3 | 0.0181 | 0.0189 | 0.0179 | 0.0033 | 18 | 0.0145-0.0210 |
| **1,2,4-Trimethylbenzene** | 8 | 0.0146 | 0.0151 | 0.0143 | 0.0032 | 22 | 0.0094-0.0186 |
| **beta-Pinene** | 6 | 0.0653 | 0.0381 | 0.0297 | 0.0707 | 108 | 0.0058-0.1669 |
| **o-Ethyltoluene** | 8 | 0.0183 | 0.0188 | 0.0181 | 0.0033 | 18 | 0.0125-0.0236 |
| **3-Carene** | 8 | 0.0248 | 0.0232 | 0.0216 | 0.0126 | 51 | 0.0082-0.0441 |
| **1,3,5-Trimethylbenzene** | 8 | 0.0619 | 0.0636 | 0.0607 | 0.0124 | 20 | 0.0402-0.0755 |
| **Benzaldehyde** | 8 | 0.4075 | 0.3661 | 0.3780 | 0.1789 | 44 | 0.2203-0.7856 |
| **Limonene** | 7 | 0.0216 | 0.0152 | 0.0148 | 0.0167 | 78 | 0.0024-0.0427 |
| **m-Cymene** | 8 | 0.0035 | 0.0036 | 0.0035 | 0.0006 | 16 | 0.0025-0.0041 |
| **p-Cymene** | 8 | 0.0386 | 0.0384 | 0.0366 | 0.0127 | 33 | 0.0212-0.0579 |
| **Ocimene** | 5 | 0.0096 | 0.0081 | 0.0081 | 0.0059 | 62 | 0.0030-0.0191 |
| **Eucalyptol** | 8 | 0.0802 | 0.0683 | 0.0768 | 0.0275 | 34 | 0.0594-0.1393 |
| **1,2,3-Trimethylbenzene** | 8 | 0.0182 | 0.0181 | 0.0179 | 0.0034 | 19 | 0.0127-0.0231 |
| **1,3-Diethylbenzene** | 8 | 0.0013 | 0.0013 | 0.0013 | 0.0003 | 21 | 0.0010-0.0019 |
| **1,4-Diethylbenzene** | 8 | 0.0127 | 0.0125 | 0.0125 | 0.0024 | 19 | 0.0093-0.0160 |
| **Phenol** | 8 | 0.9210 | 0.9316 | 0.8859 | 0.2757 | 30 | 0.5851-1.4204 |
| **1,2-Dichlorobenzene** | 8 | 0.0041 | 0.0038 | 0.0040 | 0.0011 | 27 | 0.0030-0.0062 |
| **Nonanal** | 8 | 1.0351 | 1.0147 | 0.9477 | 0.4570 | 44 | 0.5030-1.7820 |
| **Acetophenone** | 8 | 0.1775 | 0.1510 | 0.1631 | 0.0884 | 50 | 0.1003-0.3749 |
| **L-Fenchone** | 8 | 0.0063 | 0.0066 | 0.0062 | 0.0008 | 13 | 0.0050-0.0073 |
| **n-Dodecane** | 8 | 0.1354 | 0.1229 | 0.1321 | 0.0336 | 25 | 0.1017-0.1923 |
| **(+)-Camphor** | 8 | 0.1301 | 0.1264 | 0.1284 | 0.0226 | 17 | 0.1005-0.1643 |
| **1-Terpinen-4-ol** | 8 | 0.0863 | 0.0801 | 0.0843 | 0.0219 | 25 | 0.0679-0.1369 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Decanal** | 8 | 0.7561 | 0.5475 | 0.6646 | 0.4836 | 64 | 0.3795-1.8703 |
| **alpha-Terpineol** | 8 | 0.0245 | 0.0247 | 0.0196 | 0.0149 | 61 | 0.0050-0.0479 |
| **Naphthalene** | 8 | 0.0728 | 0.0717 | 0.0715 | 0.0151 | 21 | 0.0550-0.0998 |
| **n-Tridecane** | 8 | 0.2423 | 0.2302 | 0.2395 | 0.0411 | 17 | 0.1968-0.3224 |
| **Benzothiazole** | 8 | 0.0811 | 0.0813 | 0.0784 | 0.0236 | 29 | 0.0574-0.1302 |
| **n-Tetradecane** | 8 | 0.3644 | 0.3733 | 0.3551 | 0.0889 | 24 | 0.2622-0.5246 |

**Table 1.14.** Descriptive statistical parameters for VOCs determined by August 2018 sampling (μg $m^{-3}$).

| Compound | Number of samples (N) | Average | Median | Geometric mean | Standard deviation | Coeff. of variation (CV) | Min-Max |
|---|---|---|---|---|---|---|---|
| **Isoprene** | 8 | 1.1176 | 0.7502 | 0.9509 | 0.6945 | 62 | 0.4806-2.3009 |
| **n-Hexane** | 8 | 0.4712 | 0.3753 | 0.4269 | 0.2377 | 50 | 0.2086-0.9536 |
| **Methachrolein** | 8 | 0.0486 | 0.0444 | 0.0478 | 0.0099 | 20 | 0.0387-0.0694 |
| **2-Methylfuran** | 8 | 0.0261 | 0.0268 | 0.0245 | 0.0085 | 33 | 0.0098-0.0368 |
| **Methylvinylketone** | 8 | 0.0938 | 0.0942 | 0.0905 | 0.0246 | 26 | 0.0482-0.1301 |
| **Chloroform** | 8 | 0.0044 | 0.0039 | 0.0041 | 0.0016 | 36 | 0.0021-0.0068 |
| **Tetrachloromethane** | 8 | 0.1256 | 0.1331 | 0.1188 | 0.0373 | 30 | 0.0495-0.1654 |
| **Benzene** | 8 | 0.0476 | 0.0474 | 0.0453 | 0.0150 | 31 | 0.0225-0.0740 |
| **n-Heptane** | 8 | 0.1967 | 0.2106 | 0.1604 | 0.1095 | 56 | 0.0458-0.3331 |
| **Crotonaldehyde** | 8 | 0.0215 | 0.0213 | 0.0211 | 0.0039 | 18 | 0.0142-0.0266 |
| **n-Octane** | 8 | 0.1253 | 0.1350 | 0.1127 | 0.0510 | 41 | 0.0405-0.1790 |
| **Toluene** | 8 | 0.4080 | 0.4180 | 0.4008 | 0.0741 | 18 | 0.2482-0.4760 |
| **Hexanal** | 8 | 4.2743 | 4.5355 | 3.8848 | 1.7558 | 41 | 1.6538-7.0218 |
| **Chlorobenzene** | 8 | 0.4888 | 0.5624 | 0.4377 | 0.1971 | 40 | 0.1640-0.6765 |
| **Ethylbenzene** | 8 | 0.0544 | 0.0616 | 0.0457 | 0.0252 | 46 | 0.0101-0.0777 |
| **m+p Xylene** | 8 | 0.0780 | 0.0874 | 0.0651 | 0.0370 | 47 | 0.0138-0.1185 |
| **o-Xylene** | 8 | 0.0679 | 0.0745 | 0.0591 | 0.0296 | 44 | 0.0158-0.1021 |
| **Styrene** | 8 | 0.0269 | 0.0278 | 0.0222 | 0.0128 | 48 | 0.0034-0.0461 |
| **1- Heptanal** | 8 | 0.1877 | 0.2080 | 0.1721 | 0.0721 | 38 | 0.0740-0.2821 |
| **Alpha-pinene** | 8 | 0.1192 | 0.1052 | 0.0941 | 0.0772 | 65 | 0.0197-0.2528 |
| **Isopropylbenzene** | 8 | 0.0034 | 0.0039 | 0.0029 | 0.0016 | 47 | 0.0007-0.0050 |
| **Camphene** | 8 | 0.0325 | 0.0335 | 0.0258 | 0.0166 | 51 | 0.0033-0.0538 |

| | | | | | | |
|---|---|---|---|---|---|---|
| **n-Propylbenzene** | 8 | 0.0091 | 0.0106 | 0.0077 | 0.0042 | 46 | 0.0020-0.0127 |
| **m-Ethyltoluene** | 8 | 0.0287 | 0.0337 | 0.0231 | 0.0142 | 50 | 0.0042-0.0418 |
| **p-Ethyltoluene** | 8 | 0.0109 | 0.0127 | 0.0092 | 0.0052 | 47 | 0.0022-0.0158 |
| **beta-Myrcene** | 2 | 0.0178 | 0.0178 | 0.0166 | 0.0090 | 51 | 0.0114-0.0242 |
| **1,2,4-Trimethylbenzene** | 8 | 0.0104 | 0.0123 | 0.0083 | 0.0053 | 51 | 0.0014-0.0160 |
| **beta-Pinene** | 8 | 0.0186 | 0.0144 | 0.0104 | 0.0224 | 120 | 0.0021-0.0707 |
| **o-Ethyltoluene** | 8 | 0.0130 | 0.0153 | 0.0106 | 0.0064 | 49 | 0.0022-0.0186 |
| **3-Carene** | 8 | 0.0198 | 0.0194 | 0.0138 | 0.0156 | 79 | 0.0024-0.0504 |
| **1,3,5-Trimethylbenzene** | 8 | 0.0418 | 0.0483 | 0.0340 | 0.0208 | 50 | 0.0068-0.0645 |
| **Benzaldehyde** | 8 | 0.1738 | 0.1934 | 0.1546 | 0.0700 | 40 | 0.0442-0.2460 |
| **Limonene** | 7 | 0.0095 | 0.0056 | 0.0071 | 0.0100 | 106 | 0.0035-0.0319 |
| **m-Cymene** | 7 | 0.0029 | 0.0036 | 0.0026 | 0.0011 | 38 | 0.0008-0.0038 |
| **p-Cymene** | 8 | 0.0250 | 0.0287 | 0.0200 | 0.0128 | 51 | 0.0037-0.0407 |
| **Ocimene** | 5 | 0.0076 | 0.0082 | 0.0068 | 0.0037 | 49 | 0.0035-0.0114 |
| **Eucalyptol** | 8 | 0.1283 | 0.1400 | 0.1091 | 0.0661 | 52 | 0.0379-0.2407 |
| **1,2,3-Trimethylbenzene** | 8 | 0.0145 | 0.0166 | 0.0120 | 0.0071 | 49 | 0.0028-0.0220 |
| **1,3-Diethylbenzene** | 7 | 0.0011 | 0.0013 | 0.0009 | 0.0005 | 48 | 0.0002-0.0018 |
| **1,4-Diethylbenzene** | 8 | 0.0096 | 0.0114 | 0.0082 | 0.0043 | 45 | 0.0023-0.0137 |
| **Phenol** | 8 | 0.4098 | 0.3641 | 0.3467 | 0.2389 | 58 | 0.1386-0.7952 |
| **1,2-Dichlorobenzene** | 4 | 0.0012 | 0.0011 | 0.0012 | 0.0003 | 26 | 0.0010-0.0016 |
| **Nonanal** | 8 | 1.1303 | 1.1894 | 1.0399 | 0.4148 | 37 | 0.3929-1.5595 |
| **Acetophenone** | 8 | 0.0877 | 0.0996 | 0.0770 | 0.0377 | 43 | 0.0218-0.1366 |
| **L-Fenchone** | 8 | 0.0054 | 0.0060 | 0.0045 | 0.0028 | 52 | 0.0012-0.0092 |
| **n-Dodecane** | 8 | 0.0269 | 0.0292 | 0.0242 | 0.0112 | 42 | 0.0080-0.0432 |
| **(+)-Camphor** | 8 | 0.0738 | 0.0729 | 0.0635 | 0.0361 | 49 | 0.0174-0.1299 |
| **1-Terpinen-4-ol** | 8 | 0.0346 | 0.0327 | 0.0285 | 0.0207 | 60 | 0.0066-0.0745 |
| **Decanal** | 8 | 0.5396 | 0.5760 | 0.5092 | 0.1712 | 32 | 0.2239-0.7716 |
| **alpha-Terpineol** | 8 | 0.0175 | 0.0120 | 0.0140 | 0.0133 | 76 | 0.0048-0.0454 |
| **Naphthalene** | 8 | 0.0385 | 0.0387 | 0.0350 | 0.0159 | 41 | 0.0129-0.0624 |
| **n-Tridecane** | 8 | 0.1289 | 0.1309 | 0.1124 | 0.0602 | 47 | 0.0332-0.2084 |
| **Benzothiazole** | 8 | 0.0441 | 0.0441 | 0.0399 | 0.0180 | 41 | 0.0144-0.0663 |
| **n-Tetradecane** | 8 | 0.1510 | 0.1509 | 0.1302 | 0.0720 | 48 | 0.0334-0.2477 |

## APPENDIX 2 Temporal Variation of VOCs

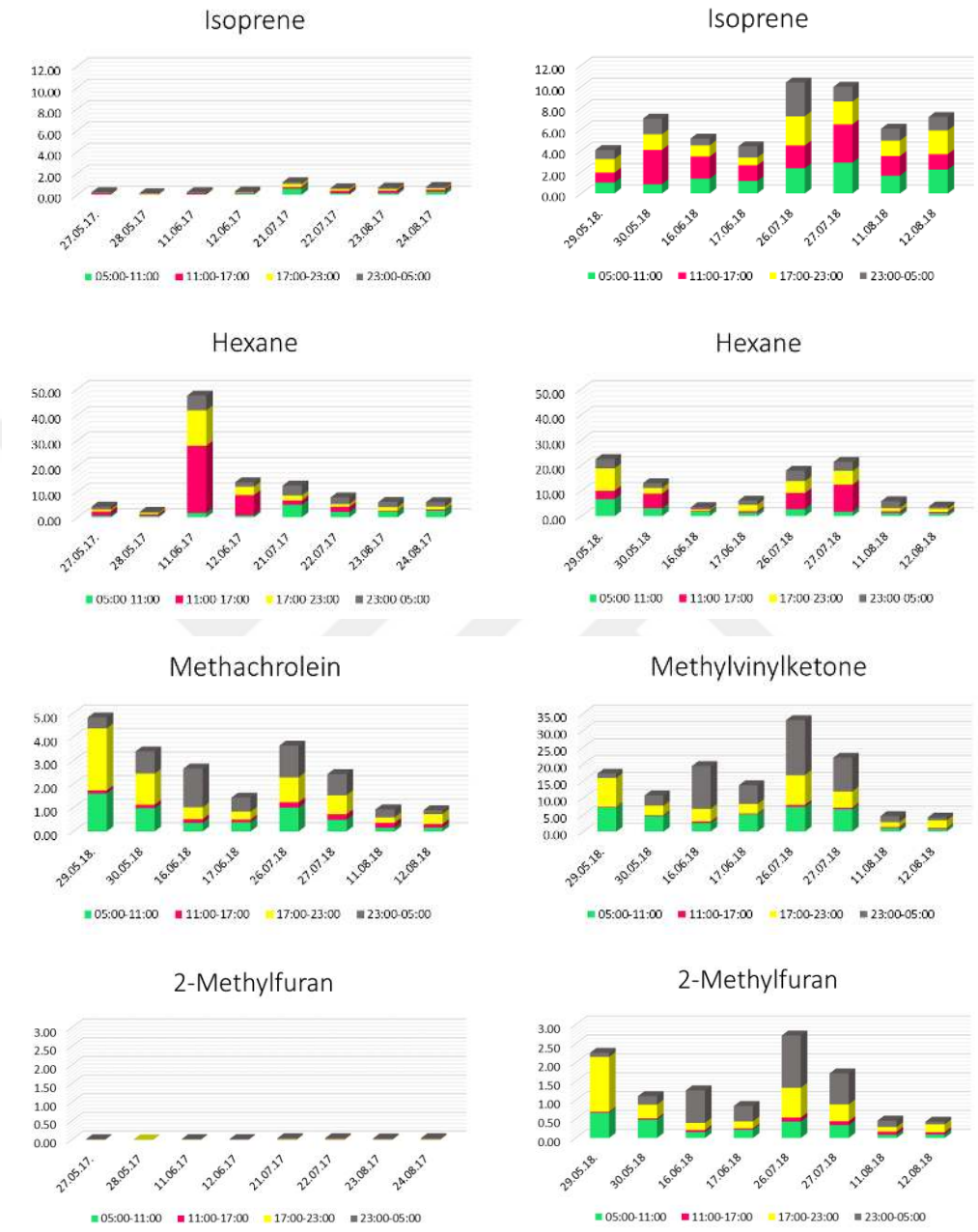


**Figure 2.1.** Intraday, interday and annual variations for each VOC.

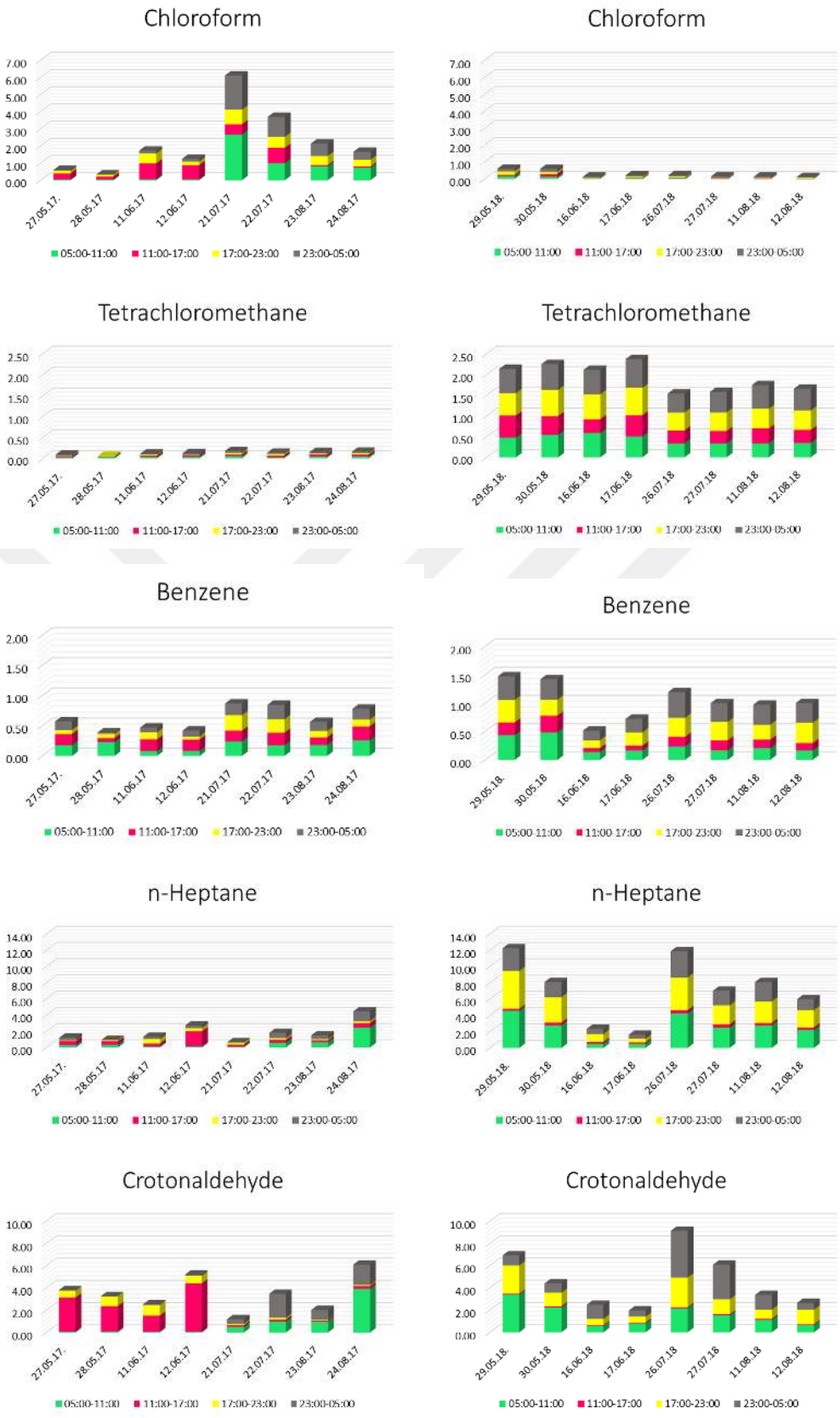


**Figure 2.1 (continued)** Intraday, interday and annual variations for each VOC.

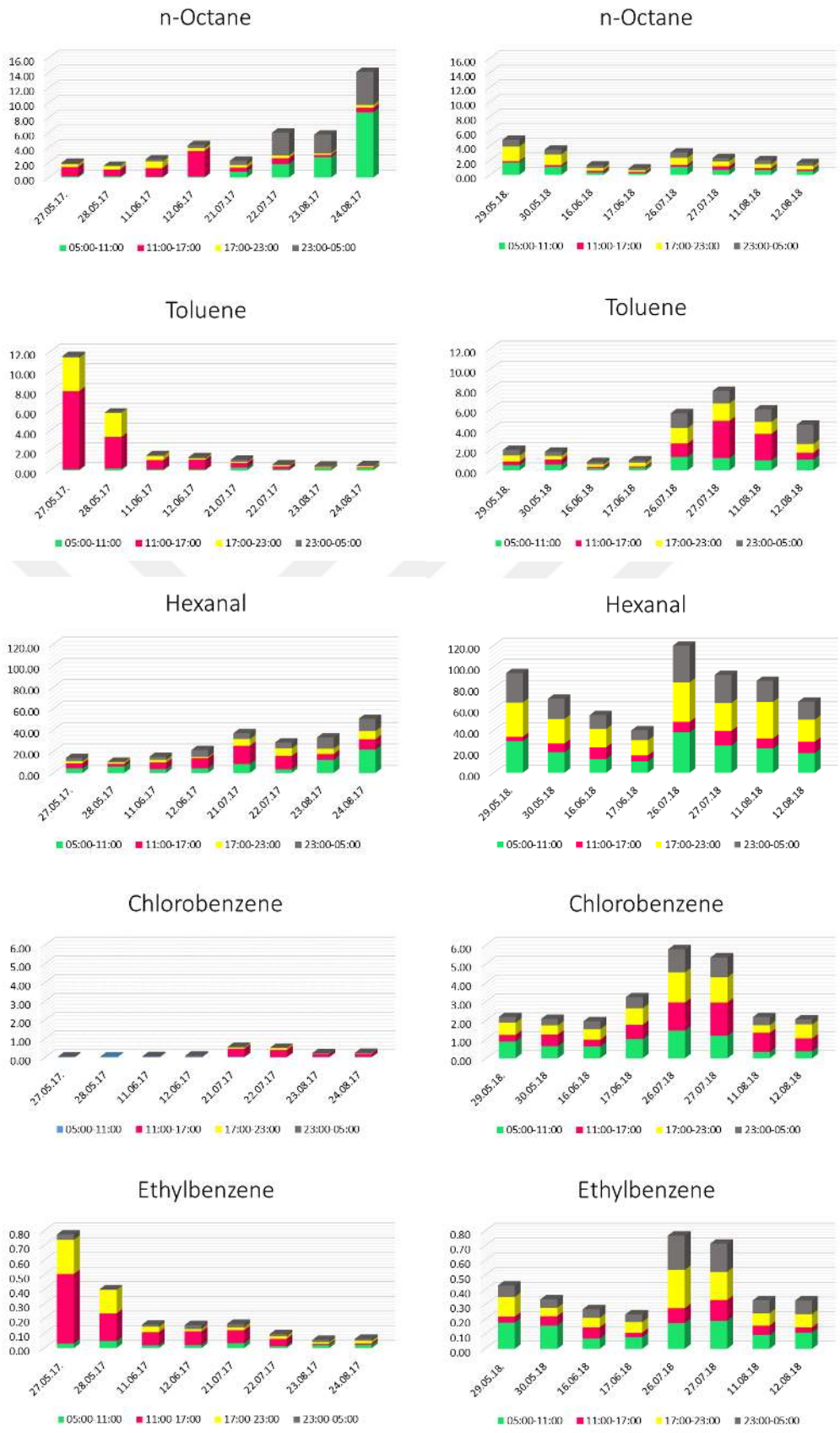


**Figure 2.1 (continued)** Intraday, interday and annual variations for each VOC.

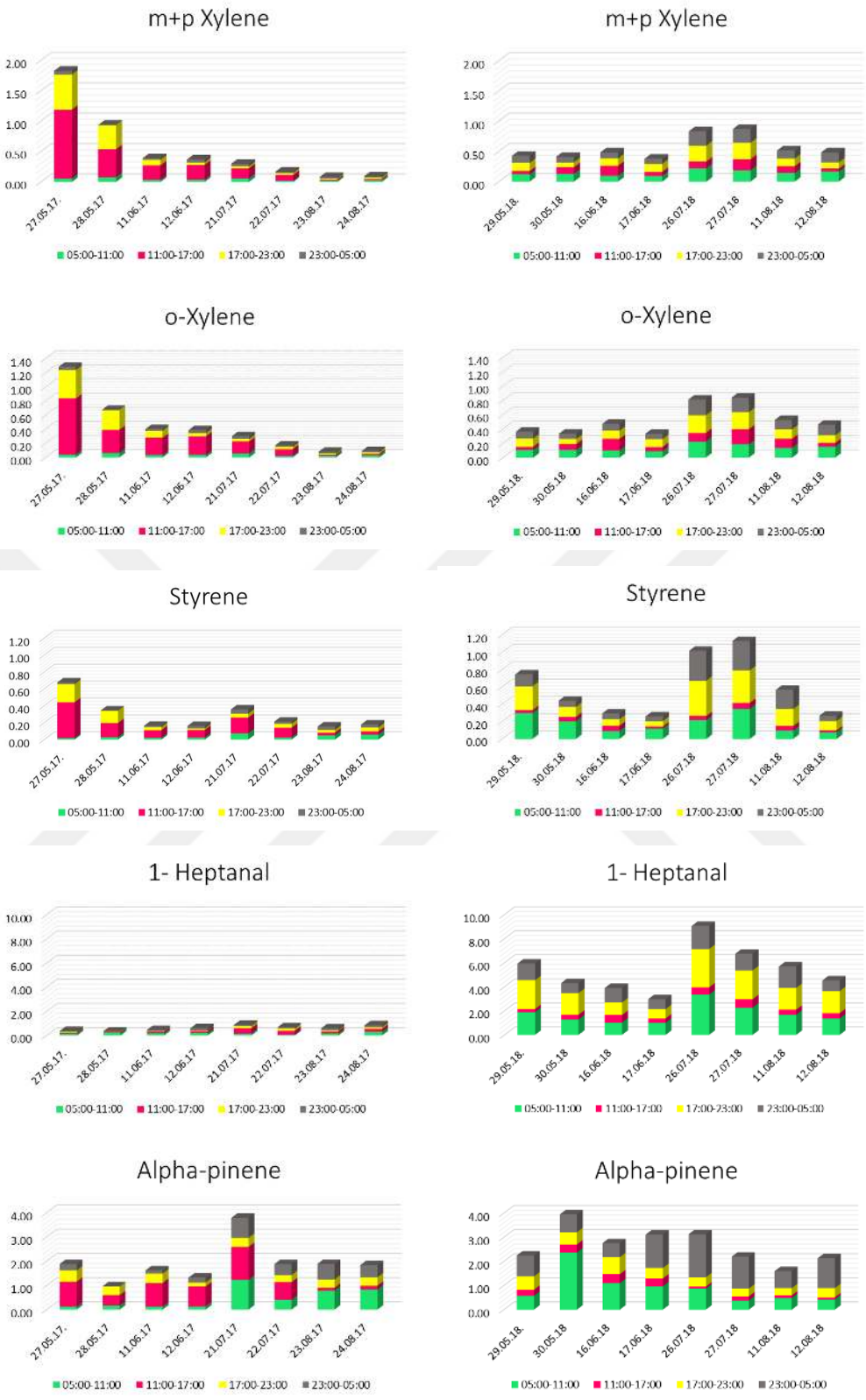


**Figure 2.1 (continued)** Intraday, interday and annual variations for each VOC.

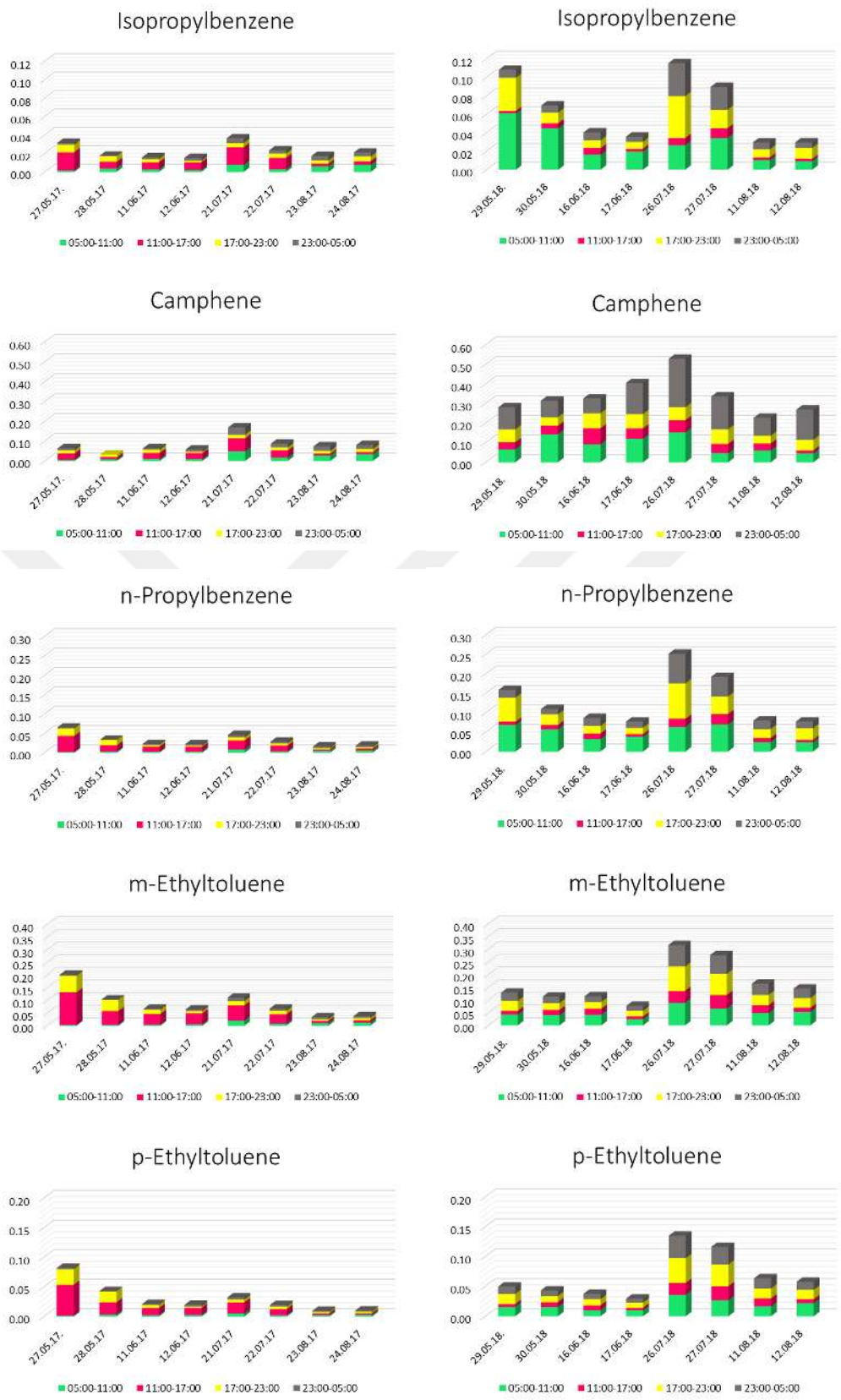


**Figure 2.1 (continued)** Intraday, interday and annual variations for each VOC.

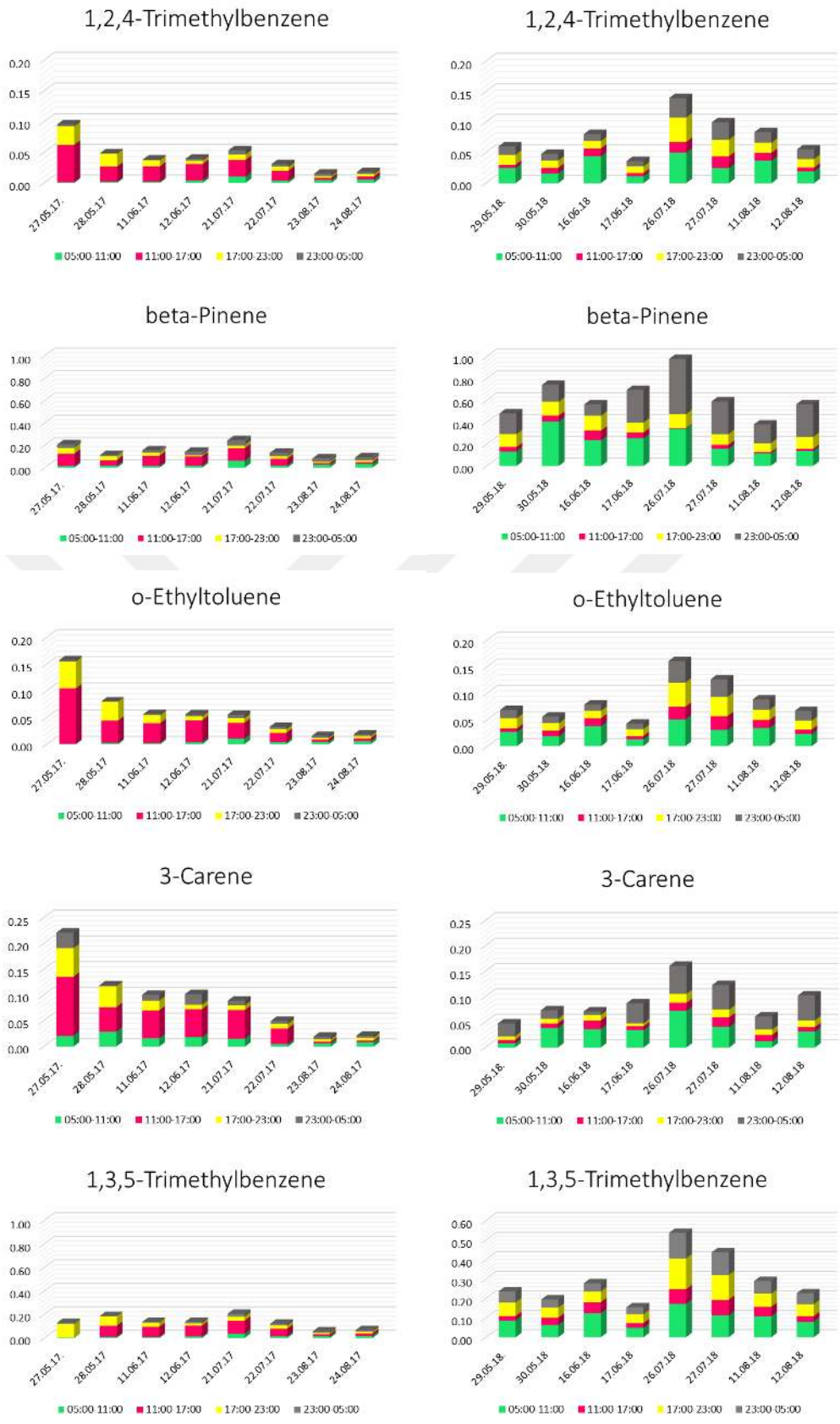


**Figure 2.1 (continued)** Intraday, interday and annual variations for each VOC.

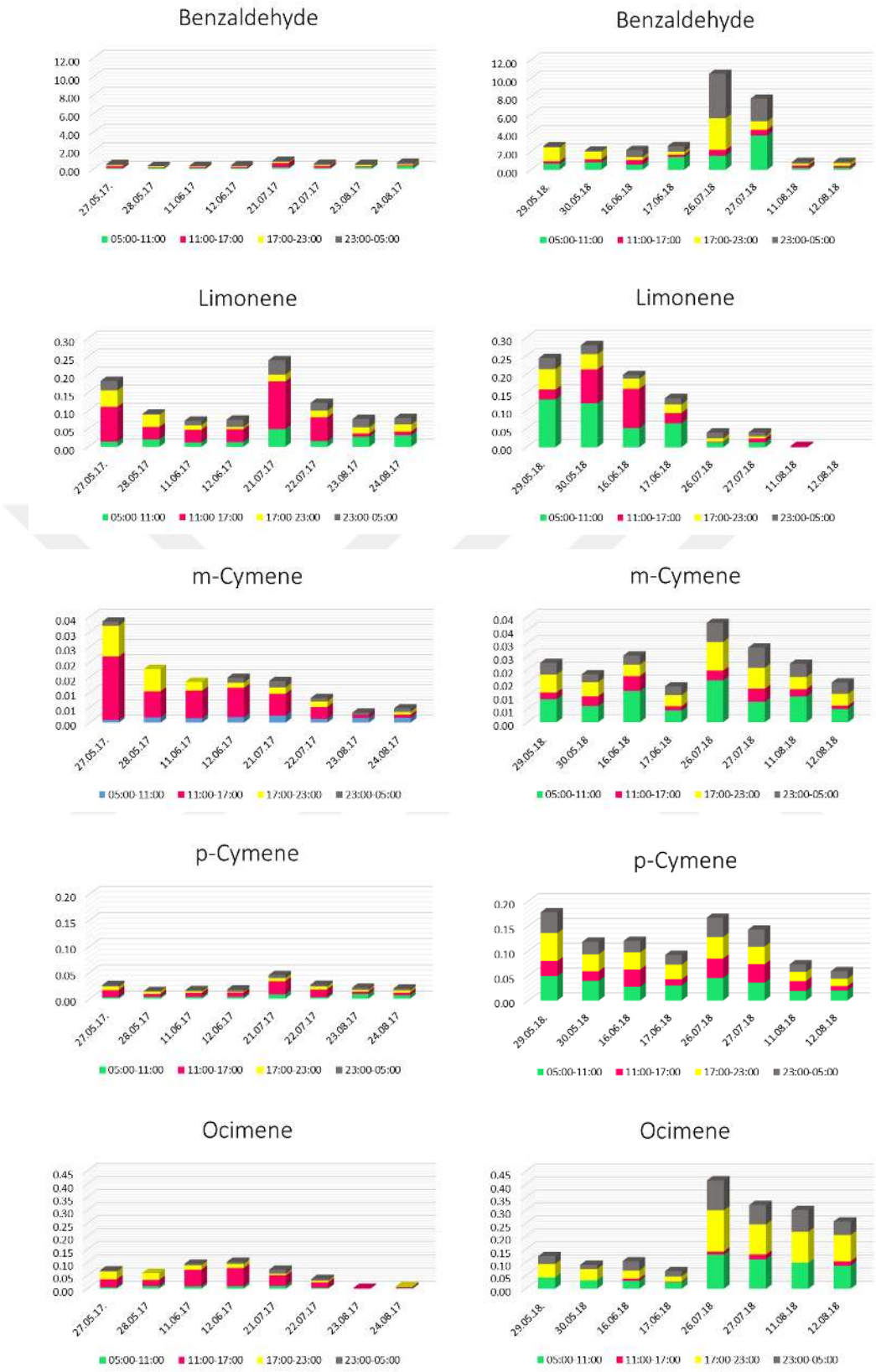


**Figure 2.1 (continued)** Intraday, interday and annual variations for each VOC.


**Figure 2.1 (continued)** Intraday, interday and annual variations for each VOC.

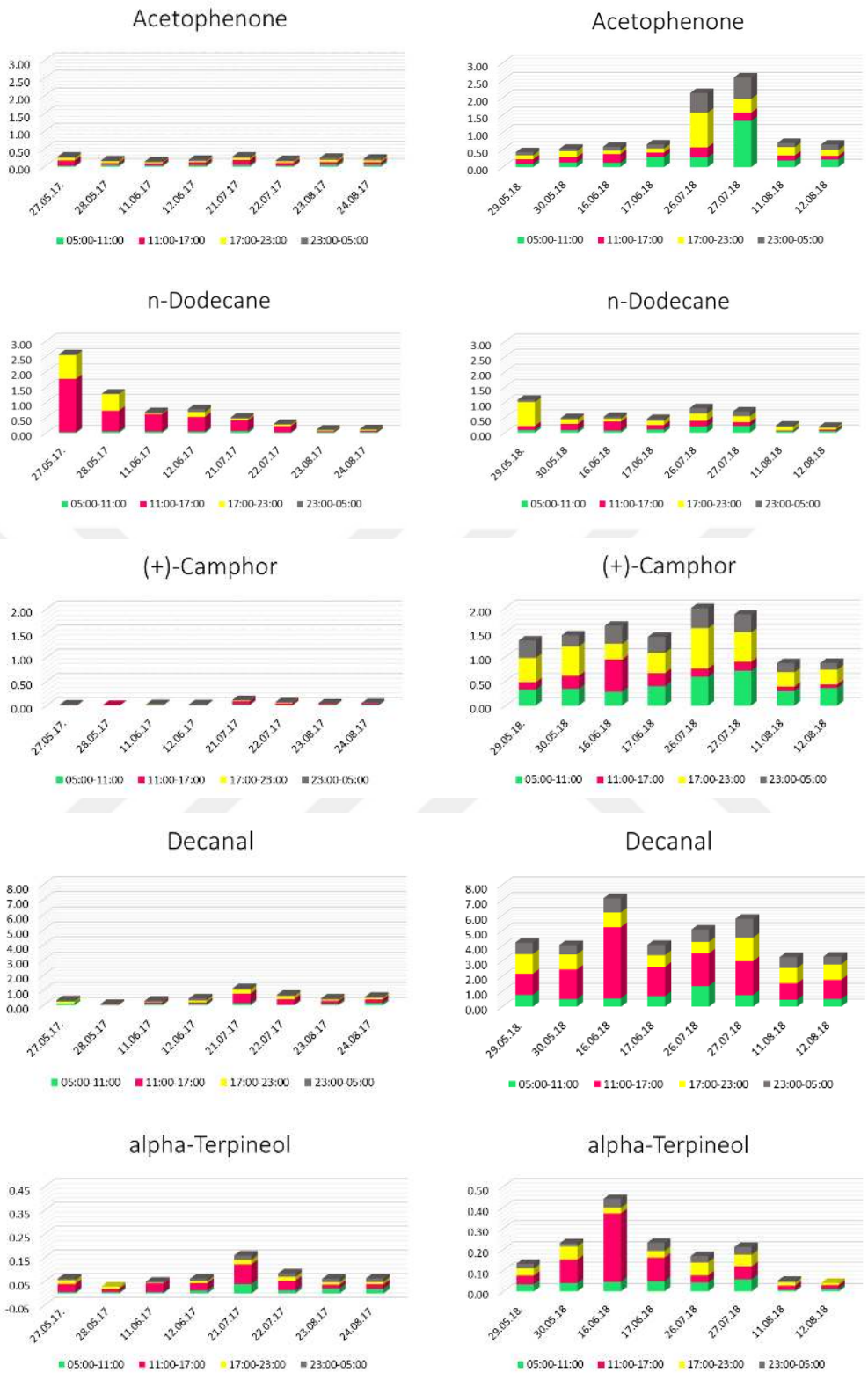


**Figure 2.1 (continued)** Intraday, interday and annual variations for each VOC.

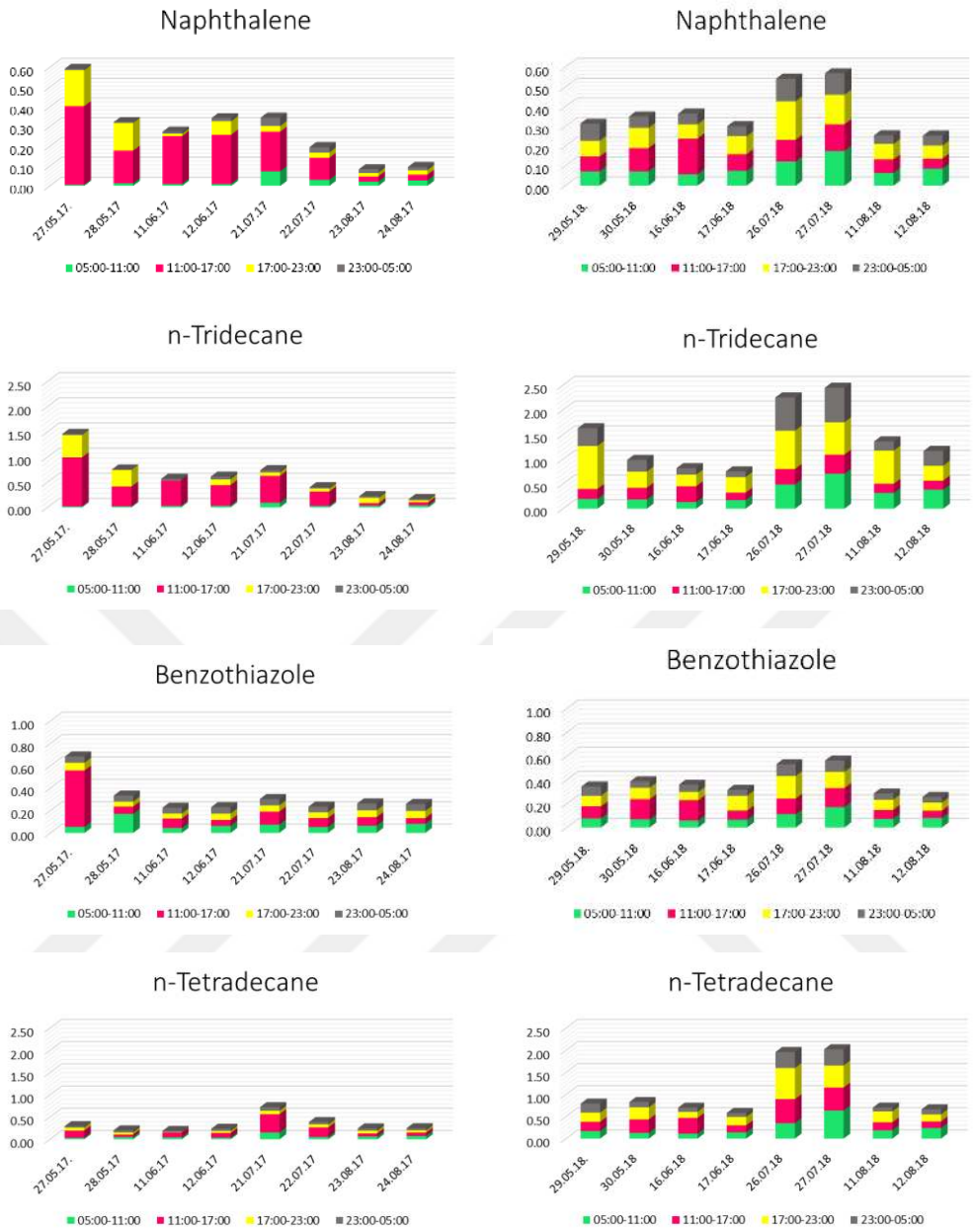


**Figure 2.1 (continued)** Intraday, interday and annual variations for each VOC.

## APPENDIX 3 Spatial Variation of VOCs

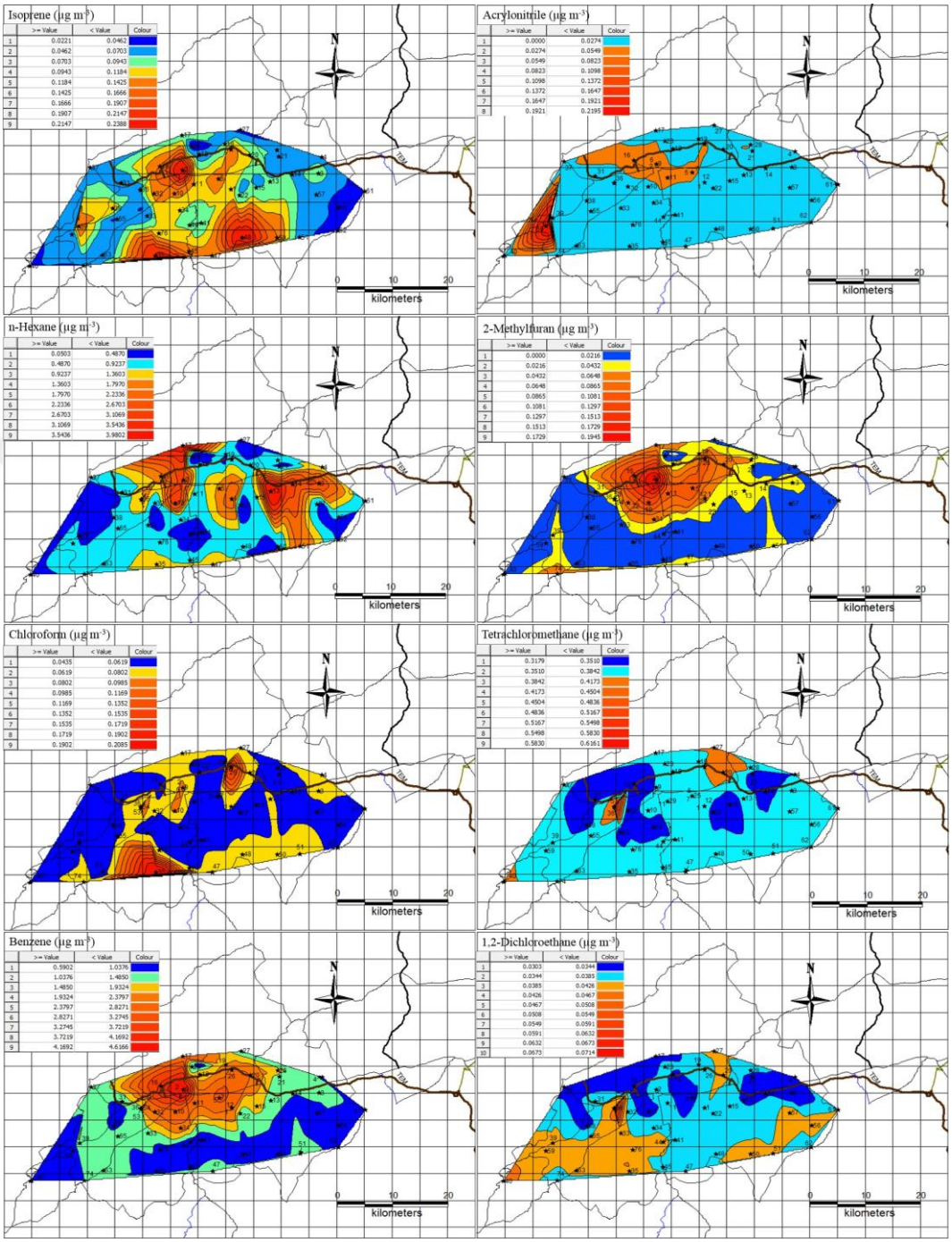


**Figure 3.1.** Pollution level distribution map of each VOC for the winter.

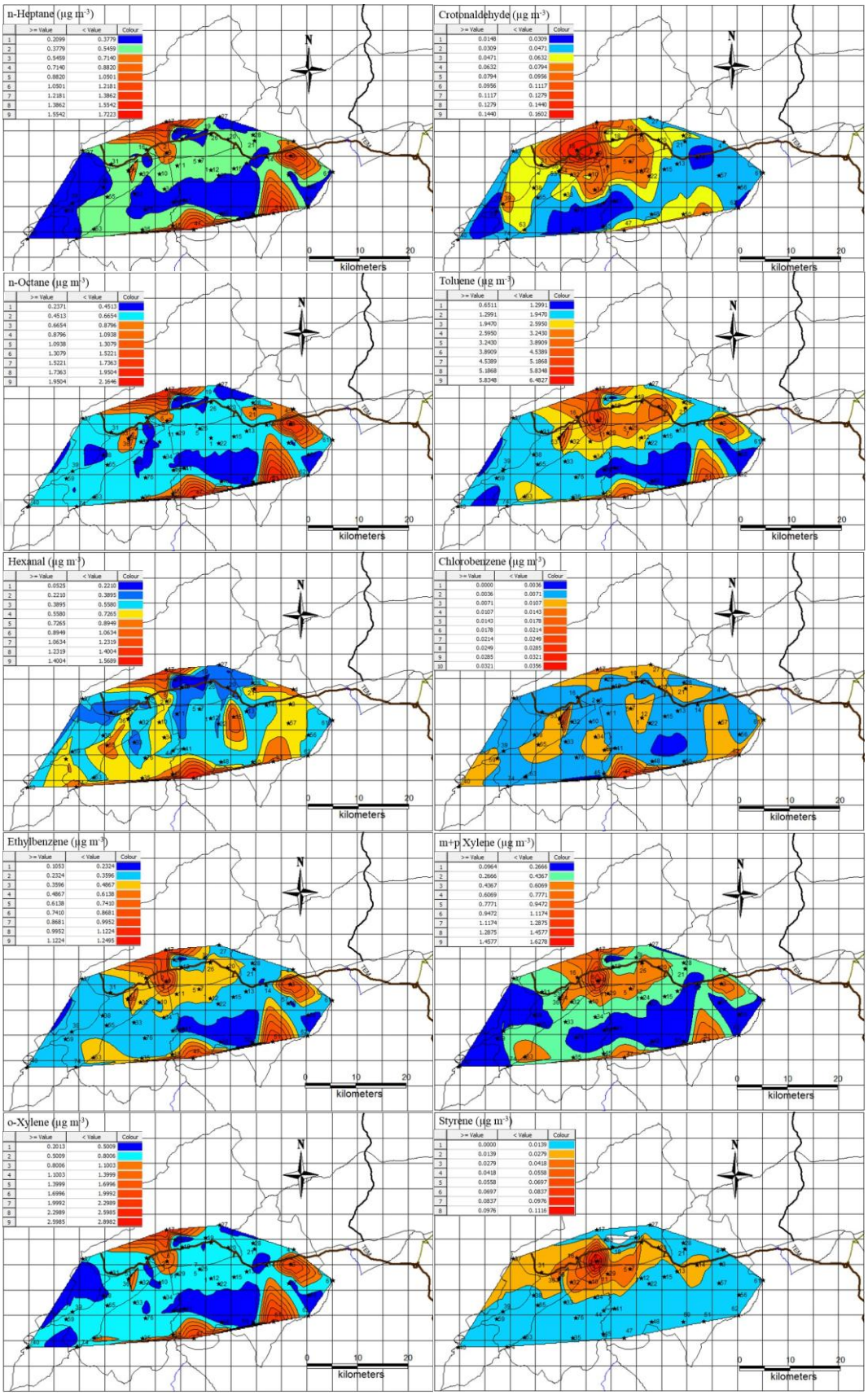


**Figure 3.1 (continued)** Pollution level distribution map of each VOC for the winter.

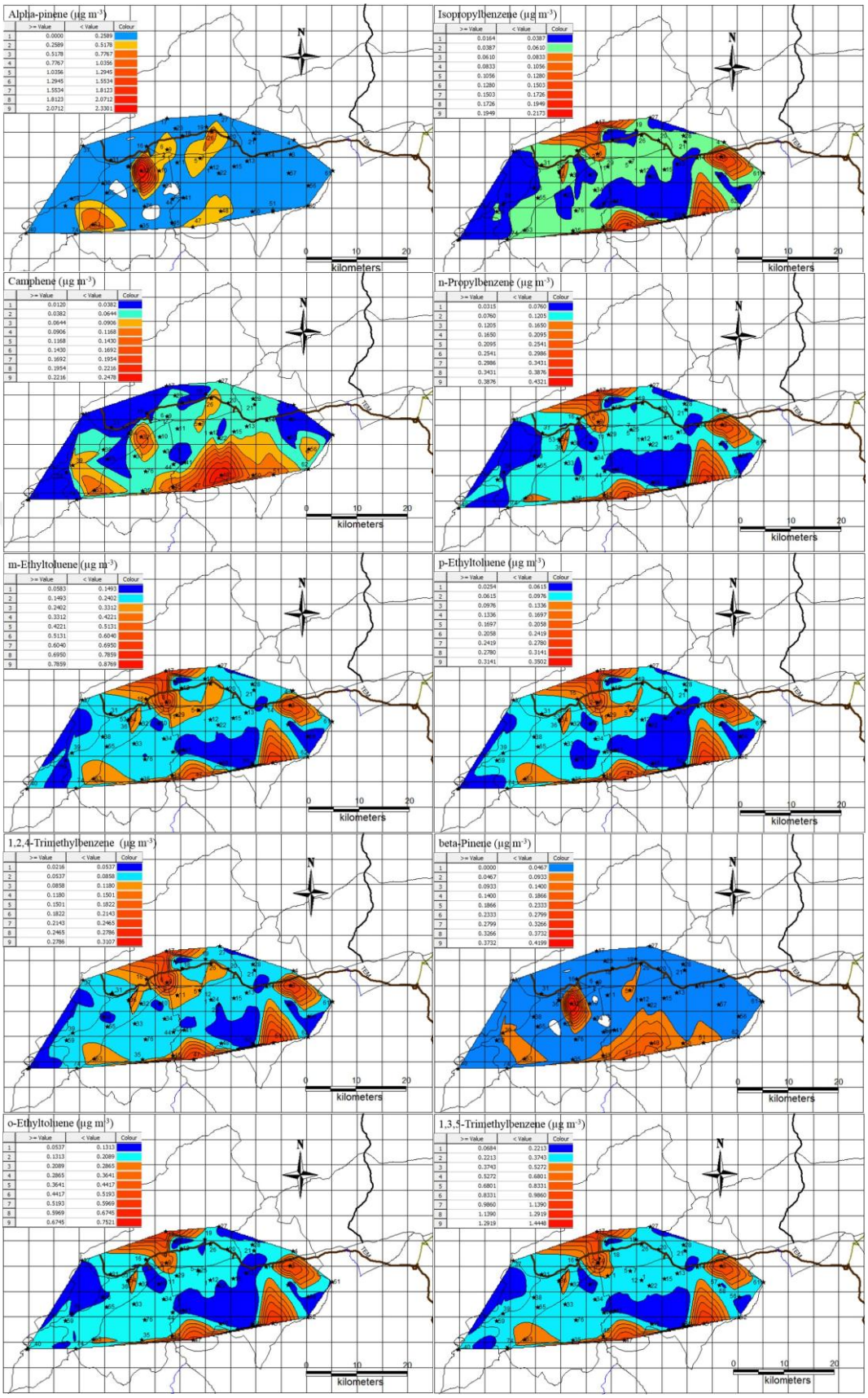


**Figure 3.1 (continued)** Pollution level distribution map of each VOC for the winter.

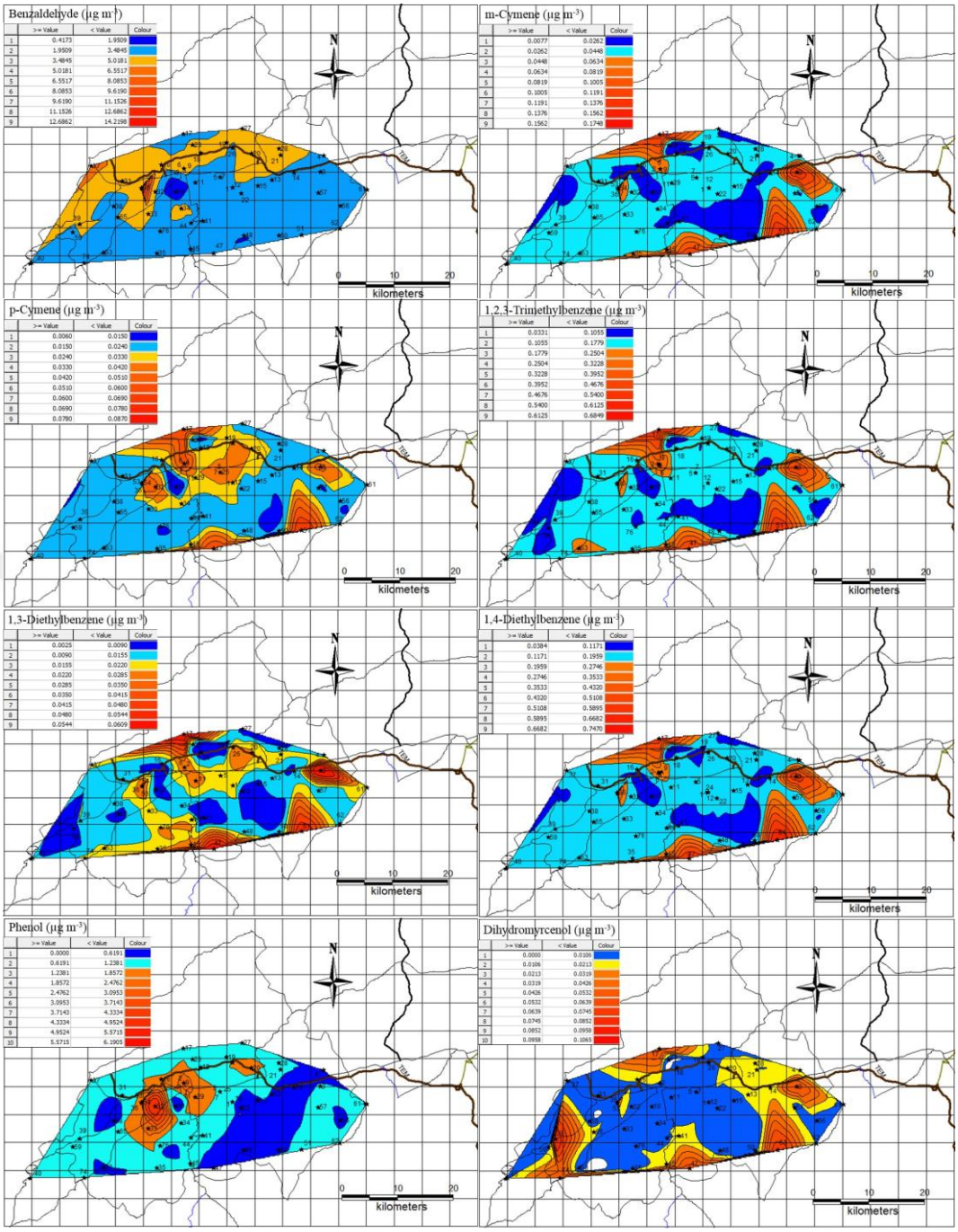


**Figure 3.1 (continued)** Pollution level distribution map of each VOC for the winter.

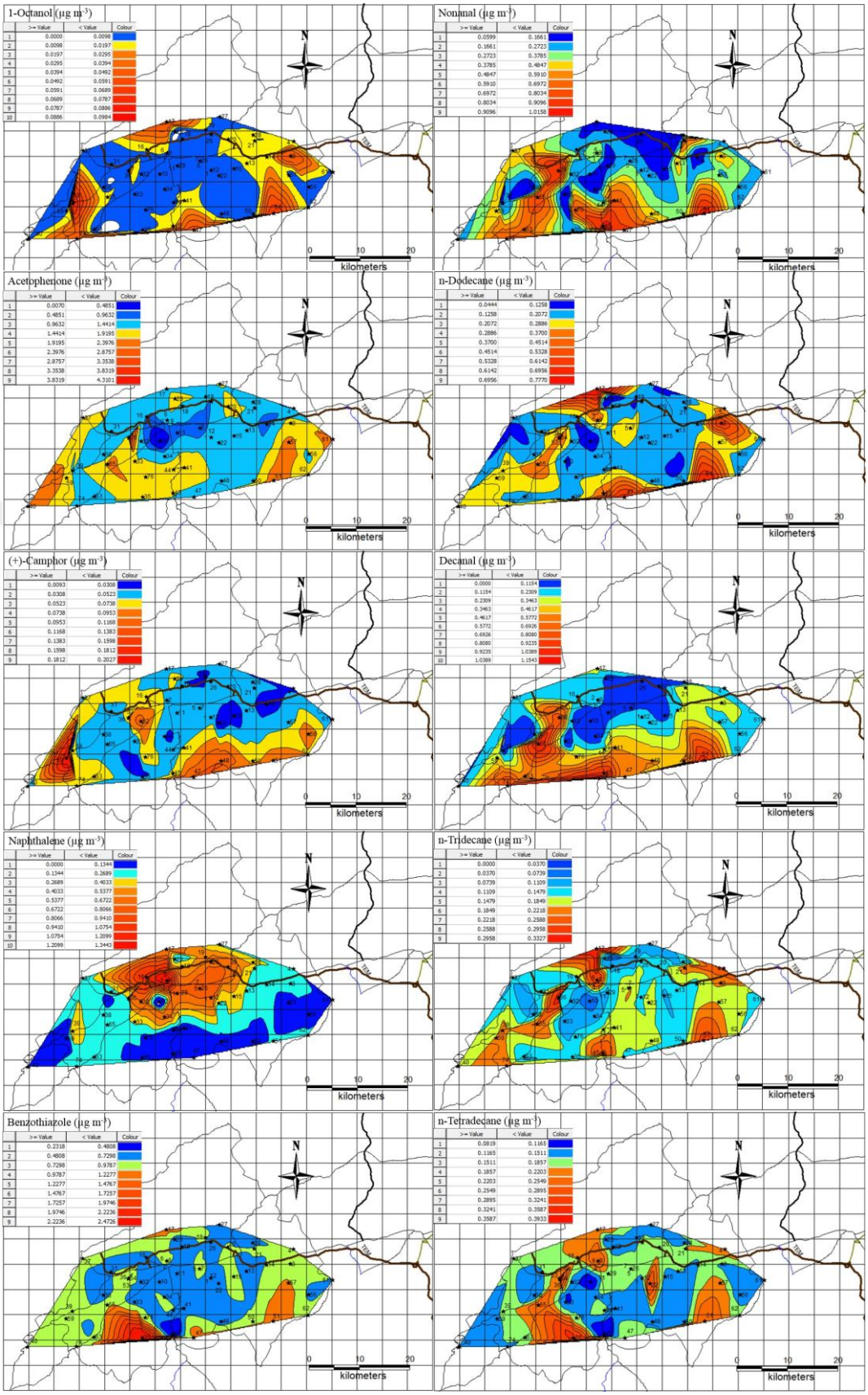


**Figure 3.1 (continued)** Pollution level distribution map of each VOC for the winter.

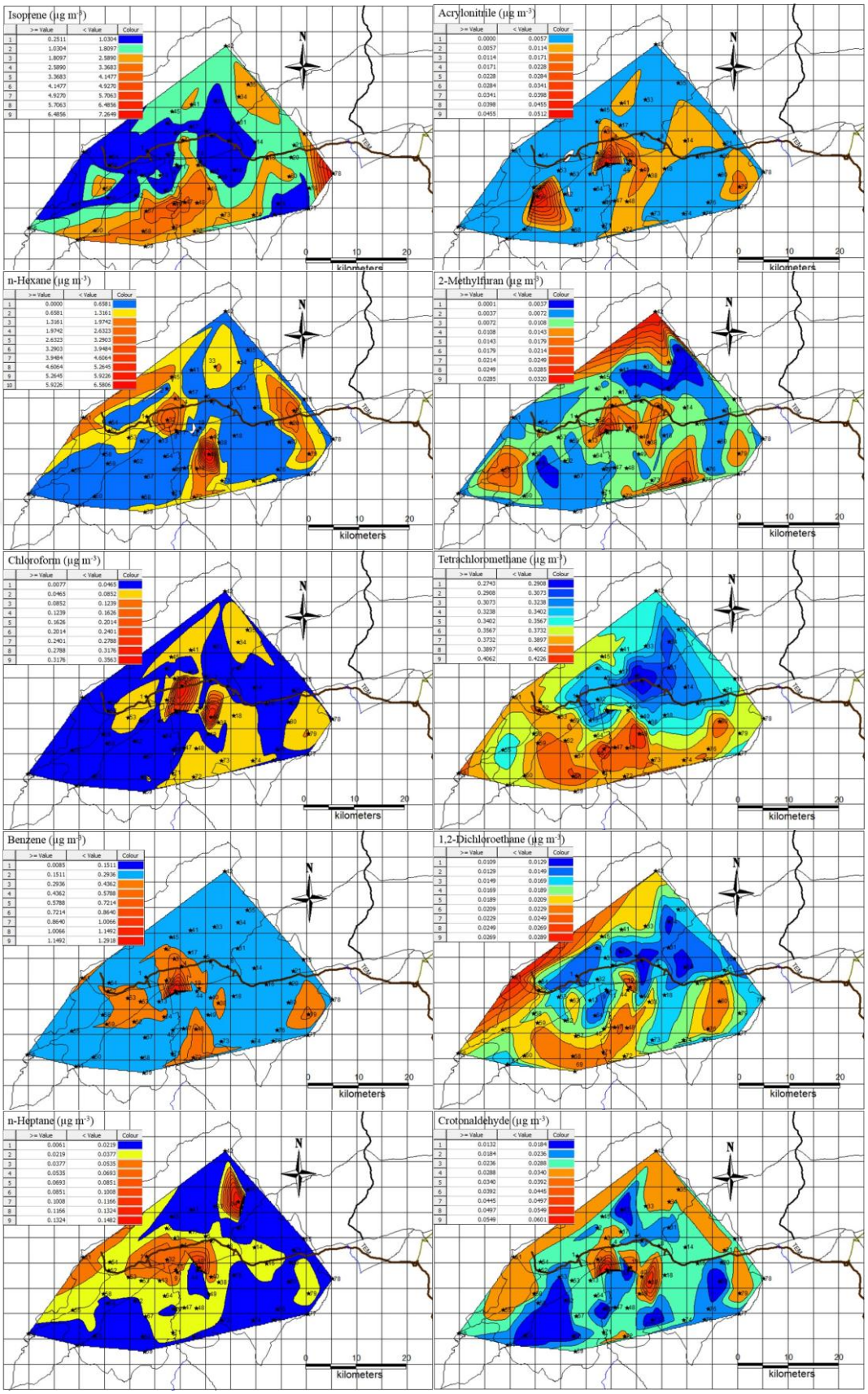


**Figure 3.2.** Pollution level distribution map of each VOC for the summer.

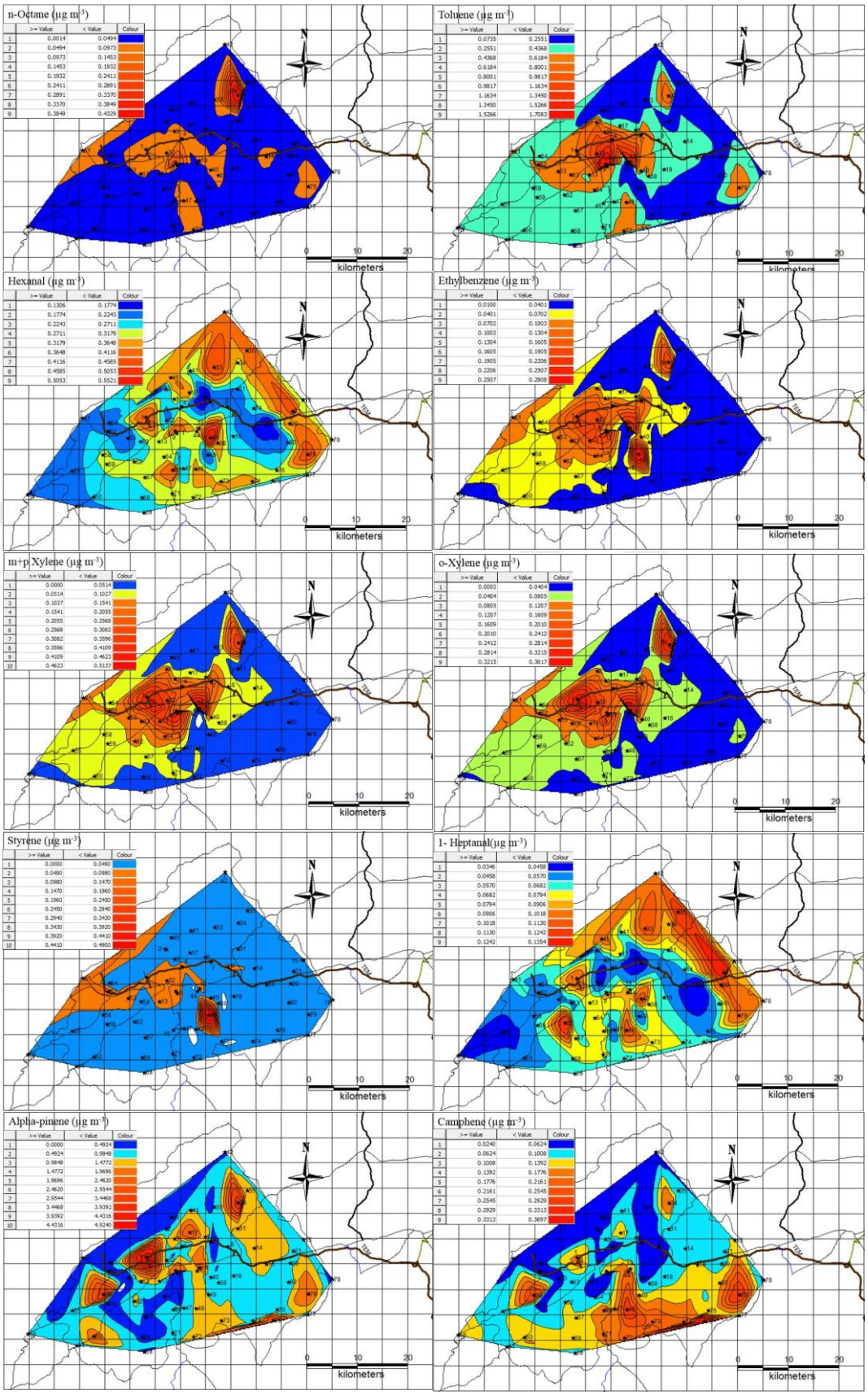


**Figure 3.2 (continued)** Pollution level distribution map of each VOC for the summer.

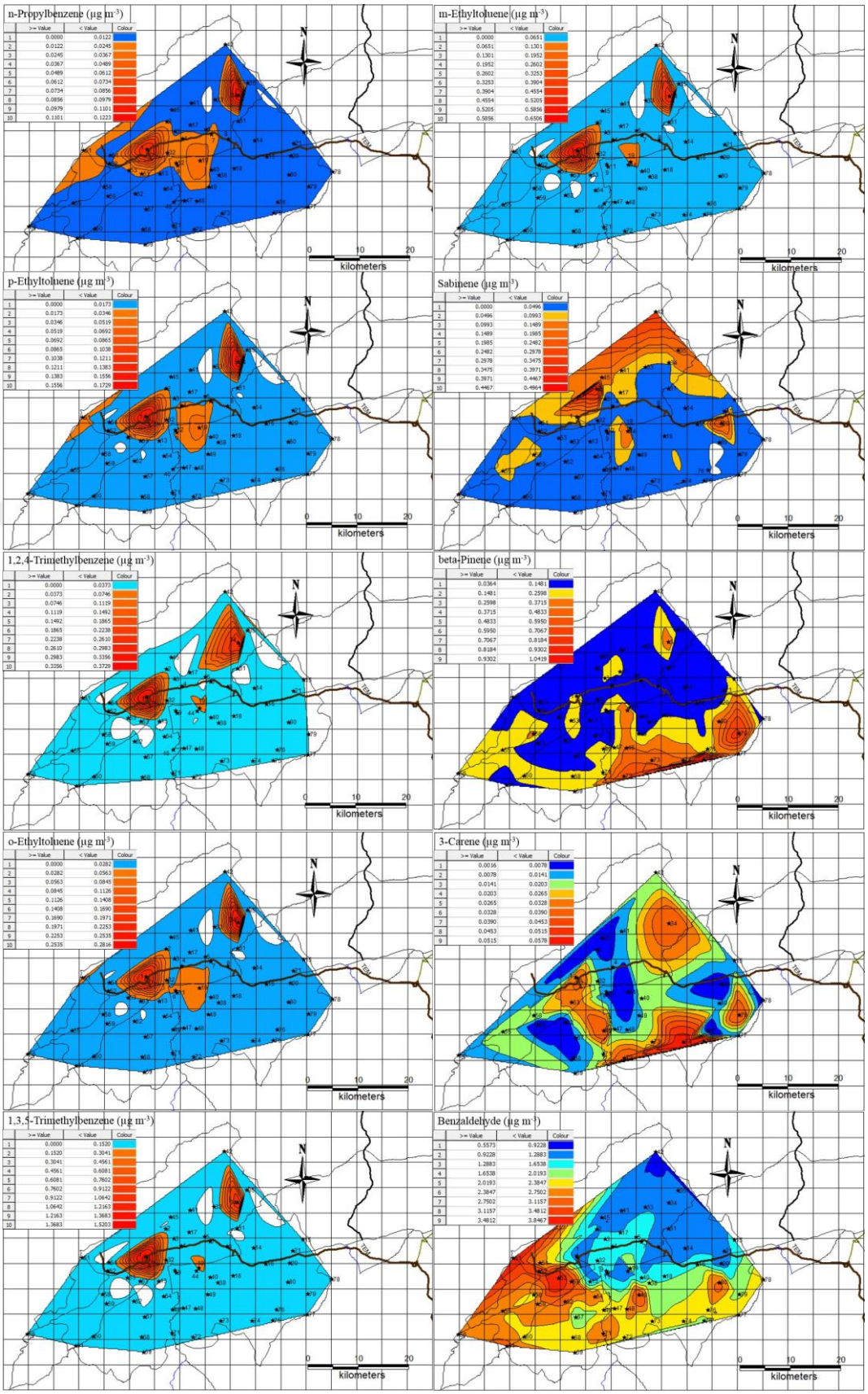


**Figure 3.2 (continued)** Pollution level distribution map of each VOC for the summer.

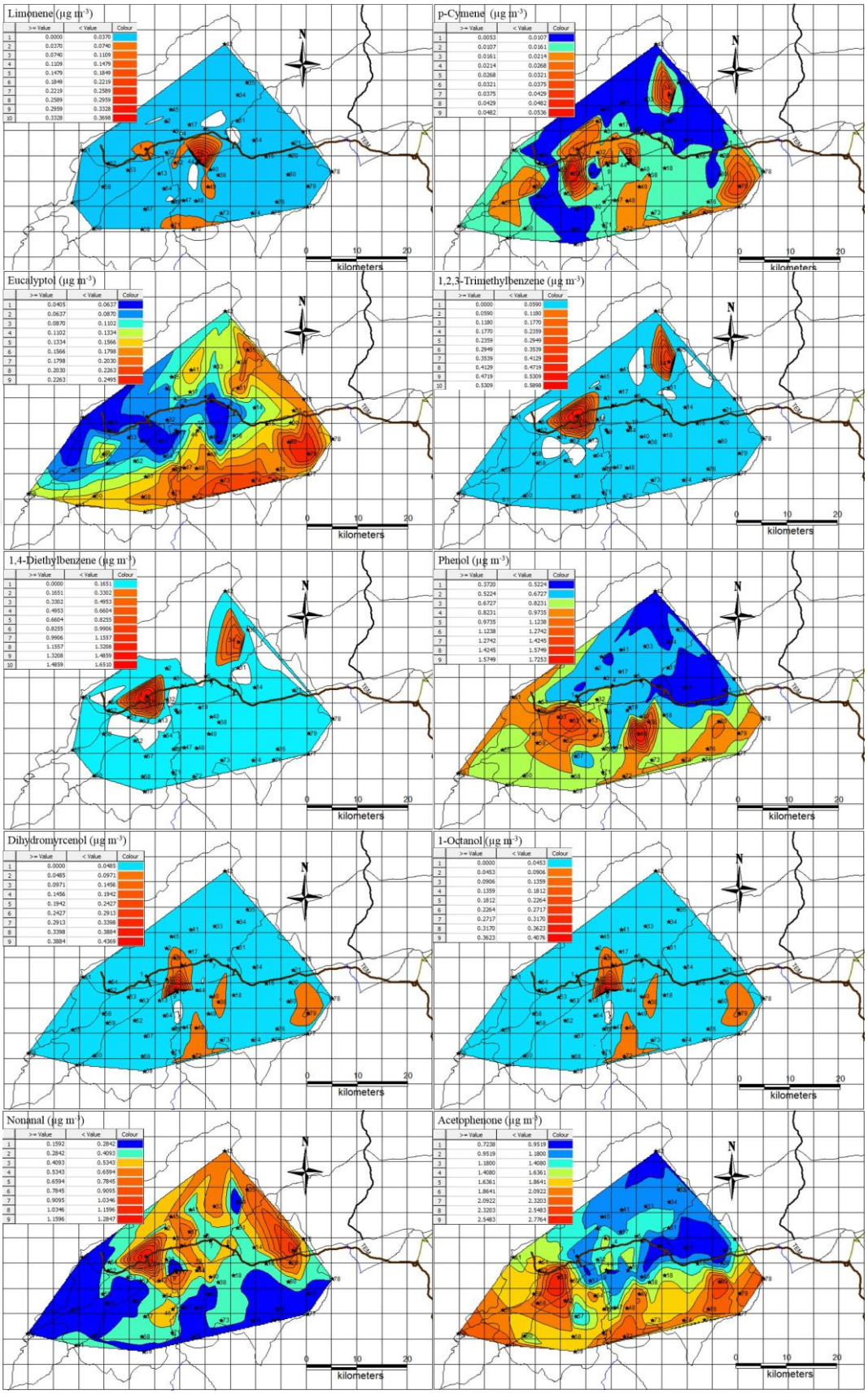


**Figure 3.2 (continued)** Pollution level distribution map of each VOC for the summer.

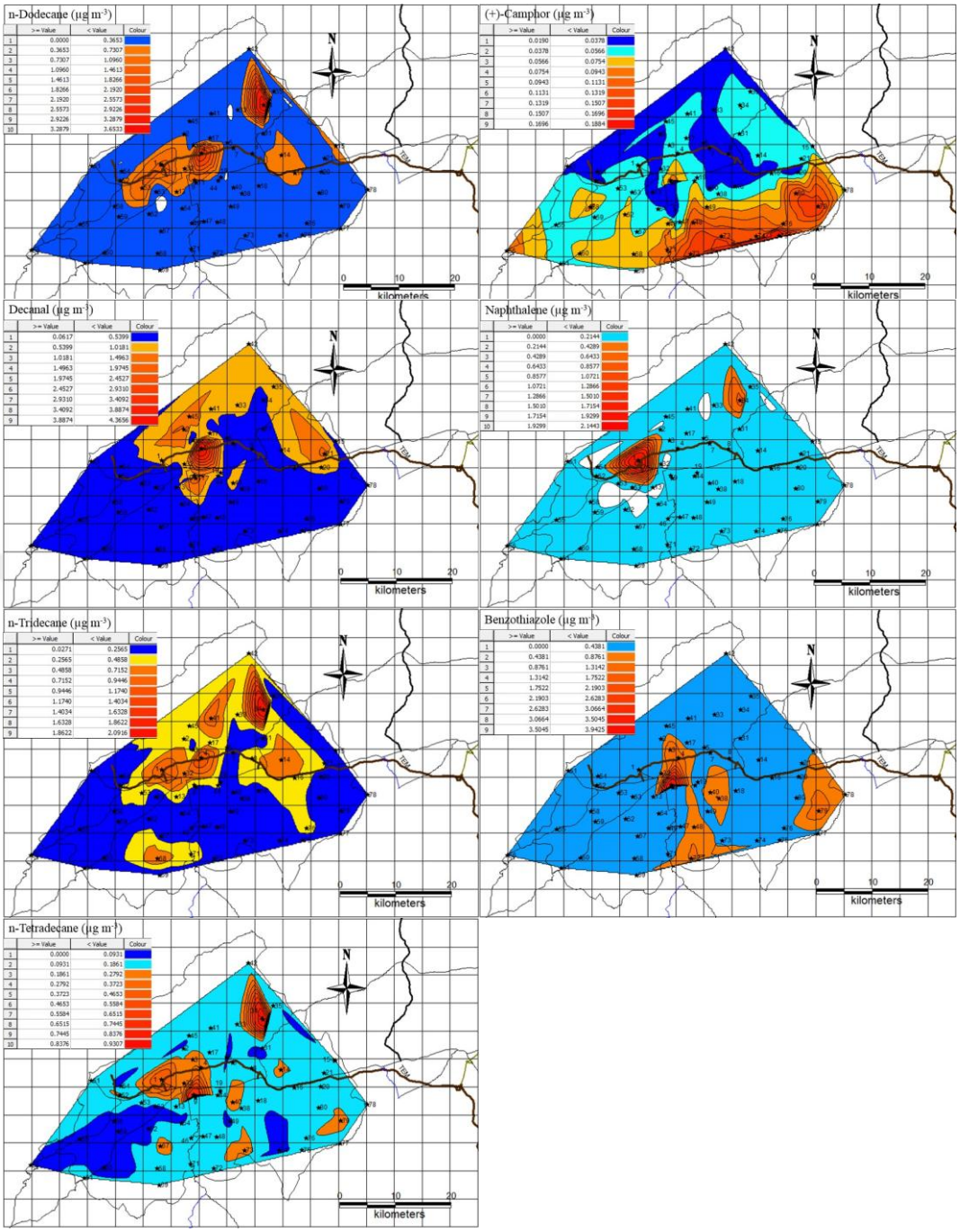


**Figure 3.2 (continued)** Pollution level distribution map of each VOC for the summer.

# 8. CURRICULUM VITAE

2017 – pr. Bolu Abant İzzet Baysal University, Chemistry Department (English) PhD

2014 – 2017 Bolu Abant İzzet Baysal University, Chemistry Department (English) MSc

2009 – 2014 Bolu Abant İzzet Baysal University, Chemistry Department (English) BS

**Employment :**

2020 – pr. Lecturer Bolu Abant İzzet Baysal University, Bolu

2019 – 2020 Lecturer Yüksek İhtisas University, Ankara

**Contributed Projects :**

2015-2019 Bolu Atmosferinde Gaz Fazı Kirleticilerin Uzun Vadeli, Alansal Değişiminin İncelenmesi: Yüksek Ozon Konsantrasyonlarına Biyojenik Uçucu Bileşiklerin Katkısı, Higher Education Student, TÜBİTAK 114Y632.

2017-2017 Yarıkırsal Alanda Gaz Fazı İnorganik Kirleticilerin Kısa ve Uzun Vadeli Ölçülmesi ve Sonuçların Organik Kirleticilerle İlişkilendirilmesi, Researcher, BAP 2017.03.03.1174.

2015–2018 Bolu Atmosferinde Uçucu Organik Bileşiklerin Alansal Değişiminin İncelenmesi, Researcher, BAP 2015.03.03.891.

2015–2018 Bolu Atmosferinde Uçucu Organik Bileşiklerin Aktif Örnekleme ile İncelenmesi ve Ozon Oluşumuna Katkısının Belirlenmesi, Researcher, BAP 2015.09.02.962.

**Publications :**

Dörter M, Odabasi M, Yenisoy-Karakaş S. Source apportionment of biogenic and anthropogenic VOCs in Bolu plateau. Sci. Total Environ. 2020;731:139201.

Yenisoy-Karakaş S, Dörter M, Odabasi M. Intraday and interday variations of 69 volatile organic compounds (BVOCs and AVOCs) and their source profiles at a semi-urban site. Sci. Total Environ. 2020;723:138028.

Dörter M, Karadeniz H, Saklangıç U, Yenisoy-Karakaş S. The use of passive lichen biomonitoring in combination with positive matrix factor analysis and stable isotopic ratios to assess the metal pollution sources in throughfall deposition of Bolu plain, Turkey. Ecol. Indic. 2020;113:106212.

Dörter M, Sağırlı E, Karakaş D, Yenisoy-Karakaş S. Investigation of washing mechanisms in volume-based fractional rain samples in high altitude semirural site by determining polycyclic aromatic hydrocarbons, elemental carbon, and organic carbon. Polycycl. Aromat. Compd. 2018;40:179-193.

**Skills and Interests :**

Experience in using GC-MS, HPLC, IC.

Working knowledge in PMF, MapInfo, Stat-graphics, XLSTAT, ChemDraw.

# 9. ORIGANILITY REPORT

T.R.
BOLU ABANT İZZET BAYSAL UNIVERSITY
DIRECTORATE OF INSTITUTE OF GRADUATE STUDIES

STUDENT & SUPERVISOR PLAGIARISM DECLARATION FORM

| | | | |
|---|---|---|---|
| Department | Chemistry PhD | | |
| Name and surname | Melike DÖRTER | | |
| Student number | 17261040203 | | |
| Postgraduate program | MSc with thesis ☐ | PhD ☑ | |
| Academic year and semester of thesis examination | 2020 / 2021 | Autumn ☐ | Spring ☑ |
| Thesis defence date | 27.04.2021 | | |
| Number of pages | 183 | | |
| Thesis title (Tr) | Yüksek rakımlı yarı-kırsal bir alanda termal desorpsiyonlu GC-MS tekniği ile belirlenen antropojenik ve biyojenik uçucu organik karbonların (UOB'ler) alansal ve mevsimsel değişimlerinin ve biyojenik UOB'lerin ozon konsantrasyonlarına katkısının incelenmesi | | |
| Thesis title (Eng) | Investigation of spatial and seasonal variations of antropogenic and biogenic volatile organic carbons (VOCs) determined by thermal desorption GC-MS technique and contribution of biogenic VOCs to ozone concentrations at high altitude semi-rural site | | |

Based on the plagiarism report that was generated on the date of 10 / 05 / 2021 by using predetermined filtrations set by Directorate of Institute of Graduate Studies of the Turnitin programme, a plagiarism detection sofware, the rate of plagiarism detected was 17 %.

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Supervisor
(Name, Surname, date ve Signature)

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