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## Temporal variations of VOC concentrations in Bursa atmosphere

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## ABSTRACT

The levels and sources of VOCs in the atmosphere of Bursa have been investigated by measuring C<sub>2</sub>–C<sub>12</sub> VOCs which include alkanes, alkenes, alkynes, aromatics and halogenated hydrocarbons in two different campaigns. The first campaign was carried out between September 14 and November 6, 2005, and the second one between March 17 and May 10, 2006. The concentrations of 112 VOCs were detected in the collected samples. The median total concentrations of VOCs were 115 and 86 µg m<sup>-3</sup> for the first and second campaigns, respectively. Alkanes ( $\bar{x}$  = 51.50 µg m<sup>-3</sup>) are the most abundant group in the Bursa airshed, which is followed by aromatics ( $\bar{x}$  = 49.38 µg m<sup>-3</sup>), alkenes ( $\bar{x}$  = 36.86 µg m<sup>-3</sup>) and halogenated compounds ( $\bar{x}$  = 13.07 µg m<sup>-3</sup>). In the present study, the VOCs showed well defined diurnal, weekday/weekend and seasonal variations. Diurnal variation of most of the measured organic compounds followed traffic rush-hours. On the other hand, some VOCs such as 1-octene, 1-nonene, 1-undecene, n-nonane, n-decane, 1,2,3-trimethylbenzene, undecane and dodecane have displayed unusual profiles that do not follow the traffic pattern during the first campaign due to asphalting operations. Moreover, the average T/B ratio obtained in the first campaign was found to be significantly higher than the second one. This relatively high difference between T/B ratios is an indication of the availability of different sources rather than the traffic. Therefore, it can be suggested that there were additional VOC sources than traffic in Bursa city center.

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## 1. Introduction

Volatile organic compounds (VOCs) are considered to be one of the most significant groups of air pollutants due to their toxic and carcinogenic effects on human health (Saeaw and Thepanondh, 2015). In addition to their adverse effects on humans, VOCs have a profound influence on the formation of tropospheric ozone and other oxidants (Rappenglück et al., 1998; Rappenglück and Fabian, 1999a; Yassaa et al., 2011; Saeaw and Thepanondh, 2015; Sahu and Saxena, 2015). Solar radiation is a key element in the atmospheric

photochemistry of VOCs and NO<sub>x</sub> because tropospheric ozone and PAN will be produced when NO<sub>x</sub> and VOCs combine in the presence of sunlight (Rappenglück et al., 1998; Sahu and Saxena, 2015). The issues of decreasing tropospheric ozone concentrations and controlling VOCs concentrations are particularly important in air pollution management throughout the world (Iqbal et al., 2014). Towards this aim, the VOCs measurements in the ambient atmosphere are essential in cities with a high population and a dense vehicle fleet (Khoder, 2007).

The ambient levels of VOCs are affected from various factors such as meteorological conditions and availability of different sources in any urban or industrially impacted urban areas. For example, more rainy days in summertime lead to decrease the concentrations of organics compared to dry winter days (Lee et al., 2002). Higher hydroxyl (OH) concentrations in summer will be more effective for removal of VOCs by chemical reaction. Indeed, higher temperatures and more sunlight will speed most of the chemical reactions (Lee et al., 2002). Furthermore, higher NMHC concentrations are observed at higher altitudes as owing to low OH accessibility in higher altitudes (Sharma et al., 2000). Seasonal

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variations of atmospheric VOCs are also affected by other meteorological conditions, including wind direction, wind pattern, precipitation, boundary layer dynamics and transport and/or dilution from the surrounding region (Rappenglück and Fabian, 1999a; Cai et al., 2010; Park et al., 2013; Menchaca-Torre et al., 2015; Valach et al., 2015; Baudic et al., 2016). Calm conditions, shallow boundary layer, stagnant wind patterns and high atmospheric stability prevent the dilution of the organics and pollutants accumulate in the atmosphere (Rappenglück et al., 2000; Dumanoglu et al., 2014; Barletta et al., 2016; Baudic et al., 2016). Variability of sources also influences on the observed seasonal variation in atmosphere (Hoque et al., 2008; Kuntasal et al., 2013; Park et al., 2013; Valach et al., 2015; Singh et al., 2016). Seasonal variations of organic compounds, with a maximum in winter and minimum in summer, have been reported in many studies (Ho et al., 2004; Na et al., 2005; Kerbachi et al., 2006; Guo et al., 2007; Qin et al., 2007; Hoque et al., 2008; Chang et al., 2009; Russo et al., 2010; Stock et al., 2010; Kuntasal et al., 2013; Singh et al., 2016). On the contrary, different seasonal patterns have been also detected in some cities depending on the location, meteorological and topographical properties of the sampling point and proximity of the sampling point to industrial sources because elevated temperature causes increased VOC concentrations due to increased vapor pressure of the both solvents and monomers in paints, adhesives, coatings, etc (Thad, 2000; Ho et al., 2004; Na et al., 2005; Elbir et al., 2007; Li and Wang, 2012; Dumanoglu et al., 2014).

Several studies also showed that VOC concentrations are higher on weekdays than those on weekends, indicating that human activities have an important effect on VOC concentrations (Cai et al., 2010; Zou et al., 2015). VOC concentrations also show variation through the day depend on the emissions, transport and dilution, and chemical removal (Rappenglück and Fabian, 1999a; Derwent et al., 2000; Leuchner and Rappenglück, 2010). The diurnal cycles of alkanes, alkenes and aromatics have a double peak pattern on weekdays, directly related with traffic rush hours (Cai et al., 2010; Valach et al., 2015). The two peaks are usually observed at 9:00 a.m. and between 15:00–20:00 p.m. during the morning and afternoon rush hours (Cai et al., 2010; Li and Wang, 2012; Olumayede and Okuo, 2012; Valach et al., 2015). This situation can be explained by higher VOC emissions due to higher traffic density during the morning and afternoon, and dilution by increase of the assimilation capacity of the atmosphere; in other words, an increase of the mixing depth and photochemical activity during the noon time (Lai et al., 2004; Kelessis et al., 2006; Yurdakul et al., 2013). In addition to traffic emissions, evaporative sources are also important in diurnal patterns depicted by some of the VOCs. Since evaporative emissions are expected to increase in the afternoon with increasing temperature, (Nguyen et al., 2009), any increase in concentrations of VOCs can be attributed to their evaporative sources.

Bursa is the fourth largest city of Turkey with a population of about 3 million. Bursa, covering an area of 10,819 km<sup>2</sup>, is located in the northwestern part of Anatolia. Bursa is an industrial city. There is approximately 8000 business working with textiles in Bursa. Cotton weaving, artificial and synthetic yarn production, woven fabric and home textile are leading sub sectors of Bursa textile industry. More than 75% of the yarn is produced in Bursa. In addition to textile industry, motor, motor parts, hydraulic and pneumatic components, rubber and rubber components motor oils and additives are major sub-industry products of Bursa. Bursa is also the automotive center of Turkey. Globally well-known automotive manufacturers were located in Bursa and 60% of the automotive production of Turkey was performed in Bursa. The number of motor vehicles was about 400,000 in Bursa in 2006 however this number was increased to 800,000 in 2016 (TSI, 2016a). Therefore, between 2006 and 2016 there was nearly 100% of increase in the number of

vehicles registered to traffic in Bursa. Same situation is also true for the population because the population of Bursa reached to about 1.5 million in 2006 and according to the Turkish Statistical Institute reached to about 3 million in 2016 (TSI, 2016b). Although, both Bursa's population and the total number of road motor vehicles registered to the traffic in Bursa have been doubled in the last 10 years, there was no significant changes in the practices, used fuel quality/type and national regulations, etc. Accordingly, the concentration of VOCs in the Bursa atmosphere probably increased even more in the last decade.

The objective of this study is to determine the level of pollution in Bursa in terms of wide range of organic pollutants, ranging from C<sub>2</sub> to C<sub>12</sub>, and to identify the factors and sources affecting temporal variations of the measured species. A significant contribution of the study is the investigation of extensive asphalt pavement activities in the city during the study, which allowed us to observe how asphaltting modified the VOC composition of the atmosphere. The asphalt profile generated is included in the follow-up paper where source apportionment by a receptor modeling, PMF, will be discussed. Finally, the ozone formation potential of individual VOCs species was calculated to estimate effect of each species on the ozone level in urban atmosphere.

## 2. Material and methods

### 2.1. Sampling

Two sampling campaigns were performed during the study. The first campaign was carried out between September 14 and November 6, 2005, and the second one between March 17 and May 10, 2006. The numbers of hourly measurements in fall and spring campaigns were 841 and 856, respectively. The online GC-FID system was placed in a shelter which was 3 m far away from the surrounding buildings and trees (in the middle of the garden). Furthermore, system was 1.5 m high from the surface.

### 2.2. Site description

The measurements were performed at the back of Bursa Hygiene Center (40.19°N, 29.05°E), which is located approximately at the city center. The location of the Hygiene Center in Bursa is given in Fig. 1. Detailed figure which shows the three industrial zones, city center and sampling location is also given in Fig. S1. Altıparmak Boulevard with four lanes of two-way traffic is a major thoroughfare in the Bursa. The boulevard with heavy traffic is the nearest main avenue and located approximately 250 m to the north of the sampling point. Intercity roads that connect Bursa to Ankara and Yalova, which are the two highways with the heaviest traffic load in the city, are approximately 1 and 1.5 km away from the Hygiene Center, respectively. Other roads with heavy traffic are further away.

Bursa, which is located in the northwestern part of the country, is the fourth largest city in Turkey with its population of 2.5 million people. There are approximately 8000 small- and large-scale facilities producing textile. Cotton weaving, artificial and synthetic yarn production, woven fabric and home textile are the leading subsectors in the textile industry. The city accounts for >75% of the annual yarn production in Turkey. Bursa is also the center of automotive industry in the country, accounting for approximately 60% of the annual automotive production in Turkey.

There was an intense asphalt pavement activity in Altıparmak Boulevard and in Hasta Yurdu Road (about 50 m to the south of the sampling point) which connected with Altıparmak Boulevard between September 20 and October 25 during the first campaign. This provided an ideal opportunity to characterize an asphalt profile and

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