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Analysis of surface ozone and nitrogen oxides at urban, semi-rural and rural sites in Istanbul, Turkey

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HIGHLIGHTS

► First dataset providing semi-urban and rural ozone levels in Istanbul.
► Higher ozone levels are observed in the rural areas compared to urban areas.
► Weekend effect is clearer in the urban sites compared to rural areas.
► Long-range transport can play an important role on the ozone levels in the city.

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ABSTRACT

Ozone (O_3) mixing ratios were measured at three different sites (urban/traffic, semi-rural and rural/island) in Istanbul from September 2007 to December 2009 in order to determine the diurnal, monthly and seasonal variations of O_3 and nitrogen oxides (NO_x) and to study the local and regional impacts. This is the first study that evaluates the O_3 levels in semi-rural and rural sites in Istanbul in addition to the urban sites. The diurnal O_3 variations are generally characterized by afternoon maxima (64 ppb at the urban, 80 ppb at the semi-rural and 100 ppb at the rural site) and the nighttime minimum being more pronounced at the polluted urban site. The monthly mean O_3 mixing ratios start to increase in March, reaching their maximum values in August for the urban (~25 ppb) and semi-rural sites (30 ppb). However, at the rural site, the monthly mean O_3 levels reach their maximum value in June (35 ppb). The O_3 mixing ratios for weekends were higher than those on weekdays at each site by up to 28%, possibly due to changes in VOC sensitivity and reduction in NO_x levels. In order to better understand and characterize the relationship between air masses and O_3 levels, cluster analysis was applied to the back-trajectories calculated by the HYSPLIT model for the semi-rural site. The analyses clearly showed that major transport is characterized by northern and western clusters, particularly from the Eastern Europe and the Mediterranean region, as well as recirculation over Istanbul due to high pressure systems leading to accumulated levels of O_3. The results clearly suggest that extended measurement networks from urban to rural sites should be considered for a more comprehensive evaluation of O_3 levels.

1. Introduction

Surface ozone (O_3) is a major component of smog and is formed through a series of photochemical reactions in the presence of volatile organic compounds (VOCs) and nitrogen oxides (NO_x) under intense solar radiation. O_3 is produced by the reaction of an oxygen molecule (O_2) with an oxygen atom, which originates from the photolysis of nitrogen dioxide (NO_2) by solar radiation. O_3 is destroyed by reacting with NO to form NO_2 and O_2. While this so-called 'null cycle' does not lead to a net production or destruction of O_3, the presence of VOCs in the atmosphere interacts with this mechanism through reactions driven by the hydroxyl radical (OH) leading to reactions with the present NO and therefore, to accumulation of O_3 (Seinfeld and Pandis, 1998). In some cases, O_3 formation is controlled almost entirely by NO_x and is largely independent of the amount of VOC

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(NO_x-sensitive), while in other cases, it increases with increasing VOC (VOC-sensitive; Sillman, 1999). As a result of complex meteorological influences and photochemical mechanisms, precursor emissions (NO_x and VOCs) can lead to elevated levels of surface O_3 locally and downwind. These meteorological and chemical conditions cause large diurnal, day-to-day, seasonal and year-to-year variations in O_3 levels (Solomon et al., 2000; Shan et al., 2009).

O_3 levels have been widely studied for many locations in the world (e.g. Davidson, 1993; Wakamatsu et al., 1996; Duenas et al., 2002; Elminir, 2005; Garcia et al., 2005; Camalier et al, 2007; Shan et al., 2009; Carvalho et al., 2010). On the other hand, very few studies have been conducted in Istanbul focusing on O_3 levels, due to the limited network on ambient O_3 measurements. In contrast to the large geographical extent and the population of Istanbul, only a few measurement stations (Sarachane in the European side and Kadikoy in the Asian side), operated by the Istanbul Metropolitan Municipality (IBB), have been monitoring O_3 levels since 1999 (Incecik et al., 2010). This available dataset has been statistically investigated for different periods in a number of studies (Topcu and Incecik, 2002, 2003; Im et al., 2006, 2008). Topcu and Incecik (2002) studied the O_3 levels and its relationship with NO_x and some meteorological parameters in Istanbul for the 1998 and 1999 datasets and found that O_3 mixing ratios generally increase with increasing temperature in the ozone season. Topcu et al. (2005) studied the interaction patterns of O_3 and NO_x during the period of 2002–2003 and found that high O_3 episodes were characterized by southwest and west–southwest winds and calm conditions. They have reported that the diurnal variations of O_3, NO_x and VOCs supported the buildup of O_3 during rush hours. Im et al. (2006) found that high summertime O_3 levels are mostly associated with southerly winds. They reported high levels (up to 300 $\mu g\ m^{-3}$) due to limited mixing heights. Im et al. (2008) found that urban O_3 levels were mainly subject to NO_x-sensitive chemistry. Karaca and Ozturk (2012) studied the weekend effect, considering Sundays as the weekend days, in Istanbul using data from 2 municipality stations between 2000 and 2005 and found higher mean ozone during weekends compared to weekdays.

There are also modeling studies investigating the O_3 levels in Istanbul (Anteplioğlu, 2000; Topcu et al., 2003; Im et al., 2011a, 2011b). Anteplioğlu (2000) studied episodic O_3 levels in Istanbul using SAIMM mesoscale meteorological and UAM-V chemistry and transport models and found that O_3 mixing ratios subsided on the late afternoon and evening hours, suggesting the significance of traffic sources on the air quality of the area. Topcu et al. (2003) studied the O_3 levels in Istanbul using MM5/CAMx modeling system and found that the MM5 meteorological model was capable of simulating the flow characteristics on city level while the lack of high resolution emission inventories was a major deficiency in simulating the pollutant levels in the area. Im et al. (2011a), using MM5/CMAQ model system on a high spatial resolution calculated an impact of biogenic emissions on the regional O_3 levels up to 25 ppb in the extended Istanbul area. Im et al. (2011b), using WRF/CMAQ model system, showed that precursor emissions from Istanbul can contribute to O_3 formation downwind in the East Mediterranean while locally, these emissions behave as a net chemical sink for O_3.

Due to the limited number of studies conducted for the O_3 levels in Istanbul and considering the urban focus of all these studies, O_3 levels in Istanbul (Asian side) were measured at three new different sites (traffic, semi-rural and rural — a small island in the Marmara Sea) in the frame of the Cost-728 Action in order to better represent the geographical features of O_3 within the extended area. Therefore, this study aims to determine the diurnal, monthly and seasonal variations of O_3 at each new site and to study the possible regional influences using back-trajectory analysis. This study also aims to investigate the variations of O_3 levels between weekdays and weekends at these monitoring sites.

2. Methodology

2.1. The study area

Istanbul is the 21st largest megacity in the world with a population over 13 million with an area of about 5300 km^2. The city is situated between the Black Sea and the internal Marmara Sea. The Bosphorus channel, which is approximately 30 km in length, separates the city to Asian and European sides in the direction of NNE/SSW (Fig. 1). The complex terrain of Istanbul has impacts on the circulation systems over the city (Anteplioğlu, 2000). The dominant wind direction is on the NE/SW axis, the first being observed generally in summer and the latter in winter. Local and international shipping as well as traffic and industry significantly contribute to the high air pollutant levels in the city (Markakis et al., 2012; Kanakidou et al., 2011). The major industrial activities consist of textile, metal and chemical production (Im et al., 2006). Local emissions and long-range transport (LRT) can lead to elevated levels of pollutants in the city and its surroundings (Kindap et al., 2006; Im et al., 2010; Koçak et al., 2011). Currently, the registered number of motor vehicles exceeds 2.7 million in the city and is increasing. Traffic rush hours behave as a sink for O_3 by the emissions of fresh NO_x (Im et al., 2006). The ratio of diesel powered cars in the city is around 45%. LPG or auto gas is widely being used by the taxies (about 18,000). Following the fuel switching in 1990s, natural gas has replaced the low-quality coal and currently is widely used in the city.

2.2. Ozone measurements

Although O_3 measurements in the urban sites of the city began in 1999, these measurements have not been sustained due to technical problems often experienced. Therefore, for the present study, new measurements have been carried out at different sites of Istanbul in the frame of the Cost-728 Action (Incecik et al., 2010). These different measurement sites provide large O_3 variations with different emission, particularly NO_x, and regional characterizations. Geographical distribution of the three new sites is depicted in Fig. 1. The urban/traffic and the semi-rural stations are 8 km apart from each other while the semi-rural and the rural/island stations have 16 km in between. The Kocaeli Gulf shown in Fig. 1 hosts the largest industrial area in Turkey in terms of petroleum production activities. The information regarding the locations, site characteristics, measurement periods and measured parameters are shown in Table 1. These stations are:

1. Göztepe (40.99 N, 29.07 E, 40 m asl): an urban/traffic site located at the garden of the State Supply Office (DMO) building where a major highway (E-5) is 10 m away. Therefore, the site is strongly influenced by high traffic emissions, particularly NO_x, throughout the day. The highway is connected to the Bosphorus Bridge, one of the two bridges connecting the Asian side to the European side. According to Traffic and Transportation Survey of Highways Report (2010), about 200,000 motor vehicles pass daily on this motorway. There are many illegal squatter buildings around the highway site. Therefore traffic and household emissions are believed to be the dominant source influencing the station, which is typical and representative of an urban/traffic site.
2. Kandilli (41.06 N, 29.06 E, 124 m asl): a semi-rural site located in the large and historical observatory campus of Kandilli Observatory on a hill overlooking the Bosphorus. There is much lower traffic density here compared to the Göztepe site and the surrounding area is mostly residential. However, the shipping emissions from the Bosphorus (about 63,000 ship transitions in 2008) can have significant influences on the air quality levels