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Characterization of volatile organic compounds and the impacts on the regional ozone at an international airport☆

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In this study, the measurement of volatile organic compounds (VOCs) was conducted at Beijing Capital International Airport (ZBAA) and a background reference site in four seasons of 2015. Total concentrations of VOCs were 72.6 ± 9.7, 65.5 ± 8.7, 95.8 ± 11.0, and 79.2 ± 10.8 $\mu g/m^3$ in winter, spring, summer, and autumn, respectively. The most abundant specie was toluene (10.1%–17.4%), followed by benzene, ethane, isopentane, ethane, acetylene, and n-butane. Seasonal variations of VOCs were analyzed, and it was found that the highest concentration occurring in summer, while the lowest in spring. For the diurnal variation, the concentration of VOCs in the daytime (9:00–15:00) was less than that at night (15:00–21:00) obviously. Ozone Formation Potential (OFP) was calculated by using Maximum Incremental Reactivity (MIR) method. The greatest contribution to OFP from alkenes and aromatics, which accounted for 27.3%–51.2% and 36.6%–58.6% of the total OFP. The WRF-CMAQ model was used to simulate the impact of airport emissions on the surrounding area. The results indicated that the maximum impact of VOCs emissions and all sources emissions at the airport on O_3 was 0.035 and -23.8 $\mu g/m^3$, respectively. Meanwhile, within 1 km from the airport, the concentration of O_3 around the airport was greatly affected by airport emitted.

1. Introduction

With the development of economic globalization, aviation as an important class of transportation plays a significant role in global economic activities and has had a profound influence on international relationships (Herndon et al., 2008; Vichi et al., 2016). Air traffic has increased continuously over the last several decades. Depending on a recent report of the International Air Transport Association (IATA), global passenger traffic is expected to increase by around 5% annually and will reach 3.8 billion by 2020 (IATA, 2017). With the rapid increase in air traffic demand, aircraft emissions as an important and special source of air pollution, have attracted more and more attention (Masiol and Harrison, 2015; Stratmann et al., 2016). Aircraft engine emissions include NO_x, CO, SO_2, volatile organic compounds (VOCs), and particulate matter (PM) (Stettler et al., 2011). In recent years, most researches have been focused on the estimation of aircraft emissions and their impact on the surroundings area (Winther et al., 2015; Simonetti et al., 2015; Rissman et al., 2013; Song and Shon, 2012; Yim et al., 2013). Research of aircraft emission characteristics was mainly concentrated on NOx, CO, and PM (Ren et al., 2016; Herndon et al., 2008). However, as one of the main pollutants in aircraft emissions, there was poorly concerned about the characteristics of VOCs components. Some studies have shown that VOCs played an important role for the production of photochemical O_3 and other oxidants, which increased the atmospheric oxidizing ability, and could make important impact on the secondary organic aerosol (SOA) production (Niu et al., 2016; Hou et al., 2015; Wei et al., 2014). In addition, VOCs contain a variety of harmful substances, which have an adverse effects on air quality and human health (Li et al., 2015a; Louie et al., 2013).

For a long time, the research on VOCs characteristics has mainly focused on fuel combustion (Ozil et al., 2009; Minguillon et al.,

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2015), biomass burning (Gilman et al., 2015; Zhu et al., 2016), industrial emissions (Zheng et al., 2016; Gallego et al., 2014), transportation sources (Ho et al., 2013; Pang et al., 2015), and fugitive emissions (Chen et al., 2015; Liu et al., 2016) at home and abroad. However, compared with other sources of pollution, research on VOCs emission characteristics of aircraft was relatively scarce. Only a few studies have analyzed the VOCs characteristics of the airport in detail. For example, Lai et al. (2013) measured the concentration of 22 VOCs at the airport apron in summer, autumn, and early winter of 2011, and they observed that aromatics accounted for the largest proportion of total VOCs (TVOCs), and the five most abundant VOCs species in all samples were toluene, m,p-xylene, o-xylene, i-pentane, and styrene. Schurmann et al. (2007) investigated the difference in the VOCs components of the aircraft emissions during ignition, idle, and taxiing, and they found that the components of the VOCs changed with the type and the status of engine, and the proportion of aromatic was higher when the engine has not yet reached the final temperature. In addition, the proportion of C_2-C_3 alkenes in the exhaust of the aircraft was obviously higher than that in the environment. Guimaraes et al., 2010 analyzed the characteristics of VOCs in downtown, airport and urban forest in Brazil, and their results showed that there was no significant difference in the ratio of toluene to benzene between the urban and the forest, but it was obviously different at the airport. Zhu et al. (2011) examined the ultrafine particles, polycyclic aromatic hydrocarbon (PAH) species, and VOCs in an international airport in USA, and they found that the concentrations of $PM_{2.5}$, PAHs, and four VOCs (i.e., acrolein, benzene, 1,3-butadiene, and formaldehyde) in the airport were higher than that of background site, especially naphthalene. Based on observation data and meteorological data Ionel et al. (2011) investigated the diurnal variation of VOCs components at the airport, and they observed that the concentration of VOCs varied with the flow of the aircraft and the high concentration was recorded when the aircraft was fueling.

In this study, we focus on the Beijing Capital International Airport (International Air Transport Association code: ZBAA), which is the second busiest airport in the world based on passenger traffic (ACI, 2016). According to recent statistics of the Civil Aviation Administration of China (CAAC), the number of passenger traffic reached about 94 million, and the total number of aircraft movements reached about 610 thousand in ZBAA in 2016 (CAAC, 2016). Therefore, there are many types of aircraft in the ZBAA, and the number of daily flights is stable. So the ZBAA as a research object is very representative. The main aim of this study is to reveal the characteristics of VOCs at the airport through the systematic collection and analysis of the samples. Furthermore, due to the significant impact of VOCs for O_3, this paper will also investigate the ozone formation potential and quantify the impact of aircraft emissions on regional air quality by using WRF-CMAQ model system. The results of the study could better understand the characteristics of airport pollution and its impact on the surrounding environment.

2. Methods

2.1. Sample collection

The ZBAA is the busiest airport in China and is located approximately 25 km away from the northeast of the city centre (Tiananmen Square) (Fig. 1) (CAAC, 2016). The airport covers 14.8 km^2, and has 3 terminals and 3 runways. The west runway (runway 1) is 3200 m long and 50 m wide. The middle runway (runway 2) and east runway (runway 3) are 3800 m long and 60 m wide. The main types of aircraft during the sampling period were Boeing 738 and 737, Airbus 320, 321, 332, and 333, accounting for 80% of the total aircraft. The main sources of emissions of VOCs at the airport included aircraft, ground support equipment, ground access vehicles, private vehicles, and airport oil depot.

The sampling site was located next to the middle runway (runway 2). Although flights in and out of ZBAA generally proceed from south to north according to the dominant wind direction, but as the changes of wind direction at the airport, the direction of aircraft take-off and landing will change. In order to make the collected samples representative, there were three sampling sites set in the middle, north, and south of the runway at a height of 1 m. After that, three samples were averaged.

In order to analyze the seasonal and diurnal variation of VOCs, the samples were collected over 28 days in January, April, August, and October of 2015, representing winter, spring, summer, and autumn, with two 6-h sampling periods (09:00–15:00 and 15:00–21:00) for each day. We use 3.2 L summa canisters to collect samples, and sampling flow rate was controlled by a flow controller at a constant flow rate of 8.9 mL/min during the 6-h sampling process (Li et al., 2014). In addition, we used the same sampling method at the same time outside of the airport in October for comparison analysis. The background reference site was set on the roof (6 m above the ground) of a building in the west of the airport, where was only affected by the traffic sources. In total, 91 VOCs samples were collected during the sampling period. Additionally, meteorological parameters, including temperature, atmospheric pressure, relative humidity (RH), wind speed, and wind direction were obtained from the airport's meteorological station and the aircraft movements during sampling were listed in Table 1.

2.2. Sample analysis

VOCs samples were analyzed by Gas Chromatography–Mass Spectrometry (GC–MS, Model 7899A/5975C, Agilent Inc.) according to Environmental Protection Agency (EPA) TO-15 methods (US EPA, 1999). Before the sample enters the GC-MS, the 400 mL of sample needed to be injected into the pre-concentrator (Model 7100, Entech Inc.) and passed through 3-stage cryotrap (Module 1–3). Module 1 was mainly used to remove H_2O, N_2, CO_2, CO, and O_2 from samples at $-165\,^{\circ}C$ by liquid nitrogen, and then recovered by desorbing at $10\,^{\circ}C$. Module 2 was mainly used to remove Ar, CH_4, CO_2, and trace water at $-50\,^{\circ}C$, and then the samples were backflushed at $180\,^{\circ}C$. After that, samples were frozen to $-160\,^{\circ}C$ in Module 3, which was constituted by the empty capillary (Liu et al., 2008). Then the Module 3 was heated to rapid evaporation of the samples and then the concentrated sample was driven into the GC-MS by helium. For GC analysis, the initial temperature was maintained at $-20\,^{\circ}C$ for 1 min, and then raised to $0\,^{\circ}C$ at a rate of $5\,^{\circ}C$/min, reaching $100\,^{\circ}C$ at a rate of $10\,^{\circ}C$/min, then the rate of $5\,^{\circ}C$/min increased to $150\,^{\circ}C$, and finally to $200\,^{\circ}C$ at the rate of $12\,^{\circ}C$/min (Cheng et al., 2016; Wei et al., 2014).

Photochemical Assessment Monitoring Stations (PAMS) certified gas were used to quantify the concentration of VOCs components. The GC-MS system was operated in SCAN mode, and could analyze all PAMS VOCs except for ethane, ethane, acetylene, and propane. The detection limit of the method was ranged from 0.1 to 1.2 ppbv. The PAMS gas was diluted to 4 different concentrations (2, 5, 10 and 20 ppbv) to quantitative the target compounds. The calibration curve of each target compound was determined by the relationship between the integrated peak area and the corresponding concentration (5 levels: 0, 2, 5, 10 and 20 ppbv), and the calibration curve was checked every day. Generally, the correlation was good and the correlation coefficient was above 0.99 (Wei et al., 2014). The concentrations of ethane, ethane, acetylene, and propane in the samples were analyzed by Gas Chromatograph-Flame Ionization Detector (GC-FID).