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Observation and analysis of atmospheric volatile organic compounds in a typical petrochemical area in Yangtze River Delta, China

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ABSTRACT

Volatile organic compounds (VOCs) are a kind of important precursors for ozone photochemical formation. In this study, VOCs were measured from November 5th, 2013 to January 6th, 2014 at the Second Jinshan Industrial Area, Shanghai, China. The results showed that the measured VOCs were dominated by alkanes (41.8%), followed by aromatics (20.1%), alkenes (17.9%), and halo-hydrocarbons (12.5%). The daily trend of the VOC concentration showed a bimodal feature due to the rush-hour traffic in the morning and at nightfall. Based on the VOC concentration, a receptor model of Positive Matrix Factorization (PMF) coupled with the information related to VOC sources was applied to identify the major VOC emissions. The result showed five major VOC sources: solvent use and industrial processes were responsible for about 30% of the ambient VOCs, followed by rubber chemical industrial emissions (23%), refinery and petrochemical industrial emissions (21%), fuel evaporations (13%) and vehicular emissions (13%). The contribution of generalized industrial emissions was about 74% and significantly higher than that made by vehicle exhaust. Using a propylene-equivalent method, alkenes displayed the highest concentration, followed by aromatics and alkanes. Based on a maximum incremental reactivity (MIR) method, the average hourly ozone formation potential (OFP) of VOCs is 220.49 ppbv. The most significant source for ozone chemical formation was identified to be rubber chemical industrial emissions, following one by vehicular emission. The data shown herein may provide useful information to develop effective VOC pollution control strategies in industrialized area.

Introduction

Volatile organic compounds (VOCs) are one of the main pollutants emitted into the atmosphere in megacities. VOCs in the atmosphere have aroused wide concern for decades because they are a kind of important precursors of secondary air pollutants *via* photochemical processes (Seinfeld and Pandis, 2006; Crutzen, 1975; Chameides and Walker, 1976).

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VOCs are known to be ingredients in the photochemical production of tropospheric ozone (O_3) in the presence of nitrogen oxides (NO_x) under sunlight (Li et al., 2017). Photochemical Assessment Monitoring Stations (PAMS) organized by the United States Environmental Protection Agency (US EPA) have particularly defined 57 critical ozone precursors ($VOCs_{PAMS}$) (Shao et al., 2016). Moreover, most VOCs also impact air quality and human health directly (Leuchner and Rappenglück, 2010; Pérez-Rial et al., 2010; Fu and Chen, 2016). Several VOCs, such as benzene, toluene, and 1,3-butadiene, have been proved to be air toxics and showed adverse effects on human health, including nose and throat irritation, asthma and leukemia, and even death (Knox, 2005; Kampa and Castanas, 2008; Wang et al., 2016).

The contribution to photochemical ozone formation is related to the characteristics of different VOC species (Geng et al., 2007, 2008, 2009a, 2009b; Tang et al., 2007, 2008). The potential of VOCs to generate ozone through photochemical reactions is defined as the reactivity of VOCs (Geng et al., 2010). The VOC reactivity is an important factor to determine the ozone formation in large cities (Chameides et al., 1992; Ran et al., 2009; Tie et al., 2009). Based on the contributions to photochemical ozone formation of each emission source of VOC species, an effective O_3 pollution control strategy could be developed (Cai et al., 2010a; Geng et al., 2007, 2008, 2009a, 2009b; Tang et al., 2007, 2008). Thus, it could be crucial to obtain the contributions to photochemical ozone formation of emission sources by two steps: identifying the emission sources of VOC species and calculating the photochemical reactivity of different VOC species.

Some VOC species can be used as the finger-prints to point out specific VOC sources, and thus they were used as "VOC-tracers" to identify VOC sources (Geng et al., 2009a, 2009b). For instance, isopentane is a tracer of gasoline evaporation (Barletta et al., 2005); propylene is the characteristic product of internal combustion engines and was reported as a good indicator of vehicle exhaust in Shanghai (Scheff and Wadden, 1993; Geng et al., 2010). Based on these studies, An et al. (2014) pointed out that industrial production sources, automobile emission sources, combustion sources, industrial production volatilization sources, solvent use sources and biogenic emission sources are the main VOC sources in an industrial area of Nanjing; in addition, the sources related to industrial production activities accounted for 45%–63% of the VOCs. Shao et al. (2016) studied the emission sources in industrial parks in Nanjing and suggested that industrial-related emission, including industrial emissions and industrial solvent usage, occupied the highest proportion, accounting for about 51.26% of the VOCs. Saeaw and Thepanondh (2015) suggested that 42%–57% of total VOC (TVOC) concentration was contributed from mobile sources, following one by industrial processes (15%–44%) in industrial areas in Thailand. Dumanoglu et al. (2014) studied the emission sources in a heavily industrialized region in Turkey and suggested that refinery and petroleum products, petrochemical industry, solvent use and industrial processes, and vehicle exhaust were the identified VOC sources, contributing 56%, 22%, 12%, and 10%.

The calculation of photochemical reactivity of each VOC species is another necessary step to obtain the contributions to photochemical ozone formation of emission sources. A propylene-equivalent concentration method proposed by Chameides et al. (1992) and a maximum incremental reactivity (MIR) method proposed by Carter (1994) were widely used to calculate the reactivity of different VOC species. Luo et al. (2011) calculated the reactivity of VOC species in Guangzhou and suggested that alkenes contributed the most photochemical reactivity. Zhang et al. (2017) pointed out that the aromatics contributed the most photochemical reactivity in 23 Chinese cities. An et al. (2014) calculated the reactivity of VOC species in Nanjing and suggested that the top 5 species were ethane, ethylene, propane, benzene and acetylene. Shao et al. (2016) indicated that alkenes were the dominant contributors to the O_3 photochemical production; without alkenes, the averaged maximum of O_3 concentration was reduced from 73.43 to about 26.42 ppbv, decreasing by 64.02%.

The study about emission sources and photochemical reactivity of VOCs is still very limited in China to date, most of the studies focused on the central area of megacities (Song et al., 2007; Yuan et al., 2009; Su et al., 2011; Shao et al., 2016). However, the information about the characteristics of VOCs in industrial areas is scarce, especially in the area at a large-scale chemical industry. During atmospheric aging and transmission, the characteristics of VOCs change because of the photochemical reactions. Such study is thus highly useful to observe original emission and characteristics of VOC emission.

Shanghai is the largest megacity with a population of more than 24 million in China, and the economy developed rapidly during the last decades. The industrial output increased from 510 billion yuan (1996) to 3.32 trillion yuan (2015); the number of automobiles increased from 470,000 (1996) to 2,820,000 (2015), accounting for a more than 600% increase (Shanghai Municipal Statistics Bureau (SMSB), 1997, 2016). As a result, air quality was deteriorated seriously during the past decades. It was reported that the surface O_3 concentrations continuously increased in last decade by 0.5–1.0 ppbv/year in eastern China (Shen and Wang, 2012; Tang et al., 2009; Wang et al., 2009). In Shanghai, the annual number of days over 1-hour average Chinese national O_3 standard (93 ppbv) arrives at 40–80 ppbv (An et al., 2008). O_3 may become one of the most important pollutants in Yangtze River Delta (YRD). In this study, we analysed the concentration of VOCs from November 5th, 2013 to January 6th, 2014, in the Second Jinshan Industrial Area of Shanghai and analysed the composition of VOCs. Furthermore, the impact of weather condition, on the variation of the VOC concentrations and the VOC reactivity were also explored. Based on such information, we further identified the emission sources of VOCs using the PMF receptor model. This study attempts to figure out: (1) which source contributes significantly to ambient VOCs and (2) what roles do the VOC sources play in the photochemical O_3 formation. This study may provide useful information to establish effective air pollution control strategies for a heavily chemical industrialized region.

1. Measurements and methods

1.1. Site description

The sampling site is located at the international trade mall (N30°43′57.94″ E121°18′19.09″) in the Second Jinshan Industrial

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