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Diurnal profiles of isoprene, methacrolein and methyl vinyl ketone at an urban site in Hong Kong

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HIGHLIGHTS

- Isoprene primarily originated from local biogenic emissions.
- Higher isoprene levels were observed on days when average daily temperature was above 30 °C.
- Traffic emissions and biogenic emissions were the major contributors to MACR/MVK.
- The use of MACR/MVK to represent the isoprene oxidation rate is inappropriate in urban Hong Kong.

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ABSTRACT

Methacrolein (MACR) and methyl vinyl ketone (MVK) are major oxidation products of isoprene, but they also have primary emissions in urban environments, for example from fuel use. To examine whether MACR and MVK could be used as a direct measurement of the oxidation rate of isoprene in an urban setting, the diurnal variations of isoprene, MACR and MVK were characterized at an urban site in Hong Kong from September to November, 2010. Ozone (O_3), carbon monoxide (CO), sulfur dioxide (SO_2), and nitrogen oxides (NO_x) were simultaneously monitored. The average isoprene mixing ratio was 252 ± 204 pptv, with a bell-shaped distribution observed on most sampling days. Higher levels of isoprene were recorded in the beginning of the sampling period, when the temperature was higher. The average mixing ratios of MACR and MVK were 101 ± 85 pptv and 175 ± 131 pptv, respectively. While isoprene, MACR and MVK experienced peak concentrations from 11 a.m. to 3 p.m., increased levels of MACR and MVK during the morning rush hour did not coincide with isoprene. The low associations between isoprene and MACR/MVK suggest that either MACR/MVK were not formed from local isoprene oxidation and/or they could partly originate from primary emissions such as fuel evaporation or combustion. Statistical analyses of linear regression and positive matrix factorization revealed that approximately 20–29% of the measured MACR and MVK was associated with biogenic emissions, and 55–71% was impacted by vehicular emissions, particularly during morning rush hours. Since MACR and MVK originated from both primary emissions and biogenic emissions at this urban site, they can therefore overestimate the actual rate of isoprene oxidation and its contribution to O_3 production in urban areas with strong primary emissions.

1. Introduction

Biogenic volatile organic compounds (BVOCs) are emitted in substantial quantities from certain types of terrestrial vegetation, and are believed to play an important role in ozone (O_3) chemistry in forests (Makar et al., 1999), mountains (Dreyfus et al., 2002), semi-rural (Starn et al., 1998) and urban areas (Biesenthal and Shepson, 1997; Fuentes et al., 2000). Isoprene (2-methyl-1,3-butadiene, C_5H_8), with an annual global emission of about 500–750 Tg, is the single highest VOC emission in the troposphere (Guenther et al., 2006). Based on measurements in 2006, biogenic sources are the biggest emission source category for VOCs in the Pearl River Delta (PRD) region of China, where air pollution has been severe due to the rapid growth of industries and population since the 1980s (Zheng et al., 2009). In particular, isoprene is the single highest VOC contributor to ozone formation potential, accounting for 15%. In Hong Kong, a highly urbanized and densely populated city, BVOCs have been shown to account for 8.8 μg m^{-3}

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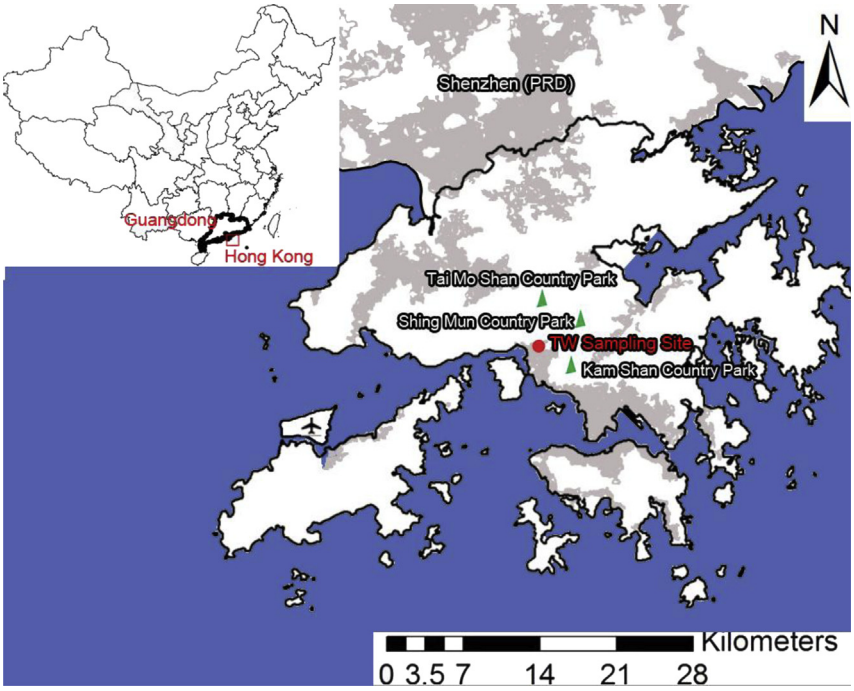

Fig. 1. Map of the sampling site (TW) and its surrounding environments. The highly developed areas are in gray, and Kowloon is located 7–15 km southeast of TW.

(49%) of ambient $PM_{2.5}$-bounded organic carbon content on days under regional transport influences, compared to 0.99 μg m^{-3} (21%) on days under mainly local emission influences (Hu et al., 2008). Given the significant contrition of BVOCs to both O_3 and SOA formation in urban areas and on a regional scale, the implications of photochemical oxidation of BVOCs need to be considered and understood for the development of effective air quality regulations.

The main removal pathway of isoprene is reaction with OH radicals during daytime and with O_3 and NO_3 radicals at night (Brown et al., 2009). In high NO_x environments, formaldehyde, MVK and MACR are the major primary oxidation products of isoprene, accounting for more than 50% of the carbon yield (Carter and Atkinson, 1996; Miyoshi et al., 1994; Zhao et al., 2004). Many previous studies have used ratios of isoprene and its oxidation products, such as MVK/MACR and [MVK + MACR]/isoprene, to investigate the magnitude and location of isoprene emission sources (Guo et al., 2012; Karl et al., 2007; Barket et al., 2004; Yokouchi, 1994; Stroud et al., 2001). In particular, MVK and MACR have been used to estimate isoprene's contribution to O_3 formation at a semi-rural site in British Columbia, Canada (Biesenthal et al., 1997) and at an urban forested site in Nashville, Tennessee, USA (Starn et al., 1998). The potential use of MVK/MACR as a direct measurement of the actual oxidation rate of isoprene allows the estimation of isoprene's contribution to O_3 production (Guo et al., 2012; Biesenthal and Shepson, 1997). However, MVK and MACR can also originate from primary emission sources including automobile exhaust (Yokouchi, 1994; Biesenthal and Shepson, 1997). Therefore, in urban areas with strong anthropogenic sources, the use of MVK/MACR to represent the isoprene oxidation rate may not be reliable due to the additional contributions of MVK/MACR from primary emissions.

Diurnal variations and species correlations at a particular site can contain information about the dominant local sources and chemical processes. Although many studies have reported time-series profiles of BVOCs in the PRD region (Li and Wang, 2012; Tang et al., 2007), limited information is available on the diurnal profile of isoprene oxidation products, particularly in urban areas in close proximity to fresh primary emissions. In this paper, the diurnal profiles of isoprene, MVK and MACR are studied at an urban site in Hong Kong and used to identify their sources and formation mechanisms. The goal of the paper is to examine the sources of MVK and MACR, and determine whether MVK/MACR is a reliable tool to represent the oxidation rate of isoprene in an urban area with local primary emissions.

2. Materials and methods

2.1. Sampling description

The Hong Kong Environmental Protection Department (HKEPD) air quality monitoring station at Tsuen Wan (TW) is used to characterize VOCs in an urban area (Fig. 1). Tsuen Wan District, located in the New Territories of Hong Kong, has an area of 60.7 km^2 with a population of around 300,000 in 2011; it is a mixed residential, commercial and light industrial district. The sampling site (22.373°N, 114.112°E) is adjacent to major roadways and surrounded by residential and industrial blocks. Previous studies have shown that vehicular exhaust is the predominant emission source of polycyclic aromatic hydrocarbons (Sin et al., 2003) and total non-methane hydrocarbons (NMHCs) (Guo et al., 2004b) at this site.

The sampling campaign lasted from September to November 2010, the season when O_3 levels are generally highest due to the long range transport of pollution-laden continental air masses, strong photochemical activity, and/or meteorological conditions that favor the accumulation of atmospheric pollutants (Chan et al., 1998; Leung and Zhang, 2001). In this study, hourly VOC samples were collected on selected O_3 episode days (Oct. 24, 29–31; Nov. 1–3, 9 and 19) and non-episode days (Sep. 28, Oct. 2, 8, 14, 18–19, 27–28; Nov. 20–21). During the sampling period, O_3 levels were predicted based on weather forecasts and meteorological data such as temperature, wind speed and vertical mixing conditions. An episode day was defined when the highest hourly O_3 level