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Characterization of volatile organic compounds at a roadside environment in Hong Kong: An investigation of influences after air pollution control strategies

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HIGHLIGHTS

- A series of control strategies has been implemented by HKSAR in recent years.
- Characteristics of VOCs were compared at roadside between 2003 and 2011/2012.
- Besides alkanes, the mixing ratios of other VOCs decreased by >50% since 2003.
- LPG fuel consumption becomes the largest contributor to the pollution.
- The sum of OFP for the target VOCs was reduced by 47% compared to that in 2003.

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ABSTRACT

Vehicular emission is one of the important anthropogenic pollution sources for volatile organic compounds (VOCs). Four characterization campaigns were conducted at a representative urban roadside environment in Hong Kong between May 2011 and February 2012. Carbon monoxide (CO) and VOCs including methane (CH_4), non-methane hydrocarbons (NMHCs), halocarbons, and alkyl nitrates were quantified. Both mixing ratios and compositions of the target VOCs show ignorable seasonal variations. Except CO, liquefied petroleum gas (LPG) tracers of propane, *i*-butane and *n*-butane are the three most abundant VOCs, which increased significantly as compared with the data measured at the same location in 2003. Meanwhile, the mixing ratios of diesel- and gasoline tracers such as ethyne, alkenes, aromatics, halogenated, and nitrated hydrocarbons decreased by at least of 37%. The application of advanced multivariate receptor modeling technique of positive matrix factorization (PMF) evidenced that the LPG fuel consumption is the largest pollution source, accounting for 60 ± 5% of the total quantified VOCs at the roadside location. The sum of ozone formation potential (OFP) for the target VOCs was 300.9 μg-O^3 m^{-3}, which was 47% lower than the value of 567.3 μg-O^3 m^{-3} measured in 2003. The utilization of LPG as fuel in public transport (i.e., taxis and mini-buses) contributed 51% of the sum of OFP, significantly higher than the contributions from gasoline- (16%) and diesel-fueled (12%) engine emissions. Our results demonstrated the effectiveness of the switch from diesel to LPG-fueled engine for taxis and mini-buses implemented by the Hong Kong Special Administrative Region (HKSAR) Government between the recent

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ten years, in additional to the execution of substitution to LPG-fueled engine and restrictions of the vehicular emissions in compliance with the updated European emission standards.

1. Introduction

Volatile organic compounds (VOCs) in the atmosphere are emitted from both biogenic (mainly from vegetation) and anthropogenic sources (e.g., vehicular and fossil-fueled power plant emission and solvent usage) (Apel et al., 2010; Atkinson, 2000; Atkinson and Arey, 2003). VOCs are important precursors to the formation of ground-level ozone (O_3) and secondary organic aerosols (SOA), and can also pose adverse health effects on human (Ho et al., 2013; Louie et al., 2013). Many studies have demonstrated that vehicular emission is one of the major sources of anthropogenic VOCs in urban areas (Cai and Xie, 2009; Niedojadlo et al., 2007; Song et al., 2007; Vega et al., 2000; Watson et al., 2001). Vega et al. reported that vehicular exhaust contributed 58.7% to non-methane hydrocarbons (NMHC) in Mexico City's atmosphere (Vega et al., 2000).

Hong Kong is one of the most densely populated cities in the world, with over 7.0 million people and more than 707,000 registered vehicles in an area of 1104 km^2 by the end of 2011 (Hong Kong Transport Department, 2012). Over the past years, urban and street-level air pollution pertaining to vehicular emission has attracted more and more public attention. As estimated by the Hong Kong Environmental Protection Department (HKEPD), local road transport contributed to 23% of the total VOCs emissions in 2011, with a number of 7567 tonnes VOCs emitted into the airs (Hong Kong Environmental Protection Department, 2011). Lau et al. (2010) found that vehicle- and marine vessel-related sources accounted for 31–48% of the ambient VOCs in Hong Kong in 2002–2003, while the contributions increased to 40–54% in 2006–2007. Guo et al. (2007) also investigated the C_1–C_8 VOCs at four urban and rural areas in Hong Kong from September 2002 to August 2003, and their results demonstrated that vehicular emissions contributed significantly to ambient VOCs levels in urban areas (65 $\pm$ 36%). Therefore, vehicular emission is confirmed as one of the key VOCs emission sources in Hong Kong. It is critical to determine the VOC emission characteristics from vehicles in order to further assess the associated human exposure risk and to understand their effects on subsequence photochemical reactions.

Methods adopted to quantify VOCs from vehicular emissions primarily include laboratory-based single-vehicle dynamometer tests (Guo et al., 2011b; Tsai et al., 2003), tunnel studies (Ho et al., 2007, 2009a; Hsu et al., 2001; Legreid et al., 2007; Lonneman et al., 1986), on-board mobile monitoring (Lau et al., 2011), and monitoring in roadside environment (Chan et al., 2002; Guo et al., 2011b; Ho et al., 2002; Ho et al., 2006; Kawashima et al., 2006; Tsai et al., 2006; Wang et al., 2002b). In the dynamometer tests, the VOCs emissions from vehicles were determined under different driving cycles which were set in advance (Guo et al., 2011b; Tsai et al., 2003). However, this method cannot accurately reflect a vehicle's emission under real-world traffic conditions. In contrast to dynamometer tests, the tunnel studies can directly determine vehicular emission profiles, and the monitoring is normally conducted under complicated on-road conditions with emissions from vehicle tailpipes and fuel evaporations (Ho et al., 2009a, b). The result from tunnel study is thus more representative and accurate to estimate the contributions of vehicle fleets to the total air pollutants in local urban areas. Ho et al. determined the emission factors for a number of 110 VOCs species in a tunnel in Hong Kong, of which the total measured VOC emission factors ranged from 67 mg veh^{-1} km^{-1} to 148 mg veh^{-1} km^{-1} (Ho et al., 2009a). However, there are several assumptions and limitations for roadway tunnel measurements, including approval by the administrative authorities for field monitoring, no cold start emissions from vehicles, bias in fleet distributions, resistance caused by tunnel walls, and speed limits established in the tunnels (Ho et al., 2009a; Kawashima et al., 2006). On-board measurement of vehicular emissions facilitates the examination of a vehicle's emission under real-world conditions. For example, Lau et al. measured the instantaneous carbon monoxide (CO), nitrogen monoxide (NO), and VOCs emissions from LPG-fueled taxis in Hong Kong using a sophisticated portable emission measurement system (Lau et al., 2011). Even though the method can accurately measure the instantaneous emission factors on-route under different operation modes (stop, start, creeping, cruising, idling and speed changes), only two vehicles can be examined per day only and the monitoring equipment procedures are complex and expensive.

In this study, we have conducted a one-year intensive VOCs monitoring program at a representative urban roadside environment in Hong Kong from May 2011 to February 2012. VOCs were collected in canister and speciated offline to investigate their mixing ratios and compositions. The results has been compared with a previous study at the same site in 2003, to demonstrate the effectiveness of VOCs control strategies implemented by the Hong Kong Special Administrative Region (HKSAR) Government between the years. The O_3 formation potential for each VOCs emission source was identified in further.

2. Methodology

2.1. Sampling site

Four characterization campaigns were conducted at an urban roadside location, namely Mong Kok Air Quality Monitoring Station (MKAQMS), in May 2011, August 2011, November 2011 and February 2012, respectively. The station is surrounded by residential and commercial building blocks with heavy daily traffic (shown in Fig. 1) (Lee et al., 2002), which is one of the three roadside monitoring stations established by the HKEPD. Based on the local geography, MKAQMS is the most representative roadside environment in Hong Kong. During the sampling period, any activity potentially generating additional pollutants (e.g., constructions sites) was prohibited near the sampling locations.

2.2. Measurement of VOCs and other trace gases

Twenty-four hour (0:00–23:59) integrated VOCs samples were collected into pre-treated and evacuated 2-L electro-polished stainless steel canisters by an ATEC automated sampler (Model 2200, Malibu, CA) once every three days during the periods of four campaigns. The final pressure of the sampled canister was 29 $\pm$ 1 psi. A Teflon PFA filter holder contains a 47 mm Teflon filter to remove particulates from the air stream prior to entering the flow lines. The sampling inlet was approximate 3 m above the