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Decadal changes in emissions of volatile organic compounds (VOCs) from on-road vehicles with intensified automobile pollution control: Case study in a busy urban tunnel in south China☆

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ABSTRACT

In the efforts at controlling automobile emissions, it is important to know in what extent air pollutants from on-road vehicles could be truly reduced. In 2014 we conducted tests in a heavily trafficked tunnel in south China to characterize emissions of volatile organic compounds (VOC) from on-road vehicle fleet and compared our results with those obtained in the same tunnel in 2004. Alkanes, aromatics, and alkenes had average emission factors (EFs) of 338, 63, and 42 mg km^{-1} in 2014 against that of 194, 129, and 160 mg km^{-1} in 2004, respectively. In 2014, LPG-related propane, n-butane and i-butane were the top three non-methane hydrocarbons (NMHCs) with EFs of 184 ± 21, 53 ± 6 and 31 ± 3 mg km^{-1}; the gasoline evaporation marker i-pentane had an average EF of 17 ± 3 mg km^{-1}; ethylene and propene were the top two alkenes with average EFs of 16 ± 1 and 9.7 ± 0.9 mg km^{-1}, respectively; isoprene had no direct emission from vehicles; toluene showed the highest EF of 11 ± 2 mg km^{-1} among the aromatics; and acetylene had an average EF of 7 ± 1 mg km^{-1}. While EFs of total NMHCs decreased only 9% from 493 ± 120 mg km^{-1} in 2004 to 449 ± 40 mg km^{-1} in 2014, their total ozone formation potential (OFP) decreased by 57% from 2.50 × 10^3 mg km^{-1} in 2004 to 1.10 × 10^3 mg km^{-1} in 2014, and their total secondary organic aerosol formation potential (SOAFP) decreased by 50% from 50 mg km^{-1} in 2004 to 25 mg km^{-1} in 2014. The large drop in ozone and SOA formation potentials could be explained by reduced emissions of reactive alkenes and aromatics, due largely to fuel transition from gasoline/diesel to LPG for taxis/buses and upgraded vehicle emission standards.

1. Introduction

Volatile organic compounds (VOCs) are precursors of tropospheric ozone and secondary organic aerosols (SOA) (Carter, 1994; Finlayson-Pitts and Pitts, 1999; Atkinson and Arey, 2003). They are emitted from both biogenic and anthropogenic sources

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(Seinfeld et al., 1998), with global biogenic emissions accounting for 10 times the amount of anthropogenic emissions (Guenther et al., 1995). However, anthropogenic VOC emissions can predominate on a global level, especially in densely populated urban areas or highly industrialized regions (Atkinson and Arey, 2003). Vehicle exhaust, an important anthropogenic source of ambient VOCs worldwide (Streets et al., 2003), contributes substantially to air pollution in China due to the increasing number of automobiles over the past three decades. The number of civilian vehicles in China has increased by approximately 20% per year, from 1.8 million in 1980 to 126.7 million in 2013 (China Statistical Yearbook, 2014). Recent emission inventories suggest that vehicle exhaust makes up approximately 36% of the anthropogenic VOCs in China (Zhang et al., 2009). In the Pearl River Delta (PRD) region of the South China, bottom-up estimates suggest that motor vehicles contribute to 40–57% of VOCs from anthropogenic emission sources (Zhang et al., 2009; Zheng et al., 2009b; Che et al., 2011; Lu et al., 2013). Similarly, field measurements in the PRD region have also demonstrated that vehicle exhaust may constitute 20–53% of anthropogenic VOCs (Guo et al., 2007a; Liu et al., 2008b; Zhang et al., 2012, 2013; Ling et al., 2011) and 24–40% of the ozone formation potentials (OFPs) (Zheng et al., 2009a; Cheng et al., 2010; Zhang et al., 2012).

To combat air pollution from vehicle exhaust, which is surging along with vehicle numbers, China has strengthened its emission standards for vehicles in the past decade. Standards have been upgraded from China I (equals to Euro I) in 2001, to China IV in 2010, and, finally, to China V in 2015. The rapidly changing vehicle fleet composition and emission standards make it difficult to estimate motor vehicle VOC emissions on regional and national scales. The uncertainties of the bottom-up on-road vehicle VOC emission estimates in the PRD region were up to -50% - +70% (Zheng et al., 2009b). Therefore, updated local emission factors (EFs) for automobiles are urgently needed for better emission estimates.

Vehicular EFs can be determined by many methods, including chassis and engine dynamometer testing under controlled conditions (Nine et al., 1999), on-road measurements (Shorter et al., 2005), remote sensing (Bishop and Stedman, 1996), and tunnel studies (Jamriska et al., 2004; Hueglin et al., 2006). Tunnel studies have the advantage of obtaining absolute emission levels by capturing a snapshot of the on-road vehicle fleet, thus representing real-world operations and conditions (Franco et al., 2013). On-road EF measurements of vehicular emissions have been extensively performed throughout China by using portable emissions measurement systems (PEMS) in locations such as Shanghai (Chen et al., 2007), Beijing (Liu et al., 2009; Huo et al., 2011; Wang et al., 2011; Shen et al., 2014; Yao et al., 2015), Macao (Hu et al., 2012; Wang et al., 2014), and Chongqing (Wang et al., 2012). Remote sensing measurements of EFs were previously conducted in Hangzhou in 2004 and 2005 (Guo et al., 2007b). In those studies total rather than speciated non-methane hydrocarbons (NMHCs) or total VOCs (TVOC) were measured, except that very recently Yao et al. (2015) measured EFs for some speciated VOCs from 18 typical diesel vehicles based on on-road measurements in Beijing.

Although the results from tunnel studies reflect emissions under real-world conditions, only a few tunnel studies have been conducted to characterize vehicular VOC emissions on mainland China. Wang et al. (2001b) and Lu et al. (2010) measured vehicular VOC emissions by sampling from the middle of tunnels in Beijing and Shanghai, respectively. Most EFs from tunnel studies in China come from field campaigns conducted in the Zhujiang Tunnel, the tunnel that is also the subject of the current study. EFs have been reported for fine particulate matter ($PM_{2.5}$) and inorganic traces gases (Wang et al., 2001a; Dai et al., 2015; Liu et al., 2014a), total NMHCs (Wang et al., 2001a), and speciated VOCs (Fu et al., 2005). In the PRD region, EFs for vehicular VOCs were determined from Hong Kong tunnel measurements of the Cross-Harbor Tunnel in 1999 (Ho et al., 2004) and the Shing Mun Tunnel in 2003 (Ho et al., 2009). The last tunnel campaign for vehicular VOC emissions in the PRD region was conducted in 2004 (Fu et al., 2005); therefore, VOC composition profiles and EFs from on-road vehicles should be upgraded to reflect the changing vehicle fleet composition and tightened emission standards. Liquefied petroleum gas (LPG)-driven taxis and buses, were not present in Guangzhou until 2004, but have already contributed substantially to ambient VOCs (Tang et al., 2008; Zhang et al., 2012, 2013).

From June 25th to July 1st, 2014, we measured the EFs of a variety of gaseous and particulate pollutants from on-road vehicles in the Zhujiang Tunnel in the urban area of Guangzhou, China. The EFs of $PM_{2.5}$, organic carbon (OC), elemental carbon (EC) and total VOCs were previously reported by Zhang et al. (2015a), and those of dicarbonyls were detailed by Zhang et al. (2016). The present study focuses on source profiles and EFs of speciated VOCs. Here, we provide the latest emission characterization of vehicular VOCs in the PRD region, which could be used to assess the effectiveness of vehicle emission policies.

2. Experimental methods

2.1. Field work

This study was conducted in 2014 from June 25th to July 1st, in the Zhujiang Tunnel, a busy underwater tunnel that crosses the Pearl River in urban Guangzhou. Trace gases were simultaneously detected with on-line instrumentations. One hour VOC samples were collected in pre-evacuated 2-L electro-polished stainless-steel canisters at a constant flow rate of 66.7 mL min^{-1} using a Model 910 Pressurized Canister Sampler (Xonteck, Inc., CA, USA) on two weekdays and two weekends. The VOC samples were collected at time intervals of 02:00-03:00, 07:00-08:00, 08:00-09:00, 09:00-10:00, 10:30-11:30, 14:00-15:00, 17:00-18:00, 18:00-19:00, and 19:00-20:00 on each sampling day. Detailed descriptions of the tunnel, *in situ* field measurements, and sample collection, can be found in our previous studies (Zhang et al., 2015a, 2016) and are also available in the supporting information.

Carbon dioxide (CO_2) was monitored *in situ* by an eddy covariance system (IRGASON, Campbell Scientific, Inc., UT, U.S.), with an integrated open-path CO_2/H_2O gas analyzer and a 3-D Sonic Anemometer. Carbon monoxide (CO) was measured from canister air samples by gas chromatography (Zhang et al., 2012).

2.2. Laboratory analysis

We analyzed VOCs by using a Model 7100 Preconcentrator (Entech Instruments Inc., California, USA) combined with an Agilent 5973N gas chromatography-mass selective detector/flame ionization detector (GC-MSD/FID, Agilent Technologies, USA). The detailed cryogenic concentration steps are described elsewhere (Zhang et al., 2013a). Briefly, VOCs were concentrated inside canisters by three-stage liquid nitrogen cryogenic trapping, then injected to the GC-MSD/FID system for quantification. Details regarding the instrumentation and parameters, analytical conditions, calibration methods, and quality control and quality assurance procedures, can be found elsewhere (Zhang et al., 2012, 2015a,b) and are also available in the supporting information.

2.3. EF calculations for individual VOCs

The average EF of individual VOCs from vehicles passing through the tunnel during a time interval, *T*, was calculated as follows