# Ambient volatile organic compounds and their effect on ozone production in Wuhan, central China

X.P. Lyu [a], N. Chen [b], H. Guo [a,*], W.H. Zhang [c,*], N. Wang [a], Y. Wang [a], M. Liu [a]

[a] *Department of Civil and Environmental Engineering, The Hong Kong Polytechnic University, Hong Kong*
[b] *Hubei Provincial Environment Monitoring Center, Wuhan, China*
[c] *Department of Environmental Sciences, School of Resource and Environmental Sciences, Wuhan University, Wuhan, China*

## HIGHLIGHTS

- First study on VOC sources and their effect on $O_3$ production in central China
- The application of PBM-MCM on RIR calculation
- Vehicular exhausts and coal burning are major contributors to VOCs in Wuhan.
- Ethene and toluene contributed the most to $O_3$ formation.

## GRAPHICAL ABSTRACT
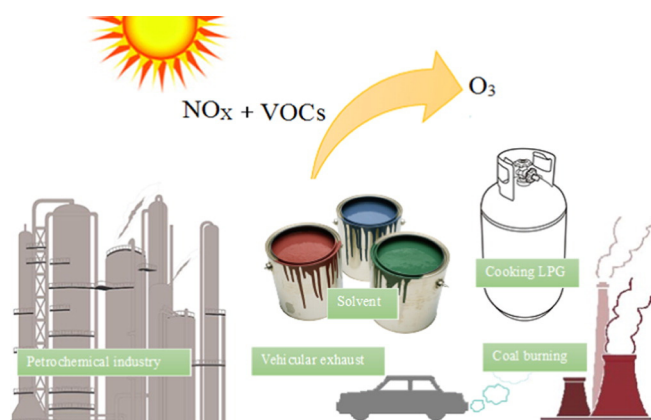
## ABSTRACT

Ambient volatile organic compounds (VOCs) were continuously measured from February 2013 to October 2014 at an urban site in Wuhan. The characteristics and sources of VOCs and their effect on ozone ($O_3$) formation were studied for the first time. The total VOC levels in Wuhan were relatively low, and of all VOCs, ethane (5.2 ± 0.2 ppbv) was the species with the highest levels. Six sources, i.e., vehicular exhausts, coal burning, liquefied petroleum gas (LPG) usage, the petrochemical industry, solvent usage in dry cleaning/degreasing, and solvent usage in coating/paints were identified, and their contributions to the total VOCs were 27.8 ± 0.9%, 21.8 ± 0.8%, 19.8 ± 0.9%, 14.4 ± 0.9%, 8.5 ± 0.5%, and 7.7 ± 0.4%, respectively. Model simulation of a photochemical box model incorporating the Master Chemical Mechanism (PBM-MCM) indicated that the contribution to $O_3$ formation of the above sources was 23.4 ± 1.3%, 22.2 ± 1.2%, 23.1 ± 1.7%, 11.8 ± 0.9%, 5.2 ± 0.4%, and 14.2 ± 1.1%, respectively. LPG and solvent usage in coating/paints were the sources that showed higher contributions to $O_3$ formation, compared to their contributions to VOCs. The relative incremental reactivity (RIR) analysis revealed that the $O_3$ formation in Wuhan was generally VOC-limited, and ethene and toluene were the primary species contributing to $O_3$ production, accounting for 34.3% and 31.5% of the total RIR-weighted concentration, respectively. In addition, the contribution of CO to the $O_3$ formation was remarkable. The $C_4$ alkanes and alkenes from the LPG usage also significantly contributed to the $O_3$ formation. The results can assist local governments in formulating and implementing control strategies for photochemical pollution.

© 2015 Elsevier B.V. All rights reserved.

\* Corresponding authors.
*E-mail addresses:* ceguohai@polyu.edu.hk (H. Guo), 00007335@whu.edu.cn (W.H. Zhang).

## 1. Introduction

Ambient VOCs are important in the formation of $O_3$ and secondary organic aerosols (SOAs) (Guo et al., 2013; Cheng et al., 2010; Camredon et al., 2007; Tsigaridis et al., 2005). As key $O_3$ precursors, VOCs react with nitrogen oxides ($NO_x$) in the presence of sunlight, leading to photochemical pollution with elevated $O_3$ concentration. Due to intense and uncontrolled emissions of VOCs, mega-cities and city clusters in China, such as Beijing (Yao et al., 2015; Wei et al., 2014), the Yangtze River Delta of eastern China (Li et al., 2014; Xue et al., 2014), and the Pearl River Delta (PRD) of southern China (Ling et al., 2011; Cheng et al., 2010) currently suffer from severe photochemical pollution.

Identifying the sources of VOCs is crucial for local government to formulate and implement emission reduction strategies, but the sources depend largely on energy consumption levels and the industrial structures of a city/region, and are often complex. In general, VOCs sources include emissions from gasoline-, diesel-, and liquefied petroleum gas (LPG)-fuelled vehicles, fuel evaporation, emissions from industries such as shoe making, furniture manufacturing and etc., solvents in paints and consumer products, and coal and biomass burning (Guo et al., 2004, 2011; Li et al., 2014; Wang et al., 2013; Cai et al., 2010). The source contributions to ambient VOCs vary between cities and regions. For example, Wang et al. (2013) found that coal burning contributed 26–39% and vehicular exhausts 31–45% to the total VOCs in Beijing in winter, while An et al. (2014) indicated that industrial emissions constituted a considerable proportion (45–63%) of the total VOCs in the Yangtze River Delta, and Cai et al. (2010) reported that industry accounted for 36% of the ambient VOCs in Shanghai. Guo et al. (2011) and Ling et al. (2011) found that solvent usage was the major source of ambient VOCs in the PRD region, whereas vehicular emissions made the most significant contribution in Hong Kong, although it is adjacent to the PRD region (Ou et al., 2015).

VOCs contribute to $O_3$ formation through a series of photochemical reactions, including the hydroxyl radical (OH) initiated oxidation of VOCs, nitrogen cycling driven by peroxyl ($RO_2$) and hydroperoxyl ($HO_2$) oxidation and photolysis, and the combination of oxygen atom (O) with molecular oxygen ($O_2$) (Ling et al., 2014; Cheng et al., 2013). The photochemical reactivity of the VOC species and the intermediates therefore significantly influences $O_3$ production, along with the level of concentration. For instance, alkenes and aromatics are highly reactive in photochemical $O_3$ formation (Ling and Guo, 2014; Ling et al., 2011). The relative incremental reactivity (RIR) method proposed by Carter and Atkinson (1989) is frequently used to evaluate the sensitivity of $O_3$ production to the changes of VOC precursors, through the application of an observation-based model (OBM) using the carbon bond IV mechanism. Ling et al. (2011) recently developed a combined application of the positive matrix factorization (PMF) model and the OBM to study the VOC source contributions to the formation of photochemical $O_3$ in Guangzhou and Hong Kong. Moreover, the maximum incremental reactivity (MIR), $O_3$ formation potential (OFP), and photochemical $O_3$ creation potential (POCP) have also been used to describe the contribution of VOC species to $O_3$ production (Barletta et al., 2002; Jenkin and Hayman, 1999).

Wuhan is the largest megacity in central China and an important transport hub, and has experienced rapid development through growth in real estate and new technology industries such as optoelectronics, biological science, environmental science, etc. Accompanying this urbanization and industrialization is air pollution, characterized by haze and photochemical smog, which has been often observed in recent years. Even so, there are virtually no published studies on ambient VOCs in Wuhan. Obtaining first-hand information on VOC characteristics and sources and their association with photochemical smog formation is therefore an urgent task. To our best knowledge, this is the first study on VOC sources and their effects on the $O_3$ formation in this region.

In this study, the characteristics of ambient VOCs and their effects on $O_3$ production in Wuhan were investigated. The abundance and temporal patterns of VOCs were discussed, and the source contributions to ambient VOCs were quantified. The dominant factors affecting the photochemical $O_3$ formation were determined using a photochemical box model incorporating the Master Chemical Mechanism (PBM-MCM), and the contributions of VOC sources to the $O_3$ formation were also quantified. The $O_3$-precursor relationships were also evaluated using RIR and RIR-weighted concentration. The outcomes will be of help to air scientists and local governments, for further study and to take measures to reduce VOC and $O_3$.

## 2. Methodology

### 2.1. Site description and chemical analysis

From February 2013 to October 2014, 99 VOCs consisting of 56 non-methane hydrocarbons, 28 halocarbons, and 15 oxygenated VOCs (OVOCs), the five trace gases $SO_2$, $NO_2$, NO, CO, and $O_3$, and two meteorological parameters (temperature and humidity) were simultaneously monitored at an urban site (30.54 N, 114.37 E, <50 m a.s.l.) in Wuhan. The site was set up on the rooftop of a six-story building (~18 m height) within the Hubei Provincial Environmental Monitoring Center, as shown in Fig. 1.

Ambient air was continuously drawn through a PFA Teflon tube with an inside diameter of 7.6 cm. The sampling tube inlet was 1.5 m above the rooftop, and the outlet was connected to a PFA-made manifold with a by-pass pump drawing air at a rate of 15 L/min. A chromatography-flame ionization detector-mass spectrometry (GC–FID–MS) system (TH_PKU-300), developed by Tianhong instrument Inc. in Wuhan and Peking University, was used to carry out real-time measurements of VOCs. The air samples were pre-concentrated by passing them through a cold trap maintaining −80 °C for the removal of water and carbon dioxide, and then trapped at −150 °C with an empty capillary column. After pre-concentration, the VOCs were desorbed by rapid heating up to 100 °C and introduced into the GC–FID–MS system (Agilent GC7820/5975MS) for chemical analysis. The detection limit range was 0.005–0.050, 0.002–0.021, 0.002–0.023, and 0.011–0.070 ppbv for $C_2$–$C_5$ hydrocarbons, $C_6$–$C_9$ hydrocarbons, halocarbons, and OVOCs with $R^2 \geq 0.996$, ≥0.993, ≥0.998, and ≥0.985, respectively (more details can be found in the supplementary material — Table S1).

Commercial instruments developed by Thermo Environmental Instruments (TEI) Inc. were used to measure the trace gases. $SO_2$, $NO_x$ ($NO_x = NO + NO_2$), CO, and $O_3$ were detected with a pulsed UV fluorescence $SO_2$ analyzer (Model 43, TEI), a chemiluminescence trace level NO–$NO_2$–$NO_x$ analyzer (Model 42iTL, TEI), an enhanced trace level CO analyzer (Model 48iTL, TEI), and an UV photometric $O_3$ analyzer (Model 49i, TEI), respectively. Details of the instruments including the operating principles, measuring ranges, and detection limits were provided by Geng et al. (2009) and Chang and Lee (2007).

### 2.2. Quality assurance and control (QA/QC)

To guarantee the data quality acquired from the TH_PKU-300 system, the calibration of sampling flow rate, mass spectrometer tuning, blank experiment, and instrument calibration were conducted regularly. The sampling flow rate was calibrated every six months with an electronic soap film flow meter (Sensidyne, Gilibrator-2) to ensure the sampling flow precision was in the range of ± 1.5%. The mass spectrometry was tuned before the MS analysis, to make sure that the half peak width ($PW_{50}$) was between 0.45–0.55 on the contour map, and the peak shape was symmetric with no bifurcation. The concentrations of VOC species in the blank experiments were all below 5% of the average concentrations of VOCs in ambient air. The GC–FID–MS system was calibrated every two weeks with six concentration levels of standard samples in the range of 0.3–25 ppbv, and the standard sample with