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Chemical loss of volatile organic compounds and its impact on the source analysis through a two-year continuous measurement

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HIGHLIGHTS

• 35% initial VOCs had been consumed during the transport from sources to the receptor.

- Reactivity of VOCs was underestimated over 60% if the removal of VOCs was ignored.
- C3-C5 alkenes and C8 aromatics contributed over 60% of the chemical loss of VOCs.
- Seven sources of VOCs were identified and quantified in Shanghai urban.

• The regional transportation contributed $\sim 20\%$ of VOCs in Shanghai urban from PMF.

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ABSTRACT

Chemical loss of volatile organic compounds (VOCs) is more important than the observed VOCs, which is the real actor of the chemical process in the atmosphere. The chemical loss of VOCs might impact on the identification of VOCs sources in ambient. For this reason, VOCs with 56 species were continuously measured in the urban area of Shanghai from 2009 to 2010, and based on the measurement the chemical loss of VOCs was calculated. According to the result, the initial VOCs in Shanghai urban was (34.8 ± 20.7) ppbv, higher than the observed one by ~35%, including alkanes (~38%), aromatics (~36%), alkenes (~17%), and acetylene (~8%). The chemical reactivity of VOCs would be underestimated by ~60% if the chemical loss were ignored. The chemical loss of VOCs showed a good agreement with Ox $(O_3 + NO_2)$. C7–C8 aromatics and C3–C5 alkenes contributed ~60% of consumed VOCs. Seven sources were identified and quantified from positive matrix factorization (PMF) analysis. Vehicular emissions were the largest anthropogenic source of VOCs in Shanghai urban, accounting for 27.6% of VOCs, followed by solvent usage (19.4%), chemical industry (13.2%), petrochemical industry (9.1%), and coal burning (~5%). The contribution of biogenic emissions to total VOCs was 5.8%. Besides the five local anthropogenic sources and one biogenic source, the regional transportation was identified as one important source, contributing about 20% of VOCs in Shanghai urban. Sources apportionment results from PMF analysis based on the initial VOCs showed some differences from those based on observed data and might be more appropriate to be applied into the formulation of air pollution control measures.

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1. Introduction

Shanghai has been experiencing a rapid economic growth in the past decades. The increase of the energy consumption due to the rapid economic growth resulted in a dramatic increase of the pollutants emissions (Huang et al., 2011) and the deterioration of the air quality in Shanghai, in term of ozone and fine particles (Gao

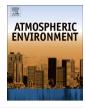
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et al., 2009; Geng et al., 2009; Tie and Cao, 2009). Volatile organic compounds (VOCs) are important precursors of the photochemical process and have been paid a large amount attention to as their great contribution to the formation of troposphere ozone and secondary organic aerosols (SOA) (IPCC, 2007; Seinfeld and Pandis, 2006).

So far, many studies have been conducted to investigate the characterization of VOCs and the key VOCs components of ozone formation in Shanghai. However, identifying the important contributors to ozone formation potential (OFP) based solely on the observed data was problematic (Shao et al., 2011). The chemical loss







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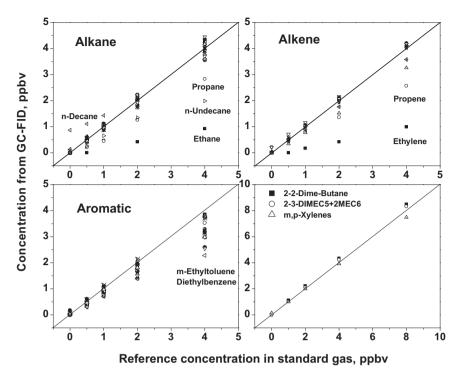


Fig. 1. Comparison of the manual calibration results and the reference concentrations in standard gas.

of the reactive VOC species during the transportation from emission sources to the receptor site played important role in the formation of ozone. As studied by Xie et al. (2008), the chemical loss of the reactive VOC species contributed more than one third of the OFP in Beijing urban. Actually, the consumed VOCs might be the real contributors to the ozone formation, which could not be taken into account by the observed data. The oxidants formation agreed better with the consumption of VOCs than with the observed VOCs in Beijing during the 2008 Olympic period (Shao et al., 2011). Furthermore, the source apportionment of VOCs would have large uncertainty for the reactive VOC species if the chemical loss was ignored (Wittig and Allen, 2008). The source apportionment of VOCs by Chemical Mass Balance model (CMB) considering the chemical loss differed a lot from that based on the observed data (Na and Kim, 2007; Shao et al., 2011). As reported by Na and Kim (2007), the contribution from vehicle exhaust was underestimated by 10% when the chemical loss effect was incorporated in the CMB calculation while the contribution from solvent usage and gasoline evaporation were overestimated. Generally, the contribution of sources with more reactive species would be underestimated based on the observed VOCs.

There were usually two kinds of methods using to estimate the consumption of VOCs in ambient. One was through estimating the photochemical age of air mass by the VOC species pairs from the same emission sources but having different reactivities with OH (McKeen et al., 1996). The other was based on the oxidation products measurement to estimate the consumption of their parent VOC species (Bertman et al., 1995; Wiedinmeyer et al., 2001). The chemical loss of VOCs has been estimated previously in different regions (Shao et al., 2011; Shiu et al., 2007; Xie et al., 2008) but not in Shanghai.

In this study, the continuous measurement of C2–C12 VOC species were carried out for two years to investigate the characterization of VOCs in urban Shanghai, China. Based on the observed data, the chemical loss of VOCs was estimated. The high response temporal variation of VOCs through over the two years was

discussed in detail combining with the oxidants variations in Sections 3.2 and 3.3. Studies of VOCs in other cities were employed to compare with that in this study, and some special result in Shanghai was obtained in Section 3.4. According to the estimation result of the chemical loss, the sources contributions were quantified by receptor model, positive matrix factorization (PMF) (Paatero, 1997), in Section 3.5. Finally, in Section 4, the conclusions of the present study were summarized and the implications were discussed.

2. Experiment

2.1. Monitoring sites

The monitoring site locates in the southwest of the urban area in Shanghai, China. It is about 8 km away from the city center. The sample inlet is on the roof of a 5-floor building at Shanghai Academy of Environmental Science (31.17°N, 121.43°E), about 15 m above the ground. There are no other large VOCs sources except the vehicular and domestic emissions in the urban area. In the south and southwest around 50 km away from the monitoring site, there are some petrochemical and chemical industrial factories in the rural area (Cai et al., 2010; Huang et al., 2011), which may have effects on the VOCs measured results at the monitoring site in the special meteorological conditions.

2.2. Measurement of VOCs

Individual VOC species were continuously measured every 30 min from January 2009 to December 2010 by two on-line high performance gas chromatograph with flame ionization detector (GC-FID) systems (Chromato-sud airmoVOC C2–C6 #5250308 and airmoVOC C6–C12 #2260308, France). For C2–C6 VOCs, the sample is preconcentrated through a trap, a fine tube containing porous substances. Three trap phases, including Carbotrap C, Carbopack B and Carboxen, are chosen so as to trap from the selected

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