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Reactivity-based industrial volatile organic compounds emission inventory and its implications for ozone control strategies in China

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HIGHLIGHTS

- Industrial speciated VOCs emission inventory in China for 2010 was developed.
- Reactivity-based (OFP-based) VOCs emission inventory was established.
- OFP-based and mass-based characteristics by species and sources were different.
- OFP-based top 15 species, top 10 sources and high-polluted regions were identified.
- Three implications about reactivity-based strategies were proposed for more efficient O_3 mitigation.

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ABSTRACT

Increasingly serious ozone (O_3) pollution, along with decreasing NOx emission, is creating a big challenge in the control of volatile organic compounds (VOCs) in China. More efficient and effective measures are assuredly needed for controlling VOCs. In this study, a reactivity-based industrial VOCs emission inventory was established in China based on the concept of ozone formation potential (OFP). Key VOCs species, major VOCs sources, and dominant regions with high reactivity were identified. Our results show that the top 15 OFP-based species, including *m*/*p*-xylene, toluene, propene, *o*-xylene, and ethyl benzene, contribute 69% of the total OFP but only 30% of the total emission. The architectural decoration industry, oil refinery industry, storage and transport, and seven other sources constituted the top 10 OFP sub-sectors, together contributing a total of 85%. The provincial and spatial characteristics of OFP are generally consistent with those of mass-based inventory. The implications for O_3 control strategies in China are discussed. We propose a reactivity-based national definition of VOCs and low-reactive substitution strategies, combined with evaluations of health risks. Priority should be given to the top 15 or more species with high reactivity through their major emission sources. Reactivity-based policies should be flexibly applied for O_3 mitigation based on the sensitivity of O_3 formation conditions.

1. Introduction

Due to the rapid urbanization and industrialization, high levels of ground-level ozone (O_3) and secondary organic aerosols (SOAs) have become more and more frequent in China in recent decades (Shao et al., 2009; Guo et al., 2014; Xue et al., 2014). Great efforts have been made to reduce severe pollution, resulting in annual averaged concentrations reductions of 24%, 10%, 38% and 32% in $PM_{2.5}$, PM_{10}, SO_2, and NO_2 in 2015 in China as compared to the levels in 2013 after the implement of the National Air Pollution Prevention and Control Action Plan in 2013 (MEP, 2013; MEP, 2016; CEMS, 2014; CEMS, 2015). However, the 8-h ozone maximum remains almost unchanged, i.e.,139 $\mu g/m^3$ in 2013 and 134 $\mu g/m^3$ in 2015, with an unexpected increase to 145 $\mu g/m^3$ in 2014 (CEMS, 2014; CEMS, 2015; CEMS, 2016).

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Volatile organic compounds (VOCs) are considered as the crucial precursors of atmospheric ozone and SOAs in the presence of NOx and solar radiation, particularly in VOCs-sensitive areas (Atkinson, 2000; Shao et al., 2009; Yuan et al., 2013). Studies have shown that O_3 chemistry is generally VOC-limited in major developed and O_3 nonattainment areas throughout the year, such as the Beijing-Tianjin area, Yangtze River Delta (YRD), and Pearl River Delta (PRD) (Liu et al., 2010; Tang et al., 2012; Ding et al., 2013; Zhang et al., 2008) Therefore, effective control of VOCs is important for alleviating O_3 pollution in China. In some developed countries, VOCs control has migrated from controlling total VOCs emissions to controlling specific VOCs species based on their reactivity to ozone formation, in an effort to implement efficient and cost-effective strategies for air quality control and regulation. The US EPA has issued guidelines for considering VOCs reactivity in the development of state implementation plans (SIPs) (US EPA, 2005). Shortly thereafter, Texas implemented reactivity-based rules to control highly reactive VOCs in the Houston/Galveston/Brazoria ozone nonattainment area (Stoeckenius and Russell, 2005). Arguably the most innovative and forceful example of the reactivity-based regulatory scheme is the Air Resources Board (ARB) Aerosol Coatings Regulation, which was approved as a pilot project by the US EPA in 2005 (CARB, 2000; US EPA, 2005). In Europe, reactivity-based strategies for stationary sources have also been investigated after great progress was achieved in transportation control, and the results show that these strategies offer significant ozone reduction compared with simple mass-based strategies. (Derwent et al., 2007).

Detailed speciated VOCs emission inventory and highly explicit chemical mechanisms are the two essential elements in the assessment of reactivity-based VOCs control strategies (Derwent et al., 2007). Speciated VOCs emission inventory have been proposed on global (Streets et al., 2003), national (Wei et al., 2008; Mo et al., 2016), and regional scales, such as for the PRD and YRD (Zheng et al., 2009; Ou et al., 2015; Huang et al., 2011; Fu et al., 2013.) However, due to the lack of local source profiles, most of these speciated inventories in China were developed by applying Western or other regional source profiles, except for the inventories by Ou et al. (2015) and Mo et al. (2016), who used updated local species databases in their studies. The 2008 national speciated VOCs inventory by Mo et al. (2016) contained only 75 species, which may not be representative of the emission behavior of various emission sources. For example, 1,2,3,5-teramethyl benzene, which is one of the top 10 most reactive species in the PRD (Ou et al., 2015), was not included in the inventory. Moreover, previous national speciated VOCs inventories are developed based on the early years (e.g. 2005 and 2008) and contain limited industrial sources. Therefore, it is necessary to update the national speciated VOCs inventory by including more typical VOCs species and industrial sources. A comparison of the improved speciated VOCs inventory in this study and other national speciated inventories is shown in Table 1.

The reactivity and subsequent ozone production potentials (OPPs) can be quantified by several metrics, such as maximum incremental reactivity (MIR) and maximum ozone incremental reactivity (MOIR) (Carter, 1994), as well as by photochemical ozone creation potential (POCP) (Derwent et al., 1996, 1998) and tagged ozone production potential (TOPP) (Butler et al., 2011). A comparison of these four scales is given in Table 2. They are all calculated under different NOx conditions and then used to estimate the corresponding OPPs in different atmospheric regimes. Of these metrics, MIR, which represents conditions where ozone is highly sensitive to VOCs emissions, has been widely used to describe the relative reactivity effects of VOCs on ozone formation potential (OFP) (Huang et al., 2011; Mo et al., 2015; Ou et al., 2015; Wu et al., 2016; An et al., 2017). In this study, we used the MIR scale to develop a reactivity-based industrial inventory in China for 2010.

In this paper, we first developed a speciated industrial VOCs emission inventory in China using the latest emission inventory and applicable species databases. Then, the updated MIR values were applied to estimate the OFP (ozone formation potential) for an OFP-based or reactivity-based emission inventory. From the reactivity-based emission inventory, we identified the key VOCs species, major VOCs sources and dominant regions with high reactivity, and estimated the corresponding disparities in mass-based emission inventory. Finally, we discussed and provided the recommendations for ozone control strategies based on current air quality and VOCs control in China.

2. Methodology

2.1. Emission inventory and source profiles

In this study, we used the industrial VOCs emission inventory of 2010 presented by us recently (Qiu et al., 2014). In compiling the VOCs emission inventory, industrial sectors were classified based on a source-tracing method, tracing the material flow of VOCs in each industrial process. Comprehensive source coverage of 98 contributing industrial sources was also considered, representing almost all industrial emission sources. Furthermore, the emission inventory adopted the latest available local emission factors, including only a few foreign emission factors for sources where data on Chinese factors were unavailable.

In this study, 188 VOCs species, divided into the six categories, i.e., alkanes, alkenes/alkynes, aromatic hydrocarbons, halocarbons, oxygenated organics and others, were estimated to develop the speciated VOCs emission inventory. "Others" included undefined species contributing less than 1.0% to the specific source or species without MIR values. Priority was given to the latest local VOCs chemical profiles, including source profiles of production of VOCs (Mo et al., 2015), storage and transport (Liu et al., 2008), industrial processes using VOCs as raw materials (Zheng et al., 2013; He et al., 2015; Shi et al., 2015; Mo et al., 2015), and processes using VOC-containing products (Liu et al., 2008; Wang et al., 2009a,b; Yuan et al., 2010; He et al., 2012; Zheng et al., 2013; Xu et al., 2014; He et al., 2015; Shi et al., 2015). Information from the US EPA

Table 1
Comparison of national speciated VOCs inventories.

Reference	Year	Source object (industrial subsector)	Total VOCs Emission (Tg)	Basic emission inventory	No. Of species included
This study	2010	Industry (98)	13.4	Qiu et al. (2014)	188 individual species
Mo et al. (2016)	2008	Anthropogenic source (83)	26.0	Bo (2012)	75 individual species
Wei et al. (2008)	2005	Anthropogenic source (37)	20.1	Wei et al. (2008)	40 individual or grouped species