Speciated NMVOCs Emission Inventories from Industrial Sources in China and Spatial Patterns of Ozone Formation Potential in 2016

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Abstract. This paper compiled a new speciated NMVOCs emission inventory for the industrial sources at the county-level by using a bottom-up approach in 2016, as well as estimated the ozone formation potential (OFP) and investigated its spatial characteristics in China. Results indicated that the total NMVOCs emissions from industrial sources estimated as 21.04 Tg in 2016. The five major source categories including “production of VOCs”, “storage and transportation”, “industrial processes using VOCs as raw material”, “processes using VOCs-containing products”, and “industrial fossil fuel combustion processes” generated 1.92 Tg, 0.94 Tg, 6.54 Tg, 10.04 Tg, and 1.60 Tg VOCs, respectively, in 2016. According to our estimates, aromatics were the largest contributor of industrial NMVOCs emissions in 2016, accounting for 36% of total NMVOCs, followed by Alkanes (29%), OVOCs (22%), Alkenes (7%), Halocarbons (4%), and Alkynes (2%). Styrene, m/p-xylene, ethylbenzene, toluene, and ethyl acetate were the top five VOC species from industrial sources in terms of abundance in 2016. Aromatics have a high potential for ozone formation, and accounted for 70% of total OFP, followed by Alkenes (14%), Alkanes (10%), and OVOCs (6%). Styrene, p-xylene, toluene, ethylbenzene, 1,3-butadiene were the five species that had the largest potential to form ozone, and plastic industry, coke industry, household appliances industry, and architectural decoration were the key contributing sectors. The emissions displayed distinct spatial characteristics, with significantly higher emissions and OFPs in coastal regions than in other inland areas of China.

Keyword: Industrial NMVOCs; Emission Inventory; Species and OFP; Spatial variation

1. Introduction

Over the past two decades, with the rapid development of China’s economy, quick urbanization, and industrialization, air pollution in China has gradually become serious. The air pollution is not only affecting climate change, visibility, and sustainable development of China’s economy but also poses a great threat to human health [1]. Therefore, in recent years, the Chinese government has issued several policies to mitigate the air pollution in China, such as “Action Plan for the Prevention and Control of Air Pollution”, “13th Five-Year Plan”, and “Blue Sky Defense” [2]. As a result, anthropogenic NOx emissions in China have decreased by 21% during 2013-2017 [3]. The concentration of fine atmospheric particles also showed a decreasing trend in this period, spatially in key regions such as Beijing-Tianjin-Hebei, Pearl River Delta, and Yangtze River Delta. Unfortunately, the Volatile Organic Compounds
(VOCs) concentration in China continued to increase due to a lack of efficient control measurements [4]. Meanwhile, ozone (O₃) pollution has become the primary pollution in most cities, and the proportion of secondary organic particulates in fine particulates continues to increase. Tropospheric O₃ and Secondary Organic Aerosols (SOA) are the secondary pollutants generated by oxidation of VOC precursors in the atmosphere [5]. Therefore, reducing ambient VOC emissions is critical and can be helpful to alleviate photochemical smog as well as to improve human health in cities and regions in China.

Non-methane Volatile Organic compounds (NMVOCs) mainly originated from primary sources, including natural (biogenic), biomass burning, and anthropogenic sources. Studies conducted in China have found that industrial sources were the top-ranking emitter, followed by transportation [6]. The total emissions of NMVOCs emitted by vehicles have been declining since peaking in around 2007 due to the stringent control measures, while industrial emissions have been increasing continually in China [4]. However, few scientists concentrated on the industrial NMVOCs emissions, and have been able to estimate the NMVOCs emission for the past decades with the provincial resolutions [7]. Therefore, it is essential to compile the industrial NMVOCs emission inventory at a high-resolution by local-based EFs as well as including the broad range of activities data.

Ozone is formed through complex chemical reactions that involve oxides of nitrogen (NOₓ), VOCs, and sunlight [5]. Different species of VOCs have different reactivity and reaction mechanisms; consequently, the O₃ formation potentials of each species greatly differ from each other. From this point, an effective controlling measure not only needs to consider the emission amounts of VOCs but also their chemical reactivities. Source profiles and emission inventories are the most important source data for analyzing air pollution conditions and making effective controlling strategies. Thus, some researchers tried to characterize the emissions and distribution of speciated VOCs in China, but most of them used foreign profiles such as EPA SPECIATE (https://www.epa.gov/air-emissions-modeling/speciate-version-45-through-32) database and neglected the oxygenated VOCs (OVOCs), which has considerable emissions and significantly contribute to the oxidant capacity of the atmosphere.

In order to address the above research questions, this paper compiles county-level emission inventory of China’s industrial speciated NMVOCs emissions in 2407 counties in mainland China for the year 2016; on the basis of this inventory, the ozone formation potentials were estimated for different species, different sources, and different regions.

2. Methodology and Data Sources

2.1. Source classification and emission estimation

In this study, industrial activities have been grouped into five main sectors based on source-tracing method and traditional source classification, including the production of NMVOCs (P-VOCs), storage and transportation (ST), industrial processes using NMVOCs as raw materials (VOCs-RM), processes using NMVOCs-containing products (VOCs-CP), and fossil fuel combustion (FFC), and include 108 particular industrial subsectors. Industrial NMVOCs emission at county-level was estimated using the bottom-up method based on activity data and emission factors (EFs) data. The following Eq1 implemented this method.

\[ E_t = \sum_{c}^{N} \left[ \sum A_{m,r} \times EF_{m,r} \times (1 - \theta_r) \right] \]

where the subscripts \( c, m \) and \( r \) respectively stand for a county (stand for province where county-level activity data absent), emission sources, and removal technological condition; \( E_t \) is the total NMVOCs emissions (Tg) in a particular year; \( \theta_r \) is the removal efficiency under the technological condition of \( r \); \( A_{m,r} \) and \( EF_{m,r} \) are the activity data and EF, referring to activity level for \( m^{th} \) source under the removal efficiency of \( r \).

The source-specific county-level activity data for more than 2000 county-level administrative regions required by this industrial emission inventory were collected from more than 300 city-level statistical
yearbooks, annual reports from relevant industry associations, and environmental survey statistics and bulletins. The detailed information about compiling activity data can be refer to Simayi et al. [8]. Moreover, the activity level of the refining industry was collected at the factory-based database from 216 existing refineries in China. Hong Kong, Macau, and Taiwan were not considered in this study due to a lack of activity data. The NMVOCs emission factors for industrial activities were mainly obtained from locally measured emission factors in this study, recently published scientific articles, various national limits of pollutant emissions, Compilation guide for the China's air pollutant emission inventory, EPA AP42 Compilation of Air Emissions Factors (https://www.epa.gov/air-emissions-factors-and-quantification/ap-42-compilation-air-emissions-factors).

2.2. Calculation of speciated NMVOCs emissions and OFP
The profiles of NMVOCs used for speciation were mainly selected from our local measurements and domestic research, and some source profiles obtained from Wu and Xie [5]. The speciated NMVOCs emissions were calculated by multiplying the total emission for specific sources by the corresponding weight percentages, as formulated in Eq 2.

\[ E_t = \sum_i E_i \times f_{i,j} \]  

(2)  

where \( E_i \) and \( E_t \) are the total emissions of species \( j \) from all the sources and emission sources \( i \), respectively; and \( f_{i,j} \) is the weighted percentage of species \( j \) from sources \( i \).

Contribution to ozone formation of different VOC species significantly differs due to differences in maximum incremental reactivity (MIR). MIR was usually applied to evaluate the influence of VOCs on \( O_3 \) formation and calculate ozone formation potentials (OFPs) in ambient air [5,9] based on Eq 3. OFP has been used to evaluate the contribution of certain species in ambient air to ozone production based on both emissions and reactivity [10].

\[ OFP_{i,j} = E_{i,j} \times MIR_j \]  

(2)  

where \( OFP_c \) is the OFP of species \( j \) from source \( i \), \( E_{i,j} \) is the emission of species \( j \) from source \( i \), and \( MIR_j \) is the maximum incremental reactivity of species \( j \).

3. Results and discussions

3.1. Industrial emission inventory of NMVOCs
The total NMVOCs emission from industrial sources in China was estimated at 21.04 Tg in 2016. The category of using VOCs containing products (10.04 Tg) and using NMVOCs as raw materials (6.54 Tg) were the two largest NMVOCs sources with the contribution of 47.7% and 31.1% to the total emissions. The production of NMVOCs (1.92 Tg), storage and transportation (0.94 Tg), and industrial fossil fuel combustion (1.60 Tg) contributed 9.1%, 4.5%, and 7.6% to the total emissions, respectively. In terms of individual sources, plastic manufacturing, synthetic leather manufacturing, row medicine manufacturing, coke production, and architectural decoration were the top five high NMVOCs emission sources related to industrial processes in China, accounting for 37.5% of total emissions.

Due to unbalanced economic developments in China, the industries were also distributed unevenly. Thus, the provinces in east China such as Shandong, Zhejiang, Jiangsu, and Shanghai had higher emissions than other parts of China, accounting for 39.4% of total emissions. Central/South China and North China also generated considerable NMVOCs emissions, contributing 26.5% and 13.5%, respectively, of the total emissions. Shandong, Guangdong, Jiangsu, Zhejiang, and Henan were the top five provinces with high NMVOCs emissions from industrial sources, which contributed 45.3% of the total industrial NMVOCs emissions. The top five county-level administrative regions with the largest emissions were Guangzhou urban area, Shanghai Pudong New Area, Hangzhou urban area, Shenzhen urban area, Zhenhai District of Ningbo city among the 2407 counties, and emitted 1096 Gg NMVOCs from industrial processes.
Figure 1. Spatial distribution of county-level industrial NMVOCs emissions.

Figure 2. Speciated NMVOCs emissions and their corresponding OFP.

Figure 3. Top 10 species in terms of emissions (left) and OFP (right) from different emission sources.
3.2. Speciated NMVOCs emissions and OFP

The calculation of speciated NMVOCs showed that aromatics (7.57 Tg) made the largest contribution and accounted 36% of the total industrial NMVOCs emissions in 2016, followed by alkanes (6.10 Tg, 29%), OVOCs (4.62 Tg, 22%), alkenes (0.84 Tg, 4%), halocarbons (0.42 Tg, 2%), and others (1.47 Tg, 7%), as shown in Fig. 2. The styrene, m/p-xylene, Ethylbenzene, toluene, and ethyl acetate were the most abundant species in nationwide, accounting for 35.1% of the total emissions, the top 10 emission contributing species were showed in Fig. 3, and they accounted 56.8% of total emissions. Aromatic species took up five places in the 10 top anthropogenic VOC species.

China's industrial NMVOCs emission in 2016 had the potential to form 59.7 Tg O₃. The aromatics were not the component only with high emissions, but also have the largest ozone formation potentials. The OFPs of the aromatics were 40 Tg-O₃, with a contribution of 70% to the total OFP. The alkenes contributed 14% of OFPs, with only 4% of emissions. Alkanes and OVOCs only contributed 10% and 6% for OFPs, respectively, while they accounted for 29% and 22% of emissions. In terms of individual species, styrene was the species with the largest OFP, contributing 25.3% (14.45 Gg) of total OFPs. m/p-xylene, toluene, and Ethylbenzene were the other species that made a large contribution to ozone formation. The top 10 species accounted for 75.5% of the total OFP. The plastic manufacturing, furniture and household appliances manufacturing, architectural decoration, coking industry, and six other sources constituted the top 10 OFP subsectors, and they together contributed 76.8% to the total OFP, while accounting 61% of emissions. As shown in Fig. 4, the provincial and spatial characteristics of OFP are generally consistent with those of total industrial NMVOCs emissions. Guangdong, Shandong, Jiangsu, Zhejiang, and Henan provinces have the largest ozone formation potentials and accounted for 48% of national industrial OFPs. The contribution of different sources to OFP varies from region to region. For example, VOCs-CP was the largest contributor in provinces such as Guangdong, Hebei, Hebei, while VOCs-RM was the largest contributor in Shandong, Henan, Zhejiang.

![Figure 4. Source contribution and spatial distribution of OFP in China in 2016](image-url)
4. Conclusions
Chinese industrial NMVOCs emission inventories at a county-level resolution were established for the year 2016. The results showed that NMVOCs emissions from industrial sources in coastal areas are significantly higher than those in inland areas in China. Besides, based on the latest local source profiles, the speciated NMVOCs emission inventory was developed, including OVOCs. Aromatics made the highest contribution (36%) of total industrial emissions, followed by the alkanes (29%), OVOCs (22%), and alkenes (4%). Aromatics not only had the highest emissions but also have the highest OFPs; 7.6 Tg aromatics had the potential to form 40 Tg-O₃, accounting 70% of total OFP. Provincial and spatial characteristics of OFP are generally consistent with those of total industrial NMVOCs emissions.

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