Improved provincial emission inventory and speciation profiles of anthropogenic non-methane volatile organic compounds: a case study for Jiangsu, China

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ABSTRACT

Non-methane volatile organic compounds (NMVOC) are the key precursors of ozone (O_3) and secondary organic aerosol (SOA) formation. Accurate estimation in their emissions plays a crucial role in air quality simulation and policy making. We developed a high-resolution anthropogenic NMVOCs emission inventory for Jiangsu in eastern China from 2005 to 2014, based on detailed information of individual local sources and the field measurements on source profiles of chemical industry. Totally 56 NMVOCs samples were collected in 9 chemical plants, and then analyzed with a gas chromatography-mass spectrometry system (GC-MS). Source profiles of stack emissions from synthetic rubber, acetate fiber, polyether, vinyl acetate, and ethylene production, and those of fugitive emissions from ethylene, butanol and octanol, propylene epoxide, polyethylene and glycol production were obtained. Various manufacturing technologies and raw materials lead to discrepancies in source profiles between our domestic field tests and foreign results for synthetic rubber and ethylene production. The provincial NMVOC emissions were calculated to increase from 1774 Gg in 2005 to 2507 Gg in 2014, and relatively large emission densities were found in cities along the Yangtze River with developed economy and industry. The estimates were larger than those from most other available inventories, due mainly to the complete inclusion of emission sources and to the elevated activity levels from plant-by-plant investigation in this work. Industrial processes and solvent use were the largest contributing sectors, and their emissions were estimated to increase respectively from 461 to 958 and from 38 to 966 Gg. Alkanes, aromatics and oxygenated VOCs (OVOCs) were the most important species, accounting for 25.9%-29.9%, 20.8%-23.2% and 18.2%-21.0% to annual total emissions respectively. Quantified with a Monte-Carlo simulation, the uncertainties of annual NMVOCs emissions vary slightly from years, and the result for 2014 was -41%~+93%, expressed as 95% confidence intervals (CI). Reduced uncertainty was achieved compared to previous national and regional inventories, attributed mainly to the detailed classification of emission sources and to the use of information at plant level.
in this work. Discrepancies in emission estimation were explored for chemical and refinery sector with various data sources and methods. Compared with Multi-resolution Emission Inventory for China (MEIC), the spatial distribution of emissions in this work were more influenced by the locations of large point sources, and smaller emissions were found in urban region for developed cities in southern Jiangsu. Besides, clear discrepancies were found between this work and MEIC in the speciation of NMVOC emissions under the atmospheric chemistry mechanisms CB05 and SAPRC99. The difference of species OLE1 resulted mainly from the updated source profile of building paint use, and the differences of other species from the varied sector contributions to emissions of the two inventories. CMAQ simulation was applied to evaluate the two inventories, and better performance (indicated by daily 1h-max O₃ concentrations in Nanjing city) was found for January, April and October 2012 when the provincial inventory was used.

1 Introduction

With strong OH and HO₂ radical chemistry reactions, non-methane volatile organic compounds (NMVOCs) are reported to play crucial roles in formation of secondary organic aerosols (SOA) and serious photochemical pollution in China, particularly in developed cities and regions. For example, Huang et al. (2014) revealed that the contribution of SOA from NMVOC conversion reached 44%-71% to ambient organic aerosols during heavy haze period in winter, based on detailed chemistry composition and source analysis of airborne particles in four important cities (Beijing, Shanghai, Guangzhou and Xi’an) across the country. Due to intensive emissions of species with strong atmospheric oxidation capability (indicated as maximum incremental reactivity, MIR), the ozone (O₃) formation were recognized as VOC-limited in developed areas including Jing-Jin-Ji (JJJ), Yangtze River Delta (YRD) and Pearl River Delta (PRD) regions (Geng et al., 2008; Shao et al., 2009; Zhang et al., 2008; Xing et al., 2011).
Given the impacts of NMVOCs on air quality, increasing attentions have been paid to their sources and emission characteristics. Although natural sources dominate the emissions at global scale (Guenther et al., 1995; Muller, 1992; GEIA, http://eccad.sedoo.fr/eccad_extract_interface), the contribution from anthropogenic sources is elevated at smaller spatial scales, attributed to intensive human activities. In mainland China, the emissions of natural and anthropogenic origin were estimated close to each other at 10-30 Tg (Tie et al., 2006; Klimont et al., 2002; Streets et al., 2003). Table S1 in the supplement briefly summarizes the estimations of China’s national NMVOC emissions of anthropogenic origin from various studies. With different methods and data sources applied, the NMVOC emissions in China were estimated to be doubled from 1990 to 2010, and the contributions of solvent use, non-combustion industrial processes and transportation were enhanced for recent years. Incorporating available information at national scale, Tsinghua University developed the Multi-resolution Emission Inventory for China (MEIC, http://www.meicmodel.org/) and calculated the national total emissions at 23.6 Tg for 2010. Among all the studies, largest estimations were made in Regional Emission inventory in Asia (REAS, Ohara et al., 2007; Kurokawa et al., 2013), reaching 28.0 Tg for 2008.

At local scale, emissions from anthropogenic sources could be much higher than natural sources. For example, the anthropogenic NMVOC emissions were estimated 6-18 times of natural emissions in Beijing (Klinger et al., 2002; Wang et al., 2003; Klimont et al., 2002; Q. Zhang et al., 2009). With information on individual plants collected, emission inventories for regions with relatively heavy air pollution in China including JJJ, YRD and PRD have been developed, and differences in sector contribution were found. Solvent use and transportation were identified as the largest NMVOC sources in PRD (Zheng et al., 2009), while industrial processes were more important in YRD (Huang et al., 2011; Fu et al., 2013). Limitation existed in current regional inventories. First, the information of local sources was still lacking. Although combustion sources (e.g., power plants) were gradually included in the regional emission inventory as point sources, the sources that contribute more to NMVOCs
including refinery and chemical engineering plants were less investigated at local
scale, resulting possibly in big bias in emission estimation. Second, with varied data
sources and methods, large discrepancies might exist between studies in the amount
and spatial pattern of emissions. Such discrepancies were rarely analyzed, and the
uncertainties in emission estimation at local scale were seldom quantified. In
particular, the performances of chemistry transport modeling with various NMVOC
inventories have not been sufficiently evaluated. Moreover, source profiles and
speciation of NMVOC emissions need further improvement. Increasing domestic field
measurements have been conducted on chemical profiles of NMVOCs for typical
types of sources including solvent use (Yuan et al., 2010; Zheng et al., 2013),
transportation (Tsai et al., 2012; Huang et al., 2015), residential stoves (Wang et al.,
2009), and biomass burning (Kudo et al., 2014). The effects of those results on
speciation of NMVOC emissions were not fully assessed, except for limited studies
(Li et al., 2014). In addition, the measurements on given sectors such as chemical
engineering are still lacking, and the data from foreign countries had to be used.

Under the heavy haze pollution in eastern China (Andersson et al., 2015; Sun et
al., 2015; Wang et al., 2015), series of measures have been conducted particularly on
power and industrial boilers to control the emissions of primary particles and the
precursors of secondary particles such as SO2 and NOX (Zhao et al., 2014). Along
with gradually reduced ambient PM levels in YRD, O3 pollution becomes a bigger
concern for air quality improvement, motivating the better understanding and
controlling of NMVOC emissions. In this work, we select Jiangsu, a typical province
with intensive refinery and chemical industry in eastern China, to develop and
evaluate the high-resolution emission inventory of anthropogenic NMVOCs. The
geographic location and cities of the province are illustrated in Figure S1 in the
supplement. Field measurements on chemical composition of NMVOC emissions
were conducted to obtain the source profiles of typical chemical engineering
processes. With detailed information of local emission sources collected and temporal
changes tracked, the provincial emission inventory of NMVOC with chemistry
profiles were developed for a ten-year period 2005-2014, and the uncertainties of the
emission estimation were quantified. Through a thorough comparison between results from varied methods and data sources, the discrepancies in emission estimation, source profiles, and spatial patterns were then evaluated. Finally, chemistry transport modeling was applied in southern Jiangsu to test the improvement of the provincial NMVOC inventory.

2 Data and methods

2.1 Sampling and analysis of NMVOC species from chemical plants

We select nine types of chemical engineering enterprises that are intensively distributed in Jiangsu to measure the chemistry composition of NMVOC emissions. Very few domestic tests were available for those sources. Based on the on-site investigation of main emission processes, the locations for stack and/or fugitive emission sampling were determined for each source type, as summarized in Table S2 in the supplement. Note the sampling cannot be conducted for all the processes in an enterprise due mainly to the limitation of pipeline layout. The SUMMA canister produced by University of California, Irvine was employed to collect the air sample. The canister was sealed with smooth stainless steel as its inner wall, and the volume and vacuum pressure range of the canister was 2 L and $1.1 \times 10^{-4}$ kPa, respectively. For stack emission measurement, as shown in Figure S2a in the supplement, the canister was connected with a stainless steel probe, and a filter pipe filled with glass wool and anhydrous sodium sulfate was applied to remove the particles and water vapor in the air sample. Under flow control, the sampling time was roughly 10 minutes indicated by the pressure gage of the canister. For fugitive emission measurement, the canister was placed 50 meters downwind the chemical production device, and the sampling time was roughly 8 minutes. Repeated sampling was conducted for each process to eliminate the bias and totally 56 samples were obtained, as shown in Table S2.

NMVOC sample was analyzed by one Gas Chromatograph Mass Spectrometer (GC-MS) system (GC6890/MS5973i, Agilent Technologies, USA), as illustrated in
Figure S2b in the supplement. Firstly, sample was pumped into a cryogenic pre-concentrator with a three-stage trapping system. In the first stage, the VOC was adsorbed on glass beads at –150°C and desorbed at 10°C. In the second stage, it was trapped on Tenax at –30°C and desorbed at 180°C. In the third stage, the VOC was focused on a transfer line at –160°C and heated rapidly to 70°C. The concentrated VOC was then injected into the gas chromatograph. The GC oven temperature was initially programmed at –50°C, and then increased to 180°C at 4°C/min and to 220°C at 15°C/min, holding 3 minutes. The VOC compounds were separated on a DB-5MS capillary column (60 m×0.25 mm×1.0 μm) and quantified using a quadrupole mass spectrometer. The mass spectrometer was operated in SCAN mode and scanned 20-42 amu and 35-270 amu before and after 8.5 minutes, respectively. The ionization method was electron impacting, and the source temperature was 230°C. The PAMS (Photochemical Assessment Monitoring System) standard mixture (Spectra Gases Inc., USA) and TO-15 standard mixture (Spectra Gases Inc., USA) were used to confirm the retention times of different compounds, and to identify them based on retention time and mass spectrum. The target species were quantified by using multipoint internal calibration method. To establish calibration curves, a certified gas mixture containing all the target compounds was dynamically diluted with pure nitrogen to five concentration gradients using mass flow controllers. Bromochloromethane, 1,2-difluorobenzene, and chlorobenzene-d5 were chosen as internal standards in samples. The method detection limit was 0.5 ppb for all species.

2.2 Development of provincial emission inventory

Anthropogenic NMVOC emissions in Jiangsu for 2005-2014 were estimated with a bottom-up method using the following equation:

\[ E(n) = \sum_i AL(i, n) \times EF(i, n) \]  

(1)

where \( i \) and \( n \) represent the source type and year, respectively; \( E \) is the annual emissions; \( AL \) is the activity level data; and \( EF \) is the emission factor (i.e., emissions per unit of \( AL \)).
As summarized in Table S3 in the supplement, the emission sources were classified into a four-level framework, including seven main categories: stationary fossil fuel combustion, industrial process, solvent use, transportation, oil distribution, biomass burning, and others. Each main category was further subdivided into subcategories according to discrepancies in fuel consumption, product manufacturing, or technology application.

For power plants, industrial boilers, industrial processes and paint use plants, the detailed information with inter-annual changes was collected and tracked at plant level from the multiple-year official Environmental Statistics (the databases of emission sources compiled by local environmental protection agency), Pollution Source Census (PSC, internal data of emission sources collected by local environmental protection agency), and on-site surveys on large emitters conducted by local environmental protection bureaus. The information included geographic location, types and amounts of raw materials, types and amounts of products, fuel quality and consumption, and combustion/manufacturing technology. For 2014, as an example, detailed information of 6023 plants was obtained, with the locations of those point sources illustrated in Figure S1.

Activity data of other emission sources were generally collected at provincial or city level based on official statistical yearbooks. In particular, as the amount of solvent use was not reported at city level, the data at the national/provincial level were first collected and then allocated into cities using the building areas, vehicle production and industrial GDP as proxies. For oil distribution, the simplified method by Wei (2009) was followed to calculate the activity levels of oil storage, transport and sale, based on the provincial energy balance statistics. The annual biofuel use for residential stoves until 2008 was taken from official energy statistics. As the data were unavailable for subsequent years, the activity level was calculated as a product of grain production, waste-to-grain ratio, and the ratio of residual material burned in stoves according to the government plan of biomass utilization (PGJP, 2009).

Similarly, the biomass combusted in open fields was calculated as a product of grain production, waste-to-grain ratio, and the percentage of residual material burned in the
2.3 Determination of emission factors

Based on extensive literature survey, the NMVOC emission factors were determined as follows with descending priorities: (1) the results from domestic measurements; (2) the emission limits of local laws and regulations; (3) the values from expert judgment specific for China; and (4) emission factors from AP-42 database (USEPA, 2002) and the EMEP/EEA guidebook (EEA, 2013) when above information was lacking. The emission factors applied in this work are summarized by sector in Tables S4-S6 in the supplement.

The emission factors for power plants and industrial boilers were taken mainly from Bo et al. (2008). Given the similar designs of boilers between China and developed countries (Wei et al., 2008), the emission factors in AP-42 database were also applied when domestic results were lacking. For residential combustion of fossil fuel, the emission factors from domestic tests (Zhang et al., 2000; Wang et al., 2009) were used, as shown in Table S4. For industrial processes, there were very few local tests on NMVOC emission factors conducted before, thus the values from expert judgment and data from AP-42 and EMEP/EEA had to be applied, as summarized in Table S5. For solvent use, the VOC contents of given products were limited by national laws and regulations, as summarized by Wei et al. (2008). The updating of regulations and their impacts on inter-annual changes in NMVOC emission factors were considered from 2005 to 2014, such as GB18583-2003 and GB18583-2008 for indoor painting. Data from AP-42, EMEP/EEA and other literatures (Bo et al., 2008; Fu et al., 2013) were also applied when local information was missing. As a result, the emission factors by source type are summarized in Table S6. Emission factors of oil distribution were taken directly from Wei et al. (2008) and Shen (2006).

For off-road transportation, the data from EMEP/EEA and expert judgment (Wei et al., 2008; Q. Zhang et al., 2009) were adopted, attributed to lack of domestic tests or relevant standards/regulations. Following He (2015), the emission factors for on-road vehicles were calculated and adjusted according to local conditions using Eq.
(2):

\[ EF = BEF \times \varphi \times \gamma \times \lambda \times \theta \]  

(2)

where \( BEF \) is the base emission factor, \( \varphi \) is the environmental correction factor, \( \gamma \) is the average traveling speed correction factor, \( \lambda \) is the vehicle deterioration correction factor, and \( \theta \) is correction factor for other conditions (e.g., vehicle loading and fuel quality).

The emission factors for biofuel burning in stoves were from the field test results by Wang et al. (2009), who measured the NMVOC emission characteristics of multiple stove-fuel combinations in China and provided the emission factors by province. For biomass open burning, the local test results by Li et al. (2007) were applied, as summarized in Table S4.

2.4 Speciation of NMVOC emissions

The total NMVOC emissions for given source type were broken down into individual species using Eq. (3):

\[ E(i, k) = E(i) \times X(i, k) \]  

(3)

where \( E \) is the emissions; \( X \) is chemical profile of NMVOCs (%); \( i \) and \( k \) represent the source type and individual NMVOCs species, respectively.

For chemical processes such as rubber, polyether, and polyethylene production, the measurement results of this work were used. The chemical profiles for other sources were mainly taken from domestic measurements, including residential fossil fuel and biomass burning (Tsai et al., 2003; Liu et al., 2008; Wang et al., 2009; Zhang et al., 2000; Wang et al., 2014a), biomass open burning (Zhang et al., 2013; Kudo et al., 2014), on-road vehicles (Liu et al., 2008; Tsai et al., 2012; Huang et al., 2015; Wang et al., 2013; Ou et al., 2014; Gao et al., 2012), iron & steel (Shi et al., 2015; He et al., 2005; Jia et al., 2009; Tsai et al., 2008; Li et al., 2014), paint and printing ink production (Zheng et al., 2013;), solvent use (Yuan et al., 2010; Zheng et al., 2013; Tang et al., 2014; Wang et al., 2014b) and refineries (Liu et al., 2008; Wei et al., 2014). For sources without sufficient local measurements, results from foreign studies were
applied including the SPECIATE database by USEPA (2014), and Theloke and Friedirch (2007).

To reduce the possibly large uncertainty of source profile from individual measurement, Li et al. (2014) developed the “composite profiles” for sources where multiple candidate profiles were available, by revising the OVOCs fraction and averaging the fractions in different profiles for each species. While Li et al. (2014) included the source profiles published before 2011, considerable local measurements were conducted after then. In this work, therefore, “composite profiles” were updated following the method by Li et al. (2014), and the most recent source profiles from domestic results were contained. Table 1 compares the source profiles of this work with those of Li et al. (2014) or SPECIATE for typical sectors, grouped as alkanes, alkenes, alkynes, aromatics, OVOCs, and others. Elevated fractions of alkanes are found in this work for almost all the sources, while the comparisons of other species are less conclusive between sources.

To evaluate the atmospheric oxidation capability from NMVOC emissions, ozone formation potentials (OFPs) were calculated by multiplying the speciated NMVOC emissions and corresponding MIR values (Carter, 1994). To meet the requirement of atmospheric modeling, NMVOC emissions were assigned to chemical mechanism species by multiplying the emissions of individual species and mechanism-specific conversion factors using the following equation:

\[
E(i,m) = \frac{E(i,k)}{M(k)} \times C(k,m) \tag{4}
\]

where \(E\) is the emissions, \(M\) is the mole weight, \(C\) is the conversion factor, and \(i, m\), and \(k\) represent the source type, individual species, and the chemical mechanism species.

2.5 Uncertainty analysis

The uncertainty of estimated provincial NMVOC emissions for each year were quantified using Monte-Carlo simulation, as described in Zhao et al. (2011). As shown in Table S7 in the supplement, normal distributions were assumed for activity levels,
with varied coefficients of variation (CV, the standard deviation divided by the mean) determined for different source types, according to the reliability of energy and economy statistics (IPCC, 2006; Zhao et al., 2011). Due to lack of sufficient measurement results to support the data fitting, the determination of probability distributions for emission factors depended largely on expert judgment (Streets et al., 2003; Zhao et al., 2011; Wei et al., 2011). As summarized in Table S8 in the supplement, the uniform distributions were conservatively assumed for most solvent use sources based on limited data points, while lognormal distributions with large CVs for other sources. Ten thousand simulations were performed to estimate the uncertainties of emissions, and the parameters that were most significant in determination of the uncertainties were identified by source type according to the rank of their contributions to variance.

3 Results

3.1 Source profiles of chemical industry from measurement

NMVOC source profiles of 14 processes (9 for stack emissions and 5 for fugitive emissions) were obtained from field measurements. With totally 61 species detected by GC-MS systems, the chemistry components were grouped into 6 types (alkanes, alkenes, halohydrocarbon, aromatics, OVOCs, and others), as illustrated in Figure 1a. Alkanes were the main species of synthetic rubber industry (SBR, SIS rubber and SEBS rubber) and the mass fractions were measured over 70%. For production of cellulose acetate fiber, alkanes, aromatics, and OVOCs were the main species in process of acetate flake production, while OVOCs dominated in the spinning process. Resulting from various raw materials applied, the source profiles of the two types of polyether production differed a lot: the mass fraction of OVOCs was close to 80% for PPG, while the main species for POP were others, aromatics and halohydrocarbon. For ethylene production, aromatics were the main composition in the stack gas of cracking furnace, while alkanes and alkenes dominated the fugitive emissions. For other types of fugitive emissions, big differences existed in the source profiles.
attributed mainly to the various raw materials and chemical reactions.

The detailed chemistry compositions for stack and fugitive emissions were summarized in Tables S9 and S10, respectively. For stack emissions of synthetic rubber production, cyclohexane was the dominating species, with the mass fractions close to or above 70% for all types of products. Besides, styrene and acetone were also important species for SBR and SIS/SEBS rubber, respectively. Used as the solvent in the chemical reactions, acetone and cyclohexane were considerably emitted during acetate flake production process, and the mass fraction of acetone reached 70% in the spinning process. As the raw materials for polyether production, acrylonitrile and ethylene oxide were the main species emitted from POP and PPG production, with the mass fractions measured at 43% and 62%, respectively. As the main product, vinyl acetate was unsurprisingly measured to take 80% of NMVOC emissions from its production process.

For fugitive emissions from ethylene production, the mass fractions of ethylene, propylene, and n-hexane reached 33%, 26% and 20%, respectively. 1,2-dichloropropane dominated the emissions from propylene oxide production, with the mass fraction measured at 65%. For polyethylene and glycol production, ethylene and xylene were identified as the largest species, with the mass fractions measured at 42% and 35%, respectively.

Since there were very few domestic tests on source profiles of chemical industry, the results obtained in this work were compared with those available in SPEICATE for synthetic rubber, ethylene and polyethylene production, as illustrated in Figure 1b-d, respectively. As can be seen in Figure 1b, large discrepancy was found for source files of SBR between this work and SPEICATE: while cyclohexane was identified as the main species in this work, SPECIATE included only styrene and 1,3-butadiene (the raw materials in SBR production). Variation in manufacturing technologies was the main source of the discrepancy. Emulsion polymerization technology was considered in SPEICATE, in which solvent was not used and thus NMVOC emissions consisted mainly of the volatile raw materials. This work, however, measured the plants with solution polymerization technology, in which
significant organic solvents would be released during the drying process. As shown in Figure 1c, both SPECIATE and our measurements on fugitive emissions indicated that ethylene and isobutene were the important species for ethylene production. In addition, much larger fractions of propylene and n-hexane were found in this work. Clear different composition was found for flue gas of cracking furnace, with abundant species from incomplete combustion. Similar source profiles were found between this work and SPECIATE for polyethylene production, dominated by ethylene (Figure 1d).

3.2 Inter-annual trends and sectoral contribution of NMVOC emissions

As shown in Table 2, the annual emissions of anthropogenic NMVOCs for Jiangsu were estimated to increase from 1774 to 2507 Gg during 2005-2014, with an average annual growth rate at 3.9%. Industrial processes and solvent use were identified as the largest two sectors contributing to the emissions. The emission fractions of the two types of sources to total anthropogenic emissions were estimated to increase from 26% in 2005 to 38% in 2014, and from 21% to 39%, respectively. In contrast, the emission contributions from transportation and biomass burning were declining from 18% to 11%, and from 26% to 4%, respectively, attributed mainly to the controlled motorcycle emissions, replacement of residential biofuel stoves with natural gas/electricity ones, and the gradual implementation of straw burning prohibition. Relatively small contributions were found for stationary fuel combustion plants, oil distribution, and other sources, and their collective fractions to total emissions ranged 7-9% during the study period.

Figure S3a-c in the supplement provided the inter-annual trends in emissions of subcategories for industrial processes, solvent use and transportation. The emissions from industrial processes were estimated to be doubled from 2005 to 2014, and the inter-annual trend in emissions was well correlated with that in industry GDP (Figure S3a). The comprehensive investigations on point sources indicated that few measures were implemented to control NMVOC till 2014, and the increased emissions were thus mainly driven by the growth of industry activities. Largest growth was found for synthetic and fine chemical industry, with the emissions elevated from 130 in 2005 to
361 Gg in 2014. Due to enhanced coking industry, the emissions of iron & steel production were estimated to increase 254% from 27 to 96 Gg.

The emissions of solvent use in Jiangsu were calculated to increase 153% from 380 in 2005 to 963 Gg in 2014, and the growth was highly consistent with that of industry plus construction GDP (Figure S3b). Despite of increased use of water soluble paint and implementation of emission standards for given processes (e.g., the VOC content of interior wall paint has been reduced from 250 to 120g/g since 2008), it was still difficult to restrain the emissions under the fast growth of solvent use, as relevant polices were not widely conducted across the sector. Paint use was the largest contributor, and its emissions were calculated to increase from 225 in 2005 to 652 Gg in 2014. The emissions from printing ink increased 355% from 25 to 115 Gg.

Although Jiangsu’s total vehicle population increased 76% from 2005 to 2014, the NMVOC emissions of on-road transportation were estimated to decline 31% from 297 to 204 Gg, with the peak emissions at 302 for 2007 (Figure S3c). The implementation of staged emission standards (State I-V, equal to Euro I-V) on new vehicles, and reduced motorcycle population were the main reasons for the declining emissions. For example, the emissions of motorcycle deceased 66% from 185 to 64 Gg, and its contribution to on-road vehicle emissions declined as well from 62% and 31%. Unsurprisingly, gasoline vehicles dominated the emissions of on-road transportation, with the fraction ranged 81%-87% during the study period.

Illustrated in Figure 2 are the spatial distributions of Jiangsu’s NMVOC emissions for various years within a 3×3 km grid system. Besides point sources which were directly allocated according to geographic locations, certain proxies were applied to allocate emissions from other sources including GDP for industrial area sources and oil distribution, population for solve use area sources, road net and traffic flow for on-road vehicles, railway and canal for off-road transportation, and rural population for biomass burning. High emission intensities were mainly found in relatively developed cities along Yangtze River in southern Jiangsu including Nanjing, Suzhou, Wuxi and Yangzhou (see Table S11 for the emissions by city). In central and northern Jiangsu, large emissions existed in areas with clustered industrial parks,
reflecting the impacts of big plants on spatial pattern of NMVOC emissions. Comparing the emissions for 2005 and 2014, increased emissions were commonly found in southern Jiangsu indicating the faster growth of industry in developed cities (Figure 2d). Moreover, reduced emissions were coincided with road net distribution, implying the benefits of emission controls on vehicles.

3.3 Speciation and OFPs of NMVOC emissions

Based on the source profiles, emissions of more than 500 hundred NMVOC species were calculated and grouped into 12 categories (alkanes, alkenes, alkynes, aromatics, alcohols, aldehydes, ketones, ethers, acids, esters, halohydrocarbons, and others). From 2005 to 2014, the mass fractions of alkanes, unsaturated hydrocarbon (alkenes and alkynes), aromatics, OVOCs (alcohols, aldehydes, ketones, ethers, acids, and esters), halohydrocarbons, and others were ranged 26-30%, 13-19%, 21-23%, 18-21%, 3-4%, and 11-12%, respectively. Shown in Figure 3 are the mass fractions of species by source for 2014. Due to varied fuel qualities and combustion conditions, large differences in the speciation of emissions were found for fossil fuel combustion, transportation and biomass burning. Dominated by coal combustion, the profile of fossil fuel stationary sources was relatively simple with little OVOCs and halohydrocarbons, and aromatics were the largest fraction (45%), followed by alkanes (29%). Alkanes, aromatics and alkenes were the main species from transportation, with the fractions estimated at 30%, 24%, and 23%, respectively. For biomass burning, elevated alkenes and less alkanes were found attributed to the highly incomplete combustion. The mass fractions of alkanes, aromatics and alkenes from industrial processes were estimated 32%, 16% and 12%. In particular, relatively close emission fractions were found between species for chemical industry, the largest emission source of industrial processes: 19%, 15%, 11%, 10% and 10% of aromatics, ketones, alkenes, alkanes, and halohydrocarbons, respectively. For solvent use, aromatics and alkanes were the most important species with the fractions estimated at 32% and 22%, respectively, and the collective fraction of OVOC species reached 27%. Alkanes and aldehydes dominated the emissions of
oil distribution and other sources, which came mainly from the oil evaporation and residential cooking, respectively.

The OFPs from NMVOC emissions in Jiangsu were calculated to increase from 3880 in 2005 to 5200 Gg in 2014, and the ratio of annual OFPs to emissions varied slightly around 2.1 for the decade. The OFP/emission ratios for 2014 were provided by source in Figure 3. With abundant aromatics and alkenes emissions that were highly active in chemistry, the largest ratio (3.68) was found for fossil fuel stationary combustion. The ratios of biomass burning and other sources reached 3.0, attributed to active aromatics and aldehydes emissions, respectively. The lowest ratio (1.58) was found for oil distribution, as its emissions were dominated by alkanes with low reactivity. Figure S4 in the supplement provided 25 species with the biggest contributions to OFPs and their emission sources for 2005 and 2014. In 2005, the 25 species were estimated to account for 44% of total NMVOC emissions and 83% of OFPs (Figure S4a). The aromatics species with (e.g., xylene and toluene) came largely from solvent use and industrial processes, while alkenes species (e.g., ethylene and propylene) were mainly from industrial processes, biomass burning, and transportation. Besides, biomass burning was the dominating sources of methyl glyoxal, methyl alcohol and glyoxal. For 2014, the 25 species were estimated to account for 38% of total NMVOC emissions and 81% of OFPs, and the contributions of solvent use and industrial processes to OFPs were clearly elevated (Figure S4b). The orders of isopropanol and n-butanol that were mostly from solvent use, for example, were moved forward. Moreover, the contribution of biomass burning significantly declined, and the glyoxal was not identified as the one of the 25 most important species to OFPs any more.

3.4 Uncertainties of provincial NMVOC emission inventory

The uncertainties of estimated annual NMVOC emissions for Jiangsu 2005-2014 are illustrated in Figure 4, expressed as the 95% confidence intervals (CIs) around the central estimates. As inter-annual changes were hardly assumed in determination of probability distributions for parameters, similar uncertainty ranges were thus
calculated for emissions of various years. As shown in Table 3, the uncertainty of emissions 2014 was quantified at -41%~+93% (95% CI), and biomass burning and other sources were estimated as the sources with largest uncertainties, followed by stationary fossil fuel combustion and oil distribution. For most emission sectors/categories, emission factors were identified as the largest sources of emission uncertainty, with an exception of solvent use. Resulting from complicated sources of stack and fugitive emissions, it is generally difficult to conduct comprehensive field measurements on NMVOC emission factors for industrial and residential sources, and large uncertainties were thus assumed for them attributed to limited domestic test samples and to heavy dependence on foreign databases. Regarding solvent use for which provincial and city statistics were lacking, the activity data had to be downscaled from national level leading to possibly big bias in emission estimation.

Provided in Table 3 as well are the uncertainties of national and YRD emissions from other studies. Compared with those results, the emission uncertainties were reduced in this work for industrial processes, solvent use and transportation. The more detailed classification of emission sources and adoption of independent emission factors for those sources should be the most important reason. For example, totally 34 vehicle type-control combinations were taken into account for calculating the on-road vehicle emissions, and emission factor for each type of combination was assumed independent from other. In addition, the errors of activity levels for big point sources were significantly reduced from the detailed investigation and on-site survey at plant level, leading to smaller uncertainty in emission estimation for industrial and solvent use sources.

4 Evaluation of provincial emission inventory

4.1 Chemical and refinery industry emissions from varied data sources and methods

As indicated in Table 2, chemical and refinery industry was one of the biggest contributors to anthropogenic NMVOC emissions. We select Nanjing, the capital city
of Jiangsu province, to evaluate the impacts of data sources and methods on emissions of this category. Besides the method described in Sections 2.2 and 2.3 that incorporated the most available information from Environmental Statistics, PSC, and on-site surveys (Method 1), two other methods based respectively on data from Environmental Statistics (Method 2) and economic statistics without any information on individual plants (Method 3) were also applied to calculate the emissions in the city for 2011. Note the emissions of area sources (i.e., not included in plant-by-plant investigations) in Methods 1 and 2 were estimated using the same data source as Method 3. Table S12 in the supplement provides the emissions calculated based on the three data sources by subcategory of chemical and refinery industry. The largest emissions estimated using Method 1 were clearly larger than those using Method 2 or 3, resulting mainly from the incomplete records of chemical products by environmental or economic statistics. For example, some basic chemistry products (e.g., ethylene oxide and ethylene glycol) and synthetic chemical products (e.g., polyether and polyethylene) were not included in current economic statistics. In addition, although most chemical and refinery plants were investigated in the Environmental Statistics, only three types of chemical products were recorded for each plant, much less than the actual (more than one hundred types for some plants). The omission of chemical product types thus led to underestimations in NMVOC emissions. With the product types fully covered, Method 1 could even underestimate the emissions, as the emission factors could not be measured or determined for all products due to the completed pipe layout or fugitive release.

Spatial distributions of the emissions estimated using the three data sources for Nanjing were illustrated in Figure 5. Similar patterns were found for Method 1 and 2 (Figure 5a and 5b), as the emissions were dominated by the big chemical and refinery plants. As labeled in Figure 5a, the largest ten plants were estimated to account for 80% of NMVOC emissions of the sector for the whole city. Without detailed information of individual plants, Method 3 had to apply the proxies (e.g., population density) to allocate the emissions, and clearly overestimate the emissions in urban downtown (Figure 5c). It could thus be inferred that big discrepancies in spatial
distribution of emissions at small scale might be caused when downscaled from larger scale without sufficient investigation on local sources, particularly for regions where emissions were dominated by large plants that were gradually moved out of urban areas. To further examine the emission estimation on individual plants, an alternative method was applied to calculate the emissions of all manufacturing processes separately including leaks of hydrocarbon vapors from process equipment (valves, flanges, seals, etc.), storage of organic liquid, loading and unloading of organic liquid, and waste water treatment (mentioned as device operation based method herein). As indicated in Table S13 in the supplement, detailed information of 15 key chemical and refinery enterprises in Nanjing (i.e., enterprises directly under the control of city government) were collected and the emissions of those plants were calculated and compared with the results using the method as described in Sections 2.2 and 2.3 (mentioned as emission factor based method herein). Although the total emissions of the 15 plants were very close between the two methods, significant discrepancies existed for individual plants. For example, much larger NMVOC emissions were calculated for plants 3 and 6 with device operation based method, as the emission factors for production of chlorobenzene alkylbenzene, and cyclohexanone were lacking, leading to underestimation by the emission factor based method. As shown in Figure S6 in the supplement, the differences in emissions from varied calculating methods for the 15 plants led to moderate changes in spatial distributions of the chemical and refinery emissions for the city. In general, the device operation based method could better capture the activities of specific plant and the actual emission characteristics; however, the method could hardly be applied in a broader scale, as it depends strongly on the completeness and quality of data collection.

4.2 Changes in speciation of NMVOC emissions

As indicated in Section 2.4, the speciation of NMVOC emissions in Jiangsu were updated by including the results of our field measurements and other most recent domestic tests, based on previous foreign database (SPECIATE) and the composite
profile by Li et al. (2014). Figure 6 illustrated the emissions of 445 species (accounting for 99.5% of total NMVOC emissions) estimated with the source profile before (SPECIATE and Li et al., 2014) and after updating (this work) for Jiangsu 2010. Due to relatively limited tests available, there were no significant changes in emissions for most species when updated profiles were applied. However, relative big changes in emissions (over 100 Gg) were found for thylacetate and certain aromatics species (benzene, xylene, ethyl benzene, and methyl benzene). Applying the source profile of paint use measured by Zheng et al. (2013) led to enhanced thylacetate. Reduced benzene and methylbenzene, and elevated ethyl benzene and xylene resulted mainly from the revisions on source profiles of coking (Jia et al., 2009; Shi et al., 2015) and solvent use (Wang et al., 2014b; Zheng et al., 2013).

To support the air quality modeling, the emissions of NMVOC species under CB05 and SAPRC99 mechanisms were calculated using Eq. (4) based on the source profiles before and after updating, and the results for 2010 were shown in Figure 7. With source profiles updated based on most recent measurements, relatively big changes were found for ALDX (see captions of Figure 7 for the detailed meanings) in CB05 and OLE1 in SAPRC99. The revisions on source profiles of solvent use were the main reason for the changes. For example, the increased ALDX was attributed mainly to the updated profiles of printing ink and automobile paint use (Zheng et al., 2013; Tang et al., 2014), while increased OLE1 was to that of building coating (Yuan et al., 2010; Wang et al., 2014b).

4.3 Comparisons with other inventories

The total anthropogenic NMVOC emissions in Jiangsu were extracted from other continental/national/regional inventories and compared with our estimates for various years, as shown in Figure 4. All the results were within the 95% CIs in this work. Except for REAS that provided extremely high emissions for China (Kurokawa et al., 2013), our estimates were generally 0-18% larger than other studies in the total emission estimation, attributed mainly to the omission of certain emission sources in other inventories and to the elevated activity levels from plant-by-plant investigation.
in this work. Figure 8 provided the NM VOC emissions by source from various inventory studies for selected years. As can be seen, much larger emissions were made in this work than the national (Wei et al., 2008) or regional inventory (Fu et al., 2013). The latter two studies missed the emissions from the manufacturing processes of certain chemical products. For example, fermentation alcohol, dye and rubber were not included in Wei et al. (2008), either glasswork, pesticide or charcoal in Fu et al. (2013). The emissions from solvent use in this work were larger than those from Bo et al. (2008), attributed to omission of carpentry coating, pesticide and adhesive using by the latter. The varied data sources also contributed to the emission discrepancies. For example, Wei et al. (2008) and Bo et al (2008) made larger estimates in transportation emissions than us, as they applied higher values of annual average miles traveled for motorcycles at national level.

The emissions of CB05 and SAPRC 99 species estimated by us and MEIC were compared in Figure 7. For CB05 mechanism, our results were smaller for TOL and XYL but larger for ETH and ETHA than MEIC (Figure 7a), while discrepancies existed for most species under SAPRC 99 (Figure 7b). Such discrepancies could result either from the various source profiles, or from the various source contributions in total emissions. For example, with updated source profile for building coating, much larger OLE1 emissions were estimated in this work than MEIC. Besides the total emissions, the differed speciations under chemical mechanisms could result in complex impacts on air quality simulation, which would be discussed in next section.

Figure 9 compares the spatial distributions of Jiangsu's NMVOC emissions for 2010 between our results and MEIC. To be consistent in resolution and to ease visualization, the high-resolution inventory obtained in this work (Figure 2) was upscaled to 0.25°×0.25°, the same as MEIC. Similar spatial patterns were found for the two inventories: high emission densities existed in southern Jiangsu with relatively developed economy and industry. As indicated in Figure 9a, the areas with big plants and large emissions were consistent with each other, indicating that the provincial NMVOC emissions were largely influenced by the locations of large point sources. Figure 9c shows that larger emissions estimated in this work than MEIC were
commonly found in areas with big plants, reflecting the impacts of detailed and complete investigation on product types and activity levels at plant level on the emission estimation. Although our result was 315 Gg or 18% larger than MEIC in total anthropogenic NMVOC emissions, lower emissions were found in this work at downtown Nanjing and the Suzhou-Wuxi-Changzhou city clusters with large populations. The result implies that downscaling of emissions depending on certain proxies (e.g., population and economy density) might overestimate the emissions in urban areas, and detailed information on individual sources should be included if possible.

4.4 Evaluation of multiple-scale inventories through air quality modeling

The Models-3/Community Multi-scale Air Quality (CMAQ) version 4.7.1 was applied to test the performances of chemistry transport simulation with various NMVOC emission inventories for Jiangsu area. As shown in Figure S6 in the supplement, three nested domains (D1, D2 and D3) were set, and the most inner D3 covered the mega city Shanghai and six most developed cities in southern Jiangsu including Nanjing, Changzhou, Zhenjiang, Wuxi, Suzhou and Nantong, with a horizontal spatial resolution at 3 km. Chemistry transport simulation was conducted separately with two inventories, i.e., MEIC and the provincial one developed in this work, for January, April, July and October 2012. The first five days for each month were chosen as spin-up period to provide initial conditions for later simulations. Other model settings on meteorological simulation and emissions of natural origin were described in Zhou et al. (2016).

Figure 10 provides the observed and predicted daily 1h-max \( O_3 \) concentrations for the four months, and Table 4 compares the model performances with MEIC and our provincial inventory, indicated as normalized mean bias (NMB) and error (NME) values. As suggested by the minus NMBs for most cases, model usually generated lower 1h-max \( O_3 \) concentrations than observation with either MEIC or provincial inventory applied, with an exception for April simulation with MEIC applied. The result thus implied NMVOC emissions of anthropogenic origin might be
underestimated, as YRD was commonly recognized as VOC-limited region for O₃ formation. Compared to MEIC, better model performances (except for July) were generally achieved when the provincial inventory was applied, indicating the improved reliability of the detailed bottom-up NMVOC inventory on high-resolution chemistry transport simulation. In particular, larger emissions were estimated for certain species with relatively high ozone formation potential (e.g., ethene and ethanol) in the provincial inventory, leading to higher and closer O₃ prediction to observation.

We should acknowledge, however, that the discrepancies between simulation and observation were still large compared to regional studies in North America (Y. Zhang et al., 2009). More efforts on improving or validating emission inventory at provincial scale are thus in great needed. Besides careful compilation of emission source information in the bottom-up method, observation constraint from ground measurements could be used to evaluate the emission level, source contribution, and speciation of VOC emissions (M. Wang et al., 2014). Moreover, the emission uncertainty of other species, i.e., NOₓ, could also partly explain the discrepancies, as the NOₓ control measures taken recently could hardly be fully tracked in the emission inventory development.

5 Conclusion

Using a bottom-up approach, we developed a high-resolution emission inventory of anthropogenic NMVOC for Jiangsu province, eastern China, with substantial detailed information on local sources and source profiles from domestic tests incorporated. Attributed largely to the elevated contribution from industrial processes and solvent use, the annual provincial emissions were estimated to increase 41% from 2005 to 2014. Influenced largely by location of big point sources, high emission densities were found in cities along the Yangtze River. Our estimations were larger than results from most other available inventories except REAS, due mainly to the omissions of certain industrial and solvent use sources by other studies and to the elevated activity levels from plant-by-plant investigation in this work. Benefiting from
more detailed classification and investigation of emission sources, reduced uncertainties in annual emissions were quantified in this work compared to previous studies. Varied data sources and methods were of significant impacts on emission estimation at city/plant level. In particular, downscaling directly from national inventories would overestimate the emissions in urban downtown. With the most recent source profiles from local measurements included, considerable changes in emissions were found for thyl acetate and certain aromatics species, and the speciation under CB05 and SAPRC99 differed a lot from the national inventory MEIC. Compared to MEIC, better model performance (indicated by daily 1h-max O3 concentrations) were achieved when the improved provincial inventory was used in CMAQ simulation, although the discrepancies between simulation and observation need further investigation. As emission controls on NMVOCs started to be implemented on industrial sources in China (e.g., the application of leak detection and repair technique in chemical and refinery plants), more field tests were recommended to better track the temporal changes in emission factors and to reduce the uncertainty of emission estimation in the future.

ACKNOWLEDGEMENT

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Wei, W.: Research and forecast on Chinese anthropogenic emissions of volatile organic compounds, Ph. D thesis, Tsinghua University, Beijing, China, 2009


FIGURE CAPTIONS

Figure 1. NMVOC source profiles by grouped species measured in chemical enterprises (a) and the comparisons with SPECIATE results for synthetic rubber (b), ethylene (c), and polyethylene production (d).

Figure 2. Spatial distribution of Jiangsu’s anthropogenic NMVOC emissions (3×3km) for 2005 (a), 2010 (b), and 2014 (c); and the differences between 2005 and 2014 (2014 minus 2005, d).

Figure 3. Fractions of NMVOC species and the ratios of OFPs to emission by sector for Jiangsu 2014.

Figure 4. The inter-annual trends in anthropogenic NMVOC emissions in Jiangsu from 2005 to 2014. The grey dotted lines indicate the 95% CIs of emissions estimated in this study. The results from other inventories are illustrated as well for comparison.

Figure 5. Spatial distributions of NMVOC emissions from chemical and refinery industry for Nanjing 2011 (3×3km), estimated using the detailed enterprise information (a), Environmental Statistics (b), and economic statistics without any information on individual sources (c). The black dots indicate the largest ten emitters in the city.

Figure 6. Emissions of NMVOC species for Jiangsu 2010 before and after source profile updating.

Figure 7. Emissions of CB05 (a) and SAPRC99 (b) species for Jiangsu 2010. The left and middle columns indicate the results before and after updating of source profiles, and the right columns indicate the results of MEIC. The CB05 species PAR represents paraffin carbon bond, UNR for unreactive parts of molecules, OLE for terminal olefin carbon bond, TOL for toluene and other monooalkylaromatics, XYL for xylene and other polyalkylaromatics, FORM for formaldehyde, ALD2 for acetaldehyde, ETH for ethene, MEOH for methanol, ETOH for ethanol, ETHA for ethane, IOLE for internal olefin carbon bond, ALDX for C3+ aldehydes, NVOL for nonvolatile mass. The
SAPRC 99 species ALK1, ALK2, ALK3, ALK4 and ALK5 represent alkanes and other non-aromatic compounds that react only with OH, and have kOH between 2 and 500, 500 and 2500, 2500 and 5000, 5000 and 10000, greater than 10000 ppm⁻¹ min⁻¹, respectively. ETHENE respect ethane, and OLE1 for alkenes with kOH smaller than 70000 ppm⁻¹ min⁻¹, OLE2 for alkenes with kOH greater than 70000 ppm⁻¹ min⁻¹, ARO1 for aromatics with kOH smaller than 20000 ppm⁻¹ min⁻¹, ARO2 for aromatics with kOH greater than 20000 ppm⁻¹ min⁻¹ and NROG for unreactive mass.

Figure 8. Jiangsu’s anthropogenic NMVOC emissions by sector for selected years estimated from this work and other inventories.

Figure 9. Spatial distributions of Jiangsu’s anthropogenic NMVOC emissions for 2010 (0.25°×0.25°) by this study (a) and MEIC (b), and the differences between the two inventories (this study minus MEIC, d). The black dots indicate the largest fifty emitters in the province.

Figure 10. Observed and simulated daily 1h-max O₃ concentrations using MEIC and provincial emission inventory in January (a), April (b), July (c) and October (d) in 2012 at the air quality monitoring sites in Nanjing. Note the different y-axis scales between panels.
Table 1 Updated NMVOC source profiles in this study and those from SPECIATE and Li et al. (2014).

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<th>Weight Percentage (%)</th>
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<th>Alkenes</th>
<th>Alkynes</th>
<th>Aromatics</th>
<th>OVOCs</th>
<th>Others</th>
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<td>OVOCs</td>
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Table 2 Anthropogenic NMVOC emissions in Jiangsu by source from 2005 to 2014 (Gg).

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</tbody>
</table>
Table 3 Uncertainties of anthropogenic NMVOC emissions (expressed 95% CI around the central estimates) and the most significant two parameters contributing to the uncertainties by sector for Jiangsu 2014. The percentages in the parentheses indicate the contributions of the parameters to the variance of emissions. The uncertainties from other inventories are provided for comparisons.

<table>
<thead>
<tr>
<th>Source Category</th>
<th>Uncertainty</th>
<th>Parameters contributing most to uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>This work</td>
<td>Wei (2009)</td>
</tr>
<tr>
<td></td>
<td>Provincial scale</td>
<td>National scale</td>
</tr>
<tr>
<td>Fuel stationary combustion</td>
<td>-66%, +190%</td>
<td>-</td>
</tr>
<tr>
<td>Industrial process</td>
<td>-58%, +152%</td>
<td>-88%, +283%</td>
</tr>
<tr>
<td>Solvent use</td>
<td>-68%, +131%</td>
<td>-82%, +223%</td>
</tr>
<tr>
<td>Transportation</td>
<td>-51%, +117%</td>
<td>-86%, +261%</td>
</tr>
<tr>
<td>Oil distribution</td>
<td>-66%, +162%</td>
<td>-</td>
</tr>
<tr>
<td>Biomass burning</td>
<td>-76%, +499%</td>
<td>-</td>
</tr>
<tr>
<td>Other</td>
<td>-98%, +490%</td>
<td>-</td>
</tr>
<tr>
<td>Total</td>
<td>-41%, +93%</td>
<td>-51%, +133%</td>
</tr>
</tbody>
</table>

1 The ratio of straw burned in stove as biofuel
Table 4 Model performance of daily 1h-max $O_3$ concentrations using MEIC and provincial inventory for January, April, July and October 2012 in Nanjing.

<table>
<thead>
<tr>
<th></th>
<th>Provincial emission inventory</th>
<th>MEIC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NMB$^1$</td>
<td>NME$^1$</td>
</tr>
<tr>
<td>January</td>
<td>-21%</td>
<td>34%</td>
</tr>
<tr>
<td>April</td>
<td>-26%</td>
<td>38%</td>
</tr>
<tr>
<td>July</td>
<td>-28%</td>
<td>33%</td>
</tr>
<tr>
<td>October</td>
<td>-20%</td>
<td>26%</td>
</tr>
</tbody>
</table>

$^1$ Normalized mean bias (NMB) and error (NME) were calculated as following equations ($P_i$ and $O_i$ indicate the results from modeling prediction and observation, respectively):

\[
NMB = \frac{\sum_{i=1}^{n}(P_i - O_i)}{\sum_{i=1}^{n}O_i} \times 100\%
\]

\[
NME = \frac{\sum_{i=1}^{n}|P_i - O_i|}{\sum_{i=1}^{n}O_i} \times 100\%.
\]
Figure 1

(a) Bar chart showing the mass fraction (%) of different emissions from SBR, SBS rubber, SEBS rubber, Acetate flake, Spinning, PEG, PPG, Vinyl acetate, Ethylene, Ethylene, Butanol and octanol, Propylene epoxide, Polyethylene, and Glycol. The emissions are classified as Stack emissions and Fugitive emissions.

(b) Bar chart showing the mass fraction (%) of specific compounds such as cyclohexane, 1,3-butadiene, methylene chloride, styrene, acetone, 2-propional, carbon disulfide, SBR (this study), SBS rubber (this study), SEBS rubber (this study), SBR (SPECIATE).
Figure 2

(a) 2005

(b) 2010

(c) 2014

(d) Difference between 2005 and 2014
Figure 3

[Diagram showing mass fraction and ratio of OFP/emission for different sources and chemical categories.]
Figure 4

![Graph showing VOC emissions from various studies over the years]

- **REAS**: Blue line and markers
- **MEIC**: Red line and markers
- **Wei et al. (2008)**: Green line and markers
- **Bo et al. (2008)**: Purple line and markers
- **Zhang et al. (2009)**: Light blue line and markers
- **Fu et al. (2013)**: Orange line and markers
- **Li (2012)**: Dark blue line and markers
- **This study**: Brown line and markers

Y-axis: VOC emissions (Gg)
X-axis: Years 2005 to 2014
Figure 5
Figure 6
Figure 7

(a) CB05

(b) SAPRC99
Figure 8
Figure 9

(a) and (b) Two maps showing VOCs emissions per tonne in different regions. The maps are color-coded to represent various emission levels, with darker colors indicating higher emissions. The legend includes categories for emissions ranging from 0 to 110,000 tonnes, with specific ranges for 0-500, 500-3000, 3000-6000, 6000-9000, 9000-15000, 15000-25000, 25000-40000, and 40000-110000 tonnes. A large point source is indicated by a symbol in one region.
Figure 9 (continued)

(c) VOCs emissions/t

-70000--50000
-50000--25000
-25000--5000
-5000--0
0-3000
3000-6000
6000-12000
12000-20000
20000-35000
35000-60000

Large point source
Figure 10

(a) Observations vs. simulations for 1-hour max O3 (mg/m³) from 6 January to 26 January.

(b) Observations vs. simulations for 1-hour max O3 (mg/m³) from 6 April to 26 April.

(c) Observations vs. simulations for 1-hour max O3 (mg/m³) from 6 July to 26 July.

(d) Observations vs. simulations for 1-hour max O3 (mg/m³) from 6 October to 31 October.