



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 (NMVOCs) are the key precursors of ozone (O₃) and secondary organic aerosol (SOA) formation. Accurate estimation of their emissions plays a crucial role in air quality simulation and policy making. We developed a high-resolution anthropogenic NMVOC emission inventory for Jiangsu in eastern China from 2005 to 2014, based on detailed information of individual local sources and field measurements of source profiles of the chemical industry. A total of 56 NMVOCs samples were collected in nine chemical plants and were 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 led 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 economies and industries. 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 NMVOC emissions vary slightly through the years, and the result for 2014 was –41 to +93%, expressed as 95% confidence intervals (CI). Reduced uncertainty was achieved compared to previous national and regional inventories, attributed partly 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 the chemical and refinery sectors with various data sources and methods. Compared with the 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 area for developed cities in southern Jiangsu. In addition,

discrepancies were found between this work and MEIC in the speciation of NMVOC emissions under the atmospheric chemistry mechanisms CB05 and SAPRC99. The difference in species OLE1 resulted mainly from the updated source profile of building paint use and the differences in other species from the varied sector contributions to emissions in the two inventories. The Community Multi-scale Air Quality (CMAQ) model simulation was applied to evaluate the two inventories, and better performance (indicated by daily 1 h maximum O₃ concentrations in Nanjing) were 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 (SOAs) 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 a heavy haze period in winter, based on detailed analysis on chemistry composition and the source 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 by maximum incremental reactivity, MIR), ozone (O₃) formation was recognized as VOC limited in developed areas including the 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 attention has 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, emissions of natural and anthropogenic origin were estimated close to each other at 10–30 Tg, and anthropogenic emissions were dominated by solvent use and industrial processes (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, NMVOC emissions in China were estimated to have doubled from 1990 to 2010, and the contributions of solvent use, non-combustion industrial processes and transportation were enhanced in 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, the largest estimations were made in the 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, anthropogenic NMVOC emissions were estimated to be 6–18 times those of natural origin 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, 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 industry plants were less investigated at local scale, resulting possibly in a big bias in emission estimation. Second, with varied data sources and methods, large discrepancies might exist between studies in the amount and spatial patterns of emissions. Such discrepancies were rarely analyzed, and the uncertainties in emission estimation at local scale were seldom quantified. In particular, the performance of chemistry transport modeling based on various NMVOC inventories has not been sufficiently evaluated. Moreover, chemical speciation of NMVOC emissions needs further improvement. Domestic measurements have increasingly been conducted on chemical profiles of NMVOCs for typical source categories 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 in limited studies (Li et al., 2014). In addition, the measurements on given sectors such as the chemical industry 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 NO_x (Zhao et al., 2014). Along with gradually reduced ambient PM levels in YRD, O₃ pollution has become a bigger concern for air quality improvement, motivating better understanding and control of NMVOC emissions. In this work, we select Jiangsu, a typical province with intensive refinery and chemical industries 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 Fig. S1 in the Supplement. Field measurements on the chemical composition of NMVOC emissions were conducted to obtain the source profiles of typical chemical industry processes. With detailed information of local emission sources collected and temporal changes tracked, a provincial emission inventory of speciated NMVOC was developed for a 10-year period (2005–2014), and the uncertainties of the emission estimation were quantified. Through a thorough comparison of 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

Chemical profiles of NMVOC emissions are still lacking for the chemical industry and oil exploitation and refinery in China due to a big variety of source categories. We select nine types of chemical engineering enterprises that are intensively distributed in Jiangsu to measure the chemistry composition of NMVOC emissions, as summarized in Table S2 in the Supplement. To our knowledge, no domestic measurement of NMVOC speciation has been conducted for those sources yet, and current work was expected to supplement the domestic source profiles for the chemical industry. 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 (see Table S2 for the details). Note that sampling could not be conducted for all processes in one 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 made out of stainless steel as its inner wall, and the volume and vacuum pressure range of the canister were 2 L and 1.1×10^{-4} kPa, respectively. For stack emission measurement, as shown in Fig. 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 min until the pressure in the canister became ambient. For fugitive emission measurement, the canister was placed 50 m downwind of the production device, and the sampling time was roughly 8 min. Repeated sampling was conducted for each process to eliminate the bias, and a total of 56 samples were obtained, as shown in Table S2.

NMVOC samples were analyzed by a gas chromatography – mass spectrometry (GC-MS) system (GC6890/MS5973i,

Agilent Technologies, USA), as illustrated in Fig. S2b in the Supplement. Firstly, the sample was pumped into a cryogenic preconcentrator with a three-stage trapping system. In the first stage, the VOC species were adsorbed on glass beads at -150°C and desorbed at 10°C . Vapor water was converted to solid water and was thus separated from the sample. In the second stage, the sample was trapped on Tenax at -30°C and desorbed at 180°C , and the target species were separated from CO_2 and other compositions in the air. In the third stage, the sample was focused on a transfer line at -160°C and heated rapidly to 70°C , and the species were concentrated. 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^{-1} and to 220°C at $15^\circ\text{C min}^{-1}$, holding 3 min. The VOC compounds were separated on a DB-5MS capillary column ($60\text{ m} \times 0.25\text{ mm} \times 1.0\ \mu\text{m}$) and quantified using a quadrupole mass spectrometer. The mass spectrometer was operated in SCAN mode and scanned 20–42 and 35–270 amu before and after 8.5 min, respectively. The ionization method was electron impacting, and the source temperature was 230°C . The PAMS (Photochemical Assessment Monitoring Station) 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 a 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

Different from national and regional inventories that relied mainly on energy and economic statistics, detailed information on individual emission sources was collected for Jiangsu, and interannual changes were tracked at plant level based on various databases. Those databases contained the multiple-year official environmental statistics (databases of emission sources routinely compiled by local environmental protection bureaus), Pollution Source Census (PSC, a thorough investigation of emission sources organized at national level), and on-site surveys of large emitters conducted by the local department of environmental supervision. 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, and the locations of those point sources are illustrated in Fig. S1. Incorporating the plant-by-plant information and the energy and industrial statistics

at provincial level, a four-level framework was established, covering all the anthropogenic NMVOC sources for Jiangsu, as summarized in Table 1. The framework included 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. The emissions of the province for 2005–2014 were calculated using the following equation:

$$E(n) = \sum_i AL(i, n) \times EF(i, n), \quad (1)$$

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 2, emission factors were collected from extensive literatures and determined as follows with descending priorities: (1) results from domestic measurements; (2) emission limits of local laws and regulations; (3) 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 domestic information was lacking. Details will be discussed by sector in Sect. 2.3.

The total NMVOC emissions for given source type were then broken down into individual species using Eq. (2):

$$E(i, k) = E(i) \times X(i, k), \quad (2)$$

where E is the emissions; i and k represent the source type and individual NMVOCs species, respectively; X is chemical profile of NMVOCs (%). To reduce the 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 OVOC fraction and averaging the fractions in different profiles for each species. As a more detailed source classification was applied in this work, some sources (e.g., biomass open burning, automobile production and repairing, and wood decoration and wooden furniture paint) were not covered by Li et al. (2014), and thus the results from SPECIATE (USEPA, 2014) were applied instead. We named the combination of Li et al. (2014) and SPECIATE as a source profile “before updating” hereinafter. While Li et al. (2014) included the source profiles published before 2011, a series of local measurements was conducted since then. In this work, therefore, “composite profiles” were updated following the method by Li et al. (2014). The most recent domestic results and the measurements conducted in this work were incorporated, as summarized by source types in Sect. 2.3.

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 (CB05 and SAPRC99) species by multiplying the emissions of individual species and mechanism-specific conversion factors using the following equation:

$$E(i, m) = \frac{E(i, k)}{M(k)} \times C(k, m), \quad (3)$$

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

The uncertainty of estimated provincial emissions was quantified using a Monte Carlo framework (Zhao et al., 2011) for each year. Probability distribution functions (PDFs) were determined for all the parameters involved in the emission calculation, and 10 000 simulations were performed to estimate the uncertainties of emissions. 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. The detailed information of PDF assumption will be provided by sector in Sect. 2.3.

2.3 Data sources of emission inventory development by category

2.3.1 Combustion sources (fossil fuel combustion and biomass burning)

For power sector and heating/industrial boilers, activity data were compiled at plant level based on the information obtained from environmental statistics, PSC and on-site surveys. The annual amount of residential fossil fuel combustion for 2005–2014 and that of biofuel use for residential stoves until 2008 were directly taken from Chinese official energy statistics (NBS, 2015a). As the data were unavailable for subsequent years for biofuel, 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). 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 field (Wang and Zhang, 2008; PGJP, 2009), as described in Zhao et al. (2011, 2013). Following the rules of IPCC (2006), the uncertainties of activity levels were determined according to the reliability of energy and economy statistics. As shown in Table S3 in the Supplement, normal distributions were assumed with the coefficient of variation (CV, the standard deviation divided by the mean) determined at 5, 10, 20 and 30 % for power, industrial, residential fossil fuel and biomass combustion sources, respectively.

As summarized in Table 2, 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), AP-42

Table 1. Categories of anthropogenic NMVOC emission sources.

Sector	Subsector	Product/fuel/solvent use	Product/technology	
Fossil fuel stationary combustion	Power plant	Coal/oil/natural gas/waste/biofuel	NA	
	Heating and industrial boiler	Coal/coke/oil/natural gas	NA	
	Residential	Coal/oil/liquified petroleum gas (LPG)/natural gas	NA	
Biomass burning	Boiler	NA	NA	
	Stove burning	Crop straw/wood	NA	
	Open burning	Crop straw	Rice/corn/wheat/other	
Industrial process	Iron and steel	Coking	Mechanical/indigenous	
		Sinter/pellet/crude steel	NA	
	Non-metallic mineral	Glass	Flat glass/glass fiber/glass work	
		Cement clinker/lime/brick and tile/ceramic	NA	
		Crude oil exploit/crude oil refinery	NA	
	Oil exploitation and refinery			
	Chemical industry	Chemical raw materials: ethylene/benzene/methanol/ acetic acid/synthesis ammonia/phthalic acid/ethylene oxide/vinyl acetate/styrene/glycol/octanol/butanol		NA
			Synthetic chemical industry: synthetic resin	Polyethylene/polypropylene/ Polystyrene/polyvinyl chloride
			Synthetic chemical industry: synthetic fiber	Viscose/cellulose acetate fiber/nylon fiber
		Synthetic chemical industry: synthetic rubber	NA	
		Fine chemical industry: pharmaceutical/chemical pesticide/paint/printing ink/adhesive/dye	NA	
		Food and wine	Fermentation alcohol/spirit/beer	NA
	Bread/cake/biscuit		NA	
Vegetable oil extraction	NA			
Plastic and rubber product	Foam plastic/plastic products/tire/other rubber product	NA		
Textile industry	Silk/cloth/woolen yarn	NA		
Carbon black		NA		
Solvent use	Paint use	Interior/exterior building coating	Water based/solvent based	
		Automobile production/repairing	NA	
		Wood decoration/wooden furniture paint	NA	
		Anticorrosive paint	NA	
		Other paint	NA	
		New-type/traditional ink	NA	
	Printing		NA	
	Dyeing		NA	
	Adhesive use	Shoe making/timber production/other	NA	
	Other solvent use	Agriculture pesticide/Dry cleaning/household solvent use/solvent degreasing	NA	
Transportation	On-road	Automobile	Load (light/heavy) fuel (gasoline/diesel)	
	Off-road	Motorcycle Train/inland ship/construction machine/tractor/ agriculture truck/agriculture machine	Gasoline NA	
Oil distribution	Crude oil/ gasoline/diesel	Storage/transport/load and unload/gas station	NA	
Others		Garbage disposal	Burning/landfill/compost	
		Cooking fume	NA	

Table 2. NMVOC emission factors for combustion sources, industrial processes and solvent use. Unless specifically noted, the units are g kg^{-1} (fuel), g kg^{-1} (products) and g kg^{-1} (solvents), respectively.

Source	Fuel/product/solvent use		EFs in this study	EFs in the references
Combustion				
Fossil fuel	Power plant	Coal	0.15	0.15 ^a , 0.81 ^b ; 0.02 ^c ; 0.03–0.03 ^d ; 0.02 ^e
		Fuel oil	0.09	3.88 ^b ; 0.04 ^c ; 0.12 ^d ; 0.09–0.14 ^e
		Natural gas (g m^{-3})	0.083	0.12 ^c ; 0.08–0.10 ^d ; 0.08–0.10 ^e
	Heating and industrial boiler	Coal	0.18	0.18 ^a ; 3.95 ^b ; 0.04 ^c ; 0.03–0.03 ^d ; 0.02 ^e
		Fuel oil	0.12	3.88 ^b ; 0.12 ^c ; 0.12 ^d ; 0.09–0.14 ^e
		Natural gas (g m^{-3})	0.094	0.1 ^c ; 0.08–0.10 ^d ; 0.08–0.10 ^e
	Residential	Coal	4.5	0.6 ^a ; 3.08 ^b ; 6.48, 4.98 ^g ; 4.5 ^c ; 6.41 ^d
		Fuel oil	0.35	0.35 ^c
		LPG	5.29	0.17 ^{a,b} ; 3.28 ^g ; 5.29 ^c ; 66 (g m^{-3}) ^e
		Natural gas (g m^{-3})	0.15	0.13 ^c ; 0.15 ^c ; 0.14 ^d ; 0.18 ^e
		Coal gas	0.00044	0.00044 ^a
	Biomass burning	Boiler	Biomass	1.1
Stove burning			3.23	1.09–4.94 ^g ; 3.23 ^c ; 5.3 ^e
Open burning		Crop straw	13.77	1.7–3.0 (corn straw) ^g , 8.89 (wheat straw) ^g ; 13.77 ^c ; 8.55 ^d ; 5.3 ^e
		Rice straw	7.48	7.48 ^h
		Wheat straw	7.48	7.48 ^h
		Corn straw	10.4	10.4 ^h
		Other straws	8.94	Average of straw open burning above
		Industrial process		
Iron and steel	Coking/sintering/steel		3.96/0.25/0.06	3.4 ^c ; 3.96 ^f /0.25 ^f /0.06 ^f
Non-metallic mineral	Flat glass/glass fiber/glass work		4.4/3.15/4.4	4.4 ^{c,f} ; 3.5 ^e /3.15 ^{a,i} /4.4 ^f
	Cement clinker/lime/brick and tile/ceramic		0.33/0.177/0.13/29.22	0.12 ^c ; 0.018 ^d ; 0.33 ^f /0.177 ^f /0.01 ^l ; 0.2 ^c ; 0.033 ^a ; 0.13 ^f /29 ^c ; 29.215 ^a ; 29.22 ^c
Oil exploitation/refinery			1.42/1.82	1.42 ^f /1.82 ^f ; 1.05 ^d ; 3.54 ^e
Chemical industry	Ethylene/benzene/methanol		0.097/0.1/5.95	0.097 ^f ; 0.6 ^d /0.1 ^f ; 0.25 ^j /5.95 ^f
	Polyethylene/polypropylene		10/8	10 ^{f,j} ; 0.33 ^e ; 3.4 ^d /8 ^{f,j} ; 0.35 ^e ; 4 ^d
	Polystyrene/polyvinyl chloride		5.4/3	5.4 ^f ; 0.21–3.34 ^e ; 0.12 ^d /3 ^{f,j} ; 0.33–8.5 ^e ; 0.096 ^d
	Acetic acid/ammonia/phthalic anhydride		1.814/4.72/21	1.81 ⁱ /4.72 ^{f,e} /1.1–6.3 ^e ; 1.3–6 ^d ; 2 ^j
	Ethylene oxide/vinyl acetate/styrene		3/4.705/0.223	3 ^f ; 0.98 ^e ; 2 ^d ; 4 ^j /4.705 ⁱ /0.223 ^f ; 1 ^d ; 3, 1 ^j
	Viscose fiber/cellulose acetate fiber/nylon fiber		14.5/73.4/3.3	14.5 ^{c,f} /73.4 ^f ; 112 ^e /2.13–3.93
	Polyester fiber/acrylic fibers polypropylene fiber		0.7/40/37.1	0.7 ^f ; 0.6 ^e /3.75–40 ^e /37.1 ^c
	Synthetic rubber		7.17	7.17 ^{f,e} ; 3.8–8.6 ^e ; 0.27–9 ^d
	Pharmaceutical/chemical pesticide		430/20	430 ^{f,e} ; 300 ^d /20 ^k
	Paint/printing ink/adhesive/dye/pigment		15/50/30/81.4/10	15 ^{f,e} ; 11 ^d /50 ^f ; 60 ^e /30 ^c ; 20 ^f /81.4 ^f /10 ⁱ

Table 2. Continued.

Source	Fuel/product/solvent use	EFs in this study	EFs in the references
Industrial process			
Plastic and rubber	Foamed plastic/plastic products	120/3.2	770 ^c ; 120 ^d /3.2 ^{f,j}
	Tire/other rubber products	0.91 (kg tire ⁻¹)/12.5	0.285 (kg tire ⁻¹) ^m ; 0.285 (kg tire ⁻¹) ^l ; 0.91 (kg tire ⁻¹) ^f ; 10 ^d ; 0.659 ⁱ /12.5 ^c
Food and wine	Fermentation alcohol/white spirit	60/25	218.25 ^f ; 60 ^d /25.35 ^l ; 25 ^{c,f} ; 150 (g L ⁻¹) ^d ; 33.105 (g L ⁻¹) ⁱ
	Beer/grape wine	0.25/0.5	0.44 ^l ; 0.4 ^c ; 0.43 (g L ⁻¹) ^a ; 0.25 ^f ; 0.35 (g L ⁻¹) ^d /0.81 ^l ; 0.5 ^{c,f} ; 0.8 (g L ⁻¹) ^d ; 0.38 (g L ⁻¹) ^e
	Cake and biscuit	1	1 ^{l,c,d,f}
	Vegetable oil extraction	3.7	3.45–10.35 ^l ; 5.5 ^c ; 3.45 ^a ; 1.57 (g L ⁻¹) ^d ; 4 ⁱ
Textile industry	Silk/cloth/woolen	10/10/10	10 ^b /10 ^b /10 ^b
Carbon black	NA	64.7	90 ^m ; 73.2 ^l ; 64.7 ^c ; 52 ^f ; 0.7 ^d ; 53.57 ^e ;
Solvent use			
Printing	New-type/traditional ink	100/750	100 ^f ; 150 ^c /750 ^f ; 650 ^c , 500
Dyeing	–	81.4	81.4 ^{e,f}
Paint use	Interior wall painting	250; 120 ^o	250 ^c /120 ⁿ
	Exterior wall painting: aqueous/solvent	120/580	120 ^f /360 ^f ; 585 ^c ; 580 ⁿ ; 230 ^d
	Vehicle manufacture/refinishing	470/720	460 ⁿ ; 470 ^c ; 475 ^l /720 ^{c,d} ; 850 ^l
	Furniture: aqueous/solvent based	250/670	250 ^c /640 ^f ; 637 ⁿ ; 550–750 ^c ;
	Anticorrosive paint use	442	442 ^c
	Other paint use	240	240 ^c
Adhesive use	Shoe making	670	664 ⁿ ; 670 ^c
	Timber production	90	88 ⁿ ; 90 ^c
	Other adhesive use	89	89 ^c ; 85 ^l
Other solvent	Agriculture pesticide	470	368–482 ^c ; 356–576 ^f
	Dry cleaning	0.16 ^p	0.8 ^e ;
	Household solvent use	0.08	0.08 ^f ; 3.7 ^d ; 4.2 ^e ; 0.1 ^a
	Degreasing	0.044	0.044 ^{a,f}

^a Bo et al. (2008). ^b Tang and Chen (2002). ^c Wei et al. (2008), Wei (2009) and Wang et al. (2009). ^d EEA (2013). ^e USEPA (2002). ^f MEP (2014). ^g Zhang et al. (2000). ^h Li et al. (2007). ⁱ ROC EPA (2009). ^j Fan et al. (2012). ^k Xia et al. (2014). ^l Wang (2006). ^m Klimont et al. (2002). ⁿ Fu et al. (2013). ^o 250 and 120 g kg⁻¹ for 2005–2007 and 2008–2014, respectively. ^p adjusted by per capital income.

database were also applied when domestic results were lacking. For residential combustion of fossil fuel, emission factors from domestic tests (Zhang et al., 2000; Wang et al., 2009) were used. Wang et al. (2009) measured the NMVOC emission characteristics of multiple stove–biofuel combinations in China, and the obtained emission factors were used in this work. For biomass open burning, the local test results by Li et al. (2007) were applied. Chemical profiles were updated by incorporating domestic measurements for residential fossil fuel and biofuel burning (Tsai et al., 2003; Liu et al., 2008; Wang et al., 2009; H. Wang et al., 2014a) and biomass open burning (Zhang et al., 2013; Kudo et al., 2014). As measurement results were insufficient for data fitting, un-

certainty of the emission factor was evaluated depending on expert judgment for combustion sources (Streets et al., 2003; Wei et al., 2011). The PDF of the emission factor was given according to reliability of data sources and/or the robustness of calculation methods (Wei et al., 2011; also the case for other sources as indicated below). As summarized in Table S4 in the Supplement, lognormal distributions were assumed with CVs set at 150 and 200 % for fossil fuel and biomass burning, respectively.

2.3.2 Industrial processes

Similar to power and industrial combustion, the activity levels of industrial processes were mainly collected at plant level by source category. However, small discrepancies existed between the compiled data at plant level and the officially reported production from economic statistics at provincial level (NBS, 2015b). In 2012, for example, the steel production aggregated from individual plants accounted for 98 % of the provincial total production (Zhou et al., 2017). In this work, we treated the individual plants as point sources, and the fraction that was not covered in plant-by-plant databases as area sources. We assumed the PDFs of industrial production to have a normal distribution, with CVs at 10 and 20 % for point and area sources, respectively.

Attributed to a wide variety of manufacturing procedures and complicated VOC exhaust processes, there were few local tests available on emission factors prior; thus, the values from expert judgment (i.e., data from routine investigations reported by the factory officials to local environmental protection bureaus) and data from AP-42 and EMEP/EEA had to be applied, as summarized in Table 2. Source profiles of chemical production including rubber, polyether and polyethylene were obtained from our measurements described in Sect. 2.1. Chemical profiles from the most recent domestic measurements were taken for other sources including iron and 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) and refineries (Liu et al., 2008; Wei et al., 2014). For sources without sufficient local tests (e.g., food and wine production), results from foreign studies were applied including the SPECIATE database by USEPA (2014) and Theloke and Friedirch (2007). Given the potential large uncertainties, a lognormal distribution with the CV set at 500 % (i.e., a long-tailed PDF) was assumed for emission factors for most industrial processes.

2.3.3 Solvent use

Although solvent-use enterprises were contained in the plant-by-plant surveys, many of them failed to report the actual solvent usage. Underestimation of activity levels and thereby emissions could be expected if the information at plant level was relied on. As the solvent usage was not directly reported at city level, we followed Wei (2009) to estimate the activity levels for the sector. The total solvent consumption at national level was first obtained according to the solvent production and imports and exports statistics (CNLIC, 2015; GAC, 2015). The provincial level was then calculated based on the intensities of activities that consume solvents (e.g., building construction and vehicle production). Finally, the provincial data were allocated to point sources according to production of individual plants and area sources according to distribution of industrial gross domestic product (GDP). Normal and lognormal distributions with CVs set at 20 and

80 % were applied for the activity levels of point and area sources of solvent use, respectively, indicating much larger uncertainty for the latter (Wei, 2009).

The VOC contents of solvents were limited by national laws and regulations, as summarized by Wei et al. (2008). The updating of regulations and their impacts on interannual changes in NMVOC emission factors were considered from 2005 to 2014, such as GB18583-2003 and GB18583-2008 for indoor painting. Bias needs to be admitted here, and possible underestimation of emissions would be expected for the sector, as the regulations were not strictly enforced particularly for small solvent-use enterprises and construction sites (area sources). Data from AP-42, EMEP/EEA and other literature (Bo et al., 2008; Fu et al., 2013) were applied when local information was missing, as provided in Table 2. The domestic tests on chemical species (Yuan et al., 2010; Zheng et al., 2013; H. Wang et al., 2014b) were included to update the source profiles of the sector. For uncertainty of the emission factors, a uniform distribution was tentatively applied (Table S4).

2.3.4 Transportation

The activity data of off-road transportation for 2005–2010 was taken from Zhao et al. (2013), and the data for other years were scaled according to the changes in passenger and freight traffic by rail and shipping, and those in numbers of agricultural and construction equipments (NBS, 2015c). For on-road transportation, activity data (total kilometers traveled) by vehicle type and control stage were calculated as the product of vehicle population and annual average kilometers traveled (VKT). The fleet composition by control stage was obtained from the survey by local government (internal data; Zhao et al., 2015), and VKTs by vehicle type were determined according to previous studies (Cai and Xie, 2007; Wang et al., 2008) and the guidebook of emission inventory development for Chinese cities (He, 2015). While the CV of transportation activities at national level was estimated at 16 % (Zhao et al., 2011), larger uncertainties were assumed at provincial level (Wei, 2009). We followed Wei (2009) and assumed normal and lognormal distribution with CVs at 30 and 50 % for on-road and off-road transportation, respectively.

For emission factors of off-road transportation, the data from EMEP/EEA and expert judgment (Wei et al., 2008; Q. Zhang et al., 2009) were adopted, attributed to a 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. (4):

$$EF = BEF \times \varphi \times \gamma \times \lambda \times \theta, \quad (4)$$

where BEF is the base emission factor, φ is the environmental correction factor, γ is the average traveling speed correction factor, λ is the vehicle deterioration correction factor and θ is the correction factor for other conditions (e.g., vehicle

loading and fuel quality). Domestic tests on chemical compositions (Liu et al., 2008; Tsai et al., 2012; Huang et al., 2015; Wang et al., 2013; Ou et al., 2014; Gao et al., 2012) were incorporated to update the source profile of on-road vehicles. Lognormal distributions with CVs at 150 and 300 % were, respectively, assumed for emission factors of on-road and off-road transportation.

2.3.5 Oil distribution and other sources

For oil distribution, Wei (2009) developed a simplified model to simulate the oil storage, transport and sale activities based on the provincial energy balance statistics, and the model was applied in this work to calculate the activity levels for the sector. Activity data from other sources were directly taken from official provincial statistics (NBS, 2015b, c). Emission factors of oil distribution and other sources were obtained from Wei et al. (2008) and Xia et al. (2014), and lognormal distributions were assumed for them as summarized in Table S4. The source profiles were obtained from Liu et al. (2008) and SPECIATE.

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 a total of 61 species detected by GC-MS systems, the chemistry components were grouped into six types (alkanes, alkenes, halohydrocarbon, aromatics, OVOCs and others), as illustrated in Fig. 1a. Alkanes were the main species of synthetic rubber industry (SBR, SIS rubber and SEBS rubber), with the mass fractions over 70 %. For production of cellulose acetate fiber, alkanes, aromatics and OVOCs were the main species in the process of acetate flake production, while OVOCs dominated in the spinning process. Resulting from various raw materials, the source profiles of the two types of polyether production differed a lot: the mass fraction of OVOCs was close to 80 % for polypropylene glycol (PPG), while the main species for polyether polyol (POP) were others, aromatics and halohydrocarbon. For ethylene production, aromatics mainly composed 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 S5 and S6, 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. In addition, 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 the 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 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. The 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 SPECIATE for synthetic rubber, ethylene and polyethylene production, as illustrated in Fig. 1b–d, respectively. As can be seen in Fig. 1b, large discrepancy was found for source files of SBR between this work and SPECIATE: 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. SPECIATE targeted emulsion polymerization technology in which solvents were not used, and 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 Fig. 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. Different compositions were 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 (Fig. 1d).

3.2 Interannual trends and sectoral contribution of NMVOC emissions

As shown in Table 3, 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, emission contributions from

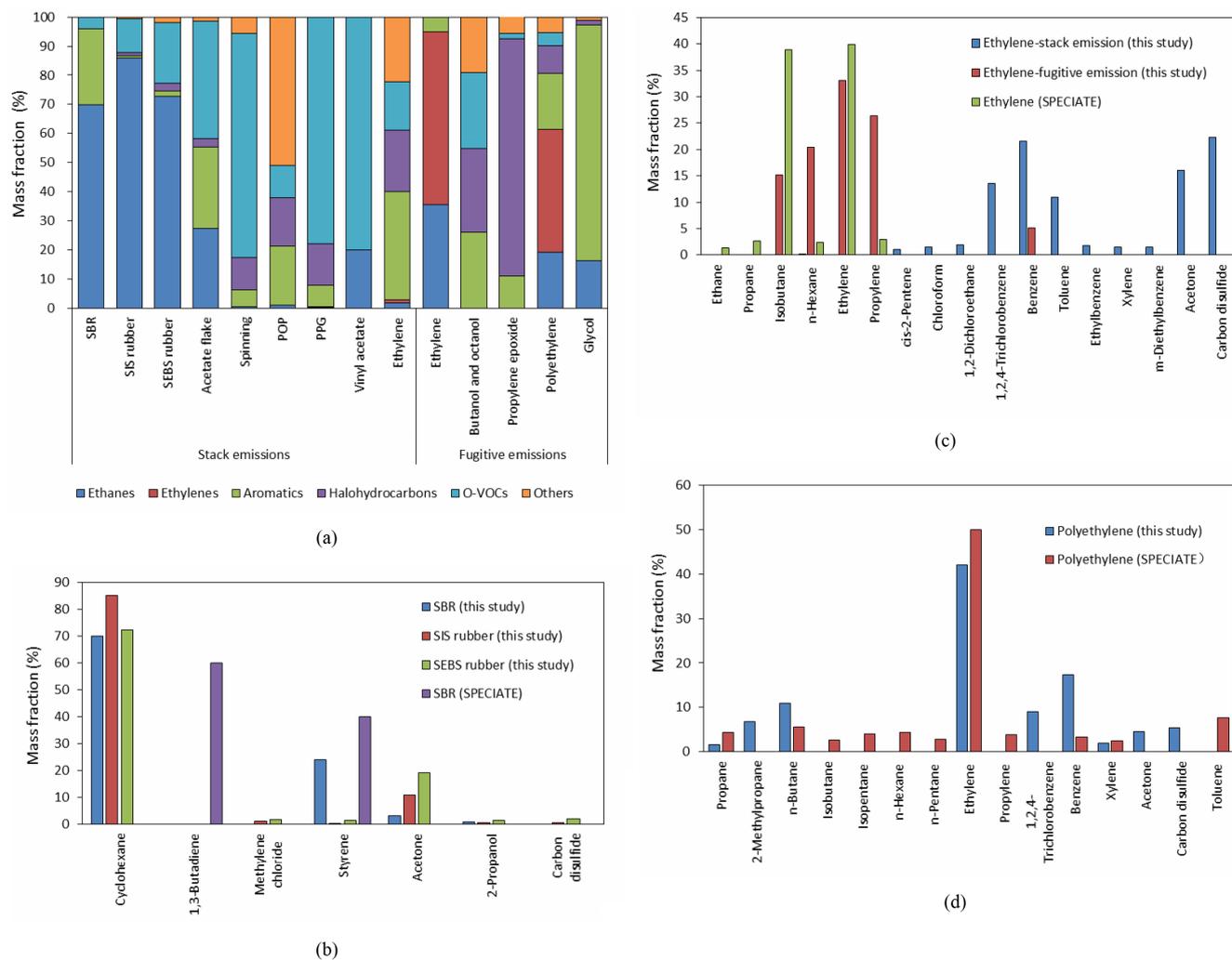


Figure 1. NMVOC source profiles by grouped species measured in chemical enterprises (a) and the comparisons with SPECIATE results for synthetic rubber (b), ethylene (c) and polyethylene production (d).

Table 3. Anthropogenic NMVOC emissions in Jiangsu by source from 2005 to 2014 (Gg).

Source	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014
Fossil fuel combustion	43	43	45	47	48	50	54	54	58	59
Industrial process	461	580	616	626	722	823	747	821	871	958
Transportation	325	321	336	331	331	317	313	302	311	280
Solvent use	380	441	492	495	606	652	697	783	809	966
Oil distribution	35	35	39	42	46	53	56	64	59	53
Biomass burning	458	343	355	147	139	131	126	119	116	110
Other	72	73	74	74	75	76	77	78	78	79
Total	1774	1835	1956	1762	1967	2102	2071	2220	2302	2507

transportation and biomass burning declined 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 provide the interannual trends in emissions of subcategories for industrial processes, solvent use and transportation. The emissions from industrial processes were estimated to double from 2005 to 2014, and the interannual trend in emissions was well correlated with that in industry GDP (Fig. S3a). The comprehensive investigations on point sources indicated that few measures were implemented to control NMVOCs until 2014, and the increased emissions were thus mainly driven by the growth of industry activities. The largest growth was found for synthetic and fine chemical industries, with the emissions elevated from 130 in 2005 to 361 Gg in 2014. Due to enhanced coking industry, the emissions of iron and 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 (Fig. S3b). Despite the 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 120 g kg⁻¹ since 2008), it was still difficult to restrain the emissions under the fast growth of solvent use, as relevant policies 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 Gg in 2007 (Fig. S3c). The implementation of staged emission standards (State I–V, equal to Euro I–V) on new vehicles and the reduced motorcycle population were the main reasons for the declining emissions. For example, emissions of motorcycles decreased 66 % from 185 to 64 Gg, and their contribution to on-road vehicle emissions declined as well from 62 to 31 %. Gasoline vehicles dominated the emissions of on-road transportation, with the fraction ranging 81–87 % during the study period.

Illustrated in Fig. 2 are the spatial distributions of Jiangsu's NMVOC emissions for various years within a 3 × 3 km grid system. The emissions of point sources were directly allocated according to their geographic locations. For other sources, certain proxies were applied to allocate emissions, including GDP for industrial area sources and oil distribution, population for solvent-use area sources, road net and traffic flow for on-road vehicles, railway and canal net for off-road transportation and rural population for biomass burning. High emission intensities were mainly found in relatively developed cities along the Yangtze River in southern Jiangsu including Nanjing, Suzhou, Wuxi and Yangzhou (see Table S7 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 the

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 (Fig. 2d). Moreover, reduced emissions coincided with road net distribution, implying the benefit of emission controls on vehicles.

3.3 Speciation and OFPs of NMVOC emissions

Table 4 compares the source profiles of this work with those of Li et al. (2014) or SPECIATE for typical source categories, 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. Based on the source profiles, emissions of more than 500 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 between 26–30, 13–19, 21–23, 18–21, 3–4 and 11–12 %, respectively.

Shown in Fig. 3 are the mass fractions of species by source category for 2014. Due to varied fuel qualities and combustion conditions, large differences in emission speciation were found for fossil fuel combustion, transportation and biomass burning. The profile of fossil fuel stationary sources was dominated by coal combustion, 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 the chemical industry, the largest emission source of industrial processes, i.e., 19, 15, 11, 10 and 10 % for 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. As the chemical profiles of emitted NMVOCs vary between source categories, the OFP-to-emission ratio for a given category could indicate the potential contribution to ozone formation of the category, as a

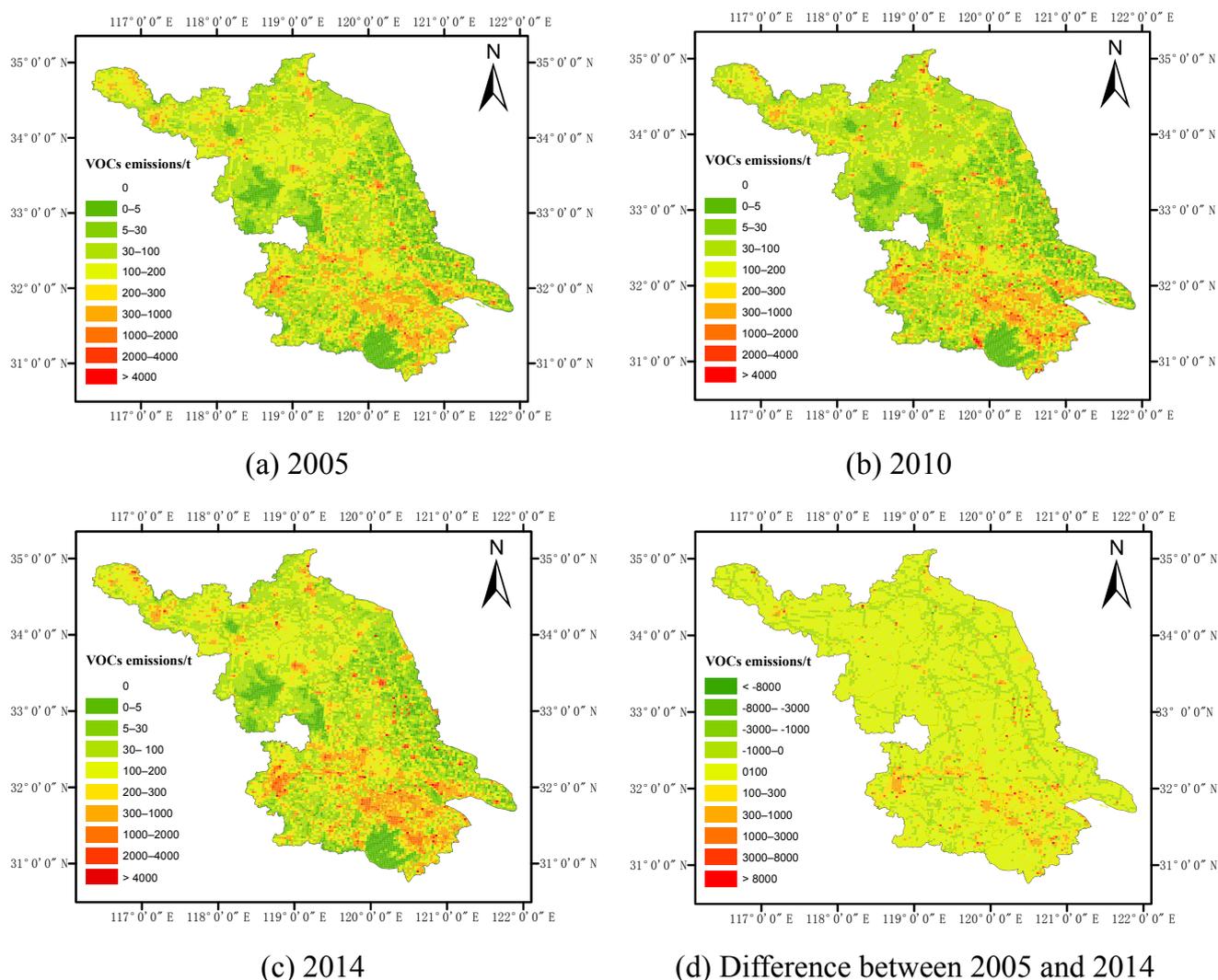


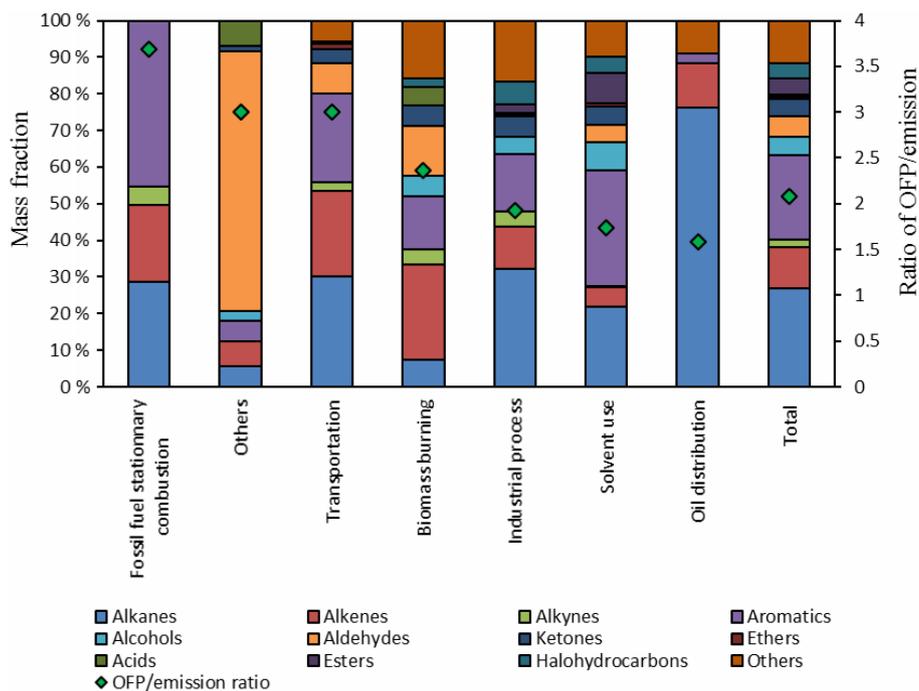
Figure 2. Spatial distribution of Jiangsu's anthropogenic NMVOC emissions (3×3 km) for 2005 (a), 2010 (b) and 2014 (c), and the differences between 2005 and 2014 (2005 data subtracted from 2014 data; d).

combined effect of multiple species emitted. The priorities of emission control for ozone abatement could thus be suggested by the ratio. The ratios for 2014 were provided by source in Fig. 3. With abundant aromatic and alkene 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 aromatic and aldehyde 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 (Fig. S4a). Xylene, ethylene and propylene were identified as the most three important species in

terms of OFP. The aromatic species with (e.g., xylene and toluene) came largely from solvent use and industrial processes, while alkene species (e.g., ethylene and propylene) were mainly from industrial processes, biomass burning and transportation. In addition, 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 (Fig. 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 one of the 25 most important species to OFPs any more.

Table 4. Updated NMVOC source profiles in this study and those from SPECIATE and Li et al. (2014).

Sector		Species (weight percentage, %)					
		Alkanes	Alkenes	Alkynes	Aromatics	OVOCs	Others
Biomass open burning	This study	14.83	17.24	2.20	10.98	52.58	2.16
	SPECIATE	14.20	20.59	2.62	1.82	57.68	3.08
Coking	This study	25.65	25.00	1.34	25.42	1.43	21.16
	SPECIATE	9.17	39.45	2.14	49.24	0.00	0.00
Iron and steel	This study	25.64	11.23	15.56	13.60	2.36	31.62
	SPECIATE	28.06	16.67	27.72	0.00	0.00	27.56
Paint production	This study	3.90	0.00	0.00	48.61	42.76	4.72
	SPECIATE	0.00	0.00	0.00	80.65	19.35	0.00
Ink production	This study	54.48	15.27	0.00	30.25	0.00	0.00
	SPECIATE	5.00	0.00	0.00	6.50	63.00	25.50
Refinery	This study	77.02	12.10	0.00	10.89	0.00	0.00
	Li et al. (2014)	67.57	9.44	0.91	1.96	0.00	20.12
Furniture painting	This study	6.15	0.14	0.00	61.61	29.23	2.87
	SPECIATE	0.00	0.00	0.00	30.00	51.42	18.58
Architecture painting	This study	28.69	9.39	0.00	61.92	0.00	0.00
	Li et al. (2014)	27.48	4.71	0.00	67.81	0.00	0.00
Vehicle varnish paint	This study	3.65	0.55	0.06	59.09	32.02	4.64
	Li et al. (2014)	2.14	0.82	0.08	96.96	0.00	0.00
Printing	This study	29.54	2.90	0.69	16.64	44.89	5.33
	Li et al. (2014)	14.78	2.79	0.66	11.03	26.96	43.78
Diesel vehicle	This study	44.30	22.41	1.79	20.10	11.39	0.00
	Li et al. (2014)	14.88	11.60	0.83	8.99	48.99	14.71
Motorcycle	This study	41.36	23.36	2.11	28.50	4.68	0.00
	Li et al. (2014)	45.88	32.18	0.56	21.37	0.00	0.00

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

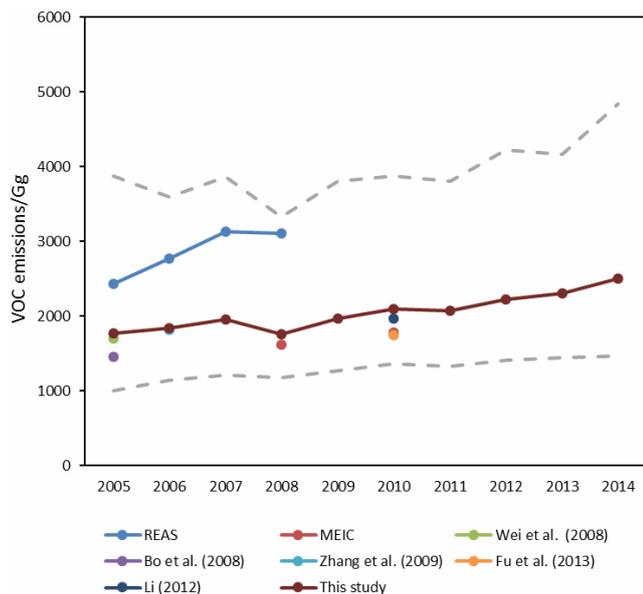


Figure 4. The interannual trends in anthropogenic NMVOC emissions in Jiangsu from 2005 to 2014. The grey dotted lines indicate the 95 % CIs of emissions estimated in this study. The results from other inventories are illustrated as well for comparison.

3.4 Uncertainties of provincial NMVOC emission inventory

The uncertainties of estimated annual NMVOC emissions for Jiangsu in 2005–2014 are illustrated in Fig. 4, expressed as the 95 % confidence intervals (CIs) around the central estimates. As interannual changes were hardly assumed in probability distributions for parameters, similar uncertainty ranges were calculated for emissions of various years. As shown in Table 5, the uncertainty of emissions for 2014 was quantified at –41 to +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 tests on emission factors for industrial and residential sources. As described in Sect. 2.3, large uncertainties had to be conservatively assumed for them due to limited domestic samples and heavy dependence on foreign databases. More measurements on actual emission characteristics are thus recommended to expand data samples for better evaluating the PDFs and effectively reducing emission uncertainty. Regarding solvent use, which provincial and city statistics were lacking, the activity data had to be downscaled from national level leading to possibly a big bias in emission estimation.

* The ratio of straw burned in stoves as biofuel.

Source category	Uncertainty					Parameters contributing most to uncertainty	
	This work Provincial scale	Wei (2009) National scale	Bo et al. (2008) National scale	Fu et al. (2013) Regional scale	Huang et al. (2011) Regional scale	This work Provincial scale	This work Provincial scale
Fuel stationary combustion	–66 %, +190 %	–	–	–	–	EF _{Power plant, coal} (68 %)	EF _{Industrial boiler, coal} (6 %)
Industrial process	–58 %, +152 %	–88 %, +283 %	–	–57 %, +152 %	–60 %, +152 %	EF _{Tire} (23 %)	EF _{Coking} (13 %)
Solvent use	–68 %, +131 %	–82 %, +223 %	–	–60 %, +147 %	–59 %, +150 %	AL _{External wall paint} (20 %)	EF _{Other paint} (14 %)
Transportation	–51 %, +117 %	–86 %, +261 %	–	–	–	EF _{Inland ship} (13 %)	EF _{Construction machine} (8 %)
Oil distribution	–66 %, +162 %	–	–	–	–	EF _{Crude oil storage} (27 %)	EF _{Gasoline sale} (23 %)
Biomass burning	–76 %, +499 %	–	–	–	–	EF _{Straw–stove} (74 %)	R* _{Straw burning in stove} (5 %)
Other	–98 %, +490 %	–	–	–	–	EF _{Cooking} (84 %)	EF _{Garbage burning} (14 %)
Total	–41 %, +93 %	–51 %, +133 %	–36 %, +94 %	–52 %, +105 %	–53 %, +113 %		

Table 5. 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 in 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 comparison.

Also provided in Table 5 are the uncertainties of national and YRD emissions from other studies. Note that all the studies applied the Monte Carlo simulation except that of Huang et al. (2011), which calculated the uncertainty of emissions based on the predetermined CVs of emission factors and activity levels at sector level. Compared with those results, the emission uncertainties were reduced in this work for industrial processes, solvent use and transportation. Besides the varied methods and assumptions of PDFs for relevant parameters, the more detailed classification of emission sources and adoption of independent emission factors for those sources should be an important reason. For example, in total, 34 vehicle-type control combinations were taken into account for calculating the on-road vehicle emissions, and the emission factor for each type of combination was assumed independent from the others. In addition, the errors of activity levels for big point sources were significantly reduced from the detailed investigation and on-site surveys 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 a part of the industrial processes, chemical and refinery industries were one of the biggest contributors to anthropogenic NMVOC emissions. We select Nanjing, the capital city of the Jiangsu province, to evaluate the impacts of data sources and methods on emissions of this category. As described in Sect. 2.2 and 2.3, the method used in this work for provincial inventory improvement incorporated the most available information from environmental statistics, PSC and on-site surveys (named Method 1 here). In addition, two other methods based, respectively, on data from environmental statistics (Method 2) and economic statistics without any information on individual plants (Method 3, which was commonly applied in national and regional inventories) were also applied to calculate the emissions in the city for 2011, and the results with different methods were compared against each other. Note that the emissions of area sources (i.e., not included in plant-by-plant investigations) in Methods 1 and 2 were the same as in Method 3. Table S8 in the Supplement provides the emissions calculated based on the three data sources by the subcategory of the chemical and refinery industries. The emissions estimated using Method 1 were clearly larger than those using Methods 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 amount (more than 100 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 in the three methods are illustrated in Fig. 5. Similar patterns were found for Methods 1 and 2 (Fig. 5a and b), as the emissions were dominated by the big chemical and refinery plants. As labeled in Fig. 5a, the largest 10 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 would overestimate the fraction of emissions in urban downtown (Fig. 5c). The comparison indicated the possible errors in spatial distribution of emissions at small scale when emissions were downscaled from larger scale without sufficient investigation of local sources, particularly for regions where large plants 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 the device-operation-based method herein). As indicated in Table S9 in the Supplement, detailed information of 15 key chemical and refinery enterprises in Nanjing (i.e., enterprises directly under the control of the city government) were collected and the emissions of those plants were calculated and compared with the results using the method as described in Sect. 2.2 and 2.3 (mentioned as the 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 the device-operation-based method, as the emission factors for production of chlorobenzene alkylbenzene and cyclohexanone were lacking, leading to underestimation of the emission-factor-based method. As shown in Fig. 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.

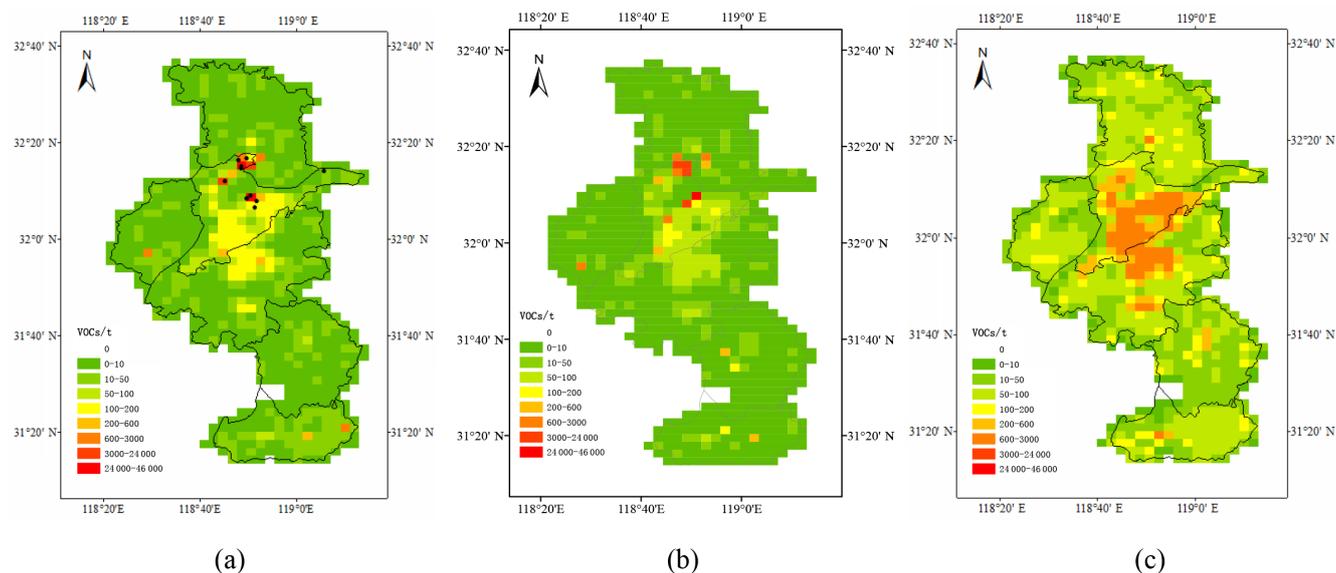


Figure 5. Spatial distributions of NMVOC emissions from the chemical and refinery industries for Nanjing 2011 (3×3 km), estimated using the detailed enterprise information (a), environmental statistics (b) and economic statistics without any information on individual sources (c). The black dots indicate the largest 10 emitters in the city

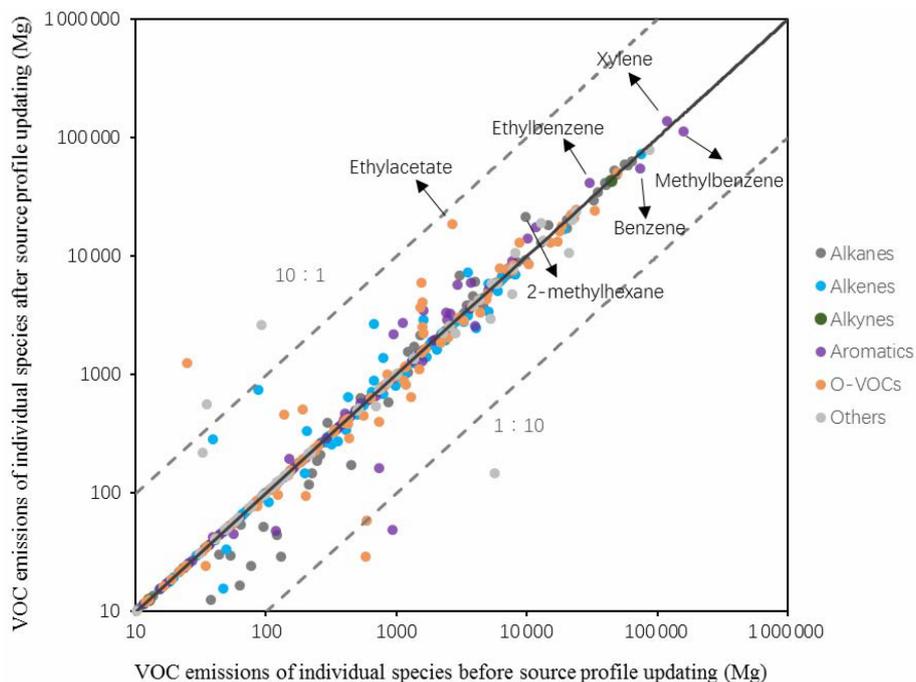


Figure 6. Emissions of NMVOC species for Jiangsu in 2010 before and after source profile updating.

4.2 Changes in speciation of NMVOC emissions

As indicated in Sect. 2.2, the speciation of NMVOC emissions in Jiangsu were updated by including our measurements and other more recent domestic tests after 2010, based on the combined profile of Li et al. (2014) and SPECIATE (i.e., the source profile before updating). The source types we

measured accounted for 9–11 % of annual NMVOC emissions from chemical industry and refinery for Jiangsu in 2005–2014. In particular, the contribution of those sources was enhanced in typical cities with intensive chemical industry. In Nanjing, as an example, the source categories we measured accounted for 19 % of annual emissions from chemical industry and refinery, and for 10 % of the total anthro-

pogenic emissions in 2010. Figure 6 illustrates the emissions of 445 species (accounting for 99.5 % of total NMVOC emissions) estimated with the source profile before and after updating for Jiangsu in 2010. As a whole, the difference between emissions of all species before and after updating was calculated at 281 Gg, i.e., 13 % of the total anthropogenic NMVOC emissions for the province. Due to relatively limited tests available, the changes in emissions were small for most species when updated profiles were applied. Relatively big changes (over 10 Gg) were found for ethylacetate and certain aromatic species (benzene, xylene, ethylbenzene and methylbenzene). Applying the source profile of paint use measured by Zheng et al. (2013) led to enhanced ethylacetate. Reduced benzene and methylbenzene, and elevated ethyl benzene and xylene resulted mainly from the revisions on source profiles of cooking (Jia et al., 2009; Shi et al., 2015) and solvent use (H. Wang et al., 2014b; Zheng et al., 2013). Although incremental information on speciation was obtained through the on-site measurements and source profile updating in current work, domestic data were still lacking for many source types, given the big variety of source categories for industrial process and solvent use. Therefore, more efforts in field measurements are still needed in order to establish a more complete database of chemical profiles for the country and the region.

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 Fig. 7 (the speciation for MEIC is illustrated in the figure as well for comparison, as discussed later in Sect. 4.3). With source profiles updated based on the most recent measurements, relatively big changes were found for ALDX (see the caption of Fig. 7 for the detailed meanings) in CB05 and OLE1 in SAPRC99. The revisions of 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), while increased OLE1 to that of building coating (Yuan et al., 2010; H. 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 in Fig. 4. All the results were within the 95 % CIs in this work. Except for REAS, which provided 37–77 % higher emissions than this work for 2005–2008 (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 NMVOC emissions by source from various inventory studies for selected years. As

can be seen, the emissions in this work were 4 and 20 % larger than the national inventory for 2005 (Wei et al., 2008) and regional inventory for 2010 (Fu et al., 2013), respectively. 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), and glasswork, pesticide and charcoal were not included 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 use 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 we did, 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 Fig. 7. While total NMVOC emissions in this work were 315 Gg or 18 % larger than MEIC for 2010, relative changes varied among species and could be bigger for certain species. In the CB05 mechanism, our results were 46 and 43 % smaller for TOL and XYL but 38 and 59 % larger for ETH and ETHA than MEIC (Fig. 7a), while discrepancies of over 30 % (relative to MEIC) existed for most species in SAPRC 99 (Fig. 7b). Such discrepancies could result either from the various source profiles or from the various source contributions to total emissions. For example, with the updated source profile for building coating, much larger OLE1 emissions were estimated in this work than in MEIC. Besides the total emissions, the different speciations under chemical mechanisms could result in complex impacts on air quality simulation and will 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 (Fig. 2) was upscaled to $0.25^\circ \times 0.25^\circ$, 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 Fig. 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 complete investigation of product types and activity levels at plant level on the emission estimation. Although our result was 18 % larger than MEIC in total anthropogenic NMVOC emissions, lower emissions were found in this work in 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

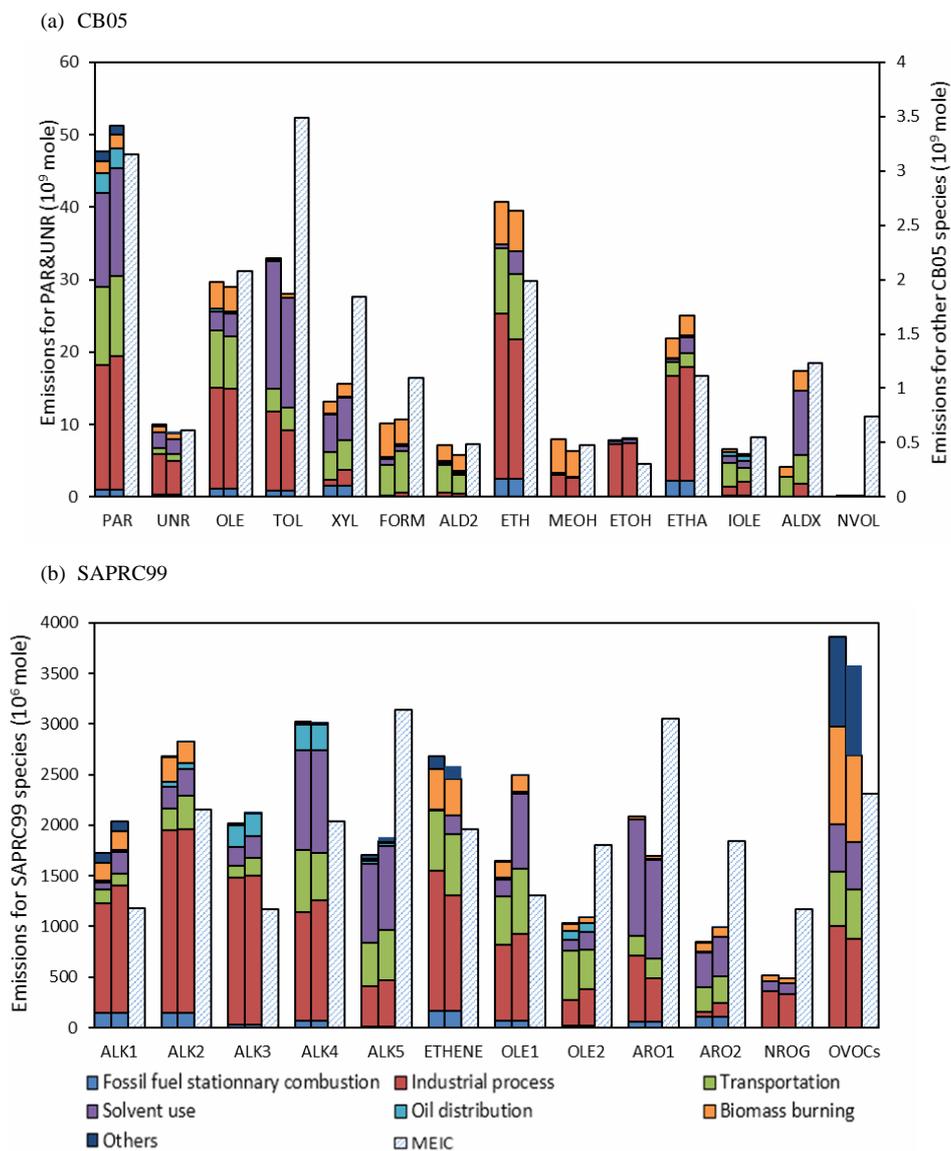


Figure 7. Emissions of CB05 (a) and SAPRC99 (b) species for Jiangsu in 2010. The left and middle columns indicate the results before and after updating of source profiles, and the right columns indicate the results of MEIC. The CB05 species PAR stands for the paraffin carbon bond, UNR for unreactive parts of molecules, OLE for terminal olefin carbon bond, TOL for toluene and other monoalkyl aromatics, XYL for xylene and other polyalkyl aromatics, 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 and NVOL for non-volatile 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 k_{OH} between 2 and 500, 500 and 2500, 2500 and 5000, 5000 and 10 000, and greater than 10 000 $\text{ppm}^{-1} \text{min}^{-1}$, respectively. ETHENE stands for ethane and OLE1 for alkenes with k_{OH} smaller than 70 000 $\text{ppm}^{-1} \text{min}^{-1}$, OLE2 for alkenes with k_{OH} greater than 70 000 $\text{ppm}^{-1} \text{min}^{-1}$, ARO1 for aromatics with k_{OH} smaller than 20 000 $\text{ppm}^{-1} \text{min}^{-1}$, ARO2 for aromatics with k_{OH} greater than 20 000 $\text{ppm}^{-1} \text{min}^{-1}$ and NROG for unreactive mass.

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 performance of chemistry transport simulations with various NMVOC emission inventories for the Jiangsu area. As shown in Fig. S6 in the

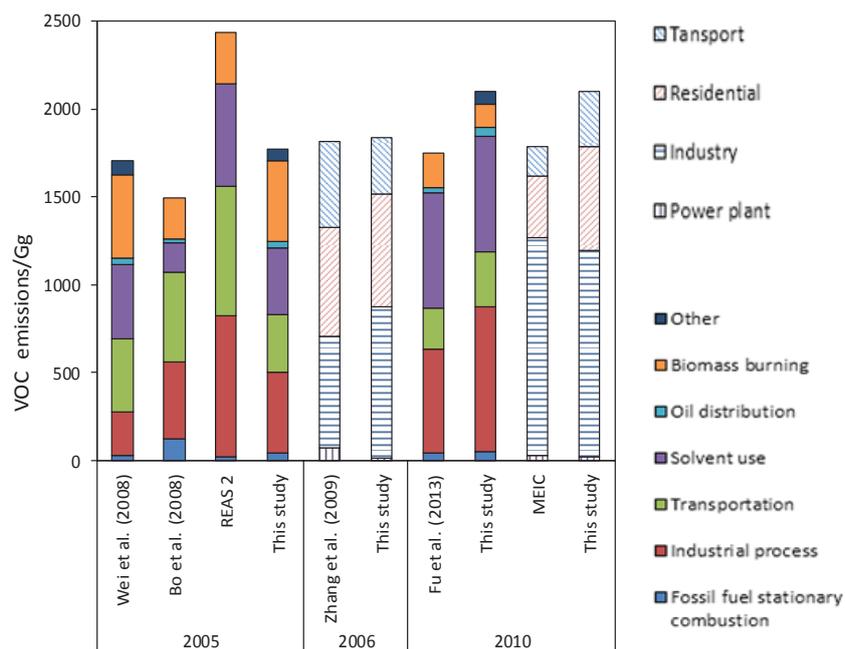


Figure 8. Jiangsu's anthropogenic NMVOC emissions by sector for selected years estimated from this work and other inventories. Note that emissions in this work are regrouped to be consistent in source categories with Zhang et al. (2009) and MEIC for direct comparison.

Supplement, three nested domains (D1, D2 and D3) were set, and the most inner D3 covered the megacity Shanghai and the 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 simulations were conducted separately with two inventories, i.e., MEIC and the provincial inventory developed in this work, for January, April, July and October 2012. Other model settings on meteorological simulation, chemistry mechanisms and emissions of natural origin were the same for the two simulations, as described in Zhou et al. (2017). The first 5 days for each month were chosen as the spin-up period to provide initial conditions for later simulations.

Figure 10 provides the observed and predicted daily 1 h maximum O_3 concentrations for the 4 months, and Table 6 compares the model performance with MEIC and our provincial inventory, indicated as normalized mean bias (NMB) and error (NME) values. As suggested by the negative NMBs for most cases, the model usually generated lower 1 h maximum O_3 concentrations than the observation with either MEIC or the provincial inventory applied, with an exception for the April simulation with MEIC applied. The result thus implied the updated anthropogenic NMVOC emission inventory at provincial scale was still likely an underestimation of the actual emissions, as YRD was commonly recognized as a VOC-limited region for O_3 formation (Xing et al., 2011). Compared to MEIC, better model performance (except for July) was generally achieved when the provincial inventory was applied, indicating the improved reliability of the de-

Table 6. Model performance of daily 1 h maximum O_3 concentrations using MEIC and the provincial inventory for January, April, July and October 2012 in Nanjing.

	Provincial emission inventory		MEIC	
	NMB*	NME*	NMB	NME
January	−21 %	34 %	−58 %	59 %
April	−26 %	38 %	35 %	55 %
July	−28 %	33 %	−23 %	29 %
October	−20 %	26 %	−50 %	50 %

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

$$\text{NMB} = \frac{\sum_{i=1}^n (P_i - O_i)}{\sum_{i=1}^n O_i} \times 100\%; \quad \text{NME} = \frac{\sum_{i=1}^n |P_i - O_i|}{\sum_{i=1}^n O_i} \times 100\%.$$

tailed bottom-up NMVOC inventory on the 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. It should be noted that the improved ozone simulation was a combined effect of the updated inventory with revisions on emission estimation, spatial distribution and source profiles for all the relevant species, and that the impacts of emission changes for individual species could not be completely validated. More chemistry transport mod-

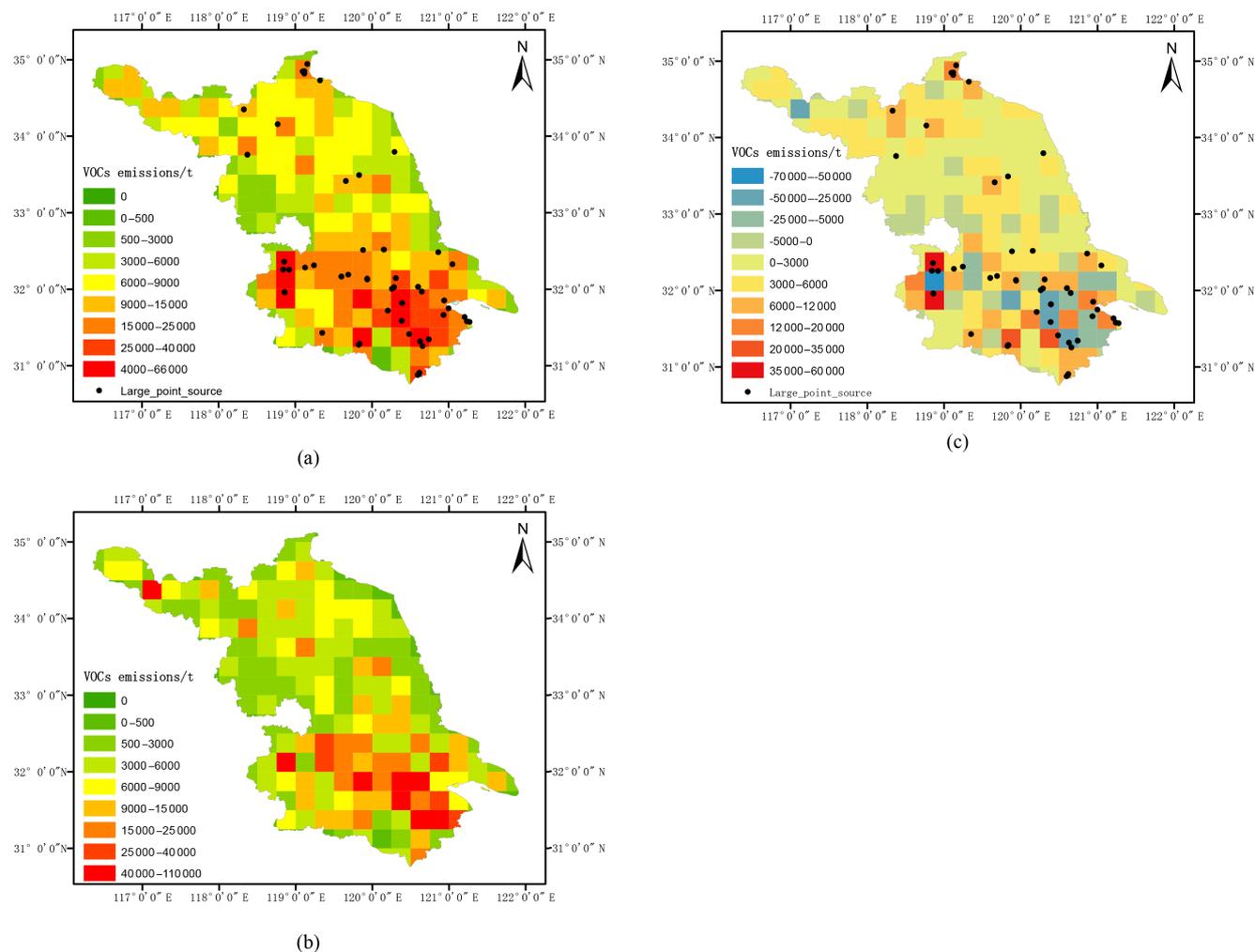


Figure 9. Spatial distributions of Jiangsu's anthropogenic NMVOC emissions for 2010 ($0.25^\circ \times 0.25^\circ$) by this study (a) and MEIC (b), and the differences between the two inventories (this study minus MEIC, c). The black dots indicate the largest 50 emitters in the province.

eling is further encouraged with intensive sensitivity analysis.

The discrepancies between simulations and observations were still large compared to regional studies in North America (Y. Zhang et al., 2009). More efforts in improving or validating emission inventory at provincial scale are thus greatly 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). Emission uncertainty of NO_x could also partly explain the discrepancies, as the NO_x control measures taken recently could hardly be fully tracked in the emission inventory development. Besides the limitation of emission input, more analysis on the impacts of chemical mechanisms and dynamics in the chemistry transport modeling are also suggested for O_3 prediction in the region.

5 Conclusion

Using a bottom-up approach, we developed a high-resolution emission inventory of anthropogenic NMVOCs for the 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 the locations 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

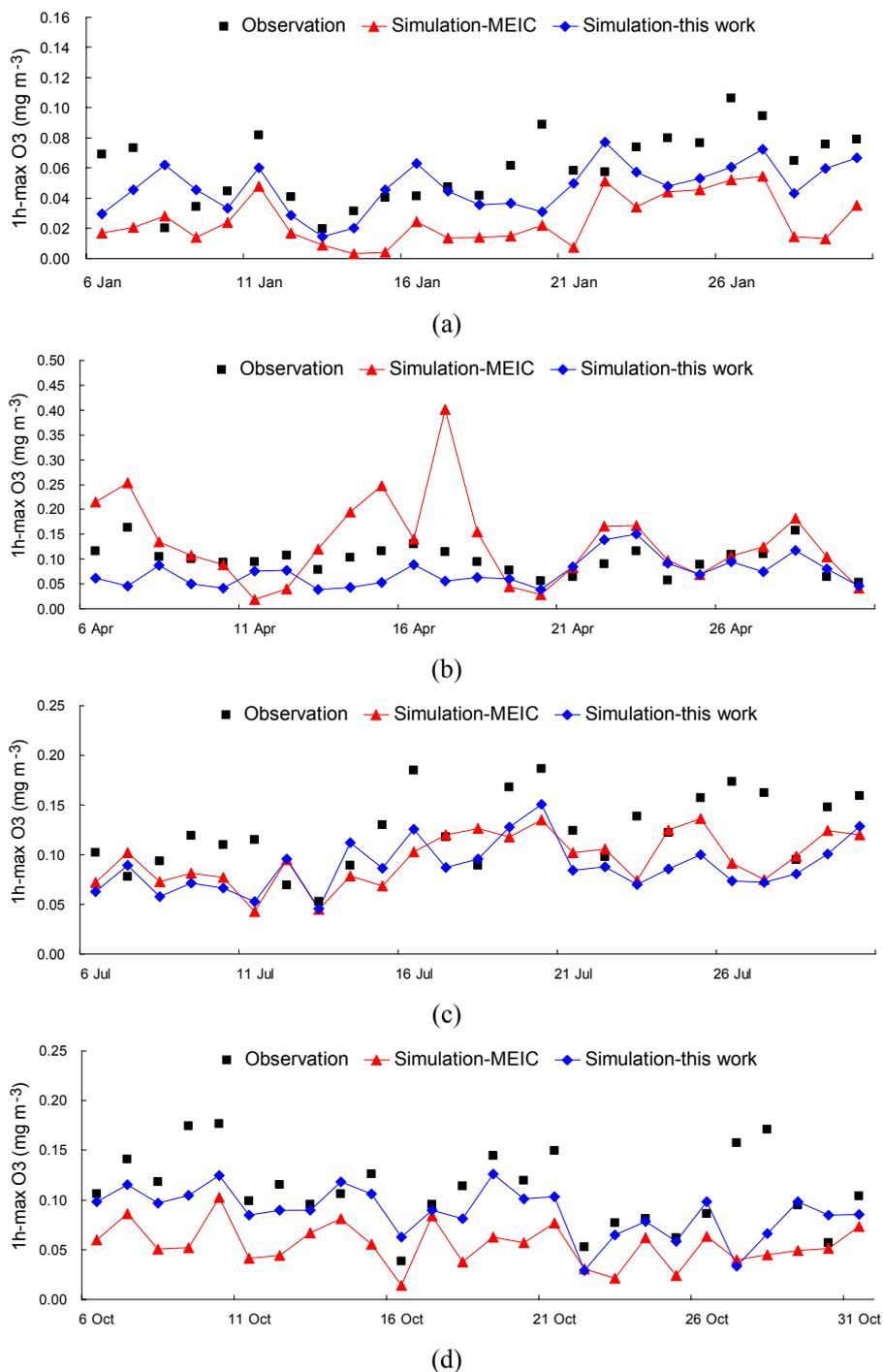


Figure 10. Observed and simulated daily 1 h maximum O₃ concentrations using MEIC and the provincial emission inventory in January (a), April (b), July (c) and October (d) in 2012 at the air quality monitoring sites in Nanjing. Note the different y-axis scales between panels.

quantified in this work compared to previous studies. Varied data sources and methods had a significant impacts on emission estimation at city/plant level. In particular, down-scaling directly from national inventories would overestimate the fraction of emissions in urban downtown. With the most

recent source profiles from local measurements included, considerable changes in emissions were found for ethylacetate and certain aromatic species, and the speciation under CB05 and SAPRC99 differed a lot from the national MEIC inventory. Compared to MEIC, better model perfor-

mance (indicated by daily 1 h maximum O₃ concentrations) was achieved when the improved provincial inventory was used in the CMAQ simulation, although the discrepancies between simulations and observations 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.

Data availability. The detailed data from field measurements have been provided in the Supplement.

The Supplement related to this article is available online at <https://doi.org/10.5194/acp-17-7733-2017-supplement>.

Competing interests. The authors declare that they have no conflict of interest.

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