TITLE PAGE

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

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1   **ABSTRACT**

2   Non-methane volatile organic compounds (NMVOCs) are the key precursors of

3   ozone (O_3) and secondary organic aerosol (SOA) formation. Accurate estimation in

4   their emissions plays a crucial role in air quality simulation and policy making. We

5   developed a high-resolution anthropogenic NMVOCs emission inventory for Jiangsu

6   in eastern China from 2005 to 2014, based on detailed information of individual local

7   sources and field measurements of source profiles of the chemical industry. A total of

8   56 NMVOCs samples were collected in 9 chemical plants, and were then analyzed

9   with a gas chromatography-mass spectrometry system (GC-MS). Source profiles of

10   stack emissions from synthetic rubber, acetate fiber, polyether, vinyl acetate, and

11   ethylene production, and those of fugitive emissions from ethylene, butanol and

12   octanol, propylene epoxide, polyethylene and glycol production were obtained.

13   Various manufacturing technologies and raw materials lead to discrepancies in source

14   profiles between our domestic field tests and foreign results for synthetic rubber and

15   ethylene production. The provincial NMVOC emissions were calculated to increase

16   from 1774 Gg in 2005 to 2507 Gg in 2014, and relatively large emission densities

17   were found in cities along the Yangtze River with developed economy and industry.

18   The estimates were larger than those from most other available inventories, due

19   mainly to the complete inclusion of emission sources and to the elevated activity

20   levels from plant-by-plant investigation in this work. Industrial processes and solvent

21   use were the largest contributing sectors, and their emissions were estimated to

22   increase respectively from 461 to 958 and from 38 to 966 Gg. Alkanes, aromatics and

23   oxygenated VOCs (OVOCs) were the most important species, accounting for

24   25.9%-29.9%, 20.8%-23.2% and 18.2%-21.0% to annual total emissions respectively.

25   Quantified with a Monte-Carlo simulation, the uncertainties of annual NMVOCs

26   emissions vary slightly from years, and the result for 2014 was -41%~+93%,

27   expressed as 95% confidence intervals (CI). Reduced uncertainty was achieved

28   compared to previous national and regional inventories, attributed partly to the

29   detailed classification of emission sources and to the use of information at plant level

30   in this work. Discrepancies in emission estimation were explored for chemical and

31   refinery sector with various data sources and methods. Compared with

32   Multi-resolution Emission Inventory for China (MEIC), the spatial distribution of

33   emissions in this work were more influenced by the locations of large point sources,

34   and smaller emissions were found in urban area for developed cities in southern

35   Jiangsu. Besides, discrepancies were found between this work and MEIC in the

36   speciation of NMVOC emissions under the atmospheric chemistry mechanisms CB05

37   and SAPRC99. The difference in species OLE1 resulted mainly from the updated

38   source profile of building paint use, and the differences in other species from the

39   varied sector contributions to emissions in the two inventories. CMAQ simulation was

40   applied to evaluate the two inventories, and better performance (indicated by daily

41   1h-max O_3 concentrations in Nanjing city) was found for January, April and October

42   2012 when the provincial inventory was used.

43

44   **1 Introduction**

45   With strong OH and HO_2 radical chemistry reactions, non-methane volatile

46   organic compounds (NMVOCs) are reported to play crucial roles in formation of

47   secondary organic aerosols (SOA) and serious photochemical pollution in China,

48   particularly in developed cities and regions. For example, Huang et al. (2014)

49   revealed that the contribution of SOA from NMVOC conversion reached 44%-71% to

50   ambient organic aerosols during a heavy haze period in winter, based on detailed

51   analysis on chemistry composition and source of airborne particles in four important

52   cities (Beijing, Shanghai, Guangzhou and Xi'an) across the country. Due to intensive

53   emissions of species with strong atmospheric oxidation capability (indicated by

54   maximum incremental reactivity, MIR), ozone (O_3) formation was recognized as

55   VOC-limited in developed areas including Jing-Jin-Ji (JJJ), Yangtze River Delta

56   (YRD) and Pearl River Delta (PRD) regions (Geng et al., 2008; Shao et al., 2009;

57   Zhang et al., 2008; Xing et al., 2011).

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58   Given the impacts of NMVOCs on air quality, increasing attentions have been

59   paid to their sources and emission characteristics. Although natural sources dominate

60   the emissions at global scale (Guenther et al., 1995; Muller, 1992; GEIA,

61   http://eccad.sedoo.fr/eccad_extract_interface), the contribution from anthropogenic

62   sources is elevated at smaller spatial scales, attributed to intensive human activities. In

63   mainland China, emissions of natural and anthropogenic origin were estimated close

64   to each other at 10-30 Tg, and anthropogenic emissions were dominated by solvent

65   use and industrial processes (Tie et al., 2006; Klimont et al., 2002; Streets et al., 2003).

66   Table S1 in the supplement briefly summarizes the estimations of China's national

67   NMVOC emissions of anthropogenic origin from various studies. With different

68   methods and data sources applied, NMVOC emissions in China were estimated to be

69   doubled from 1990 to 2010, and the contributions of solvent use, non-combustion

70   industrial processes and transportation were enhanced in recent years. Incorporating

71   available information at national scale, Tsinghua University developed the

72   Multi-resolution Emission Inventory for China (MEIC, http://www.meicmodel.org/)

73   and calculated the national total emissions at 23.6 Tg for 2010. Among all the studies,

74   largest estimations were made in Regional Emission inventory in Asia (REAS, Ohara

75   et al., 2007; Kurokawa et al., 2013), reaching 28.0 Tg for 2008.

76   At local scale, emissions from anthropogenic sources could be much higher than

77   natural sources. For example, anthropogenic NMVOC emissions were estimated 6-18

78   times those of natural origin in Beijing (Klinger et al., 2002; Wang et al., 2003;

79   Klimont et al., 2002; Q. Zhang et al., 2009). With information on individual plants

80   collected, emission inventories for regions with relatively heavy air pollution in China

81   including JJJ, YRD and PRD have been developed, and differences in sector

82   contribution were found. Solvent use and transportation were identified as the largest

83   NMVOC sources in PRD (Zheng et al., 2009), while industrial processes were more

84   important in YRD (Huang et al., 2011; Fu et al., 2013). Limitation existed in current

85   regional inventories. First, information of local sources was still lacking. Although

86   combustion sources (e.g., power plants) were gradually included in the regional

87   emission inventory as point sources, the sources that contribute more to NMVOCs

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88   including refinery and chemical industry plants were less investigated at local scale,

89   resulting possibly in big bias in emission estimation. Second, with varied data sources

90   and methods, large discrepancies might exist between studies in the amount and

91   spatial pattern of emissions. Such discrepancies were rarely analyzed, and the

92   uncertainties in emission estimation at local scale were seldom quantified. In

93   particular, the performances of chemistry transport modeling based on various

94   NMVOC inventories have not been sufficiently evaluated. Moreover, chemical

95   speciation of NMVOC emissions needs further improvement. Domestic

96   measurements have increasingly been conducted on chemical profiles of NMVOCs

97   for typical source categories including solvent use (Yuan et al., 2010; Zheng et al.,

98   2013), transportation (Tsai et al., 2012; Huang et al., 2015), residential stoves (Wang

99   et al., 2009), and biomass burning (Kudo et al., 2014). The effects of those results on

100   speciation of NMVOC emissions were not fully assessed, except for limited studies

101   (Li et al., 2014). In addition, the measurements on given sectors such as chemical

102   industry are still lacking, and the data from foreign countries had to be used.

103   Under the heavy haze pollution in eastern China (Andersson et al., 2015; Sun et

104   al., 2015; Wang et al., 2015), series of measures have been conducted particularly on

105   power and industrial boilers to control the emissions of primary particles and the

106   precursors of secondary particles such as SO_2 and NO_X (Zhao et al., 2014). Along

107   with gradually reduced ambient PM levels in YRD, O_3 pollution becomes a bigger

108   concern for air quality improvement, motivating better understanding and controlling

109   of NMVOC emissions. In this work, we select Jiangsu, a typical province with

110   intensive refinery and chemical industry in eastern China, to develop and evaluate the

111   high-resolution emission inventory of anthropogenic NMVOCs. The geographic

112   location and cities of the province are illustrated in Figure S1 in the supplement. Field

113   measurements on chemical composition of NMVOC emissions were conducted to

114   obtain the source profiles of typical chemical industry processes. With detailed

115   information of local emission sources collected and temporal changes tracked, a

116   provincial emission inventory of speciated NMVOC were developed for a ten-year

117   period 2005-2014, and the uncertainties of the emission estimation were quantified.

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118   Through a thorough comparison between results from varied methods and data

119   sources, the discrepancies in emission estimation, source profiles, and spatial patterns

120   were then evaluated. Finally, chemistry transport modeling was applied in southern

121   Jiangsu to test the improvement of the provincial NMVOC inventory.

122

123   **2 Data and methods**

124   **2.1 Sampling and analysis of NMVOC species from chemical plants**

125   Chemical profiles of NMVOC emissions are still lacking for chemical industry

126   and oil exploitation and refinery in China, due to a big variety of source categories.

127   We select nine types of chemical engineering enterprises that are intensively

128   distributed in Jiangsu to measure the chemistry composition of NMVOC emissions, as

129   summarized Table S2 in the supplement. To our knowledge, no domestic

130   measurement on NMVOC speciation has been conducted for those sources yet, and

131   current work was expected to supplement the domestic source profiles for chemical

132   industry. Based on the on-site investigation of main emission processes, the locations

133   for stack and/or fugitive emission sampling were determined for each source type (see

134   Table S2 for the details). Note sampling could not be conducted for all processes in

135   one enterprise due mainly to the limitation of pipeline layout. The SUMMA canister

136   produced by University of California, Irvine was employed to collect the air sample.

137   The canister was made out of stainless steel as its inner wall, and the volume and

138   vacuum pressure range of the canister were 2 L and 1.1×10^{-4} kPa, respectively. For

139   stack emission measurement, as shown in Figure S2a in the supplement, the canister

140   was connected with a stainless steel probe, and a filter pipe filled with glass wool and

141   anhydrous sodium sulfate was applied to remove the particles and water vapor in the

142   air sample. Under flow control, the sampling time was roughly 10 minutes until the

143   pressure in the canister reached ambient. For fugitive emission measurement, the

144   canister was placed 50 meters downwind of the production device, and the sampling

145   time was roughly 8 minutes. Repeated sampling was conducted for each process to

146   eliminate the bias and a total of 56 samples were obtained, as shown in Table S2.

147   NMVOC samples were analyzed by one Gas Chromatograph Mass Spectrometer

148   (GC-MS) system (GC6890/MS5973i, Agilent Technologies, USA), as illustrated in

149   Figure S2b in the supplement. Firstly, the sample was pumped into a cryogenic

150   pre-concentrator with a three-stage trapping system. In the first stage, the VOC

151   species were adsorbed on glass beads at −150°C and desorbed at 10°C. Vapour water

152   was converted to solid water and was thus separated from the sample. In the second

153   stage, the sample was trapped on Tenax at −30°C and desorbed at 180°C, and the

154   target species were separated from CO_2 and other compositions in the air. In the third

155   stage, the sample was focused on a transfer line at −160°C and heated rapidly to 70°C,

156   and the species were concentrated. The concentrated VOC was then injected into the

157   gas chromatograph. The GC oven temperature was initially programmed at −50°C,

158   and then increased to 180°C at 4°C/min and to 220°C at 15°C/min, holding 3minutes.

159   The VOC compounds were separated on a DB-5MS capillary column (60 m×0.25

160   mm×1.0 μm) and quantified using a quadrupole mass spectrometer. The mass

161   spectrometer was operated in SCAN mode and scanned 20-42 amu and 35-270 amu

162   before and after 8.5 minutes, respectively. The ionization method was electron

163   impacting, and the source temperature was 230°C. The PAMS (Photochemical

164   Assessment Monitoring System) standard mixture (Spectra Gases Inc., USA) and

165   TO-15 standard mixture (Spectra Gases Inc., USA) were used to confirm the retention

166   times of different compounds, and to identify them based on retention time and mass

167   spectrum. The target species were quantified by using multipoint internal calibration

168   method. To establish calibration curves, a certified gas mixture containing all the

169   target compounds was dynamically diluted with pure nitrogen to five concentration

170   gradients using mass flow controllers. Bromochloromethane, 1,2-difluorobenzene,

171   and chlorobenzene-d5 were chosen as internal standards in samples. The method

172   detection limit was 0.5 ppb for all species.

173

174   **2.2 Development of provincial emission inventory**

175　　　Different from national and regional inventories that relied mainly on energy and

176　economic statistics, detailed information on individual emission sources was collected

177　for Jiangsu, and inter-annual changes were tracked at plant level based on various

178　databases. Those databases contained the multiple-year official Environmental

179　Statistics (databases of emission sources routinely compiled by local environmental

180　protection bureaus), Pollution Source Census (PSC, thorough investigation on

181　emission sources organized at national level), and on-site surveys on large emitters

182　conducted by local department of environmental supervision. The information

183　included geographic location, types and amounts of raw materials, types and amounts

184　of products, fuel quality and consumption, and combustion/manufacturing technology.

185　For 2014, as an example, detailed information of 6023 plants was obtained, and the

186　locations of those point sources are illustrated in Figure S1. Incorporating the

187　plant-by-plant information and the energy and industrial statistics at provincial level, a

188　four-level framework was established, covering all the anthropogenic NMVOC

189　sources for Jiangsu, as summarized in Table 1. The framework included seven main

190　categories: stationary fossil fuel combustion, industrial process, solvent use,

191　transportation, oil distribution, biomass burning, and others. Each main category was

192　further subdivided into subcategories according to discrepancies in fuel consumption,

193　product manufacturing, or technology application. The emissions of the province for

194　2005-2014 were calculated using the following equation:

195　$E(n) = \sum_i AL(i,n) \times EF(i,n)$ （1）

196　where i and n represent the source type and year, respectively; E is the annual

197　emissions; AL is the activity level data; and EF is the emission factor (i.e., emissions

198　per unit of AL). As summarized in Table 2, emission factors were collected from

199　extensive literatures and determined as follows with descending priorities: (1) results

200　from domestic measurements; (2) emission limits of local laws and regulations; (3)

201　values from expert judgment specific for China; and (4) emission factors from AP-42

202　database (USEPA, 2002) and the EMEP/EEA guidebook (EEA, 2013) when domestic

203　information was lacking. Details will be discussed by sector in Section 2.3.

204   The total NMVOC emissions for given source type were then broken down into

205 individual species using Eq. (2):

206 $E(i,k) = E(i) \times X(i,k)$ (2)

207 where E is the emissions; i and k represent the source type and individual NMVOCs

208 species, respectively; X is chemical profile of NMVOCs (%). To reduce the

209 uncertainty of source profile from individual measurement, Li et al. (2014) developed

210 the "composite profiles" for sources where multiple candidate profiles were available,

211 by revising the OVOCs fraction and averaging the fractions in different profiles for

212 each species. As a more detailed source classification was applied in this work, some

213 sources (e.g., biomass open burning, automobile production & repairing, and wood

214 decoration & wooden furniture paint) were not covered by Li et al. (2014) and thus

215 the results from SPECIATE were applied instead. We named the combination of Li et

216 al. (2014) and SPECIATE as a source profile "before updating" hereinafter. While Li

217 et al. (2014) included the source profiles published before 2011, a series of local

218 measurements were conducted after then. In this work, therefore, "composite profiles"

219 were updated following the method by Li et al. (2014). The most recent domestic

220 results and the measurements conducted in this work were incorporated as

221 summarized by source type in Section 2.3.

222   To evaluate the atmospheric oxidation capability from NMVOC emissions,

223 ozone formation potentials (OFPs) were calculated by multiplying the speciated

224 NMVOC emissions and corresponding MIR values (Carter, 1994). To meet the

225 requirement of atmospheric modeling, NMVOC emissions were assigned to chemical

226 mechanism (CB05 and SAPRC99) species by multiplying the emissions of individual

227 species and mechanism-specific conversion factors using the following equation:

228 $E(i,m) = \dfrac{E(i,k)}{M(k)} \times C(k,m)$

229   (3)

230 where E is the emissions, M is the mole weight, C is the conversion factor, and i, k,

231 and m represent the source type, individual species, and the chemical mechanism

  species.

232   The uncertainty of estimated provincial emissions was quantified using a

233   Monte-Carlo framework (Zhao et al., 2011) for each year. Probability distribution

234   functions (PDF) were determined for all the parameters involved in the emission

235   calculation, and 10 000 simulations were performed to estimate the uncertainties of

236   emissions. The parameters that were most significant in determination of the

237   uncertainties were identified by source type according to the rank of their

238   contributions to variance. The detailed information of PDF assumption will be

239   provided by sector in Section 2.3.

240   **2.3 Data sources of emission inventory development by category**

241   **Combustion sources (fossil fuel combustion and biomass burning)**

242   For power sector and heating/industrial boilers, activity data were compiled at

243   plant level based on the information obtained from Environmental Statistics, PSC and

244   on-site survey. The annual amount of residential fossil fuel combustion for 2005-2014

245   and that of biofuel use for residential stoves until 2008 were directly taken from

246   Chinese official energy statistics (NBS, 2015a). As the data were unavailable for

247   subsequent years for biofuel, the activity level was calculated as a product of grain

248   production, waste-to-grain ratio, and the ratio of residual material burned in stoves

249   according to the government plan of biomass utilization (PGJP, 2009). The biomass

250   combusted in open fields was calculated as a product of grain production,

251   waste-to-grain ratio, and the percentage of residual material burned in the field (Wang

252   and Zhang, 2008; PGJP, 2009), as described in Zhao et al. (2011; 2013). Following

253   the rules of IPCC (2006), the uncertainties of activity levels were determined

254   according to the reliability of energy and economy statistics. As shown in Table S3 in

255   the supplement, normal distributions were assumed with the coefficients of variation

256   (CV, the standard deviation divided by the mean) determined at 5%, 10%, 20% and

257   30% for power, industrial, residential fossil fuel and biomass combustion sources,

258   respectively.

259   As summarized in Table 2, emission factors for power plants and industrial

260   boilers were taken mainly from Bo et al. (2008). Given the similar designs of boilers

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261 between China and developed countries (Wei et al., 2008), AP-42 database were also

262 applied when domestic results were lacking. For residential combustion of fossil fuel,

263 emission factors from domestic tests (Zhang et al., 2000; Wang et al., 2009) were used.

264 Wang et al. (2009) measured the NMVOC emission characteristics of multiple

265 stove-biofuel combinations in China and the obtained emission factors were used in

266 this work. For biomass open burning, the local test results by Li et al. (2007) were

267 applied. Chemical profiles were updated by incorporating domestic measurements for

268 residential fossil fuel and biofuel burning (Tsai et al., 2003; Liu et al., 2008; Wang et

269 al., 2009; Wang et al., 2014a), and biomass open burning (Zhang et al., 2013; Kudo et

270 al., 2014). As measurement results were insufficient for data fitting, uncertainty of

271 emission factor was evaluated depending on expert judgment for combustion sources

272 (Streets et al., 2003; Wei et al., 2011). PDF of emission factor was given according to

273 reliability of data sources and/or the robustness of calculation methods (Wei et al.,

274 2011; also the case for other sources as indicated below). As summarized in Table S4

275 in the supplement, lognormal distributions were assumed with CVs set at 150% and

276 200% for fossil fuel and biomass burning, respectively.

277 **Industrial processes**

278 Similar with power and industrial combustion, the activity levels of industrial

279 processes were mainly collected at plant level by source category. However, small

280 discrepancies existed between the compiled data at plant level and the officially

281 reported production from economic statistics at provincial level (NBS, 2015b). In

282 2012, for example, the steel production aggregated from individual plants accounted

283 for 98% of the provincial total production (Zhou et al., 2017). In this work, we treated

284 the individual plants as point sources, and the fraction that was not covered in

285 plant-by-plant databases as area sources. We assumed the PDFs of industrial

286 production as normal distribution with CVs at 10% and 20% for point and area

287 sources, respectively.

288 Attributed to a wide variety of manufacturing procedures and complicated VOC

289 exhaust processes, there were few local tests available on emission factors before,

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290   thus the values from expert judgment (i.e., data from routine investigations reported

291   by the factory officials to local environmental protection bureaus) and data from

292   AP-42 and EMEP/EEA had to be applied, as summarized in Table 2. Source profiles

293   of chemical production including rubber, polyether, and polyethylene were obtained

294   from our measurements described in Section 2.1. Chemical profiles from most recent

295   domestic measurements were taken for other sources including iron & steel (Shi et al.,

296   2015; He et al., 2005; Jia et al., 2009; Tsai et al., 2008; Li et al., 2014), paint and

297   printing ink production (Zheng et al., 2013), and refineries (Liu et al., 2008; Wei et al.,

298   2014). For sources without sufficient local tests (e.g., food and wine production),

299   results from foreign studies were applied including the SPECIATE database by

300   USEPA (2014), and Theloke and Friedirch (2007). Given the potential large

301   uncertainties, lognormal distribution with CV set at 500% (i.e., a long-tailed PDF)

302   was assumed for emission factors for most industrial processes.

303   **Solvent use**

304   Although solvent-use enterprises were contained in the plant-by-plant surveys,

305   many of them failed to report the actual solvent usage. Underestimation in activity

306   levels and thereby emissions could be expected if the information at plant level was

307   relied on. As the solvent usage was not directly reported at city level, we followed

308   Wei (2009) to estimate the activity levels for the sector. The total solvent consumption

309   at national level was first obtained according to the solvent production and imports &

310   exports statistics (CNLIC, 2015; GAC, 2015). The provincial level was then

311   calculated based on the intensities of activities that consume solvent (e.g., building

312   construction and vehicle production). Finally, the provincial data were allocated to

313   point sources according to production of individual plants and area sources according

314   to distribution of industrial GDP. Normal and lognormal distributions with CVs set at

315   20% and 80% were applied for the activity levels of point and area sources of solvent

316   use, respectively, indicating much larger uncertainty for the latter (Wei, 2009).

317   The VOC contents of solvent were limited by national laws and regulations, as

318   summarized by Wei et al. (2008). The updating of regulations and their impacts on

319   inter-annual changes in NMVOC emission factors were considered from 2005 to 2014,

320   such as GB18583-2003 and GB18583-2008 for indoor painting. Bias needs to be

321   admitted here and possible underestimation in emissions would be expected for the

322   sector, as the regulations were not strictly enforced particularly for small solvent use

323   enterprises and construction sites (area sources). Data from AP-42, EMEP/EEA and

324   other literatures (Bo et al., 2008; Fu et al., 2013) were applied when local information

325   was missing, as provided in Table 2. The domestic tests on chemical species (Yuan et

326   al., 2010; Zheng et al., 2013; Tang et al., 2014; Wang et al., 2014b) were included to

327   update the source profiles of the sector. For uncertainty of the emission factors,

328   uniform distribution was tentatively applied (Table S4).

329   **Transportation**

330   The activity data of off-road transportation for 2005-2010 was taken from Zhao

331   et al. (2013), and the data for other years were scaled according to the changes in

332   passenger and freight traffic by rail and shipping, and those in numbers of agricultural

333   and construction equipments (NBS, 2015c). For on-road transportation, activity data

334   (total kilometers traveled) by vehicle type and control stage were calculated as the

335   product of vehicle population and annual average kilometers traveled (VKT). The

336   fleet composition by control stage was obtained from the survey by local government

337   (internal data, Zhao et al., 2015), and VKT by vehicle type were determined according

338   to previous studies (Cai and Xie, 2007; Wang et al., 2008) and the guidebook of

339   emission inventory development for Chinese cities (He, 2015). While the CV of

340   transportation activities at national level was estimated at 16% (Zhao et al., 2011),

341   larger uncertainties were assumed at provincial level (Wei, 2009). We followed Wei

342   (2009) and assumed normal and lognormal distribution with CVs at 30% and 50% for

343   on-road and non-road transportation, respectively.

344   For emission factors of off-road transportation, the data from EMEP/EEA and

345   expert judgment (Wei et al., 2008; Q. Zhang et al., 2009) were adopted, attributed to

346   lack of domestic tests or relevant standards/regulations. Following He (2015), the

347   emission factors for on-road vehicles were calculated and adjusted according to local

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348 conditions using Eq. (4):

349 $EF = BEF \times \varphi \times \gamma \times \lambda \times \theta$ (4)

350 where BEF is the base emission factor, φ is the environmental correction factor, γ is

351 the average traveling speed correction factor, λ is the vehicle deterioration correction

352 factor, and θ is correction factor for other conditions (e.g., vehicle loading and fuel

353 quality). Domestic tests on chemical compositions (Liu et al., 2008; Tsai et al., 2012;

354 Huang et al., 2015; Wang et al., 2013; Ou et al., 2014; Gao et al., 2012) were

355 incorporated to update the source profile of on-road vehicles. Lognormal distributions

356 with CVs at 150% and 300% were respectively assumed for emission factors of

357 on-road and off-road transportation.

358 **Oil distribution and other sources**

359 For oil distribution, Wei (2009) developed a simplified model to simulate the oil

360 storage, transport and sale activities based on the provincial energy balance statistics,

361 and the model was applied in this work to calculate the activity levels for the sector.

362 Activity data from other sources were directly taken from official provincial statistics

363 (NBS, 2015b; c). Emission factors of oil distribution and other sources were obtained

364 from Wei et al. (2008), Shen (2006) and Xia et al. (2014), and lognormal distributions

365 were assumed for them as summarized in Table S4. The source profiles were obtained

366 from Liu et al. (2008) and SPECIATE.

367 **3 Results**

368 **3.1 Source profiles of chemical industry from measurement**

369 NMVOC source profiles of 14 processes (9 for stack emissions and 5 for fugitive

370 emissions) were obtained from field measurements. With totally 61 species detected

371 by GC-MS systems, the chemistry components were grouped into 6 types (alkanes,

372 alkenes, halohydrocarbon, aromatics, OVOCs, and others), as illustrated in Figure 1a.

373 Alkanes were the main species of synthetic rubber industry (SBR, SIS rubber and

374 SEBS rubber), with the mass fractions over 70%. For production of cellulose acetate

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375   fiber, alkanes, aromatics, and OVOCs were the main species in process of acetate

376   flake production, while OVOCs dominated in the spinning process. Resulting from

377   various raw materials, the source profiles of the two types of polyether production

378   differed a lot: the mass fraction of OVOCs was close to 80% for PPG, while the main

379   species for POP were others, aromatics and halohydrocarbon. For ethylene production,

380   aromatics were the main composition in the stack gas of cracking furnace, while

381   alkanes and alkenes dominated the fugitive emissions. For other types of fugitive

382   emissions, big differences existed in the source profiles attributed mainly to the

383   various raw materials and chemical reactions.

384   The detailed chemistry compositions for stack and fugitive emissions were

385   summarized in Tables S5 and S6, respectively. For stack emissions of synthetic rubber

386   production, cyclohexane was the dominating species, with the mass fractions close to

387   or above 70% for all types of products. Besides, styrene and acetone were also

388   important species for SBR and SIS/SEBS rubber, respectively. Used as the solvent in

389   the chemical reactions, acetone and cyclohexane were considerably emitted during

390   acetate flake production process, and the mass fraction of acetone reached 70% in the

391   spinning process. As the raw materials for polyether production, acrylontitrile and

392   ethylene oxide were the main species emitted from POP and PPG production, with the

393   mass fractions measured at 43% and 62%, respectively. As the main product,

394   vinyl acetate was measured to take 80% of NMVOC emissions from its production

395   process. For fugitive emissions from ethylene production, the mass fractions of

396   ethylene, propylene, and n-hexane reached 33%, 26% and 20%, respectively.

397   1,2-dichloropropane dominated the emissions from propylene oxide production, with

398   the mass fraction measured at 65%. For polyethylene and glycol production, ethylene

399   and xylene were identified as the largest species, with the mass fractions measured at

400   42% and 35%, respectively.

401   Since there were very few domestic tests on source profiles of chemical industry,

402   the results obtained in this work were compared with those available in SPECIATE

403   for synthetic rubber, ethylene and polyethylene production, as illustrated in Figure

404   1b-d, respectively. As can be seen in Figure 1b, large discrepancy was found for

15

405   source files of SBR between this work and SPECIATE: while cyclohexane was

406   identified as the main species in this work, SPECIATE included only styrene and 1,3-

407   butadiene (the raw materials in SBR production). Variation in manufacturing

408   technologies was the main source of the discrepancy. SPECIATE targeted emulsion

409   polymerization technology in which solvent was not used and NMOVC emissions

410   consisted mainly of the volatile raw materials. This work, however, measured the

411   plants with solution polymerization technology, in which significant organic solvents

412   would be released during the drying process. As shown in Figure 1c, both SPECIATE

413   and our measurements on fugitive emissions indicated that ethylene and isobutene

414   were the important species for ethylene production. In addition, much larger fractions

415   of propylene and n-hexane were found in this work. Different compositions were

416   found for flue gas of cracking furnace, with abundant species from incomplete

417   combustion. Similar source profiles were found between this work and SPECIATE for

418   polyethylene production, dominated by ethylene (Figure 1d).

419   **3.2 Inter-annual trends and sectoral contribution of NMVOC emissions**

420   As shown in Table 3, the annual emissions of anthropogenic NMVOCs for Jiangsu

421   were estimated to increase from 1774 to 2507 Gg during 2005-2014, with an average

422   annual growth rate at 3.9%. Industrial processes and solvent use were identified as the

423   largest two sectors contributing to the emissions. The emission fractions of the two

424   types of sources to total anthropogenic emissions were estimated to increase from

425   26% in 2005 to 38% in 2014, and from 21% to 39%, respectively. In contrast,

426   emission contributions from transportation and biomass burning were declining from

427   18% to 11%, and from 26% to 4%, respectively, attributed mainly to the controlled

428   motorcycle emissions, replacement of residential biofuel stoves with natural

429   gas/electricity ones, and the gradual implementation of straw burning prohibition.

430   Relatively small contributions were found for stationary fuel combustion plants, oil

431   distribution, and other sources, and their collective fractions to total emissions ranged

432   7-9% during the study period.

433   Figure S3a-c in the supplement provided the inter-annual trends in emissions of

16

434   subcategories for industrial processes, solvent use and transportation. The emissions

435   from industrial processes were estimated to be doubled from 2005 to 2014, and the

436   inter-annual trend in emissions was well correlated with that in industry GDP (Figure

437   S3a). The comprehensive investigations on point sources indicated that few measures

438   were implemented to control NMVOC till 2014, and the increased emissions were

439   thus mainly driven by the growth of industry activities. Largest growth was found for

440   synthetic and fine chemical industry, with the emissions elevated from 130 in 2005 to

441   361 Gg in 2014. Due to enhanced coking industry, the emissions of iron & steel

442   production were estimated to increase 254% from 27 to 96 Gg.

443   The emissions of solvent use in Jiangsu were calculated to increase 153% from

444   380 in 2005 to 963 Gg in 2014, and the growth was highly consistent with that of

445   industry plus construction GDP (Figure S3b). Despite of increased use of water

446   soluble paint and implementation of emission standards for given processes (e.g., the

447   VOC content of interior wall paint has been reduced from 250 to 120 g/kg since 2008),

448   it was still difficult to restrain the emissions under the fast growth of solvent use, as

449   relevant polices were not widely conducted across the sector. Paint use was the largest

450   contributor, and its emissions were calculated to increase from 225 in 2005 to 652 Gg

451   in 2014. The emissions from printing ink increased 355% from 25 to 115 Gg.

452   Although Jiangsu's total vehicle population increased 76% from 2005 to 2014,

453   the NMVOC emissions of on-road transportation were estimated to decline 31% from

454   297 to 204 Gg, with the peak emissions at 302 in 2007 (Figure S3c). The

455   implementation of staged emission standards (State I-V, equal to Euro I-V) on new

456   vehicles, and reduced motorcycle population were the main reasons for the declining

457   emissions. For example, emissions of motorcycles deceased 66% from 185 to 64 Gg,

458   and its contribution to on-road vehicle emissions declined as well from 62% to 31%.

459   Gasoline vehicles dominated the emissions of on-road transportation, with the fraction

460   ranged 81%-87% during the study period.

461   Illustrated in Figure 2 are the spatial distributions of Jiangsu's NMVOC

462   emissions for various years within a 3×3 km grid system. The emissions of point

463   sources were directly allocated according to their geographic locations. For other

17

464   sources, certain proxies were applied to allocate emissions, including GDP for

465   industrial area sources and oil distribution, population for solve use area sources, road

466   net and traffic flow for on-road vehicles, railway and canal net for off-road

467   transportation, and rural population for biomass burning. High emission intensities

468   were mainly found in relatively developed cities along Yangtze River in southern

469   Jiangsu including Nanjing, Suzhou, Wuxi and Yangzhou (see Table S7 for the

470   emissions by city). In central and northern Jiangsu, large emissions existed in areas

471   with clustered industrial parks, reflecting the impacts of big plants on spatial pattern

472   of NMVOC emissions. Comparing the emissions for 2005 and 2014, increased

473   emissions were commonly found in southern Jiangsu indicating the faster growth of

474   industry in developed cities (Figure 2d). Moreover, reduced emissions were coincided

475   with road net distribution, implying the benefit of emission controls on vehicles.

476   **3.3 Speciation and OFPs of NMVOC emissions**

477   Table 4 compares the source profiles of this work with those of Li et al. (2014) or

478   SPECIATE for typical source categories, grouped as alkanes, alkenes, alkynes,

479   aromatics, OVOCs, and others. Elevated fractions of alkanes are found in this work

480   for almost all the sources, while the comparisons of other species are less conclusive

481   between sources. Based on the source profiles, emissions of more than 500 NMVOC

482   species were calculated and grouped into 12 categories (alkanes, alkenes, alkynes,

483   aromatics, alcohols, aldehydes, ketones, ethers, acids, esters, halohydrocarbons, and

484   others). From 2005 to 2014, the mass fractions of alkanes, unsaturated hydrocarbon

485   (alkenes and alkynes), aromatics, OVOCs (alcohols, aldehydes, ketones, ethers, acids,

486   and esters), halohydrocarbons, and others were between 26-30%, 13-19%, 21-23%,

487   18-21%, 3-4%, and 11-12%, respectively.

488   Shown in Figure 3 are the mass fractions of species by source category for 2014.

489   Due to varied fuel qualities and combustion conditions, large differences in emission

490   speciation were found for fossil fuel combustion, transportation and biomass burning.

491   The profile of fossil fuel stationary sources was dominated by coal combustion, and

492   aromatics were the largest fraction (45%), followed by alkanes (29%). Alkanes,

18

493 aromatics and alkenes were the main species from transportation, with the fractions

494 estimated at 30%, 24%, and 23%, respectively. For biomass burning, elevated alkenes

495 and less alkanes were found attributed to the highly incomplete combustion. The mass

496 fractions of alkanes, aromatics and alkenes from industrial processes were estimated

497 32%, 16% and 12%. In particular, relatively close emission fractions were found

498 between species for chemical industry, the largest emission source of industrial

499 processes, i.e., 19%, 15%, 11%, 10% and 10% for aromatics, ketones, alkenes,

500 alkanes, and halohydrocarbons, respectively. For solvent use, aromatics and alkanes

501 were the most important species with the fractions estimated at 32% and 22%,

502 respectively, and the collective fraction of OVOC species reached 27%. Alkanes and

503 aldehydes dominated the emissions of oil distribution and other sources, which came

504 mainly from the oil evaporation and residential cooking, respectively.

505   The OFPs from NMVOC emissions in Jiangsu were calculated to increase from

506 3880 in 2005 to 5200 Gg in 2014, and the ratio of annual OFPs to emissions varied

507 slightly around 2.1 for the decade. As the chemical profiles of emitted NMVOC vary

508 between source categories, the OFP to emission ratio for a given category could

509 indicate the potential contribution to ozone formation of the category, as a combined

510 effect of multiple species emitted. The priorities of emission control for ozone

511 abatement could thus be suggested by the ratio. The ratios for 2014 were provided by

512 source in Figure 3. With abundant aromatics and alkenes emissions that were highly

513 active in chemistry, the largest ratio (3.68) was found for fossil fuel stationary

514 combustion. The ratios of biomass burning and other sources reached 3.0, attributed to

515 active aromatics and aldehydes emissions, respectively. The lowest ratio (1.58) was

516 found for oil distribution, as its emissions were dominated by alkanes with low

517 reactivity. Figure S4 in the supplement provided 25 species with the biggest

518 contributions to OFPs and their emission sources for 2005 and 2014. In 2005, the 25

519 species were estimated to account for 44% of total NMVOC emissions and 83% of

520 OFPs (Figure S4a). Xylene, ethylene, and propylene were identified as the most three

521 important species in terms of OFP. The aromatics species with (e.g., xylene and

522 toluene) came largely from solvent use and industrial processes, while alkenes species

19

523   (e.g., ethylene and propylene) were mainly from industrial processes, biomass burning,

524   and transportation. Besides, biomass burning was the dominating sources of methyl

525   glyoxal, methyl alcohol and glyoxal. For 2014, the 25 species were estimated to

526   account for 38% of total NMVOC emissions and 81% of OFPs, and the contributions

527   of solvent use and industrial processes to OFPs were clearly elevated (Figure S4b).

528   The orders of isopropanol and n-butanol that were mostly from solvent use, for

529   example, were moved forward. Moreover, the contribution of biomass burning

530   significantly declined, and the glyoxal was not identified as one of the 25 most

531   important species to OFPs any more.

532   **3.4 Uncertainties of provincial NMVOC emission inventory**

533   The uncertainties of estimated annual NMVOC emissions for Jiangsu 2005-2014

534   are illustrated in Figure 4, expressed as the 95% confidence intervals (CIs) around the

535   central estimates. As inter-annual changes were hardly assumed in probability

536   distributions for parameters, similar uncertainty ranges were calculated for emissions

537   of various years. As shown in Table 5, the uncertainty of emissions for 2014 was

538   quantified at -41%~+93% (95% CI), and biomass burning and other sources were

539   estimated as the sources with largest uncertainties, followed by stationary fossil fuel

540   combustion and oil distribution. For most emission sectors/categories, emission

541   factors were identified as the largest sources of emission uncertainty, with an

542   exception of solvent use. Resulting from complicated sources of stack and fugitive

543   emissions, it is generally difficult to conduct comprehensive field tests on emission

544   factors for industrial and residential sources. As described in Section 2.3, large

545   uncertainties had to be conservatively assumed for them due to limited domestic

546   samples and to heavy dependence on foreign databases. More measurements on actual

547   emission characteristics are thus recommended to expand data samples for better

548   evaluating the PDFs and effectively reducing emission uncertainty. Regarding solvent

549   use for which provincial and city statistics were lacking, the activity data had to be

550   downscaled from national level leading to possibly big bias in emission estimation.

551   Provided in Table 5 as well are the uncertainties of national and YRD emissions

552　from other studies. Note all the studies applied Monte-Carlo simulation except Huang

553　et al. (2011), which calculated the uncertainty of emissions based on the

554　predetermined CVs of emission factors and activity levels at sector level. Compared

555　with those results, the emission uncertainties were reduced in this work for industrial

556　processes, solvent use and transportation. Besides the varied methods and

557　assumptions of PDFs for relevant parameters, the more detailed classification of

558　emission sources and adoption of independent emission factors for those sources

559　should be an important reason. For example, totally 34 vehicle type-control

560　combinations were taken into account for calculating the on-road vehicle emissions,

561　and emission factor for each type of combination was assumed independent from

562　other. In addition, the errors of activity levels for big point sources were significantly

563　reduced from the detailed investigation and on-site survey at plant level, leading to

564　smaller uncertainty in emission estimation for industrial and solvent use sources.

565　**4 Evaluation of provincial emission inventory**

566　**4.1 Chemical and refinery industry emissions from varied data sources and**
567　**methods**

568　　　As a part of industrial process, chemical and refinery industry was one of the

569　biggest contributors to anthropogenic NMVOC emissions. We select Nanjing, the

570　capital city of Jiangsu province, to evaluate the impacts of data sources and methods

571　on emissions of this category. As described in Sections 2.2 and 2.3, the method used

572　in this work for provincial inventory improvement incorporated the most available

573　information from Environmental Statistics, PSC, and on-site surveys (named Method

574　1 here). Besides, two other methods based respectively on data from Environmental

575　Statistics (Method 2) and economic statistics without any information on individual

576　plants (Method 3, which was commonly applied in national and regional inventories)

577　were also applied to calculate the emissions in the city for 2011, and the results with

578　different methods were compared against each other. Note the emissions of area

579　sources (i.e., not included in plant-by-plant investigations) in Methods 1 and 2 were

21

580　the same as Method 3. Table S8 in the supplement provides the emissions calculated

581　based on the three data sources by subcategory of chemical and refinery industry. The

582　emissions estimated using Method 1 were clearly larger than those using Method 2 or

583　3, resulting mainly from the incomplete records of chemical products by

584　environmental or economic statistics. For example, some basic chemistry products

585　(e.g., ethylene oxide and ethylene glycol) and synthetic chemical products (e.g.,

586　polyether and polyethylene) were not included in current economic statistics. In

587　addition, although most chemical and refinery plants were investigated in the

588　Environmental Statistics, only three types of chemical products were recorded for

589　each plant, much less than the actual (more than one hundred types for some plants).

590　The omission of chemical product types thus led to underestimations in NMVOC

591　emissions. With the product types fully covered, Method 1 could even underestimate

592　the emissions, as the emission factors could not be measured or determined for all

593　products due to the completed pipe layout or fugitive release.

594　　　Spatial distributions of the emissions in the three methods are illustrated in

595　Figure 5. Similar patterns were found for Method 1 and 2 (Figure 5a and 5b), as the

596　emissions were dominated by the big chemical and refinery plants. As labeled in

597　Figure 5a, the largest ten plants were estimated to account for 80% of NMVOC

598　emissions of the sector for the whole city. Without detailed information of individual

599　plants, Method 3 had to apply the proxies (e.g., population density) to allocate the

600　emissions, and would overestimate the fraction of emissions in urban downtown

601　(Figure 5c). The comparison indicated the possible errors in spatial distribution of

602　emissions at small scale when emissions were downscaled from larger scale without

603　sufficient investigation on local sources, particularly for regions where large plants

604　were gradually moved out of urban areas.

605　　　To further examine the emission estimation on individual plants, an alternative

606　method was applied to calculate the emissions of all manufacturing processes

607　separately including leaks of hydrocarbon vapors from process equipment (valves,

608　flanges, seals, etc.), storage of organic liquid, loading and unloading of organic liquid,

609　and waste water treatment (mentioned as device operation based method herein). As

22

610   indicated in Table S9 in the supplement, detailed information of 15 key chemical and

611   refinery enterprises in Nanjing (i.e., enterprises directly under the control of city

612   government) were collected and the emissions of those plants were calculated and

613   compared with the results using the method as described in Sections 2.2 and 2.3

614   (mentioned as emission factor based method herein). Although the total emissions of

615   the 15 plants were very close between the two methods, significant discrepancies

616   existed for individual plants. For example, much larger NMVOC emissions were

617   calculated for plants 3 and 6 with device operation based method, as the emission

618   factors for production of chlorobenzene alkylbenzene and cyclohexanone were

619   lacking, leading to underestimation in the emission factor based method. As shown in

620   Figure S6 in the supplement, the differences in emissions from varied calculating

621   methods for the 15 plants led to moderate changes in spatial distributions of the

622   chemical and refinery emissions for the city. In general, the device operation based

623   method could better capture the activities of specific plant and the actual emission

624   characteristics; however, the method could hardly be applied in a broader scale, as it

625   depends strongly on the completeness and quality of data collection.

626   **4.2 Changes in speciation of NMVOC emissions**

627   As indicated in Section 2.2, the speciation of NMVOC emissions in Jiangsu were

628   updated by including our measurements and other most recent domestic tests after

629   2010, based on the combination profile of Li et al. (2014) and SPECIATE (i.e., the

630   source profile before updating). The source types we measured accounted for 9-11%

631   of annual NMOVC emissions from chemical industry and refinery for Jiangsu

632   2005-2014. In particular the contribution of those sources was enhanced in typical

633   cities with intensive chemical industry. In Nanjing, as an example, the source

634   categories we measured accounted for 19% of annual emissions from chemical

635   industry and refinery, and for 10% of the total anthropogenic emissions in 2010.

636   Figure 6 illustrates the emissions of 445 species (accounting for 99.5% of total

637   NMVOC emissions) estimated with the source profile before and after updating for

638   Jiangsu 2010. As a whole, the difference between emissions of all species before and

639 after updating was calculated at 281 Gg, i.e., 13% of the total anthropogenic NMVOC

640 emissions for the province. Due to relatively limited tests available, the changes in

641 emissions were small for most species when updated profiles were applied. Relative

642 big changes (over 10 Gg) were found for ethylacetate and certain aromatics species

643 (benzene, xylene, ethylbenzene, and methylbenzene). Applying the source profile of

644 paint use measured by Zheng et al. (2013) led to enhanced ethylacetate. Reduced

645 benzene and methylbenzene, and elevated ethyl benzene and xylene resulted mainly

646 from the revisions on source profiles of cooking (Jia et al., 2009; Shi et al., 2015) and

647 solvent use (Wang et al., 2014b; Zheng et al., 2013). Although incremental

648 information on speciation was obtained through the on-site measurements and source

649 profile updating in current work, domestic data were still lacking for many source

650 types, given the big variety of source categories for industrial process and solvent use.

651 Therefore more efforts on field measurements are still needed in order to establish a

652 more complete database of chemical profiles for the country and the region.

653   To support the air quality modeling, the emissions of NMVOC species under

654 CB05 and SAPRC99 mechanisms were calculated using Eq. (4) based on the source

655 profiles before and after updating, and the results for 2010 were shown in Figure 7

656 (the speciation for MEIC is illustrated in the figure as well for comparison, as

657 discussed later in Section 4.3). With source profiles updated based on most recent

658 measurements, relatively big changes were found for ALDX (see captions of Figure 7

659 for the detailed meanings) in CB05 and OLE1 in SAPRC99. The revisions on source

660 profiles of solvent use were the main reason for the changes. For example, the

661 increased ALDX was attributed mainly to the updated profiles of printing ink and

662 automobile paint use (Zheng et al., 2013; Tang et al., 2014), while increased OLE1 to

663 that of building coating (Yuan et al., 2010; Wang et al., 2014b) .

664 **4.3 Comparisons with other inventories**

665   The total anthropogenic NMVOC emissions in Jiangsu were extracted from other

666 continental/national/regional inventories and compared with our estimates for various

667 years in Figure 4. All the results were within the 95% CIs in this work. Except for

24

668   REAS that provided 37-77% higher emissions than this work for 2005-2008

669   (Kurokawa et al., 2013), our estimates were generally 0-18% larger than other studies

670   in the total emission estimation, attributed mainly to the omission of certain emission

671   sources in other inventories and to the elevated activity levels from plant-by-plant

672   investigation in this work. Figure 8 provided the NMVOC emissions by source from

673   various inventory studies for selected years. As can be seen, the emissions in this

674   work were 4% and 20% larger than the national inventory for 2005 (Wei et al., 2008)

675   and regional inventory for 2010 (Fu et al., 2013), respectively. The latter two studies

676   missed the emissions from the manufacturing processes of certain chemical products.

677   For example, fermentation alcohol, dye and rubber were not included in Wei et al.

678   (2008), and glasswork, pesticide and charcoal were not included in Fu et al. (2013).

679   The emissions from solvent use in this work were larger than those from Bo et al.

680   (2008), attributed to omission of carpentry coating, pesticide and adhesive using by

681   the latter. The varied data sources also contributed to the emission discrepancies. For

682   example, Wei et al. (2008) and Bo et al. (2008) made larger estimates in transportation

683   emissions than us, as they applied higher values of annual average miles traveled for

684   motorcycles at national level.

685   The emissions of CB05 and SAPRC 99 species estimated by us and MEIC were

686   compared in Figure 7. While total NMVOC emissions in this work were 315 Gg or

687   18% larger than MEIC for 2010, relative changes varied among species and could be

688   bigger for certain ones. In CB05 mechanism, our results were 46% and 43% smaller

689   for TOL and XYL but 38% and 59% larger for ETH and ETHA than MEIC (Figure

690   7a), while discrepancies of over 30% (relative to MEIC) existed for most species in

691   SAPRC 99 (Figure 7b). Such discrepancies could result either from the various source

692   profiles, or from the various source contributions to total emissions. For example,

693   with updated source profile for building coating, much larger OLE1 emissions were

694   estimated in this work than MEIC. Besides the total emissions, the differed

695   speciations under chemical mechanisms could result in complex impacts on air quality

696   simulation, and it would be discussed in next section.

697   Figure 9 compares the spatial distributions of Jiangsu's NMVOC emissions for

25

698 2010 between our results and MEIC. To be consistent in resolution and to ease

699 visualization, the high-resolution inventory obtained in this work (Figure 2) was

700 upscaled to 0.25°×0.25°, the same as MEIC. Similar spatial patterns were found for

701 the two inventories: high emission densities existed in southern Jiangsu with

702 relatively developed economy and industry. As indicated in Figure 9a, the areas with

703 big plants and large emissions were consistent with each other, indicating that the

704 provincial NMVOC emissions were largely influenced by the locations of large point

705 sources. Figure 9c shows that larger emissions estimated in this work than MEIC were

706 commonly found in areas with big plants, reflecting the impacts of complete

707 investigation on product types and activity levels at plant level on the emission

708 estimation. Although our result was 18% larger than MEIC in total anthropogenic

709 NMVOC emissions, lower emissions were found in this work at downtown Nanjing

710 and the Suzhou-Wuxi-Changzhou city clusters with large populations. The result

711 implies that downscaling of emissions depending on certain proxies (e.g., population

712 and economy density) might overestimate the emissions in urban areas, and detailed

713 information on individual sources should be included if possible.

714 **4.4 Evaluation of multiple-scale inventories through air quality modeling**

715   The Models-3/Community Multi-scale Air Quality (CMAQ) version 4.7.1 was

716 applied to test the performances of chemistry transport simulation with various

717 NMVOC emission inventories for Jiangsu area. As shown in Figure S6 in the

718 supplement, three nested domains (D1, D2 and D3) were set, and the most inner D3

719 covered the mega city Shanghai and six most developed cities in southern Jiangsu

720 including Nanjing, Changzhou, Zhenjiang, Wuxi, Suzhou and Nantong, with a

721 horizontal spatial resolution at 3 km. Chemistry transport simulations were conducted

722 separately with two inventories, i.e., MEIC and the provincial one developed in this

723 work, for January, April, July and October 2012. Other model settings on

724 meteorological simulation, chemistry mechanisms and emissions of natural origin

725 were the same for the two simulations, as described in Zhou et al. (2017). The first

726 five days for each month were chosen as spin-up period to provide initial conditions

26

727   for later simulations.

728   Figure 10 provides the observed and predicted daily 1h-max O_3 concentrations

729   for the four months, and Table 6 compares the model performances with MEIC and

730   our provincial inventory, indicated as normalized mean bias (NMB) and error (NME)

731   values. As suggested by the minus NMBs for most cases, model usually generated

732   lower 1h-max O_3 concentrations than observation with either MEIC or provincial

733   inventory applied, with an exception for April simulation with MEIC applied. The

734   result thus implied the updated anthropogenic NMVOC emission inventory at

735   provincial scale was still likely an underestimation of the actual emissions, as YRD

736   was commonly recognized as VOC-limited region for O_3 formation (Xing et al., 2011).

737   Compared to MEIC, better model performances (except for July) were generally

738   achieved when the provincial inventory was applied, indicating the improved

739   reliability of the detailed bottom-up NMVOC inventory on high-resolution chemistry

740   transport simulation. In particular, larger emissions were estimated for certain species

741   with relatively high ozone formation potential (e.g., ethene and ethanol) in the

742   provincial inventory. It should be noted that the improved ozone simulation was a

743   combined effect of the updated inventory with revisions on emission estimation,

744   spatial distribution and source profiles for all the relevant species, and that the impacts

745   of emission changes for individual species could not be completely validated. More

746   chemistry transport modeling is further encouraged with intensive sensitivity analysis.

747   The discrepancies between simulation and observation were still large compared

748   to regional studies in North America (Y. Zhang et al., 2009). More efforts on

749   improving or validating emission inventory at provincial scale are thus in great

750   needed. Besides careful compilation of emission source information in the bottom-up

751   method, observation constraint from ground measurements could be used to evaluate

752   the emission level, source contribution, and speciation of VOC emissions (M. Wang et

753   al., 2014). Emission uncertainty of NO_X could also partly explain the discrepancies, as

754   the NO_X control measures taken recently could hardly be fully tracked in the emission

755   inventory development. Besides the limitation of emission input, more analysis on the

756   impacts of chemical mechanisms and dynamics in the chemistry transport modeling

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757   are also suggested for O_3 prediction in the region.

758   **5 Conclusion**

759   Using a bottom-up approach, we developed a high-resolution emission inventory

760   of anthropogenic NMVOC for Jiangsu province, eastern China, with substantial

761   detailed information on local sources and source profiles from domestic tests

762   incorporated. Attributed largely to the elevated contribution from industrial processes

763   and solvent use, the annual provincial emissions were estimated to increase 41% from

764   2005 to 2014. Influenced largely by location of big point sources, high emission

765   densities were found in cities along the Yangtze River. Our estimations were larger

766   than results from most other available inventories except REAS, due mainly to the

767   omissions of certain industrial and solvent use sources by other studies and to the

768   elevated activity levels from plant-by-plant investigation in this work. Benefiting from

769   more detailed classification and investigation of emission sources, reduced

770   uncertainties in annual emissions were quantified in this work compared to previous

771   studies. Varied data sources and methods were of significant impacts on emission

772   estimation at city/plant level. In particular, downscaling directly from national

773   inventories would overestimate the fraction of emissions in urban downtown. With the

774   most recent source profiles from local measurements included, considerable changes

775   in emissions were found for ethylacetate and certain aromatics species, and the

776   speciation under CB05 and SAPRC99 differed a lot from the national inventory

777   MEIC. Compared to MEIC, better model performance (indicated by daily 1h-max O_3

778   concentrations) were achieved when the improved provincial inventory was used in

779   CMAQ simulation, although the discrepancies between simulation and observation

780   need further investigation. As emission controls on NMVOCs started to be

781   implemented on industrial sources in China (e.g., the application of leak detection and

782   repair technique in chemical and refinery plants), more field tests were recommended

783   to better track the temporal changes in emission factors and to reduce the uncertainty

784   of emission estimation in the future.

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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 monoalkylaromatics, 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 yeas estimated from this work and other inventories. Note emissions in this work are regrouped to be consistent in source categories with Zhang et al. (2009) and MEIC for direct comparison.

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 O$_3$ 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 Categories of anthropogenic NMVOC emission sources.

Sector	Subsector	Product/fuel/solvent used	Product/technology
Fossil fuel stationary combustion	Power plant	Coal/oil/natural gas/waste/biofuel	N.A.
	Heating and industrial boiler	Coal/coke/oil/natural gas	N.A.
	Residential	Coal/oil/LPG/natural gas	N.A.
Biomass burning	Boiler	N.A.	N.A.
	Stove burning	Crop straw/wood	N.A.
	Open burning	Crop straw	Rice/corn/wheat/other
Industrial process	Iron and steel	Coking	Mechanical/indigenous
		Sinter/pellet/crude steel	N.A.
	Non-metallic mineral	Glass	Flat glass/glass fiber/glass work
		Cement clinker/lime/brick and tile/ceramic	N.A.
	Oil exploitation and refinery	Crude oil exploit/crude oil refinery	N.A.
	Chemical industry	Chemical raw materials: Ethylene/benzene/methanol/ acetic acid/synthesis ammonia/phthalic acid/ethylene oxide/vinylacetate/styrene/glycol/octanol/butanol	N.A.
		Synthetic chemical industry: synthetic resin	Polyethylene/polypropylene/Polystyrene/polyvinylchloride
		Synthetic chemical industry: synthetic fiber	viscose/cellulose acetate fiber/nylon fiber
		Synthetic chemical industry: synthetic rubber	N.A.
		Fine chemical industry: pharmaceutical/chemical pesticide/paint/printing ink/adhesive/dye	N.A.
	Food and wine	fermentation alcohol/spirit/beer	N.A.
		Bread/cake/biscuit	N.A.
		Vegetable oil extraction	N.A.

Table 1 (continued)

Sector	Subsector	Product/fuel/solvent used	Product/technology
Industrial process	Plastic and rubber product	Foam plastic/plastic products/tire/other rubber product	N.A.
	Textile industry	Silk/cloth/woolen yarn	N.A.
	Carbon black		N.A.
Solvent use	Paint use	Interior/exterior building coating	Water-based/solvent-based
		Automobile production/repairing	N.A.
		Wood decoration/wooden furniture paint	N.A.
		Anticorrosive paint	N.A.
		Other paint	N.A.
	Printing	New-type/traditional ink	N.A.
	Dyeing		N.A.
	Adhesive use	Shoe making/timber production/other	N.A.
	Other solvent use	Agriculture pesticide/Dry cleaning/household solvent use/solvent degreasing	N.A.
Transportation	On-road	Automobile	Load (light/heavy)-fuel (gasoline/diesel)
		Motorcycle	Gasoline
	Off-road	Train/inland ship/construction machine/ tractor/agriculture truck/agriculture machine	N.A.
Oil distribution	Crude oil/gasoline/diesel	Storage/transport/load & unload/gas station	N.A.
Others		Garbage disposal	Burning/landfill/compost
		Cooking fume	N.A.

Table 2 NMVOC emission factors for combustion sources, industrial processes and solvent use. Unless specifically noted, the units are g/kg-fuel, g/kg-product and g/kg-solvent, respectively.

Source	Fuel/product/solvent used		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	0.0015[e]; 1.1[f]
	Stove burning	Wood	3.23	1.09-4.94[g]; 3.23[c]; 5.3[e]
		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]
	Open burning	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 straws 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[i]; 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]; 21[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]

Table 2 (continued)

Source	Fuel/product/solvent used	EFs in this study	EFs in the references
Industrial process			
Chemical industry	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]
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)/12.5	0.285(kg/tire)[m]; 0.285(kg/tire)[l]; 0.91 (kg/tire)[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)[d]; 33.105(g/L)[i]
	Beer/grape wine	0.25/0.5	0.44[l]; 0.4[c]; 0.43(g/L)[a]; 0.25[f]; 0.35 (g/L)[d]/0.81[l]; 0.5[c,f]; 0.8 (g/L)[d]; 0.38(g/L)[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)[d]; 4[i]
Textile industry	Silk/cloth/woolen	10/10/10	10[b]/10[b]/10[b]
Carbon black	N.A.	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*	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**	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)
*250 and 120 g/kg for 2005-2007 and 2008-2014, respectively; **Adjusted by per capital income.

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

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& 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

Table 4 (continued)

Sector		Species (weight percentage, %)					
		Alkanes	Alkenes	Alkynes	Aromatics	OVOCs	Others
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

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 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.

Source Category	Uncertainty					Parameters contributing most to uncertainty	
	This work	Wei (2009)	Bo et al. (2008)	Fu et al. (2013)	Huang et al. (2011)	This work	
	Provincial scale	National scale	National scale	Regional scale	Regional scale	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%)	$R_{Straw\ burning\ in\ stove}$ [1] (5%)
Other	-98%, +490%	-	-		-	$EF_{Cooking}$ (84%)	$EF_{Garbage\ burning}$ (14%)
Total	-41%, +93%	-51%, +133%	-36%, +94%	-52%, +105%	-53%, +113%		

[1] The ratio of straw burned in stove as biofuel

Table 6 Model performance of daily 1h-max O$_3$ concentrations using MEIC and provincial inventory for January, April, July and October 2012 in Nanjing.

	Provincial emission inventory		MEIC	
	NMB[1]	NME[1]	NMB	NME
January	-21%	34%	-58%	59%
April	-26%	38%	35%	55%
July	-28%	33%	-23%	29%
October	-20%	26%	-50%	50%

[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):

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

;

Figure 1

(a)

(b)

47
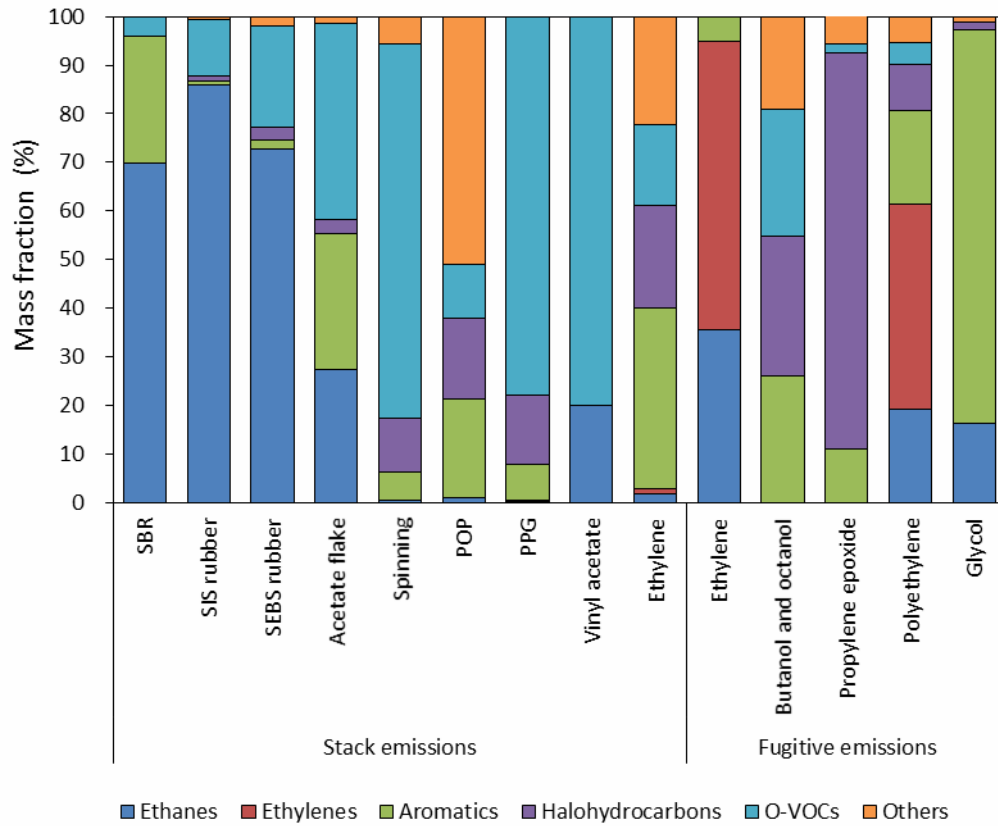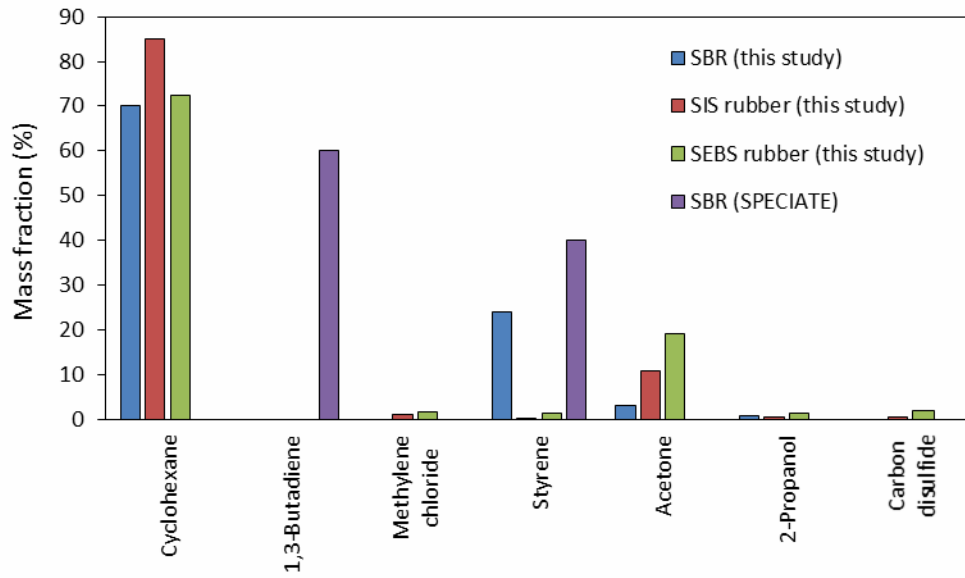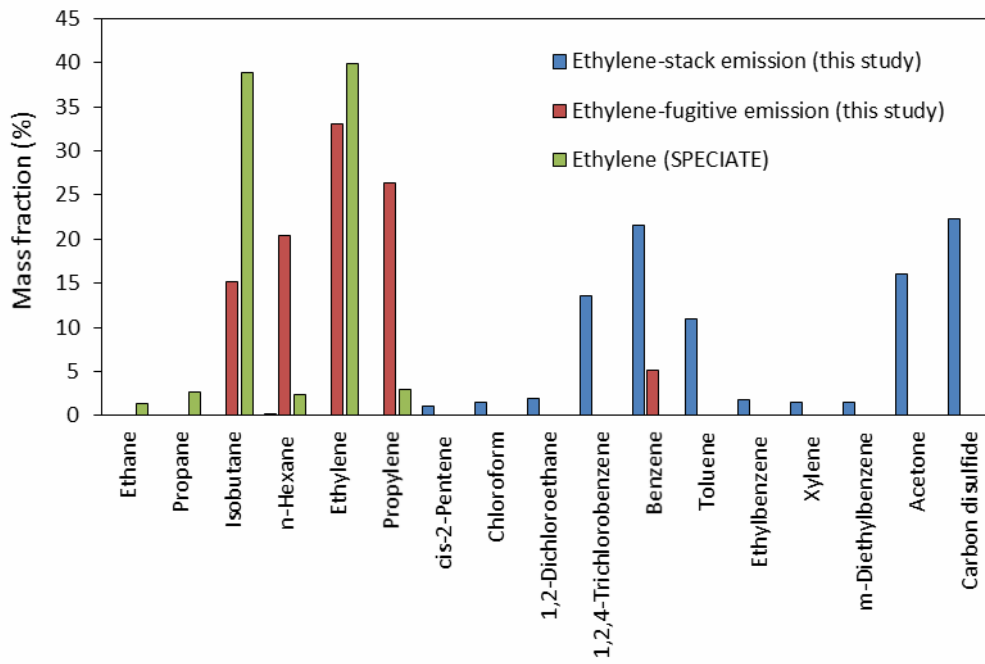
(c)
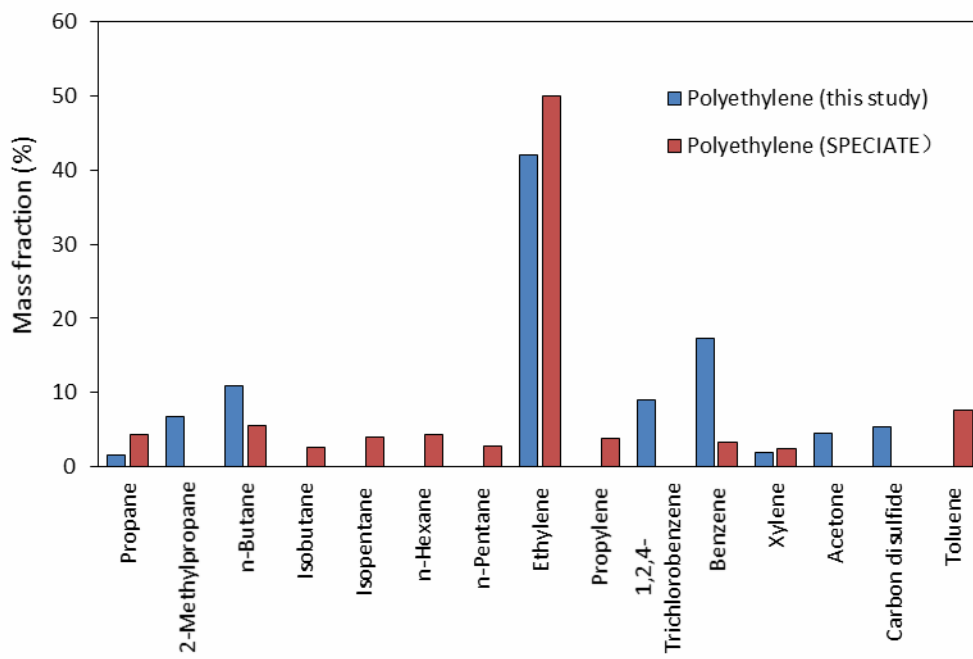
(d)
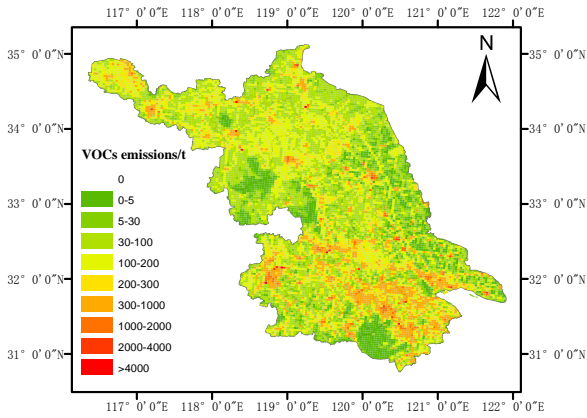
Figure 2

(a) 2005
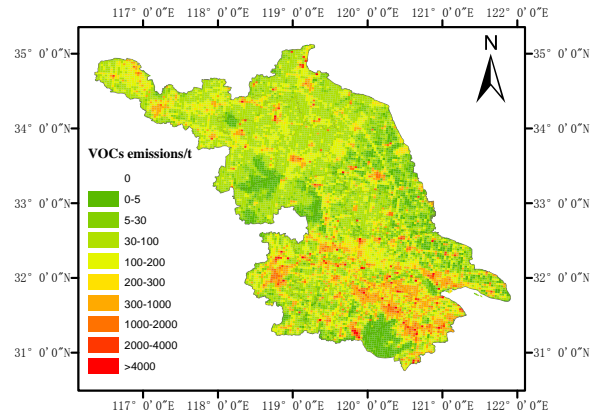
(b) 2010
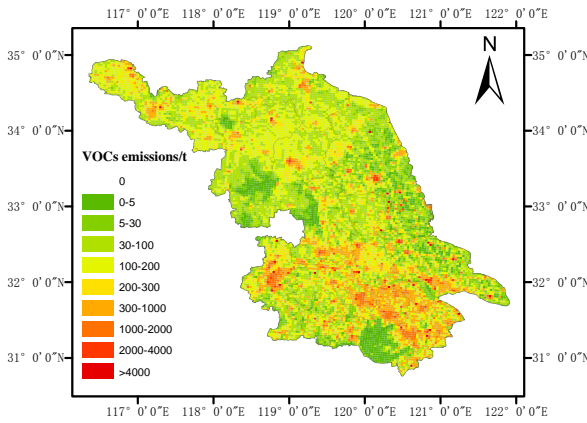
(c) 2014
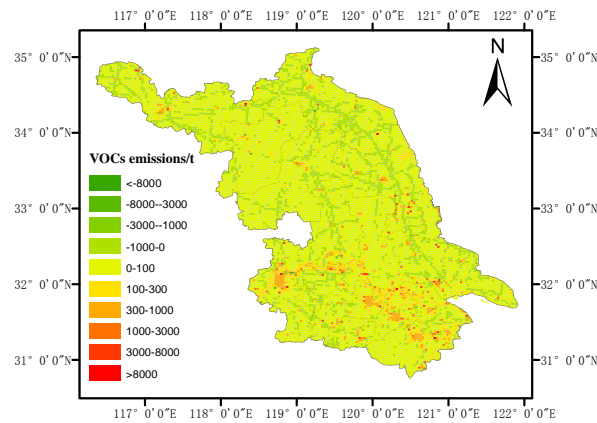
(d) Difference between 2005 and 2014

49

Figure 3

Figure 4

Figure 5

(a) (b) (c)
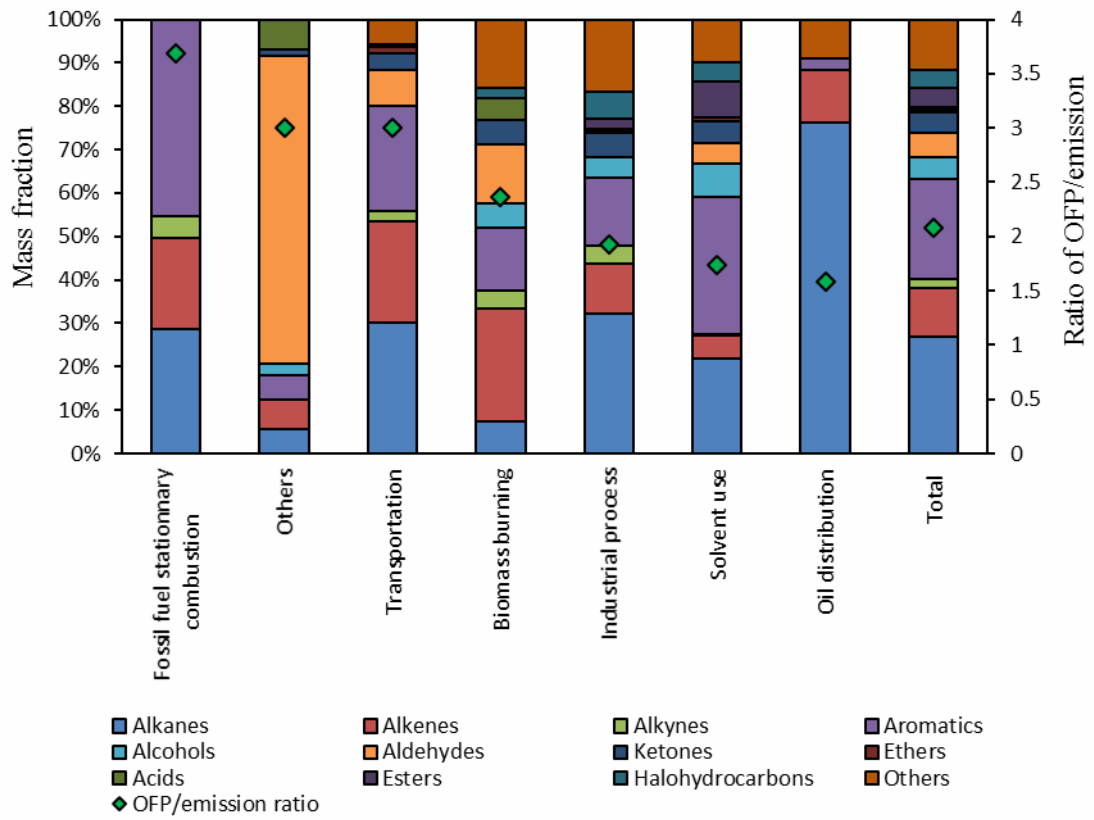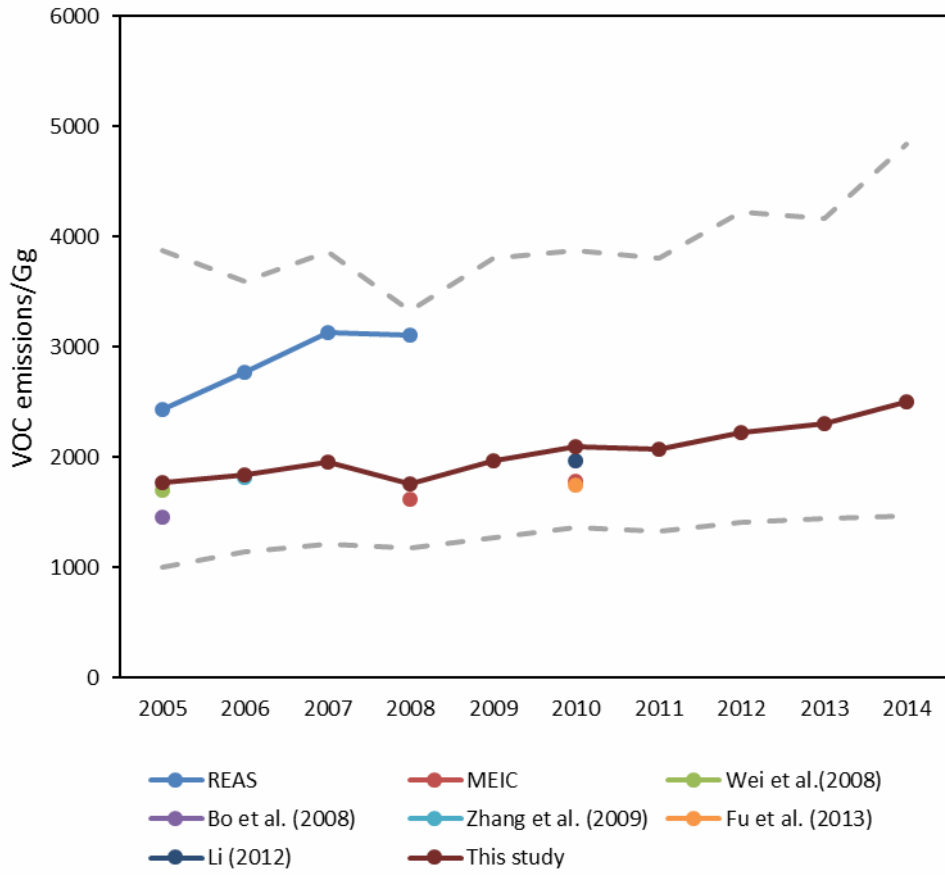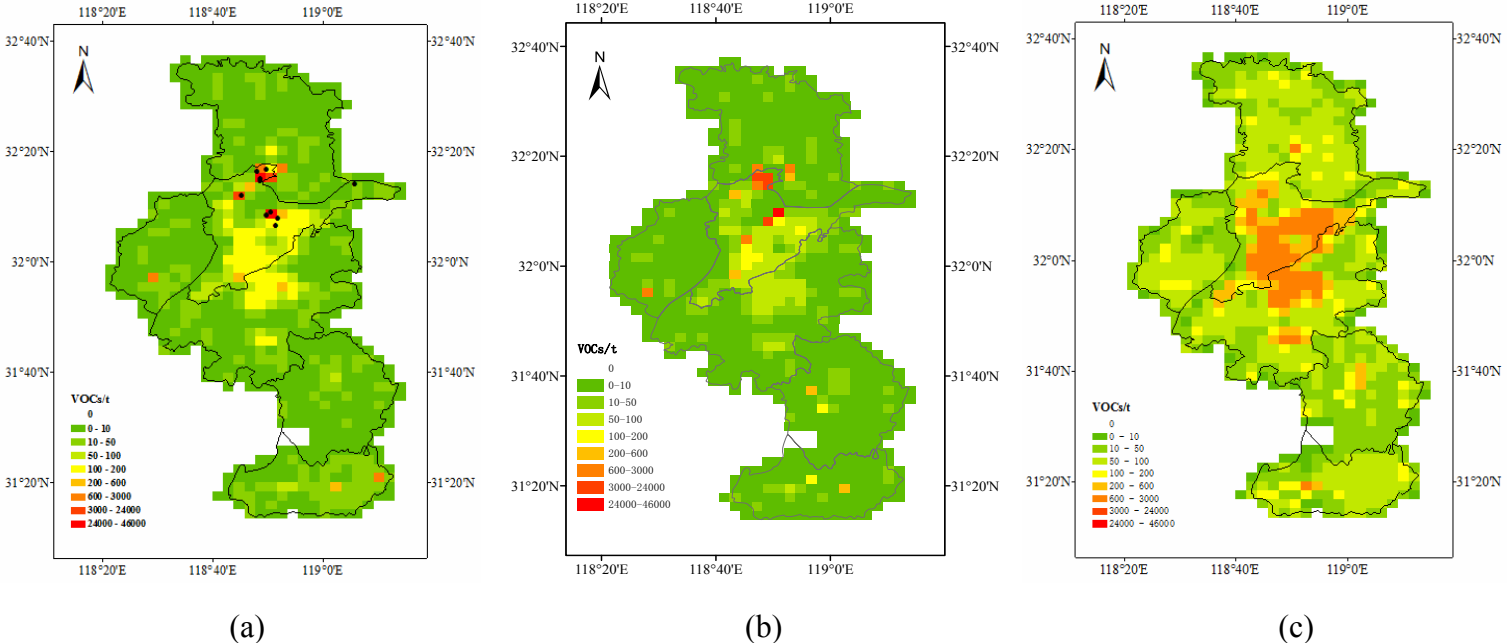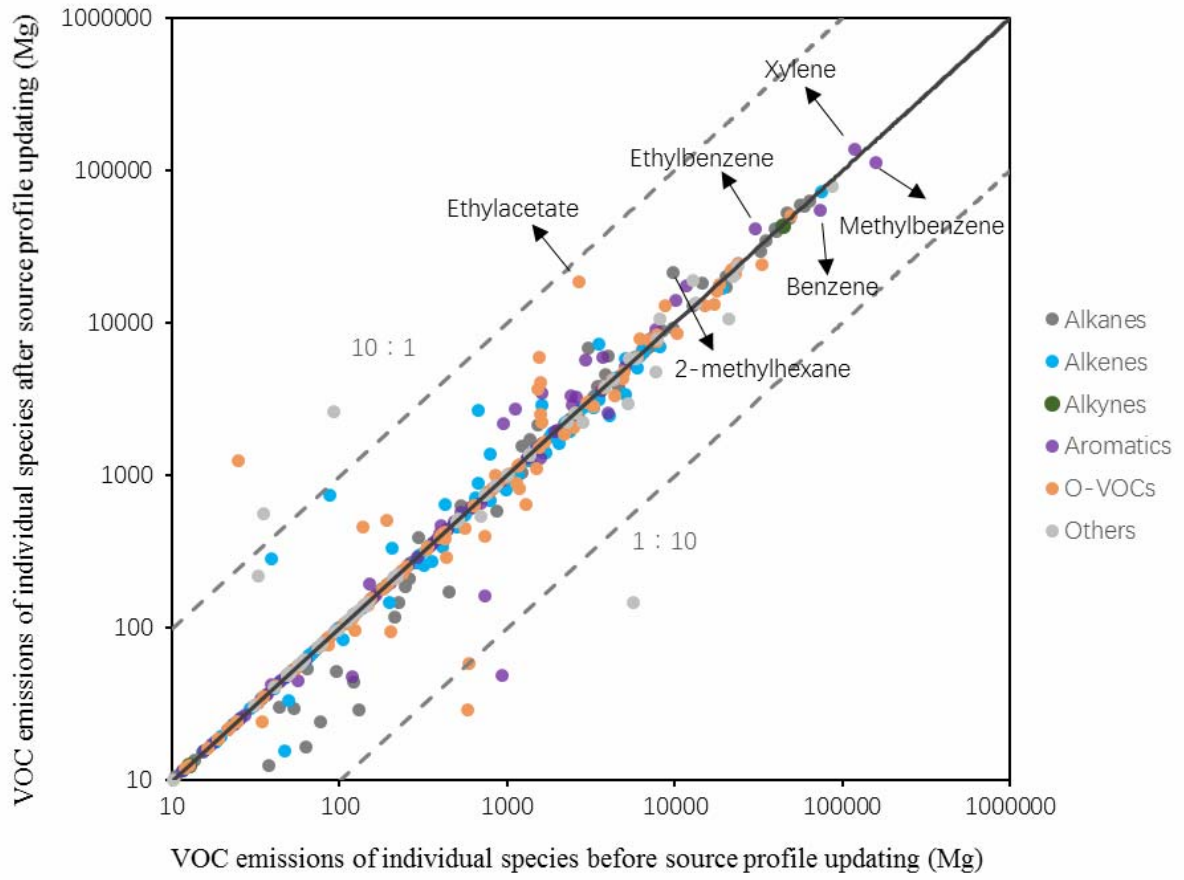
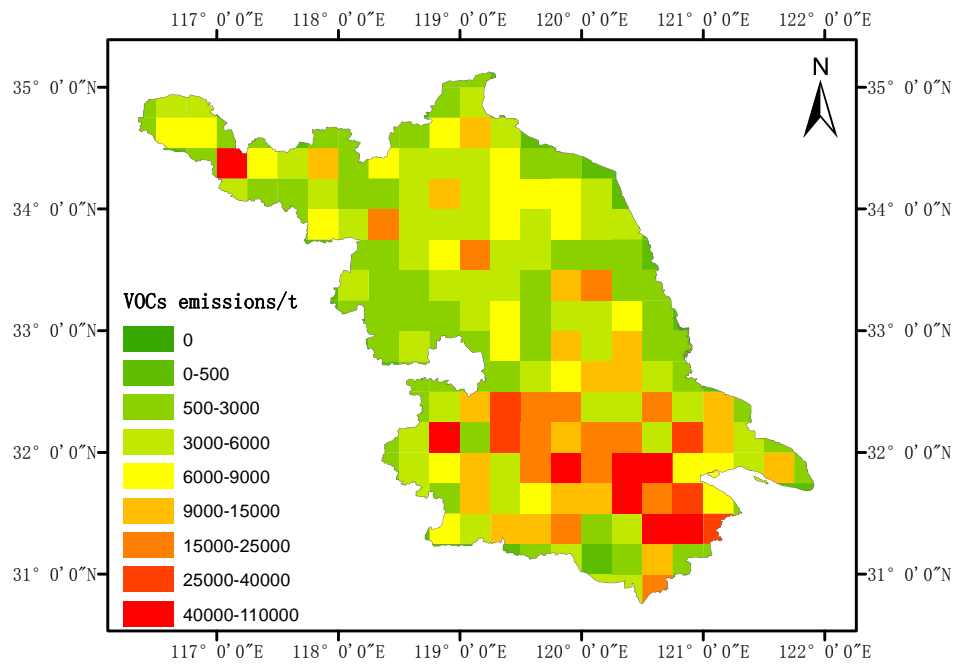**Figure 6**

Figure 7

(a) CB05
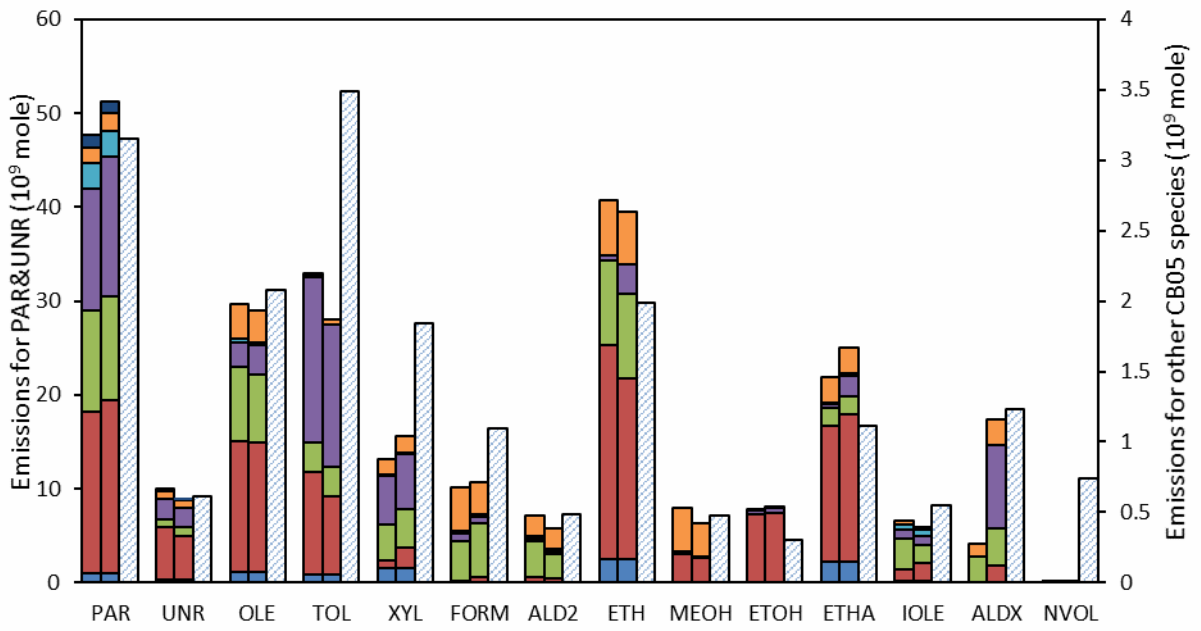
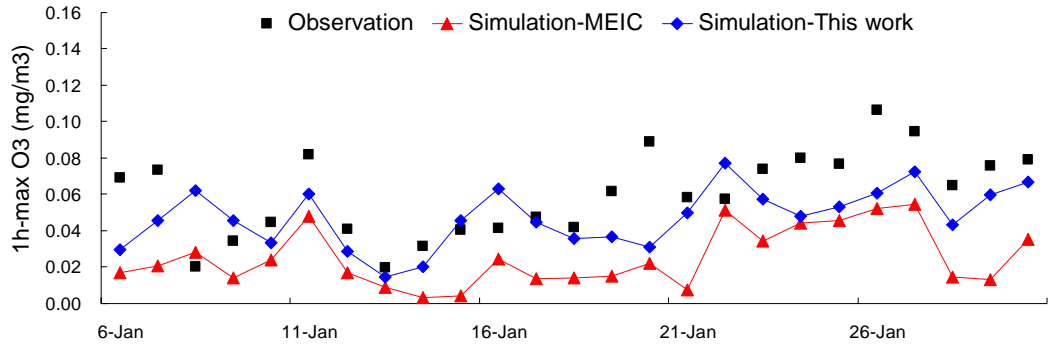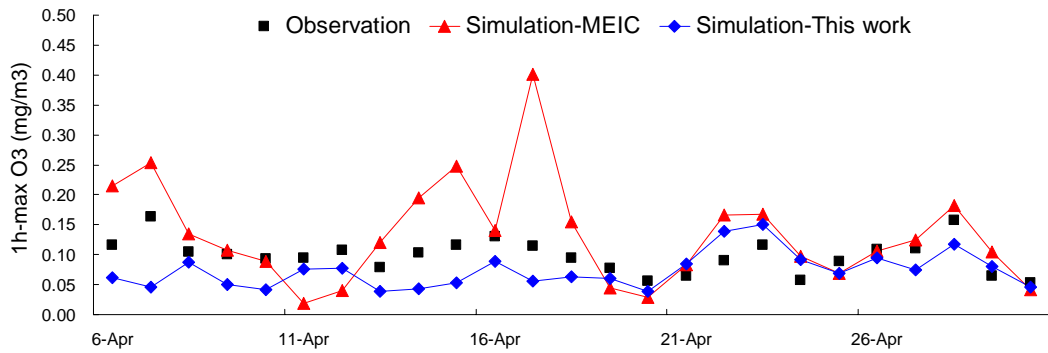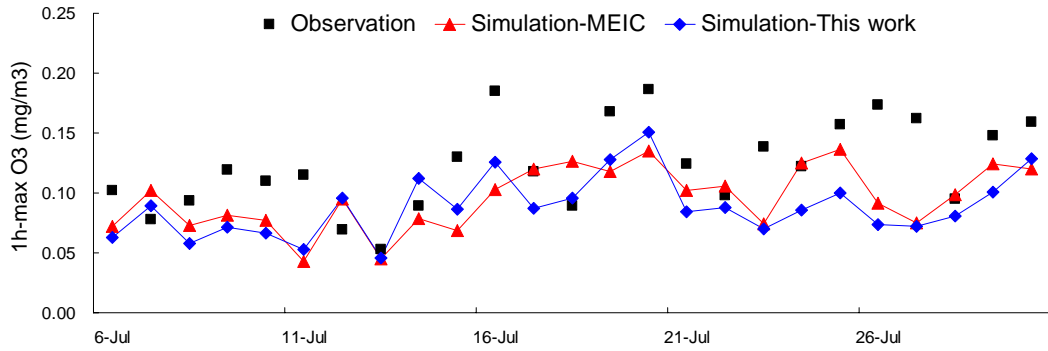(b) SAPRC99
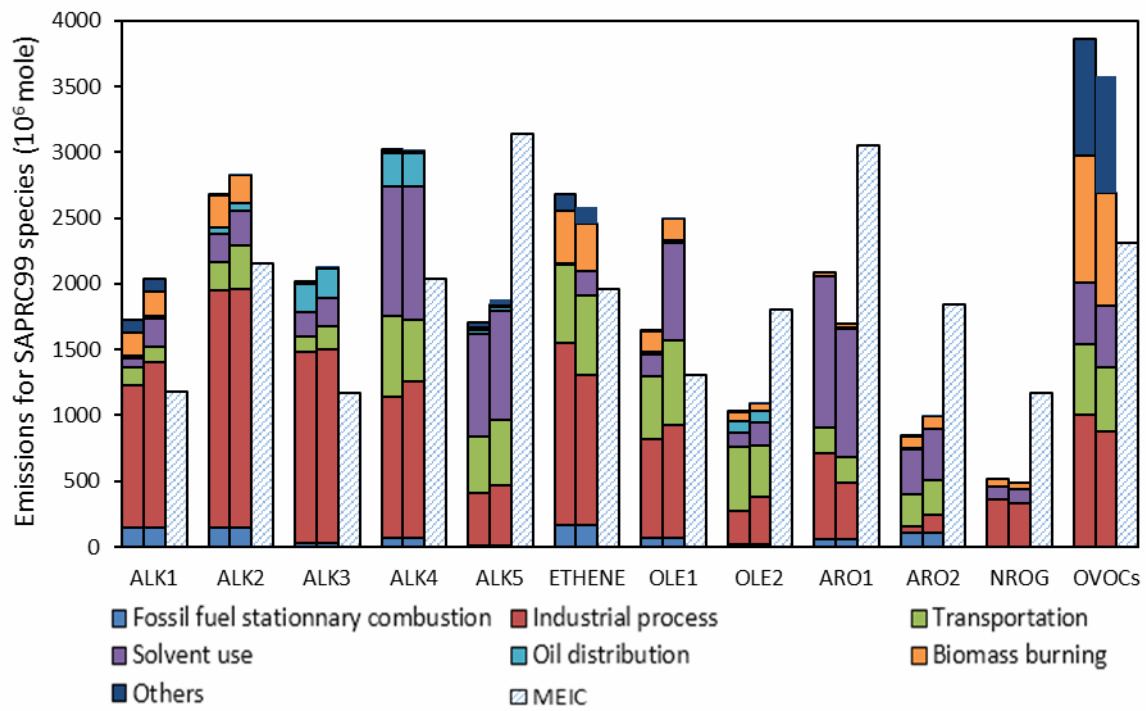
Figure 8
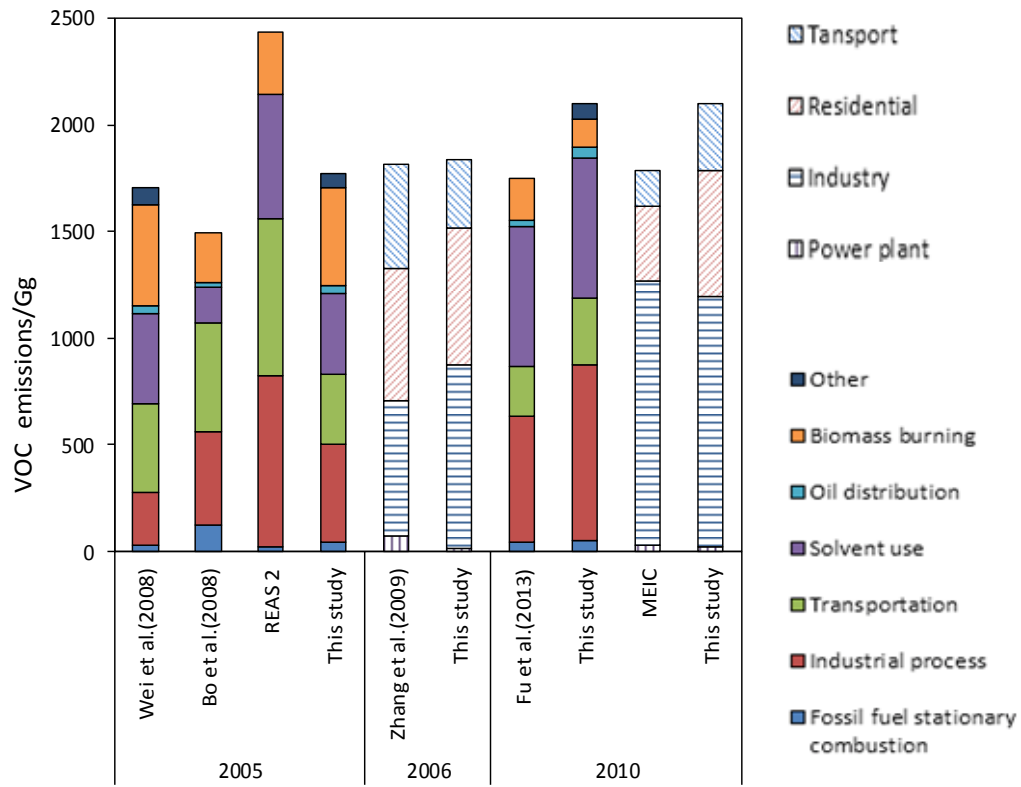
Figure 9

(a)

(b)

Figure 9 (continued)

(c)

Figure 10

(a)

(b)

(c)

(d)