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 (NMVOC) 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 the field measurements on source profiles of chemical industry. Totally 56

8   NMVOCs samples were collected in 9 chemical plants, and then analyzed with a gas

9   chromatography-mass spectrometry system (GC-MS). Source profiles of stack

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

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

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

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

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

15   production. The provincial NMVOC emissions were calculated to increase from 1774

16   Gg in 2005 to 2507 Gg in 2014, and relatively large emission densities were found in

17   cities along the Yangtze River with developed economy and industry. The estimates

18   were larger than those from most other available inventories, due mainly to the

19   complete inclusion of emission sources and to the elevated activity levels from

20   plant-by-plant investigation in this work. Industrial processes and solvent use were the

21   largest contributing sectors, and their emissions were estimated to increase

22   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 mainly 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 region for developed cities in southern

35   Jiangsu. Besides, clear 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 of species OLE1 resulted mainly from the updated

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

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

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

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

42   October 2012 when the provincial inventory was used.

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 heavy haze period in winter, based on detailed

51   chemistry composition and source analysis 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 as

54   maximum incremental reactivity, MIR), the ozone (O_3) formation were 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).

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, the emissions of natural and anthropogenic origin were estimated

64   close to each other at 10-30 Tg (Tie et al., 2006; Klimont et al., 2002; Streets et al.,

65   2003). Table S1 in the supplement briefly summarizes the estimations of China's

66   national NMVOC emissions of anthropogenic origin from various studies. With

67   different methods and data sources applied, the NMVOC emissions in China were

68   estimated to be doubled from 1990 to 2010, and the contributions of solvent use,

69   non-combustion industrial processes and transportation were enhanced for recent

70   years. Incorporating available information at national scale, Tsinghua University

71   developed   the   Multi-resolution   Emission   Inventory   for   China   (MEIC,

72   http://www.meicmodel.org/) and calculated the national total emissions at 23.6 Tg for

73   2010. Among all the studies, largest estimations were made in Regional Emission

74   inventory in Asia (REAS, Ohara et al., 2007; Kurokawa et al., 2013), reaching 28.0

75   Tg for 2008.

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

77   natural sources. For example, the anthropogenic NMVOC emissions were estimated

78   6-18 times of natural emissions 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, the 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

88   including refinery and chemical engineering plants were less investigated at local

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

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

91   and 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 with various NMVOC

94   inventories have not been sufficiently evaluated. Moreover, source profiles and

95   speciation of NMVOC emissions need further improvement. Increasing domestic field

96   measurements have been conducted on chemical profiles of NMVOCs for typical

97   types of sources including solvent use (Yuan et al., 2010; Zheng et al., 2013),

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

99   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 engineering 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 the better understanding and

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

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

111 evaluate the high-resolution emission inventory of anthropogenic NMVOCs. The

112 geographic location and cities of the province are illustrated in Figure S1 in the

113 supplement. Field measurements on chemical composition of NMVOC emissions

114 were conducted to obtain the source profiles of typical chemical engineering

115 processes. With detailed information of local emission sources collected and temporal

116 changes tracked, the provincial emission inventory of NMVOC with chemistry

117 profiles were developed for a ten-year period 2005-2014, and the uncertainties of the

118 emission estimation were quantified. Through a thorough comparison between results

119 from varied methods and data sources, the discrepancies in emission estimation,

120 source profiles, and spatial patterns were then evaluated. Finally, chemistry transport

121 modeling was applied in southern Jiangsu to test the improvement of the provincial

122 NMVOC inventory.

123 **2 Data and methods**

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

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

126 distributed in Jiangsu to measure the chemistry composition of NMVOC emissions.

127 Very few domestic tests were available for those sources. Based on the on-site

128 investigation of main emission processes, the locations for stack and/or fugitive

129 emission sampling were determined for each source type, as summarized in Table S2

130 in the supplement. Note the sampling cannot be conducted for all the processes in an

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

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

133 The canister was sealed with smooth stainless steel as its inner wall, and the volume

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

135 For stack emission measurement, as shown in Figure S2a in the supplement, the

136 canister was connected with a stainless steel probe, and a filter pipe filled with glass

137 wool and anhydrous sodium sulfate was applied to remove the particles and water

138 vapor in the air sample. Under flow control, the sampling time was roughly 10

139 minutes indicated by the pressure gage of the canister. For fugitive emission

140 measurement, the canister was placed 50 meters downwind the chemical production

141 device, and the sampling time was roughly 8 minutes. Repeated sampling was

142 conducted for each process to eliminate the bias and totally 56 samples were obtained,

143 as shown in Table S2.

144   NMVOC sample was analyzed by one Gas Chromatograph Mass Spectrometer

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

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

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

148 adsorbed on glass beads at –150°C and desorbed at 10°C. In the second stage, it was

149 trapped on Tenax at –30°C and desorbed at 180°C. In the third stage, the VOC was

150 focused on a transfer line at –160°C and heated rapidly to 70°C. The concentrated

151 VOC was then injected into the gas chromatograph. The GC oven temperature was

152 initially programmed at –50°C, and then increased to 180°C at 4°C/min and to 220°C

153 at 15°C/min, holding 3minutes. The VOC compounds were separated on a DB-5MS

154 capillary column (60 m×0.25 mm×1.0 μm) and quantified using a quadrupole mass

155 spectrometer. The mass spectrometer was operated in SCAN mode and scanned 20-42

156 amu and 35-270 amu before and after 8.5 minutes, respectively. The ionization

157 method was electron impacting, and the source temperature was 230°C. The PAMS

158 (Photochemical Assessment Monitoring System) standard mixture (Spectra Gases Inc.,

159 USA) and TO-15 standard mixture (Spectra Gases Inc., USA) were used to confirm

160 the retention times of different compounds, and to identify them based on retention

161 time and mass spectrum. The target species were quantified by using multipoint

162 internal calibration method. To establish calibration curves, a certified gas mixture

163 containing all the target compounds was dynamically diluted with pure nitrogen to

164 five concentration gradients using mass flow controllers. Bromochloromethane,

165 1,2-difluorobenzene, and chlorobenzene-d5 were chosen as internal standards in

166 samples. The method detection limit was 0.5 ppb for all species.

167 **2.2 Development of provincial emission inventory**

168 Anthropogenic NMVOC emissions in Jiangsu for 2005-2014 were estimated

169 with a bottom-up method using the following equation:

170 $$E(n) = \sum_i AL(i,n) \times EF(i,n) \tag{1}$$

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

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

173 per unit of AL).

174   As summarized in Table S3 in the supplement, the emission sources were

175   classified into a four-level framework, including seven main categories: stationary

176   fossil fuel combustion, industrial process, solvent use, transportation, oil distribution,

177   biomass burning, and others. Each main category was further subdivided into

178   subcategories according to discrepancies in fuel consumption, product manufacturing,

179   or technology application.

180   For power plants, industrial boilers, industrial processes and paint use plants, the

181   detailed information with inter-annual changes was collected and tracked at plant

182   level from the multiple-year official Environmental Statistics (the databases of

183   emission sources compiled by local environmental protection agency), Pollution

184   Source Census (PSC, internal data of emission sources collected by local

185   environmental protection agency), and on-site surveys on large emitters conducted by

186   local environmental protection bureaus. The information included geographic location,

187   types and amounts of raw materials, types and amounts of products, fuel quality and

188   consumption, and combustion/manufacturing technology. For 2014, as an example,

189   detailed information of 6023 plants was obtained, with the locations of those point

190   sources illustrated in Figure S1.

191   Activity data of other emission sources were generally collected at provincial or

192   city level based on official statistical yearbooks. In particular, as the amount of solvent

193   use was not reported at city level, the data at the national/provincial level were first

194   collected and then allocated into cities using the building areas, vehicle production

195   and industrial GDP as proxies. For oil distribution, the simplified method by Wei

196   (2009) was followed to calculate the activity levels of oil storage, transport and sale,

197   based on the provincial energy balance statistics. The annual biofuel use for

198   residential stoves until 2008 was taken from official energy statistics. As the data were

199   unavailable for subsequent years, the activity level was calculated as a product of

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

201   stoves according to the government plan of biomass utilization (PGJP, 2009).

202   Similarly, the biomass combusted in open fields was calculated as a product of grain

203   production, waste-to-grain ratio, and the percentage of residual material burned in the

204   field (Wang and Zhang, 2008; PGJP, 2009), as described in Zhao et al. (2011; 2013).

205   **2.3 Determination of emission factors**

206   Based on extensive literature survey, the NMVOC emission factors were

207   determined as follows with descending priorities: (1) the results from domestic

208   measurements; (2) the emission limits of local laws and regulations; (3) the values

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

210   database (USEPA, 2002) and the EMEP/EEA guidebook (EEA, 2013) when above

211   information was lacking. The emission factors applied in this work are summarized by

212   sector in Tables S4-S6 in the supplement.

213   The emission factors for power plants and industrial boilers were taken mainly

214   from Bo et al. (2008). Given the similar designs of boilers between China and

215   developed countries (Wei et al., 2008), the emission factors in AP-42 database were

216   also applied when domestic results were lacking. For residential combustion of fossil

217   fuel, the emission factors from domestic tests (Zhang et al., 2000; Wang et al., 2009)

218   were used, as shown in Table S4. For industrial processes, there were very few local

219   tests on NMVOC emission factors conducted before, thus the values from expert

220   judgment and data from AP-42 and EMEP/EEA had to be applied, as summarized in

221   Table S5. For solvent use, the VOC contents of given products were limited by

222   national laws and regulations, as summarized by Wei et al. (2008). The updating of

223   regulations and their impacts on inter-annual changes in NMVOC emission factors

224   were considered from 2005 to 2014, such as GB18583-2003 and GB18583-2008 for

225   indoor painting. Data from AP-42, EMEP/EEA and other literatures (Bo et al., 2008;

226   Fu et al., 2013) were also applied when local information was missing. As a result, the

227   emission factors by source type are summarized in Table S6. Emission factors of oil

228   distribution were taken directly from Wei et al. (2008) and Shen (2006).

229   For off-road transportation, the data from EMEP/EEA and expert judgment (Wei

230   et al., 2008; Q. Zhang et al., 2009) were adopted, attributed to lack of domestic tests

231   or relevant standards/regulations. Following He (2015), the emission factors for

232   on-road vehicles were calculated and adjusted according to local conditions using Eq.

233   (2):

234    $EF = BEF \times \varphi \times \gamma \times \lambda \times \theta$ (2)

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

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

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

238   quality).

239   The emission factors for biofuel burning in stoves were from the field test results

240   by Wang et al. (2009), who measured the NMVOC emission characteristics of

241   multiple stove-fuel combinations in China and provided the emission factors by

242   province. For biomass open burning, the local test results by Li et al. (2007) were

243   applied, as summarized in Table S4.

244   **2.4 Speciation of NMVOC emissions**

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

246   individual species using Eq. (3):

247    $E(i, k) = E(i) \times X(i, k)$ (3)

248   where *E* is the emissions; *X* is chemical profile of NMVOCs (%); *i* and *k* represent the

249   source type and individual NMVOCs species, respectively.

250   For chemical processes such as rubber, polyether, and polyethylene production,

251   the measurement results of this work were used. The chemical profiles for other

252   sources were mainly taken from domestic measurements, including residential fossil

253   fuel and biomass burning (Tsai et al., 2003; Liu et al., 2008; Wang et al., 2009; Zhang

254   et al., 2000; Wang et al., 2014a), biomass open burning (Zhang et al., 2013; Kudo et

255   al., 2014), on-road vehicles (Liu et al., 2008; Tsai et al., 2012; Huang et al., 2015;

256   Wang et al., 2013; Ou et al., 2014; Gao et al., 2012), iron & steel (Shi et al., 2015; He

257   et al., 2005; Jia et al., 2009; Tsai et al., 2008; Li et al., 2014), paint and printing ink

258   production (Zheng et al., 2013;), solvent use (Yuan et al., 2010; Zheng et al., 2013;

259   Tang et al., 2014; Wang et al., 2014b) and refineries (Liu et al., 2008; Wei et al., 2014).

260   For sources without sufficient local measurements, results from foreign studies were

261   applied including the SPECIATE database by USEPA (2014), and Theloke and

262   Friedirch (2007).

263   To reduce the possibly large uncertainty of source profile from individual

264   measurement, Li et al. (2014) developed the "composite profiles" for sources where

265   multiple candidate profiles were available, by revising the OVOCs fraction and

266   averaging the fractions in different profiles for each species. While Li et al. (2014)

267   included the source profiles published before 2011, considerable local measurements

268   were conducted after then. In this work, therefore, "composite profiles" were updated

269   following the method by Li et al. (2014), and the most recent source profiles from

270   domestic results were contained. Table 1 compares the source profiles of this work

271   with those of Li et al. (2014) or SPECIATE for typical sectors, grouped as alkanes,

272   alkenes, alkynes, aromatics, OVOCs, and others. Elevated fractions of alkanes are

273   found in this work for almost all the sources, while the comparisons of other species

274   are less conclusive between sources.

275   To evaluate the atmospheric oxidation capability from NMVOC emissions, ozone

276   formation potentials (OFPs) were calculated by multiplying the speciated NMVOC

277   emissions and corresponding MIR values (Carter, 1994). To meet the requirement of

278   atmospheric modeling, NMVOC emissions were assigned to chemical mechanism

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

280   mechanism-specific conversion factors using the following equation:

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

(4)

282

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

283

        and k represent the source type, individual species, and the chemical mechanism

284

        species.

285   **2.5 Uncertainty analysis**

286   The uncertainty of estimated provincial NMVOC emissions for each year were

287   quantified using Monte-Carlo simulation, as described in Zhao et al. (2011). As shown

288   in Table S7 in the supplement, normal distributions were assumed for activity levels,

289   with varied coefficients of variation (CV, the standard deviation divided by the mean)

290   determined for different source types, according to the reliability of energy and

291   economy statistics (IPCC, 2006; Zhao et al., 2011). Due to lack of sufficient

292   measurement results to support the data fitting, the determination of probability

293   distributions for emission factors depended largely on expert judgment (Streets et al.,

294   2003; Zhao et al., 2011; Wei et al., 2011). As summarized in Table S8 in the

295   supplement, the uniform distributions were conservatively assumed for most solvent

296   use sources based on limited data points, while lognormal distributions with large

297   CVs for other sources. Ten thousand simulations were performed to estimate the

298   uncertainties of emissions, and the parameters that were most significant in

299   determination of the uncertainties were identified by source type according to the rank

300   of their contributions to variance.

3 Results

3.1 Source profiles of chemical industry from measurement

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

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

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

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

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

308   SEBS rubber) and the mass fractions were measured over 70%. For production of

309   cellulose acetate fiber, alkanes, aromatics, and OVOCs were the main species in

310   process of acetate flake production, while OVOCs dominated in the spinning process.

311   Resulting from various raw materials applied, the source profiles of the two types of

312   polyether production differed a lot: the mass fraction of OVOCs was close to 80% for

313   PPG, while the main species for POP were others, aromatics and halohydrocarbon.

314   For ethylene production, aromatics were the main composition in the stack gas of

315   cracking furnace, while alkanes and alkenes dominated the fugitive emissions. For

316   other types of fugitive emissions, big differences existed in the source profiles

317   attributed mainly to the various raw materials and chemical reactions.

318   The detailed chemistry compositions for stack and fugitive emissions were

319   summarized in Tables S9 and S10, respectively. For stack emissions of synthetic

320   rubber production, cyclohexane was the dominating species, with the mass fractions

321   close to or above 70% for all types of products. Besides, styrene and acetone were

322   also important species for SBR and SIS/SEBS rubber, respectively. Used as the

323   solvent in the chemical reactions, acetone and cyclohexane were considerably emitted

324   during acetate flake production process, and the mass fraction of acetone reached 70%

325   in the spinning process. As the raw materials for polyether production, acrylontitrile

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

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

328   vinyl acetate was unsurprisingly measured to take 80% of NMVOC emissions from

329   its production process.

330   For fugitive emissions from ethylene production, the mass fractions of ethylene,

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

332   1,2-dichloropropane dominated the emissions from propylene oxide production, with

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

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

335   42% and 35%, respectively.

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

337   the results obtained in this work were compared with those available in SPEICATE

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

339   1b-d, respectively. As can be seen in Figure 1b, large discrepancy was found for

340   source files of SBR between this work and SPEICATE: while cyclohexane was

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

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

343   technologies was the main source of the discrepancy. Emulsion polymerization

344   technology was considered in SPEICATE, in which solvent was not used and thus

345   NMOVC emissions consisted mainly of the volatile raw materials. This work,

346   however, measured the plants with solution polymerization technology, in which

347   significant organic solvents would be released during the drying process. As shown in

348   Figure 1c, both SPECIATE and our measurements on fugitive emissions indicated that

349   ethylene and isobutene were the important species for ethylene production. In addition,

350   much larger fractions of propylene and n-hexane were found in this work. Clear

351   different composition was found for flue gas of cracking furnace, with abundant

352   species from incomplete combustion. Similar source profiles were found between this

353   work and SPECIATE for polyethylene production, dominated by ethylene (Figure 1d).

354   **3.2 Inter-annual trends and sectoral contribution of NMVOC emissions**

355   As shown in Table 2, the annual emissions of anthropogenic NMVOCs for Jiangsu

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

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

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

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

360   26% in 2005 to 38% in 2014, and from 21% to 39%, respectively. In contrast, the

361   emission contributions from transportation and biomass burning were declining from

362   18% to 11%, and from 26% to 4%, respectively, attributed mainly to the controlled

363   motorcycle emissions, replacement of residential biofuel stoves with natural

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

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

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

367   7-9% during the study period.

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

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

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

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

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

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

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

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

376 361 Gg in 2014. Due to enhanced coking industry, the emissions of iron & steel

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

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

379 380 in 2005 to 963 Gg in 2014, and the growth was highly consistent with that of

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

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

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

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

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

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

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

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

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

389 297 to 204 Gg, with the peak emissions at 302 for 2007 (Figure S3c). The

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

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

392 emissions. For example, the emissions of motorcycle deceased 66% from 185 to 64

393 Gg, and its contribution to on-road vehicle emissions declined as well from 62% and

394 31%. Unsurprisingly, gasoline vehicles dominated the emissions of on-road

395 transportation, with the fraction ranged 81%-87% during the study period.

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

397 emissions for various years within a 3×3 km grid system. Besides point sources which

398 were directly allocated according to geographic locations, certain proxies were

399 applied to allocate emissions from other sources including GDP for industrial area

400 sources and oil distribution, population for solve use area sources, road net and traffic

401 flow for on-road vehicles, railway and canal for off-road transportation, and rural

402 population for biomass burning. High emission intensities were mainly found in

403 relatively developed cities along Yangtze River in southern Jiangsu including Nanjing,

404 Suzhou, Wuxi and Yangzhou (see Table S11 for the emissions by city). In central and

405 northern Jiangsu, large emissions existed in areas with clustered industrial parks,

406   reflecting the impacts of big plants on spatial pattern of NMVOC emissions.

407   Comparing the emissions for 2005 and 2014, increased emissions were commonly

408   found in southern Jiangsu indicating the faster growth of industry in developed cities

409   (Figure 2d). Moreover, reduced emissions were coincided with road net distribution,

410   implying the benefits of emission controls on vehicles.

3.3 Speciation and OFPs of NMVOC emissions

412   Based on the source profiles, emissions of more than 500 hundred NMVOC

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

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

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

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

417   and esters), halohydrocarbons, and others were ranged 26-30%, 13-19%, 21-23%,

418   18-21%, 3-4%, and 11-12%, respectively.

419   Shown in Figure 3 are the mass fractions of species by source for 2014. Due to

420   varied fuel qualities and combustion conditions, large differences in the speciation of

421   emissions were found for fossil fuel combustion, transportation and biomass burning.

422   Dominated by coal combustion, the profile of fossil fuel stationary sources was

423   relatively simple with little OVOCs and halohydrocarbons, and aromatics were the

424   largest fraction (45%), followed by alkanes (29%). Alkanes, aromatics and alkenes

425   were the main species from transportation, with the fractions estimated at 30%, 24%,

426   and 23%, respectively. For biomass burning, elevated alkenes and less alkanes were

427   found attributed to the highly incomplete combustion. The mass fractions of alkanes,

428   aromatics and alkenes from industrial processes were estimated 32%, 16% and 12%.

429   In particular, relatively close emission fractions were found between species for

430   chemical industry, the largest emission source of industrial processes: 19%, 15%, 11%,

431   10% and 10% of aromatics, ketones, alkenes, alkanes, and halohydrocarbons,

432   respectively. For solvent use, aromatics and alkanes were the most important species

433   with the fractions estimated at 32% and 22%, respectively, and the collective fraction

434   of OVOC species reached 27%. Alkanes and aldehydes dominated the emissions of

435 oil distribution and other sources, which came mainly from the oil evaporation and

436 residential cooking, respectively.

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

438 3880 in 2005 to 5200 Gg in 2014, and the ratio of annual OFPs to emissions varied

439 slightly around 2.1 for the decade. The OFP/emission ratios for 2014 were provided

440 by source in Figure 3. With abundant aromatics and alkenes emissions that were

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

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

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

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

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

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

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

448 OFPs (Figure S4a). The aromatics species with (e.g., xylene and toluene) came largely

449 from solvent use and industrial processes, while alkenes species (e.g., ethylene and

450 propylene) were mainly from industrial processes, biomass burning, and

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

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

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

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

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

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

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

458 important species to OFPs any more.

459 **3.4 Uncertainties of provincial NMVOC emission inventory**

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

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

462 central estimates. As inter-annual changes were hardly assumed in determination of

463 probability distributions for parameters, similar uncertainty ranges were thus

464   calculated for emissions of various years. As shown in Table 3, the uncertainty of

465   emissions 2014 was quantified at -41%~+93% (95% CI), and biomass burning and

466   other sources were estimated as the sources with largest uncertainties, followed by

467   stationary fossil fuel combustion and oil distribution. For most emission

468   sectors/categories, emission factors were identified as the largest sources of emission

469   uncertainty, with an exception of solvent use. Resulting from complicated sources of

470   stack and fugitive emissions, it is generally difficult to conduct comprehensive field

471   measurements on NMVOC emission factors for industrial and residential sources, and

472   large uncertainties were thus assumed for them attributed to limited domestic test

473   samples and to heavy dependence on foreign databases. Regarding solvent use for

474   which provincial and city statistics were lacking, the activity data had to be

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

476   Provided in Table 3 as well are the uncertainties of national and YRD emissions

477   from other studies. Compared with those results, the emission uncertainties were

478   reduced in this work for industrial processes, solvent use and transportation. The more

479   detailed classification of emission sources and adoption of independent emission

480   factors for those sources should be the most important reason. For example, totally 34

481   vehicle type-control combinations were taken into account for calculating the on-road

482   vehicle emissions, and emission factor for each type of combination was assumed

483   independent from other. In addition, the errors of activity levels for big point sources

484   were significantly reduced from the detailed investigation and on-site survey at plant

485   level, leading to smaller uncertainty in emission estimation for industrial and solvent

486   use sources.

487   **4 Evaluation of provincial emission inventory**

488   **4.1 Chemical and refinery industry emissions from varied data sources and**
489   **methods**

490   As indicated in Table 2, chemical and refinery industry was one of the biggest

491   contributors to anthropogenic NMVOC emissions. We select Nanjing, the capital city

492 of Jiangsu province, to evaluate the impacts of data sources and methods on emissions

493 of this category. Besides the method described in Sections 2.2 and 2.3 that

494 incorporated the most available information from Environmental Statistics, PSC, and

495 on-site surveys (Method 1), two other methods based respectively on data from

496 Environmental Statistics (Method 2) and economic statistics without any information

497 on individual plants (Method 3) were also applied to calculate the emissions in the

498 city for 2011. Note the emissions of area sources (i.e., not included in plant-by-plant

499 investigations) in Methods 1 and 2 were estimated using the same data source as

500 Method 3. Table S12 in the supplement provides the emissions calculated based on the

501 three data sources by subcategory of chemical and refinery industry. The largest

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

503 3, resulting mainly from the incomplete records of chemical products by

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

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

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

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

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

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

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

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

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

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

514 Spatial distributions of the emissions estimated using the three data sources for

515 Nanjing were illustrated in Figure 5. Similar patterns were found for Method 1 and 2

516 (Figure 5a and 5b), as the emissions were dominated by the big chemical and refinery

517 plants. As labeled in Figure 5a, the largest ten plants were estimated to account for

518 80% of NMVOC emissions of the sector for the whole city. Without detailed

519 information of individual plants, Method 3 had to apply the proxies (e.g., population

520 density) to allocate the emissions, and clearly overestimate the emissions in urban

521 downtown (Figure 5c). It could thus be inferred that big discrepancies in spatial

522 distribution of emissions at small scale might be caused when downscaled from larger

523 scale without sufficient investigation on local sources, particularly for regions where

524 emissions were dominated by large plants that were gradually moved out of urban

525 areas.

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

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

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

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

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

531 indicated in Table S13 in the supplement, detailed information of 15 key chemical and

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

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

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

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

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

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

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

539 factors for production of chlorobenzene alkylbenzene, and cyclohexanone were

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

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

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

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

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

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

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

547 **4.2 Changes in speciation of NMVOC emissions**

548   As indicated in Section 2.4, the speciation of NMVOC emissions in Jiangsu were

549 updated by including the results of our field measurements and other most recent

550 domestic tests, based on previous foreign database (SPECIATE) and the composite

551   profile by Li et al. (2014). Figure 6 illustrated the emissions of 445 species

552   (accounting for 99.5% of total NMVOC emissions) estimated with the source profile

553   before (SPECIATE and Li et al., 2014) and after updating (this work) for Jiangsu

554   2010. Due to relatively limited tests available, there were no significant changes in

555   emissions for most species when updated profiles were applied. However, relative big

556   changes in emissions (over 100 Gg) were found for thylacetate and certain aromatics

557   species (benzene, xylene, ethyl benzene, and methyl benzene). Applying the source

558   profile of paint use measured by Zheng et al. (2013) led to enhanced thylacetate.

559   Reduced benzene and methylbenzene, and elevated ethyl benzene and xylene resulted

560   mainly from the revisions on source profiles of coking (Jia et al., 2009; Shi et al.,

561   2015) and solvent use (Wang et al., 2014b; Zheng et al., 2013).

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

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

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

565   With source profiles updated based on most recent measurements, relatively big

566   changes were found for ALDX (see captions of Figure 7 for the detailed meanings) in

567   CB05 and OLE1 in SAPRC99. The revisions on source profiles of solvent use were

568   the main reason for the changes. For example, the increased ALDX was attributed

569   mainly to the updated profiles of printing ink and automobile paint use (Zheng et al.,

570   2013; Tang et al., 2014), while increased OLE1 was to that of building coating (Yuan

571   et al., 2010; Wang et al., 2014b) .

572   **4.3 Comparisons with other inventories**

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

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

575   years, as shown in Figure 4. All the results were within the 95% CIs in this work.

576   Except for REAS that provided extremely high emissions for China (Kurokawa et al.,

577   2013), our estimates were generally 0-18% larger than other studies in the total

578   emission estimation, attributed mainly to the omission of certain emission sources in

579   other inventories and to the elevated activity levels from plant-by-plant investigation

580 in this work. Figure 8 provided the NMVOC emissions by source from various

581 inventory studies for selected years. As can be seen, much larger emissions were made

582 in this work than the national (Wei et al., 2008) or regional inventory (Fu et al., 2013).

583 The latter two studies missed the emissions from the manufacturing processes of

584 certain chemical products. For example, fermentation alcohol, dye and rubber were

585 not included in Wei et al. (2008), either glasswork, pesticide or charcoal in Fu et al.

586 (2013). The emissions from solvent use in this work were larger than those from Bo et

587 al. (2008), attributed to omission of carpentry coating, pesticide and adhesive using by

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

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

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

591 motorcycles at national level.

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

593 compared in Figure 7. For CB05 mechanism, our results were smaller for TOL and

594 XYL but larger for ETH and ETHA than MEIC (Figure 7a), while discrepancies

595 existed for most species under SAPRC 99 (Figure 7b). Such discrepancies could result

596 either from the various source profiles, or from the vairous source contributions in

597 total emissions. For example, with updated source profile for building coating, much

598 larger OLE1 emissions were estimated in this work than MEIC. Besides the total

599 emissions, the differed speciations under chemical mechanisms could result in

600 complex impacts on air quality simulation, which would be discussed in next section.

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

602 2010 between our results and MEIC. To be consistent in resolution and to ease

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

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

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

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

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

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

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

610   commonly found in areas with big plants, reflecting the impacts of detailed and

611   complete investigation on product types and activity levels at plant level on the

612   emission estimation. Although our result was 315 Gg or 18% larger than MEIC in

613   total anthropogenic NMVOC emissions, lower emissions were found in this work at

614   downtown Nanjing and the Suzhou-Wuxi-Changzhou city clusters with large

615   populations. The result implies that downscaling of emissions depending on certain

616   proxies (e.g., population and economy density) might overestimate the emissions in

617   urban areas, and detailed information on individual sources should be included if

618   possible.

4.4 Evaluation of multiple-scale inventories through air quality modeling

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

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

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

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

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

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

626   horizontal spatial resolution at 3 km. Chemistry transport simulation was conducted

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

628   work, for January, April, July and October 2012. The first five days for each month

629   were chosen as spin-up period to provide initial conditions for later simulations. Other

630   model settings on meteorological simulation and emissions of natural origin were

631   described in Zhou et al. (2016).

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

633   for the four months, and Table 4 compares the model performances with MEIC and

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

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

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

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

638   result thus implied NMVOC emissions of anthropogenic origin might be

639   underestimated, as YRD was commonly recognized as VOC-limited region for O_3

640   formation. Compared to MEIC, better model performances (except for July) were

641   generally achieved when the provincial inventory was applied, indicating the

642   improved reliability of the detailed bottom-up NMVOC inventory on high-resolution

643   chemistry transport simulation. In particular, larger emissions were estimated for

644   certain species with relatively high ozone formation potential (e.g., ethene and ethanol)

645   in the provincial inventory, leading to higher and closer O_3 prediction to observation.

646   We should acknowledge, however, that the discrepancies between simulation and

647   observation were still large compared to regional studies in North America (Y. Zhang

648   et al., 2009). More efforts on improving or validating emission inventory at provincial

649   scale are thus in great needed. Besides careful compilation of emission source

650   information in the bottom-up method, observation constraint from ground

651   measurements could be used to evaluate the emission level, source contribution, and

652   speciation of VOC emissions (M. Wang et al., 2014). Moreover, the emission

653   uncertainty of other species, i.e., NO_X, could also partly explain the discrepancies, as

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

655   inventory development.

5 Conclusion

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

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

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

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

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

662   2005 to 2014. Influenced largely by location of big point sources, high emission

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

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

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

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

more detailed classification and investigation of emission sources, reduced uncertainties in annual emissions were quantified in this work compared to previous studies. Varied data sources and methods were of significant impacts on emission estimation at city/plant level. In particular, downscaling directly from national inventories would overestimate the emissions in urban downtown. With the most recent source profiles from local measurements included, considerable changes in emissions were found for thyl acetate and certain aromatics species, and the speciation under CB05 and SAPRC99 differed a lot from the national inventory MEIC. Compared to MEIC, better model performance (indicated by daily 1h-max O_3 concentrations) were achieved when the improved provincial inventory was used in CMAQ simulation, although the discrepancies between simulation and observation need further investigation. As emission controls on NMVOCs started to be implemented on industrial sources in China (e.g., the application of leak detection and repair technique in chemical and refinery plants), more field tests were recommended to better track the temporal changes in emission factors and to reduce the uncertainty of emission estimation in the future.

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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.

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

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

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 2 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 3 Uncertainties of anthropogenic NMVOC emissions (expressed 95% CI around the central estimates) and the most significant two parameters contributing to the uncertainties by sector for Jiangsu 2014. The percentages in the parentheses indicate the contributions of the parameters to the variance of emissions. The uncertainties from other inventories are provided for comparisons.

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	
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%	-	-	-	-	$EF_{Straw\text{-}stove}$ (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 4 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):

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

Figure 1

(a)

(b)

(c)

(d)

Figure 2

(a) 2005 (b) 2010

(c) 2014 (d) Difference between 2005 and 2014

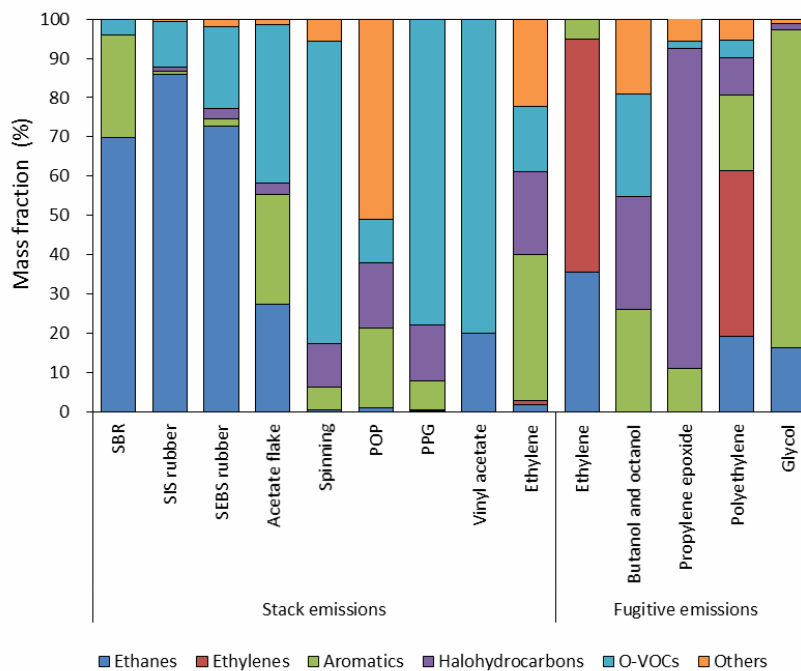
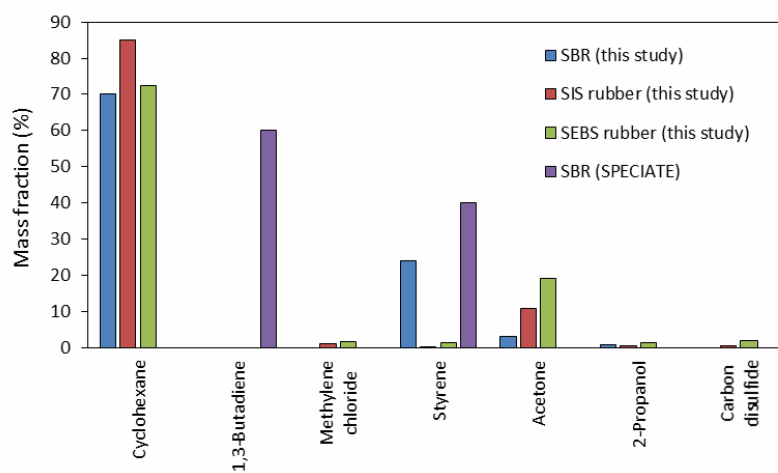
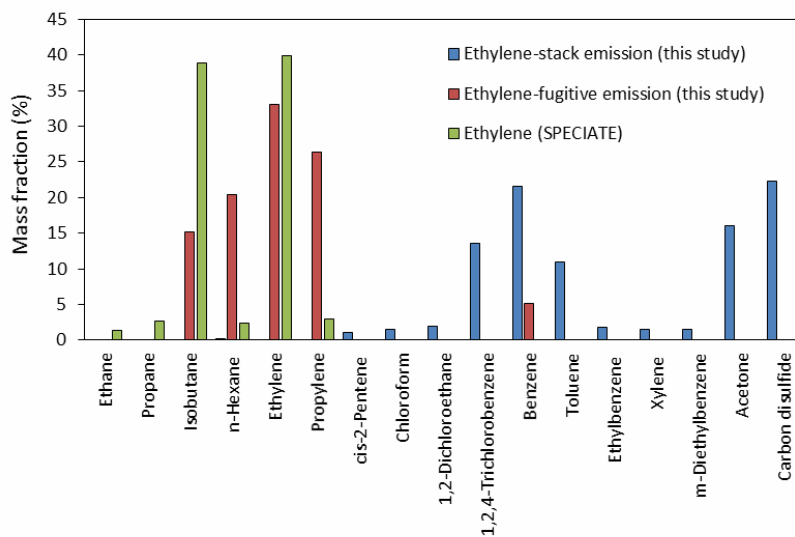
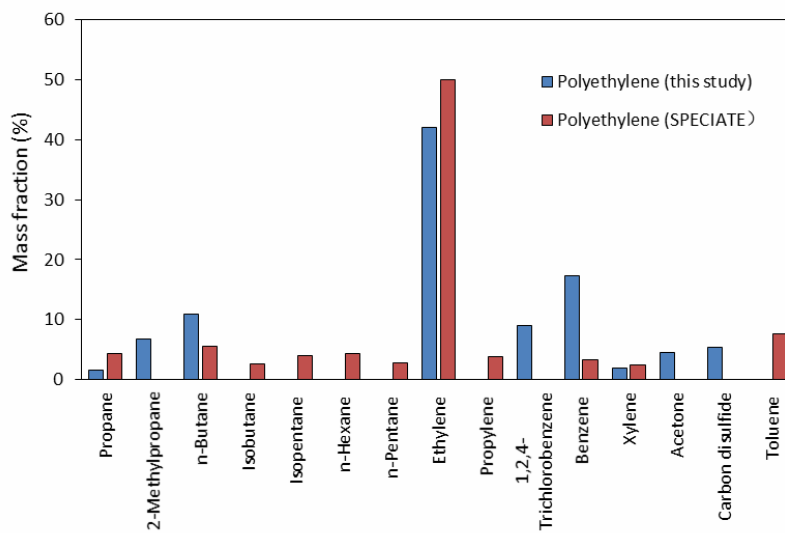
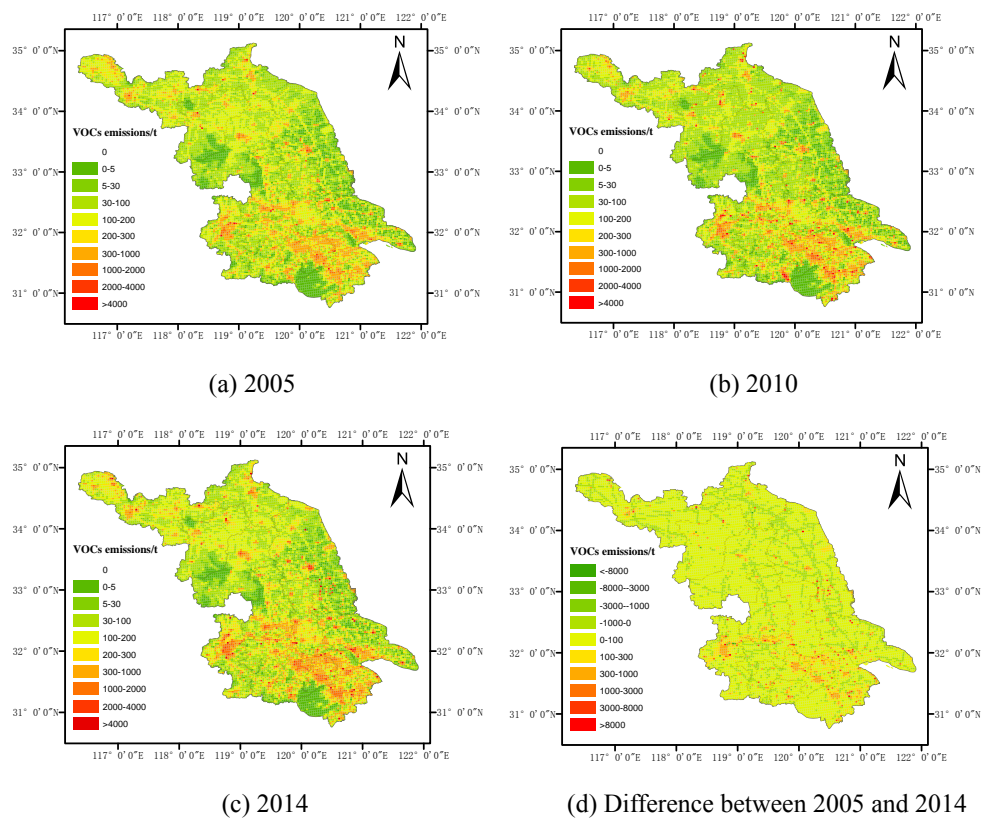
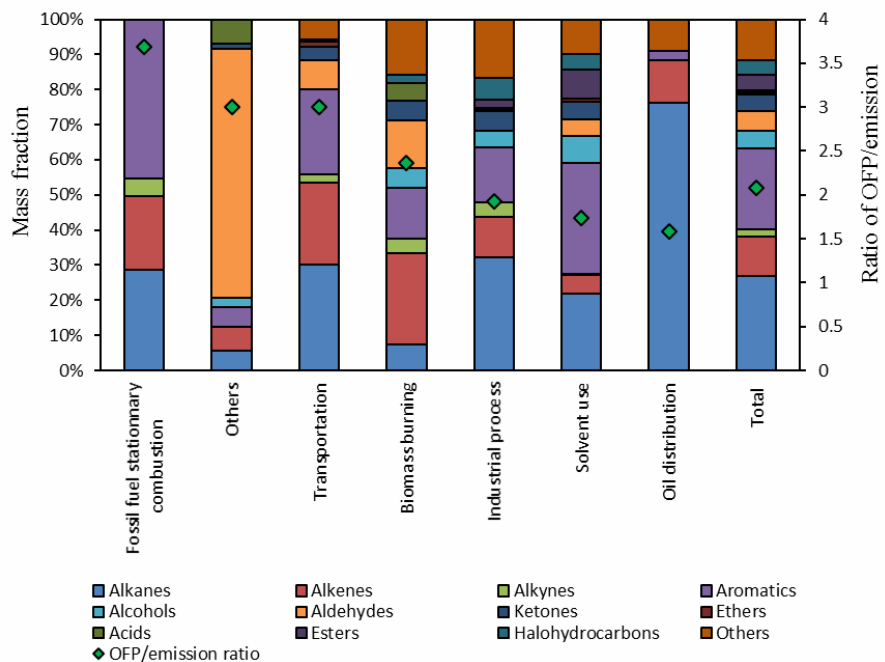
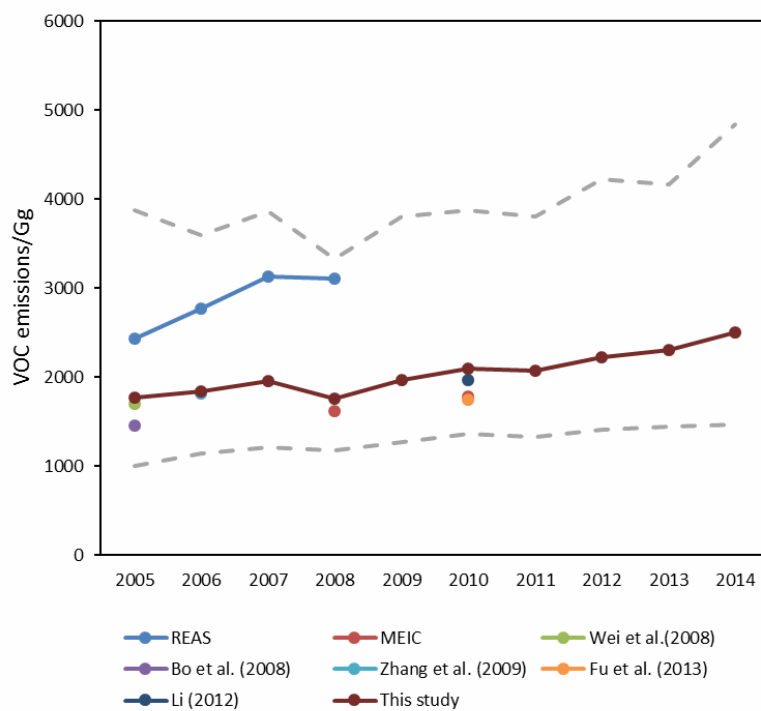
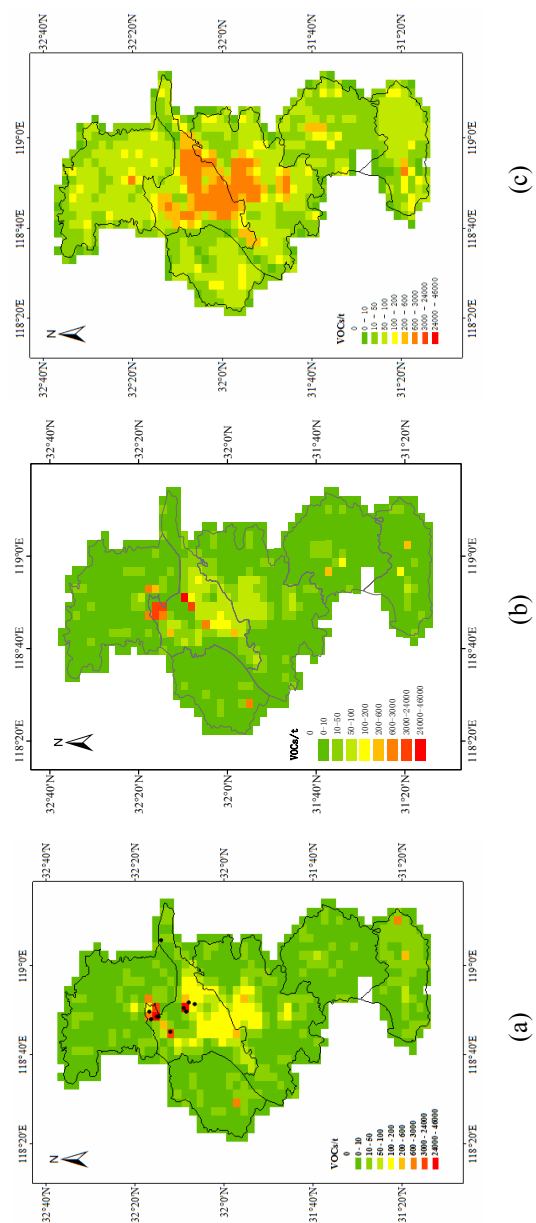



Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

(a) CB05

(b) SAPRC99

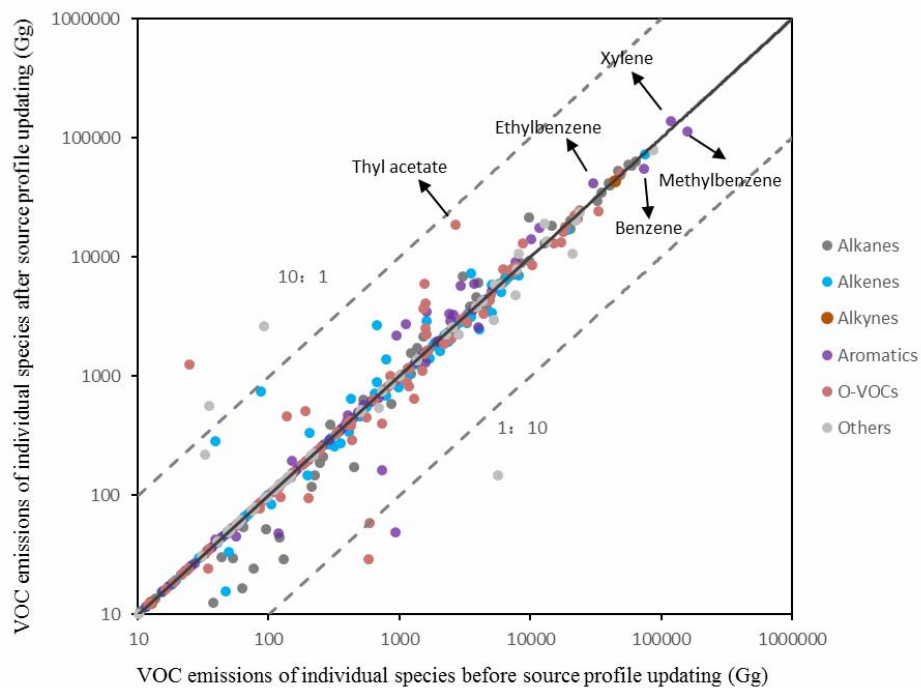
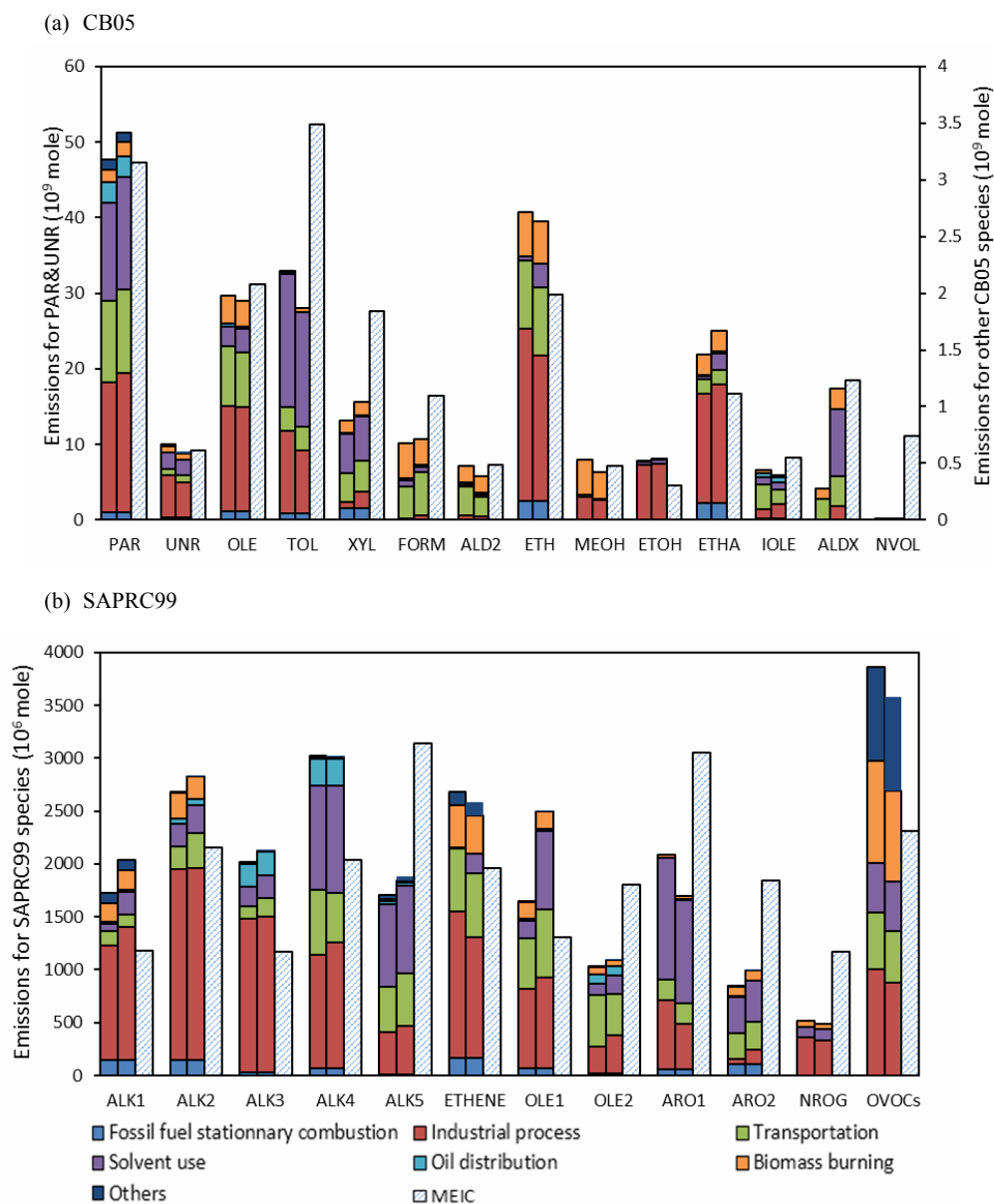
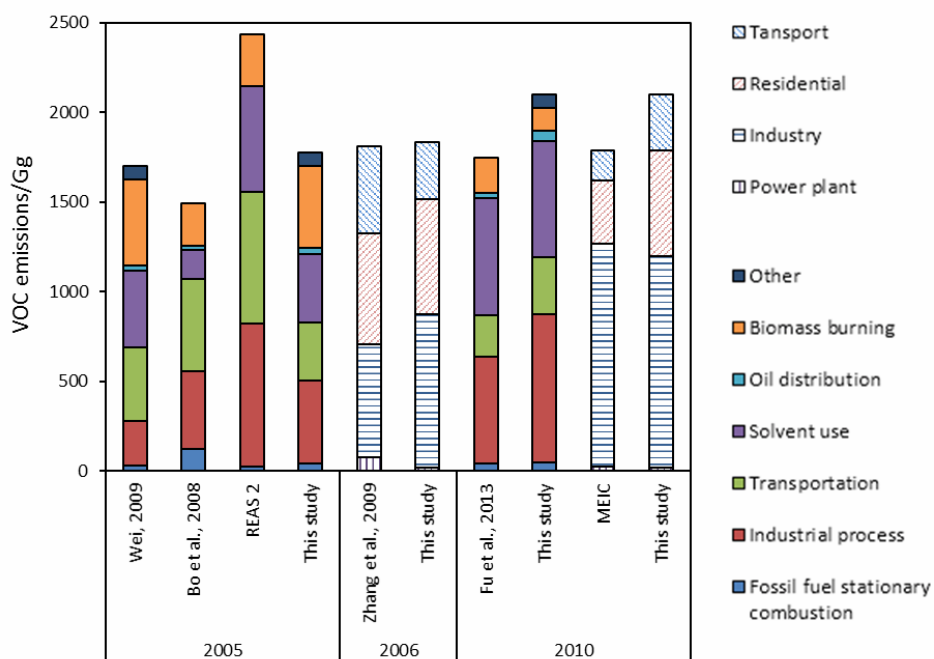
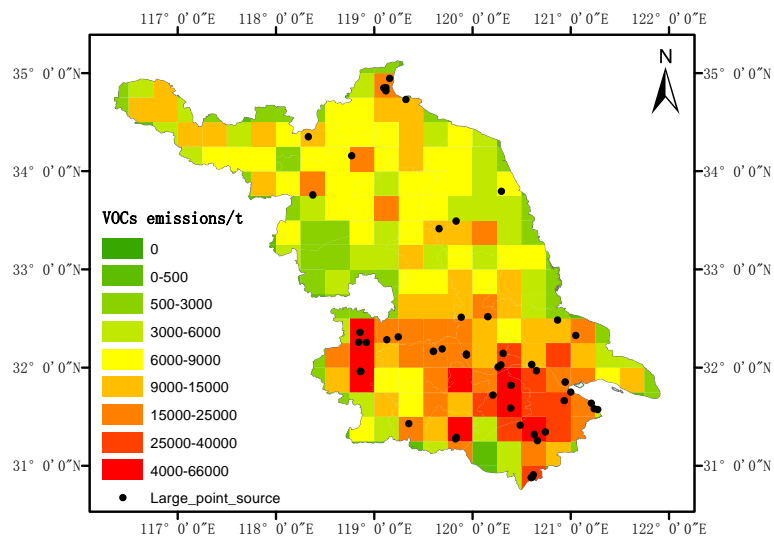



Figure 8

Figure 9

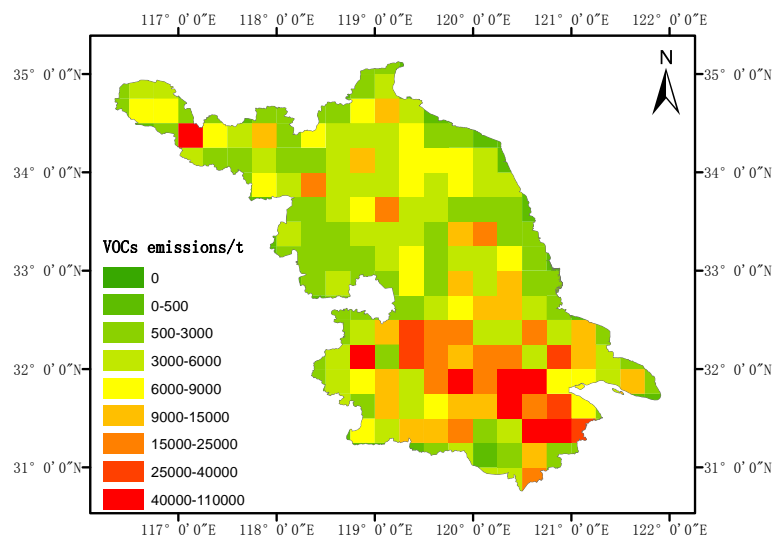
(a)

(b)

Figure 9 (continued)

(c)

Figure 10