

Main revisions and response to reviewers' comments

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Title: Advantages of city-scale emission inventory for urban air quality research and policy: the case of Nanjing, a typical industrial city in the Yangtze River Delta, China

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We thank very much for the valuable comments from the two reviewers, which help us improve the quality of our manuscript. Following is our point-by-point responses to the comments and corresponding revisions.

Reviewer #1

0. The authors' survey approach to estimate stationary emissions is a significant and novel contribution to modelling air pollution in China, and highlights that more work is needed to improve emissions characterization of Chinese power generation and industrial activity. My main critique relates to some of the emissions and observational comparisons made in the analysis (detailed below), as well as highlighting areas where additional documentation would be helpful. Overall, the manuscript reads well and the presentation is clear (except where noted). I recommend that with revision, this manuscript be considered for publication in ACP.

Response and revisions:

We thank the reviewer's positive comment on the paper.

1. Some summary tables or figures are needed on activity levels (2010-2012) used in this analysis either in the supplemental material or main text, especially for coal-fired power plants, and other major industrial sectors. The authors highlight significant uncertainties in energy statistics for China (Section 4.6), so it is important that activity estimates are clearly summarized for reference.

Response and revisions:

We thank the reviewer's important comment. We have added **a new Table S1 in the revised supplement**, summarizing the activity levels for the continuous three years 2010-2012 in Nanjing by sector. We also added a paragraph **in Section 4.6 (lines 872-891, Pages 33-34 in the revised manuscript)** to discuss the uncertainty by source:

"The uncertainties of China's national emission inventories have been estimated using Monte-Carlo simulation, as described in our previous studies (Zhao et al., 2011; 2013). Targeting city scale, however, the uncertainty of current inventory for Nanjing is more difficult to be systematically quantified, as many emission factors are city- or device-dependent and their probability distributions could not be fully defined without sufficient field measurement records. In general, the uncertainties of emissions from power and industry sectors are expected to be reduced compared to the national level, as the "key sources" in the city contribute significantly to the fuel consumption and production of those sectors. As described in Section 2, the activity levels and emission factors for those key sources were compiled plant by plant or obtained through onsite survey, leading to relatively small biases in emission estimation. For most area sources, the emission factors used in this work were hardly improved compared to previous national/regional inventories, thus large uncertainties remain in those sources. Given the tiny fractions of emissions by those sources in Nanjing, however, their contribution on the uncertainty of total city emissions is expected to be limited. Very high uncertainty is expected for fugitive dusts that are

generally not included in national/regional inventory, as little local information is available to improve the emission factors. Given the large shares of fugitive dusts to primary PM emissions (Figure S2), field measurements on construction sites and road dusts are suggested for better emission estimation in Nanjing. "

In the paper, however, we cannot fully provide the detailed activity levels plant by plant in Nanjing, as we had a agreement with local Environmental Protection Agency, that the detailed unit/plant-based information should not be published without permission.

2. Captions are needed for all figures in the supplemental material.

Response and revisions:

We thank the reviewer's comment. The captions of all the figures in the supplement are provided **in Pages S2-S3 in the revised supplement.**

3. Abstract. The horizontal resolution of the emissions inventory should be included. It is not clear what the authors mean by "high-resolution" for a reader just glancing at the manuscript.

Response and revisions:

We thank the reviewer's comment. **In lines 4-6, Page 2 of the revised manuscript,** the horizontal resolution information has been included:

"In this paper, a high-resolution emission inventory (with a horizontal resolution at 3×3 km) of air pollutants and CO₂ for Nanjing,"

4. Section 2.1. This is where a table on activity of point and area sources (like Table S3 for EF) would be helpful.

Response and revisions:

We thank the reviewer's suggestion and have added **a new Table S1 in the revised supplement**, which summarizes the annual activity levels for the main point and area sources for 2010-2012.

5. Page 18699, Line 13. How comprehensive is the spatial coverage of the Intelligent Traffic Violation Monitoring System? Does it cover all roads, or mostly highways? Could some traffic be missing from the monitoring system, which would contribute to underestimating emissions from motor vehicles? Also, can the authors provide a short description of how the monitoring system derives traffic flows (e.g. loop detectors, cameras, mobile cellphone data, etc.)?

Response and revisions:

We thank the reviewer's important comment and admit that the relevant information was not clearly stated in the original manuscript. Cameras are used in the Intelligent Traffic Violation Monitoring System to continuously record the real-time traffic flows for most arterial roads and highways, and part of residential roads in the city. The system does not cover all the roads (particularly for residential roads), and the traffic flows in those roads were simulated from the real-time monitoring data for similar roads that are covered by the system. Since the emissions from on-road vehicles were first calculated with CORPERT based on the registered vehicle population and investigated mileages traveled for the whole city, and then spatially distributed to the road net of the city according to the monitored and simulated traffic flow intensities, there is little underestimation on the total emissions resulting from the missed traffic by Intelligent Traffic Violation Monitoring System. However, uncertainty does exist in the spatial distribution of emissions, particularly for areas with fewer cameras installed. We have described the system **in lines 187-196, Pages 8-9 in the revised manuscript:**

"The traffic flows in the city are compiled from the observations of the Intelligent Traffic Violation Monitoring System (internal data of NJEPB). In the system, cameras are used to continuously record the real-time traffic flows for most arterial roads and highways, and part of residential roads in the city. The system does not cover all the roads (particularly for residential roads), and the traffic flows in those roads were simulated from the real-time monitoring data for similar roads that are covered by the system. Combining the information of traffic flows and the road net, the spatial and diurnal distributions of emissions from CORPERT can be derived. It should be noted, however, uncertainty exists in the allocation of vehicle emissions, particularly for areas with fewer cameras installed."

6. Section 3.1. What explains the growth and then decrease in NO_x emissions shown in Figure 1a?

Response and revisions:

We thank the reviewer for the comment. In general, the inter-annual variation of emissions results from the combination of varied activity levels (e.g., coal consumption) and emission factors that are significantly influenced by emission control measures. In this case, the coal consumption in Nanjing increased largely from 31 million metric tons in 2010 to 35 in 2011, and it dominated the growth of NO_x emissions, even with improved use of SCR in power sector. From 2011 to 2012, the growth in coal consumption was limited while the average removal efficiencies of SCR are significantly improved (as shown in Table 1), leading to reduced NO_x emissions for the whole city. We have clarified this **in lines 279-284, Page 12 in the revised manuscript.**

"For NO_x, the large increase in coal consumption from 31 million metric tons (Mt) in 2010 to 35 in 2011 dominated the growth of NO_x emissions, even with improved use of SCR in power sector. From 2011 to 2012, the growth in coal

consumption was limited while the average removal efficiencies of SCR are significantly improved (as shown in Table 1), leading to reduced NO_x emissions for the whole city. "

7. Figure S2. A caption with acronym meanings would be helpful here. The color coding scheme is also hard to follow? It may help to color major source categories a single color (e.g. transportation, power plant, industrial, area, etc.), and different shades of that color for subcategories (e.g. cement, iron & steel production, etc.).

Response and revisions:

We thank the reviewer's reminder. We have added the acronym meanings **in the caption of Figure S2 in Page S2 of the revised supplement:**

Figure S2. Source contributions to the total emissions by species and those to coal consumption in Nanjing from 2010 to 2012. Recall from Section 2.1 of the main text that CPP represents coal-fired power plants, IND total industry, ISP iron & steel plants, CEM cement plants, RCP refineries and chemical plants, OIN other industry plants, SOL solvent use, RES residential & commercial sector, TRA transportation, and FUD fugitive dust.

The figure has been modified as suggested.

8. Section 3.1. If the penetration and removal efficiency dramatically increased for NO_x control at coal-fired power plants (Table 1) between 2010 and 2012, why did the NO_x emissions distribution among sources not change much year-to-year (Figure S2)?

Response and revisions:

We thank the reviewer for the important comment. The small inter-annual variation in sector distribution of NO_x emissions is attributed mainly to following

issues. First, as discussed in the response to Question 6, the variation in annual emissions from power sector resulted from the combination of the varied emission control levels and coal consumed by the sector. The growth in coal consumption of power plants partly offset the benefits of improved penetration and removal efficiency of SCR on NO_x control, and the NO_x emissions from power sector did not vary much for the three years (97, 112 and 94 Gg for 2010, 2011, and 2012, respectively). Second, besides power sector, emission controls were also improved for other sources, including the increased use of retrofitted low-NO_x burner for industrial boilers, and the implementation of strict emission standards for new gasoline and diesel vehicles. For example, the emissions from other industrial combustion (OIN) were estimated to decrease from 22 to 14 Gg from 2010 to 2012, and the emissions from on-road vehicles did not change a lot despite of vehicle population growth. As a result, the fractions of NO_x emissions from power plants, industrial boilers and on-road vehicles to total were estimated to change slightly from 2010 to 2012.

We have clarified this **in lines 300-312, Page 13 in the revised manuscript:**

"It can be found that the sector distribution of NO_x emissions did not change much annually, even with clear enhancement of NO_x control in coal-fired power plants as shown in Table 1. The growth in coal consumption of power plants partly offset the benefits of improved penetration and removal efficiency of SCR on NO_x control, and the NO_x emissions from power sector did not vary much for the three years (97, 112 and 94 Gg for 2010, 2011, and 2012, respectively). Besides power sector, in addition, emission controls were also improved for other sources, including the increased use of retrofitted low-NO_x burner for industrial boilers, and the implementation of strict emission standards for vehicles. For example, the emissions from other industrial combustion (OIN) were estimated to decrease from 22 to 14 Gg from 2010 to 2012, and the emissions from on-road vehicles did not change a lot despite of vehicle population growth, leading to relatively small variation in sector distribution of emissions for the three years."

9. Figures S3a and S3b. It is not clear in the figure which line refers to MEIC and which refers to emissions from this study. Also, a caption is needed. What does A and B refer to in panel a?

Response and revisions:

We thank the reviewer's reminder. A and B in panel (a) refer to MEIC and this study, respectively. We have modified the caption and added the information **in Page S2 of the revised supplement:**

Figure S3. (a) Monthly variation of SO₂ emissions by source from MEIC (2010) and our estimates (2012). A and B refer to MEIC and our estimates, respectively. (b) Monthly variation of emissions by species from our estimates (2012).

10. Section 4.1. I have some questions with regards to the inter-annual comparison of the emissions inventory with satellite NO₂ column data, and the statement that NO_x levels in the atmosphere decreased along with decreases in emissions (Line 24). First, what explains the large fluctuations in the vertical column densities in the beginning of 2010, 2011, and 2012 that are not seen in the preceding years? To what extent do year-to-year changes in meteorology affect the trend? Second, what are the uncertainties bars on the satellite-derived trends in NO₂, and are these uncertainties larger than the changes in NO_x emissions? If there is a decreasing trend after 2011, the analysis would be strengthened if additional years of satellite data were added beyond 2012.

Response and revisions:

We thank the reviewer's important comment, and admit that uncertainties exist in the comparison between the inter-annual variations in NO_x emissions and NO₂ VCDs and, and that the results should be interpreted cautiously. First, we have clarified **in lines 432-434, Page 17 in the revised manuscript** that each data point in Figure 4 is

the 12-month moving averages, calculated as the means of the data for the previous and subsequent six months. Thus the VCD fluctuations at 2010, 2011 and 2012 were not at the beginning but the middle of the years. The fluctuations come mainly from inclusion or exclusion of extremely high monthly mean VCDs in winter. In particular, the lacking of data for certain months in the moving average calculation would exaggerate the fluctuations. The inter-annual changes in meteorology in Nanjing are summarized **in a new Figure S5 in the revised supplement**. During the study period (2010-2012), the variations were small for most parameters except for precipitation. Although varied precipitation has limited direct impacts on ambient NO₂ level, it could change the data sampling of retrieval. Therefore we admit that the NO₂ VCD from OMI could partly be influenced by the meteorology (particularly precipitation) besides the varied emissions, and we have discussed this **in lines 456-460, Page 18 in the revised manuscript**:

"Another uncertainty comes from meteorology. As shown in Figure S5 in the supplement, the inter-annual changes in meteorological parameters were small except for precipitation during 2010-2012 in Nanjing. The varied precipitation could change the data sampling of retrieval, and thereby influence the NO₂ VCD levels."

Second, the biases of NO₂ VCD retrieval from OMI could reach 40% (Boersma et al., 2007; 2011), and the uncertainties are larger than the inter-annual changes in NO_x emissions in the three years. However, since the emissions in this work are not directly compared with absolute values of VCDs but the relative trends, the uncertainties from NO₂ VCD observation could be less influential on the reliability of result. We have added the discussion **in lines 450-456, Page 18 in the revised manuscript**:

"First, the biases of NO₂ VCD retrieval from OMI were reported to reach 40% attributed probably to the errors in the air mass factor calculations (Boersma et al., 2007; 2011). Such uncertainties are potentially larger than the inter-annual changes in NO_x emissions of Nanjing between 2010 and 2012, and

thus weaken the comparison. However, since the bottom-up emissions are not evaluated by the absolute values but the relative trends of VCDs, the effects of NO₂ VCD retrieval uncertainties on the comparison could partly be mitigated."

We have agreed with the reviewer that the period for emission and VCD comparison is short, and have modified Figure 4 with the latest information on NO₂ VCDs included. As can be seen in the revised figure, the NO₂ level in Nanjing did not increase after 2012. Analysis on long-term trend in emissions from the bottom-up method is further recommended for better understanding the NO_x pollution in the area. We have added this **in lines 460-465, Pages 18-19 in the revised manuscript:**

"Finally, the period for emission and VCD comparison is relatively short. Even the NO₂ VCDs kept decreasing slightly after 2012, the benefits of NO_x emission control could not be fully confirmed as the emission inventory for the most recent years are still unavailable due to the delay of activity data report. Analysis on long-term trend in emissions from the bottom-up method is further suggested for better understanding the NO_x pollution in the area."

Reference:

Boersma, K. F., Eskes, H. J., Dirksen, R. J., van der A, R. J., Veefkind, J. P., Stammes, P., Huijnen, V., Kleipool, Q. L., Sneep, M., Claas, J., Leitao, J., Richter, A., Zhou, Y., and Brunner, D.: An improved tropospheric NO₂ column retrieval algorithm for the Ozone Monitoring Instrument, *Atmos. Meas. Tech.*, 4, 1905-1928, 2011.

Boersma, K. F., Eskes, H. J., Veefkind, J. P., Brinksma, E. J., vander A, R. J., Sneep, M., van den Oord, G. H. J., Levelt, P. F., Stammes, P., Gleason, J. F., and Bucsela, E. J.: Near-real time retrieval of tropospheric NO₂ from OMI, *Atmos. Chem. Phys.*, 7, 2103–2118, 2007.

II. Section 4.1, last paragraph. Could atmospheric chemistry and transport of urban

emissions also be important for NO_x enhancements seen over the Yangtze River? Are these areas downwind of Nanjing?

Response and revisions:

We thank the reviewer's important comment. The area with high NO₂ VCDs along the Yangtze River was located in eastern Nanjing. Given the dominating east wind of the city, it is upwind instead of downwind of Nanjing. However, we agree with the reviewer that sources other than ships (e.g., factories located along the river) could contribute to the high VCDs, and we have added this **in lines 518-519, Pages 20-21 in the revised manuscript:**

"Besides the ships, the emissions from factories along the river could also contribute to the high VCDs."

12. Figure 5. For clarity, the caption should mention that panel (a) refers to city-scale emissions from "this study".

Response and revisions:

We thank the reviewer's reminder and have revised the caption of Figure 5 as suggested:

Figure 5. (a) Spatial distribution of city-scale NO_x emissions in this study, (b) summer NO₂ vertical column density (VCD) from OMI, and (c) NO_x emissions from MEIC for Nanjing, 2010. The resolution is 0.125°×0.125°.

13. Section 4.2. Given that NO_x has a relatively short atmospheric lifetime, why is the slope in the correlation of emissions and concentrations so flat? What explains the large y-intercept? A more direct comparison of local emissions is to plot emissions versus enhancements in NO_x, SO₂, and CO above regional background levels.

Response and revisions:

We thank the reviewer's important comment and admit that the limitation of the

correlation analysis was not fully discussed in the original manuscript, particularly for NO₂ concentrations versus NO_x emissions. In urban areas with plenty of emission sources and relatively large emission density, NO was found to account for large fraction of NO_x in the ambient atmosphere (Zhou et al., 2008). As the dominating component of primary NO_x directly from emission sources, NO is more difficult to be oxidized to NO₂ in urban than in rural or remote regions, attributed to less resident time for chemistry conversion in urban. Given the 9 state-operated monitoring sites are all located in urban/suburban Nanjing, the observed NO₂ concentrations were less sensitive or correlated to the NO_x emissions, compared to the case of SO₂ or CO. That partly explains the small slope of ambient NO₂ levels to NO_x emissions in Figure 7(a), and the lowest correlation coefficient among all the concerned species.

The y-intercepts can be considered as the approximation of regional background levels of corresponding air pollutants. As pointed by the reviewer, the value for NO₂ is relatively high compared to SO₂. Since the YRD is a developed region with large economy, high energy consumption, and, particularly, large vehicle population and intensive transportation, the background levels of NO₂ could be enhanced, and the local emissions in Nanjing thus have a less significant impact on NO₂ concentrations. We agree with the reviewer that comparisons between the emissions and enhancements in pollutants above regional background levels are more useful. Attributed to the limitation of observation sites (all of which are in urban areas), however, the background levels for the region have not been sufficiently observed and reported, and are thus currently unavailable for the analysis. (Note the y-intercepts are rough estimates as mentioned in the beginning of this paragraph, and the correlation coefficients between the emissions and the concentration enhancements above the y-intercepts would remain the same as those between the emissions and the original observed concentrations.) We are currently conducting the simulation on the regional background levels of certain air pollutants (SO₂, NO₂ and PM_{2.5}) for the city using chemistry transport model, and more accurate estimates could be expected in near future. We have added the relevant discussions **in lines 539-554, Pages 21-22 in the revised manuscript:**

"The y-intercepts in Figure 7(a) can be considered as the approximations of regional background levels of SO₂ and NO₂, and the value for NO₂ is relatively high compared to SO₂. Since the YRD is a developed region with large economy, high energy consumption, and, particularly large vehicle population and intensive transportation, the background levels of NO₂ could be enhanced, and the local emissions in Nanjing city thus have a less significant impact on NO₂ concentrations. Moreover, in urban areas with plenty of emission sources and relatively large emission density, NO was found to account for large fraction of NO_x in the ambient atmosphere (Zhou et al., 2008). As the dominating component of primary NO_x directly from emission sources, NO is more difficult to be oxidized to NO₂ in urban than in rural or remote regions, attributed to less resident time for chemistry conversion in urban. Given the 9 state-operated monitoring sites are all located in urban/suburban Nanjing, the observed NO₂ concentrations were less sensitive or correlated to the NO_x emissions, compared to the case of SO₂, and it leads to the smaller slope of ambient NO₂ levels to NO_x emissions and the lower correlation coefficient in Figure 7(a)."

Reference:

Zhou, W., Wang X., Zhang, Y., Su, H., and Lu, K.: Current status of nitrogen oxides related pollution in China and integrated control strategy, Acta Scientiarum Naturalium Universitatis Pekinensis, 44, 323-330, 2008 (in Chinese).

14. Section 4.3.2. What was the basis for why the authors used the lowest daily OC/EC value observed as a surrogate for the primary emissions ratio? Also a figure with time series data of the OC/EC ratio should be included in supplemental material.

Response and revisions:

We thank the reviewer's important comment. The principle of determining the primary OC to EC, i.e., (OC/EC)_{pri}, in the EC-tracer method is to exclude the effects of SOC formation as much as possible (Castro et al., 1999). (OC/EC)_{pri} can be

estimated by various ways, including the OC to EC ratio from emission inventory, OC to EC concentration ratio from observation when SOC formation is weak and thus the concentrations are dominated by emissions, or the lowest OC to EC concentration ratio during the observation. Given the relatively small offline sampling size in Li et al. (2015), they chose the lowest daily OC/EC as $(OC/EC)_{pri}$ to estimate the SOC level using the EC-tracer method. In this work, therefore, we have adopted their assumption and results. We admit the uncertainty from the limited data availability and recommend further improvement on observation. We have discussed this **in lines 647-656, Page 25-26 in the revised manuscript.**

"EC and primary OC result from incomplete combustion, and the ratio of OC to EC concentrations is used to evaluate carbonaceous aerosol emissions and the formation of secondary organic aerosols (SOA) through the EC-tracer method (Castro et al., 1999). From 2011 to 2013, ambient EC and OC in downwind Nanjing were collected using quartz filters and analyzed with a DRI Model 2001 Thermal/Optical Carbon Analyzer by season (Li et al., 2015). The ratios of primary OC to EC, $(OC/EC)_{pri}$, were then determined based on the observation. Attributed to limited sampling size, Li et al. (2015) chose the lowest daily OC/EC during the sampling period for each season as the seasonal $(OC/EC)_{pri}$ to exclude the effects of SOA (see Figure S7 for the observed time series of ambient OC to EC ratio)."

The time series data of OC/EC ratios are taken directly from Li et al. (2015) and illustrated **in a new Figure S7 in the revised supplement** as required by the reviewer.

Reference:

Castro, L. M., Pio C.A., Harrison, R. M., and Smith. D. J. T.: Carbonaceous aerosol in urban and rural European atmospheres: estimation of secondary organic carbon concentrations, *Atmos. Environ.*, 33, 2771-2781, 1999.

Li, B., Zhang, J., Zhao, Y., Yuan, S. Y., Zhao, Q. Y., Shen. G. F., and Wu, H. S.: Seasonal variation of urban carbonaceous aerosols in a typical city Nanjing in Yangtze

River Delta, China, Atmos. Environ., 106, 223-231, 2015.

15. Section 4.3.2, Line 15. McDonald et al. also found factor of 2 higher OC/EC ratios from Los Angeles filter samples that did not use backup filters to correct for a positive OC artifact. Given the large uncertainty in the OC measurements used in this study, how confident can the authors be that their emissions ratio is closer to the artifact corrected ambient OC/EC ratio than MEIC (Line 4)? It is possible that the true ambient OC/EC ratio is lower than the two emission inventories.

McDonald, B.C., A.H. Goldstein, and R.A. Harley, Long-term trends in California mobile source emissions and ambient concentrations of black carbon and organic aerosols. Environmental Science & Technology, 2015. DOI: 10.1021/es505912b.

Response and revisions:

We thank the reviewer's crucial comment and agree that different sampling/analytical methods can lead to considerable uncertainties in observation of ambient carbonaceous aerosol concentrations, and that such uncertainty could be important for evaluation of emission inventories. We have cited the study suggested by the reviewer, and have stated that the artifacts of OC measurement can vary between cities. In Nanjing, such artifacts have not been well quantified, and it is thus difficult to make a conclusive evaluation or comparison on the results from different bottom-up emission inventories, as indicated by the reviewer. Therefore, we have revised the text and deleted the words that imply a better estimate by this work over MEIC **in lines 672-680, Page 26 in the revised manuscript:**

"Moreover, the carbonaceous aerosol sampling procedure used by Li et al. (2015) would lead to positive artifacts of OC measurement and elevated OC to EC, since usage of quartz filters adsorbs some semivolatile organic compounds (SVOC) in the ambient atmosphere (Cheng et al., 2009). The system bias of OC quantification from this sampling approach was estimated to reach 50% in US (Chow et al., 2010; McDonald et al., 2015), and it was found to be 100% in

certain city in China (Hu et al., 2008). However, the bias can vary largely between cities, and it has not been well quantified for Nanjing, making the evaluation of emission inventories of carbonaceous aerosols less conclusive."

Improved analysis on artifacts of OC observation has also been recommended for the city (**lines 680-685, Page 26-27 in the revised manuscript**):

"Finally, uncertainty also exists in the $(OC/EC)_{pri}$ determination by Li et al. (2015), as the sample size from off-line measurements was small. To better evaluate the city-level OC and BC emissions, therefore, more observational research with improved (e.g., long-term and continuous) measurements is strongly recommended at sites where local sources dominate, and the artifacts of the measurement should be sufficiently analyzed."

16. Section 4.3.3. The authors suggest that oxidation of NMVOCs could be an important source of secondary CO (Page 18716, Line 17). To control for chemistry, the authors could also see how ambient ratios of CO₂/CO compare during morning periods (i.e., when photochemistry is slower).

Response and revisions:

We thank the reviewer's important comment. Following the reviewer's suggestion, we have checked the observation data during the night till early morning (i.e., from 6pm to 6am) for the subset (2), and the ambient CO₂ to CO ratio is estimated at 89.2, larger than the value based on daily average concentrations, at 91.9. The results thus confirm the reviewer's judgment that photochemistry is slower at relatively lower temperature, leading to less secondary CO formation in the atmosphere, and thereby larger CO₂ to CO ratio. If the CO concentrations are further revised based on the description in Section 4.4, the modified ambient CO₂ to CO ratio is calculated at 70.7 for 6pm to 6am period. Compared to the ratio based on daily average concentrations at 66.8, the ratio for 6pm to 6am period is closer to the result from city-scale emission inventory at 76.1. We have added the discussions **in lines**

738-742, Page 29 and lines 800-802, Page 31 in the revised manuscript.

"To partly exclude the effects of NMVOC oxidation, we recalculated the ambient CO₂ to CO ratio at 91.9 based on the hourly concentration data from 6pm to 6am for subset (2), when the temperature was lower and photochemistry was slower. The value is larger than 86.9 based on daily average concentration data, attributed mainly to less formation of secondary CO."

"If only hourly data from 6pm to 6am are applied to mitigate the effects of secondary CO formation from NMVOC oxidation, an even closer ambient CO₂ to CO ratio to emission inventory result would be estimated at 70.7."

17. Table 1. What does "Gas release ratio" mean?

Response and revisions:

It means the fraction of flue gas that is not recycled or collected for purification treatment, and is thus directly released to the atmosphere. We have added the information as a note of Table 1:

18. Figure 1(b). The points are hard to see when they overlap. Maybe a bar chart would be better here, similar to panel (a).

Response and revisions:

We thank the reviewer's suggestion and have revised the figure accordingly.

19. Table S1. What do stages mean?

Response and revisions:

"Stages" mean the staged emission standards for vehicles. China I-IV are equivalent to Euro I-IV, respectively, as stated **in line 184, Page 8 in the revised**

manuscript:

" ..., fleet composition by control stage (China I-IV, equivalent to Euro I-IV), ..."

To avoid confusion, we have changed to words to China I-IV **in the revised Table S2.**

20. Table S3. For completeness, emission factors for coal-fired power plants and cement facilities should be added to the table.

Response and revisions:

We thank the reviewer's comment, and have added the information on emission factors for coal-fired power plants and cement facilities **in Table S4 in the revised supplement.**

*21. Title: Should read "Advantages of *a* city-scale emission inventory".*

Response and revisions:

We thank the reviewer's reminder and have revised the title as suggested.

22. Figure 8. "Original" observation is misspelled in the figure.

Response and revisions:

We thank the reviewer's reminder and have revised the figure as suggested.

Reviewer #2

1. The manuscript is complete and excellent. It would be a great addition (perhaps in Supplementary Information?) to discuss uncertainty in a sector by sector fashion. It

may be unrealistic to perform a detailed spatial/temporal sector by sector uncertainty analysis but it may be a good complement to the already thorough analysis.

Response and revisions:

We thank the reviewer's positive comment on the paper. We have added a paragraph to qualitatively discuss the emission uncertainty by source **in lines 872-891, Pages 33-34 in the revised manuscript:**

"The uncertainties of China's national emission inventories have been estimated using Monte-Carlo simulation, as described in our previous studies (Zhao et al., 2011; 2013). Targeting city scale, however, the uncertainty of current inventory for Nanjing is more difficult to be systematically quantified, as many emission factors are city- or device-dependent and their probability distributions could not be fully defined without sufficient field measurement records. In general, the uncertainties of emissions from power and industry sectors are expected to be reduced compared to the national level, as the "key sources" in the city contribute significantly to the fuel consumption and production of those sectors. As described in Section 2, the activity levels and emission factors for those key sources were compiled plant by plant or obtained through onsite survey, leading to relatively small biases in emission estimation. For most area sources, the emission factors used in this work were hardly improved compared to previous national/regional inventories, thus large uncertainties remain in those sources. Given the tiny fractions of emissions by those sources in Nanjing, however, their contribution on the uncertainty of total city emissions is expected to be limited. Very high uncertainty is expected for fugitive dusts that are generally not included in national/regional inventory, as little local information is available to improve the emission factors. Given the large shares of fugitive dusts to primary PM emissions (Figure S2), field measurements on construction sites and road dusts are suggested for better emission estimation in Nanjing. "

As we admit, quantifying the uncertainty for city-scale inventory using Monte-Carlo simulation is more difficult than that for national one, as many emission

factors are device-dependent and their probability distributions could not be fully defined without sufficient field measurement records. We agree with the reviewer that the uncertainty analysis for emission inventory at city-scale, and comparisons with national/regional-level ones are important, and will conduct the research in details once more local information gets available.

TITLE PAGE

Advantages of a city-scale emission inventory for urban air quality research and policy: the case of Nanjing, a typical industrial city in the Yangtze River Delta, China

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ABSTRACT

1
2 With most eastern Chinese cities facing major air quality challenges, there is a
3 strong need for city-scale emission inventories for use in both chemical transport
4 modeling and the development of pollution control policies. In this paper, a
5 high-resolution emission inventory (with a horizontal resolution at 3×3 km) of air
6 pollutants and CO₂ for Nanjing, a typical large city in the Yangtze River Delta, is
7 developed incorporating the best available information on local sources. Emission
8 factors and activity data at the unit or facility level are collected and compiled using a
9 thorough onsite survey of major sources. Over 900 individual plants, which account
10 for 97% of the city's total coal consumption, are identified as point sources, and all of
11 the emission-related parameters including combustion technology, fuel quality, and
12 removal efficiency of air pollution control devices (APCD) are analyzed. New
13 data-collection approaches including continuous emission monitoring systems and
14 real-time monitoring of traffic flows are employed to improve spatiotemporal
15 distribution of emissions. Despite fast growth of energy consumption between 2010
16 and 2012, relatively small inter-annual changes in emissions are found for most air
17 pollutants during this period, attributed mainly to benefits of growing APCD
18 deployment and the comparatively strong and improving regulatory oversight of the
19 large point sources that dominate the levels and spatial distributions of Nanjing
20 emissions overall. The improvement of this city-level emission inventory is indicated
21 by comparisons with observations and other inventories at larger spatial scale.
22 Relatively good spatial correlations are found for SO₂, NO_x, and CO between the
23 city-scale emission estimates and concentrations at 9 state-operated monitoring sites
24 ($R=0.58$, 0.46 , and 0.61 , respectively). The emission ratios of specific pollutants
25 including BC to CO, OC to EC, and CO₂ to CO compare well to top-down constraints
26 from ground observations. The inter-annual variability and spatial distribution of NO_x
27 emissions are consistent with NO₂ vertical column density measured by the Ozone

28 Monitoring Instrument (OMI). In particular, the Nanjing city-scale emission inventory
29 correlates better with satellite observations than the downscaled Multi-resolution
30 Emission Inventory for China (MEIC) does when emissions from power plants are
31 excluded. This indicates improvement in emission estimation for sectors other than
32 power generation, notably industry and transportation. High-resolution emission
33 inventory may also provide a basis to consider the quality of instrumental
34 observations. To further improve emission estimation and evaluation, more
35 measurements of both emission factors and ambient levels of given pollutants are
36 suggested; the uncertainties of emission inventories at city scale should also be fully
37 quantified and compared with those at national scale.

38

39

1 INTRODUCTION

40 Emission inventories are crucial for atmospheric science research, particularly
41 chemical transport modeling (CTM), and for air quality policymaking that seeks to
42 identify and control pollution sources. Given China's important role in the origins and
43 transport of air pollutants in East Asia and beyond, a number of emission inventories
44 at national scale have been established in recent years. These include the Transport
45 and Chemical Evolution over the Pacific Mission (TRACE-P, Streets et al., 2003), the
46 Intercontinental Chemical Transport Experiment-Phase B (INTEX-B, Zhang et al.,
47 2009), the Regional Emission inventory in ASia (REAS, Ohara et al., 2007;
48 Kurokawa et al., 2013), and the Multi-resolution Emission Inventory for China
49 (MEIC, <http://www.meicmodel.org/>). Based on "bottom-up" principles and
50 frameworks similar to those described in Streets et al. (2003), more detailed source
51 categories and expanded domestic information on emission factors and activity levels
52 have been integrated into most recent work, yielding improved inter-annual trends in
53 national estimates of anthropogenic air pollutant emissions (e.g., MEIC; Zhao et al.,
54 2012a; 2012b; 2013). Aside from the national-level work, regional emission

55 inventories have also been established with improved understanding of local
56 conditions for key areas with high densities of population, industry, and energy
57 consumption, e.g., the Jing-Jin-Ji region including Beijing and Tianjin (JJJ; S. Wang
58 et al., 2010), the Yangtze River Delta (YRD; Fu et al., 2013; Huang et al., 2011), and
59 the Pearl River Delta (PRD; Zheng et al., 2009).

60 There is still need for improvement of bottom-up emission inventories, however,
61 particularly at smaller spatial scales. First, data for activity levels and emission factors
62 used in current Chinese inventories come mostly from coarse statistics or surveys at
63 the provincial level, except for select sectors (e.g., power generation, Zhao et al.,
64 2008). Underlying information that is crucial to emission levels (e.g., combustion or
65 manufacturing technologies, fuel qualities, and penetrations and removal efficiencies
66 of various emission control devices) has often been overlooked or assumed to be
67 uniform, inevitably reducing the accuracy and reliability of emission estimates.
68 Without sufficient source-specific information, in particular, it is hard to identify and
69 characterize “super-emitting” sources, which can strongly affect aggregate emission
70 estimates. Second, the spatial and temporal distributions of emissions are often not
71 well characterized. Emissions from most sectors are spatially allocated according to
72 proxies, e.g., population or economic densities. However, the distribution of large
73 sources in China is changing quickly because much industrial production is being
74 relocated out of urban cores, and the correlations between emissions and the usual
75 proxies like population density are getting weaker, particularly in developed cities
76 (Zhang et al., 2012a; Zhao et al., 2013). This introduces error into the spatial
77 allocations. The time distribution of emissions is commonly based on expert judgment,
78 with little reliance on real-time data sources, e.g., continuous emission monitoring
79 systems (CEMS). Finally, some sources that may play important roles in local
80 emissions are often missed in regional emission inventories, e.g., fugitive dust from
81 construction and road transportation, and volatile organic compounds (VOC) from gas
82 stations, mainly due to data limits on such sources. Such limitations weaken capacities

83 to research atmospheric chemistry using inventories as inputs to CTMs, and also
84 undermine the efficacy of pollution control decision-making.

85 Several studies have illustrated the benefits of city-scale emission inventories
86 that integrate more detailed local information. Timmermans et al. (2013), for example,
87 concluded that the results of NO₂ and PM₁₀ simulations were more consistent with
88 observations for Paris when a local emission inventory was used. In the U.S., model
89 simulations of NO₂ columns based on actual hourly NO_x emissions from CEMS
90 agreed better with satellite observations than those based on default emission inputs
91 from the U. S. Environmental Protection Agency (USEPA; Kim et al., 2009). In
92 China, vehicle emission inventories resolved at the county level, rather than provincial
93 level, were shown to better support air quality simulations for small regions (Zheng et
94 al., 2014).

95 China is experiencing frequent severe haze episodes (Zhang et al., 2012b; Wang
96 et al., 2013; Wang et al., 2014; R. Huang et al., 2014). Cities are being required to
97 expand efforts at air pollution control, and use of CTMs for air quality assessment and
98 policy making is becoming more routine. Due in part to weak emission inputs,
99 however, atmospheric simulations for cities are often disappointingly inaccurate
100 (personal communication with Zifa Wang from Institute of Atmospheric Physics,
101 Chinese Academy of Science, 2014). Without integrating more detailed local
102 information, some cities simply downscale a national emission inventory into
103 high-resolution emission inputs for a CTM or develop local inventories based on the
104 same source data and methods used for national ones. Despite improvements from
105 some information (e.g., the precise location of large point sources), the quality and
106 reliability of those inventories have not been well evaluated using, for example,
107 integrated observational data as top-down constraints. Thus the emission estimates
108 introduce large uncertainties into the city-scale air quality simulations.

109 It should be noted that such improvements in emission inventories for a few
110 megacities, including Beijing and Shanghai, have been driven by air quality planning

111 for major events like the 2008 Summer Olympic Games and 2010 World Expo.
112 During recent years, however, satellite observations have detected that the most
113 significant growth in air pollution (indicated for example by vertical column densities
114 of tropospheric NO₂) across the country is occurring not within such megacities but in
115 the less-developed regions around them, due to faster growth in the economies and
116 emission sources in those areas (Zhang et al., 2012a). This finding highlights the
117 importance of developing and assessing air pollutant emission inventories for regions
118 other than China's much-studied megacities.

119 We select Nanjing, a typical large city in the YRD, to establish and evaluate a
120 high-resolution emission inventory at city scale. As shown in Figure S1(a) in the
121 supplement, Nanjing is the capital city of Jiangsu Province and the second largest city
122 in central east China following Shanghai, with a total area of 6587 km² and population
123 of 8 million in 2012 (NJNBS, 2013). Intensively industrial, Nanjing consumes much
124 more coal than many other Chinese cities with economies of similar size (e.g.,
125 Hangzhou, Qingdao, and Shenyang), and in 2012 suffered the highest number of days
126 of haze (226) of all of China's provincial capital cities (data provided by the Nanjing
127 Meteorological Bureau). The share of coal use in primary energy reached 89% in
128 2012 (Environmental Statistics, an internal database of the Nanjing Environmental
129 Protection Bureau, NJEPB; NJNBS, 2013), much higher than the national level of
130 71% (NBSC, 2013). Large coal consumption and industrial and chemical production
131 have resulted in high emissions of anthropogenic atmospheric pollutants. As the host
132 city of the 2nd Asian Youth Games (AYG) in August 2013, Nanjing undertook various
133 measures to control emissions in industry but allowed construction activities at
134 thousands of sites, leading to large changes in the levels and the temporal and spatial
135 distributions of emissions. Such changes are captured by a comprehensive city-scale
136 emission inventory.

137

2 DATA AND METHODS

138 2.1 The basic methodology

139 The annual emissions in Nanjing from 2010 to 2012 are estimated with a
140 bottom-up approach for 10 atmospheric pollutants (SO_2 , NO_x , total suspended
141 particulates (TSP), PM_{10} , $\text{PM}_{2.5}$, black carbon (BC) or elemental carbon (EC), organic
142 carbon (OC), CO, VOCs, and NH_3) and the greenhouse gas CO_2 . At the largest scale,
143 sources fall into six main categories: coal-fired power plants (CPP), industry (IND),
144 transportation (TRA, including on-road and non-road subcategories), the residential &
145 commercial sector (RES, including fossil fuel, biofuel, and biomass open burning
146 subcategories, along with gas stations for VOC estimation only), agriculture (AGR,
147 including livestock farming and fertilizer use for NH_3 estimation only), and fugitive
148 dust (FUD, including that from construction sites and roads). IND is further divided
149 into cement plants (CEM), iron & steel plants (ISP), refineries and chemical plants
150 (RCP), solvent use (SOL; although some solvent is not used in industry, we include it
151 in this category for classification simplicity) and other industry plants (OIN).

152 To improve the accuracy and reliability of the city-level emission inventory, new
153 data are collected from various sources and modified methods are applied compared
154 to previous studies, as briefly summarized below.

155 With sufficient information related to emission estimation now available, more
156 sources can be characterized as point sources in the current inventory. These include
157 power plants (total number in 2012, similarly for subsequent categories: 18), cement
158 plants (23), iron & steel plants (2), chemical plants (173), non-ferrous metal smelters
159 (14), lime plants (9), brick plants (31), factories representing a portion of other
160 industrial sectors (434), and gas-fueling stations (269). The locations of point sources
161 by category are shown in Figure S1 (b) and (c) in the supplement. The annual
162 emissions of point sources are calculated with Equation (1):

163
$$E_i = \sum_{j,m} A_{i,j,m} \times EF_{i,j,m} \times (1 - \eta_{i,j,m}) \quad (1)$$

164 where i , j and m represent the species, individual plant, and fuel/technology type,
165 respectively; A is the activity level data; EF is the uncontrolled emission factor; and η
166 is removal efficiency of air pollutant control device (APCD).

167 For all the point sources, information from the Environmental Statistics database
168 and Pollution Source Census (internal data of NJEPB) is collected and compiled to
169 obtain the activity levels (energy consumption or industrial production) and
170 parameters related to emission factors, plant by plant. Moreover, we conduct onsite
171 surveys individually for all of the CPP, CEM, ISP and RCP sources (labeled “key
172 sources” in this paper), to get further information that is crucial for emission
173 estimation but not covered by the official census or statistics (see details in Section
174 2.2). In 2012, all of the point sources and all of the key sources in Nanjing accounted
175 for 97% and 96% of the city’s total coal consumption, respectively, reflecting the
176 highly centralized energy use of Nanjing. The annual activity levels for the key
177 sources for 2010-2012 are summarized in Table S1 in the supplement.

178 Besides annual levels, monthly energy consumption, industrial production, and
179 flue-gas concentrations from CEMS are obtained whenever possible through our
180 plant-by-plant onsite investigations. The monthly distribution of emissions from key
181 sources is then revised based on these data.

182 Emissions from on-road transportation are calculated using COPERT 4 (version
183 9.0) (EEA, 2012). The parameters required by the model, including vehicle population
184 by type, **fleet composition by control stage (China I-IV, equivalent to Euro I-IV)**, and
185 annual average kilometers traveled (VKT), are taken from investigations by NJEPB.
186 The detailed information for 2012 is summarized in Tables S2 and S3 in the
187 supplement. **The traffic flows in the city are compiled from the observations of the**
188 **Intelligent Traffic Violation Monitoring System (internal data of NJEPB). In the**
189 **system, cameras are used to continuously record the real-time traffic flows for most**

190 arterial roads and highways, and part of residential roads in the city. The system does
191 not cover all the roads (particularly for residential roads), and the traffic flows in those
192 roads were simulated from the real-time monitoring data for similar roads that are
193 covered by the system. Combining the information of traffic flows and the road net,
194 the spatial and diurnal distributions of emissions from CORPERT can be derived. It
195 should be noted, however, uncertainty exists in the allocation of vehicle emissions,
196 particularly for areas with fewer cameras installed.

197 For area sources including other small industry, solvent use, residential
198 combustion, agricultural activity, and non-road transportation, emissions are estimated
199 following previous work (Zhao et al., 2012a; 2012b; 2013), with up-to-date emission
200 factors from domestic measurements and city-scale activity levels. The energy
201 consumption data are taken from the Environmental Statistics (internal data of NJEPB)
202 and the agricultural and industrial outputs are mainly from the Nanjing Statistical
203 Yearbook (NJBNS, 2013). Fire counts and intensity observed from MODIS
204 (Moderate Resolution Imaging Spectroradiometer, [https://earthdata.nasa.gov/
205 data/near-real-time-data/firms](https://earthdata.nasa.gov/data/near-real-time-data/firms)) are used to determine the spatial and temporal
206 distribution of emissions from biomass open burning. Regarding fugitive dust,
207 information about individual construction sites in the city is obtained from NJEPB to
208 improve the estimation of emission levels and spatial and temporal distributions. This
209 includes location, period of operations, construction area, and amount of earthworks).
210 The largest 221 construction sites in Nanjing in 2012 (accounting for 45% of the total
211 construction area) are shown in Figure S1 (c) in the supplement. The annual activity
212 levels for the main area sources for 2010-2012 are summarized in Table S1.

213 **2.2 Emission factors**

214 As mentioned previously, parameters related to emission factors for key sources
215 (CPP, CEM, ISP, and RCP) are obtained through onsite surveys for each plant. The
216 parameters for CPP include boiler type, combustion technology, fuel quality (sulfur,

217 ash, and volatile matter contents), types and pollutant removal efficiencies of APCDs
218 (flue gas desulphurization (FGD), selective catalytic reduction (SCR)/selective
219 non-catalytic reduction (SNCR), dust collection). Emission factors can then be
220 determined or calculated based on the method described by Zhao et al. (2010). For
221 cement production, the kiln type, PM removal efficiency of dust collectors, and fuel
222 quality are investigated and emission factors are calculated following Lei et al. (2011)
223 and Zhao et al. (2012a; 2013). For ISP, key parameters in four main processes (coking,
224 sintering, pig iron production, and steelmaking) are obtained, including the SO₂
225 removal rate of FGD for sintering, PM removal rate of dust collectors, and the gas
226 release ratios of coke ovens, blast furnaces, and basic oxygen furnaces. Emission
227 factors for each process are then calculated following Zhao et al. (2012a; 2013). For
228 the chemical industry, the surveyed parameters include the types and amounts of raw
229 materials and products, the types and volumes of tanks, and technologies applied for
230 VOC control. In particular, the emission factors for refineries are determined by
231 industrial process, including production, storage, loading, and unloading (Wei et al.,
232 2008; USEPA, 2002; EEA, 2013). Inter-annual variations in these parameters for
233 major sources are tracked in the survey so that changing emission factors over time
234 (2010-2012) can be determined. Table 1 summarizes the penetrations and removal
235 efficiencies of APCDs for CPP and typical industries in Nanjing from 2010 to 2012.
236 For other industrial sources, emission factors are taken mainly from the database by
237 Zhao et al. (2011; 2013), after incorporating the most recent results from domestic
238 measurements. Table S4 in the supplement summarizes the emission factors for main
239 industrial processes.

240 For other sources for which local emission factors are currently unavailable,
241 emission factors are determined based on existing studies in other parts of China. If no
242 domestic studies are available, recommendations of USEPA (2002) are applied. Road
243 dust emissions are estimated following USEPA (2002), based mainly on the average
244 weight of vehicles, silt loading of the road surface, and traffic flow. Those parameters

245 are taken from Fan et al. (2007) and Huang et al. (2006), with some adjustments of
246 road types for Nanjing. Emission factors of construction dust recommended by
247 USEPA (2002) are used in this work, i.e., 0.026, 0.106, and 0.191 (kg/m²)/month for
248 PM_{2.5}, PM₁₀, and TSP, respectively. The mass fractions of BC and OC in construction
249 PM_{2.5} are assumed to be 2.4% and 3.4%, respectively, from measurements by Zhao et
250 al. (2009).

251 For gasoline stations, Nanjing completed installation of vapor recovery systems
252 at all stations at the end of 2012. VOC emission factors for gas storage, loading,
253 unloading and sales are determined at 0.03, 0.87, 0.10 and 2.44 g/kg, respectively
254 (Wei et al., 2008; Fu et al., 2013). Solvents include paints for buildings and furniture,
255 ink, fabric coating adhesives, and pesticides. VOC emission factors for decorative
256 adhesives, interior wall paints, and wood paints are taken from Fu et al. (2013), while
257 those for other solvent use come mainly from Wei et al. (2008).

258 Emission factors for non-road transportation are mainly from Zhang et al. (2010)
259 and Ye et al. (2014). Emission factors for household biofuel use are estimated based
260 on results of various domestic measurements as summarized in Zhao et al. (2013) and
261 Cui et al. (2015), while those for biomass open burning are from Li et al. (2007). NH₃
262 emissions from livestock farming and fertilizer use are taken from Dong et al. (2010),
263 Yang (2008), and Yin et al. (2010).

264 **3 RESULTS**

265 **3.1 Inter-annual variability and sector distribution of emissions**

266 The annual emissions of various air pollutants and CO₂ from anthropogenic
267 sources in Nanjing are shown in Figure 1(a) for 2010-2012. In 2010, the total
268 emissions of SO₂, NO_x, CO, VOCs, NH₃, PM_{2.5}, PM₁₀, TSP, CO₂, BC and OC are
269 estimated at 165, 216, 774, 224, 21, 71, 94, 158, 79976, 6.2, and 6.7 Gigagrams (Gg),
270 respectively. Note the numbers here for PM emissions do not include fugitive dust

271 from construction and transportation, to facilitate comparison with inventories that
272 omit the source. Despite large growth in coal consumption from 2010 to 2012, the
273 emissions of SO₂ and NO_x in 2012 are estimated to be smaller than those in 2010,
274 implying the effectiveness of emission control measures for the city in recent years.
275 These measures include mainly the increased use of flue gas desulfurization (FGD)
276 and selective catalytic reduction (SCR) systems in the power generation sector (see
277 the detailed information in Table 1). The slight increase in SO₂ emissions between
278 2011 and 2012 resulted mainly from the growth in coal consumption in industries
279 other than power generation, where FGD systems have not been widely deployed. For
280 NO_x, the large increase in coal consumption from 31 million metric tons (Mt) in 2010
281 to 35 in 2011 dominated the growth of NO_x emissions, even with improved use of
282 SCR in power sector. From 2011 to 2012, the growth in coal consumption was limited
283 while the average removal efficiencies of SCR are significantly improved (as shown
284 in Table 1), leading to reduced NO_x emissions for the whole city. PM emissions are
285 estimated to be quite stable for the three years, with small increases in PM_{2.5} and PM₁₀.
286 Rising mass fractions of PM_{2.5} to TSP (from 45% to 48%) indicate the difficulty in
287 controlling emissions of finer primary particles compared to coarser ones. For VOCs
288 and NH₃, which have not been well regulated in national action plans for air pollution
289 prevention and control (Zhao et al., 2014), the inter-annual variabilities of emissions
290 are small and driven mainly by relative stability in chemical and agricultural
291 production, respectively. While CO₂ continues to rise, no growth is estimated for CO
292 from 2011 to 2012, implying improved overall combustion efficiency in the city.

293 Figure S2 in the supplement shows the sector contributions to total emissions by
294 year and species. From 2010 to 2012, power plants, iron & steel plants, and other
295 industrial plants are the largest SO₂ sources, contributing 41%-42%, 14%-19%, and
296 32%-23% of total emissions, respectively. NO_x emissions come mainly from power
297 plants (45%) and on-road transportation (20%) throughout the time period. The shares
298 of SO₂ and NO_x emissions from the power sector are clearly smaller than its shares of

299 coal consumption (57%-64%) or CO₂ emissions (48%-57%), due largely to relatively
300 stringent emission controls in the sector. It can be found that the sector distribution of
301 NO_x emissions did not change much annually, even with clear enhancement of NO_x
302 control in coal-fired power plants as shown in Table 1. The growth in coal
303 consumption of power plants partly offset the benefits of improved penetration and
304 removal efficiency of SCR on NO_x control, and the NO_x emissions from power sector
305 did not vary much for the three years (97, 112 and 94 Gg for 2010, 2011, and 2012,
306 respectively). Besides power sector, in addition, emission controls were also improved
307 for other sources, including the increased use of retrofitted low-NO_x burner for
308 industrial boilers, and the implementation of strict emission standards for vehicles.
309 For example, the emissions from other industrial combustion (OIN) were estimated to
310 decrease from 22 to 14 Gg from 2010 to 2012, and the emissions from on-road
311 vehicles did not change a lot despite of vehicle population growth, leading to
312 relatively small variation in sector distribution of emissions for the three years.

313 Fugitive dust, particularly that of road origin, is identified as the dominant
314 anthropogenic source of PM emissions. The fugitive dust shares of TSP are estimated
315 to range 64%-70% during the research period, while smaller fractions are found for
316 finer particles and carbonaceous aerosols. Apart from fugitive dust, iron & steel
317 production plays a significant role in PM emissions in Nanjing, with its shares of TSP,
318 PM₁₀, and PM_{2.5} calculated at 15%-16%, 20%-23%, and 35%-41%, respectively. This
319 results mainly from the large coal use by the sector, and relatively poor PM control
320 measures of certain plants compared to other major coal-consuming sources, e.g.,
321 power plants. Iron & steel production is also identified as the biggest contributor of
322 CO emissions for the city with its share reaching 60% in 2012, even though emission
323 factors for the sector in Nanjing (based on field investigations) are smaller than the
324 national average (Zhao et al., 2012a). This is partly attributed to relatively little
325 inefficient coal combustion at other sources in the city (e.g., in small industry and
326 residential use), resulting in much lower fractions of CO emissions from those sources

327 than the national averages. VOCs come mainly from chemical production (52%) and
328 solvent use (29%-30%). With vapor recovery systems increasingly applied, VOC
329 emissions from gas stations decline during the research period. Despite an increase in
330 vehicle population, the fractions of on-road transportation emissions for most species
331 decrease from 2010 to 2012, attributed mainly to implementation of increasingly strict
332 vehicle emission standards. From effective prohibition of burning of agricultural
333 wastes, the emission contributions of this source, mainly of particles, carbonaceous
334 aerosols, and CO, are also considerably reduced.

335 **3.2 Spatial and temporal distribution**

336 For simulation of atmospheric transport and chemistry, the emission inventories
337 are allocated into a 3×3 km grid system. For sources lacking specific location
338 information, their emissions are assumed to be correlated with population density,
339 with the exception of NH₃, which is allocated based on the density of agricultural
340 GDP. Shown in Figure 2 are the spatial distributions of SO₂, NO_x, PM_{2.5} (excluding
341 fugitive dust from construction and roads) and VOC emissions for Nanjing in 2012,
342 and the locations of the ten largest point sources of each species. Relatively high
343 emission densities are found in the urban area, particularly around certain large power
344 generation and industrial sources. As illustrated Figure 3, the fractions of emissions
345 from point sources for all concerned species are estimated to exceed 50%, as are those
346 from the collective four key source types, with the exception of BC, at 38%.

347 Monthly distributions of SO₂ emissions by sector and that of total emissions of
348 all species for 2012 are respectively shown in Figure S3 (a) and (b) in the supplement.
349 Note again that fugitive dust from construction sites and roads is excluded. The results
350 of MEIC are also provided in Figure S3(a) for comparison. It can be seen that the
351 temporal distributions of the two studies are similar except for residential emissions,
352 which are smaller overall in this work compared to MEIC. As indicated by MODIS
353 fire counts, over 90% of biomass open burning occurred in May-July, leading to much

354 higher OC emissions in those three months compared to any other time of the year.
355 For other species, the temporal distributions of emissions correlate closely with those
356 of activity levels, with a drop in February attributed mainly to reduced energy supply
357 and industrial production during the Spring Festival. Pronounced diurnal variations of
358 on-road transportation emissions are illustrated in Figure S4 in the supplement, with
359 two peaks at the rush hours. The daily shares of CO and VOC emissions in the
360 morning rush hour (16%) are slightly higher than those of NO_x (14%) and PM_{2.5}
361 (15%). Based on the assumptions of COPERT, the cold start of most vehicles occurs
362 in the morning, leading to larger CO and VOC emission factors during this time
363 compared to those during stable operation of vehicles. The influence of vehicle cold
364 starts on emissions of NO_x and PM_{2.5} is smaller.

365 **3.3 Comparisons with other studies in emission estimates**

366 Figure 1(b) compares our estimates of Nanjing emissions with those from other
367 inventories (Fu et al., 2013; MEIC) for a common year, 2010. In the other studies,
368 national or regional average levels for some parameters related to emissions, e.g., the
369 penetrations and pollutant removal rates of emission control devices, are applied.
370 These values can vary considerably from those based on plant-by-plant field
371 investigations, leading to clear differences in emission estimates compared to the
372 current work.

373 Our estimate of SO₂ emissions for Nanjing is 25% and 22% higher than those of
374 Fu et al. (2013) and MEIC, respectively, even though the plant-by-plant survey
375 indicates an FGD penetration rate of 92% of installed power generating capacity,
376 higher than the provincial average of 85% used in Fu et al. (2013). The higher
377 estimate results because: 1) the total coal consumption from the Environmental
378 Statistics applied in this work is 14% larger than that provided by the Nanjing
379 Almanac used in other studies (NJCLCC, 2011; see Section 4.6 for more discussion);
380 and 2) a relatively lower removal efficiency of FGD is obtained from the onsite

381 survey for 2010. Similar NO_x emission levels are found between current work and
382 MEIC, while lower emissions were provided by Fu et al. (2013). According to filed
383 survey, the penetration rate of SCR/SNCR increased from 44% to 67%, and the NO_x
384 removal efficiency increased from 18% to 77% during 2010-2012 (Table 1). The
385 penetration rate is much larger compared to the provincial average of 22% applied in
386 MEIC and Fu et al. (2013), partly offsetting a discrepancy in estimated emissions
387 caused by larger activity levels used in current city-scale inventory.

388 Our estimates for PM_{2.5}, PM₁₀, and BC emissions (without fugitive dust
389 emissions) are larger than those of Fu et al. (2013) or MEIC in 2010. This results
390 mainly from larger emissions from industry (particularly iron & steel production), as
391 the survey revealed that relatively old and inefficient wet dust collectors were still
392 used at some plants. OC emissions, however, are estimated to be lower than MEIC
393 indicates, due mainly to very little coal or biomass burning in the city-level statistics.

394 VOC emissions estimated in this work in 2010 are 34% larger than Fu et al.
395 (2013) and 36% larger than MEIC. In particular, emissions from refineries and
396 chemical plants, calculated using detailed information on each plant's inputs of raw
397 materials and the product types and amounts, are 116% higher than those in regional
398 inventories (Fu et al., 2013). Thus the fraction of total VOC emissions attributed to
399 industrial processes is estimated at 48% by us, larger than the YRD average level of
400 34% (Fu et al., 2013). Given Nanjing is a city with large petroleum refining and
401 chemical industries, and that much higher production of crude oil, gasoline, diesel and
402 liquefied petroleum gas is reported than in other YRD cities in 2010 (NJNBS, 2013),
403 the higher VOCs emissions indicated by the plant-based inventory is believed to
404 better reflect the city's true industrial structure.

405 For CO, our estimates are 12% higher for industry than those of MEIC, but 26%
406 and 37% lower respectively for residential and transportation sectors, resulting in 2%
407 lower emissions for anthropogenic sources as a whole. The discrepancy in sector
408 contributions is caused mainly by the high percentage of centralized coal combustion

409 in the city: power, iron & steel, cement, and chemical plants consumed over 95% of
410 the city's coal, based on our field survey. Our CO₂ emission estimate is 22% higher
411 than that of MEIC, resulting mainly from the difference in coal consumption reported
412 by the Environmental Statistics database and the city almanac.

413

414 **4 ASSESSMENT OF THE CITY-SCALE EMISSION INVENTORY**

415 The current inventory is assessed to gauge improvements of emission estimates
416 using a city-scale framework. The inter-annual variability, spatial distributions, and
417 correlations of a number of species of the inventory are evaluated by comparison to
418 available satellite and ground observations, and to downscaled national emission
419 inventories.

420 **4.1 Evaluation of inter-annual trends and spatial distribution of NO_x emissions** 421 **with satellite observations**

422 The inter-annual trend in NO_x emissions estimated bottom-up is compared with
423 that of NO₂ vertical column densities (VCDs) based on satellite observations. The
424 VCDs of tropospheric NO₂ are retrieved from the Ozone Monitoring Instrument (OMI)
425 by the Royal Netherlands Meteorological Institute (Boersma et al., 2007; 2011), using
426 monthly data with spatial resolution of 0.125°×0.125° (data source:
427 http://www.temis.nl/airpollution/no2col/no2regioomimonth_v2.php). Illustrated in
428 Figure 4 are annual emissions estimated in this work for Nanjing from 2010 to 2012
429 and VCDs from 2005 to 2012 for 4 regions: Nanjing, Shanghai, 4 provinces in the
430 YRD (including Jiangsu, Zhejiang, Anhui and Shanghai), and a rectangular region
431 containing Nanjing (see Figure S1(a) for reference). The first two represent NO₂ at
432 city levels while the latter two represent regional levels. To eliminate seasonal
433 variations, NO₂ VCDs are presented as 12-month moving averages, calculated as the
434 means of the data for the previous and subsequent six months. All the data are

435 normalized to the 2010 level of Nanjing. While NO₂ VCDs started declining around
436 2008 for Shanghai, it kept increasing for the rest of the YRD region including Nanjing
437 until 2012. Clearly higher than the regional levels, the average NO₂ VCD for Nanjing
438 approached that of Shanghai after 2010. This implies, on one hand, the benefits of
439 Shanghai's strict emission controls of on-road vehicles and big power plants (K.
440 Huang et al., 2014), implemented in advance of other regions. On the other hand, the
441 growth of NO₂ for the rest of the YRD demonstrates the spread of air pollution source
442 regions from major metropolitan areas to less developed cities nearby, and suggests
443 the need for increased efforts in emission and pollution abatement in those areas, as
444 indicated by Zhang et al. (2012a). Decreased emissions in Nanjing are clearly
445 indicated by this work after 2011, attributed mainly to the national policy of
446 compulsory installation and running of SCR devices in the power sector. This
447 inter-annual variation shows good consistency with that of OMI NO₂ VCD.

448 It should be noted that uncertainties exist in the comparison between the
449 inter-annual variations in emissions and VCDs and the results should be interpreted
450 cautiously. First, the biases of NO₂ VCD retrieval from OMI were reported to reach
451 40% attributed probably to the errors in the air mass factor calculations (Boersma et
452 al., 2007; 2011). Such uncertainties are potentially larger than the inter-annual
453 changes in NO_x emissions of Nanjing between 2010 and 2012, and thus weaken the
454 comparison. However, since the bottom-up emissions are not evaluated by the
455 absolute values but the relative trends of VCDs, the effects of NO₂ VCD retrieval
456 uncertainties on the comparison could partly be mitigated. Another uncertainty comes
457 from meteorology. As shown in Figure S5 in the supplement, the inter-annual changes
458 in meteorological parameters were small except for precipitation during 2010-2012 in
459 Nanjing. The varied precipitation could change the data sampling of retrieval, and
460 thereby influence the NO₂ VCD levels. Finally, the period for emission and VCD
461 comparison is relatively short. Even the NO₂ VCDs kept decreasing slightly after
462 2012, the benefits of NO_x emission control could not be fully confirmed as the

463 emission inventory for the most recent years are still unavailable due to the delay of
464 activity data report. Analysis on long-term trend in emissions from the bottom-up
465 method is further suggested for better understanding the NO_x pollution in the area.

466 To further assess possible improvement of emission estimates by the current
467 city-level inventory, the spatial distribution of monthly means of OMI NO₂ VCD in
468 summer (June-August) 2010 over Nanjing is compared with that of two emission
469 studies: 1) city-level emissions at spatial resolution of 3×3 km by the current work,
470 and 2) MEIC emissions developed at the provincial level with a resolution of 5×5 km.
471 For the purpose of visualization and further analysis, the emissions are reallocated to a
472 0.125°×0.125° grid system from the original spatial distributions, consistent with the
473 resolution of retrieved OMI NO₂ VCD. We assume that the NO₂ VCD from satellite
474 observations reflect the anthropogenic NO_x emissions of the city for the following
475 reasons. NO_x emissions in East China are predominantly anthropogenic (Mijling et al.,
476 2013); lightning and soil sources as a share of total emissions are estimated to peak in
477 July, when they account for 9% and 12%, respectively (Lin, 2012). NO_x emissions in
478 Nanjing are clearly larger than in surrounding areas (Huang et al., 2011), and the NO₂
479 VCD over the city is believed to be most influenced by local emissions.

480 As shown in Figure 5, a similar spatial pattern of NO_x is captured by the gridded
481 emissions and satellite observations, and relatively higher pollution in the urban area
482 in the center of the city is indicated, attributed mainly to the combined effects of
483 intensive transportation and large point sources. The emission inventories, however,
484 underestimate the high-pollution areas compared to OMI observations, particularly
485 MEIC. To further gauge improvement in spatial distribution by the city-scale
486 emissions, correlations between the gridded emissions and the VCD are analyzed. As
487 shown in Figure 6 (a), the correlation coefficients (R) between the emissions and the
488 VCDs are calculated at 0.450 and 0.408 for this work and MEIC, respectively,
489 indicating better agreement by the city-scale inventory. Moreover, a sensitivity test on
490 the correlation coefficients is conducted through step-wise exclusion of the grid cells

491 with the largest emissions. Along with the increase in excluded grid cells, the R for
492 this city-scale emission inventory remains above 0.43, while those of MEIC sharply
493 decrease (Figure 6 (b)). In order to estimate emissions of the whole country, the MEIC
494 is based mainly on energy and economic statistics at the provincial level, though it
495 includes a limited number of major point sources, e.g., power plants with relatively
496 good documentation and large emissions. Emissions from other point sources are
497 based on coarser inputs due to constraints of time, labor, and data availability. The
498 current study, in contrast, compiled detailed information for all power plants and most
499 other industrial sources in Nanjing through comprehensive survey investigation, as
500 described in Section 2. Better estimates of emission levels and spatial distributions
501 should thus be expected, particularly for small or medium-size emission sources.
502 Once the grid cells dominated by major power plants are excluded from the two
503 inventories, as shown in Figure 6 (c), the current city-scale emissions still correlate
504 well with satellite observations ($R=0.436$) while MEIC shows little correlation
505 ($R=0.085$). The results reflect that inventories compiled at the provincial or regional
506 level better estimate emissions of large sources than small or medium-sized ones, due
507 to relative availability of information on power plants but much poorer nationwide
508 data availability for other industrial plants. When focusing on smaller regions like
509 cities, however, detailed information on more emission sources from onsite survey
510 becomes crucial for improving emission estimates.

511 It should be noted that high NO_2 VCDs are found over the Yangtze River by
512 OMI (roughly following the dark red zone in Figure S6 in the supplement) while
513 current emission inventories cannot capture this. Possible underestimation of
514 emissions from ships is indicated. Due to data limits, only ships arriving or leaving
515 the port of Nanjing are taken into account in the current city-scale inventory, while
516 those passing through Nanjing are omitted. Further investigation of the vessel flow
517 along the Yangtze River is thus necessary to improve the estimation of ship emissions,
518 which may be particularly influential at small spatial scales. Besides the ships, the

519 emissions from factories along the river could also contribute to the high VCDs.

520 **4.2 Spatial correlations between pollutant emissions and ambient concentrations** 521 **from ground observations**

522 Ambient concentrations for selected pollutants from ground observations are
523 used to test the city-scale emission inventory. Daily averages of SO₂, NO₂, CO, and
524 PM_{2.5} concentrations for 2012 are obtained from the 9 state-operated monitoring
525 stations in urban/suburban Nanjing, mapped in Figure S1 (d). The SO₂, NO₂, CO, and
526 PM_{2.5} concentrations were measured by Ecotech EC9850B, Ecotech EC9841B,
527 Ecotech EC9830B and Met One 1020 analyzers, respectively. The emissions of
528 specific pollutants around each site with a grid cell size of 0.04°×0.04° are calculated
529 from the 3×3 km gridded inventories, and correlations with annual mean
530 concentrations of corresponding species are analyzed. Since none of the city's key
531 sources (CPP, CEM, ISP or RCP) are located in those grid cells, the effects of
532 individual big sources on the correlation between emissions and observation are
533 assumed to be limited.

534 As shown in Figure 7(a), modest agreement is found in spatial patterns between
535 the observed concentrations and the emissions for SO₂ and NO_x (NO₂), with the R
536 calculated at 0.58 and 0.46, respectively. SO₂ and NO_x have average atmospheric
537 lifetimes of several days and one day, respectively, thus the ambient concentrations
538 are expected to partly reflect emission intensities nearby and the correlation analysis
539 adds support for the reliability of the city-scale emission inventory. The y-intercepts in
540 Figure 7(a) can be considered as the approximations of regional background levels of
541 SO₂ and NO₂, and the value for NO₂ is relatively high compared to SO₂. Since the
542 YRD is a developed region with large economy, high energy consumption, and,
543 particularly large vehicle population and intensive transportation, the background
544 levels of NO₂ could be enhanced, and the local emissions in Nanjing city thus have a
545 less significant impact on NO₂ concentrations. Moreover, in urban areas with plenty

546 of emission sources and relatively large emission density, NO was found to account
547 for large fraction of NO_x in the ambient atmosphere (Zhou et al., 2008). As the
548 dominating component of primary NO_x directly from emission sources, NO is more
549 difficult to be oxidized to NO₂ in urban than in rural or remote regions, attributed to
550 less resident time for chemistry conversion in urban. Given the 9 state-operated
551 monitoring sites are all located in urban/suburban Nanjing, the observed NO₂
552 concentrations were less sensitive or correlated to the NO_x emissions, compared to
553 the case of SO₂, and it leads to the smaller slope of ambient NO₂ levels to NO_x
554 emissions and the lower correlation coefficient in Figure 7(a).

555 As shown in Figure 7(b), the correlation coefficient for CO is calculated at 0.61,
556 and it reaches 0.86 when the observation of the Caochangmen site is excluded, where
557 extremely high emissions are calculated but low ambient levels were observed (to be
558 further discussed in Section 4.4). Even with a longer lifetime (weeks to months) than
559 SO₂ or NO_x, CO in the atmosphere over Nanjing results mainly from primary
560 emissions from incomplete combustion, implying reasonable agreement between
561 emissions and concentrations. However, emissions from small coal combustion
562 sources still cannot be fully tracked or precisely quantified, and this evidence is thus
563 tentative.

564 **4.3 Evaluation of emissions against top-down constraints from observations**

565 For certain pairs of pollutants that come from common sources and thus share
566 emission characteristics, or weakly reactive species that are relatively stable in the
567 atmosphere, correlations of ambient concentrations can provide useful “top-down”
568 constraints on “bottom-up” estimates of primary emissions. In this work, the
569 correlations of three pairs of species in the atmosphere—BC and CO, OC and EC, and
570 CO₂ and CO—are analyzed based on daily mean concentrations from ground
571 observations in 2012. Combining the mass or molar ratios of emissions for
572 corresponding species allows further evaluation of the city-scale inventory.

573 **BC and CO**

574 BC and CO both result from incomplete combustion of solid fuels and certain
575 industrial processes such as coking. With relatively long atmospheric lifetime, CO is
576 usually recognized as a tracer of pollution transport. Combined with BC levels, it can
577 also be used to test emission inventories of the two species (most at regional or
578 national scale), which is particularly useful for BC given its relatively large emission
579 uncertainties (Kondo et al., 2011; Wang et al., 2011; Zhao et al., 2011; 2012a). We
580 follow the method presented in Wang et al. (2011) but focus on evaluating the
581 city-level, top-down emission ratio of BC to CO based on observations at
582 Caochangmen in Nanjing (point A in Figure S1(d) in the supplement). We choose this
583 site for emission evaluation for two main reasons. First, it is an urban site and thus
584 assumed to be more representative for the city emissions, compared to suburban/rural
585 sites that are more influenced by emissions from broader areas. Second,
586 Caochangmen is the biggest and the most comprehensive state-operated station in the
587 city. Among all the 9 state-operated sites in Nanjing, it is one and only station that
588 conducts observation not only for the six criterion pollutants (i.e., SO₂, NO₂, CO, O₃,
589 PM₁₀, and PM_{2.5}) but also for certain species including BC used here and CO₂ used
590 later. Daily means of BC and CO concentrations are calculated based on the hourly
591 data from continuous observations using Magee AE 31 and Ecotech EC9830B
592 analyzers, respectively, and the correlation between the two species are then evaluated
593 and used to check the bottom-up emission inventories. Since ambient levels of BC
594 and CO depend not only on emissions but also on atmospheric processes (e.g., wet
595 and dry depositions of BC, chemical reactions of CO with OH, and mixing of both
596 BC and CO) that exert different influences on the two species (Wang et al., 2011), the
597 top-down emission ratio of BC to CO ($BC/CO|_{E,top-down}$) is calculated from the
598 observed BC/CO ($dBC/dCO|_t$) by excluding the influence of the above-mentioned
599 atmospheric processes, as indicated in Equation (2):

$$dBC/dCO|_t = BC/CO|_{E,top-down} F_{dry} F_{chem} F_{mixing} F_{wet} \quad (2)$$

601 F_{wet} indicates the wet deposition screening. Based on precipitation data from the
 602 Weather Underground weather site (<http://www.wunderground.com/history/>), the data
 603 in precipitation days were excluded to eliminate the effects of wet deposition. F_{dry} ,
 604 F_{chem} and F_{mixing} indicate the screening of dry deposition of BC, chemical reactions of
 605 CO with OH, and mixing of both BC and CO, respectively. Following the methods by
 606 Wang et al. (2011), F_{mixing} is set at 1 and $F_{chem+dry}$ is calculated at 0.88 based on the
 607 lifetime of BC and CO in the atmosphere.

608 As shown in Figure 8, the annual ratio of BC to CO from observations is
 609 estimated at $0.0071 \mu\text{gm}^{-3} \text{ppbv}^{-1}$ by linear regression with the reduced major axis
 610 method (Hirsch and Gilroy, 1984), and it is $0.0073 \mu\text{gm}^{-3} \text{ppbv}^{-1}$ if the days of wet
 611 deposition are excluded. Once influence from other atmospheric processes are further
 612 eliminated, $BC/CO|_{E,top-down}$ rises to 0.0084, lower than the ratio from the city-scale
 613 bottom-up emission inventory at 0.0097, or that from the MEIC national inventory at
 614 0.0095. It should be noted that the downtown observation site is influenced heavily by
 615 local transportation, particularly gasoline vehicles that have relatively high CO but
 616 low BC emissions. Therefore, the top-down ratio of BC to CO observed at the site is
 617 expected to be somewhat lower than that of emissions over the entire city. The
 618 comparison of top-down and bottom-up results is thus roughly consistent with the
 619 city-scale emission inventory, although possible overestimation of BC, or
 620 underestimation of CO emissions are indicated.

621 Aside from mean annual levels, comparisons are also conducted for seasonal BC
 622 to CO ratios, as summarized in Table 2. The highest $BC/CO|_{E,top-down}$ is found in
 623 summer while the lowest is in winter. Such seasonal variation, however, is not
 624 indicated in the current bottom-up emission inventory, for the following possible
 625 reasons. First, as described in Section 2, the temporal distribution of emissions is
 626 based on investigation of large and medium enterprises. However, the species of
 627 concern here, especially BC, come largely from small industrial and residential

628 sources, for which temporal information is still lacking. For transportation, the
629 increased cold start of vehicles in winter also leads to higher CO emissions that
630 cannot be fully captured by COPERT (Cai and Xie, 2010; Xiao et al., 2004) and could
631 then lead to an overestimate of BC/CO from the bottom-up method. Second, although
632 Caochangmen is located in urban Nanjing, it would inevitably be influenced by
633 emissions from wider regions outside the city that are not quantified in the city-scale
634 inventory. For example, biomass burning, which has a higher BC to CO ratio than
635 exists in the ambient atmosphere, occurs more frequently in less-developed areas such
636 as northern Jiangsu and Anhui provinces than in Nanjing. According to MODIS, 79%
637 of agricultural fire points in Jiangsu 2012 were found in summer, elevating the
638 ambient BC/CO in this season. Third, uncertainty exists about the estimation of F_{chem} .
639 In winter, the lowest OH densities in the boundary layer resulting from the weakest
640 radiation lead to the smallest CO sink, and the opposite is true in summer (Seiler et al.,
641 1984; Huang et al., 2013). The elevated F_{chem} in summer should thus lead to reduced
642 $BC/CO|_{E,top-down}$. In this work, however, the seasonal difference in F_{chem} cannot be
643 precisely quantified precisely based on existing studies, and the same F_{chem} has to be
644 used for all seasons, leading to possible overestimation of $BC/CO|_{E,top-down}$ for summer
645 and underestimation for winter.

646 **OC and EC**

647 EC and primary OC result from incomplete combustion, and the ratio of OC to
648 EC concentrations is used to evaluate carbonaceous aerosol emissions and the
649 formation of secondary organic aerosols (SOA) through the EC-tracer method (Castro
650 et al., 1999). From 2011 to 2013, ambient EC and OC in downwind Nanjing were
651 collected using quartz filters and analyzed with a DRI Model 2001 Thermal/Optical
652 Carbon Analyzer by season (Li et al., 2015). The ratios of primary OC to EC,
653 $(OC/EC)_{pri}$, were then determined based on the observation. Attributed to limited

654 sampling size, Li et al. (2015) chose the lowest daily OC/EC during the sampling
655 period for each season as the seasonal $(OC/EC)_{pri}$, to exclude the effects of SOA (see
656 Figure S7 for the observed time series of ambient OC to EC ratio). The $(OC/EC)_{pri}$
657 were then estimated at 1.70, 1.27, 1.53, and 1.85 for spring, summer, autumn, and
658 winter, respectively, with an annual average of 1.59. In this work, we adopt those
659 results and assume that they serve as a top-down constraint of carbonaceous aerosol
660 emissions. From the bottom-up estimates, the emission ratios of OC to BC in our
661 city-scale emission inventory and MEIC are respectively 1.38 (for 2012) and 1.24 (for
662 2010, the most recent year for which MEIC emissions are available), both of which
663 are lower than the top-down $(OC/EC)_{pri}$ from observations. With few emission sources
664 nearby, the observation site is thought to be less influenced by local sources (e.g.,
665 on-road transportation that has a relatively low emission OC to BC ratio) than the
666 regional transport of pollutants (Li et al., 2015). Thus some sources with high OC to
667 BC ratios that are uncommon in Nanjing but more dispersed outside the city
668 contribute significantly to the observed concentrations at the site. Those sources
669 include residential fossil and biomass combustion and biomass open burning. The OC
670 to BC emission ratios of Jiangsu and Anhui provinces surrounding Nanjing are
671 estimated respectively at 1.91 and 2.13 (Zhao et al., 2013), clearly larger than the
672 local emission ratio of Nanjing. Moreover, the carbonaceous aerosol sampling
673 procedure used by Li et al. (2015) would lead to positive artifacts of OC measurement
674 and elevated OC to EC, since usage of quartz filters adsorbs some semivolatile
675 organic compounds (SVOC) in the ambient atmosphere (Cheng et al., 2009). The
676 system bias of OC quantification from this sampling approach was estimated to reach
677 50% in US (Chow et al., 2010; McDonald et al., 2015), and it was found to be 100%
678 in certain city in China (Hu et al., 2008). However, the bias can vary largely between
679 cities, and it has not been well quantified for Nanjing, making the evaluation of
680 emission inventories of carbonaceous aerosols less conclusive. Finally, uncertainty
681 also exists in the $(OC/EC)_{pri}$ determination by Li et al. (2015), as the sample size from

682 off-line measurements was small. To better evaluate the city-level OC and BC
683 emissions, therefore, more observational research with improved (e.g., long-term and
684 continuous) measurements is strongly recommended at sites where local sources
685 dominate, and the artifacts of the measurement should be sufficiently analyzed.

686 **CO₂ and CO**

687 CO₂ is a well-known greenhouse gas, with the main anthropogenic sources fossil
688 energy combustion and industrial processes. The ratios of CO₂ to CO emissions differ
689 between source types, reflecting varying combustion efficiencies. The observed ratio
690 of CO₂ to CO levels in the atmosphere can thus be used as an indicator of energy
691 efficiency, as well as a top-down test of emissions estimated bottom-up. The annual
692 molar ratios of CO₂ to CO emissions in Nanjing are calculated at 65.7, 73.6, and 76.1
693 for 2010, 2011, and 2012, respectively, significantly higher than that in Beijing in
694 2008 (32.8, Zhao et al., 2012a). They are also higher than the mixing ratios observed
695 in rural Beijing in 2008 (26.8, Y. Wang et al., 2010) or at Hatetuma Island (HAT), a
696 remote site located off the coast of continental East Asia and influenced by air masses
697 transported from East Asian countries from late fall to early spring (34.5, Tohjima et
698 al., 2014). Given the large discrepancy, data from measurements in urban Nanjing
699 (Caochangmen, Point A in Figure S1 (d)) are further analyzed to test the emissions.
700 Daily mean concentrations of CO₂ and CO are derived from hourly observations using
701 Thermo 410i and Ecotech EC9830B analyzers, respectively, for all of 2012. To
702 exclude the effects of biogenic emissions that prevail in warm seasons, data for the
703 winter months (January, February, and December) are used. The prevailing wind
704 directions over Nanjing in winter are east and northeast, and large point sources,
705 accounting for 64% of the city's CO₂ emissions, are located to the east and northeast
706 of Caochengmen, supporting use of the observational data for the current purpose.

707 The average observed concentrations of CO₂ and CO in winter were 421 ppmv

708 and 608 ppbv, respectively. Based on the cumulative probability distribution of daily
709 CO concentrations (as shown in Figure S8 in the supplement), the whole dataset is
710 divided into three subsets: (1) below the 30th percentile (with average CO and CO₂
711 concentrations at 350 ppbv and 410 ppmv, respectively), (2) between the 30th and 95th
712 percentile (677 ppbv for CO and 424 ppmv for CO₂), and (3) above the 95th percentile
713 (above 1200 ppbv for CO and 448ppmv for CO₂). We consider that subset (1)
714 represents air masses from relatively clean areas outside Nanjing, and subset (2) a
715 well-mixed blend of sources of CO₂ and CO over Nanjing. Subset (3) is assumed to
716 indicate extremely serious regional pollution episodes, in which pollutants were
717 trapped in a shallow inversion layer (Y. Wang et al., 2010). Subset (2) is believed to
718 best reflect the typical effects of local emissions and is used for bottom-up emission
719 comparisons.

720 Illustrated in Figure 9 is the CO₂-CO correlation estimated with the reduced
721 major axis method based on surface observations and the CO₂ to CO ratios from
722 bottom-up emission inventories for Nanjing. Our estimate of the CO₂ to CO ratio
723 (76.1) is closer to observations (86.9) than MEIC (52.8), implying improvement in the
724 current city-scale inventory. The observed CO₂ to CO ratio, however, should
725 theoretically be lower than that from emissions for the following three reasons. First,
726 compared to CO, the observation of CO₂ at an urban site would be more influenced by
727 sources within a broader region than the city, as CO₂ has a longer lifetime in the
728 atmosphere. Thus it is not fully representative of the very centralized and large CO₂
729 emissions inside the city, particularly those from large point sources (e.g., 17 power
730 plants and 2 iron & steel plants, which are estimated to account for 78% of total CO₂
731 emissions in Nanjing), and the CO₂ to CO ratio from observations should be reduced.
732 Second, the current emission inventory includes only the primary CO emissions while
733 there may be a fair amount of secondary CO from the oxidation of NMVOC. Duncan
734 et al. (2007) estimated that CO from NMVOC oxidation equaled nearly 50% of global
735 primary CO emissions. Given the intensive refineries and chemical plants and thereby

736 elevated NMVOC emissions in Nanjing, considerable secondary CO from NMVOC
737 oxidation can be expected, leading to a lower ratio of CO₂ to CO from observations
738 than that from primary emissions. To partly exclude the effects of NMVOC oxidation,
739 we recalculated the ambient CO₂ to CO ratio at 91.9 based on the hourly
740 concentration data from 6pm to 6am for subset (2), when the temperature was lower
741 and photochemistry was slower. The value is larger than 86.9 based on daily average
742 concentration data, attributed mainly to less formation of secondary CO. Third, as
743 discussed previously, the Caochangmen site is influenced heavily by local
744 transportation that exhibits a lower CO₂ to CO emission ratio than industry. We
745 believe that the higher CO₂ to CO ratio from observations than bottom-up emissions
746 reflect the uncertainties from both approaches. On one hand, emissions from certain
747 species and sectors need to be further improved, e.g., CO from vehicles might be
748 underestimated by the current work, since relatively poor management of vehicle
749 emissions in China cannot be tracked by COPERT. On the other hand, we speculate
750 that possible bias also exists in observations, with more discussion to follow in
751 Section 4.4.

752 The larger molar ratios of CO₂ to CO in Nanjing than in Beijing, both from
753 observations and emissions, are attributed mainly to the structure of emission sources.
754 Nanjing is a city with intensive heavy industry, and over 90% of coal was consumed
755 by power plants, iron & steel plants, cement plants, and large chemical enterprises
756 with relatively high energy efficiencies, leading to elevated ratios of CO₂ to CO in
757 emissions and thereby concentrations. Transportation, particularly gasoline vehicles,
758 is additionally a significant emission source of CO compared to CO₂, and plays
759 important roles in molar ratios of CO₂ to CO. For instance, Y. Wang et al. (2010)
760 found significantly increased ambient CO₂/CO in September 2008 (46.4 ppmv/ppmv)
761 compared to September 2005-2007 (23–29 ppmv/ppmv) in Beijing, resulting mainly
762 from the temporary ban of vehicles for the Beijing Olympic Games and thereby
763 decreased CO emissions. In 2012 the vehicle population in Beijing was 3.5 times that

764 of Nanjing (NHNBS, 2013). Transportation was estimated to contribute 29%-37% of
765 anthropogenic CO emissions in Beijing from various studies (MEIC; Zhao et al.,
766 2013), but the value is much smaller in Nanjing (10%), elevating the molar ratio of
767 CO₂ to CO in the city.

768 **4.4 Evaluation of local ground observations based on the city-scale emission** 769 **inventory**

770 While ground observations can be used as top-down constraints on emissions, we
771 suggest that a high-resolution emission inventory can also be used to evaluate
772 observational data. Although detailed local information demonstrably improves
773 emission estimation, inconsistencies still exist between the city-scale emission
774 inventory and ground observations of CO at Caochangmen. These inconsistencies
775 include: 1) the significant increase in correlation coefficients between CO emissions
776 and ambient concentrations at state-operated monitoring sites when the data at
777 Caochangmen are excluded (from 0.61 to 0.86), as described in Section 4.2 and
778 Figure 7(b); and 2) the higher CO₂/CO from observations at Caochangmen than that
779 from city-scale emissions, which contradicts expectations based on atmospheric
780 chemistry principles, as described in Section 4.3 and shown in Figure 9. This suggests
781 the possibility of instrumental or other error reflected in the relatively low CO
782 concentrations observed at Caochangmen in 2012. Thus we conduct a comparison of
783 CO concentrations between Caochangmen and another state-operated site, Shanxilu,
784 for 2012 and 2014. Similar to Caochangmen, Shanxilu is also an urban site, 3.5 km
785 from Caochangmen. Frequency histograms of hourly CO concentrations at the two
786 sites for 2012 and 2014 are shown in Figure S9. It can be seen that CO levels at
787 Caochangmen were significantly lower than those at Shanxilu in 2012 (Figure S9(a))
788 but the CO levels were quite similar at the two sites in 2014 (Figure S9(b)). Moreover,
789 a clear difference (~30%) in CO levels between 2012 and 2014 were found at
790 Caochangmen (Figure S9(c)) but not at Shanxilu (Figure S9(d)). Given the very close

791 distance and similar characteristics of the two sites, we tentatively assume that there
792 should not be a significant difference in CO levels between them. Thus we conduct a
793 sensitivity test by increasing the CO concentrations at Caochangmen by 30% in 2012,
794 and repeat the assessment of the city-scale emission inventory with the revised CO
795 dataset. The correlation coefficient between CO emissions and ambient concentrations
796 at the 9 state-operated sites would be increased substantially, from 0.62 to 0.83. The
797 ratio of CO₂ to CO in winter from the revised observational data would decrease from
798 to 86.9 to 66.8, close to and lower than the ratio from the bottom-up city-scale
799 inventory (76.1), consistent with the expectation that observed CO₂/CO should be
800 smaller than emissions. **If only hourly data from 6pm to 6am are applied to mitigate**
801 **the effects of secondary CO formation from NMVOC oxidation, an even closer**
802 **ambient CO₂ to CO ratio to emission inventory result would be estimated at 70.7.**
803 Such data revision is clearly speculative, but encourages further analysis when
804 observational data for a longer period become available at both sites. The city-scale
805 emission inventory may thus provide a basis to raise questions about the quality of
806 local ground observations, which should not be taken for granted.

807 **4.5 Comparison between city and national inventories for certain sources**

808 To further explore the effects of methods and data employed in emission
809 estimation at city and national levels, we conduct comparisons of emission levels and
810 spatial distributions between the current inventory and MEIC for given pollutants
811 from typical sources, including SO₂ from power generation, NO_x from transportation,
812 and PM_{2.5} from industry, for 2010 in Nanjing. Our estimates are reallocated to a
813 resolution of 5 × 5 km, the same as MEIC, so that spatial correlations between the two
814 inventories can be quantified.

815 As shown in Figure 10(a), relatively good correlation in the spatial distributions
816 of SO₂ emissions from power generation is found for the two inventories, with the R
817 estimated at 0.74. The result indicates consistency between the emission estimates of

818 the two studies for large point sources, as might be expected given their shared
819 reliance on relatively transparent, publicly available information on power plants
820 nationwide. Lacking detailed field investigation of individual sources, however,
821 national inventory studies have to rely on standard information for which routine
822 updates or revisions are not guaranteed, and the latest changes in individual plants,
823 including the closure of small power units or relocation of some power plants, cannot
824 be tracked fully or on a timely basis. This is reflected by a number of data points in
825 Figure 10(a) with positive emission values on one axis but zero on the other.
826 Regarding the total emission levels, MEIC is 35% lower than our estimate, attributed
827 mainly to the different SO₂ removal efficiencies of FGD applied in the two studies.
828 Based on the field measurement data that were reported by individual plants and
829 verified by the local environmental protection bureau, the average removal efficiency
830 of FGD for power plants in Nanjing in 2010 is estimated at 66%, lower than the
831 values commonly applied by researchers in national emission assessments (e.g., above
832 70%, Zhao et al., 2013). The discrepancy reveals the value of site-specific
833 investigation of key parameters influencing emission estimates, including the
834 SO₂-removal rate of FGD.

835 For NO_x from transportation, the spatial R is calculated at 0.652 between the two
836 estimates, and the value would rise to 0.75 if the two grid cells with the largest
837 emissions in the city-scale inventory were excluded, as shown in Figure 10(b). Similar
838 to the power sector, the general spatial pattern of emissions from transportation for the
839 two inventories is largely consistent. The emissions in MEIC, however, are much
840 more concentrated in downtown urban regions compared to our estimate, resulting
841 from differences in spatial densities of population versus transportation flows based
842 on road networks. The former is commonly applied in spatial distribution of national
843 emission inventories while the latter, when available through field investigation or
844 real-time recording, are used in city-scale ones like ours. The total NO_x emissions
845 from transportation estimated by MEIC are 27% lower than those by the city-scale

846 inventory, suggesting introduction of considerable uncertainty when emissions
847 estimated at the national level are downscaled to the city level based on proxies like
848 population or economic activity.

849 In contrast to the above two cases, little correlation is found between the two
850 estimates in the spatial distribution of PM_{2.5} emissions from industrial sources (Figure
851 10(c)). Shown in the maps of Figure 10(c) are not only the PM_{2.5} emissions but also
852 the locations of the 20 largest emitting industrial enterprises. A clear discrepancy is
853 observed between the distribution of those sources and emissions from MEIC, while
854 much stronger consistency is found in the current work. Without sufficient
855 information on individual sources, inventories developed at the national level tend to
856 allocate large fractions of emissions into urban regions with relatively high densities
857 of population and/or economic activity, assuming good spatial correlation between
858 emissions and those proxies. Such correlation, however, likely weakens as pollution
859 control in urban regions is implemented because it includes significant relocation of
860 emission sources to suburban or rural areas (a primary element of urban pollution
861 control policy in China). The total PM_{2.5} emissions from industrial sources estimated
862 by MEIC are 50% lower than our estimate, moreover, because: 1) a national emission
863 inventory based on the sector-average levels of controls and emission factors cannot
864 capture atypical, extremely large sources (super emitters); and 2) coal consumption
865 from the official statistics used by MEIC is much lower than the aggregate of
866 individual sources evaluated in the field survey (3.0 versus 5.0 Mt for Nanjing, 2010).
867 Comparisons and correlation analyses between inventories developed at different
868 spatial scales, therefore, show the advantages of thorough investigation of individual
869 emission sources, particularly for cities with many large industrial enterprises like
870 Nanjing.

871 **4.6 Uncertainty assessment of city-scale emission inventory**

872 **The uncertainties of China's national emission inventories have been estimated**

873 using Monte-Carlo simulation, as described in our previous studies (Zhao et al., 2011;
874 2013). Targeting city scale, however, the uncertainty of current inventory for Nanjing
875 is more difficult to be systematically quantified, as many emission factors are city- or
876 device-dependent and their probability distributions could not be fully defined without
877 sufficient field measurement records. In general, the uncertainties of emissions from
878 power and industry sectors are expected to be reduced compared to the national level,
879 as the “key sources” in the city contribute significantly to the fuel consumption and
880 production of those sectors. As described in Section 2, the activity levels and emission
881 factors for those key sources were compiled plant by plant or obtained through onsite
882 survey, leading to relatively small biases in emission estimation. For most area
883 sources, the emission factors used in this work were hardly improved compared to
884 previous national/regional inventories, thus large uncertainties remain in those sources.
885 Given the tiny fractions of emissions by those sources in Nanjing, however, their
886 contribution on the uncertainty of total city emissions is expected to be limited. Very
887 high uncertainty is expected for fugitive dusts that are generally not included in
888 national/regional inventory, as little local information is available to improve the
889 emission factors. Given the large shares of fugitive dusts to primary PM emissions
890 (Figure S2), field measurements on construction sites and road dusts are suggested for
891 better emission estimation in Nanjing.

892 We try further to identify some common sources of uncertainty in the
893 development of city-level emission inventories, including: 1) the inconsistencies of
894 activity-level data from various sources; and 2) the downscaling of activity data or
895 emissions due to lack of city-level information.

896 There has been continuing concern about the accuracy and reliability of China’s
897 energy statistics for more than a decade (Sinton, 2001). Statistics from various sources
898 report divergent energy consumption levels for the country, and the choice of
899 activity-level data for emission inventories continues to be debated. For example,
900 China’s total energy use from national statistics has been inconsistent with that

901 aggregated from provincial statistics, driving considerable differences in national
902 emission estimates (Akimoto et al., 2006; Guan et al., 2012; Zhao et al., 2013). While
903 Akimoto et al. (2006) concluded that an emission inventory based on
904 province-by-province statistics were in better agreement with satellite observations,
905 Guan et al. (2012) indicated that over-reporting in provincial energy statistics could be
906 a factor. At the city level, however, there are far fewer evaluations of the accuracy of
907 energy statistics. We find a clear discrepancy in energy consumption data in statistical
908 sources for Nanjing: the total coal consumption in 2010 was reported at 27.9 Mt in the
909 Nanjing Almanac (NJCLCC, 2011), while the value from the Environmental Statistics
910 was 14% higher, 31.9 Mt. The disparity results mainly from differences in data
911 collection for small emission sources (enterprises). While data reporting systems and
912 resulting data quality have been gradually improved for large- and medium-scale
913 enterprises, many small-scale ones still do not maintain well-documented records on
914 energy consumption, and the energy use of those enterprises is poorly captured by the
915 city almanac (personal communications with officials from Nanjing Municipal
916 Commission of Economy and Information Technology, 2014). Aimed at pollution
917 control, the environmental statistical system obtains and verifies energy data for each
918 enterprise through field surveys, and we thus believe that these energy consumption
919 data are more complete and reliable for emission inventory development. The
920 uncertainty from such varied statistical sources could be reduced as retirement of
921 small boilers and/or closure of small enterprises increases. Although the Nanjing
922 Almanac stopped reporting coal consumption for the city after 2010, the
923 Environmental Statistics indicates that the combined share of coal consumption by
924 large- and medium-sized sources increased from 84% in 2010 to 91% in 2012,
925 attributed to closure of small enterprises reporting highly uncertain energy data during
926 the period.

927 Besides problems in the energy data, uncertainty in the city-scale emission
928 inventory can also result from lack of information on certain industrial sectors in the

929 city statistics. If field surveys of individual sources cannot be conducted due to labor
930 or time constraints, emissions have to be estimated by downscaling national or
931 provincial estimates. To evaluate the resulting uncertainty, air pollutant emissions
932 from non-ferrous metal smelting and the production of brick and lime in Nanjing 2012
933 are recalculated by the downscaling provincial estimates method (method B). In this
934 method, emissions in Jiangsu province are first calculated based on the provincial
935 statistics and provincial average levels of emission control. Emissions in Nanjing are
936 then obtained according to Nanjing's fraction of certain proxy (industrial GDP in this
937 case) out of the whole province. The results are compared with those based on
938 detailed source investigations (method A). Shown in Table 3 are the product output
939 (activity level) and pollutant emissions estimated by methods A and B. The activity
940 levels estimated from provincial-level information are much higher than the actual
941 industrial production aggregated from individual plants, suggesting downscaling
942 produces emission overestimates. For example, gaseous pollutant emissions
943 calculated with method B are 2, 10, and 30 times larger than those produced by
944 method A for brick, lime, and copper production, respectively. For PM emissions, the
945 discrepancies in emissions between the two methods are smaller, attributed partly to
946 the compensating effects of divergent removal efficiencies of dust collectors applied
947 in the two methods, obtained either from plant-by-plant surveys (method A) or from
948 national or provincial average levels (method B). The differences are believed to
949 reflect disparities in the considerable fractions of total emissions from OIN (i.e.,
950 industrial sources excluding iron & steel, cement, and chemical plants, for which
951 information is relatively clear, as defined in Section 2.1), specifically 6%, 22%, 15%,
952 and 24% of SO₂, NO_x, PM_{2.5}, and CO for lime production, as shown in Table 3. The
953 results suggest relatively large uncertainties in city-level emission estimates lacking
954 sufficient individual source information. In this case, moreover, the overestimates in
955 Nanjing's emissions from downscaling provincial emissions would inevitably lead to
956 underestimates for other cities within the province, weakening understanding of

957 emission sources and the quantitative basis of regional control policies.

958

959

5 POLICY IMPLICATIONS

960 **5.1 The effects of pollution control policies on emission abatement and air quality**

961 Substantial efforts have been undertaken in specific Chinese sectors to achieve
962 national targets in both energy conservation and emission reduction (Zhao et al.,
963 2013). Under the air pollution control measures, clear benefits in emission abatement,
964 particularly in the power and transportation sectors, are found for Nanjing from 2010
965 to 2012, a relatively short period. In the power sector, electricity generation increased
966 by 58% during 2010-2012 while that specifically from coal-fired plants grew by 47%,
967 reflecting the switch of coal to gas combustion and other diversification of power
968 generation in the city. Meanwhile, coal consumption of the power sector increased by
969 only 25%, much slower than the resulting electricity generation, reflecting improved
970 energy efficiency due to replacement of small and old power units with larger and
971 more energy-efficient ones. As shown in Figure S10(a) in the supplement, the capacity
972 share of large units (above 300 MW) increased from 72% in 2010 to 78% in 2012
973 while that of small ones (below 100 MW) decreased from 20% to 16%. The
974 penetration of large units raised as well the use of APCD for SO₂, NO_x, and PM,
975 leading to significant reduction of emission factors by 30%, 23%, and 22%,
976 respectively. The decrease in emission factors can also be seen for vehicles. With
977 implementation of staged emission standards for new vehicles from 2010 to 2012, the
978 emission factors of SO₂, NO_x, CO, and VOCs are estimated to have declined by 66%,
979 33%, 34%, and 37% for gasoline vehicles (Figure S10(b)), those of NO_x, CO, and
980 VOCs by 12%, 13%, and 24% for diesel vehicles (Figure S10(c)), and those of CO
981 and VOCs by 25% and 34% for motorcycles (Figure S10(d)), respectively. The SO₂,
982 CO, and VOCs emissions from on-road transportation decreased by 39%, 11%, and

983 27%, respectively, while the vehicle population increased by 27% in the city over the
984 three years.

985 The benefits of emission control on air quality can be partly confirmed by
986 comparisons of changes in emissions and ambient concentrations. During August
987 16-24, 2013 when the 2nd Asian Youth Games (AYG) were held in Nanjing, a series of
988 extra emission controls measures were undertaken by the government to improve air
989 quality for the Games. Those measures included increasing use of low-sulfur coal at
990 power plants, closing small factories with relatively large pollutant emissions,
991 stopping construction in some regions, and restricting traffic. Taking these extra
992 measures into account, the emissions of SO₂, NO_x, PM_{2.5}, PM₁₀, and CO over August
993 16-24, 2013 are estimated to have declined 23%, 31%, 21%, 14%, and 33%,
994 respectively, compared to those in the same period in 2012, based on the monthly
995 distributions described in Section 3.2 (see Table S5 in the supplement).
996 Correspondingly, the daily average concentrations for those pollutants in Nanjing
997 during the AYG period were found to decline by 22%, 27%, 10%, 5%, and 22%,
998 respectively, compared to the same period in 2012 (Yu et al., 2014). Although changes
999 in other factors including meteorological conditions also influenced air quality, the
1000 consistency between the reduced emissions and concentrations suggests that local
1001 emission abatement played a primary role in the air quality improvement.

1002 **5.2 Effects of super emitters and small sources on emission levels and spatial** 1003 **distributions**

1004 For cities with intensive, heavily polluting industries like Nanjing, large point
1005 sources with significant energy consumption and/or industrial production are
1006 estimated to dominate the levels and spatial distribution of emissions of the city. As
1007 shown in Figure 3, the areas with high emission densities in Nanjing are in good
1008 agreement with geographical locations of point sources for all pollutants. The ten
1009 largest point sources of SO₂ emissions are estimated to account for 54% of total

1010 emissions in the city (Figure 2(a)), and the analogous number for NO_x is 43% (Figure
1011 2(b)). For PM_{2.5}, as shown in Figure 2(c), the ten largest sources are estimated to be
1012 responsible for 75% of total primary emissions in Nanjing (excluding construction
1013 and road dust). In particular, extremely high emissions are found for iron & steel
1014 plants, resulting mainly from the high production of steel and reliance on wet
1015 scrubbers with relatively low removal efficiencies (annual average of 85%) in the
1016 exhaust streams of basic oxygen furnaces. Similarly, the ten largest refineries and
1017 chemical plants shown in Figure 2(d) are responsible for 52% of VOC emissions in
1018 Nanjing. The dominant roles of these big sources on emission levels and spatial
1019 distributions indicate that careful investigation and analysis of source-specific
1020 parameters relevant to emissions from these super emitters (e.g., removal efficiency of
1021 APCDs) are particularly crucial to the reliability of city-scale emission inventories.

1022 Although large point sources dominate emissions at the city level, the
1023 contributions from scattered small sources cannot be overlooked. As shown in Figure
1024 3, the fractions of air pollutant emissions from power, cement, iron & steel, and
1025 chemical plants to the city's total emissions are estimated to range from 38% to 88%,
1026 significantly lower than that of coal consumption (96%). Despite the tiny share of coal
1027 use, decentralized small coal combustion sources have a relatively high proportion of
1028 emissions, resulting from poorer emission control technologies and management than
1029 big enterprises. Regarding emission abatement and air quality improvement, it is
1030 imperative to expand pollution control from large sources to small- and medium-sized
1031 enterprises, as the potential for further reductions from the major sources are
1032 diminishing due to near-saturation of APCDs. As for improvement of emission
1033 inventories, more varied and uncertain emission factors for small boilers and kilns
1034 result from much greater diversities of manufacturing technologies. This necessitates
1035 more field measurements in the future to inform the application of emission factors in
1036 inventories and to better understand the emission characteristics of small sources.

1037

6 CONCLUSION

1038

1039 With updated methods and substantial new data on local emission sources, a
1040 city-scale emission inventory of air pollutants and CO₂ is developed for Nanjing for
1041 three years, 2010-2012. Through plant-by-plant onsite surveys, emission factors,
1042 spatial and temporal emission distributions, and estimates of total emissions for major
1043 sources (power, cement, iron & steel, and refineries and chemical plants) are
1044 especially improved. Emissions in the city are dominated by large point sources, or
1045 super emitters. Despite large increases in energy consumption and industrial
1046 production, the emissions of most concerned pollutants were largely stable during the
1047 period, particularly SO₂ and NO_x, attributed to increased use and air pollutant
1048 removal rates of APCDs under national policies of air pollution control. The current
1049 estimates are consistent with the inter-annual variability of NO₂ VCD observed from
1050 OMI. The improvement of emission estimates by city-scale assessment is further
1051 indicated by analyses of spatial correlations with observations by satellite (for NO_x)
1052 and ground stations (for SO₂, NO_x, and CO), as well as by top-down constraints
1053 (BC/CO, OC/EC, and CO₂/CO) provided by ground-based observations. Analyses of
1054 bottom-up emission inventories, moreover, can identify possible errors in
1055 observational datasets, encouraging further investigation.

1056 Limitations remain in the current work. First, some available and potentially
1057 valuable information cannot yet be fully exploited to improve emission estimates.
1058 CEMS data help to determine the time distribution of emissions, for example, but are
1059 currently less useful for estimating absolute emission levels, due to incompleteness
1060 and systematic errors in relevant parameters (e.g., flue gas flow rate). Second, since
1061 emission factors for some sources are still based on provincial or national assessments
1062 due to lack of local information, the uncertainties of the city-scale emission inventory
1063 have not yet been systematically quantified. In particular, the degree of uncertainty in
1064 the city-scale inventory compared to that of national ones remains unknown. Finally,

1065 it is currently difficult to assess emissions of some species believed to have high
1066 emission uncertainty, e.g., VOC and NH₃, due to lack of sufficient instrumental
1067 observations. More field measurements of both emissions and ambient levels of these
1068 species are thus recommended in the future.

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1070

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FIGURE CAPTIONS

Figure 1. (a) The inter-annual variability of Nanjing emissions for 2010-2012 and (b) comparisons in annual emissions with other studies for 2010. The left-hand vertical axis indicates SO₂, NO_x, CO, VOCs, NH₃, PM_{2.5}, PM₁₀, TSP, and CO₂ while the right-hand indicates BC and OC. 2010(A) and 2010(B) refer to the emissions of current estimates with and without fugitive dust, respectively.

Figure 2. Spatial distribution of emissions for Nanjing 2012, with locations of largest point sources indicated. (a) SO₂; (b) NO_x; (c) PM_{2.5} (fugitive dust from construction and road sources excluded) and (d) VOC.

Figure 3. The emission fractions of point sources, area sources, and on-road transportation, and those of key sources of total emissions in Nanjing, 2012

Figure 4. The inter-annual trends in NO₂ vertical column density (VCD) from OMI for selected regions (see Figure S1(a) for reference) and the bottom-up NO_x emissions for 2010-2012. All the data are normalized to 2010 level in Nanjing.

Figure 5. (a) Spatial distribution of city-scale NO_x emissions in this study, (b) summer NO₂ vertical column density (VCD) from OMI, and (c) NO_x emissions from MEIC for Nanjing, 2010. The resolution is 0.125°×0.125°.

Figure 6. Spatial correlation between NO_x emissions from city- and national-scale inventories and NO₂ vertical column density (VCD) from OMI, in Nanjing, 2010 for (a) all grids, (b) step-wise exclusion of grid cells with largest emissions and (c) grid cells without power plant emissions.

Figure 7. Linear regression of emissions and concentrations at the 9 state-operated stations in Nanjing, 2012. (a) SO₂ and NO_x/NO₂; (b) CO.

Figure 8. The correlation of daily BC and CO concentrations at Caochangmen site and the emission ratios of BC to CO from bottom-up inventories for Nanjing, 2012.

Figure 9. The correlation of daily CO₂ and CO concentrations at Caochangmen site and the emission ratios of CO₂ to CO from bottom-up inventories for Nanjing, 2012. The wintertime concentrations with CO between the 30th and 90th percentiles are used for the correlation analysis.

Figure 10. Spatial distribution and linear regression of emissions from city-scale and national inventories (MEIC) for (a) SO₂ from power generation, (b) NO_x from transportation, and (c) PM_{2.5} from industry for Nanjing, 2010.

TABLES

Table 1. The capacity penetrations, average removal efficiencies of APCDs, and flue gas release ratios for key sources in Nanjing.

	CPP-FGD		CPP -SCR/SNCR		CEM-dust collector ^a
	Penetration	SO ₂ removal efficiency	Penetration	NO _x removal efficiency	TSP removal efficiency
2010	92.4%	66.0%	43.7%	17.7%	96.9%
2011	97.0%	78.5%	66.6%	41.8%	97.0%
2012	98.3%	81.2%	67.4%	77.0%	99.6%
	ISP coke oven Gas release ratio ^b	ISP blast furnace Gas release ratio ^b	ISP sintering-FGD SO ₂ removal efficiency	ISP pig iron production-fabric filter TSP removal efficiency	ISP steelmaking- dust collector ^c TSP removal efficiency
2010	0.5%	1.5%	70.0%	98.9%	97.3%
2011	0.5%	1.5%	70.0%	98.9%	96.7%
2012	0.5%	1.5%	70.0%	98.8%	96.7%

^a Including the fabric filter and the electrostatic precipitator.

^b The fraction of flue gas that is not recycled or collected for purification treatment, and is thus directly released to the atmosphere

^c Including the fabric filter and the wet scrubber.

Table 2. The average concentrations of BC and CO and correlation of BC to CO from observations at Caochangmen and the ratios of bottom-up BC to CO emissions by season in Nanjing, 2012.

	Urban observation						Bottom-up inventory	
	Avg. BC ^a (μgm^{-3})	Avg. CO ^a (ppbv)	Avg. BC ^b (μgm^{-3})	Avg. CO ^b (ppbv)	BC/CO ^a ($\mu\text{gm}^{-3} \text{ppbv}^{-1}$)	BC/CO ^b ($\mu\text{gm}^{-3} \text{ppbv}^{-1}$)	$BC/CO _{E,\text{top-down}}$ ^c ($\mu\text{gm}^{-3} \text{ppbv}^{-1}$)	$BC/CO _{E,\text{bottom-up}}$ ($\mu\text{gm}^{-3} \text{ppbv}^{-1}$)
Spring	2.946	661.3	3.009	684.9	0.0070	0.0072	0.0082	0.0101
Summer	2.644	490.3	3.000	491.0	0.0083	0.0085	0.0097	0.0096
Autumn	4.206	619.6	3.822	627.1	0.0081	0.0081	0.0092	0.0095
Winter	3.007	615.0	3.068	637.7	0.0051	0.0060	0.0068	0.0096
Overall	3.156	588.0	3.264	600.5	0.0071	0.0074	0.0084	0.0097

^a All the observation data included.

^b The influence of wet deposition excluded.

^c The influence of wet and dry deposition, chemical reactions with OH radicals, and mixing excluded.

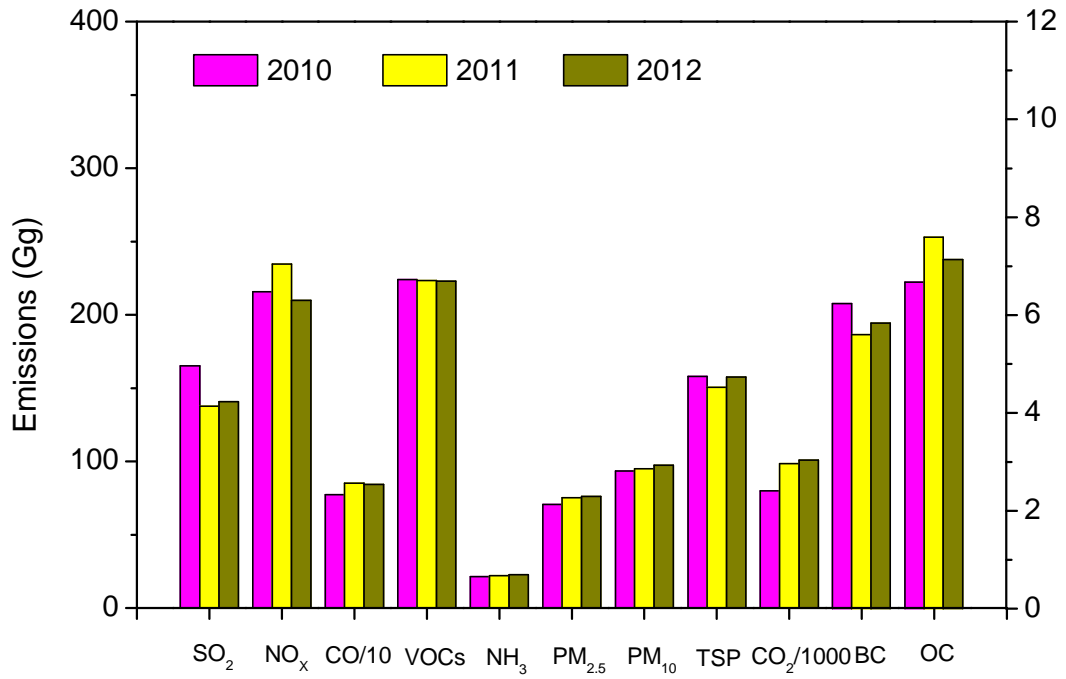
Table 3. Comparisons of emission estimations using method A (plant-by-plant survey) and B (downscaling from provincial levels) for brick, lime, and copper production in Nanjing, 2012.

	Production ¹		SO ₂ emissions		NO _x emissions		PM _{2.5} emissions		CO emissions	
	Method A	Method B	B/A	(B-A)/OIN ²	B/A	(B-A)/OIN	B/A	(B-A)/OIN	B/A	(B-A)/OIN
Brick	14	29			2.0	10%	2.0	19%	2.0	13%
Lime	207	2050	9.9	6%	9.9	22%	3.6	15%	9.9	24%
Copper	1.3	39	31.1	24%			3.6	13%		

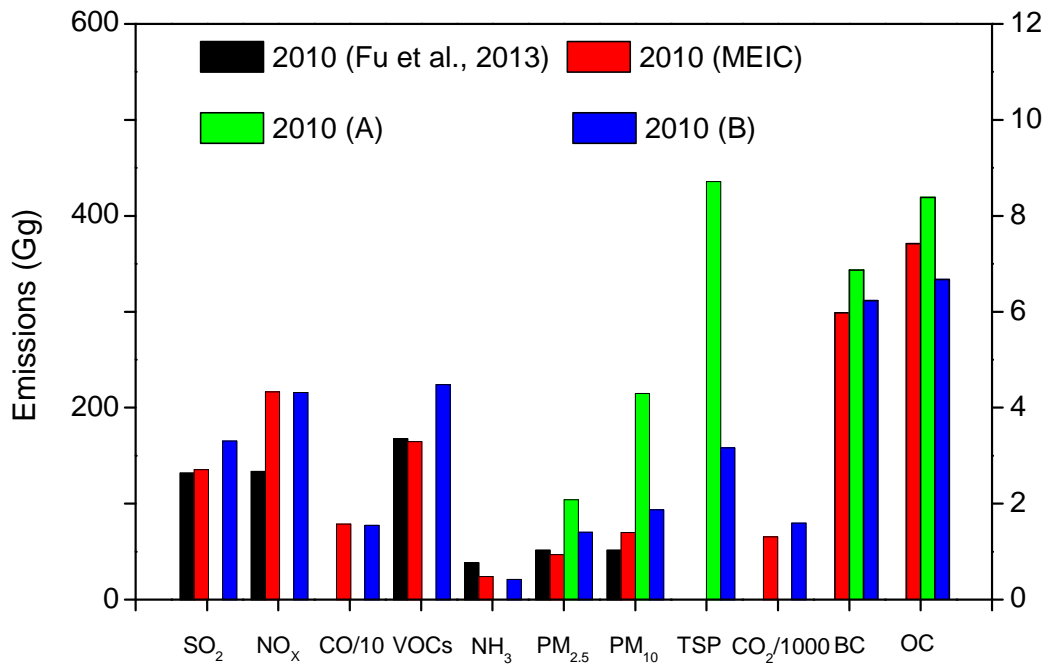
^a The units are 10⁹ bricks, 10³ t-lime and 10³ t-copper, respectively.

^b Recall from Section 2.1 that OIN indicates emissions from other industry (iron & steel, cement production and chemical industry excluded) estimated at city level.

Figure 1

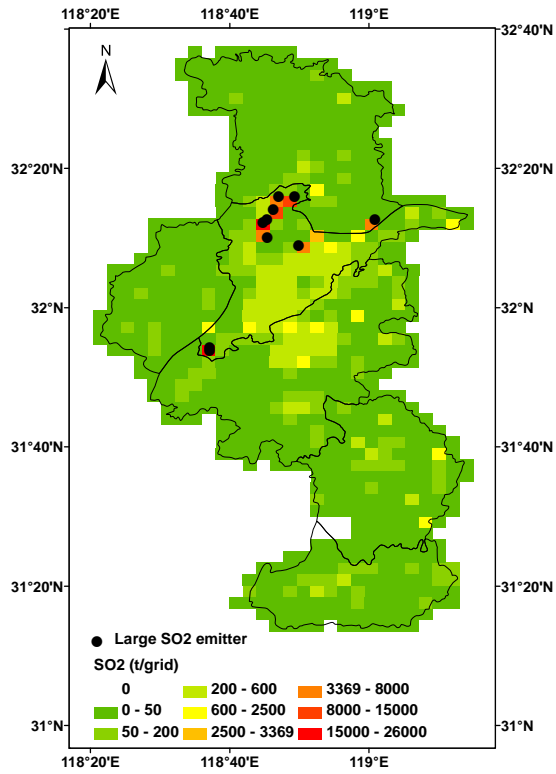


(a)

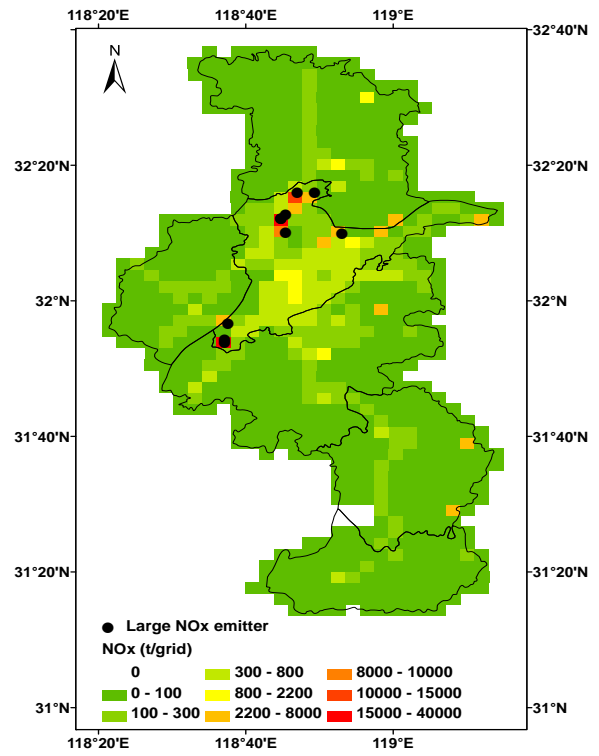


(b)

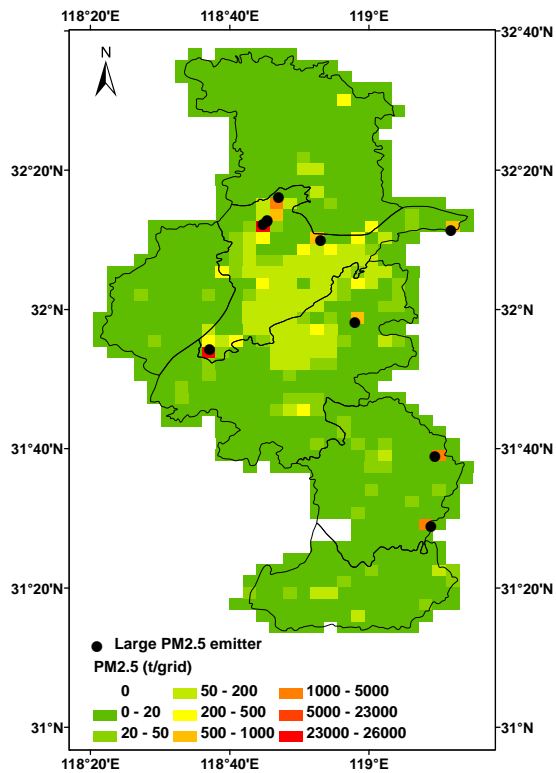
Figure 2



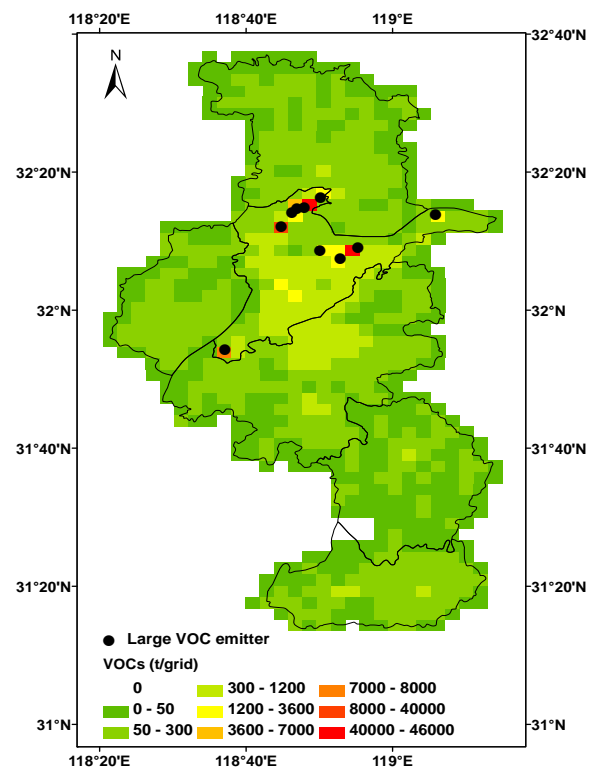
(a) SO₂



(b) NO_x



(c) PM_{2.5}



(d) VOC

Figure 3

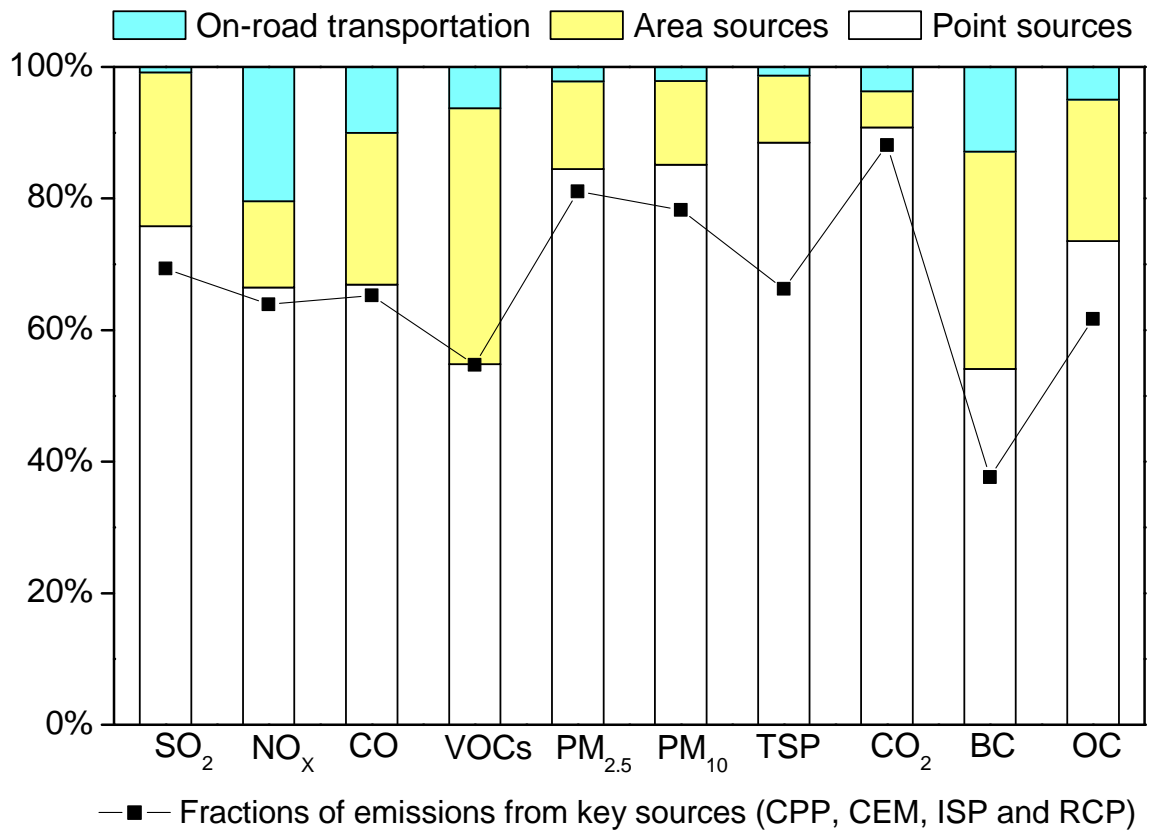


Figure 4

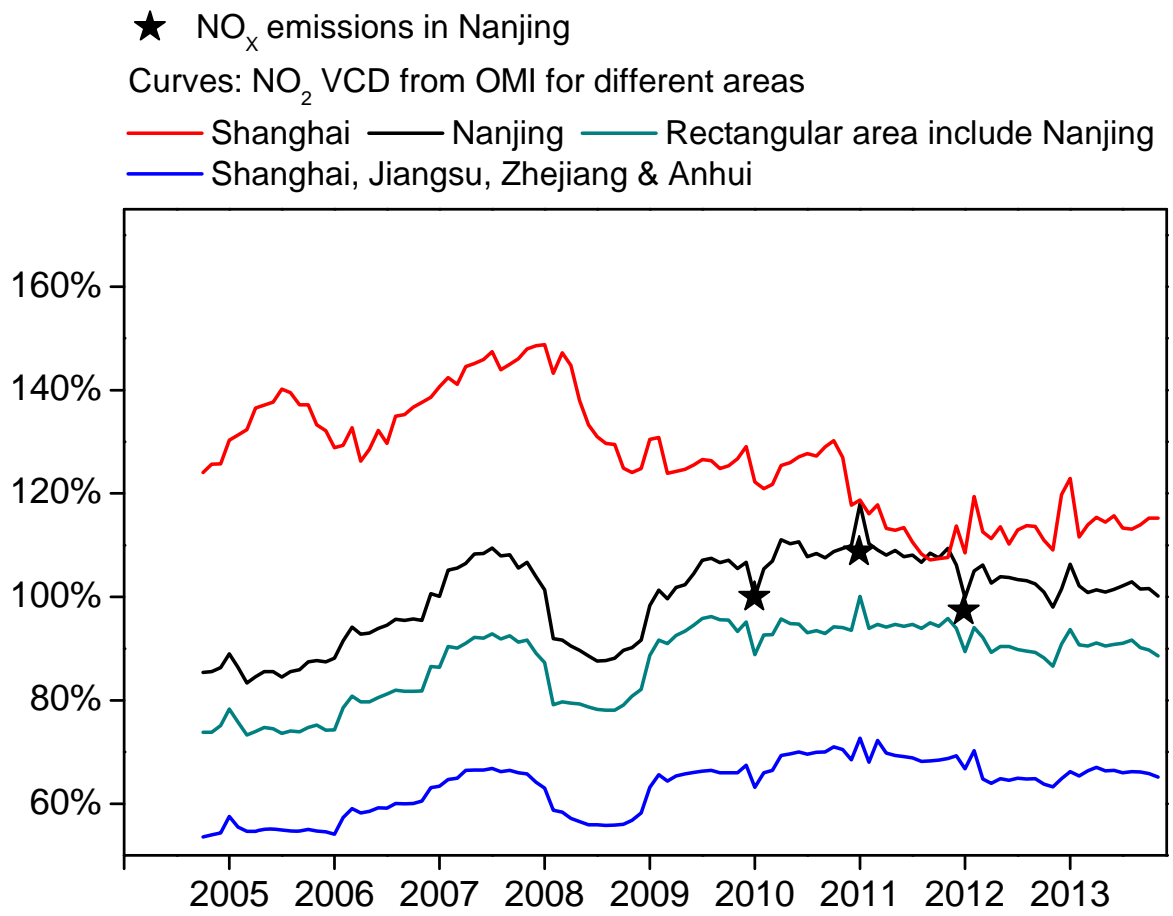
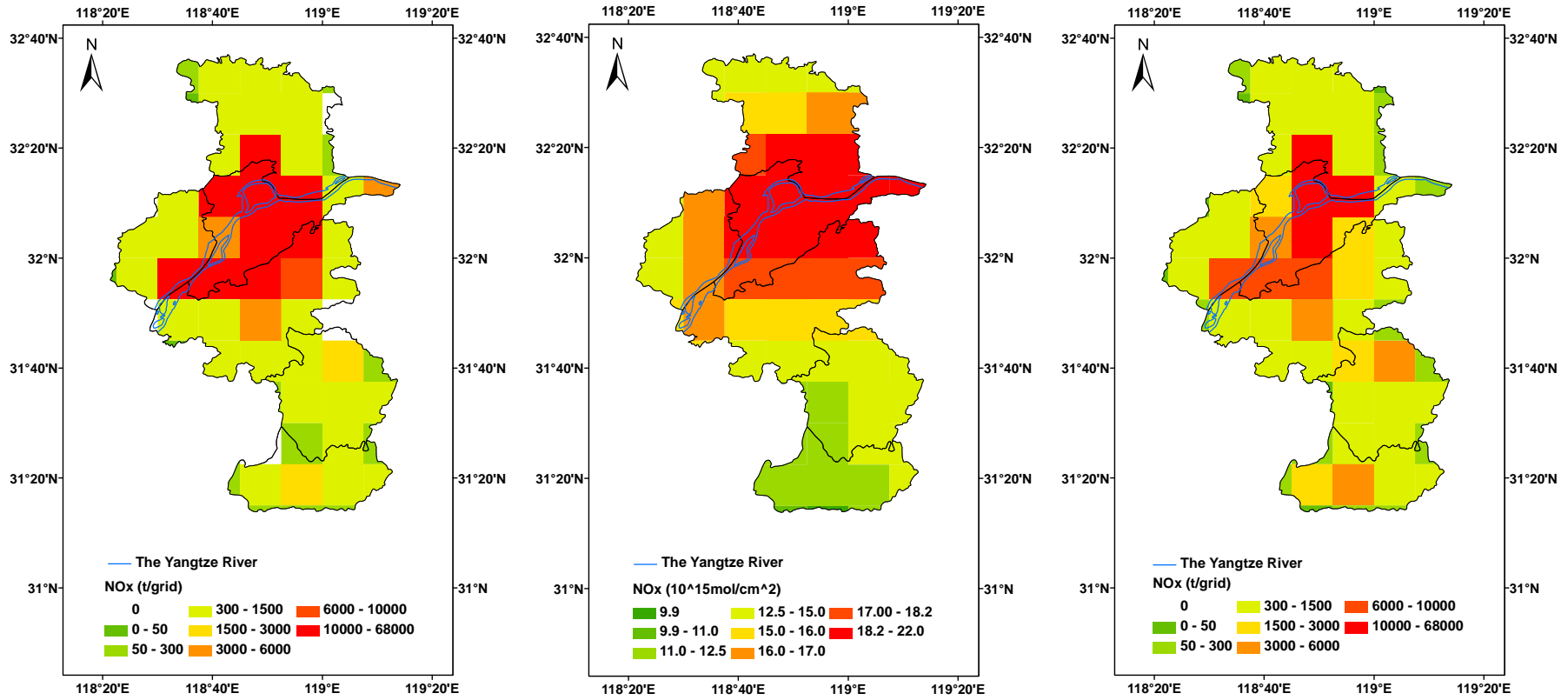


Figure 5



(a) Emissions: This study

(b) VCD from OMI

(c) Emissions: MEIC

Figure 6

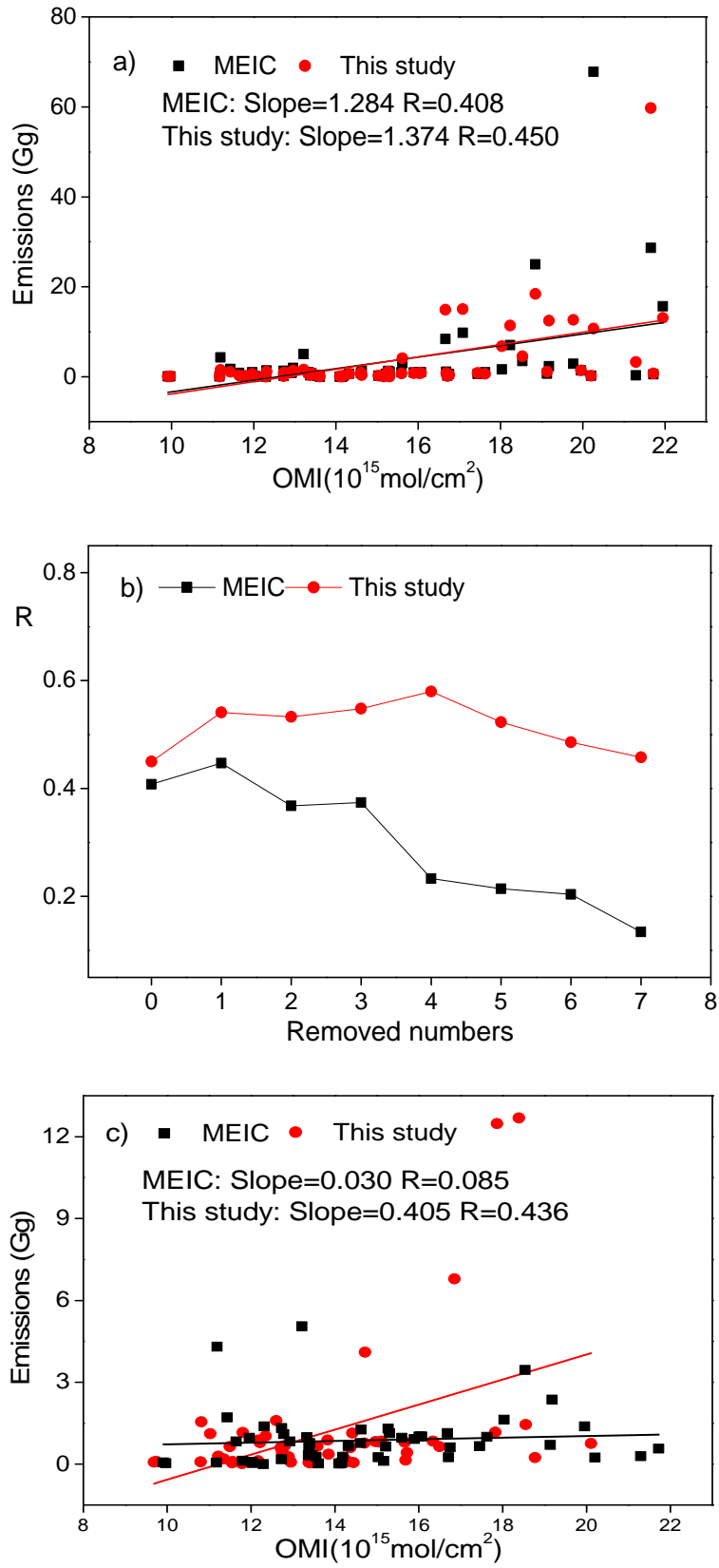


Figure 7

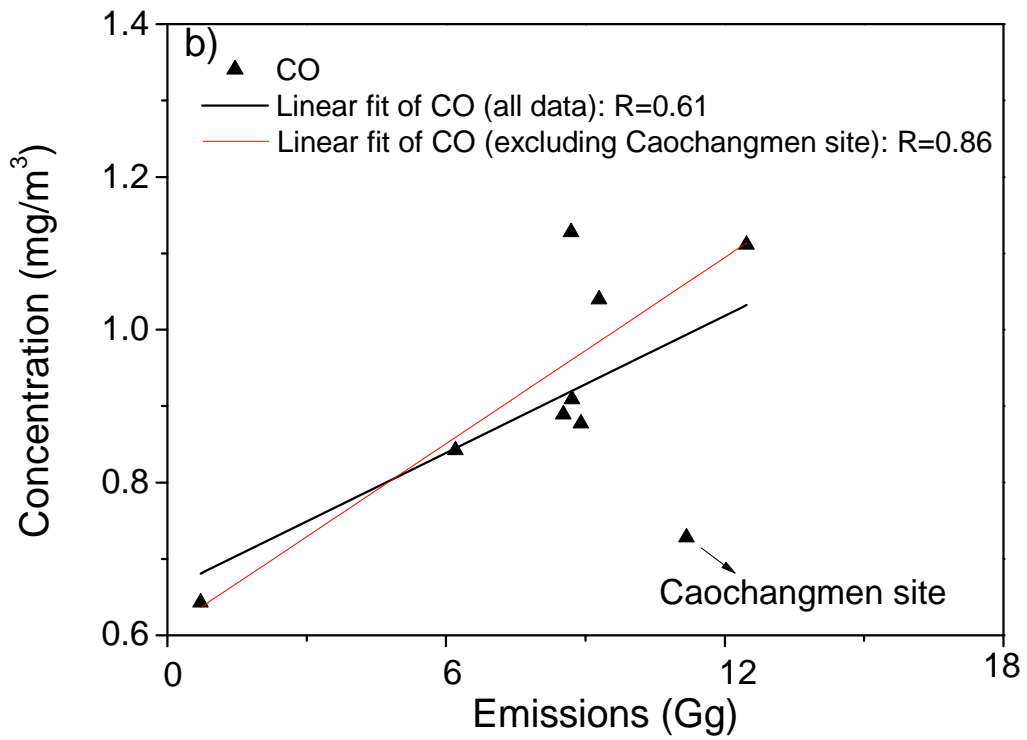
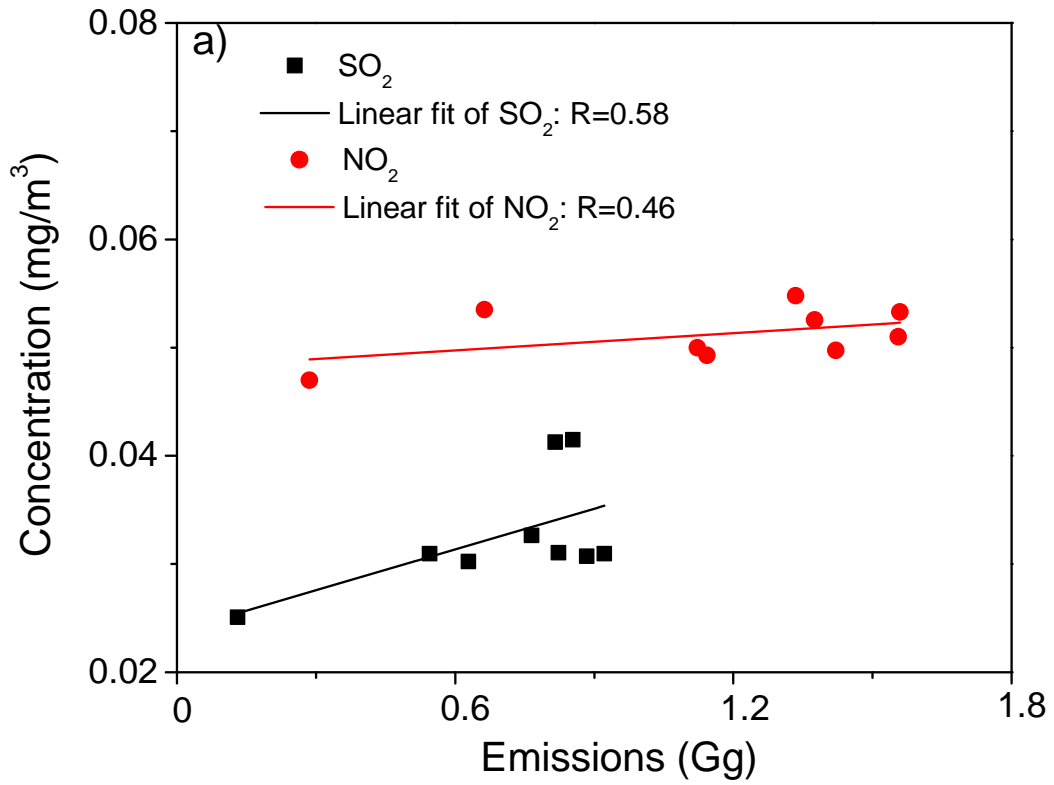


Figure 8

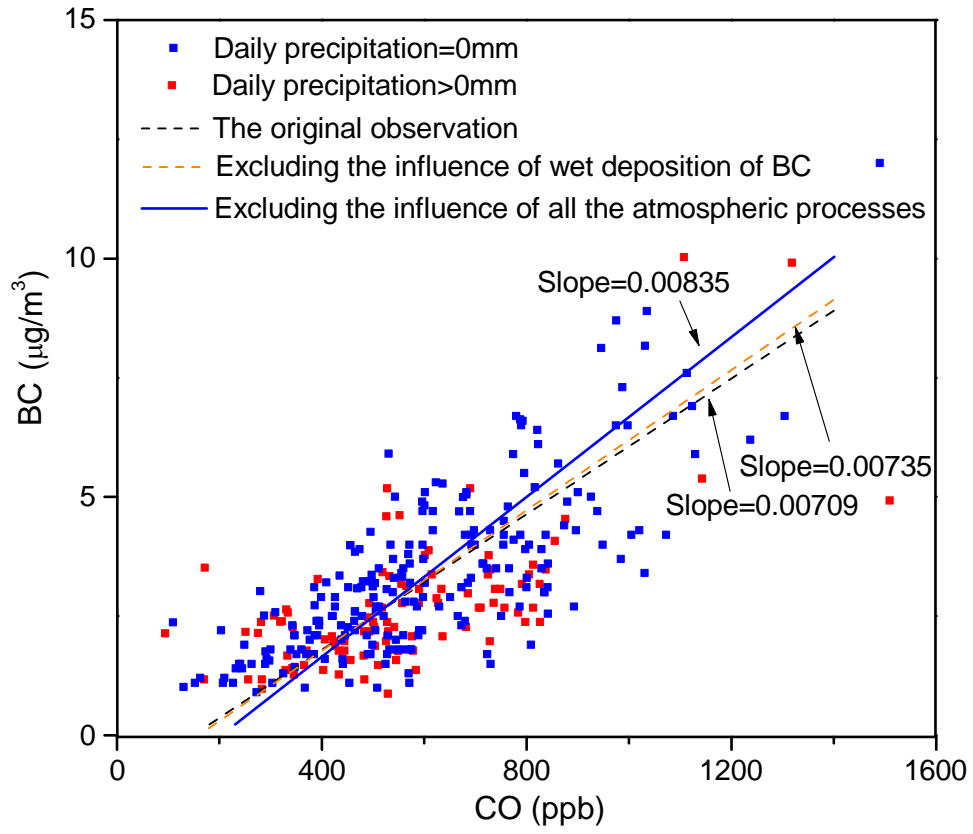


Figure 9

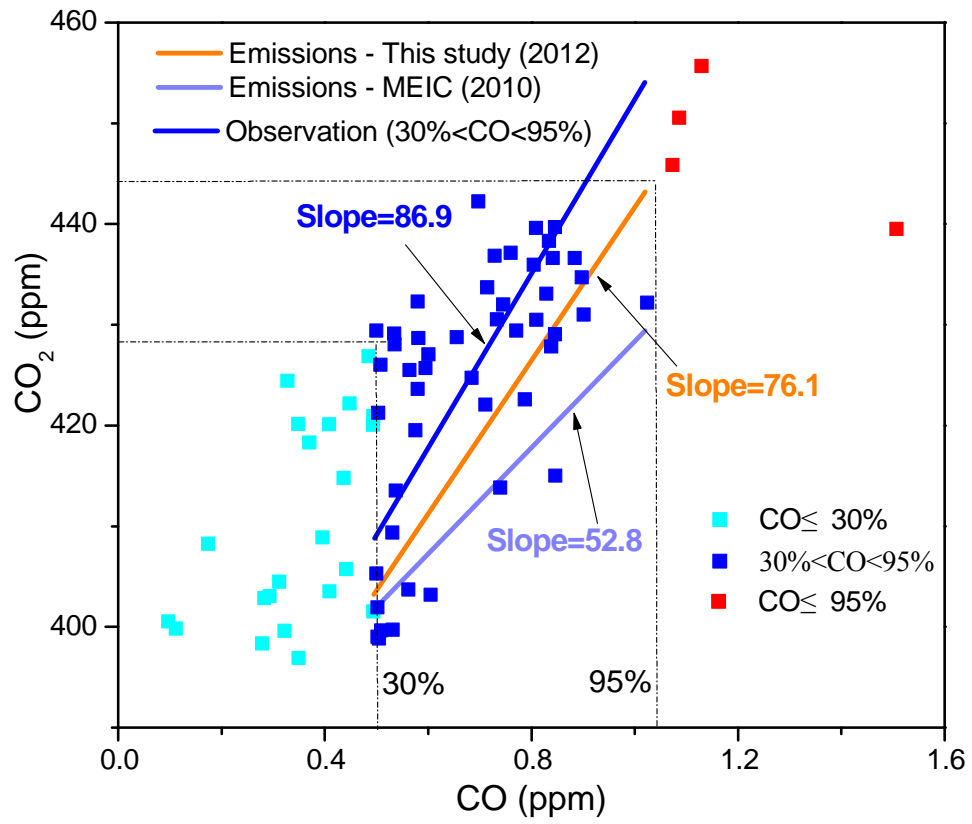
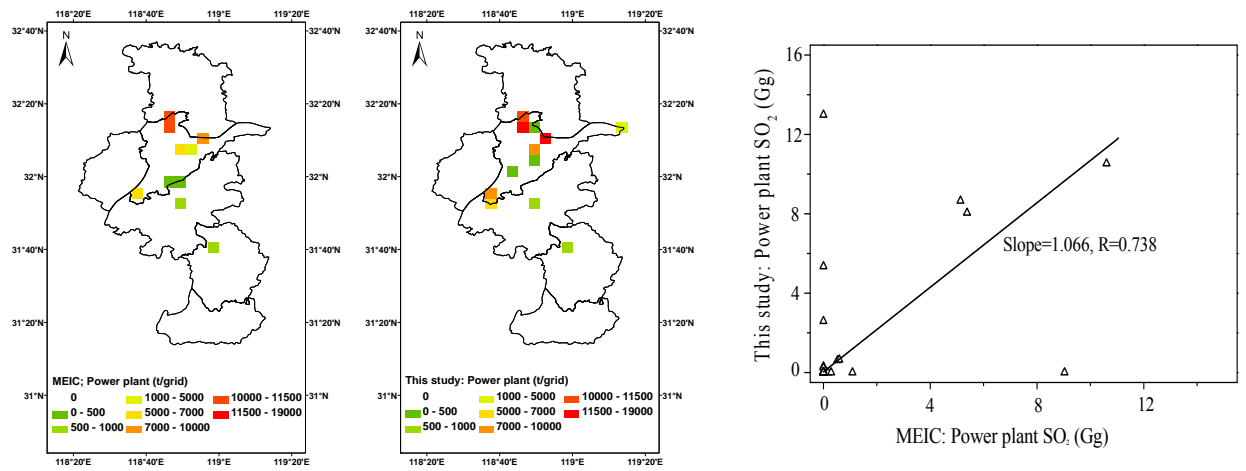
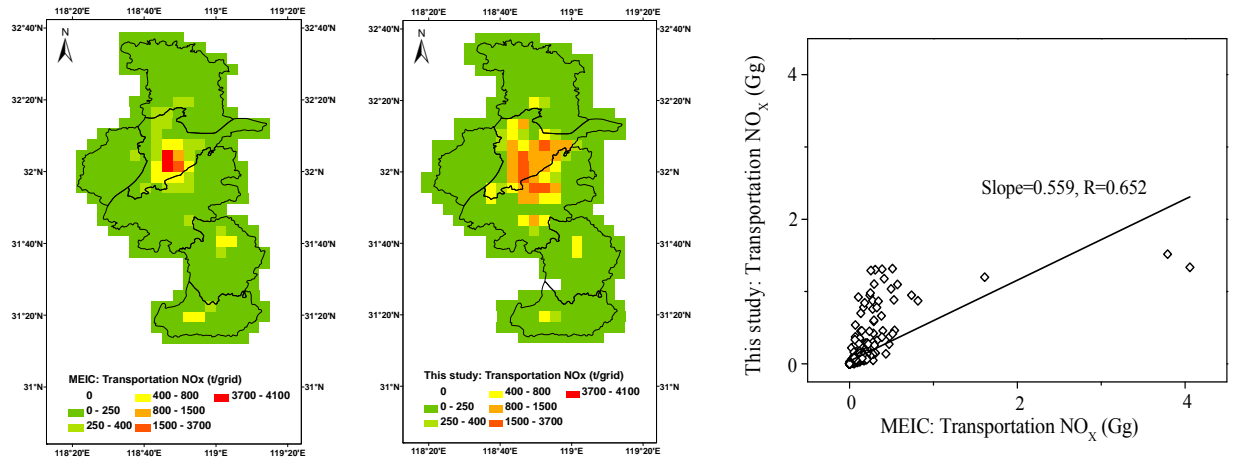


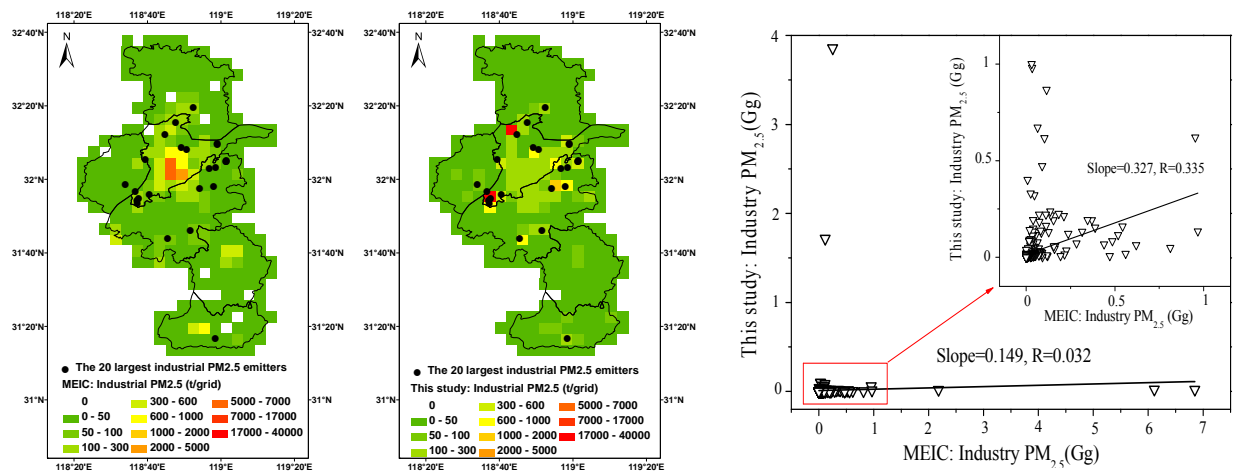
Figure 10



(a) Power plant: SO₂



(b) Transportation: NO_x



(c) Industry: PM_{2.5}