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 an 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 NOx 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 NOx 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 NOx emissions for the whole city. We have clarified this in lines 279-284, Page 12 in the revised manuscript.

"For NOx, the large increase in coal consumption from 31 million metric tons (Mt) in 2010 to 35 in 2011 dominated the growth of NOx 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 NOX 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 NOx control at coal-fired power plants (Table 1) between 2010 and 2012, why did the NOx 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 NOX 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 NOX control, and the NOX 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-NOX 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 NOX 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 NOX emissions did not change much annually, even with clear enhancement of NOX 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 NOX control, and the NOX 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-NOX 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 NOₓ 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 NOₓ 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 NOₓ emissions and NO₂ VCDs 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 NO$_2$ level, it could change the data sampling of retrieval. Therefore we admit that the NO$_2$ 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 NO$_2$ 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 NO$_2$ 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 NO$_2$ 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 NOX 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 NOX 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 NOX pollution in the area."

Reference:

II. Section 4.1, last paragraph. Could atmospheric chemistry and transport of urban
emissions also be important for NOx 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 NO\textsubscript{2} 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 NOX emissions in this study, (b) summer NO\textsubscript{2} vertical column density (VCD) from OMI, and (c) NOX emissions from MEIC for Nanjing, 2010. The resolution is 0.125\degree×0.125\degree.

13. Section 4.2. Given that NO\textsubscript{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\textsubscript{x}, SO\textsubscript{2}, 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 NO$_2$ 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 NO$_2$ 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 NO$_2$ concentrations were less sensitive or correlated to the NO$_X$ emissions, compared to the case of SO$_2$ or CO. That partly explains the small slope of ambient NO$_2$ levels to NOx 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 NO$_2$ is relatively high compared to SO$_2$. 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 NO$_2$ could be enhanced, and the local emissions in Nanjing thus have a less significant impact on NO$_2$ 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 (SO$_2$, NO$_2$ 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 SO\textsubscript{2} and NO\textsubscript{2}, and the value for NO\textsubscript{2} is relatively high compared to SO\textsubscript{2}. 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 NO\textsubscript{2} could be enhanced, and the local emissions in Nanjing city thus have a less significant impact on NO\textsubscript{2} 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\textsubscript{X} in the ambient atmosphere (Zhou et al., 2008). As the dominating component of primary NO\textsubscript{X} directly from emission sources, NO is more difficult to be oxidized to NO\textsubscript{2} 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 NO\textsubscript{2} concentrations were less sensitive or correlated to the NO\textsubscript{X} emissions, compared to the case of SO\textsubscript{2}, and it leads to the smaller slope of ambient NO\textsubscript{2} levels to NO\textsubscript{X} emissions and the lower correlation coefficient in Figure 7(a)."

Reference:

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)\textsubscript{pri}, in the EC-tracer method is to exclude the effects of SOC formation as much as possible (Castro et al., 1999). (OC/EC)\textsubscript{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 \((\text{OC/EC})_{\text{pri}}\) 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, \((\text{OC/EC})_{\text{pri}}\), 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 \((\text{OC/CE})_{\text{pri}}\) 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:


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
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.


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 CO$_2$ 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 CO$_2$ to CO ratio. If the CO concentrations are further revised based on the description in Section 4.4, the modified ambient CO$_2$ 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
"To partly exclude the effects of NMVOC oxidation, we recalculated the ambient CO$_2$ 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 CO$_2$ 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.
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

With most eastern Chinese cities facing major air quality challenges, there is a strong need for city-scale emission inventories for use in both chemical transport modeling and the development of pollution control policies. In this paper, a high-resolution emission inventory (with a horizontal resolution at $3 \times 3$ km) of air pollutants and CO$_2$ for Nanjing, a typical large city in the Yangtze River Delta, is developed incorporating the best available information on local sources. Emission factors and activity data at the unit or facility level are collected and compiled using a thorough onsite survey of major sources. Over 900 individual plants, which account for 97% of the city’s total coal consumption, are identified as point sources, and all of the emission-related parameters including combustion technology, fuel quality, and removal efficiency of air pollution control devices (APCD) are analyzed. New data-collection approaches including continuous emission monitoring systems and real-time monitoring of traffic flows are employed to improve spatiotemporal distribution of emissions. Despite fast growth of energy consumption between 2010 and 2012, relatively small inter-annual changes in emissions are found for most air pollutants during this period, attributed mainly to benefits of growing APCD deployment and the comparatively strong and improving regulatory oversight of the large point sources that dominate the levels and spatial distributions of Nanjing emissions overall. The improvement of this city-level emission inventory is indicated by comparisons with observations and other inventories at larger spatial scale. Relatively good spatial correlations are found for SO$_2$, NO$_X$, and CO between the city-scale emission estimates and concentrations at 9 state-operated monitoring sites ($R=0.58$, 0.46, and 0.61, respectively). The emission ratios of specific pollutants including BC to CO, OC to EC, and CO$_2$ to CO compare well to top-down constraints from ground observations. The inter-annual variability and spatial distribution of NO$_X$ emissions are consistent with NO$_2$ vertical column density measured by the Ozone
Monitoring Instrument (OMI). In particular, the Nanjing city-scale emission inventory correlates better with satellite observations than the downscaled Multi-resolution Emission Inventory for China (MEIC) does when emissions from power plants are excluded. This indicates improvement in emission estimation for sectors other than power generation, notably industry and transportation. High-resolution emission inventory may also provide a basis to consider the quality of instrumental observations. To further improve emission estimation and evaluation, more measurements of both emission factors and ambient levels of given pollutants are suggested; the uncertainties of emission inventories at city scale should also be fully quantified and compared with those at national scale.

1 INTRODUCTION

Emission inventories are crucial for atmospheric science research, particularly chemical transport modeling (CTM), and for air quality policymaking that seeks to identify and control pollution sources. Given China’s important role in the origins and transport of air pollutants in East Asia and beyond, a number of emission inventories at national scale have been established in recent years. These include the Transport and Chemical Evolution over the Pacific Mission (TRACE-P, Streets et al., 2003), the Intercontinental Chemical Transport Experiment-Phase B (INTEX-B, Zhang et al., 2009), the Regional Emission inventory in ASia (REAS, Ohara et al., 2007; Kurokawa et al., 2013), and the Multi-resolution Emission Inventory for China (MEIC, http://www.meicmodel.org/). Based on “bottom-up” principles and frameworks similar to those described in Streets et al. (2003), more detailed source categories and expanded domestic information on emission factors and activity levels have been integrated into most recent work, yielding improved inter-annual trends in national estimates of anthropogenic air pollutant emissions (e.g., MEIC; Zhao et al., 2012a; 2012b; 2013). Aside from the national-level work, regional emission
inventories have also been established with improved understanding of local conditions for key areas with high densities of population, industry, and energy consumption, e.g., the Jing-Jin-Ji region including Beijing and Tianjin (JJJ; S. Wang et al., 2010), the Yangtze River Delta (YRD; Fu et al., 2013; Huang et al., 2011), and the Pearl River Delta (PRD; Zheng et al., 2009).

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

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

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

It should be noted that such improvements in emission inventories for a few megacities, including Beijing and Shanghai, have been driven by air quality planning
for major events like the 2008 Summer Olympic Games and 2010 World Expo. During recent years, however, satellite observations have detected that the most significant growth in air pollution (indicated for example by vertical column densities of tropospheric NO₂) across the country is occurring not within such megacities but in the less-developed regions around them, due to faster growth in the economies and emission sources in those areas (Zhang et al., 2012a). This finding highlights the importance of developing and assessing air pollutant emission inventories for regions other than China’s much-studied megacities.

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

2.1 The basic methodology

The annual emissions in Nanjing from 2010 to 2012 are estimated with a bottom-up approach for 10 atmospheric pollutants (SO$_2$, NO$_X$, total suspended particulates (TSP), PM$_{10}$, PM$_{2.5}$, black carbon (BC) or elemental carbon (EC), organic carbon (OC), CO, VOCs, and NH$_3$) and the greenhouse gas CO$_2$. At the largest scale, sources fall into six main categories: coal-fired power plants (CPP), industry (IND), transportation (TRA, including on-road and non-road subcategories), the residential & commercial sector (RES, including fossil fuel, biofuel, and biomass open burning subcategories, along with gas stations for VOC estimation only), agriculture (AGR, including livestock farming and fertilizer use for NH$_3$ estimation only), and fugitive dust (FUD, including that from construction sites and roads). IND is further divided into cement plants (CEM), iron & steel plants (ISP), refineries and chemical plants (RCP), solvent use (SOL; although some solvent is not used in industry, we include it in this category for classification simplicity) and other industry plants (OIN).

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

With sufficient information related to emission estimation now available, more sources can be characterized as point sources in the current inventory. These include power plants (total number in 2012, similarly for subsequent categories: 18), cement plants (23), iron & steel plants (2), chemical plants (173), non-ferrous metal smelters (14), lime plants (9), brick plants (31), factories representing a portion of other industrial sectors (434), and gas-fueling stations (269). The locations of point sources by category are shown in Figure S1 (b) and (c) in the supplement. The annual emissions of point sources are calculated with Equation (1):
where \(i, j\) and \(m\) represent the species, individual plant, and fuel/technology type, respectively; \(A\) is the activity level data; \(EF\) is the uncontrolled emission factor; and \(\eta\) is removal efficiency of air pollutant control device (APCD).

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

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

Emissions from on-road transportation are calculated using COPERT 4 (version 9.0) (EEA, 2012). The parameters required by the model, including vehicle population by type, fleet composition by control stage (China I-IV, equivalent to Euro I-IV), and annual average kilometers traveled (VKT), are taken from investigations by NJEPB. The detailed information for 2012 is summarized in Tables S2 and S3 in the supplement. 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 network, 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.

For area sources including other small industry, solvent use, residential combustion, agricultural activity, and non-road transportation, emissions are estimated following previous work (Zhao et al., 2012a; 2012b; 2013), with up-to-date emission factors from domestic measurements and city-scale activity levels. The energy consumption data are taken from the Environmental Statistics (internal data of NJEPB) and the agricultural and industrial outputs are mainly from the Nanjing Statistical Yearbook (NJNBS, 2013). Fire counts and intensity observed from MODIS (Moderate Resolution Imaging Spectroradiometer, https://earthdata.nasa.gov/data/near-real-time-data/firms) are used to determine the spatial and temporal distribution of emissions from biomass open burning. Regarding fugitive dust, information about individual construction sites in the city is obtained from NJEPB to improve the estimation of emission levels and spatial and temporal distributions. This includes location, period of operations, construction area, and amount of earthworks.

The largest 221 construction sites in Nanjing in 2012 (accounting for 45% of the total construction area) are shown in Figure S1 (c) in the supplement. The annual activity levels for the main area sources for 2010-2012 are summarized in Table S1.

**2.2 Emission factors**

As mentioned previously, parameters related to emission factors for key sources (CPP, CEM, ISP, and RCP) are obtained through onsite surveys for each plant. The parameters for CPP include boiler type, combustion technology, fuel quality (sulfur,
ash, and volatile matter contents), types and pollutant removal efficiencies of APCDs (flue gas desulphurization (FGD), selective catalytic reduction (SCR)/selective non-catalytic reduction (SNCR), dust collection). Emission factors can then be determined or calculated based on the method described by Zhao et al. (2010). For cement production, the kiln type, PM removal efficiency of dust collectors, and fuel quality are investigated and emission factors are calculated following Lei et al. (2011) and Zhao et al. (2012a; 2013). For ISP, key parameters in four main processes (coking, sintering, pig iron production, and steelmaking) are obtained, including the SO$_2$ removal rate of FGD for sintering, PM removal rate of dust collectors, and the gas release ratios of coke ovens, blast furnaces, and basic oxygen furnaces. Emission factors for each process are then calculated following Zhao et al. (2012a; 2013). For the chemical industry, the surveyed parameters include the types and amounts of raw materials and products, the types and volumes of tanks, and technologies applied for VOC control. In particular, the emission factors for refineries are determined by industrial process, including production, storage, loading, and unloading (Wei et al., 2008; USEPA, 2002; EEA, 2013). Inter-annual variations in these parameters for major sources are tracked in the survey so that changing emission factors over time (2010-2012) can be determined. Table 1 summarizes the penetrations and removal efficiencies of APCDs for CPP and typical industries in Nanjing from 2010 to 2012. For other industrial sources, emission factors are taken mainly from the database by Zhao et al. (2011; 2013), after incorporating the most recent results from domestic measurements. Table S4 in the supplement summarizes the emission factors for main industrial processes.

For other sources for which local emission factors are currently unavailable, emission factors are determined based on existing studies in other parts of China. If no domestic studies are available, recommendations of USEPA (2002) are applied. Road dust emissions are estimated following USEPA (2002), based mainly on the average weight of vehicles, silt loading of the road surface, and traffic flow. Those parameters
are taken from Fan et al. (2007) and Huang et al. (2006), with some adjustments of road types for Nanjing. Emission factors of construction dust recommended by USEPA (2002) are used in this work, i.e., 0.026, 0.106, and 0.191 (kg/m²)/month for PM$_{2.5}$, PM$_{10}$, and TSP, respectively. The mass fractions of BC and OC in construction PM$_{2.5}$ are assumed to be 2.4% and 3.4%, respectively, from measurements by Zhao et al. (2009).

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

Emission factors for non-road transportation are mainly from Zhang et al. (2010) and Ye et al. (2014). Emission factors for household biofuel use are estimated based on results of various domestic measurements as summarized in Zhao et al. (2013) and Cui et al. (2015), while those for biomass open burning are from Li et al. (2007). NH$_3$ emissions from livestock farming and fertilizer use are taken from Dong et al. (2010), Yang (2008), and Yin et al. (2010).

### 3 RESULTS

#### 3.1 Inter-annual variability and sector distribution of emissions

The annual emissions of various air pollutants and CO$_2$ from anthropogenic sources in Nanjing are shown in Figure 1(a) for 2010-2012. In 2010, the total emissions of SO$_2$, NO$_X$, CO, VOCs, NH$_3$, PM$_{2.5}$, PM$_{10}$, TSP, CO$_2$, BC and OC are estimated at 165, 216, 774, 224, 21, 71, 94, 158, 79976, 6.2, and 6.7 Gigagrams (Gg), respectively. Note the numbers here for PM emissions do not include fugitive dust
from construction and transportation, to facilitate comparison with inventories that omit the source. Despite large growth in coal consumption from 2010 to 2012, the emissions of SO$_2$ and NO$_X$ in 2012 are estimated to be smaller than those in 2010, implying the effectiveness of emission control measures for the city in recent years. These measures include mainly the increased use of flue gas desulfurization (FGD) and selective catalytic reduction (SCR) systems in the power generation sector (see the detailed information in Table 1). The slight increase in SO$_2$ emissions between 2011 and 2012 resulted mainly from the growth in coal consumption in industries other than power generation, where FGD systems have not been widely deployed. 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. PM emissions are estimated to be quite stable for the three years, with small increases in PM$_{2.5}$ and PM$_{10}$. Rising mass fractions of PM$_{2.5}$ to TSP (from 45% to 48%) indicate the difficulty in controlling emissions of finer primary particles compared to coarser ones. For VOCs and NH$_3$, which have not been well regulated in national action plans for air pollution prevention and control (Zhao et al., 2014), the inter-annual variabilities of emissions are small and driven mainly by relative stability in chemical and agricultural production, respectively. While CO$_2$ continues to rise, no growth is estimated for CO from 2011 to 2012, implying improved overall combustion efficiency in the city.

Figure S2 in the supplement shows the sector contributions to total emissions by year and species. From 2010 to 2012, power plants, iron & steel plants, and other industrial plants are the largest SO$_2$ sources, contributing 41%-42%, 14%-19%, and 32%-23% of total emissions, respectively. NO$_X$ emissions come mainly from power plants (45%) and on-road transportation (20%) throughout the time period. The shares of SO$_2$ and NO$_X$ emissions from the power sector are clearly smaller than its shares of
coal consumption (57%-64%) or CO\textsubscript{2} emissions (48%-57%), due largely to relatively stringent emission controls in the sector. It can be found that the sector distribution of NO\textsubscript{X} emissions did not change much annually, even with clear enhancement of NO\textsubscript{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\textsubscript{X} control, and the NO\textsubscript{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\textsubscript{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.

Fugitive dust, particularly that of road origin, is identified as the dominant anthropogenic source of PM emissions. The fugitive dust shares of TSP are estimated to range 64%-70% during the research period, while smaller fractions are found for finer particles and carbonaceous aerosols. Apart from fugitive dust, iron & steel production plays a significant role in PM emissions in Nanjing, with its shares of TSP, PM\textsubscript{10}, and PM\textsubscript{2.5} calculated at 15%-16%, 20%-23%, and 35%-41%, respectively. This results mainly from the large coal use by the sector, and relatively poor PM control measures of certain plants compared to other major coal-consuming sources, e.g., power plants. Iron & steel production is also identified as the biggest contributor of CO emissions for the city with its share reaching 60% in 2012, even though emission factors for the sector in Nanjing (based on field investigations) are smaller than the national average (Zhao et al., 2012a). This is partly attributed to relatively little inefficient coal combustion at other sources in the city (e.g., in small industry and residential use), resulting in much lower fractions of CO emissions from those sources.
than the national averages. VOCs come mainly from chemical production (52%) and solvent use (29%-30%). With vapor recovery systems increasingly applied, VOC emissions from gas stations decline during the research period. Despite an increase in vehicle population, the fractions of on-road transportation emissions for most species decrease from 2010 to 2012, attributed mainly to implementation of increasingly strict vehicle emission standards. From effective prohibition of burning of agricultural wastes, the emission contributions of this source, mainly of particles, carbonaceous aerosols, and CO, are also considerably reduced.

**3.2 Spatial and temporal distribution**

For simulation of atmospheric transport and chemistry, the emission inventories are allocated into a 3×3 km grid system. For sources lacking specific location information, their emissions are assumed to be correlated with population density, with the exception of NH$_3$, which is allocated based on the density of agricultural GDP. Shown in Figure 2 are the spatial distributions of SO$_2$, NO$_x$, PM$_{2.5}$ (excluding fugitive dust from construction and roads) and VOC emissions for Nanjing in 2012, and the locations of the ten largest point sources of each species. Relatively high emission densities are found in the urban area, particularly around certain large power generation and industrial sources. As illustrated Figure 3, the fractions of emissions from point sources for all concerned species are estimated to exceed 50%, as are those from the collective four key source types, with the exception of BC, at 38%.

Monthly distributions of SO$_2$ emissions by sector and that of total emissions of all species for 2012 are respectively shown in Figure S3 (a) and (b) in the supplement. Note again that fugitive dust from construction sites and roads is excluded. The results of MEIC are also provided in Figure S3(a) for comparison. It can be seen that the temporal distributions of the two studies are similar except for residential emissions, which are smaller overall in this work compared to MEIC. As indicated by MODIS fire counts, over 90% of biomass open burning occurred in May-July, leading to much
higher OC emissions in those three months compared to any other time of the year. For other species, the temporal distributions of emissions correlate closely with those of activity levels, with a drop in February attributed mainly to reduced energy supply and industrial production during the Spring Festival. Pronounced diurnal variations of on-road transportation emissions are illustrated in Figure S4 in the supplement, with two peaks at the rush hours. The daily shares of CO and VOC emissions in the morning rush hour (16%) are slightly higher than those of NO\textsubscript{X} (14%) and PM\textsubscript{2.5} (15%). Based on the assumptions of COPERT, the cold start of most vehicles occurs in the morning, leading to larger CO and VOC emission factors during this time compared to those during stable operation of vehicles. The influence of vehicle cold starts on emissions of NO\textsubscript{X} and PM\textsubscript{2.5} is smaller.

3.3 Comparisons with other studies in emission estimates

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

Our estimate of SO\textsubscript{2} emissions for Nanjing is 25% and 22% higher than those of Fu et al. (2013) and MEIC, respectively, even though the plant-by-plant survey indicates an FGD penetration rate of 92% of installed power generating capacity, higher than the provincial average of 85% used in Fu et al. (2013). The higher estimate results because: 1) the total coal consumption from the Environmental Statistics applied in this work is 14% larger than that provided by the Nanjing Almanac used in other studies (NJCLCC, 2011; see Section 4.6 for more discussion); and 2) a relatively lower removal efficiency of FGD is obtained from the onsite
survey for 2010. Similar NO\textsubscript{X} emission levels are found between current work and MEIC, while lower emissions were provided by Fu et al. (2013). According to filed survey, the penetration rate of SCR/SNCR increased from 44\% to 67\%, and the NO\textsubscript{X} removal efficiency increased from 18\% to 77\% during 2010-2012 (Table 1). The penetration rate is much larger compared to the provincial average of 22\% applied in MEIC and Fu et al. (2013), partly offsetting a discrepancy in estimated emissions caused by larger activity levels used in current city-scale inventory.

Our estimates for PM\textsubscript{2.5}, PM\textsubscript{10}, and BC emissions (without fugitive dust emissions) are larger than those of Fu et al. (2013) or MEIC in 2010. This results mainly from larger emissions from industry (particularly iron & steel production), as the survey revealed that relatively old and inefficient wet dust collectors were still used at some plants. OC emissions, however, are estimated to be lower than MEIC indicates, due mainly to very little coal or biomass burning in the city-level statistics.

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

For CO, our estimates are 12\% higher for industry than those of MEIC, but 26\% and 37\% lower respectively for residential and transportation sectors, resulting in 2\% lower emissions for anthropogenic sources as a whole. The discrepancy in sector contributions is caused mainly by the high percentage of centralized coal combustion
in the city: power, iron & steel, cement, and chemical plants consumed over 95% of
the city’s coal, based on our field survey. Our CO₂ emission estimate is 22% higher
than that of MEIC, resulting mainly from the difference in coal consumption reported
by the Environmental Statistics database and the city almanac.

4 ASSESSMENT OF THE CITY-SCALE EMISSION INVENTORY

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

4.1 Evaluation of inter-annual trends and spatial distribution of NOₓ emissions
with satellite observations

The inter-annual trend in NOₓ emissions estimated bottom-up is compared with
that of NO₂ vertical column densities (VCDs) based on satellite observations. The
VCDs of tropospheric NO₂ are retrieved from the Ozone Monitoring Instrument (OMI)
by the Royal Netherlands Meteorological Institute (Boersma et al., 2007; 2011), using
monthly data with spatial resolution of 0.125°×0.125° (data source:
http://www.temis.nl/airpollution/no2col/no2regioomimonth_v2.php). Illustrated in
Figure 4 are annual emissions estimated in this work for Nanjing from 2010 to 2012
and VCDs from 2005 to 2012 for 4 regions: Nanjing, Shanghai, 4 provinces in the
YRD (including Jiangsu, Zhejiang, Anhui and Shanghai), and a rectangular region
containing Nanjing (see Figure S1(a) for reference). The first two represent NO₂ at
city levels while the latter two represent regional levels. To eliminate seasonal
variations, NO₂ VCDs are presented as 12-month moving averages, calculated as the
means of the data for the previous and subsequent six months. All the data are
normalized to the 2010 level of Nanjing. While NO$_2$ VCDs started declining around
2008 for Shanghai, it kept increasing for the rest of the YRD region including Nanjing
until 2012. Clearly higher than the regional levels, the average NO$_2$ VCD for Nanjing
approached that of Shanghai after 2010. This implies, on one hand, the benefits of
Shanghai’s strict emission controls of on-road vehicles and big power plants (K.
Huang et al., 2014), implemented in advance of other regions. On the other hand, the
growth of NO$_2$ for the rest of the YRD demonstrates the spread of air pollution source
regions from major metropolitan areas to less developed cities nearby, and suggests
the need for increased efforts in emission and pollution abatement in those areas, as
indicated by Zhang et al. (2012a). Decreased emissions in Nanjing are clearly
indicated by this work after 2011, attributed mainly to the national policy of
compulsory installation and running of SCR devices in the power sector. This
inter-annual variation shows good consistency with that of OMI NO$_2$ VCD.

It should be noted that uncertainties exist in the comparison between the
inter-annual variations in emissions and VCDs and the results should be interpreted
cautiously. First, the biases of NO$_2$ 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 NO$_2$ VCD retrieval
uncertainties on the comparison could partly be mitigated. 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 NO$_2$ VCD levels. Finally, the period for emission and VCD
comparison is relatively short. Even the NO$_2$ 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 NOX pollution in the area.

To further assess possible improvement of emission estimates by the current city-level inventory, the spatial distribution of monthly means of OMI NO2 VCD in summer (June-August) 2010 over Nanjing is compared with that of two emission studies: 1) city-level emissions at spatial resolution of 3×3 km by the current work, and 2) MEIC emissions developed at the provincial level with a resolution of 5×5 km.

For the purpose of visualization and further analysis, the emissions are reallocated to a 0.125°×0.125° grid system from the original spatial distributions, consistent with the resolution of retrieved OMI NO2 VCD. We assume that the NO2 VCD from satellite observations reflect the anthropogenic NOX emissions of the city for the following reasons. NOX emissions in East China are predominantly anthropogenic (Mijling et al., 2013); lightning and soil sources as a share of total emissions are estimated to peak in July, when they account for 9% and 12%, respectively (Lin, 2012). NOX emissions in Nanjing are clearly larger than in surrounding areas (Huang et al., 2011), and the NO2 VCD over the city is believed to be most influenced by local emissions.

As shown in Figure 5, a similar spatial pattern of NOX is captured by the gridded emissions and satellite observations, and relatively higher pollution in the urban area in the center of the city is indicated, attributed mainly to the combined effects of intensive transportation and large point sources. The emission inventories, however, underestimate the high-pollution areas compared to OMI observations, particularly MEIC. To further gauge improvement in spatial distribution by the city-scale emissions, correlations between the gridded emissions and the VCD are analyzed. As shown in Figure 6 (a), the correlation coefficients (R) between the emissions and the VCDs are calculated at 0.450 and 0.408 for this work and MEIC, respectively, indicating better agreement by the city-scale inventory. Moreover, a sensitivity test on the correlation coefficients is conducted through step-wise exclusion of the grid cells
with the largest emissions. Along with the increase in excluded grid cells, the R for this city-scale emission inventory remains above 0.43, while those of MEIC sharply decrease (Figure 6 (b)). In order to estimate emissions of the whole country, the MEIC is based mainly on energy and economic statistics at the provincial level, though it includes a limited number of major point sources, e.g., power plants with relatively good documentation and large emissions. Emissions from other point sources are based on coarser inputs due to constraints of time, labor, and data availability. The current study, in contrast, compiled detailed information for all power plants and most other industrial sources in Nanjing through comprehensive survey investigation, as described in Section 2. Better estimates of emission levels and spatial distributions should thus be expected, particularly for small or medium-size emission sources.

Once the grid cells dominated by major power plants are excluded from the two inventories, as shown in Figure 6 (c), the current city-scale emissions still correlate well with satellite observations (R=0.436) while MEIC shows little correlation (R=0.085). The results reflect that inventories compiled at the provincial or regional level better estimate emissions of large sources than small or medium-sized ones, due to relative availability of information on power plants but much poorer nationwide data availability for other industrial plants. When focusing on smaller regions like cities, however, detailed information on more emission sources from onsite survey becomes crucial for improving emission estimates.

It should be noted that high NO\textsubscript{2} VCDs are found over the Yangtze River by OMI (roughly following the dark red zone in Figure S6 in the supplement) while current emission inventories cannot capture this. Possible underestimation of emissions from ships is indicated. Due to data limits, only ships arriving or leaving the port of Nanjing are taken into account in the current city-scale inventory, while those passing through Nanjing are omitted. Further investigation of the vessel flow along the Yangtze River is thus necessary to improve the estimation of ship emissions, which may be particularly influential at small spatial scales. Besides the ships, the
emissions from factories along the river could also contribute to the high VCDs.

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

Ambient concentrations for selected pollutants from ground observations are used to test the city-scale emission inventory. Daily averages of SO$_2$, NO$_2$, CO, and PM$_{2.5}$ concentrations for 2012 are obtained from the 9 state-operated monitoring stations in urban/suburban Nanjing, mapped in Figure S1 (d). The SO$_2$, NO$_2$, CO, and PM$_{2.5}$ concentrations were measured by Ecotech EC9850B, Ecotech EC9841B, Ecotech EC9830B and Met One 1020 analyzers, respectively. The emissions of specific pollutants around each site with a grid cell size of 0.04°×0.04° are calculated from the 3×3 km gridded inventories, and correlations with annual mean concentrations of corresponding species are analyzed. Since none of the city’s key sources (CPP, CEM, ISP or RCP) are located in those grid cells, the effects of individual big sources on the correlation between emissions and observation are assumed to be limited.

As shown in Figure 7(a), modest agreement is found in spatial patterns between the observed concentrations and the emissions for SO$_2$ and NO$_X$ (NO$_2$), with the R calculated at 0.58 and 0.46, respectively. SO$_2$ and NO$_X$ have average atmospheric lifetimes of several days and one day, respectively, thus the ambient concentrations are expected to partly reflect emission intensities nearby and the correlation analysis adds support for the reliability of the city-scale emission inventory. The y-intercepts in Figure 7(a) can be considered as the approximations of regional background levels of SO$_2$ and NO$_2$, and the value for NO$_2$ is relatively high compared to SO$_2$. 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 NO$_2$ could be enhanced, and the local emissions in Nanjing city thus have a less significant impact on NO$_2$ 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 NO\(_2\) 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 NO\(_2\) concentrations were less sensitive or correlated to the NO\(_X\) emissions, compared to the case of SO\(_2\), and it leads to the smaller slope of ambient NO\(_2\) levels to NO\(_X\) emissions and the lower correlation coefficient in Figure 7(a).

As shown in Figure 7(b), the correlation coefficient for CO is calculated at 0.61, and it reaches 0.86 when the observation of the Caochangmen site is excluded, where extremely high emissions are calculated but low ambient levels were observed (to be further discussed in Section 4.4). Even with a longer lifetime (weeks to months) than SO\(_2\) or NO\(_X\), CO in the atmosphere over Nanjing results mainly from primary emissions from incomplete combustion, implying reasonable agreement between emissions and concentrations. However, emissions from small coal combustion sources still cannot be fully tracked or precisely quantified, and this evidence is thus tentative.

4.3 Evaluation of emissions against top-down constraints from observations

For certain pairs of pollutants that come from common sources and thus share emission characteristics, or weakly reactive species that are relatively stable in the atmosphere, correlations of ambient concentrations can provide useful “top-down” constraints on “bottom-up” estimates of primary emissions. In this work, the correlations of three pairs of species in the atmosphere—BC and CO, OC and EC, and CO\(_2\) and CO—are analyzed based on daily mean concentrations from ground observations in 2012. Combining the mass or molar ratios of emissions for corresponding species allows further evaluation of the city-scale inventory.
BC and CO

BC and CO both result from incomplete combustion of solid fuels and certain industrial processes such as coking. With relatively long atmospheric lifetime, CO is usually recognized as a tracer of pollution transport. Combined with BC levels, it can also be used to test emission inventories of the two species (most at regional or national scale), which is particularly useful for BC given its relatively large emission uncertainties (Kondo et al., 2011; Wang et al., 2011; Zhao et al., 2011; 2012a). We follow the method presented in Wang et al. (2011) but focus on evaluating the city-level, top-down emission ratio of BC to CO based on observations at Caochangmen in Nanjing (point A in Figure S1(d) in the supplement). We choose this site for emission evaluation for two main reasons. First, it is an urban site and thus assumed to be more representative for the city emissions, compared to suburban/rural sites that are more influenced by emissions from broader areas. Second, Caochangmen is the biggest and the most comprehensive state-operated station in the city. Among all the 9 state-operated sites in Nanjing, it is one and only station that conducts observation not only for the six criterion pollutants (i.e., SO₂, NO₂, CO, O₃, PM₁₀, and PM₂.₅) but also for certain species including BC used here and CO₂ used later. Daily means of BC and CO concentrations are calculated based on the hourly data from continuous observations using Magee AE 31 and Ecotech EC9830B analyzers, respectively, and the correlation between the two species are then evaluated and used to check the bottom-up emission inventories. Since ambient levels of BC and CO depend not only on emissions but also on atmospheric processes (e.g., wet and dry depositions of BC, chemical reactions of CO with OH, and mixing of both BC and CO) that exert different influences on the two species (Wang et al., 2011), the top-down emission ratio of BC to CO \((\frac{BC}{CO})_{E,\text{top-down}}\) is calculated from the observed BC/CO \((\frac{dBC}{dCO})_t\) by excluding the influence of the above-mentioned atmospheric processes, as indicated in Equation (2):
$dBC/dCO|_t = BC/CO|_{E,top-down} F_{dry} F_{chem} F_{mixing} F_{wet}$  

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

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

Aside from mean annual levels, comparisons are also conducted for seasonal BC to CO ratios, as summarized in Table 2. The highest $BC/CO|_{E,top-down}$ is found in summer while the lowest is in winter. Such seasonal variation, however, is not indicated in the current bottom-up emission inventory, for the following possible reasons. First, as described in Section 2, the temporal distribution of emissions is based on investigation of large and medium enterprises. However, the species of concern here, especially BC, come largely from small industrial and residential
sources, for which temporal information is still lacking. For transportation, the increased cold start of vehicles in winter also leads to higher CO emissions that cannot be fully captured by COPERT (Cai and Xie, 2010; Xiao et al., 2004) and could then lead to an overestimate of BC/CO from the bottom-up method. Second, although Caochangmen is located in urban Nanjing, it would inevitably be influenced by emissions from wider regions outside the city that are not quantified in the city-scale inventory. For example, biomass burning, which has a higher BC to CO ratio than exists in the ambient atmosphere, occurs more frequently in less-developed areas such as northern Jiangsu and Anhui provinces than in Nanjing. According to MODIS, 79% of agricultural fire points in Jiangsu 2012 were found in summer, elevating the ambient BC/CO in this season. Third, uncertainty exists about the estimation of $F_{chem}$. In winter, the lowest OH densities in the boundary layer resulting from the weakest radiation lead to the smallest CO sink, and the opposite is true in summer (Seiler et al., 1984; Huang et al., 2013). The elevated $F_{chem}$ in summer should thus lead to reduced $BC/CO|_{E,top-down}$. In this work, however, the seasonal difference in $F_{chem}$ cannot be precisely quantified precisely based on existing studies, and the same $F_{chem}$ has to be used for all seasons, leading to possible overestimation of $BC/CO|_{E,top-down}$ for summer and underestimation for winter.

**OC and EC**

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/CE)$_{pri}$, to exclude the effects of SOA (see Figure S7 for the observed time series of ambient OC to EC ratio). The (OC/EC)$_{pri}$ were then estimated at 1.70, 1.27, 1.53, and 1.85 for spring, summer, autumn, and winter, respectively, with an annual average of 1.59. In this work, we adopt those results and assume that they serve as a top-down constraint of carbonaceous aerosol emissions. From the bottom-up estimates, the emission ratios of OC to BC in our city-scale emission inventory and MEIC are respectively 1.38 (for 2012) and 1.24 (for 2010, the most recent year for which MEIC emissions are available), both of which are lower than the top-down (OC/EC)$_{pri}$ from observations. With few emission sources nearby, the observation site is thought to be less influenced by local sources (e.g., on-road transportation that has a relatively low emission OC to BC ratio) than the regional transport of pollutants (Li et al., 2015). Thus some sources with high OC to BC ratios that are uncommon in Nanjing but more dispersed outside the city contribute significantly to the observed concentrations at the site. Those sources include residential fossil and biomass combustion and biomass open burning. The OC to BC emission ratios of Jiangsu and Anhui provinces surrounding Nanjing are estimated respectively at 1.91 and 2.13 (Zhao et al., 2013), clearly larger than the local emission ratio of Nanjing. 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. 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.

**CO$_2$ and CO**

CO$_2$ is a well-known greenhouse gas, with the main anthropogenic sources fossil energy combustion and industrial processes. The ratios of CO$_2$ to CO emissions differ between source types, reflecting varying combustion efficiencies. The observed ratio of CO$_2$ to CO levels in the atmosphere can thus be used as an indicator of energy efficiency, as well as a top-down test of emissions estimated bottom-up. The annual molar ratios of CO$_2$ to CO emissions in Nanjing are calculated at 65.7, 73.6, and 76.1 for 2010, 2011, and 2012, respectively, significantly higher than that in Beijing in 2008 (32.8, Zhao et al., 2012a). They are also higher than the mixing ratios observed in rural Beijing in 2008 (26.8, Y. Wang et al., 2010) or at Hatetuma Island (HAT), a remote site located off the coast of continental East Asia and influenced by air masses transported from East Asian countries from late fall to early spring (34.5, Tohjima et al., 2014). Given the large discrepancy, data from measurements in urban Nanjing (Caochangmen, Point A in Figure S1 (d)) are further analyzed to test the emissions. Daily mean concentrations of CO$_2$ and CO are derived from hourly observations using Thermo 410i and Ecotech EC9830B analyzers, respectively, for all of 2012. To exclude the effects of biogenic emissions that prevail in warm seasons, data for the winter months (January, February, and December) are used. The prevailing wind directions over Nanjing in winter are east and northeast, and large point sources, accounting for 64% of the city’s CO$_2$ emissions, are located to the east and northeast of Caochengmen, supporting use of the observational data for the current purpose.

The average observed concentrations of CO$_2$ and CO in winter were 421 ppmv
and 608 ppbv, respectively. Based on the cumulative probability distribution of daily CO concentrations (as shown in Figure S8 in the supplement), the whole dataset is divided into three subsets: (1) below the 30th percentile (with average CO and CO$_2$ concentrations at 350 ppbv and 410 ppmv, respectively), (2) between the 30th and 95th percentile (677 ppbv for CO and 424 ppmv for CO$_2$), and (3) above the 95th percentile (above 1200 ppbv for CO and 448ppmv for CO$_2$). We consider that subset (1) represents air masses from relatively clean areas outside Nanjing, and subset (2) a well-mixed blend of sources of CO$_2$ and CO over Nanjing. Subset (3) is assumed to indicate extremely serious regional pollution episodes, in which pollutants were trapped in a shallow inversion layer (Y. Wang et al., 2010). Subset (2) is believed to best reflect the typical effects of local emissions and is used for bottom-up emission comparisons.

Illustrated in Figure 9 is the CO$_2$-CO correlation estimated with the reduced major axis method based on surface observations and the CO$_2$ to CO ratios from bottom-up emission inventories for Nanjing. Our estimate of the CO$_2$ to CO ratio (76.1) is closer to observations (86.9) than MEIC (52.8), implying improvement in the current city-scale inventory. The observed CO$_2$ to CO ratio, however, should theoretically be lower than that from emissions for the following three reasons. First, compared to CO, the observation of CO$_2$ at an urban site would be more influenced by sources within a broader region than the city, as CO$_2$ has a longer lifetime in the atmosphere. Thus it is not fully representative of the very centralized and large CO$_2$ emissions inside the city, particularly those from large point sources (e.g., 17 power plants and 2 iron & steel plants, which are estimated to account for 78% of total CO$_2$ emissions in Nanjing), and the CO$_2$ to CO ratio from observations should be reduced. Second, the current emission inventory includes only the primary CO emissions while there may be a fair amount of secondary CO from the oxidation of NMVOC. Duncan et al. (2007) estimated that CO from NMVOC oxidation equaled nearly 50% of global primary CO emissions. Given the intensive refineries and chemical plants and thereby
elevated NMVOC emissions in Nanjing, considerable secondary CO from NMVOC oxidation can be expected, leading to a lower ratio of CO₂ to CO from observations than that from primary emissions. 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. Third, as discussed previously, the Caochangmen site is influenced heavily by local transportation that exhibits a lower CO₂ to CO emission ratio than industry. We believe that the higher CO₂ to CO ratio from observations than bottom-up emissions reflect the uncertainties from both approaches. On one hand, emissions from certain species and sectors need to be further improved, e.g., CO from vehicles might be underestimated by the current work, since relatively poor management of vehicle emissions in China cannot be tracked by COPERT. On the other hand, we speculate that possible bias also exists in observations, with more discussion to follow in Section 4.4.

The larger molar ratios of CO₂ to CO in Nanjing than in Beijing, both from observations and emissions, are attributed mainly to the structure of emission sources. Nanjing is a city with intensive heavy industry, and over 90% of coal was consumed by power plants, iron & steel plants, cement plants, and large chemical enterprises with relatively high energy efficiencies, leading to elevated ratios of CO₂ to CO in emissions and thereby concentrations. Transportation, particularly gasoline vehicles, is additionally a significant emission source of CO compared to CO₂, and plays important roles in molar ratios of CO₂ to CO. For instance, Y. Wang et al. (2010) found significantly increased ambient CO₂/CO in September 2008 (46.4 ppmv/ppmv) compared to September 2005-2007 (23–29 ppmv/ppmv) in Beijing, resulting mainly from the temporary ban of vehicles for the Beijing Olympic Games and thereby decreased CO emissions. In 2012 the vehicle population in Beijing was 3.5 times that
of Nanjing (NZNBS, 2013). Transportation was estimated to contribute 29%-37% of
anthropogenic CO emissions in Beijing from various studies (MEIC; Zhao et al.,
2013), but the value is much smaller in Nanjing (10%), elevating the molar ratio of
CO₂ to CO in the city.

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

While ground observations can be used as top-down constraints on emissions, we
suggest that a high-resolution emission inventory can also be used to evaluate
observational data. Although detailed local information demonstrably improves
emission estimation, inconsistencies still exist between the city-scale emission
inventory and ground observations of CO at Caochangmen. These inconsistencies
include: 1) the significant increase in correlation coefficients between CO emissions
and ambient concentrations at state-operated monitoring sites when the data at
Caochangmen are excluded (from 0.61 to 0.86), as described in Section 4.2 and
Figure 7(b); and 2) the higher CO₂/CO from observations at Caochangmen than that
from city-scale emissions, which contradicts expectations based on atmospheric
chemistry principles, as described in Section 4.3 and shown in Figure 9. This suggests
the possibility of instrumental or other error reflected in the relatively low CO
concentrations observed at Caochengmen in 2012. Thus we conduct a comparison of
CO concentrations between Caochangmen and another state-operated site, Shanxilu,
for 2012 and 2014. Similar to Caochangmen, Shanxilu is also an urban site, 3.5 km
from Caochangmen. Frequency histograms of hourly CO concentrations at the two
sites for 2012 and 2014 are shown in Figure S9. It can be seen that CO levels at
Caochangmen were significantly lower than those at Shanxilu in 2012 (Figure S9(a))
but the CO levels were quite similar at the two sites in 2014 (Figure S9(b)). Moreover,
a clear difference (~30%) in CO levels between 2012 and 2014 were found at
Caochangmen (Figure S9(c)) but not at Shanxilu (Figure S9(d)). Given the very close
distance and similar characteristics of the two sites, we tentatively assume that there
should not be a significant difference in CO levels between them. Thus we conduct a
sensitivity test by increasing the CO concentrations at Caochangmen by 30% in 2012,
and repeat the assessment of the city-scale emission inventory with the revised CO
dataset. The correlation coefficient between CO emissions and ambient concentrations
at the 9 state-operated sites would be increased substantially, from 0.62 to 0.83. The
ratio of CO₂ to CO in winter from the revised observational data would decrease from
to 86.9 to 66.8, close to and lower than the ratio from the bottom-up city-scale
inventory (76.1), consistent with the expectation that observed CO₂/CO should be
smaller than emissions. 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.
Such data revision is clearly speculative, but encourages further analysis when
observational data for a longer period become available at both sites. The city-scale
emission inventory may thus provide a basis to raise questions about the quality of
local ground observations, which should not be taken for granted.

4.5 Comparison between city and national inventories for certain sources

To further explore the effects of methods and data employed in emission
estimation at city and national levels, we conduct comparisons of emission levels and
spatial distributions between the current inventory and MEIC for given pollutants
from typical sources, including SO₂ from power generation, NOₓ from transportation,
and PM₂.₅ from industry, for 2010 in Nanjing. Our estimates are reallocated to a
resolution of 5×5 km, the same as MEIC, so that spatial correlations between the two
inventories can be quantified.

As shown in Figure 10(a), relatively good correlation in the spatial distributions
of SO₂ emissions from power generation is found for the two inventories, with the R
estimated at 0.74. The result indicates consistency between the emission estimates of
the two studies for large point sources, as might be expected given their shared reliance on relatively transparent, publicly available information on power plants nationwide. Lacking detailed field investigation of individual sources, however, national inventory studies have to rely on standard information for which routine updates or revisions are not guaranteed, and the latest changes in individual plants, including the closure of small power units or relocation of some power plants, cannot be tracked fully or on a timely basis. This is reflected by a number of data points in Figure 10(a) with positive emission values on one axis but zero on the other. Regarding the total emission levels, MEIC is 35% lower than our estimate, attributed mainly to the different SO₂ removal efficiencies of FGD applied in the two studies. Based on the field measurement data that were reported by individual plants and verified by the local environmental protection bureau, the average removal efficiency of FGD for power plants in Nanjing in 2010 is estimated at 66%, lower than the values commonly applied by researchers in national emission assessments (e.g., above 70%, Zhao et al., 2013). The discrepancy reveals the value of site-specific investigation of key parameters influencing emission estimates, including the SO₂-removal rate of FGD.

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

In contrast to the above two cases, little correlation is found between the two estimates in the spatial distribution of PM$_{2.5}$ emissions from industrial sources (Figure 10(c)). Shown in the maps of Figure 10(c) are not only the PM$_{2.5}$ emissions but also the locations of the 20 largest emitting industrial enterprises. A clear discrepancy is observed between the distribution of those sources and emissions from MEIC, while much stronger consistency is found in the current work. Without sufficient information on individual sources, inventories developed at the national level tend to allocate large fractions of emissions into urban regions with relatively high densities of population and/or economic activity, assuming good spatial correlation between emissions and those proxies. Such correlation, however, likely weakens as pollution control in urban regions is implemented because it includes significant relocation of emission sources to suburban or rural areas (a primary element of urban pollution control policy in China). The total PM$_{2.5}$ emissions from industrial sources estimated by MEIC are 50% lower than our estimate, moreover, because: 1) a national emission inventory based on the sector-average levels of controls and emission factors cannot capture atypical, extremely large sources (super emitters); and 2) coal consumption from the official statistics used by MEIC is much lower than the aggregate of individual sources evaluated in the field survey (3.0 versus 5.0 Mt for Nanjing, 2010).

Comparisons and correlation analyses between inventories developed at different spatial scales, therefore, show the advantages of thorough investigation of individual emission sources, particularly for cities with many large industrial enterprises like Nanjing.

### 4.6 Uncertainty assessment of city-scale emission inventory

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.

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

There has been continuing concern about the accuracy and reliability of China’s energy statistics for more than a decade (Sinton, 2001). Statistics from various sources report divergent energy consumption levels for the country, and the choice of activity-level data for emission inventories continues to be debated. For example, China’s total energy use from national statistics has been inconsistent with that
aggregated from provincial statistics, driving considerable differences in national
emission estimates (Akimoto et al., 2006; Guan et al., 2012; Zhao et al., 2013). While
Akimoto et al. (2006) concluded that an emission inventory based on
province-by-province statistics were in better agreement with satellite observations,
Guan et al. (2012) indicated that over-reporting in provincial energy statistics could be
a factor. At the city level, however, there are far fewer evaluations of the accuracy of
energy statistics. We find a clear discrepancy in energy consumption data in statistical
sources for Nanjing: the total coal consumption in 2010 was reported at 27.9 Mt in the
Nanjing Almanac (NJCLCC, 2011), while the value from the Environmental Statistics
was 14% higher, 31.9 Mt. The disparity results mainly from differences in data
collection for small emission sources (enterprises). While data reporting systems and
resulting data quality have been gradually improved for large- and medium-scale
enterprises, many small-scale ones still do not maintain well-documented records on
energy consumption, and the energy use of those enterprises is poorly captured by the
city almanac (personal communications with officials from Nanjing Municipal
Commission of Economy and Information Technology, 2014). Aimed at pollution
control, the environmental statistical system obtains and verifies energy data for each
enterprise through field surveys, and we thus believe that these energy consumption
data are more complete and reliable for emission inventory development. The
uncertainty from such varied statistical sources could be reduced as retirement of
small boilers and/or closure of small enterprises increases. Although the Nanjing
Almanac stopped reporting coal consumption for the city after 2010, the
Environmental Statistics indicates that the combined share of coal consumption by
large- and medium-sized sources increased from 84% in 2010 to 91% in 2012,
attributed to closure of small enterprises reporting highly uncertain energy data during
the period.

Besides problems in the energy data, uncertainty in the city-scale emission
inventory can also result from lack of information on certain industrial sectors in the
city statistics. If field surveys of individual sources cannot be conducted due to labor
or time constraints, emissions have to be estimated by downscaling national or
provincial estimates. To evaluate the resulting uncertainty, air pollutant emissions
from non-ferrous metal smelting and the production of brick and lime in Nanjing 2012
are recalculated by the downscaling provincial estimates method (method B). In this
method, emissions in Jiangsu province are first calculated based on the provincial
statistics and provincial average levels of emission control. Emissions in Nanjing are
then obtained according to Nanjing’s fraction of certain proxy (industrial GDP in this
case) out of the whole province. The results are compared with those based on
detailed source investigations (method A). Shown in Table 3 are the product output
(activity level) and pollutant emissions estimated by methods A and B. The activity
levels estimated from provincial-level information are much higher than the actual
industrial production aggregated from individual plants, suggesting downscaling
produces emission overestimates. For example, gaseous pollutant emissions
calculated with method B are 2, 10, and 30 times larger than those produced by
method A for brick, lime, and copper production, respectively. For PM emissions, the
discrepancies in emissions between the two methods are smaller, attributed partly to
the compensating effects of divergent removal efficiencies of dust collectors applied
in the two methods, obtained either from plant-by-plant surveys (method A) or from
national or provincial average levels (method B). The differences are believed to
reflect disparities in the considerable fractions of total emissions from OIN (i.e.,
industrial sources excluding iron & steel, cement, and chemical plants, for which
information is relatively clear, as defined in Section 2.1), specifically 6%, 22%, 15%,
and 24% of SO₂, NOₓ, PM₂.₅, and CO for lime production, as shown in Table 3. The
results suggest relatively large uncertainties in city-level emission estimates lacking
sufficient individual source information. In this case, moreover, the overestimates in
Nanjing’s emissions from downscaling provincial emissions would inevitably lead to
underestimates for other cities within the province, weakening understanding of
emission sources and the quantitative basis of regional control policies.

5 POLICY IMPLICATIONS

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

Substantial efforts have been undertaken in specific Chinese sectors to achieve national targets in both energy conservation and emission reduction (Zhao et al., 2013). Under the air pollution control measures, clear benefits in emission abatement, particularly in the power and transportation sectors, are found for Nanjing from 2010 to 2012, a relatively short period. In the power sector, electricity generation increased by 58% during 2010-2012 while that specifically from coal-fired plants grew by 47%, reflecting the switch of coal to gas combustion and other diversification of power generation in the city. Meanwhile, coal consumption of the power sector increased by only 25%, much slower than the resulting electricity generation, reflecting improved energy efficiency due to replacement of small and old power units with larger and more energy-efficient ones. As shown in Figure S10(a) in the supplement, the capacity share of large units (above 300 MW) increased from 72% in 2010 to 78% in 2012 while that of small ones (below 100 MW) decreased from 20% to 16%. The penetration of large units raised as well the use of APCD for SO₂, NOₓ, and PM, leading to significant reduction of emission factors by 30%, 23%, and 22%, respectively. The decrease in emission factors can also be seen for vehicles. With implementation of staged emission standards for new vehicles from 2010 to 2012, the emission factors of SO₂, NOₓ, CO, and VOCs are estimated to have declined by 66%, 33%, 34%, and 37% for gasoline vehicles (Figure S10(b)), those of NOₓ, CO, and VOCs by 12%, 13%, and 24% for diesel vehicles (Figure S10(c)), and those of CO and VOCs by 25% and 34% for motorcycles (Figure S10(d)), respectively. The SO₂, CO, and VOCs emissions from on-road transportation decreased by 39%, 11%, and
27%, respectively, while the vehicle population increased by 27% in the city over the three years.

The benefits of emission control on air quality can be partly confirmed by comparisons of changes in emissions and ambient concentrations. During August 16-24, 2013 when the 2nd Asian Youth Games (AYG) were held in Nanjing, a series of extra emission controls measures were undertaken by the government to improve air quality for the Games. Those measures included increasing use of low-sulfur coal at power plants, closing small factories with relatively large pollutant emissions, stopping construction in some regions, and restricting traffic. Taking these extra measures into account, the emissions of SO$_2$, NO$_X$, PM$_{2.5}$, PM$_{10}$, and CO over August 16-24, 2013 are estimated to have declined 23%, 31%, 21%, 14%, and 33%, respectively, compared to those in the same period in 2012, based on the monthly distributions described in Section 3.2 (see Table S5 in the supplement). Correspondingly, the daily average concentrations for those pollutants in Nanjing during the AYG period were found to decline by 22%, 27%, 10%, 5%, and 22%, respectively, compared to the same period in 2012 (Yu et al., 2014). Although changes in other factors including meteorological conditions also influenced air quality, the consistency between the reduced emissions and concentrations suggests that local emission abatement played a primary role in the air quality improvement.

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

For cities with intensive, heavily polluting industries like Nanjing, large point sources with significant energy consumption and/or industrial production are estimated to dominate the levels and spatial distribution of emissions of the city. As shown in Figure 3, the areas with high emission densities in Nanjing are in good agreement with geographical locations of point sources for all pollutants. The ten largest point sources of SO$_2$ emissions are estimated to account for 54% of total
emissions in the city (Figure 2(a)), and the analogous number for NOX is 43% (Figure 2(b)). For PM$_{2.5}$, as shown in Figure 2(c), the ten largest sources are estimated to be responsible for 75% of total primary emissions in Nanjing (excluding construction and road dust). In particular, extremely high emissions are found for iron & steel plants, resulting mainly from the high production of steel and reliance on wet scrubbers with relatively low removal efficiencies (annual average of 85%) in the exhaust streams of basic oxygen furnaces. Similarly, the ten largest refineries and chemical plants shown in Figure 2(d) are responsible for 52% of VOC emissions in Nanjing. The dominant roles of these big sources on emission levels and spatial distributions indicate that careful investigation and analysis of source-specific parameters relevant to emissions from these super emitters (e.g., removal efficiency of APCDs) are particularly crucial to the reliability of city-scale emission inventories.

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

With updated methods and substantial new data on local emission sources, a city-scale emission inventory of air pollutants and CO$_2$ is developed for Nanjing for three years, 2010-2012. Through plant-by-plant onsite surveys, emission factors, spatial and temporal emission distributions, and estimates of total emissions for major sources (power, cement, iron & steel, and refineries and chemical plants) are especially improved. Emissions in the city are dominated by large point sources, or super emitters. Despite large increases in energy consumption and industrial production, the emissions of most concerned pollutants were largely stable during the period, particularly SO$_2$ and NO$_X$, attributed to increased use and air pollutant removal rates of APCDs under national policies of air pollution control. The current estimates are consistent with the inter-annual variability of NO$_2$ VCD observed from OMI. The improvement of emission estimates by city-scale assessment is further indicated by analyses of spatial correlations with observations by satellite (for NO$_X$) and ground stations (for SO$_2$, NO$_X$, and CO), as well as by top-down constraints (BC/CO, OC/EC, and CO$_2$/CO) provided by ground-based observations. Analyses of bottom-up emission inventories, moreover, can identify possible errors in observational datasets, encouraging further investigation.

Limitations remain in the current work. First, some available and potentially valuable information cannot yet be fully exploited to improve emission estimates. CEMS data help to determine the time distribution of emissions, for example, but are currently less useful for estimating absolute emission levels, due to incompleteness and systematic errors in relevant parameters (e.g., flue gas flow rate). Second, since emission factors for some sources are still based on provincial or national assessments due to lack of local information, the uncertainties of the city-scale emission inventory have not yet been systematically quantified. In particular, the degree of uncertainty in the city-scale inventory compared to that of national ones remains unknown. Finally,
it is currently difficult to assess emissions of some species believed to have high emission uncertainty, e.g., VOC and NH₃, due to lack of sufficient instrumental observations. More field measurements of both emissions and ambient levels of these species are thus recommended in the future.

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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 SO$_2$, NO$_X$, CO, VOCs, NH$_3$, PM$_{2.5}$, PM$_{10}$, TSP, and CO$_2$ 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) SO$_2$; (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 NO$_2$ 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 NO$_2$ 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 NO$_2$ 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) SO$_2$ and NO$_X$/NO$_2$; (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 CO$_2$ and CO concentrations at Caochangmen site and the emission ratios of CO$_2$ to CO from bottom-up inventories for Nanjing, 2012. The wintertime concentrations with CO between the 30$^{th}$ and 90$^{th}$ 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) SO$_2$ from power generation, (b) NO$_X$ from transportation, and (c) PM$_{2.5}$ from industry for Nanjing, 2010.
### Table 1. The capacity penetrations, average removal efficiencies of APCDs, and flue gas release ratios for key sources in Nanjing.

<table>
<thead>
<tr>
<th>Source</th>
<th>CPP-FGD</th>
<th>CPP -SCR/SNCR</th>
<th>CEM-dust collector(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Penetration</td>
<td>SO(_2) removal efficiency</td>
<td>Penetration</td>
</tr>
<tr>
<td>2010</td>
<td>92.4%</td>
<td>66.0%</td>
<td>43.7%</td>
</tr>
<tr>
<td>2011</td>
<td>97.0%</td>
<td>78.5%</td>
<td>66.6%</td>
</tr>
<tr>
<td>2012</td>
<td>98.3%</td>
<td>81.2%</td>
<td>67.4%</td>
</tr>
<tr>
<td>ISP coke oven</td>
<td>0.5%</td>
<td>1.5%</td>
<td>70.0%</td>
</tr>
<tr>
<td>ISP blast furnace</td>
<td>0.5%</td>
<td>1.5%</td>
<td>70.0%</td>
</tr>
<tr>
<td>ISP sintering-FGD</td>
<td>0.5%</td>
<td>1.5%</td>
<td>70.0%</td>
</tr>
<tr>
<td>ISP pig iron production-fabric filter</td>
<td>0.5%</td>
<td>1.5%</td>
<td>70.0%</td>
</tr>
<tr>
<td>ISP steelmaking- dust collector(^c)</td>
<td>0.5%</td>
<td>1.5%</td>
<td>70.0%</td>
</tr>
</tbody>
</table>

\(^a\) 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.

<table>
<thead>
<tr>
<th>Season</th>
<th>Avg. BC $^a$ (μgm$^{-3}$)</th>
<th>Avg. CO $^a$ (ppbv)</th>
<th>Avg. BC $^b$ (μgm$^{-3}$)</th>
<th>Avg. CO $^b$ (ppbv)</th>
<th>BC/CO $^a$ (μgm$^{-3}$ ppbv$^{-1}$)</th>
<th>BC/CO $^b$ (μgm$^{-3}$ ppbv$^{-1}$)</th>
<th>BC/CO $^c$E,top-down (μgm$^{-3}$ ppbv$^{-1}$)</th>
<th>BC/CO $^c$E,bottom-up (μgm$^{-3}$ ppbv$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spring</td>
<td>2.946</td>
<td>661.3</td>
<td>3.009</td>
<td>684.9</td>
<td>0.0070</td>
<td>0.0072</td>
<td>0.0082</td>
<td>0.0101</td>
</tr>
<tr>
<td>Summer</td>
<td>2.644</td>
<td>490.3</td>
<td>3.000</td>
<td>491.0</td>
<td>0.0083</td>
<td>0.0085</td>
<td>0.0097</td>
<td>0.0096</td>
</tr>
<tr>
<td>Autumn</td>
<td>4.206</td>
<td>619.6</td>
<td>3.822</td>
<td>627.1</td>
<td>0.0081</td>
<td>0.0081</td>
<td>0.0092</td>
<td>0.0095</td>
</tr>
<tr>
<td>Winter</td>
<td>3.007</td>
<td>615.0</td>
<td>3.068</td>
<td>637.7</td>
<td>0.0051</td>
<td>0.0060</td>
<td>0.0068</td>
<td>0.0096</td>
</tr>
<tr>
<td>Overall</td>
<td>3.156</td>
<td>588.0</td>
<td>3.264</td>
<td>600.5</td>
<td>0.0071</td>
<td>0.0074</td>
<td>0.0084</td>
<td>0.0097</td>
</tr>
</tbody>
</table>

$^a$ 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.

<table>
<thead>
<tr>
<th>Production</th>
<th>Method A</th>
<th>Method B</th>
<th>SO₂ emissions</th>
<th>NOₓ emissions</th>
<th>PM₂.₅ emissions</th>
<th>CO emissions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>B/A</td>
<td>B/A</td>
<td>B/A</td>
<td>B/A</td>
</tr>
<tr>
<td>Brick</td>
<td>14</td>
<td>29</td>
<td>2.0</td>
<td>10%</td>
<td>2.0</td>
<td>13%</td>
</tr>
<tr>
<td>Lime</td>
<td>207</td>
<td>2050</td>
<td>9.9</td>
<td>6%</td>
<td>9.9</td>
<td>24%</td>
</tr>
<tr>
<td>Copper</td>
<td>1.3</td>
<td>39</td>
<td>31.1</td>
<td>24%</td>
<td>3.6</td>
<td>13%</td>
</tr>
</tbody>
</table>

*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) Emissions (Gg) over the years 2010, 2011, and 2012 for various emissions:
- NH3
- OCS
- SO2
- NOx
- CO/10
- VOCs
- PM_{2.5}
- PM_{10}
- TSP
- CO2/1000
- BC
- OC

(b) Comparison of emissions data from different sources for 2010:
- Fu et al., 2013
- MEIC
- A
- B
Figure 2

(a) SO₂

(b) NOₓ

(c) PM₂.₅

(d) VOC
Figure 3

Fractions of emissions from key sources (CPP, CEM, ISP and RCP)
Figure 4

★ NO\textsubscript{x} emissions in Nanjing
Curves: NO\textsubscript{2} VCD from OMI for different areas

- Red: Shanghai
- Black: Nanjing
- Cyan: Rectangular area include Nanjing
- Blue: Shanghai, Jiangsu, Zhejiang & Anhui
Figure 5

(a) Emissions: This study
(b) VCD from OMI
(c) Emissions: MEIC
Figure 6

(a) Emissions (Gg) vs. OMI (10^{15} \text{mol/cm}^2)
- MEIC: Slope=1.284 R=0.408
- This study: Slope=1.374 R=0.450

(b) R vs. Removed numbers
- MEIC
- This study: Slope=0.405 R=0.436

(c) Emissions (Gg) vs. OMI (10^{15} \text{mol/cm}^2)
- MEIC: Slope=0.030 R=0.085
- This study: Slope=0.405 R=0.436
Figure 7

(a) Linear fit of SO$_2$: $R = 0.58$

(b) Linear fit of CO (all data): $R = 0.61$
Linear fit of CO (excluding Caochangmen site): $R = 0.86$
Excluding the influence of wet deposition of BC

Excluding the influence of all the atmospheric processes

Daily precipitation=0mm

Daily precipitation>0mm

The original observation

Slope=0.00835

Slope=0.00735

Slope=0.00709
Figure 9

- Emissions - This study (2012)
- Emissions - MEIC (2010)
- Observation (30%<CO<95%)

- CO (ppm)
- CO₂ (ppm)

- Slope=52.8
- Slope=86.9
- Slope=76.1

- Observation (30%<CO<95%)
Figure 10

(a) Power plant: SO$_2$

Slope=1.066, R=0.738

(b) Transportation: NO$_X$

Slope=0.559, R=0.652

(c) Industry: PM$_{2.5}$

Slope=0.327, R=0.335

Slope=0.149, R=0.032