

Dear editor,

We are very grateful to you and reviewers for the constructive comments. We respectfully submit our revised manuscript. In our revised manuscript, we addressed all comments raised by the reviewers. Our point-by-point responses to the reviewers' comments are listed below in yellow color. All changes in our manuscript are also labeled in yellow.

As concluded by the reviewers, "The present paper is a timely study on using a top-down approach for estimating benzene and toluene emissions in Pearl River Delta (PRD) and Hong Kong, China", and "it is quite encouraging to note the use of a top-down approach to compare with the existing bottom-up emission estimates of benzene and toluene". This paper conveys important information about the important pollutants in China. In particular, this paper also suggests the need for more measurements to better constrain these emissions.

This manuscript has NOT been published or is under consideration for publication elsewhere.

Thank you very much for your consideration.

Please contact myself via e-mail fangxk@mit.edu or +1-6179559144.

Sincerely,

Xuekun Fang

Center for Global Change Science, Massachusetts Institute of Technology, 77 Massachusetts Ave., Cambridge, MA 02139, United States

Anonymous Referee #1

Received and published: 27 September 2015

General comments

This paper provides estimates of Benzene and Toluene for the Pearl Delta Region and Hong Kong in China, using an inversion method. To the author's and my knowledge, these are the first top-down estimates produced for this region. The author uses data from two sites in this study: data from the Heshan site was used within the inversion, whereas data from the Tai Mo Shan site were used for model validation. Emission estimates were made for the month of November 2010. Estimates were compared to various bottom-up estimates for this month and also for annual estimates. I would recommend this paper for publishing once to comments below have been addressed. The paper is well structured and written clearly. Some figures are too small to be able to see the details discussed in the paper however. More detail about the uncertainties associated with the setup and with the emission results are needed. This study could be strengthened further with an additional discussion into where the bottom-up inventories could be limited / inaccurate (see comments below) – if this information is available to the author.

Response:

In our revised manuscript, the figures have been enlarged and made clearer, especially the Figure 1.

More detail about the uncertainties associated with the setup and with the emission results have been added, e.g., "The a posteriori uncertainty of the emissions in each grid cell was calculated as described by Seibert et al. (2011), and the uncertainty reduction in each grid cell represents the difference (as a percentage) between the a posteriori and priori emission uncertainties in the corresponding grid cell" in the section 2.3.

As for the "inventories could be limited / inaccurate", right now, it is hard to say "which sources may be incorrectly", mainly because the activity data, emission factors, source profile data behind the bottom-up estimates are not shown. Thus, we cannot say which source is incorrect for sure. Nevertheless, our study gives the light that bottom-up estimates need to be improved/investigated.

Specific comments

Page 24842 Lines 15-17: Are the minor sources for both benzene and toluene or just toluene? I think this just needs to be made clearer.

Response: They are for both benzene and toluene, according to the study by Ou et al. (2015). In our revised manuscript, to be clearer, we have changed to "while minor sources for both benzene and toluene include stationary combustion, gasoline evaporation, biomass burning, etc. (Ou et al., 2015)"

Page 24843-4 Section 2.1: I would describe both sites using m.a.s.l as well as describing that the Heshan site is 60 m.a.g.l. It is easier to understand the differences between the two sites. Is the TMS site also rural?

Response: We agree with the comments. In our revised manuscript, we have added “; ~100 m above sea level” in the section. The TMS site is at an elevation of 640 m above sea level and rural.

Page 24844 Section 2.2: I think the relationship between the FELXPART model and how emission sensitivities are produced needs to be described in further detail here. Otherwise, it’s difficult for readers to understand how this is produced. For example, how do particles being measured backwards in time, driven by meteorological data, produce the emissions sensitivities with units $\text{s g}^{-1} \text{m}^2$? I realise this is explained in Stohl’s paper but this is a key part to understanding how your modelled observations are synthesised and should therefore be explained within this paper.

Response: In our revised manuscript, we have added “In FLEXPART, the trajectories of tracer particles are calculated using the mean winds interpolated from the analysis fields plus random motions representing turbulence (Stohl and Thomson, 1999). The emission sensitivity value in a particular grid cell is proportional to the particle residence time in that cell (Seibert and Frank, 2004). Residence time is specifically for the layer from the surface up to a specified height in the planetary boundary layer (100 m used by this study and previous studies, e.g., Stohl et al. (2009))” in section 2.2.

Page 24844 Lines 22-23: Is there any particular reason why you chose a RMSE cost function? How are modelling uncertainties incorporated into this cost function?

Response: Observation-model mismatch errors (including transport model errors) are determined as the root mean square error (RMSE) of the model-observation mismatch (Stohl et al., 2009; Stohl et al., 2010)

Page 24848 Line 25: ‘between the simulations and the observations’ – do you mean the agreement between the a posteriori simulations and the observations are better than the a priori simulations and the observations? If yes, make this clearer.

Response: Yes. According to this suggestion, in our revised manuscript, we have added “the agreement between the a posteriori simulations and the observations are better than the a priori simulations and the observations” into this sentence.

Page 24849 Line 13: The term ‘Uncertainty reduction’ should be further explained to how these values are calculated. How are uncertainties calculated within this inversion model?

Response: Thanks for this suggestion. In our revised manuscript, we have added “A posteriori uncertainty of the emissions in each grid cell was calculated as described by Seibert et al. (2011), and uncertain reduction in each grid cell represents the difference (%) between the a posteriori and priori emission uncertainties in the corresponding grid cell”.

Page 24850 Lines 10-21: Out of interest, was there a particular reason why the Heshan site data was used in the inversion and the Mt. TMS was chosen to verify? Did you try the inversion the other way around and compare the a posteriori emissions produced? Did you try a 2-site inversion? If you have specific reasons for doing it this way, I think the readers would be interested in these reasons.

Response: We also tried a 2-site inversion from which we found that the a posteriori benzene emissions for PRD were 4.6 Gg/month, compared to the 4.0 Gg/month from the only-Heshan inversion (used in our study). Thus, the difference is only about 15% which is within the a posteriori uncertainty. The reasons why Mt. TMS was not used as well in the inversion are those 1) measurements at two stations are calibrated in difference scales so that using two data sets in one inversion is not a scientific approach, according to the review paper by Weiss and Prinn (2011), 2) the number of measurement data at the TMS site (totally 75 in Nov. 2010) is much less than that at Heshan site (totally 419), which means limited help from adding measurement data at the TMS site into inversion, and 3) TMS is relatively close to central Urban Hong Kong (~7 km given by Guo et al. (2013)) so that the TMS is likely of a high risk to be influenced by relative local sources.

In our revised manuscript, we have added these sentences in section 2.1.

Page 24853 Line 6: Suggested re-phrase – ‘have not changed much’ to ‘have remained relatively stable’

Response: We have incorporated this change in our revised manuscript.

Page 24853 Paragraphs 2-3: A suggestion, if you know how the bottom-up inventories differ to each other you could draw some potentially useful comments about which sources may be incorrectly represented.

Response: Right now, it is hard to say “which sources may be incorrectly”, mainly because the activity data, emission factors, source profile data behind the bottom-up estimates are not shown. Thus, we cannot say which source is incorrect for sure. Nevertheless, our study gives the light that bottom-up estimates need to be improved/investigated.

Page 24854 Section 3.6: Would be worth also suggesting multiple site inversion analysis, with more thorough measurement data, to better constrain the inversion. For example, many US and global studies have incorporated more than one measurement site within their analysis.

Response: Yes, we agree with this suggestion. In our revised manuscript, we have changed to “then the major emission sources in PRD and HK regions could be “viewed” from different angles (multiple-site inversion)”. Given the short lifetime of toluene, to optimize fluxes over a region, the sites need to be sufficiently close so that they receive a significant signal, e.g. sites in the US probably would not help optimizing fluxes in China.

Figure 1: I think the place labels are too small and should be made bigger, especially as you refer to these place names throughout the paper. The units of the scale are also small and should maybe be increased to the same size as the equivalent units in Figure 2.

Response: We have incorporated these changes in our revised manuscript.

Figure 3: The two maps under the time series are too small to read the text clearly.

Response: In the ACPD, the figures are small. They are fine to read in a relative large figure, if this paper is finally published in ACP.

Figure 6: The figures here are too small to look at in detail. I would suggest orientating them differently. This comment applies to the equivalent Toluene figure in the supplementary material.

Response: In the ACPD, the figures are small. They are fine to read in a relative large figure, if this paper is finally published in ACP.

Figure 8: The arrows needs to be explained in the figure caption. Explain how their gradients are determined and what they are showing. If they are not scientifically determined (i.e. through regression) then I do not think they add much to the figure and would suggest removing them.

Response: In our revised manuscript, we have added an explanation of arrows in Figure 8.

Technical corrections

Title: 'in Pearl River Delta' to 'in the Pearl River Delta'

Response: We have incorporated this change in our revised manuscript.

Page 24841 Line 6: 'in Pearl River Delta' to 'in the Pearl River Delta'

Response: We have incorporated this change in our revised manuscript.

Page 24842 Line 7: 'Guangzhou, Shenzen in PDR, and Hong Kong are' to 'Guangzhou and Shenzen, located in the PRD, and Hong Kong are' : : Otherwise it reads like Guangzhou is in a separate regions to the PRD and HK.

Response: We have incorporated this change in our revised manuscript.

Page 24842 Line 19: add a comma (,) after 'For example'

Response: We have incorporated this change in our revised manuscript.

Page 24842 Line 14: 'In PRD' to 'In the PRD'

Response: We have incorporated this change in our revised manuscript.

Page 24842 Line 11: delete 'the most' as it's written twice

Response: We have incorporated this change in our revised manuscript.

Page 24843 Line 15: 'period at Heshan site' to 'period at the Heshan site'

Response: We have incorporated this change in our revised manuscript.

Page 24849 Line 9: 'of PRD' to 'of the PRD'

Response: We have incorporated this change in our revised manuscript.

Page 24849 Line 12: 'of PRD' to 'of the PRD'

Response: We have incorporated this change in our revised manuscript.

Page 24850 Line 1: 'in PRD' to 'in the PRD'

Response: We have incorporated this change in our revised manuscript.

Page 24850 Line 3: 'for PRD' to 'for the PRD'

Response: We have incorporated this change in our revised manuscript.

Page 24852 Line 1: 'in PRD' to 'in the PRD'

Response: We have incorporated this change in our revised manuscript.

Page 24852 Line 10: 'in PRD' to 'in the PRD'

Response: We have incorporated this change in our revised manuscript.

Page 24853 Line 18: 'in PRD' to 'in the PRD'

Response: We have incorporated this change in our revised manuscript.

Page 24853 Line 22: 'in PRD' to 'in the PRD'

Response: We have incorporated this change in our revised manuscript.

Page 24854 Line 5: 'in PRD' to 'in the PRD'

Response: We have incorporated this change in our revised manuscript.

Page 24854 Line 17: Remove 'in the future' It is not needed when using the term 'are urgently needed'

Response: We have incorporated this change in our revised manuscript.

Page 24854 Line 19: 'in PRD' to 'in the PRD'

Response: We have incorporated this change in our revised manuscript.

Page 24854 Line 21: 'in PRD' to 'in the PRD' and 'of PRD' to 'of the PRD'

Response: We have incorporated this change in our revised manuscript.

Page 24855 Line 6: 'in PRD' to 'in the PRD'

Response: We have incorporated this change in our revised manuscript.

Page 24855 Line 10: 'in PRD' to 'in the PRD'

Response: We have incorporated this change in our revised manuscript.

Page 24868 Line 6: 'for PRD' to 'for the PRD' and 'within PRD' to 'within the PRD' (Figure 6)

Response: We have incorporated this change in our revised manuscript.

Reference:

- Guo, H., Ling, Z. H., Cheung, K., Jiang, F., Wang, D. W., Simpson, I. J., Barletta, B., Meinardi, S., Wang, T. J., Wang, X. M., Saunders, S. M., and Blake, D. R.: Characterization of photochemical pollution at different elevations in mountainous areas in Hong Kong, *Atmos. Chem. Phys.*, 13, 3881-3898, 10.5194/acp-13-3881-2013, 2013.
- Ou, J., Zheng, J., Li, R., Huang, X., Zhong, Z., Zhong, L., and Lin, H.: Speciated OVOC and VOC emission inventories and their implications for reactivity-based ozone control strategy in the Pearl River Delta region, China, *Sci. Total Environ.*, 530-531, 393-402, 2015.
- Seibert, P., and Frank, A.: Source-receptor matrix calculation with a Lagrangian particle dispersion model in backward mode, 4, 51-63, 10.5194/acp-4-51-2004, 2004.
- Seibert, P., Kristiansen, N. I., Richter, A., Eckhardt, S., Prata, A. J., and Stohl, A.: Uncertainties in the inverse modelling of sulphur dioxide eruption profiles, *Geomat. Nat. Hazards Risk*, 2, 201-216, 10.1080/19475705.2011.590533, 2011.
- Stohl, A., and Thomson, D.: A Density Correction for Lagrangian Particle Dispersion Models, *Boundary-Layer Meteorology*, 90, 155-167, 10.1023/A:1001741110696, 1999.
- Stohl, A., Seibert, P., Arduini, J., Eckhardt, S., Fraser, P., Grealley, B. R., Lunder, C., Maione, M., Mühle, J., O'Doherty, S., Prinn, R. G., Reimann, S., Saito, T., Schmidbauer, N., Simmonds, P. G., Vollmer, M. K., Weiss, R. F., and Yokouchi, Y.: An analytical inversion method for determining regional and global emissions of greenhouse gases: Sensitivity studies and application to halocarbons, *Atmos. Chem. Phys.*, 9, 1597-1620, 2009.
- Stohl, A., Kim, J., Li, S., O'Doherty, S., Mühle, J., Salameh, P. K., Saito, T., Vollmer, M. K., Wan, D., Weiss, R. F., Yao, B., Yokouchi, Y., and Zhou, L. X.: Hydrochlorofluorocarbon and hydrofluorocarbon emissions in East Asia determined by inverse modeling, *Atmos. Chem. Phys.*, 10, 3545-3560, 2010.
- Weiss, R. F., and Prinn, R. G.: Quantifying greenhouse-gas emissions from atmospheric measurements: a critical reality check for climate legislation, 369, 1925-1942, 10.1098/rsta.2011.0006, 2011.

Anonymous Referee #2

Received and published: 29 September 2015

General Comments The present paper is a timely study on using a top-down approach for estimating benzene and toluene emissions in Pearl River Delta (PRD) and Hong Kong, China. In general PRD is currently suffering from high ozone levels. Clearly, effective and robust control policy formulation very often relies on good emission inventory and supported by associated modeling work on control scenarios. Unfortunately, the so-called “accurate emission inventory” does not exist and we may never know the “true value”. Nevertheless, more independent work on estimating VOC emissions will certainly help and reduce uncertainty. Therefore, it is quite encouraging to note the use of a top-down approach to compare with the existing bottom-up emission estimates of benzene and toluene. Hopefully, this kind of work will shed more light on the effective evidence-base control policy formulation and useful for decision makers when tackling the regional ozone problem.

Specific Comments 1. In the abstract and introduction sections, there is a lack of analysis on the significance of the present work and its implications in terms of control policy formulation. For example, in the abstract section the discrepancy issue articulated in section 3.5 and the conclusion section was not mentioned. RE: page 24853 (lines 24 to 28). In other words, the authors should point out the implications of underestimating the emissions of these highly reactive aromatic compounds on the control of vehicular emissions and/or evaporative loss and solvent emissions. Also, the implications on underestimating these aromatic compounds on ozone formation should be highlighted.

Response: Thank you for reminding us about the significance of the present work and its implications in terms of control policy formulation. The main topic this study wants to present is the difference between the top-down and bottom-up estimates in terms of either the total emissions or spatial distribution. Readers from various fields will pick up the information they want. Based on this study, conclusion cannot be drawn on “implications of underestimating the emissions of these highly reactive aromatic compounds the control of vehicular emissions and/or evaporative loss and solvent emissions”, since the inversion could not distinguish emissions at sector level.

2. Fig 8, the use of yellow color as a label/legend may not reproduce well in black & white copying. Better annotation is recommended.

Response: The symbols in Figure 8 are not the same, so they are suitable even in black & white copying

3. RE: page 24847, lines 3 to 6. “in agreement with previous studies, mixing ratio levels of benzene and toluene in PRD region are overall higher than those in Hong Kong, which is most likely due to the fact that Hong Kong often receives clean air masses from the ocean.”. Clarification on the root cause of

finding higher levels of toluene and benzene in PRD when comparing with HK should be made here. First of all, Hong Kong is part of PRD, so when Hong Kong receives clean air masses from the ocean so do PRD. Therefore I would suggest the key issue here is about emissions from high emitting areas. Furthermore, the Heshan site in PRD is located downwind of Guangzhou and other rapidly developing cities. High VOC levels are therefore reflected in the measurement results.

Response: We agree with the comments. Hong Kong can directly receive clean air masses from the ocean, while the air masses have to cross over some land (emission sources) before reaching central PRD. We agree that emission strength in PRD is higher than that in Hong Kong, which contributes to the higher VOC concentrations in PRD than in Hong Kong. Thus, in our revised manuscript, we have changed to “which is in part due to the fact that Hong Kong often receives clean air masses from over the ocean and that emissions in Hong Kong are lower than in the PRD”. By the way, in this study and many previous studies, Hong Kong is not defined as part of PRD, though in some studies, Hong Kong is.

Anonymous Referee #3

The authors have conducted inverse modeling to estimate benzene and toluene emissions in PRD and HK for November 2010. The inversion was based on the PRIDE---PRD2010 campaign. They extrapolate the November estimate to the annual and compare with existing bottom---up estimates. The paper is well written and considering the limited number of inverse modeling studies focused on these species, I recommend the publication after some minor revisions. I have several specific comments, followed by some minor ones.

Specific comments

Echoing one of the other reviewers, why one measurement site (Heshan) was chosen for inversion, while the other one (Mt. Tai Mo Shan) was used for validation needs to be explained better in the text. I also feel that what is suggested by this reviewer (including both measurements as well as using only the Mt. Tai Mo Shan measurement in inversion) would be extremely helpful for the reader.

Response: We also tried a 2-site inversion, and we found the a posteriori benzene emissions for PRD was 4.6 Gg/month, compared to the 4.0 Gg/month from the only-Heshan inversion. Thus, the difference is only about 15% which is within the a posteriori uncertainty. The reasons why Mt. TMS was not used as well in the inversion are those 1) measurements at two stations are calibrated in difference scales so that using two data sets in one inversion is not a scientific approach, according to the review paper by Weiss and Prinn (2011), 2) the number of measurement data at TMS (totally 75 in Nov. 2010) is much less than that at Heshan (totally 419), which means limited help from adding TMS station into inversion, and 3) TMS is relatively close to central Urban Hong Kong (~7 km given by Guo et al. (2013)) so that the TMS is likely of a high risk to be influenced by relative local sources.

Authors have used the term “RCP 3PD”, but in my opinion this scenario is better known as “RCP 2.6”. I would recommend using RCP 2.6 instead of RCP 3PD in the paper. I believe the authors should also explain why they have chosen this specific scenario versus others (RCP 4.5, etc.). It would also be interesting to check if using different emissions scenarios as their prior has any impacts on posterior estimates, especially because background mixing ratios are considered to be zero. For some species, RCP 2.6 provides the highest emissions estimates in 2010 and that might be the case for the species considered here.

Response:

We agree that “RCP 2.6” is better known than “RCP 3PD”, although “RCP 3PD” is also a correct way to call this inventory. Thus, in our revised manuscript, we have changed it to “RCP 2.6” in texts and figures. Yes, there are four scenarios in RCPs. We just chose one of them. The choice of RCP specific scenarios influences our inversion only marginally, since the RCP emissions were only used as emissions outside of China (emissions in PRD and rest of China use MEIC v1.2 and Yin et al. (2015)). Benzene and toluene emissions outside of China could hardly reach observation stations in our study.

In terms of the prior emissions, why did the authors use the averaged emissions using MEIC v1.2 and Yin et al. (2015) for toluene for the PRD region? Did the posterior emissions change much if only MEIC v1.2 was used instead? And why was this approach not used for benzene? I feel that a similar type of sensitivity analysis using different emissions inventories might be more interesting, in addition to changing simulation length and chemical loss as currently done in the paper.

Response: According to the comments, we tested the impact of the choice of a priori emissions. A posteriori emissions for PRD from inversions using MEIC v1.2, Yin et al. (2015) and the averaged emissions using MEIC v1.2 and Yin et al. (2015), respectively, were 13.8 Gg/month, 11.1 Gg/month and 12.0 Gg/month. Thus the difference is less than 15% which is not a big value and within the a posteriori uncertainty reported in this study. We also did the tests for benzene, and we found the difference of a posteriori emissions is about 10% using different a priori emissions. The estimated emissions for toluene by MEIC v1.2 and Yin et al. (2015) are quite different, thus we used the averaged value as the a priori emission; while the estimated emissions for benzene by MEIC v1.2 and Yin et al. (2015) are relatively close, thus we used one of them (MEIC v1.2 used in our study).

I am also curious if the inversion is conducted for the two species together or separately. I would also like to see a better justification as to why 100 and 70% were chosen for prior emissions uncertainty for benzene and toluene, respectively. Also, it would be good to include an equation showing how the posterior uncertainty is calculated.

Response: The inversion is conducted separately for benzene and toluene. As for the a priori uncertainty, we determined it by looking at the variations of different bottom-up estimates for that particular species. For benzene, our priori emissions were 3.1 Gg/month, while the RCP 2.6 was 3.7 Gg/month, Yin et al. (2015) was 4.4 Gg/month, REAS v1.1 was 0.7 Gg/month. Thus, the largest deviation is about $1 - 0.7/3.1 = 80\%$, and then we set the a priori uncertainty as 100%. For toluene, our priori emissions were 11.5 Gg/month, while the RCP 2.6 was 3.6 Gg/month, Yin et al. (2015) was 5.2 Gg/month, REAS v1.1 was 3.8 Gg/month and MEIC v1.2 was 14.9. Thus, the largest deviation is about $1 - 3.6/11.5 = 69\%$, and then we set the a priori uncertainty as 70%.

Authors wrote on p. 24848 “Notice that systematic errors in the simulated chemical loss would lead to smaller errors (i.e., compared to the extreme case of no loss) in the a posteriori emissions retrieved by the inversion,” but I am not sure where I can see this change in the systematic errors.

Response: Systematic errors were not analyzed in our paper and in our revised manuscript, we have deleted this sentence.

The authors mentioned in the introduction that the two major source sectors of benzene and toluene are industry and road transport. Is it possible to assess which emissions estimates need improvement in the bottom-up estimates from your inversion? Is it possible to conduct inversion at the source sector level?

Response: it is not possible to assess the emissions at source sector level, since the emissions estimated by the inversion is at grid cell scale. Emissions from different sector could not be distinguished within one grid cell.

Minor comments

1. l. 11, p. 24842. “the most the most” the most

Response: We have incorporated this change in our revised manuscript.

2. The dark blue color used for PRD is very difficult to see on Figure 1

Response: It is fine for reading.

3. The authors state on p. 24849 that “Figure 4 shows the benzene a priori and a posteriori emission fields, their differences and uncertainty reduction. The a priori fields show that emission hot spots

are located in Guangzhou, Shenzhen and Hong Kong megacities.” I think it would be helpful if you can show these locations on the map.

Response: In our revised manuscript, the cities are labeled in Figure 1 with a larger text font size.

4. Why is the correlation so much worse for toluene compared to benzene?

Response: The reasons are complicated and not clearly known. The reasons may be those 1) toluene has relatively much shorter lifetime and more complicated atmospheric reactions that may not be well simulated by the model, 2) more variations of diurnal and weekday/weekend emissions, 3) some emissions sources not far from the observatory which could not be well distinguished by the 0.25 degree grid cells.

Reference:

- Guo, H., Ling, Z. H., Cheung, K., Jiang, F., Wang, D. W., Simpson, I. J., Barletta, B., Meinardi, S., Wang, T. J., Wang, X. M., Saunders, S. M., and Blake, D. R.: Characterization of photochemical pollution at different elevations in mountainous areas in Hong Kong, *Atmos. Chem. Phys.*, 13, 3881-3898, 10.5194/acp-13-3881-2013, 2013.
- Weiss, R. F., and Prinn, R. G.: Quantifying greenhouse-gas emissions from atmospheric measurements: a critical reality check for climate legislation, 369, 1925-1942, 10.1098/rsta.2011.0006, 2011.

Anonymous Referee #4

Received and published: 24 October 2015

General comments: This paper presents one of the first estimates of benzene and toluene emissions in China using atmospheric measurement data from a rural site in the region and inverse modeling. This paper conveys important information about the toxic pollutants in China. In particular, this paper suggests the need for more measurements to better constrain these emissions.

Specific comments:

Although the result is promising, the authors need to address a few important issues before publication. First, with regard to transport model evaluation, I don't see enough description or result on this. In terms of the methodology, it should be addressed in Section 2.2, but there is no information about potential model biases. The simple question I can ask is how reliable the NCEP meteorology is in this region of China.

This is not about random errors we consider in the inversion. If the transport model is biased, then we get the biased mean estimate for the posterior emissions. The authors need to evaluate the transport model only for less than a month (pretty short period compared to other many studies). I suggest that the authors evaluate the transport model for potential biases (e.g., wind bias, planetary boundary layer height).

Response: It is almost impossible to quantify model biases, unless large-scale atmospheric experiment is carried out to quantify the biases of a model for a specific region and for a specific species. For example, some independent measurement data like radiosondes not used in the assimilation can be used to validate the model simulation. However, this is out of scope of the present study. As indicated by the reviewer, the meteorology datasets may perform different simulation (and inversion) results. Thus we tested the dataset from the European Centre for Medium-Range Weather Forecasts (ECMWF). The a posteriori emissions for PRD are very close when using these two meteo. dataset, e.g. for benzene, 4.0 Gg/month from inversion using CFSR and 4.2 Gg/month from inversion using ECMWF. Although Fang et al. (2014) shows ECMWF data set performed slightly better than the NCEP CFSR dataset for the SF6 simulations in East Asia for Hateruma, Gosan and Cape Ochiishi stations, we found CFSR dataset performed slightly better than the ECMWF dataset in the benzene simulations at the Heshan site. Thus, the CFSR dataset was used in our paper.

Table. Performance of different meteorology datasets for the benzene simulation

A priori benzene emissions	Meteo. datasets	Performance		
		<i>E</i>	<i>B</i>	<i>r</i> ²
MEIC v1.2	CFSR	1.53	0.96	0.20
	ECMWF	1.67	1.09	0.17
	CFSR performed better than ECMWF?	yes	yes	yes
RCP 2.6	CFSR	1.40	0.78	0.20

	ECMWF	1.54	0.85	0.13
	CFSR performed better than ECMWF?	yes	yes	yes

With respect to observation–model mismatch errors, just using the RMSE value of model minus observation is a convenient way, but not a correct way. I assume that “model” in L22 of P24845 means the model prediction for mixing ratios based on the a priori emission. The way inversion works is that the difference between predictions and measurements are minimized in a statistically consistent way with the two error covariance matrices. Thus if the error covariance is not properly defined, then the results are not reliable. What fraction of the observation-model mismatch is from the transport error? Was the background error included in the total mismatch error? If so, what fraction? After inversion, the RMSE is usually reduced compared to that before inversion. If I read the description in Section 2.3 as it is, the authors assign all of the average difference between “model” and observation to the random errors (i.e., the mismatch error). However, the difference between (prior) “model” and observation is also due to the lower or higher emission inventory (used as the a priori emission) than the true emission. Since the detail is not provided here, this is how I interpret L21 - L22). This important issue should be addressed.

Response: Yes, observation–model mismatch errors were defined as RMSE value of model minus observation. It cannot be determined that “What fraction of the observation-model mismatch is from the transport error”. The background was zero, since the 20 days backward simulation could cover all emission sources from which benzene and toluene can be transported to the Heshan site. Thus, the background and its error are zero.

I also wonder how the authors evaluate the uncertainty of the OH simulations from GEOS-Chem. Ideally, this uncertainty should be explicitly estimated and included in the observation–model mismatch errors

Now, with respect to background, the authors set the background to zero. However, the initial values at the domain boundary, which represents the atmospheric background, are not zero. I agree that these background concentrations (which contribute to the receptor) will dissipate in 10 or 20 days. However, what is not clear is how large the modeling domain is. If the authors used 20-day backward simulations to remove the effect of the background, then the back trajectories would have gone outside China. I wonder if the authors used a large enough domain such that the background effect is negligible. From the figures in the paper, the domain is very small, all regional.

Response: It is right that “the back trajectories would have gone outside China”. The modeling domain is globe. Thus, domain is large enough such that the background effect is negligible. The boundary condition is not the space domain but in the time domain. Therefore if the lifetime is \ll 20 days, then the background is probably zero or at least very close to it.

Minor comments:

P24841, L25: too much use of ‘crucial’

Response: In our revised manuscript, 'crucial' has been changed to 'important'.

P24842, L2 - L3: sudden jump in the logic. Why spatial and temporal distribution all of sudden? Is this related to the main conclusion of this study?

Response: it looks not "sudden jump in the logic". In this paragraph, we first introduce the health of benzene and toluene on health and air quality, and then we summary emission information is important to evaluate these impacts.

L11: typo in "the most the most"

Response: We have incorporated this change in our revised manuscript.

P24843, L15: From the perspective of inversion, one day in December would not make a big difference for the less than a month-long dataset. It is weak reasoning that the authors say "Data from 1 December 2010 were not used, since we focused on mixing ratios and emissions in November". There should be a better explanation to not to use the December data (e.g., poor measurement accuracy). The measurements are not enough here.

Response: We agree with that "one day in December would not make a big difference for the less than a month-long dataset". However, for the sake of accuracy, "Data from 1 December 2010 were not used, since we focused on mixing ratios and emissions in November". If we used the data from December as well, the reviewers and readers would argue that the estimated emissions are not only for November but Nov and Dec combined.

Also, in the abstract it says "a rural site". Is it only one site? In Section 2.1, it says "atmospheric measurements of benzene and toluene at two sites were used," It looks like the Mt. TMS site was not used for inversion. The authors need to be clear about this at the beginning of this measurement section.

Response: At the very beginning of the measurement section, we present that "In this study, atmospheric measurements of benzene and toluene at two sites were used, the Heshan site (used for the inversion) and the Mt. Tai Mo Shan (TMS) site (used for validation)".

P24848, L18 - L20. How small? Is there a reference or supporting material?

Response: Systematic errors were not analyzed in our paper and in our revised manuscript, we have deleted this sentence.

Reference:

Fang, X., Thompson, R. L., Saito, T., Yokouchi, Y., Kim, J., Li, S., Kim, K. R., Park, S., Graziosi, F., and Stohl, A.: Sulfur hexafluoride (SF₆) emissions in East Asia determined by inverse modeling, Atmos. Chem. Phys., 14, 4779-4791, 10.5194/acp-14-4779-2014, 2014.

1 Top-down estimates of benzene and toluene emissions in
2 the Pearl River Delta and Hong Kong, China

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21 Abstract

22 Benzene (C_6H_6) and toluene (C_7H_8) are toxic to humans and the environment. They
23 are also important precursors of ground-level ozone and secondary organic aerosols
24 and contribute substantially to severe air pollution in urban areas in China.
25 Discrepancies exist between different bottom-up inventories for benzene and toluene
26 emissions in the Pearl River Delta (PRD) and Hong Kong (HK), which are emission
27 hot spots in China. This study provides top-down estimates of benzene and toluene
28 emissions in the PRD and HK using atmospheric measurement data from a rural site
29 in the area, Heshan, an atmospheric transport model, and an inverse modeling method.
30 The model simulations captured the measured mixing ratios during most pollution
31 episodes. For the PRD and HK, the benzene emissions estimated in this study for
32 2010 were 44 (12–75) Gg yr⁻¹ and 5 (2–7) Gg yr⁻¹ for the PRD and HK, respectively,
33 and the toluene emissions were 131 (44–218) Gg yr⁻¹ and 6 (2–9) Gg yr⁻¹,
34 respectively. Temporal and spatial differences between the inversion estimate and four
35 different bottom-up emission estimates are discussed, and it is proposed that more
36 observations at different sites are urgently needed to better constrain benzene and
37 toluene (and other air pollutant) emissions in the PRD and HK in the future.

1 Introduction

Benzene and toluene, two volatile organic compounds (VOCs), are toxic to humans and the environment. For example, a sufficiently high exposure of toluene will lead to health issues like intra-uterine growth retardation, premature delivery, congenital malformations, and postnatal developmental retardation (Donald et al., 1991). VOCs, including benzene and toluene, are also important precursors of ground-level ozone, which is produced from the reaction between VOCs and NO_x in the presence of sunlight (Xue et al., 2014), and contribute to the formation of secondary organic aerosols (Henze et al., 2008). VOCs emitted from anthropogenic activities are important contributors to severe urban haze pollution in China (Guo et al., 2014). Therefore, information about the spatial and temporal distribution of benzene and toluene emissions is crucial for air quality simulations and predictions, health risk assessments, and emission control policy.

The Pearl River Delta (PRD) and Hong Kong (HK) are located along the coast of southern China, which is one of the most economically developed areas in the country. It is also where the densely populated mega-cities, Guangzhou and Shenzhen (in the PRD) and Hong Kong are located. The PRD and HK regions experience severe air pollution, namely toxic trace gases and particulates, as observed by satellites (e.g. van Donkelaar et al., 2010) and ground-based measurements (e.g. Guo et al., 2009). Toluene and benzene were found to be two of the most abundant VOCs in the PRD (Chan et al., 2006). Toluene and benzene, respectively, had the largest and second

largest emissions of all anthropogenic VOCs in the PRD in 2010 (Ou et al., 2015), which highlights the importance of accurately quantifying these emissions. In the PRD, the two major sources of benzene are industrial processes and road transport, and those of toluene are industrial solvents and road transport, while minor sources for both benzene and toluene include stationary combustion, gasoline evaporation, biomass burning, etc. (Ou et al., 2015).

Although some bottom-up inventories exist for benzene and toluene emissions in the PRD, there are discrepancies among them. For example, for benzene emissions in 2010, the Regional Emission inventory in Asia (REAS) v1.1 reference scenario (from here on referred to as REAS REF v1.1) estimates the emissions to be 8 Gg yr⁻¹ (Ohara et al., 2007), while the Multi-resolution Emission Inventory (MEIC) v1.2 (available at <http://www.meicmodel.org>) estimate is 33 Gg yr⁻¹, the Representative Concentration Pathways Scenario 2.6 (RCP 2.6) estimate is 45 Gg yr⁻¹ (van Vuuren et al., 2007), and the Yin et al. (2015) estimate is 54 Gg yr⁻¹. Thus, estimates of the total emissions vary by a factor of approximately seven. For toluene emissions in 2010, the estimates are also quite different: The RCP 2.6 and REAS v1.1 REF estimates are 44 Gg yr⁻¹ and 46 Gg yr⁻¹, respectively, the Yin et al. (2015) estimate is 64 Gg yr⁻¹, and the MEIC v1.2 estimate is 181 Gg yr⁻¹. Atmospheric-measurement-based estimates are needed to validate benzene and toluene emissions estimated from bottom-up methods. However, to date no top-down estimate is available for PRD and HK.

High-frequency online measurements of VOCs (including benzene and toluene)

were made during the PRIDE-PRD2010 Campaign (Program of Regional Integrated Experiments on Air Quality over Pearl River Delta) during November and December 2010. This study uses these measurement data and an inverse modeling approach to infer benzene and toluene emissions in the PRD and HK. This top-down estimate is important to test and improve the existing bottom-up inventories.

2 Methodology

2.1 Measurement data

In this study, atmospheric measurements of benzene and toluene at two sites were used, the Heshan site (used for the inversion) and the Mt. Tai Mo Shan (TMS) site (used for validation). The Heshan site (112.929 °E, 22.728 °N) is a rural observatory located on the top of a small hill (~60 m above the surrounding terrain; ~100 m above sea level) in Jiangmen (see Figure 1). The measurement period at the Heshan site was from November 11, 2010 to December 1, 2010. Data from December 1, 2010 were not used, since we focused on mixing ratios and emissions in November. Detailed information of the measurement system and procedure can be found in Wang et al. (2014). Here we provide only a brief description. Ambient mixing ratios of VOCs were measured using an online automatic gas chromatograph system equipped with a mass spectrometer and a flame ionization detector (GC-MS/FID). Most C₂-C₅ hydrocarbons were measured by the FID Channel with a porous layer open tubular (PLOT) column, whereas other VOCs, including benzene and toluene, were measured by the Mass Selective Detector (MSD) Channel with a DB-624 column. The time

101 resolution of the VOC measurements was 60 minutes. The detection limits of this
102 system for benzene and toluene are 0.006 ppb and 0.015 ppb, respectively, which are
103 much lower values than the typical benzene and toluene mixing ratio levels of 2 ppb
104 and 6 ppb during the observation period at the Heshan site.

105 The Mt. TMS site (114.118 E, 22.405 N) was not used for the inversion but for
106 validating the emissions derived from the inversions in this study. The sample air inlet
107 at the TMS site was located on the rooftop of a building at Mt. TMS at an elevation of
108 640 m above sea level. A total of 75 canisters of air samples were taken over different
109 times of day and night on November 1–3, 9, and 19–21, 2010. Detailed information on
110 the sampling time schedule can be found in Guo et al. (2013). After sampling, the
111 VOC canister samples were sent to a laboratory at the University of California, Irvine
112 for chemical analysis. Simpson et al. (2010) provide a full description of the
113 analytical system, which uses a multi-column gas chromatograph (GC) with five
114 column-detector combinations. The measurement detection limit of this system for
115 both benzene and toluene is 0.003 ppb, which is much lower than the typical mixing
116 ratio levels of 0.7 ppb for benzene and 1.6 ppb for toluene during the observation
117 period at the Mt. TMS site.

118 The TMS data were not used in the inversion because: 1) The measurements
119 performed at the two stations were calibrated according to different scales, which
120 could cause problems in the inversion (see also Weiss and Prinn (2011)). 2) The
121 number of measurement data at the TMS site (totally 75 in Nov. 2010) is much

smaller than that at the Heshan site (totally 419), which means that the inversion results would anyway be dominated by the Heshan data. 3) TMS is relatively close to central Urban Hong Kong (~7 km; Guo et al., 2013) so that the TMS site might be influenced by local sources and this is not desirable for the inversion. Tests with inversions including TMS data have shown that the PRD benzene emissions would be only ~15% higher from those using Heshan data only, which is within the a posteriori emission uncertainty.

2.2 Model simulations using FLEXPART

The source-receptor relationships (SRRs, often also called “emission sensitivities”, in units of $\text{m}^2 \text{s g}^{-1}$) were calculated using the backwards in time mode of the Lagrangian particle dispersion model, FLEXPART (<http://www.flexpart.eu>) (Stohl et al., 2005; Stohl et al., 1998). The model was driven by hourly meteorological data of $0.5^\circ \times 0.5^\circ$ horizontal resolution and 37 vertical levels from the NCEP Climate Forecast System Reanalysis (CFSR) (available at <http://rda.ucar.edu/datasets/ds093.0/>). During 3-hourly intervals throughout the sampling period, 80,000 virtual particles were released at the site’s location and at the height of the sampling inlet above model ground level, and followed backwards in time for 20 days. In FLEXPART, the trajectories of tracer particles are calculated using the mean winds interpolated from the analysis fields plus random motions representing turbulence (Stohl and Thomson, 1999). The emission sensitivity value in a particular grid cell is proportional to the particle residence time in that cell (Seibert and Frank, 2004). Residence time is

specifically for the layer from the surface up to a specified height in the planetary boundary layer (100 m used by this study and previous studies, e.g., (Stohl et al. (2009))). The spatial resolution of the output from the backward simulations is $0.25^\circ \times 0.25^\circ$. Loss of benzene and toluene by reaction with the hydroxyl (OH) radical in the atmosphere was considered in the backward simulation. Rate constant values for reaction with OH radicals were expressed for benzene as:

$$k = 2.308 \times 10^{-12} \times \exp\left(-\frac{190}{T}\right) \quad (1);$$

and for toluene as:

$$k = 1.275 \times 10^{-18} \times T^2 \times \exp\left(\frac{1192}{T}\right) \quad (2),$$

where T is the ambient temperature (K). Gridded OH fields (hourly for the period Oct to Dec 2010, at a resolution of $0.5^\circ \times 0.667^\circ$, 47 vertical levels) were derived from the atmospheric chemistry transport model, GEOS-Chem v5 (<http://acmg.seas.harvard.edu/geos/>). A reference simulation was run backwards for 20 days with atmospheric chemical loss, and additional alternative FLEXAPRT simulations were run backwards for 10 and 40 days with atmospheric chemical loss, and 20 days without atmospheric chemical loss (see Section 3.2 shows).

2.3 Inverse algorithm

Simulated benzene and toluene mixing ratios at the measurement site were obtained by integrating the gridded emission sensitivities ($\text{m}^2 \text{s g}^{-1}$) multiplied by the gridded emissions ($\text{g m}^{-2} \text{s}^{-1}$). The Bayesian inversion method used in this study is almost the

same as described and evaluated by Stohl et al. (2009) and Stohl et al. (2010), and as used in recent studies of SF₆ emissions (Fang et al., 2014) and HFC-23 emissions (Fang et al., 2015) in East Asia. Briefly, in this study a Bayesian inversion technique is employed, based on least-squares optimization, to estimate both the spatial distribution and strength of the emissions in the domain to which the measurements are sensitive. The inversion adjusts the emissions to minimize the differences between the observed and modeled mixing ratios while also considering the deviation of the optimized emissions from an a priori emission field. Observation-model mismatch errors (which include transport model errors) are determined as the root mean square error (RMSE) of the model-observation mismatch (Stohl et al., 2009; Stohl et al., 2010). In this study, mixing ratio background values were set to zero. This is because the backward simulations were run for 20 days and benzene and toluene in the air parcel from emissions occurring prior to this time would have been largely removed from the atmosphere by reaction with OH (typical atmospheric lifetimes of benzene and toluene are ~10 days and ~2 days, respectively).

For benzene, gridded a priori emission fields for mainland China were derived from MEIC v1.2 for November 2010 (0.25° × 0.25°, monthly mean), and for the rest of the world the emissions were taken from RCP Scenario 2.6 (0.5° × 0.5°, annual mean) (van Vuuren et al., 2007). For toluene, a priori emission fields for mainland China were derived from MEIC v1.2 for November 2010 (0.25° × 0.25°, monthly mean), while for the PRD region in mainland China, a priori emissions were derived by averaging the estimates from MEIC v1.2 (0.25° × 0.25°, monthly mean) and from

Yin et al. (2015) ($0.25^{\circ} \times 0.25^{\circ}$, monthly mean) for November 2010. For the rest of the world, a priori emissions were taken from RCP 2.6 inventory ($0.5^{\circ} \times 0.5^{\circ}$, yearly mean) (van Vuuren et al., 2007). Both monthly inventories of MEIC v1.2 and Yin et al. (2015) were obtained through personal communication with the dataset authors. A priori emission uncertainty in each grid cell for benzene and toluene, respectively, was set to 100% and 70% according to the differences among the bottom-up inventories and was assumed uncorrelated in space. The a posteriori uncertainty of the emissions in each grid cell was calculated as described by Seibert et al. (2011), and the uncertainty reduction in each grid cell represents the difference (as a percentage) between the a posteriori and priori emission uncertainties in the corresponding grid cell.

3 Results and Discussion

3.1 Benzene and toluene ambient mixing ratios

Table 1 shows ambient mixing ratios of benzene and toluene measured at the Heshan site and other sites all over the world. Mixing ratios of benzene at the Heshan site ranged from 0.59 ppb to 20.23 ppb and had an average of 2.27 ± 1.65 (mean \pm standard deviation) ppb during our observation period. Mixing ratios of toluene at the Heshan site ranged from 0.87 ppb to 25.05 ppb and had an average of 5.6 ± 4.15 ppb. The mixing ratios of benzene (0.67 ± 0.21 ppb) and toluene (1.58 ± 1.25 ppb) at the Mt. TMS were only ~30% of those at the Heshan site. In agreement with previous studies (e.g. Lau et al., 2010; Liu et al., 2008), mixing ratio levels of benzene and toluene in

the PRD region are overall higher than those in Hong Kong (Table 1), which is in part due to the fact that Hong Kong often receives clean air masses from over the ocean and that emissions in Hong Kong are lower than in the PRD.

Mixing ratios of benzene and toluene in some cities in Europe (e.g. Ait-Helal et al., 2014; Langford et al., 2010) and United States (e.g. USEPA, 1989; Baker et al., 2008) have been found to be approximately 0.5 ppb and 1 ppb (Table 1), respectively, which is about 20% of the mean observed values in the PRD in this study. Mixing ratios of benzene and toluene in Thompson Farm, United States were even 0.08 ± 0.002 ppb and 0.09 ± 0.005 ppb, respectively, which are much lower than the lowest mixing ratios at both Heshan and Mt. TMS sites. Levels of benzene and toluene mixing ratios at different sites mainly reflect the combined influence of emission strength, seasonal changes in atmospheric OH concentration and mixing depth.

3.2 Benzene and toluene emission sensitivities

Figure 2 shows the spatial distribution of average emission sensitivity of benzene and toluene for the Heshan site for November 12-November 30, 2010. During the observation period, air masses transported to the Heshan site mainly came from easterly and northerly directions. Considering that the major emission sources in the PRD are located to the east of the Heshan site (Figure 1), this measurement location is ideally situated for constraining emissions from this region for this period and, as the emission sensitivities show, PRD, HK, and neighboring regions, are relatively well constrained by the observations at the Heshan site. Benzene and toluene emissions in

the PRD and HK are much higher than emissions in neighboring regions (Figure 1) and, consequently, the overall mixing ratio contributions (the integral of the emission sensitivities multiplied by emissions) from PRD and HK to the observation site comprise more than 80% of the total simulated mixing ratios. Note that the emission sensitivities for benzene and toluene are different because there are differences in the chemical loss of these two compounds during atmospheric transport and in the molecular weight. Specifically, the emission sensitivities for toluene are spatially more confined because of its shorter lifetime.

As a sensitivity study, alternative simulations in which FLEXPART was ran backwards for 10 days were made. The derived emission sensitivities are almost identical to the reference simulations with 20 days duration (Supporting Information Figure S1 for benzene and Figure S2 for toluene), confirming that 20-day-backward simulations are sufficiently long to account for all benzene and toluene emission sources that can influence the mixing ratios at the Heshan site. Since the lifetime of benzene is ~10 days (much longer than that of toluene), we also made a 40-day-backward simulation from which the emission sensitivities for benzene are also almost identical to the reference simulation of 20 days (Figure S3). Without accounting for the loss by reaction with OH in the atmosphere, the emission sensitivities for benzene would only be a little higher (by ~10% in central PRD) (Figure S4). On the other hand, the emission sensitivities for toluene would be much higher (by ~50% in central PRD) (Figure S5). This indicates that accounting for chemical loss has a relatively small effect for simulating benzene mixing ratios at

Heshan, whereas it has a profound effect on toluene mixing ratios. Thus, errors in the retrieved emissions due to errors in chemical loss are marginal for benzene but could be significant for toluene.

3.3 Inversion results

Figure 3 shows the observed and simulated mixing ratios at the Heshan site. The simulations captured most pollution episodes and the inversion improved the agreement between the simulations and the observations as expected (the agreement between the a posteriori simulations and the observations is better than for the a priori simulations and the observations). For benzene, the RMSE between the observed and simulated mixing ratios decreased from 1.53 ppb, using a priori emissions, to 1.26 ppb, using a posteriori emissions, and the mean bias between the simulated mixing ratios and observations decreased from 0.96 ppb, using a priori emissions, to 0.41 ppb, using a posteriori emissions. For toluene, the RMSE between the observed and simulated mixing ratios decreased from 4.77 ppb, using a priori emissions, to 4.30 ppb, using a posteriori emissions and the mean bias between the observed and simulated mixing ratios decreased from 2.35 ppb, using a priori emissions, to 1.99 ppb, using a posteriori emissions.

Figure 3 also shows examples of spatial distributions of toluene emission sensitivities for two observed mixing ratios. The toluene mixing ratio at 00:00 UTC on 16 November 2010 was about 2 ppb and the corresponding air mass had not passed over the strong emission sources in the central part of PRD and HK (see the backward

emission sensitivities map in Figure 3c), while the toluene mixing ratio at 00:00 UTC on 24 November 2010 was about 15 ppb and the corresponding air mass had passed over the strong emission sources in the central part of PRD and HK (Figure 3d).

Figure 4 shows the benzene a priori and a posteriori emission fields, their differences and uncertainty reduction. The a priori fields show that emission hot spots are located in the megacities, Guangzhou, Shenzhen and Hong Kong. Emission changes by the inversion are positive in some grid cells and negative in some other grid cells, which shows that the a priori emissions are not systematically lower or higher everywhere than the a posteriori emissions. The biggest emission changes by the inversion occur in two boxes in Guangzhou where the a priori emissions were enhanced by ~50% in one box and decreased by more than 50% in the other box. The emission hot spot in Shenzhen did not change much. To test the sensitivity to the a priori emission in this grid cell, we performed an additional inversion in which the a priori emission in this grid cell was reduced, and a high a posteriori emission in this grid cell was still found, as in the reference inversion.

Figure 5 shows the a priori and a posteriori emissions of toluene and their difference. Emission hot spots are located in Guangzhou and Shenzhen. The uncertainty reduction map in Figure 4d and Figure 5d shows significant error reductions, of 40% or more, in boxes close to the observation site, while only low emission uncertainty reductions were achieved in boxes far from the observation site. Overall, the emission uncertainties have been reduced by the inversion in the PRD and HK, where the strongest emission sources are located.

292 The total a posteriori benzene emissions for PRD and HK, respectively, are 4.0
293 (1.1–6.9) Gg/month (for all cases the range represents one sigma uncertainty) and 0.4
294 (0.1–0.7) Gg/month. A posteriori toluene emissions are 12 (4–20) Gg/month for PRD
295 and 0.5 (0.2–0.9) Gg/month for HK. The inversion sensitivity tests, i.e., using other
296 bottom-up emission inventories for the a priori estimate (listed in Table 2), all produce
297 toluene emission estimates that fall within the uncertainty range of the a posteriori
298 emissions from the reference inversion.

299 Benzene and toluene measurement data at the Mt. TMS site were not used in the
300 inversion but for validating the posterior emissions. For benzene, using the a priori
301 and a posteriori emission fields, respectively, the RMSE between the simulated and
302 observed mixing ratios at Mt. TMS site are 0.367 ppb and 0.312 ppb, and the mean
303 bias between the simulated and observed mixing ratios are 0.314 ppb and 0.208 ppb.
304 For toluene, the RMSE (1.50 ppb) between the observed and simulated mixing ratios
305 using the a posteriori emission fields from the inversion was smaller than that (1.55
306 ppb) using the a priori field; the mean bias (1.06 ppb) between the observations and
307 simulated mixing ratios using a posteriori emission fields was also smaller than that
308 (1.12 ppb) using the a priori field. Both the RMSEs and mean bias suggest that the a
309 posteriori emissions are more accurate than the a priori emissions.

310 We also made FLEXPART simulations driven by operational meteorological
311 analyses from the European Centre for Medium-Range Weather Forecasts (ECMWF)
312 instead of CFSR data. The a posteriori emissions for the PRD are very similar when
313 using the emission sensitivities from the two alternative FLEXPART simulations, e.g.

for benzene we obtained 4.0 Gg/month from the inversion using CFSR and 4.2 Gg/month from the inversion using ECMWF. Although Fang et al. (2014) showed that FLEXPART simulations driven with ECMWF data performed slightly better than the CFSR-driven simulations for SF₆ in East Asia for Hateruma, Gosan and Cape Ochiishi stations, we found that CFSR-driven FLEXPART simulations performed slightly better than the ECMWF-driven simulations for the benzene simulations at the Heshan site. Thus, the CFSR dataset was used in this paper.

3.4 Comparison with other estimates

Figure 6 and Figure S6, respectively, show spatial distributions of benzene and toluene emissions estimated by the inversion in this study, four bottom-up inventories, and the differences among these estimates. For benzene, the spatial emission distributions in the REAS v1.1 REF have the biggest difference from our top-down emissions. Gridded emissions in the REAS v1.1 REF are always lower than the inversion emissions, while emissions in the Yin et al. (2015), MEIC v1.2 and RCP 2.6 estimates are less systematically biased. The simulated benzene mixing ratios using the REAS v1.1 inventory are much lower than the observed mixing ratios (Figure 7). Statistics of the RMSE, mean bias and squared Pearson correlation coefficients between the simulated and observed mixing ratios show that emission fields obtained from the inversion performed better in simulating the benzene mixing ratios than all four bottom-up inventories (See Table S1).

For toluene, in most grid cells over the PRD, emissions estimated by RCP 2.6, Yin

et al. (2015) and REAS v1.1 REF are lower than the inversion estimates, while MEIC v1.2 emissions are higher than the inversion estimates (Figure S6). Model simulations show that the simulated mixing ratios using emission estimates from RCP 2.6, Yin et al. (2015) and REAS v1.1 REF are much lower than the observed mixing ratios at the Heshan site (Figure S7). The simulated mixing ratios using MEIC v1.2 emission fields are not consistent with some observed pollution peaks (Figure S7). Statistics of RMSE and squared Pearson correlation coefficients show that inversion emission fields performed better at simulating toluene mixing ratios at the Heshan site than the four bottom-up emission fields (see Table S1).

Table 2 shows five estimates of total benzene and toluene emissions in the PRD and HK regions for the year 2010. The a posteriori emissions for November 2010 obtained from the inversion were extrapolated to an annual mean emission rate for the whole year 2010 by multiplying the November emissions by the ratio of emissions for the whole year 2010 to those in November 2010. For toluene, this ratio is 10.8, and was calculated from both the MEIC v1.2 and Yin et al. (2015) estimate (the November/annual emission ratio was the same in both datasets). For toluene, the factor is 10.9 (10.4–11.4), and is the average of 10.4, calculated from the MEIC v1.2 estimate, and 11.4, calculated from the Yin et al. (2015) estimate. Data in November 2010 and the whole year 2010 were obtained through personal communication with the dataset authors. Using these ratios, the benzene emissions in the PRD and HK for 2010 were estimated to be 44 (12–75) Gg yr⁻¹ and 5 (2–7) Gg yr⁻¹, respectively, and the toluene emissions were estimated to be 131 (44–218) Gg yr⁻¹ and 6 (2–9) Gg yr⁻¹,

respectively.

For benzene, emissions in the PRD in 2010 calculated from the four bottom-up estimates were 45 Gg yr⁻¹ from RCP 2.6 (van Vuuren et al., 2007), 54 Gg yr⁻¹ from Yin et al. (2015), 8 Gg yr⁻¹ from REAS v1.1 REF (Ohara et al., 2007), and 33 Gg yr⁻¹ from MEIC v1.2. Our inverse estimate agrees within its uncertainties with these bottom-up estimates, except that the REAS estimate is substantially lower than the other bottom-up and the top-down estimates. Emissions in HK were 5 (2–7) Gg yr⁻¹ estimated by this study, which agrees within uncertainties with the RCP 2.6 estimate and is much higher than the REAS v1.1 REF (no estimates are available from MEIC v1.2 or Yin et al. (2015)).

For toluene, emissions in PDR in 2010 calculated from the four bottom-up estimates were 44 Gg yr⁻¹ from RCP 2.6 estimate (van Vuuren et al., 2007), 64 Gg yr⁻¹ from Yin et al. (2015), 46 Gg yr⁻¹ from REAS v1.1 REF (Ohara et al., 2007), and 181 Gg yr⁻¹ from MEIC v1.2. The bottom-up estimate MEIC v1.2 meets the high uncertainty range of our inversion estimates, while the other three bottom-up estimates meet the low uncertainty range of our inversion estimates. For the HK toluene emissions, estimates are not available in MEIC v1.2 or Yin et al. (2015); both RCP 2.6 and REAS v1.1 REF estimates are about 4 Gg yr⁻¹, which agree with our inversion results within uncertainties.

3.5 Benzene and toluene emissions during 2000–2010

Figure 8 shows different estimates of benzene and toluene emissions in the PRD

region for the period 2000–2010. For benzene, the estimate of 8 Gg yr⁻¹ in 2000 by REAS v2.1 (Kurokawa et al., 2013) agrees with that of 13 Gg yr⁻¹ by the Reanalysis of the Tropospheric chemical composition over the past 40 years project (RETRO) (Schultz et al., 2007), which are substantially smaller than that of 43 Gg yr⁻¹ in the Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP) (Lamarque et al., 2010). For the years 2005 and 2006, different studies show substantial differences. For the year 2005, the emission estimate by RCP 2.6 was ~4 times the estimates by REAS v2.1. For the year 2006, the emission estimate by REAS v2.1 agrees with the estimate in the Intercontinental Chemical Transport Experiment-Phase B (INTEX-B) project (Zhang et al., 2009), which were only ~20% of the estimate by Zheng et al. (2009). More studies are available for the year 2010 than for other years. For the year 2010, the estimates by RCP 2.6, MEIC v1.2 and Yin et al. (2015) agree with the inversion estimate by this study, which are higher than the estimate by REAS v1.1 REF. According to these bottom-up and top-down estimates (Figure 8), it is likely that the benzene emissions in the PRD have remained relatively stable during the 2000–2010 period, although emissions are uncertain due to limited number of estimates.

For toluene, the estimate of 45 Gg yr⁻¹ in 2000 by REAS v2.1 (Kurokawa et al., 2013) agrees relatively well with the value of 36 Gg yr⁻¹ by ACCMIP (Lamarque et al., 2010), but both are substantially larger than the RETRO estimate of 14 Gg yr⁻¹ (Schultz et al., 2007). For the years 2005 and 2006, estimates of toluene emission are also quite different. For the year 2005, the emission estimate by REAS v2.1 was ~4

times the estimates by RCP 2.6. For the year 2006, the emission estimate by REAS v2.1 was ~2 times the estimate by Zheng et al. (2009) and even ~11 times the estimate by INTEX-B (Zhang et al., 2009). For the year 2010, the estimates by REAS v1.1 REF and Yin et al. (2015) meet the low end of uncertainty of inversion estimate by this study, while MEIC v1.2 estimate meets the high end. According to these estimates over 2000–2010 (Figure 8), it is likely that the toluene emissions in the PRD have increased during this period, although emissions are uncertain due to limited number of estimates.

Based on glyoxal (CHOCHO) data retrieved from satellite and inversion method, Liu et al. (2012) found their emission estimates of the lumped artificial compound ARO1 (benzene, toluene and ethylbenzene) in the PRD in 2006 were >10 times larger than the bottom-up INTEX-B estimates (also for 2006), but they did not specify which compound was responsible for the difference. As for benzene, the ratio of emissions in 2006 estimated by Zheng et al. (2009) (60 Gg yr^{-1}) to the INTEX-B estimate (15 Gg yr^{-1}) is ~4 times, much less than the factor >10 discrepancy reported by Liu et al. (2012). Inversion estimate of benzene emissions ($44 (12\text{--}75) \text{ Gg yr}^{-1}$) in 2010 is ~3 (1–5) times the INTEX-B emissions for 2006. Thus, we suggest that the big discrepancy is likely not due to emissions of benzene but emissions of toluene and/or ethylbenzene. As for toluene emissions, the ratios of bottom-up estimates by REAS v2.1 (190 Gg yr^{-1}) and Zheng et al. (2009) (103 Gg yr^{-1}) for 2006 to the INTEX-B bottom-up estimate (18 Gg yr^{-1}) are 11–6 times. Thus, considering the satellite-based estimate and other bottom-up estimates, the bottom-up INTEX-B

estimate of toluene emissions for the PRD region for 2006 was likely too low, and estimation of toluene emissions in the PRD is attributed as an important factor contributing to the big discrepancy of ARO1 emission estimates between Liu et al. (2012) and INTEX-B.

3.6 Suggestions for more top-down studies

To the best of our knowledge, this study provides the only available top-down estimate for toluene emissions in the PRD and HK regions. All other studies in Figure 8 are bottom-up estimates. More top-down estimates are needed to validate the bottom-up estimates in previous years and in the future. In this study, inversions using the Heshan measurement data reduced emission uncertainties in the PRD and HK regions. However, the emission uncertainty reductions were not large because there was only one observation site suitable for the inversion (some measurements in urban environments are available but not suitable for inverse modeling) and the observation period was not long. Thus, we propose that in the future, observations with better spatial and temporal coverage are urgently needed to better constrain benzene and toluene (and other VOC) emissions in the PRD and HK regions. Inversion-suited observation sites could be situated in rural places outside of the major emission sources located in the central part of PRD and HK regions, and then the major emission sources in the PRD and HK regions could be “viewed” from different angles (multiple-site inversion) to better constrain the benzene and toluene (and other VOC) emissions.

4 Conclusions

Using atmospheric measurements at the Heshan site, a transport model and an inversion algorithm, this study provides the first top-down estimate of benzene and toluene emissions in the Pearl River Delta (PRD) and Hong Kong (HK) regions, which are emission hot spots in China. According to the measurement data in this study and previous studies, mixing ratio levels of benzene and toluene in the PRD region are overall higher than those in Hong Kong, which are much higher than those measured in the United States and Europe. Considering that air masses transported to the Heshan site mainly came from easterly and northerly directions during the observation period, and that the major emissions sources in the PRD are located to the east of the Heshan site, the Heshan measurement site was ideally situated for constraining emissions from these regions. Based on the measurement data, model simulations and inverse technique, the PRD and HK benzene emissions for 2010 estimated in this study were 44 (12–75) Gg yr⁻¹ and 5 (2–7) Gg yr⁻¹, respectively and the PRD and HK toluene emissions for 2010 were 131 (44–218) Gg yr⁻¹ and 6 (2–9) Gg yr⁻¹, respectively. We have discussed the spatial distributions of benzene and toluene emissions obtained by inversion in this study in the context of four different existing bottom-up inventories. The discrepancies among these bottom-up estimates for the period 2000–2010 are substantial (up to a factor of seven), while this study is the only one available top-down estimate. We propose that observations with better spatial and temporal coverage are urgently needed to constrain benzene and toluene (and other VOC) emissions in the PRD and HK regions more strongly.

Supporting Information

Supplementary material related to this article is available online at

<http://www.atmos-chem-phys.net/>

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631 Tables

632 Table 1. Ambient mixing ratios (ppb) of benzene and toluene measured at the Heshan site and other sites all over the world (SD represents Standard Deviation; NG indicates
633 Not Given).

Location	Type	Time	Benzene			Toluene			Reference
			Sample number	Range	Mean±SD	Sample number	Range	Mean±SD	
(1) PRD and Hong Kong regions, China									
Heshan, PRD	Rural	11–30 Nov. 2010	419	0.59–20.23	2.27±1.65	419	0.87–25.05	5.65±4.15	This study
Guangzhou, PRD	Urban	4 Oct. to 3 Nov. 2004	111	0.66–11.35	2.39±1.99	111	0.76–36.91	7.01±7.33	(Liu et al., 2008)
Xinken, PRD	Rural	4 Oct. to 3 Nov. 2004	83	0.52–6.26	1.42±0.98	83	0.54–56.41	8.46±9.94	(Liu et al., 2008)
Dongguan, PRD	Urban	Sep. 2005	48	0.27–6.45	1.26±0.14	48	0.53–25.30	6.13±0.81	(Barletta et al., 2008)
Guangzhou, PRD	Urban	Sep. 2006	42	0.65–6.80	2.05±1.49	42	0.72–19.60	5.87±4.11	(Barletta et al., 2008)
Industrial Area, PRD	Industrial	Late summer 2000	15	NG	2.80±1.70	15	NG	13.5±1.8	(Chan et al., 2006)
Mt. Tai Mo Shan, Hong Kong	Mountain	1–3, 9, 19–21 Nov. 2010	75	0.38–1.79	0.67±0.21	75	0.26–6.30	1.58±1.25	This study
Tap Mun, Hong Kong	Rural	Nov. 2006 to Oct. 2007	39	0.05-1.67	0.56±0.41	39	0.15-7.12	1.61±1.55	(Lau et al., 2010)
Central West, Hong Kong	Urban	Nov. 2006 to Oct. 2007	40	0.05-1.91	0.60±0.50	40	0.28-8.81	2.64±2.07	(Lau et al., 2010)
(2) Other sites in China									
43 cities, China	Urban	Jan.–Feb. 2001	158	0.7–10.4	NG	158	0.4–11.2	NG	(Barletta et al., 2005)
Beijing, China	Urban	Aug. 2005	1046	NG	3.03±1.72	1039	NG	1.76±0.89	(Song et al., 2007)
Shanghai, China	Urban	15 Jun. 2006 to 14 Jun. 2007	~365	NG	6.07±11.70	~365	NG	32.80±21.60	(Ran et al., 2009)
(3) Sites in other countries									
Karachi, Pakistan	Urban	Winter of 1998–1999	78	0.34–19.3	5.20±4.50	78	0.19–37.0	7.10±7.60	(Barletta et al., 2002)

Tokyo, Japan	Urban	Summer 2007	50	NG	0.78±0.61	50	NG	2.14±0.99	(Yoshino et al., 2012)
Tokyo, Japan	Urban	Winter 2007	16	NG	0.82±0.28	16	NG	10.10±5.23	(Yoshino et al., 2012)
London, UK	Urban	Oct. 2010	601	NG	0.15±0.11	589	NG	0.68±0.57	(Langford et al., 2010)
Paris, France	Suburban	15 Jan.–15 Feb. 2010	246	NG	0.32±0.16	246	NG	0.32±0.22	(Ait-Helal et al., 2014)
Mexico City, Mexico	Urban	Feb. 2002 and Apr.–May 2003	~115	NG	3.17±1.75	~86	NG	13.5±9.33	(Velasco et al., 2007)
Mexico City, Mexico	Rural	Feb. 2002 and Apr.–May 2003	~115	NG	0.80±0.91	~86	NG	1.89±1.92	(Velasco et al., 2007)
39 cities, U.S.A.	Urban	Jun.–Sep. 1984–1986	835	0.001–0.27	NG	836	0.003–1.30	NG	(USEPA, 1989)
28 cities, U.S.A.	Urban	Summer 1999–2005	530	(0.06±0.024)– (0.48±0.24) ^a	NG	530	(0.12±0.055) –(1.54±0.88) ^a	NG	(Baker et al., 2008)
Thompson Farm, U.S.A.	Rural	Fall 2004–2006	201	NG	0.08±0.002	201	NG	0.09±0.005	(White et al., 2009)

634 ^aIt represents the range of the minimal mean value (the corresponding standard deviation) in one of 28 cities and maximal mean value (the corresponding standard
635 deviation) in another city.

Table 2. Benzene and toluene emissions (Gg yr⁻¹) in the PRD and HK regions derived from different estimates for the year 2010.

Estimate	Benzene emissions		Toluene emissions	
	PRD	HK	PRD	HK
RCP 2.6	45	3	44	4
Yin et al. (2015)	54	NE	64	NE
REAS v1.1 REF	8	0.4	46	4
MEIC v1.2	33	NE	181	NE
This study	44 (12–75)	5 (2–7)	131 (44–218)	6 (2–9)

^aNE indicates “Not Estimated”.

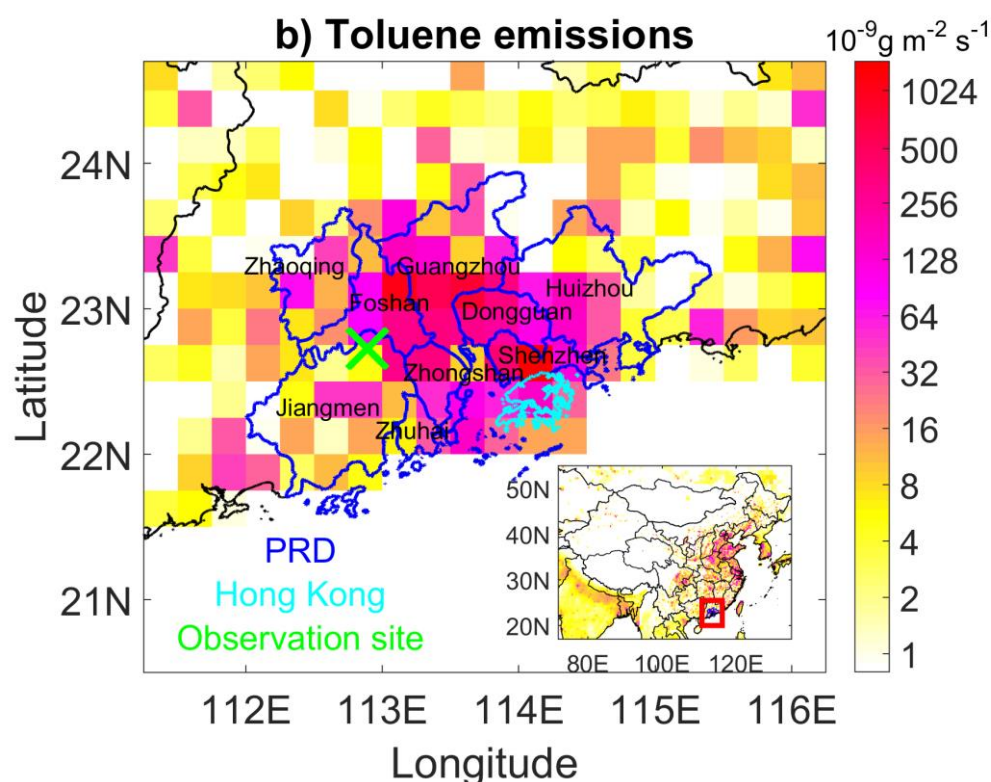
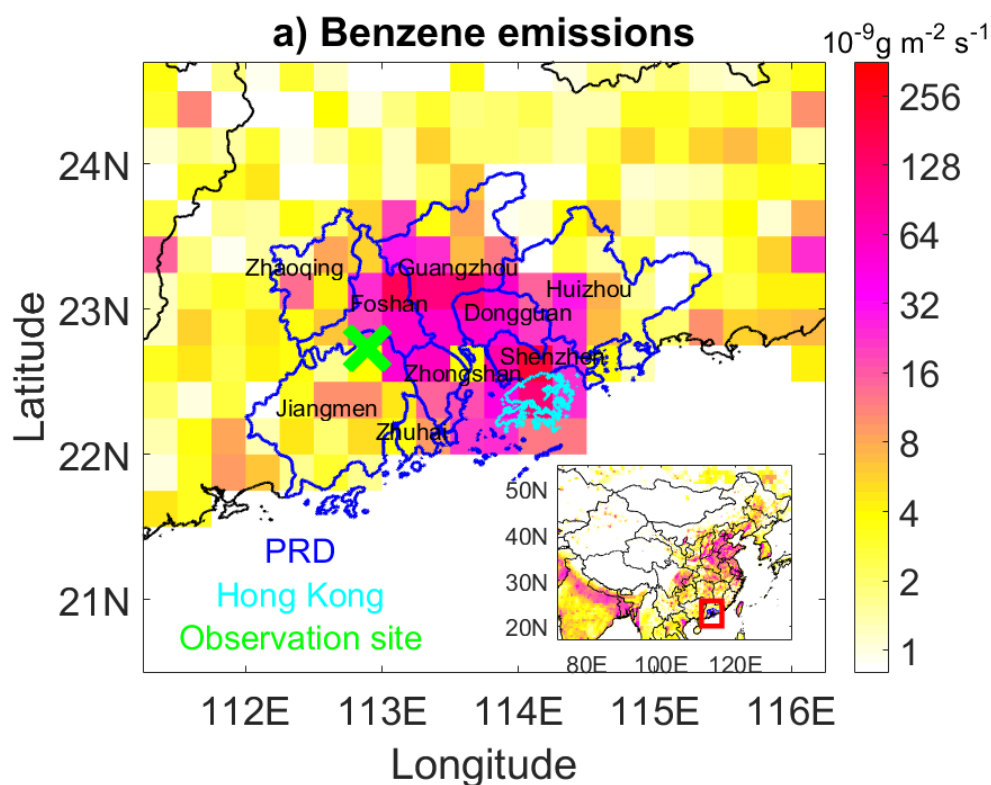
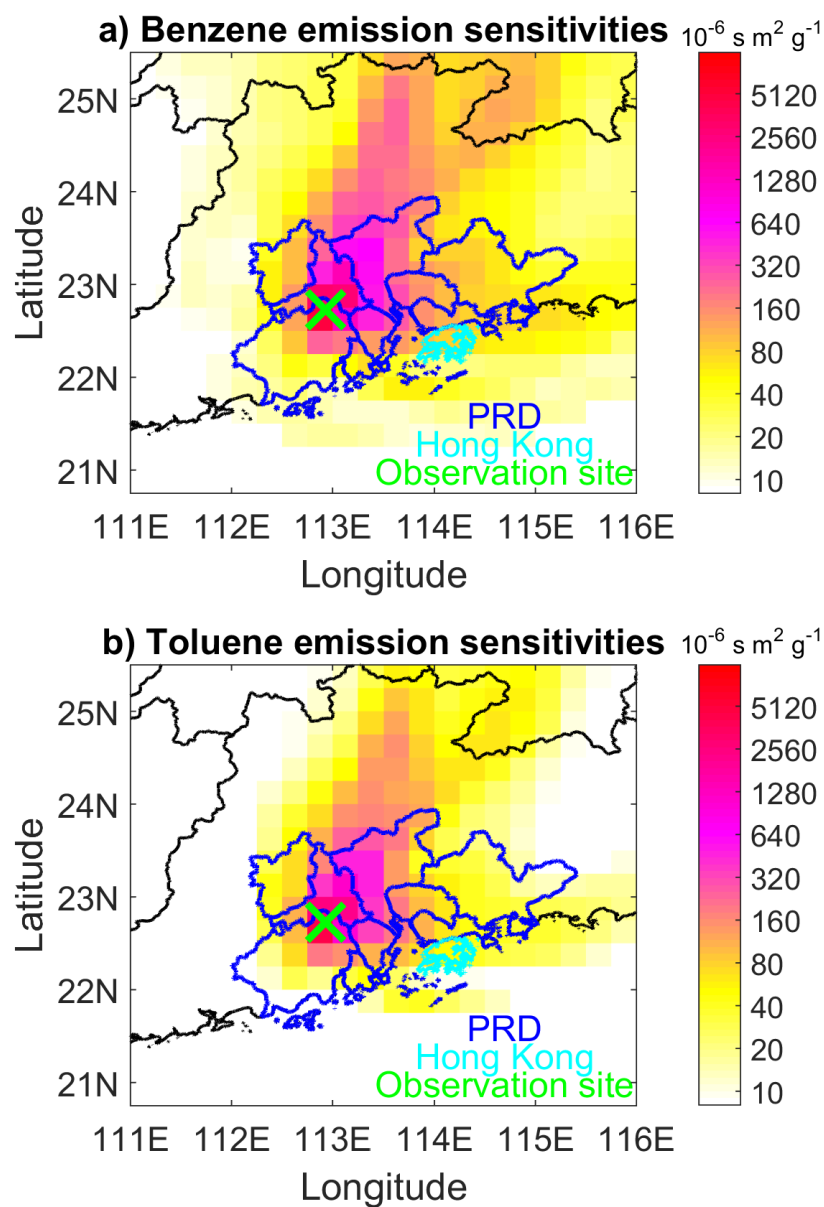


Figure 1. Map of a) benzene and b) toluene emissions from the MEIC v1.2 for China and the RCP 2.6 for outside China (inset panels), and that for the PRD and Hong Kong regions (mother panel). The PRD region is plotted with dark blue boundary lines, the Hong Kong region with cyan boundary lines. The green cross indicates the location of the Heshan observation site.



647

648 Figure 2. Average emission sensitivities of a) benzene and b) toluene for the Heshan
 649 observation site for November 12-November 31, 2010. The green cross indicates the location
 650 of Heshan site. The blue and cyan lines represent PRD and Hong Kong boundary lines,
 651 respectively.

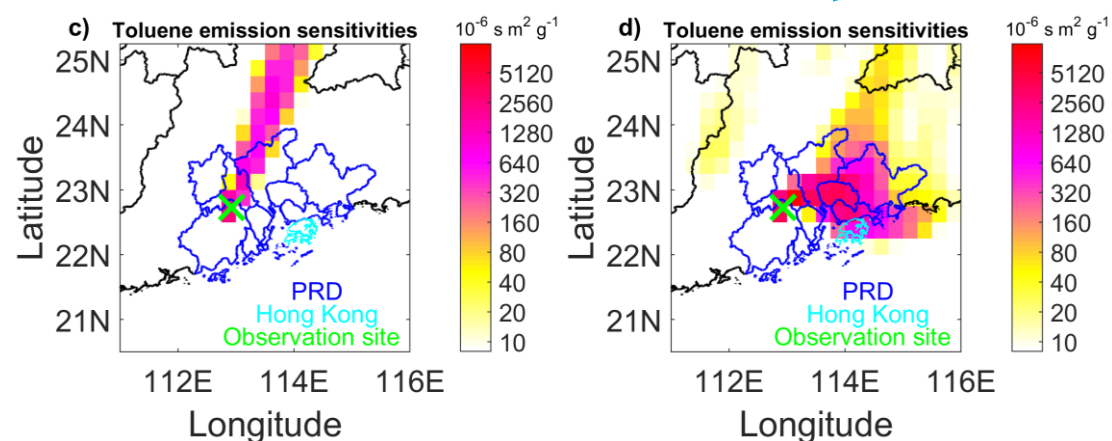
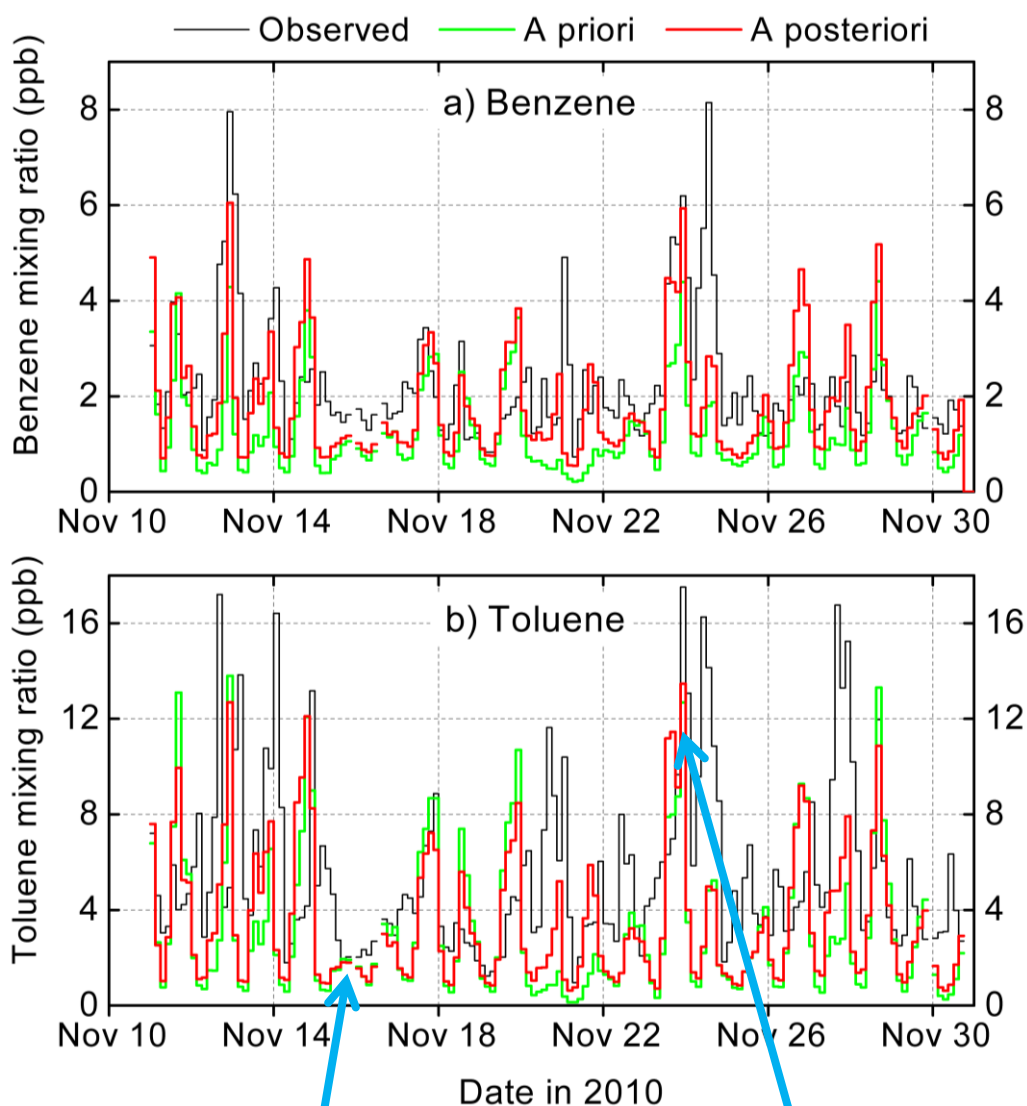


Figure 3. Observed and simulated a) benzene and b) toluene mixing ratios at the Heshan site, and two examples of spatial distributions of toluene emission sensitivities at c) 00:00 UTC on 16 November 2010 and d) 00:00 UTC on 24 November 2010.

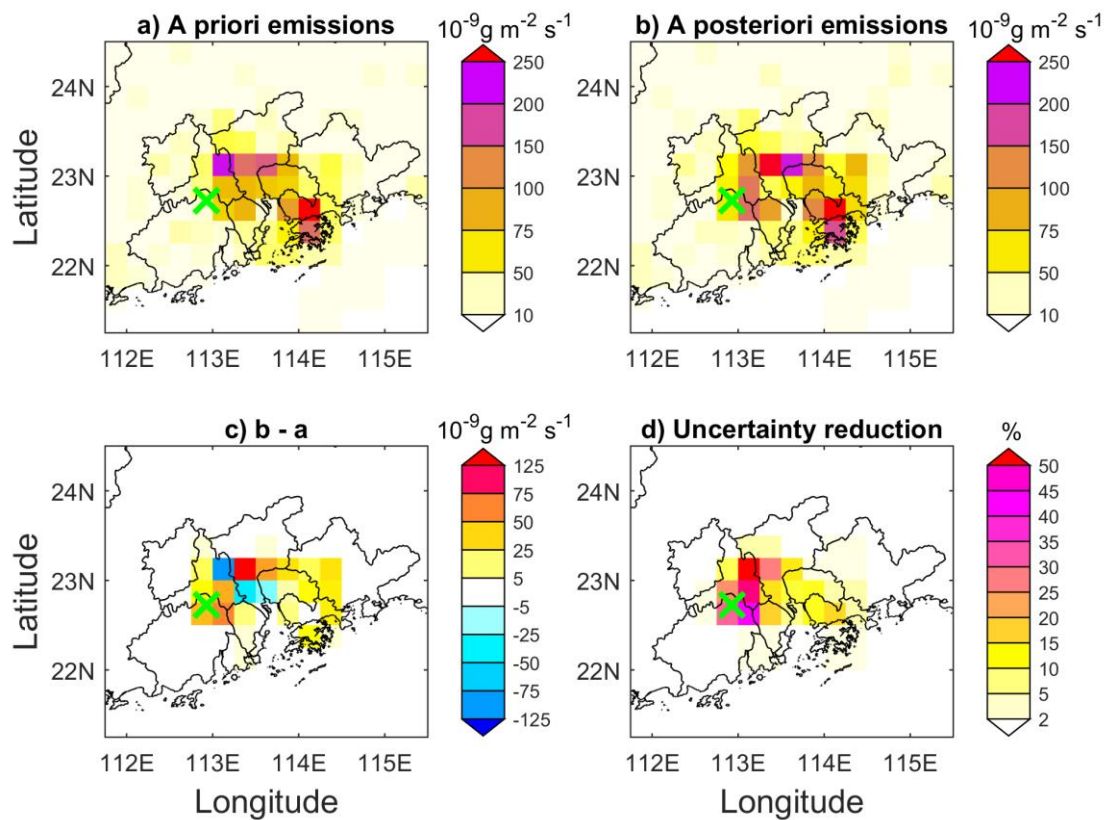


Figure 4. Maps of a) a priori benzene emissions, b) a posteriori benzene emissions, c) differences between b) and a), and d) uncertainty reduction. The observation site is marked with a green cross.

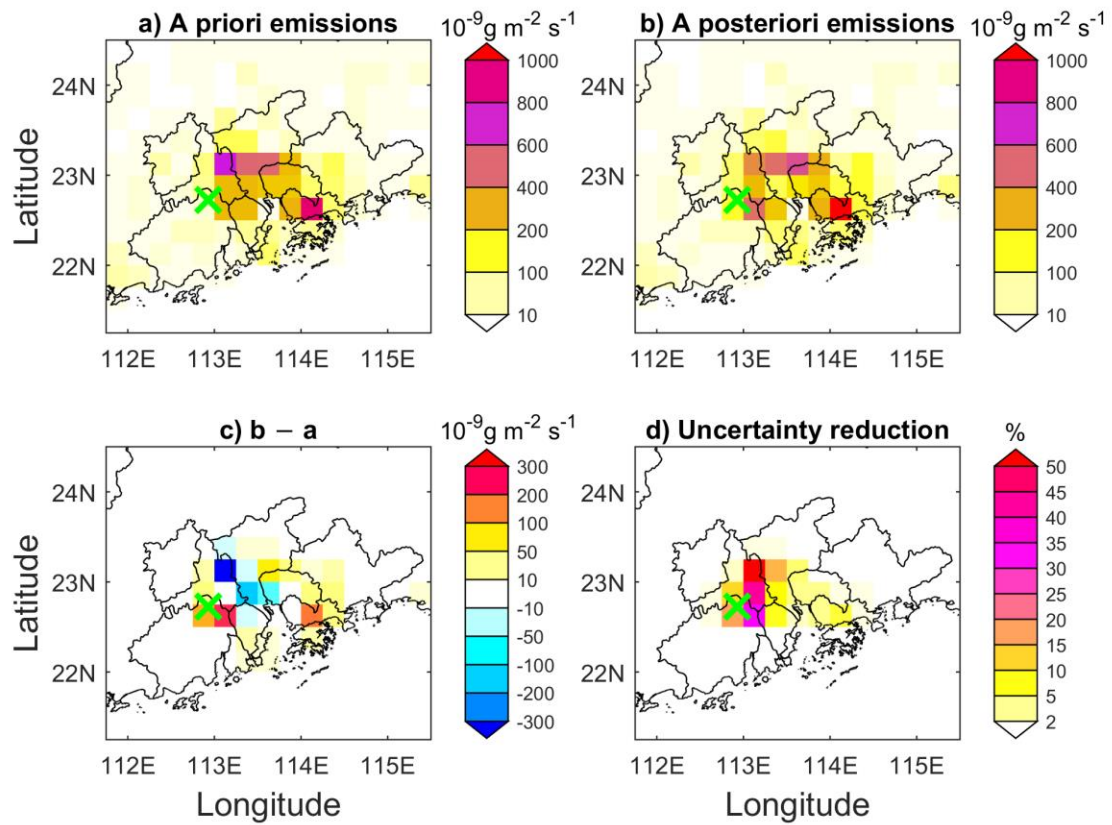


Figure 5. Maps of a) a priori toluene emissions, b) a posteriori toluene emissions, c) differences between b) and a), and d) uncertainty reduction. The Heshan observation site is marked with a green cross.

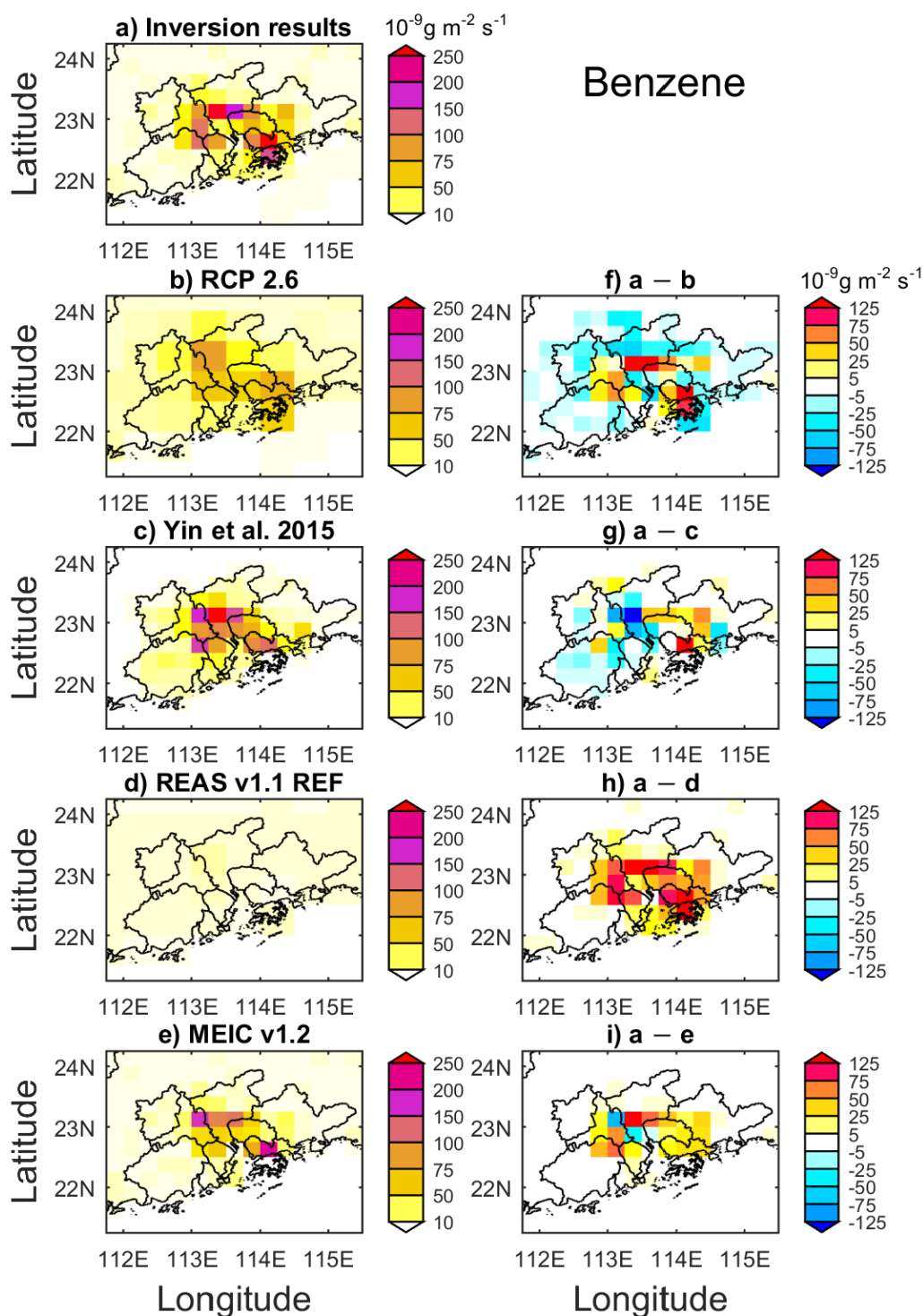


Figure 6. Maps of benzene emissions for the PRD, HK and surrounding regions from a) inversion, b) RCP 2.6, c) Yin et al. (2015), d) REAS v1.1 REF, e) MEIC v1.2, and the difference between inversion results (a) and the bottom-up inventories (b, c, d, e). Note that in c) and g) only emissions within the PRD are plotted since Yin et al. (2015) only estimated emissions within PRD, and that in e) and i) emissions within HK are not plotted since MEIC v1.2 has not estimated benzene emission in HK.

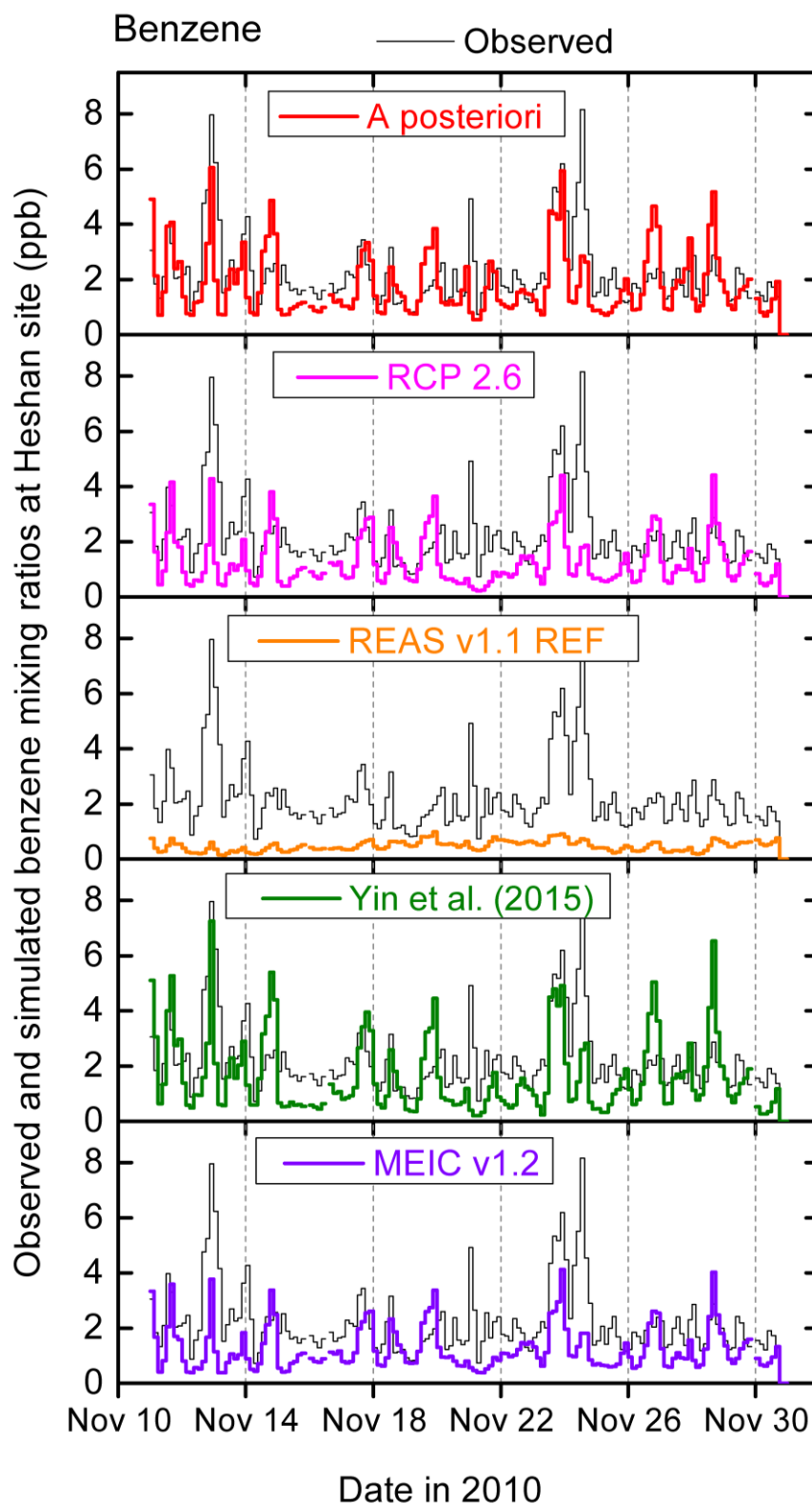
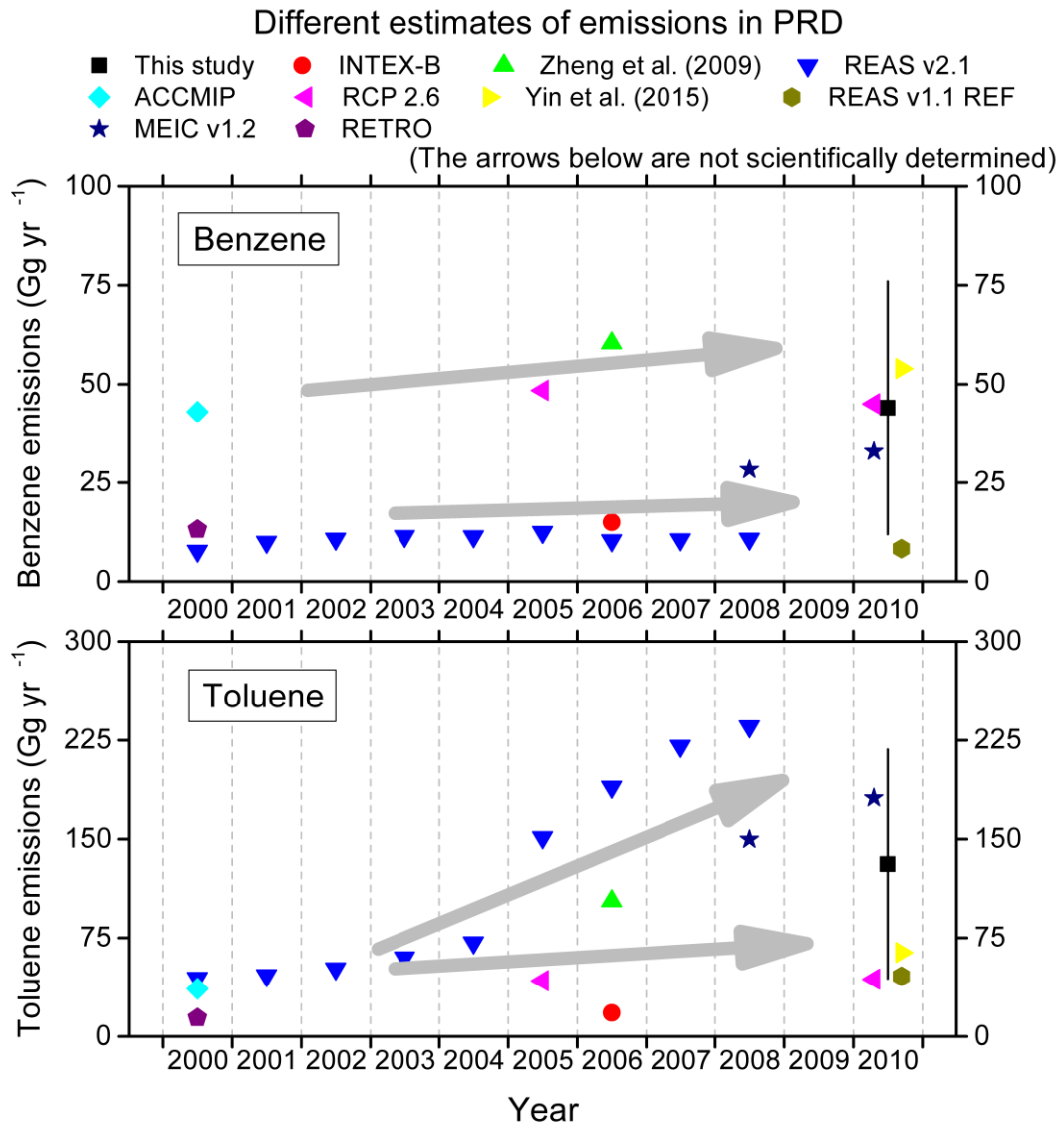


Figure 7. Time series of observed and simulated benzene mixing ratios at the Heshan site. The simulations use emission fields from inversion in this study, RCP 2.6, REAS v1.1 REF, Yin et al. (2015) and MEIC v1.2, respectively.



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677 Figure 8. Estimates of benzene and toluene emissions in the PRD region for the period

678 2000–2010.