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Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on "Evaluation of anthropogenic emissions of carbon monoxide in East Asia derived from observations of atmospheric radon-222 over the Western North Pacific" *by* A. Wada et al.

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We would like to thank the reviewer for valuable and constructive comments and suggestions. Incorporating them into the paper has resulted in a significant improvement in the paper. We confirm that all of the co-authors have concurred with this revised version of the manuscript. Our responses to the comments of Reviewer #2 are described below in details.

For General comments: This manuscript analyzes 2007-2011 observations of CO and

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Radon at 3 sites in the Western North Pacific that often sample Asian pollution outflow events. The analysis focuses on periods of enhanced Rn to select for observations that were influenced by continental sources. The atmospheric enhancements of CO/Rn are compared with global chemical-transport model simulations of this ratio for the same time period. The differences between the observed and modeled enhancement ratios are used to adjust the anthropogenic emissions of CO for several East Asian countries. The results are then compared to other emissions estimates for East Asia from bottom-up and inverse methods. This work is relevant and new. The Rn tracer methodology has been demonstrated in other regions, but this manuscript is novel in its application of the approach to East Asia, where emissions are large and recent changes have been rapid. There are significant inconsistencies between official and scientific inventories for East Asia, as well as differences in these bottom-up datasets and top-down estimates inferred from observations. This manuscript follows from recent previous work of these authors, particularly the 2011 paper by Wada et al. in Atmospheric Environment. In my opinion, the current manuscript adds significant new analyses in its use of the Rn tracer methodology and the application of a chemical-transport model to interpret the observations. The writing overall is clear (although there are numerous English errors, as noted below) and the figures are good. Some changes are needed to make this manuscript suitable for publication. While my specific recommendations are detailed below, some general issues include the following: - More details of the methods and analysis should be included. The authors too often cite the Wada et al., 2011 paper without further explanation, but this manuscript must stand on its own without the need to read the earlier paper to understand the results. - The authors must be more careful to qualify statements about the causes of specific events in their observations without further supporting evidence. In some cases, the Wada 2011 paper could help to provide such support. - Some of the assumptions and simplifications in the analysis need better justification. - Error and sensitivity analyses are critical to understand how robust the results are. - While the writing is reasonably clear, there are many grammatical and other English errors. I've listed some of them below in the Technical

Corrections, but there are too many for me to note here. I suggest that the manuscript undergo a thorough review by a native English speaker before final submission.

Ans. In our revised manuscript, we believe we have addressed much, if not all, of the concerns raised by the reviewer in the general comments above, as well as in the specific comments below. A detailed explanations of the analytical method based on Wada et al. (2011) are now added in the text. In addition, an overall error estimation is included in the results section. Finally, although the first manuscript was checked by a native English speaker, this revised manuscript has also been checked again by a native speaker.

************ Specific Comments: Section 2.1: Mention Wada et al. 2011 observations and trajectory model results that support the influence of Asian outflow events on these stations, as well as the lack of significant local sources at MNM and YON. Ans. The trajectory analysis reported by Wada et al. 2011 has been mentioned.

Section 2.2: Define the explicit measurement frequency of the Rn instrument. The hourly means are presumably averages of more frequently measured data. Ans. The measurements are obtained every 10 minutes. This information has been added in the revised manuscript.

p. 15342, line 12-13. State the Rn measurement period at the RYO station. Ans. The measurement of 222Rn at RYO started in March 2009 by using a commercially available 222Rn monitor with a detection limit of about 0.5 Bq m-3 (Wada et al., 2010). This information is now included in the text.

Section 2.3: STAG is run on a global domain, but this is never stated explicitly. Add this to the description of the model here. Ans. We have added the following phrase “a 3-D global chemical transport model” in reference to the STAG model.

Section 2.3: Biomass burning is not included in the model emissions. Are biomass burning events also excluded from the observational record? If so, how are these

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events discriminated from those that are purely anthropogenic? If not, can you quantify the possible impact of biomass burning on the observational data set and the results? Ans. In addressing the issue of CO emission from biomass burning and its effect on the measurements at MNM, we carried out an additional CO simulation by using biomass burning emission (GFED ver. 3.1 from 2005 to 2010) as a driver for the CO field in STAG. Simulated CO values at MNM from November to April showed a steady "background" concentration of 7 - 8 ppb, with a couple of noticeable peaks greater than 20 ppb, one on 26 April 2008 (Fig.1) and another one on 29 March 2010. In our analysis, these two peaks were not included in our estimation because of low correlation between Rn and CO resulting from the fact that they likely have different source regions. Thus our peak selection method excludes biomass burning effect and efficiently extracted enhanced events related to anthropogenic sources.

Section 2.3: CO produced photochemically from hydrocarbon oxidation is treated as a constant value in the model analysis, presumably to simplify the modeling. The amount of CO present downwind will depend on what sources influenced the sampled air masses and the transit time before sampling, and there will surely be seasonal differences in this photochemistry. What is the impact of this simplifying assumption in the modeling? Since a chemical-transport model is used here, why not calculate the photochemical CO production, instead of assuming a constant amount? Ans. The contribution from NMHCs produces a nearly background level at MNM because the rate constants of NMHCs with OH radical are larger than that of CO by one or more orders of magnitude. In addition MNM is located 2000 km from any source regions. Liang et al. (2004) showed almost constant contribution of CO concentration from NMHCs in their simulation.

Section 3.1: Much of the findings in this section are similar to the findings of Wada et al 2011; this should be noted here. Ans. "As reported by Wada et al., 2011" was added to the text.

p. 15344, line 11-14: This line should say " . . .are usually caused by. . .". It is too strong of a statement to say that every high CO concentration observed at these stations are caused by transport from the Asian continent. Ans. It has been corrected.

p. 15344, line 28: Add “likely” before “influenced”. This assertion has not been proven with the evidence provided up to this point. You could cite the previous results of Wada et al. 2011 as support here. Ans. It has been corrected.

p. 15345, line 3-6: Again, these conclusions are presented without proof that the proposed physical mechanisms actually produced the observed behavior. Reword these sentences to be less strong: “This behavior is consistent with the diurnal. . .” and “These results support a strong local. . .”. Ans. It has been corrected.

p. 15345, line 10: See comments above. Reword as “These peaks are consistent with the transport. . .”. Ans. It has been corrected.

p. 15345, line 24-25: Simply citing Wada et al. 2011 is not enough here to understand how the residual Rn was derived. Briefly describe the curve fitting procedure, etc. Ans. The 26th Butterworth filter with 30 days cut-off was applied for the low path filter to obtain the fitting curve. It has been added to the text.

Section 3.3: Once a ERN event is identified by analysis of delta(Rn), is it actually necessary to derive enhancements in CO? The correlation of absolute concentrations of CO vs Rn data for just the points within each Asian plume should have the same slope as the correlations of the enhancements of each species. Ans. The reviewer is completely right. The slope of the enhancement ratio (delta)CO/(delta)Rn is the same as the slope of the absolute concentration (CO/Rn). The enhancement ratios are commonly used in other studies (e.g. Levin et al., 1999; Schmidt et al., 2001, 2003).

Figure 5. It would be useful to note the slopes for each of the lines, or else plot all panels on the same scale. This way the relative slopes at each station could be compared. Ans. In Figure 5, it is important to show the high correlation of CO with Rn at MNM and

YON, whereas comparison of the slopes with the three stations is not essential. We added a statement that the x and y axes is different in the figure caption of Figure 5 to avoid any misunderstanding.

p. 15346, line 14-16. The photochemical production of CO from hydrocarbons should also vary with transport time. This would be most significant for the far-downwind MNM station. How do you know that different photochemical conditions do not contribute to the enhancement ratios? Ans. The transport time from the east coast of the Asian continent to MNM is estimated to be about 100 hours on average during the winter season based on the backward trajectory calculation. For the concentration of OH radical in the winter (Spivakovsky et al., 2000) and the rate constant of CO, a calculated chemical loss rate of CO is only about 1.1 %. This is not significant when compared with an overall error estimation of about 14 %.

p. 15349, line 14-16. Transport errors could still be an issue, because Rn and CO sources have different spatial distributions. Can you put a constraint on the impacts of transport errors on your analysis? Ans. It is difficult to estimate transport errors because all transport models have uncertainties associated with the transport mechanism. For more precise estimation, a regional model could help this problem.

p. 15351, line 15-17. State here the original inventory estimates for these regions, and note the relative changes represented by the new estimates. Ans. The original inventory of EDGAR for these regions and a comparison with the new emission estimates have been added in the text.

Results section. No explicit uncertainty estimates on the observations-derived emissions estimates are given. The sensitivity to the assumptions used in this analysis, such as variability in photochemical CO production and transport errors, is not tested. Error ranges for the derived emissions should be quantified and discussed here. Ans. The variability in the observed (delta)CO/(delta)Rn was estimated to be 10.8%. Variability of the sensitivity test of the peak selection criterion was 8.3%. Variability of the

Rn flux density used for STAG was 3.2%. These error estimates have been added in section 3.7. Thus an overall uncertainty was estimated to be about 14% using the error propagation method. It is difficult to estimate the transport error, as mentioned above. The contribution of the photochemical loss rate of CO with the reaction of OH radical is not significant, as also mentioned above.

*********** Technical Corrections: Just a few of the grammatical and other typographical errors are mentioned here. Many more errors need to be corrected before publication.

p. 15339, line 21. Begin sentence with "The" p. 15339, line 23. Add "and" before "chlorofluourocarbons", which should be lower case. p. 15340, line 1. Begin sentence with "The" p. 15340, line 4. Change to "Our study is the first to utilize the radon tracer method . . ." p. 15341, line 18. Change to ". . . YON is situated immediately downwind of the. . ." p. 15341, line 20. Change to ". . . is small, lightly populated, and has little traffic, . . ." p. 15341, line 22. Add "the" before "northeastern" p. 15342, line 7. Define "PIN" Ans. PIN is not acronym. This is a light sensitive photodiode with P, I, and N layers. p. 15342, line 20. Change "has been" to "was". p. 15346, line 13. Start new paragraph at sentence that begins "Delta(CO)/delta(Rn) obtained . . .". p. 15347, line 22. Change "special" to "spatial" p. 15348, line 10. Change "slightly lower" to "lower" p. 15348, line 14. Change "underestunated" to "underestimated". p. 15348, line 23. Add "from the regions detected" before "at the stations". p. 15349, line 4-5. Change to "We applied the method to our sites in the Western North Pacific region." p. 15350, line 15-16. Change to "Other peaks were not well reproduced, probably because these events were relatively small."

Ans. All corrections mentioned above have been implemented in the revised text. Finally, we added acknowledgement to the editors and reviewers for these constructive comments and detail corrections.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 15337, 2012.

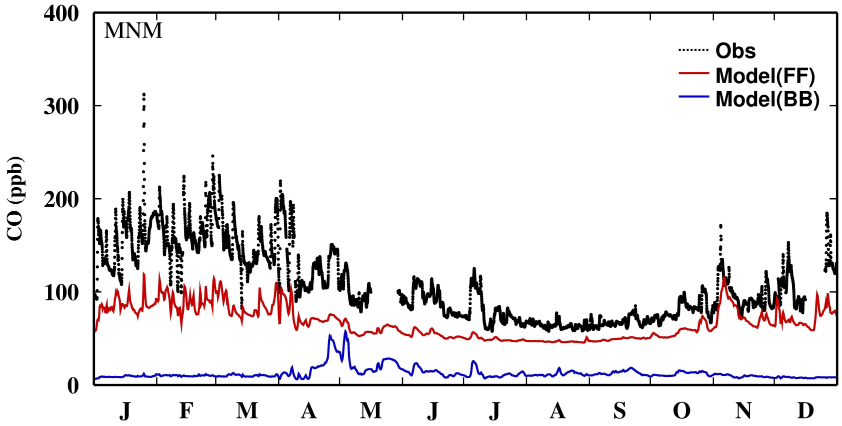

Fig. 1. Fig.1. Time series of observed CO (dots), simulated CO by using anthropogenic emission of EDGAR ver. 4.1 (red), and simulated CO by using biomass burning emission of GFED ver. 3.1 (blue) in 2008.