

1 **Model simulated trend of surface carbon monoxide for the**
2 **2001-2010 decade**

3
4 **J. Yoon¹ and A. Pozzer¹**

5 [1]{Atmospheric Chemistry Department, Max-Planck Institute of Chemistry, P.O. Box 3060,
6 55020 Mainz, Germany}

7 Correspondence to: J. Yoon (jongmin.yoon@mpic.de)

8
9 We thank the reviewer for the constructive and valuable comments, and will revise and
10 improve the manuscript soon as your comments.

11
12 ***General Comments***

13
14 *This manuscript first compares model results from simulations using decadal constant*
15 *emissions to results using the similar base conditions but including the RCP and GFED time*
16 *varying emissions. Regional mean CO concentrations using the time-varying sources are*
17 *found to be more similar to MOPITT than constant emissions. This section could be*
18 *shortened.*

19 **-> Some parts, which do overlap or are unnecessary, will be removed or shortened as**
20 **suggested by the referee. For example, the Taylor diagram is enough to provide a**
21 **concise statistical summary of spatial pattern correlation between satellite observation**
22 **and model simulation, so that the scattering plot (Figure 5 in the manuscript) is not**
23 **needed and will be removed.**

24
25 *The time varying anthropogenic and biomass burning emissions were used with chemistry to*
26 *derive a more realistic model response. Model CO distributions give reasonably good*
27 *agreement with the MOPITT surface product, although there are very large aggregation*
28 *errors in both data sets. Decadal trends from the model are compared to those determined*

1 *from a number surface sites, again with good agreement. In addition to model/surface site*
2 *comparisons in the manuscript, I suggest the model also be compared to trends in the*
3 *MOPITT products.*

4 **-> We are reluctant to compare the trends derived from MOPITT products against the**
5 **model-simulated trends. In fact, the MOPITT trend has an inevitable error caused by**
6 **time-varying averaging kernels and a priori CO profiles, as demonstrated in Yoon et al.**
7 **(2013). The MOPITT surface CO trend is therefore not realistic, with a possible bias,**
8 **ranging from -10.71 to +13.21 ppbv yr⁻¹ (-5.68 to +8.84%yr⁻¹) depending on location.**
9 **Unfortunately, it is not possible to eliminate the uncertainty of averaging kernels and a**
10 **priori solely based on satellite observations, as the true state is unknown. This is the**
11 **reason why in this study we used only the ground-based observations to evaluate the**
12 **model-simulated trend.**

13

14 *There is a brief discussion on trends in OH, CO and NOx trends from the model and the*
15 *influence of NOx on OH. This section is relatively weak and could be removed. Some*
16 *conclusions, such as the observed decreases in concentration over Europe and the US are due*
17 *to decreased anthropogenic emissions, are not new.*

18 **-> We agree that the section referring to the influences of NOx and OH is not enough to**
19 **identify explicitly the influence on the CO trend. Therefore, we will remove Figure 14**
20 **and corresponding discussion.**

21 **The simulated decreases in surface CO from anthropogenic emissions over Europe and**
22 **USA are not new, but confirmed in this study by comparing the simulation with satellite**
23 **and ground-based observations.**

24

25 *Specific Comments*

26

27 *P. 12410, line 13. It should be noted that the downward trends observed in the 1990s have*
28 *been attributed primarily to decreases in anthropogenic emissions (Duncan et al. 2007,*
29 *Novelli et al., 2003, among others).*

1 -> We will additionally mention in the manuscript that the downward trends observed
2 in the 1990s have been attributed primarily to decreases in anthropogenic emissions and
3 cite the relevant references (Duncan et al. 2007, Novelli et al., 2003, among others) in the
4 introduction.

5

6 *P. 12410-12411. All the satellites which measure CO need not be mentioned. It would be*
7 *better to say the MOPITT results are used here because of their rigorous evaluation/*
8 *validation and their 13 year continuous record. The pros and cons of using satellite retrievals*
9 *to validate models and to estimate long-term trends should be given.*

10 -> Accordingly to the comment, we will modify the manuscript.

11

12 *P. 12414, Section 2.3. This section would benefit from more detail on the MOPITT surface*
13 *product, including the pressure levels that define the surface product, its precision and any*
14 *bias.*

15 -> We will provide more details about the MOPITT TIR surface product as follows:

16 “The Measurements of Pollution in the Troposphere (MOPITT) instrument, launched
17 on board the EOS-Terra spacecraft in 1999, has been providing continuous global
18 products of atmospheric profiles of CO volume mixing ratio from 1000 to 100 hPa with
19 100 hPa interval and CO total column values (Deeter et al., 2003). The global MOPITT
20 retrieved CO data with high accuracy (expected precisions: 10%) has been applied to
21 various researches on its sources, transports, and sinks (e.g., publications at
22 <http://www.acd.ucar.edu/mopitt/publications.shtml>). In this study, the MOPITT Version
23 5 (V5) Level 3 (L3) thermal infrared (TIR) surface CO products in daytime are used
24 since they have been improved in the retrieval sensitivity and accuracy for the lower
25 tropospheric CO (Clerbaux et al., 2009; Worden et al., 2010, 2013; Deeter et al., 2007,
26 2011, 2012, 2013). MOPITT TIR products are based on thermal-infrared radiation at
27 4.7 μm . Even though a new joint (multispectral) TIR/NIR product features the
28 maximum sensitivity to near-surface CO, the TIR-based MOPITT can avoid significant
29 random errors in NIR-based MOPITT products (near-infrared radiation at 2.3 μm).”

30

1 *Section 3.1, P. 12415-12416. I found it hard to follow how the model data were transformed*
2 *to reflect the pressure and a priori constraints of the MOPITT retrieval. Is there something*
3 *missing in equation 1? This section needs to be written more clearly (e.g. see Deeter et al.,*
4 *JGR, 2010).*

5 **-> To clarify the description of Equation 1, we will rephrase the description of Equation**
6 **1 and refer to Deeter et al. (JGR, 2010) as follows:**

7 **“The EMAC-simulated surface CO can be transformed into a comparable quantity (so**
8 **called pseudo-retrieval, \hat{x}), to the MOPITT-retrieved surface CO as follows (Deeter et**
9 **al., 2003, 2010):**

10
$$\hat{x} \cong x_0 + A(x - x_0) = Ax + (I - A)x_0 \quad (1)$$

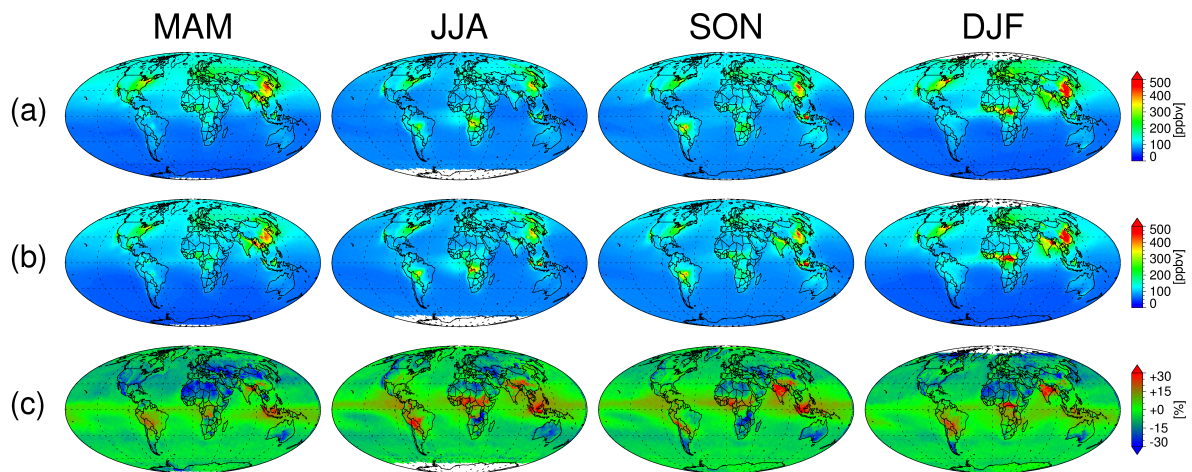
11 **where x_0 , A , I and x represent the MOPITT a priori CO, the MOPITT averaging**
12 **kernels, the identity matrices, and the EMAC-simulated CO profiles from surface to 100**
13 **hPa, respectively.”**

14

15 *P. 12416, lines 8-21, Figures 4, 5 and 6. These figures all depict the correlation of the model*
16 *and MOPITT CO. I think the Taylor diagram (Figure 6) contains the most information and*
17 *the other 2 can be removed. The authors should briefly say why this type of diagram is useful*
18 *(e.g. Taylor, JGR, 2001).*

19 **-> As noticed by the referee, the Taylor diagram contains all the statistical values (i.e.**
20 **the spatial correlation coefficient, normalized standard deviation, normalized centred**
21 **root-mean-square difference, and relative difference) used in this study. Therefore,**
22 **Figure 5 is unnecessary and will be removed. For Figure 4, we will change it to show the**
23 **seasonal distribution of MOPITT observation and RG simulation, and therefore provide**
24 **how different they are at each season as below.**

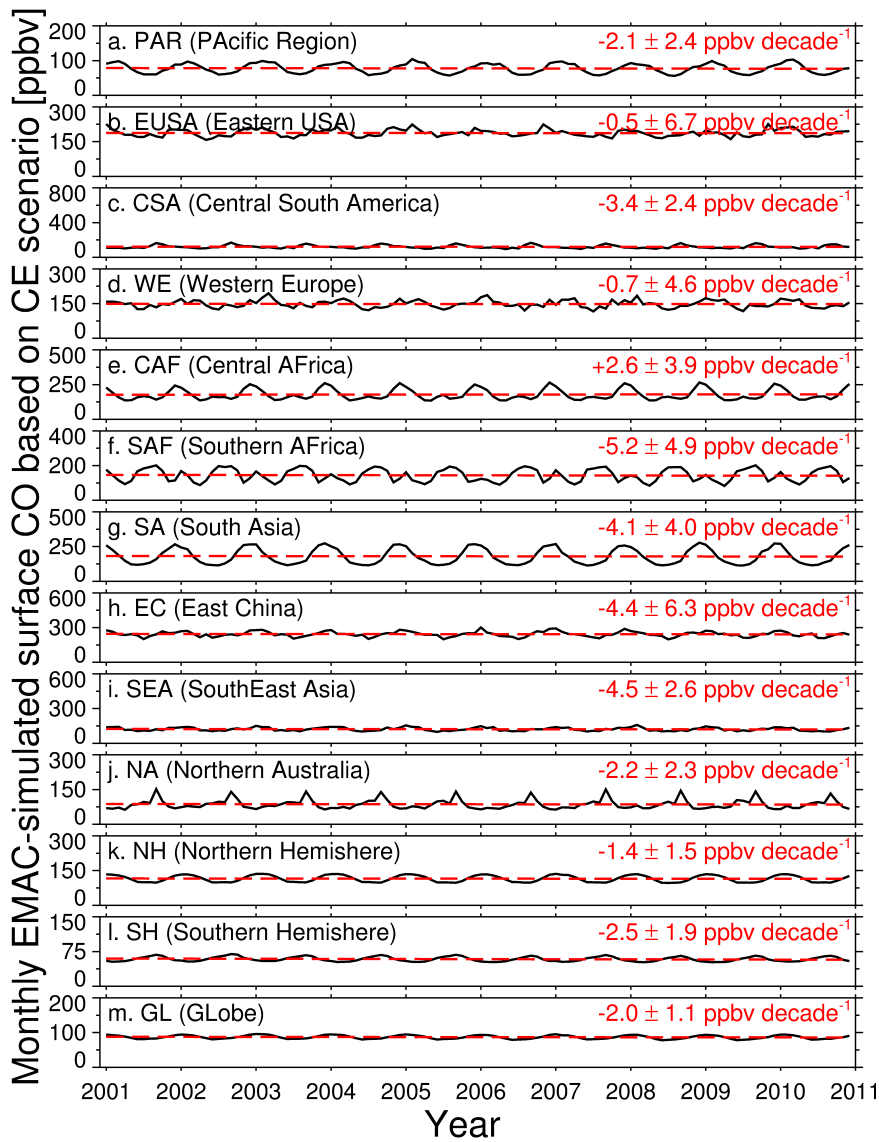
25



1
 2 Figure S1. Global distributions of seasonal (a) MOPITT-retrieved surface CO, (b) pseudo-retrievals of EMAC-simulated
 3 surface CO based on RG scenarios, and (c) their relative difference from 2001 to 2010.

4
 5 *P. 12417, Table 3. The mean decadal model results for the constant source and time varying*
 6 *source runs are compared. Mean CO over the Eastern USA and Western Europe are greater*
 7 *in the time varying scenario even though emissions have decreased. In Figure 12 a decadal*
 8 *decrease trend is shown for most regions. Transport from Central South America (the only*
 9 *region showing a strong increase in emissions) seems unlikely. Shouldn't have mean CO*
 10 *decreased?*

11 **-> The monthly means of surface CO over Eastern USA and Western Europe based RG**
 12 **scenario should be smaller than the monthly means on CE scenario as shown in Figure**
 13 **S2 below (please compare it with b. EUSA and d. WE in Figure 11 in the manuscript)**
 14 **since the RG emissions have decreased.**



1

2 Figure S2. Regional and global trend estimates of monthly EMAC-simulated surface CO based on CE scenario with $\pm 2\sigma$
 3 errors from 2001 to 2010.

4 **However, the values in Table 3 and Figure 6 are not the surface CO, but pseudo-**
 5 **retrievals of simulated surface CO. In other words, because the pseudo-retrievals are the**
 6 **weighted mean contributions of the EMAC-simulated CO profiles (x_{EMAC}) and the**
 7 **MOPITT surface a priori CO profiles (\bar{x}_{MOPITT}) in multiple layers from surface to 100**
 8 **hPa as shown in Equation 1, the pseudo-retrievals of simulated surface CO based on RG**
 9 **scenario can be larger than the pseudo-retrievals on CE scenario over Eastern USA and**
 10 **Western Europe.**

11

12

1 *P. 12416, line 23. Is 'resume' the correct word?*

2 **-> It will be changed into "show".**

3

4 *P. 12418, Table 4. Would the authors comment on why the model gives statistically*
5 *significant trends at about twice as many sites as the measurements.*

6 **-> The simulations on the resolution, 1.875 by 1.875 degrees can diminish extreme**
7 **values. Therefore, the model simulations can lead to more statistically significant trends.**

8

9 *P. 12418-12419, Figures 7, 8. A majority of the trends determined from the WDCGG surface*
10 *data and the model (Table 4) fall in the range of 0-20 ppb decade-1. The high statistical*
11 *agreement between model and measured trends in Figures 7 and 8 appears to be driven by a*
12 *few locations. Is this the case? Are there commonalities among the sites falling outside of the*
13 *cluster?*

14 **-> The correlation coefficients and linear fittings in Figures 7 and 8 show the statistical**
15 **correlation between two variables on X and Y axes. We have calculated the statistical**
16 **dependence between them with the same weights. As you see in Figures 7 and 8, only two**
17 **points are perfectly on the linear regression line, so the statistical correlation driven by**
18 **the most of variables except the two points little changes.**

19

20 *P. 12420, Figure 9a. Why do the model results with constant emissions show decreasing*
21 *trends in the Southern Pacific, Indian and Southern Oceans?*

22 **-> The changes in CO in simulation CE are purely due to meteorological changes in the**
23 **atmosphere. The changes could be due for example to changes in transport patterns**
24 **and/or increase or decrease in precipitation (which in turn influences the chemistry of**
25 **CO).**

26

27 *P. 12421, line 9. The oxidation of non-methane hydrocarbons should be included as a major*
28 *source of CO (Duncan et al., JGR, 2007 and references therein).*

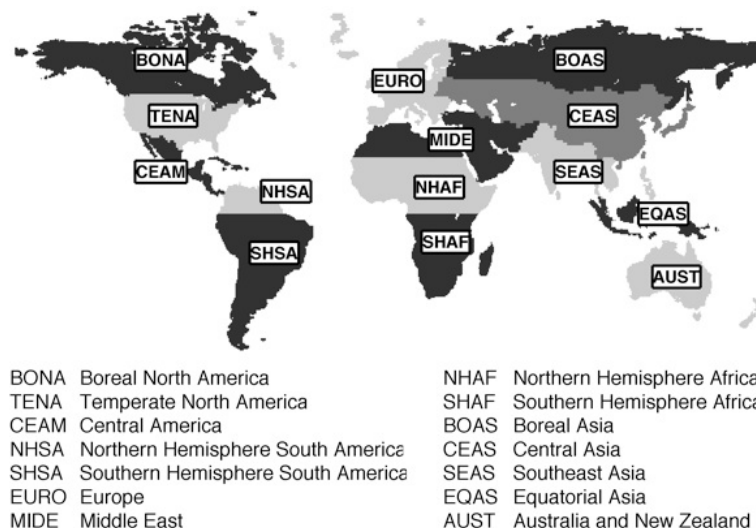
1 -> We will include the oxidation of non-methane hydrocarbons in the manuscript as a
2 major source of CO with relevant references.

3

4 *P. 12421, Figure 12. GFED 3.1 reports SEAS CO emissions from fires in 2010 were the*
5 *greatest for the decade but high emissions in Asia are not shown in Figure 12. Would the*
6 *authors comment on this.*

7 -> You can see higher emissions of biomass burning in South Asia (SA) in 2010 in Figure
8 12. The SEAS (Southeast Asia) region defined in GFED is partially similar to our South
9 Asia (SA) region as shown in Figure S3 below. Simply we used similar names (here and
10 in GFED v3.1) for different regions.

11



12

13 Figure S3. 14 basis regions for GFED annual cumulative emissions [<http://www.globalfiredata.org/Tables/index.html>].

14

15 *P. 12422, Section 4.2, lines 5-29. The trends discussed here are given in four or five different*
16 *units. Can they be normalized to % change per decade? The trends from MOPITT and AIRS*
17 *instrument come from Worden et al. 2013 and represent the total column. I would like this*
18 *work to compare model trends with trends calculated from the MOPITT surface product. The*
19 *model and MOPITT could also be compared in the mid and upper troposphere.*

20 -> It is difficult to unify the unit of the trends from several references due to the missing
21 values for normalization provided in the references. Additionally, as mentioned before,
22 since it is impossible to remove the uncertainty from MOPITT surface data, the

1 **MOPITT trends cannot be used to compare with the model-simulated trends (see Yoon**
2 **et al., 2013).**

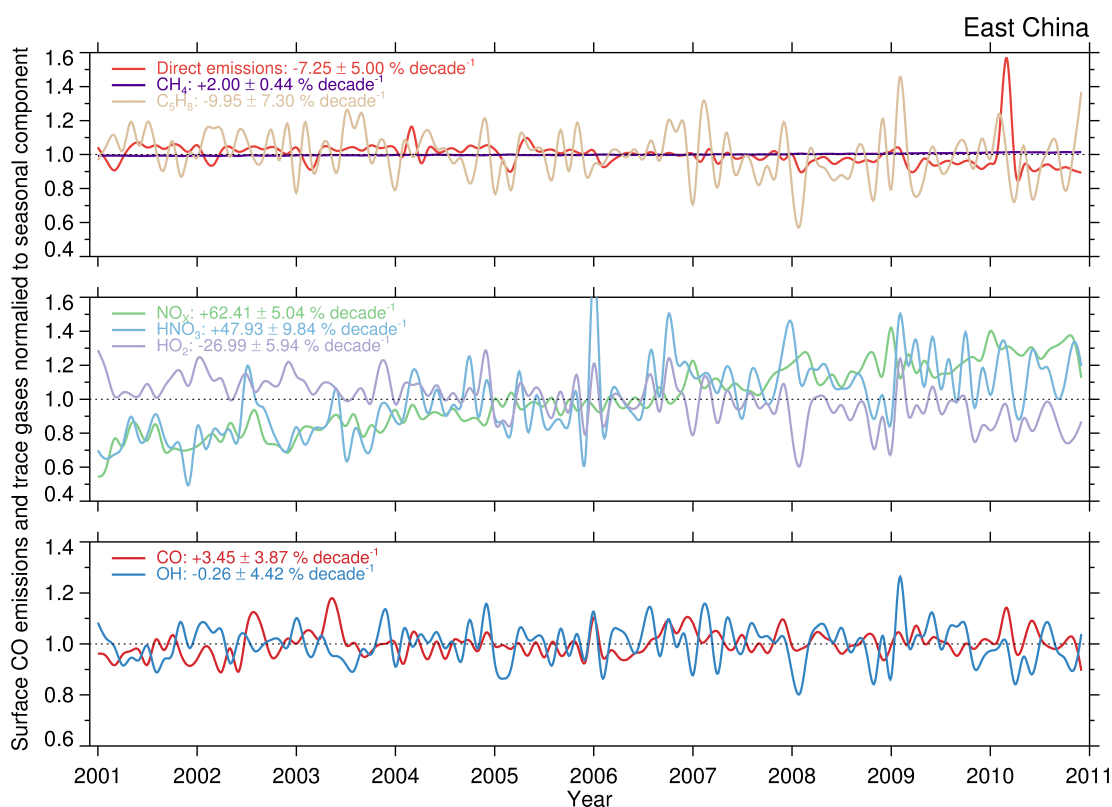
3

4 *Pp. 12422-12423, Figure 13. The changes in CO from the model are compared its emissions.*
5 *I don't think it is surprising they are similar. This rather long discussion could be shortened.*
6 *Perhaps say that regional-scale model trends generally reflect trends in the emissions, except*
7 *for Eastern China. Then examine China more closely.*

8 *P. 12423, lines 9-14. Worden et al., 2013 report a strong decrease in MOPITT column CO*
9 *over E. China during the 2000s. Emissions from Eastern China in the model show a marginal*
10 *decrease with time however the model results show an increase. The authors suggest this*
11 *surprising result may come from transport or secondary chemical production. The results*
12 *from the constant emission model run (Figure 3) don't seem to support transport. The*
13 *possibility that chemical production from hydrocarbons are referenced to Tohjima et al.,*
14 *2014 and Anglebratt et al., 2011, but neither of these papers quantitatively examine how*
15 *reasonable changes in VOCs would effect CO trends. This manuscript should look into the E*
16 *Asia emissions/surface changes in more detail.*

17 **-> As mentioned before, the trend estimates from MOPITT CO data can be biased by**
18 **the uncertainty from time-varying averaging kernels and a priori, so that we didn't used**
19 **the MOPITT CO data to evaluate the model-simulated trends. Nevertheless, we agree**
20 **with the comment. We will more closely examine the trends over Eastern China using**
21 **Figure S4 as follows;**

22



1
2 Figure S4. Long-term time series of surface CO emissions and relevant trace gases normalised to seasonal component over
3 East China from 2001 to 2010.

4
5 **“Notwithstanding a significant decrease in the CO emissions over East China, the**
6 **simulated trend in surface CO shows an insignificant increase. This is opposite to the**
7 **results from Worden et al. (2013) that showed a negative trend in MOPITT tropospheric**
8 **column CO over East China. Figure S3 shows long-term time series of surface CO**
9 **emissions and trace gases relevant to chemical production of CO and OH over East**
10 **China from 2001 to 2010. Hydroxyl radical (OH) is the main oxidant of many trace**
11 **gases and therefore one of the most important species in the atmospheric chemistry**
12 **(Lawrence et al., 2001; Wallace and Hobbs, 2006). CO removal from the troposphere is**
13 **almost exclusively by reaction with OH (Hauglustaine et al., 1998; IPCC, 1996) and, on**
14 **the other hand, CO provides the most important sink for OH (Lelieveld et al., 2002;**
15 **Thompson et al., 1992). As mentioned, the direct emissions from biomass burning and**
16 **fossil/domestic fuel has the most influence on the surface CO change, and show**
17 **significantly negative trend in the East China region ($-7.25 \pm 5.00 \text{ \% decade}^{-1}$).**
18 **Additionally, biomass burning in 2010 is the greatest for the decade in Asia (Giglio et al.,**
19 **2010). Oxidation of CH₄ is another primary chemical production of the CO, and the**

1 surface CH₄ significantly increases, $+2.00 \pm 0.44$ % decade⁻¹. In contrast, isoprene
2 (C₅H₈) occupied a majority in biogenic NMHC (Holloway et al., 2000) presents for
3 estimating the change in chemical production of CO by oxidation of NMHC, and it
4 changes by -9.95 ± 7.30 % decade⁻¹. These trends show that both direct emissions and
5 chemical formation of CO over EC region decreased during the decade 2001-2010.

6 Nevertheless the surface NO_x drastically increased during the same decade ($+62.41 \pm$
7 5.04 % decade⁻¹), which contributed to the decrease of the HO₂ (-26.99 ± 5.94 % decade⁻¹)
8 via HNO₃ formation ($+47.93 \pm 9.84$ % decade⁻¹) (see also Lelieveld et al, 2002, 2004).

9 The decrease in OH concentration (-0.26 ± 4.42 % decade⁻¹) implies a reduce oxidation
10 of CO, and therefore the presence over the EC region of a slightly positive trends of CO.
11 It must be underline that this trend is not significant, and it is calculated only for the
12 surface. The total tropospheric column of CO is strongly influenced by the long-range
13 transport of CO, which has a lifetime of around 1 month. The results of simulation CE,
14 where the pure CO transport induce a slight negative trends in the CO concentration
15 over EC, are therefore in agreement with the results of Worden et al. (2013).”

16
17 *P. 12423, Section 5. From model calculated trends of OH, CO and NO_x, the authors conclude*
18 *OH trends are largely controlled by NO_x. The discussion would benefit from a description of*
19 *CO-OH-CH₄-NO_x-O₃ chemistry. (e.g. Tables 1 and 2 in Lelieveld et al., ACP, 2004). The*
20 *authors should temper this conclusion, e.g. ‘These results suggest that more than just the CO*
21 *trend effects trends in OH’.*

22 **-> Thanks for your valuable suggestion. As the section will be removed, we do not think**
23 **it is necessary to described CO-OH-CH₄-NO_x-O₃ chemistry, as this is done in many**
24 **publications and textbooks. Nevertheless we will add the sentence suggested by the**
25 **referee, enhancing the fact that CO is controlled by multiple factors.**

26
27 *The changes in OH and NO_x shown in Figure 14 are very small and contain large*
28 *uncertainties. A more robust conclusion would require a multivariate analysis of the*
29 *important species in the OH cycle.*

1 -> We agree your comment and will remove Figure 14. As your previous comments, we
2 will more closely examine the trends over Eastern China using Figure S4 and temper the
3 conclusion.

5 *References*

6
7 *I suggest the number of citations for each reference be limited to no more than 3-4 carefully*
8 *chosen papers.*

9 -> We will choose 3 or 4 references for each citation.

11 *Tables and Figures*

12
13 *Table 2. Note that 'GC-HgO' is the method, RGD is the instrument.*

14 -> The information about instrument and analyses measurement method is from GAW
15 Report No. 188 (WMO, 2009). We will change the label, "Measurement Method" into
16 "Instrument or Analyses Measurement Method".

17
18 *Table 3. Mean MOPITT CO for PAR is reported as 91.78 ± 33.4 with standard deviation of*
19 *7.32 ± 5.28 . Are these values the mean and aggregation errors? Please clarify this in the*
20 *caption*

21 -> They are the mean values of monthly means, standard deviations, spatial correlation
22 coefficient, centred root-mean-square (RMS) difference, and relative bias from 2001 to
23 2010 with $\pm 2\sigma$.

24
25 *Table 4. As for Table 3. Also add in the caption that $(\omega/\omega\sigma) > 2$ is significant.*

26 -> We will add it in the caption.

1 *Figures 1a, b. The maps of global mean CO emissions show the general distribution of the*
2 *fossil fuel and biomass burning emission strengths but say little about changing emissions.*
3 *Figures showing model emissions by region over time would better serve in discussions of*
4 *trends.*

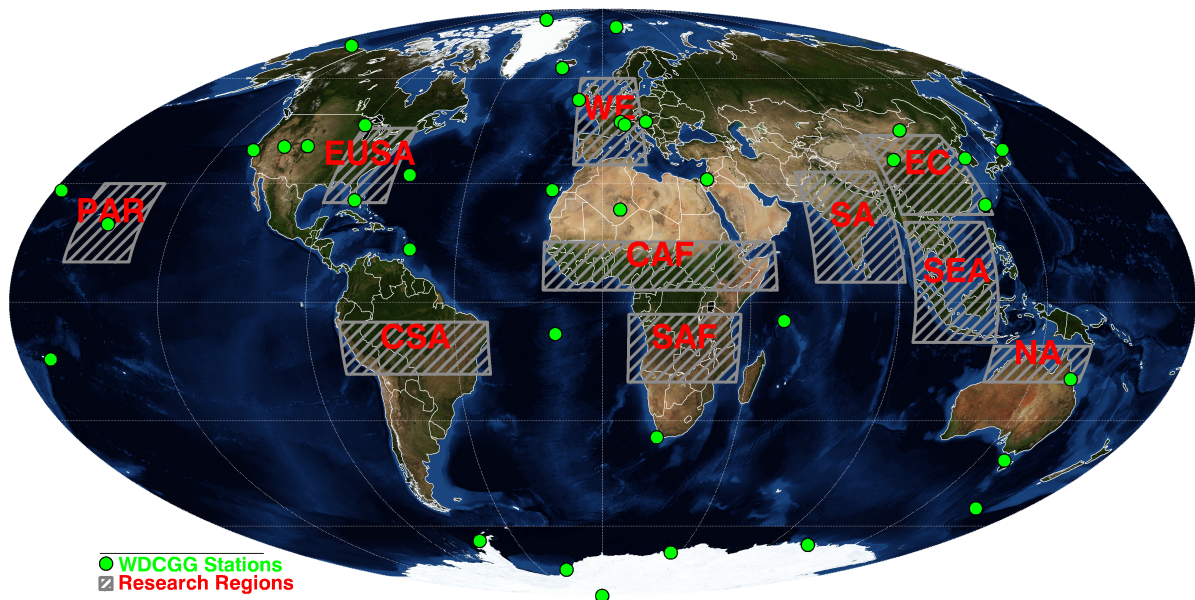
5 **-> The model emissions by region over time have been shown already in Figure 12.**

6

7 *Figure 3. The names of the regions cannot be read. The dots showing the site locations are*
8 *hard to see these should all be larger.*

9 **-> As your comment, the figure will be modified as below.**

10



11

12 Figure S5. Research region domains and geolocations of WDCGG stations listed on Tables 1 and 2, respectively.

13

14 *Figure 5. What do the yellow, blue and black dots show?*

15 **-> Black, blue, and yellow respectively indicate larger points than 1, 10, and 100 falling**
16 **into each of bins (bin size: 5 ppbv).**

17

18

19

1 *Figure 6. What are the standard deviations normalized to?*

2 **-> The simulated standard deviations are normalized to the corresponding observed**
3 **standard deviation (σ_r).**

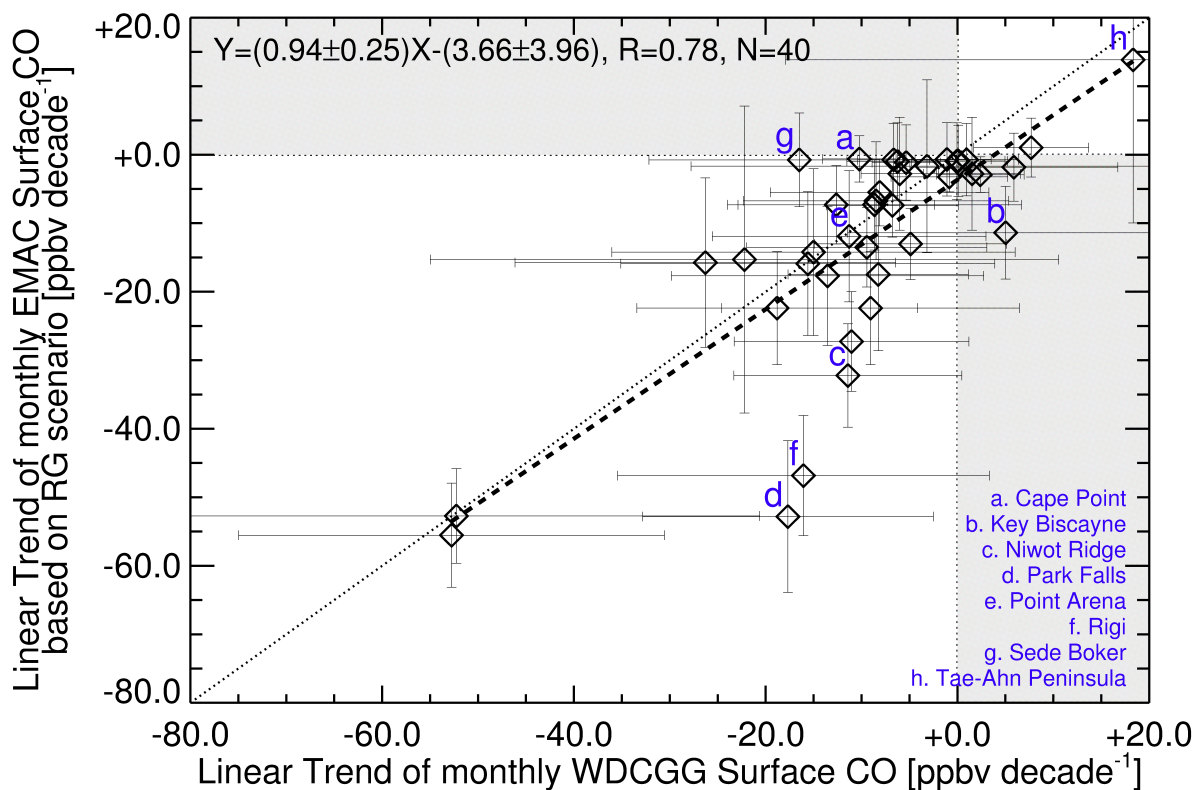
4

5 *Figure 8. There are 4-5 sites which fall outside of the general cluster. Which these are they?*

6 *Perhaps they can be labelled as in Figures 13 and 14 or defined in the figure caption.*

7 **-> As your suggestion, they will be labelled in Figure 8 as below.**

8



9

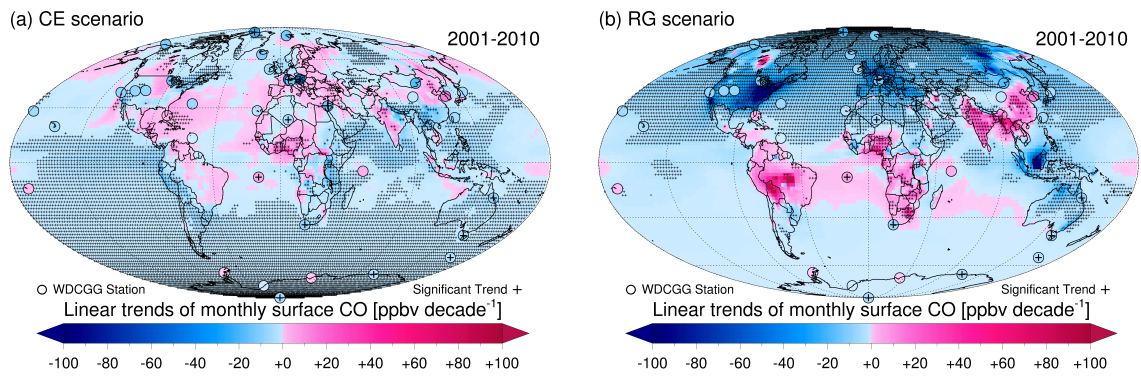
10 Figure S6. As in Figure 7 (b), but the trends of monthly EMAC-simulated surface CO from a model grid-box to the upwind
11 direction at the stations (i.e. Cape Point, Key Biscayne, Niwot Ridge, Park Falls, Point Arena, Rigi, Sede Boker, and Tae-ahn
12 Peninsula).

13

14 *Figure 9. The site symbols should be larger.*

15 **-> They will be enlarged as below.**

16



1

2 Figure S7. Global trend estimates of monthly WDCGG-archived and EMAC-simulated surface CO based on (a) CE and (b)

3 RG scenarios from 2001 to 2010. The significant trends are shown as a plus symbol (+).

4

5 *Figure 10. The colored panels are not very useful. The trend data are given in several other*

6 *places. These figures could be removed.*

7 **-> We agree with your comment. Figure 10 will be removed.**