Review Response 3

June 2024

1 Major Comments:

This manuscript provides a detailed analysis of the observed carbon monoxide mixing ratios above several regions sampled by the IAGOS program, and their associated emissions source regions. I find the analysis to be scientifically sound and the conclusions are consistent with the other papers submitted so far to the TOAR-II Community Special Issue. However, to increase this papers relevance to the TOAR-II effort I would like to recommend four areas for further analysis and discussion:

We thank the reviewer for her/his comments that will help improving our study. We respond below to each specific point.

1) There are some previous TOAR papers and other peer-reviewed studies that are relevant to this work and they should be cited (see papers referenced below).

Thank you, as advised the following citations have been added :

- Novelli et al. [1998]
- Kim et al. [2023]
- Gaudel et al. [2020]
- Gaudel et al. [2018]
- Lal et al. [2014]
- Lawrence and Lelieveld [2010]
- Lelieveld et al. [2001]
- Li et al. [2001]
- Nowak et al. [2004]
- Lu et al. [2018]

- Chang et al. [2017b]

2) This study touches on two important topics that have received little attention in the peer-reviewed literature, and the authors have an excellent opportunity to expand upon these topics. Specifically, these topics are the exceptionally high ozone mixing ratios in the UT above Siberia, and the high ozone levels in the lower, mid- and upper troposphere above the Middle East. Figure 5 (top left panel) of Gaudel et al. (2018) shows that the highest ozone values in the upper troposphere in June-July-August are found above Siberia. Figure 3c of Gaudel et al. (2020) shows that the ozone above the Middle East is even greater than ozone above China. These two regions have received relatively little attention in the peer-reviewed literature (an exception is Li et al., 2001). It would be helpful if these two regions can be given greater attention and highlighted in the abstract and conclusions as regions with exceptionally high ozone. Please elaborate on the potential contribution of biomass burning and anthropogenic emissions to the observed high ozone levels. The authors mention a potential contribution of the Asian summer monsoon to the high ozone levels above Siberia (i.e. the monsoon transports pollution from South and East Asia to Siberia). This is an excellent hypothesis and I think it should receive further attention.

Thank you for this comment that will improve the manuscript. As you noted, the two regions, Siberia and Middle-East present on average really high values of Ozone. As suggested these two regions will be highlighted and further discussed in the abstract, in the results section and in the conclusions (see below in blue).

- Among the studied regions, the troposphere above Middle-East and the UT of Siberia presented extremely high O3 values. lines (13-14)

- Previous studies already noticed the O_3 maximum over Siberia [Gaudel et al., 2018]. [Cohen et al., 2018] suggested that this maximum could be due to a higher stratospheric influence over the region. In the anthropogenic CO anomalies, the O_3 values are close to the background. However, as demonstrated in Fig.**??** a significant portion of polluted air masses are transported from the surface of East Asia to the UT of Siberia via the East Asian summer monsoon, which could potentially influence the production of O_3. On average for the other regions, O_3 mixing ratios in CO anomalies are 13 ppb higher than their respective median and this difference can reach 21 ppb for the CO anomalies associated with Biomass Burning emissions. Lines (347-352)

- In the Middle East, O_3 values are among the highest in JJASO in the LT and MT. The summertime median is also higher than the median from East Asia (see Fig.13 and Fig.14) which is a region with identified extreme O_3 values [Chang et al., 2017a, Lu et al., 2018]. Li et al. [2001] suggested that the important tropospheric O_3 in Middle East were due to the constant import of pollution from different regions trapped in the upper level anticyclone and the strong subsidence associated to it cause an accumulation in the region. Here the CO anomalies detected are mostly caused by emissions from the Middle east rather than from long range transport. In the Middle East LT, values of O_3 inside CO anomalies attributed to anthropogenic emissions are lower than the 25th percentile, which is similar to the observation

made on the northern hemisphere mid-latitudes. In the MT, the anthropogenic anomalies are close to the median during both seasons. Lines (436-443)

- In the UT O_3 values are maximum over Siberia. The O_3 measured within the BB anomalies are 15 ppb higher than the median but no no elevated values are measured in the anthropogenic anomalies coming from Eastern Asia. Further investigations are needed to explain the extremely high values of O_3 measured in the UT of Siberia in JJA. Lines (536-538)

- In the lower and middle troposphere, the maximum O_3 values are found in Middle East. Previous studies assumed that the high O_3 in the regions were due to long range transport of polluted air masses followed by chemical production in the regions [Li et al., 2001, Duncan et al., 2008]. In the LT and MT most of the detected CO anomalies are from local anthropogenic emissions which either show low values of O_3 or values close to the median. In the UT, in JJASO CO anomalies are mostly from anthropogenic emissions from South East Asia. Those anomalies show enhanced values of O_3. Lines (579-584)

This paper is about CO anomalies and as such will focus on those two regions with this prism only, so the focus is made on the O_3 values inside the CO anomalies, but a further analysis on the high background of O_3 in these two regions is out of scope of the current paper and could be the subject of a future study.

3) Previous studies (Nowak et al., 2004, Figure 3; Cooper et al., 2002, Figure 8) have shown that scatter plots of ozone vs. CO are an effective way to highlight air pollution episodes and stratospheric intrusions (or air in the UTLS that is of stratospheric origin). These types of plots would be helpful for this study. For example, on line 277 the authors speculate that some of the high ozone values may be due to stratospheric influence. A scatter plot ozone vs CO could indicate instances of stratospheric intrusions.

This study focuses on the extreme values of CO and the stratospheric air masses are discarded in this study thanks to a filtering based on 2 PVU. Therefore, the high ozone values are not attributed to the stratosphere (or it is an outlier that should be further monitored as a case study). It can also be the (aged) stratospheric influence in the troposphere and we cannot see that with a scatter plot because we are only looking at the "high CO" branch of the scatter plot. So we believe that the suggested scatter plot is not meaningful for this analysis.

Objectives of the paper will be further clarified to avoid any "frustration" in the introduction, the following sentences have been added in blue below:

"Ozone values are presented as additional information. However, detailed analysis of the ozone values and climatology is outside the scope of the current paper."

4) Many of the study regions have well known trends in ozone and CO since 2000, but these trends are not addressed. The plots of average ozone and CO can therefore be misleading for certain regions. For example, during summertime, lower tropospheric ozone has decreased strongly in eastern North America since 2000, while it has increased in wintertime (see Figures 14 and 15 of Gaudel et al.; also see Chang et al., 2017). Lower tropospheric ozone has also increased

in East Asia (Lu et al., 2018; Kim et al., 2023). Globally, CO has decreased since the 1990s. For example, trends of global CO levels can be found at the bottom of this webpage maintained by the NOAA Global Monitoring Laboratory: `https://gml.noaa.gov/ccgg/figures/` *(The figure called cotr_global.pdf shows a decrease of CO since the year 2000). Also, extreme CO air pollution events have decreased across the USA since 2000: https://www.epa.gov/air-trends/carbon-monoxide-trends Because ozone and CO have changed in many regions since the year 2000 it would be helpful to compare regions using data from the most recent years, when possible, rather than using 20-year averages.*

This analysis is not dedicated to trend analysis (already done by e.g. Cohen et al. [2018] regarding the IAGOS dataset). As the objective here is to characterise the "extremes of CO" over the entire IAGOS data set (to maximise the statistical robustness of the results), our strategy was to define the "extreme" as above the regional and seasonal Q95, assuming that the seasonal and regional differences (to be discussed) are "larger" than the global trend of CO. We believe our methodology is then of interest to detect and assess the variability of extreme events, occurring whatever the global trend. It thus provides a diagnostic picture of the origin (type of source and area) of the extreme CO that is important information to be further used in the model's evaluation (the right CO/O3 for the right reasons).

As advised, we also made the same analysis with only the last 10 years of the IAGOS datasets. The tables 1 and 2 below shows the 95th percentile computed with the full data period (2002 to 2019) to the one computed with the data from 2010 to 2019.

The differences between the two data sets can be seen in the figure below, which shows the results of the analysis conducted using the full data period and the figure using only the measurements from the last 10 years. This confirms that the trend of CO can be strong in some regions for the 95th percentile, however the differences between the two figures are not significant, and the origins and sources of the anomalies remain similar in regions with sufficient number of data. Consequently, our conclusions remain the same and it was decided to retain the full data period in order to have a larger dataset and to ensure greater statistical robustness. Indeed, it can be seen from figure B1 in the appendix that some regions are predominantly sampled in between 2002 to 2009. Removing this part of the data would result in a significant reduction in the number of measurements for those regions.

A paragraph regarding the trend and the sensitivity of our diagnostics to the period used in the analysis has been added to the conclusion (lines 594-598):

Our study focused on CO anomalies measured between 2002 to 2019, but important trends in CO and O_3 in the atmosphere have been observed in several of the studied regions (e.g. Novelli et al. [1998], Kim et al. [2023], Gaudel et al. [2020]). So, we performed the same analysis with only the last 10 years of the IAGOS measurments. Several regions, showed a decreased 95th percentile in this datasets (see tables below). However, the origins and sources of the anomalies remain similar in regions with sufficient number of data. The conclusion the study remained largely unchanged for the CO anomalies of the last 10 years.

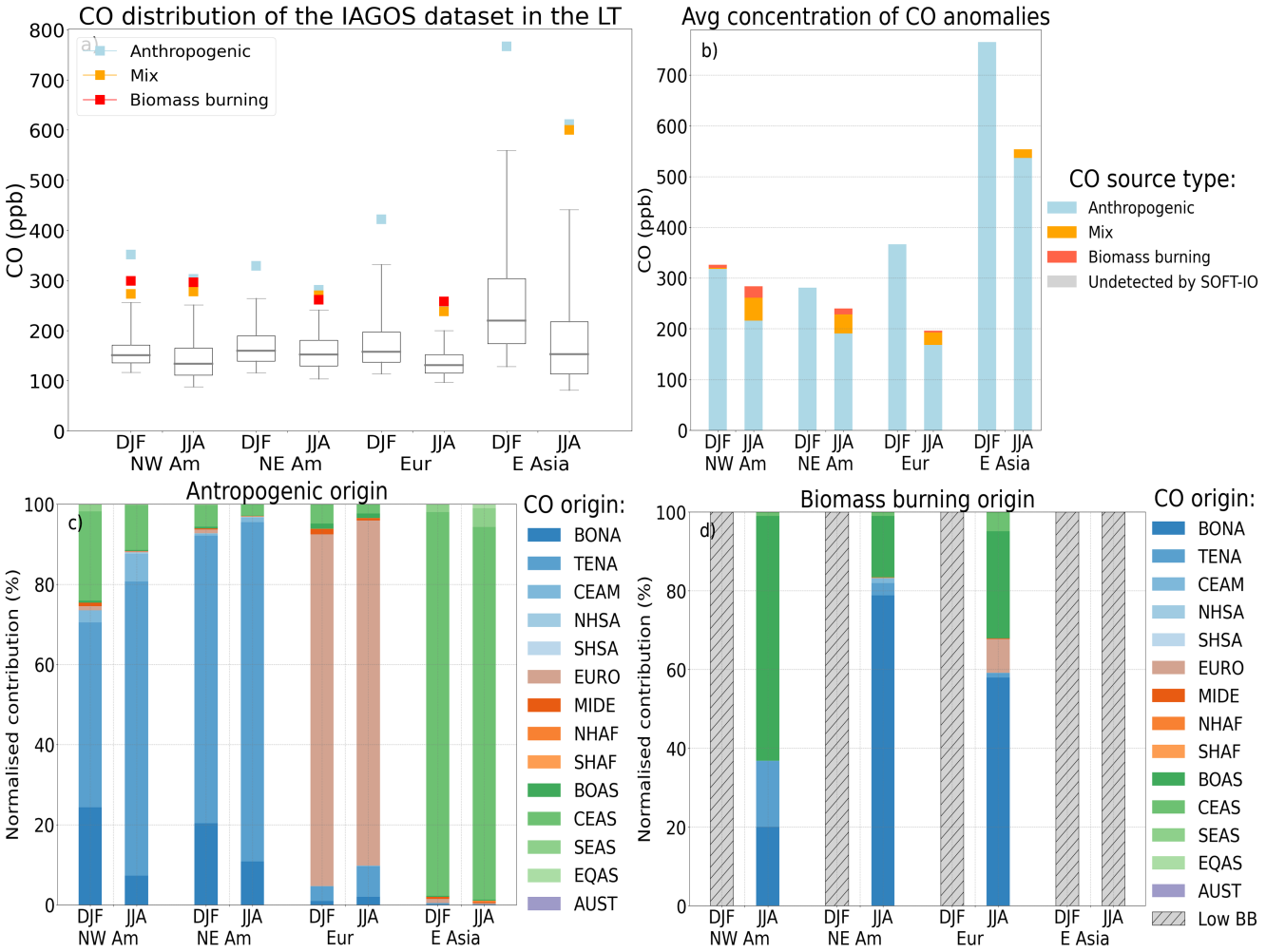

Figure 1: a) CO measured by IAGOS in the LT (below 2km). The box-plot represents the 5th, 25th, 50th, 75th and 95th percentiles of the CO distribution, while the coloured squares represent the mean values of CO inside the detected anomalies (each colour represents a type of CO anomaly attributed to a different source with SOFT-IO: red for biomass burning, blue for anthropogenic and orange for mix sources). b) Bar-plot showing the averaged mixing ratios of CO in all the detected anomalies (¿q95) in the LT in each region for JJA and DJF (given by the total height of the bar), and their proportion according to the different sources (blue for anthropogenic, red for biomass burning and orange for mix, the relative height of the coloured blocks represents the proportion of each type of anomaly). The proportion of plumes where no contribution is modelled by SOFT-IO are represented in grey (in this figure no anomalies are undetected by SOFT-IO over the 4804 observed). c) Regional origin (according to GFED regions, as in Fig. 1) of the anthropogenic contributions of the anomalies associated with mix and anthropogenic sources in the LT in NH extra-tropics (the hatched part cover region/season with not enough anomalies attributed to the mixed or anthropogenic categories) d) Same for the origin of the biomass burning contributions associated with mix and biomass burning anomalies. The Low BB patched (hatched grey patches) is applied if a regions has less than 3% of its plumes attributed to either mix or BB sources.

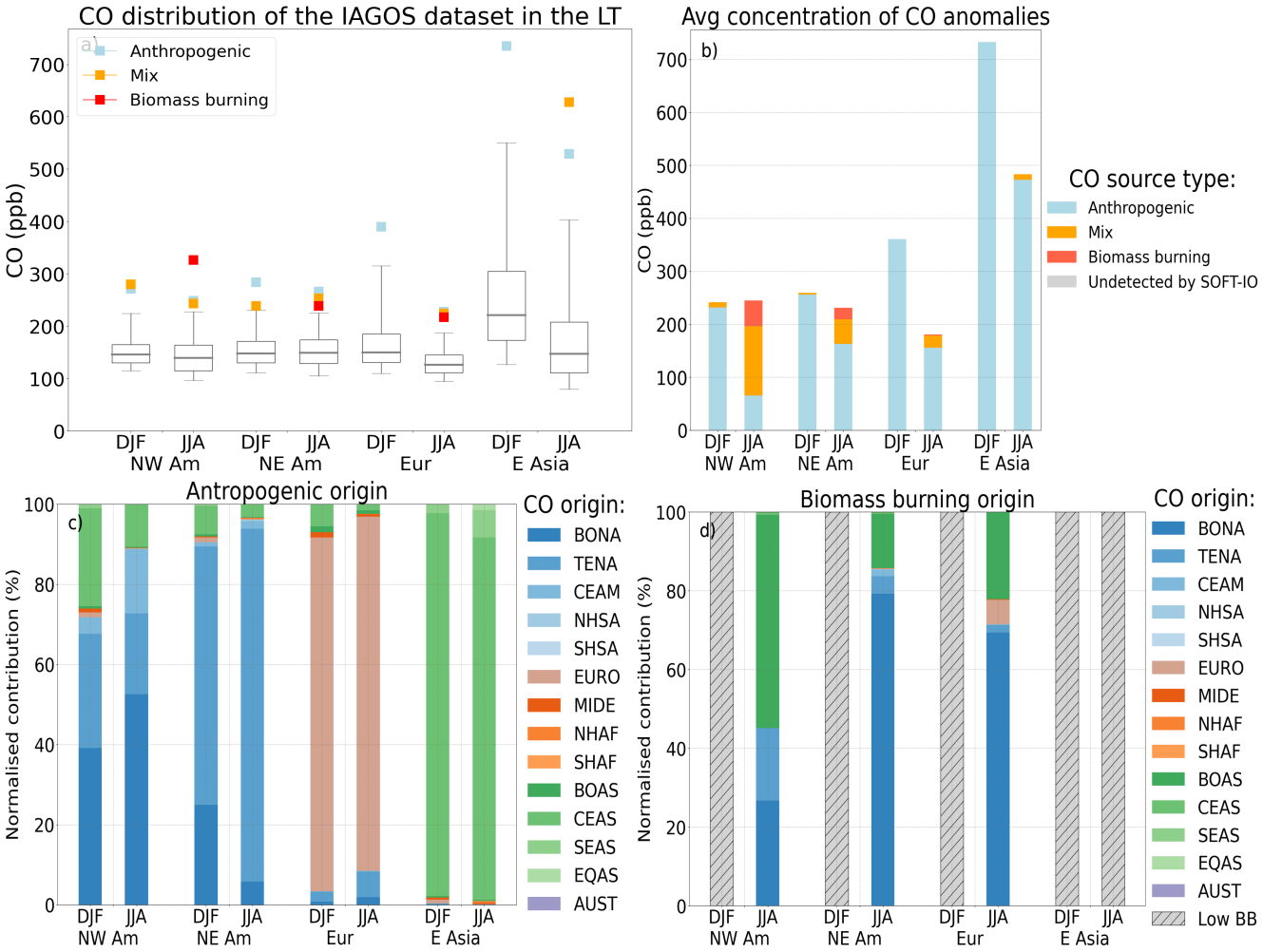

Figure 2: Same as figure with only the data from 2002 to 2019.

2 Minor Comments:

The paper contains many grammatical errors that should be corrected. A co-author with excellent English skills should carefully proofread the entire text.

Thank you for your comment. A thorough proofreading has been made by one of the co-author, native english speaker.

Line 191 In addition to increased CO emissions in winter, there is also a well-known increase in CO lifetime in winter (due to less ozone and OH), which also explains the higher wintertime concentrations (Novelli et al., 1998).

Corrected.

		LT	FT	UT
NW Am	DJF	256	160	146
	JJA	251	149	145
NE Am	DJF	264	159	126
	JJA	241	156	132
Eur	DJF	332	158	126
	JJA	200	140	123
Sib	DJF	no data	no data	127
	JJA	no data	no data	181
E Asia	DJF	559	209	129
	JJA	441	173	162

		LT	FT	UT
NW Am	DJF	224	155	142
	JJA	227	168	140
NE Am	DJF	230	148	112
	JJA	225	156	126
Eur	DJF	315	150	117
	JJA	187	135	118
Sib	DJF	no data	no data	119
	JJA	no data	no data	168
E Asia	DJF	550	205	128
	JJA	403	160	153

Table 1: q95 values (in ppb) used as thresholds for the different regions using data from 2002 to 2019 on the left and using data from 2010 to 2019 on the right

		LT	FT	UT
India	DJF	424	157	132
	MAM	305	191	130
	JJA	267	134	131
	SON	470	150	150
North Af	DJFM	no data	no data	145
	JJASO	no data	no data	110
Middle E	DJFM	253	148	135
	JJASO	300	129	113
Gulf of G	DJFM	724	297	190
	JJASO	280	192	147
South Af	DJFM	219	132	172
	JJASO	400	245	197

		LT	FT	UT
India	DJF	399	155	131
	MAM	310	194	130
	JJA	237	132	132
	SON	468	140	155
North Af	DJFM	no data	no data	137
	JJASO	no data	no data	110
Middle E	DJFM	238	143	140
	JJASO	239	125	115
Gulf of G	DJFM	708	283	183
	JJASO	289	196	146
South Af	DJFM	252	165	162
	JJASO	457	263	195

Table 2: q95 values (in ppb) used as thresholds for the different regions using data from 2002 to 2019 on the left and using data from 2010 to 2019 on the right

Discussion of transport processes impacting India should reference previous work on this topic, e.g. Lal et al. 2014; Lawrence and Lelieveld, 2010; Lelieveld et al., 2001.

Thank you for the comment and as advised the paragraphs on India have been modified in the revised version.

- It is also the period of the winter monsoon in Southern Asia, this season is characterised by week convective activity and Northern prevailing wind transporting pollution at low altitude toward the Indian ocean [Lelieveld et al., 2001, Lawrence and Lelieveld, 2010] and explaining the rather high values of CO in the LT and MT during this period and the low contribution

from SEAS in the UT, at this altitude the anthropogenic CO anomalies receive an influence from CEAS and SEAS but also from NHAF. In JJA, it is the wet phase of the monsoon in India so the important convective activity and precipitation associated with this period [Kar et al., 2004] leads to rapid transport of the South-Asian emission to the UT while preventing BB: almost all the CO anomalies are caused by anthropogenic emissions from India or the close proximity (SEAS and CEAS). (Lines 377-384)

- The O_3 cycle shown here is similar to the cycle described in Lal et al. [2014] and obtained by a radiosonde, here the focus is on the O3 measured in the CO anomalies. In the LT, the minimum values of O_3 are reached during the summer monsoon in JJA. The low values can be explained by the increased marine influence during this period [Lawrence and Lelieveld, 2010]. At this altitude the O_3 values recorded simultaneously as the CO anomalies are low and show the low O_3 production in those plumes.

  In the MT and UT, the maximum of the O_3 is reached during MAM, and the minimum is reached during DJF. In the UT, in DJF and MAM an important part of the CO anomalies come from northern African BB. Those plumes are associated with higher values of O_3 (11 and 10 ppb above the median respectively for DJF and MAM). CO anomalies in JJA are caused by the local emission of anthropogenic CO rapidly transported to the UT by the important convective activity of the South Asian Summer Monsoon (SAMA). This rapid transport could explain that the associated values of O_3 are close to the median (65 ppb). In the post monsoon season (SON) BB anomalies from Equatorial Asia are added to the local anthropogenic anomalies. The values of O_3 in the BB plumes are low and close to the 25th percentile (44 ppb) which is explained by the lower background values of O_3 in Equatorial Asia compared to India [Cohen et al., 2018]. (Lines 390-402)

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