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Interactive comment on “Analysis of $\Delta O_2/\Delta CO_2$ ratios for the pollution events observed at Hateruma Island, Japan” by C. Minejima et al.

Anonymous Referee #1

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General comments

The authors investigate the possibility of using simultaneous oxygen and CO_2 measurements for source attribution of pollution events at the station Hateruma Island, Japan. This station is in the unique position to receive polluted airmasses from several Asian countries with different fuel mix, resulting in different O_2/CO_2 emission ratios. Using back trajectory analysis to determine the origin of airmasses, the authors find a significant difference in the atmospheric $\Delta O_2/\Delta CO_2$ ratios originating from China versus those from Japan/Korea. They further use a particle dispersion model, coupled with a global transport model, to get a more detailed insight on the contributions of individual sources (biosphere, ocean, local vs more distant fossil fuel emissions) on the atmospheric signals. Their results show a predominant influence of local fossil fuel

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emissions, mainly from China, as well as a high sensitivity to the Chinese fuel mix. They therefore conclude that future O_2 and CO_2 observations at Hateruma Island could be useful in detecting changes in the Chinese fuel mix. On the other hand, their model simulations seem to overestimate the contribution of Chinese emissions on pollution events that have been attributed to Japan/Korea by the back trajectory analysis, which shows the need for further improvement in the model setup.

The influence of different fossil fuel emission sources on atmospheric to $\Delta O_2/\Delta CO_2$ ratios has been discussed in several studies recently, but is especially interesting at the location Hateruma Island, as this station received airmasses from countries which a significant difference in the fuel composition. Therefore, this study and the results presented here are definitely of interest for the scientific community and should be published in ACP after some minor revisions which are listed in the Specific Comments below. These mainly concern the structure of the paper and the order/way things are presented. Besides, I would like to see the conclusion stating the message of the paper a bit more clearly (What is possible to learn from the $\Delta O_2/\Delta CO_2$ at Hateruma and what (currently) not?) It would as well be nice to have some kind of outlook (Are there plans to investigate this topic further, and if yes, are e.g. ideas for improvements in the model setup?).

Some general comments on the terminology used in the paper:

I would in general rather use the term ' O_2 and CO_2 mixing ratios' instead of 'concentrations'. However, I am guessing you are using 'concentrations' to avoid the confusing of 'mixing ratios' with O_2/CO_2 ratios? In any case, the use should be consistent ('mixing ratio' is also used once or twice in the paper)

Although ' $-\Delta O_2/\Delta CO_2$ ratio' is absolutely correct in combination with the positive numbers given here, you might consider introducing the term 'oxidative ratio' that is widely used in the literature, since it might look better in the flow of the text. You can

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define this in the beginning, also saying that is the molar ratio of the two species (this way you also avoid to add the ‘molar’ from time to time, as you have it now).

To distinguish the atmospheric ratios from the emission ratios, you are using the terms ‘ $\Delta O_2/\Delta CO_2$ ’ ratios respectively ‘ O_2/CO_2 emission ratios’. However, you sometimes left out the word ‘emission’, just writing ‘national O_2/CO_2 ratios’ or just ‘ O_2/CO_2 ratios’. In most cases, it is still obvious from the context that are talking about the fossil fuel part, but not everywhere. You might consider to add ‘FFBC’ as a subscript in these cases.

Specific comments

Page 15632, line 17-19: It is not really clear (before reading the paper) what you want to say with the last sentence in the abstract. Maybe rephrase to ‘A sensitivity test suggest that the atmospheric $\Delta O_2/\Delta CO_2$ ratio (or oxidative ratio) is especially sensitive to changes in the Chinese fuel mix.’ (you might add another sentence with the 90% number, but this might not be necessary here)

Page 15633, line 7 – 13: I suggest to rephrase the beginning of this paragraph: Whereas you mention both biospheric and anthropogenic/burning influences in the first sentence, the next sentence talks about ‘such pollution events’ which is a bit confusing.

Page 15633, line 13 – 23: It would probably be good to give some numbers here for the range of observed $\Delta O_2/\Delta CO_2$ ratios, to give the reader some idea how well they agree with the theoretical values (useful in terms of comparison with your observations/simulations later). Besides, I suggest citing here as well Sirignano et al (ACP, 2009) and van der Laan-Luijckx et al (ACP, 2010) (both investigating the influence of the Dutch fuel mix on observed $\Delta O_2/\Delta CO_2$ ratios) and Steinbach et al (ACP, 2011) (global overview of variations in $\Delta O_2/\Delta CO_2$ due to differences in the fuel mix).

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Page 15634, line 3: The numbers for the different O_2/CO_2 ratios of the contributing countries should be already mentioned here. Actually, it would be best if you give the whole explanation from page 15639 here instead of later. Besides, it might be interesting for the reader to show the fuel composition for the different countries at some point in the paper, maybe add a a pie chart here showing how much coal, oil and gas is used (and cement produced).

Page 15634, line 21-24: You might leave out the details on the pump specification and inlet protection diameters, since these are for sure included in one of the papers you cite for the sampling details and not important for the purpose of this paper.

Page 15635/15636: As it is usually done, you report the oxygen changes in terms of changes in the O_2/N_2 ratio. However, when analyzing the pollution events, you switch back to the O_2 mixing ratio – which absolutely makes sense for the calculation of the $\Delta O_2/\Delta CO_2$ ratios. However, since you do not really mention this change in the text, it might be confusing for readers who are not so familiar with the terminology of O_2 measurements. Thus you should consider using the O_2 mixing ratio already in the plot in Figure 1; this makes it also easier to compare Figures 1 and 2. In this case, you might still mention that O_2 is usually reported as O_2/N_2 ratio, but that you rather use the O_2 mixing ratios in the following because it is required for the $\Delta O_2/\Delta CO_2$ ratios.

Page 15636, line 4-15: Here it is not completely clear that you do the analysis for the whole time period and not just for this one month. So either start with the description of how you selected the peaks and add the reference to the plot and its identified peaks later (after “we analyzed 67 peak in the following”) or state at the beginning of the paragraph that this is an example.

Page 15636, line 9-10: ‘It should be noted that the start and end times of events

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are determined by peak like variations by visual inspection.' I do not understand this sentence – do you just mean you just picked the start and end time of the peaks manually/ by eye? Please rephrase to clarify. Another question: It seems most reasonable to determine the duration of the pollution event manually (at least I could not think of any automatic criterion for this), but did you check how sensitive the $O_2/\Delta CO_2$ ratios are to the choice of the start and end points? (e.g. if one data point more or less makes a significant difference?)

Page 15637, line 2: What exactly do you mean by "flux categories"?

Page 15637, line 21ff: I am a bit confused by your description of the fossil fuel fluxes. If I understand it correctly, you use the Transcom fossil98 flux - which is the spatial distribution from EDGAR for the year 1990 (!), scaled to the emission level of 1998 using CDIAC totals. Then you further extrapolate the emission totals for the years 2006-2008 while keeping the spatial distribution constant, correct? (please clarify this description a bit) Why did you choose these data for your extrapolation and not some of the more recent EDGAR products? I would guess with the strong increases/changes in the Asian emissions it should be important to have an up-to-date emission inventory that not only matches the total country-level emissions, but also the spatial distribution of these emissions. The current EDGAR Version (4.1) provides data until 2005 – additionally, it provides a higher spatial resolution (0.1x0.1) which might be useful for your rather local application.

Page 15638, line 7ff: You don't explain here how you get the national O_2/CO_2 ratios/the fuel mix. In the abstract, you have mention CDIAC shortly, and you give a detailed explanation later in section 3.1. I suggest giving this information (and how you obtain it) already earlier in the paper (see my comment to page 15634). Besides, you write here 'The national $O_2 : CO_2$ ratios of . . . are used for the fluxes in 2006' What about 2007-2008? Do you use the same values here, or does the fuel mix change with

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time (if yes, what are the values you use for 2007 and 2008?)

Page 15639, line 11-15 and 18-22: As mentioned before, I suggest to move this explanation to an earlier part of the paper.

Page 15639, line 25-26: Well, theoretically there could be biospheric contributions – the $O_2 : CO_2$ ratio of China is not so different from the biospheric ratio... (but since you use the term 'suggest' and clarify later that the dominant contribution is indeed fossil fuel, you might just leave it like that.)

Page 15640, first paragraph: Figure 4 shows no data between April and September – what is the reason for that? Did you only analyze the times where air masses are coming from the Asian continent (if yes, you should mention it in the text)? Or are all the data from these months remove by your filter criteria (if yes, could you explain what is the reason for that – just less peaks with sufficient height because the airmasses are not so strongly influenced by continental air, or stronger phase shift)?

Do you have any possible explanation for the phase differences between the model and the observations? Is this difference for sure caused caused by something in the fossil fuel component or is it related to something in biosphere/ocean? The contributions from these components look really small in Fig. 7, but this is for winter time, might be different in summer?

Page 15640, second paragraph: Did you consider that one reason for the bad agreement in the $\Delta O_2 / \Delta CO_2$ ratios for individual events might be temporal variations in the fuel mix? (Or maybe spatial variations on a sub-country scales - with influences from different parts of the country for the different events? For example, air being strongly influenced by a cement producing plant should lead to a significantly lower ratio.) Looking at the variability in the observed ratios in Figure 4 makes me wonder whether this is just a coincidence...

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Page 15641, line 4-5: Can you add a short sentence here how the oceanic O_2 and CO_2 fluxes look, just to clarify why the ratio is lower for the ocean component? Later, you write that CO_2 is slightly absorbed by the ocean at this time of the year, but what about O_2 ?

P15641, line 20-23: This sentence is a bit confusing – maybe you rather should start with localized nature of CO_2 emissions vs the homogenous signal from the biosphere, and then mention the order of magnitude of the different fluxes relative to each other. Maybe it would be nice as well to add a map with the spatial distribution of CO_2 emissions as an illustration?

Some additional thoughts on Figure 7:

1. Is it just a coincidence that most peaks in the biospheric signal seem to be correlated with fossil fuel events?
2. Maybe it is an optical illusion, but to me the black line sometimes looks lower than I would expect from the sum of TB and FF? (the ocean signal seems negligible here).
3. How does the oceanic oxygen signal look for this time period? The TB and FF signals for oxygen can be guessed quite well from the CO_2 emissions, but since the O_2 and CO_2 ocean signals are not correlated, that could be quite different. . .anything interesting there? Or is it also just small compared to the other components?

Page 15643, line 12ff: Here you are giving a list of possible reasons for disagreements between simulated and observed oxidative ratios. I think here it needs to be clarified

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which of the mentioned points refer to the specific problem of the model overestimating the contribution from the Chinese emission, and which could generally improve the agreement between observations and model. Besides, a bit more details on whether you have any favorite theories or if already tested some of them would be nice.

Addressing the reasons in detail:

1. Particles seem to spread more than in reality – from the way you write it, it sounds as there is some indication for this theory? However, the footprint in Figure 8b looks rather localized – so just from that I am guessing that it is not a general problem. Besides, the influence area in Fig. 8c looks not just widespread, but completely different from the back trajectory. . .
2. Using higher spatially and temporally resolved meteorological fields sounds like a good idea, but I do not understand exactly what you mean with “both problems”: (a) the overestimation of the Chinese emission and (b) the fact that O₂/CO₂ is closer to the Chinese one? Isn't that the same problem (you get (b) because of (a))?
3. Using higher spatially (and maybe also temporal?) resolved input fluxes (maybe more up-to-date fossil fuel emission data) sounds good as well – but not as a solution to the problem with the overestimation of the Chinese emissions. This is clearly a transport problem, I think. However, higher resolved input fluxes might help to improve the agreement between simulated and observed individual events.
4. Improvement of model setup/ treatment of the boundary layer: You wrote earlier that the altitude at which particles absorb the flux does not seem to have an effect. Can you specify what else can be changed in the model setup, maybe also what options you have already tested?

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Page 15644, line 3ff: As mentioned in the General comments, I think this second part of the conclusion needs a bit more structure, showing more clearly what you have achieved in this paper, what your results can be used for and also what does not work (so far) and what could be done (or maybe is already planned?) about this.

Technical comments/suggested text edits

General: Some sentences in the paper, especially in the Discussion section, are quite long and contain a lot of information. To facilitate reading and understanding, it would be better to split them up into shorter ones.

Page 15635, line 24: I would suggest to rephrase the sentence like that: ‘Besides, CO_2 and O_2/N_2 show short-term variations on synoptic time scales associated with pollution events, especially in the late fall to early spring. In the following, we will focus on the analysis of this short-term component of the atmospheric signals.’

Page 15636, line 2-3: To be completely correct, you might write here ‘The extracted short-term variations are denoted as ΔCO_2 and ΔO_2 **in the following**’, as you have used ΔCO_2 and ΔO_2 before as a general term for the atmospheric changes.

Page 15636, line 4: should read ‘as follows bf:’

Page 15636, line 14: Should read ‘in the following’ (without s)

Page 15636, line 19: ‘close to’ instead of ‘close with’

Page 15636, line 23: to be consistent with the way you introduced abbreviations earlier, it should rather read: ‘Meteorological Data Explorer (METEX, <http://db.cger.nies.go.jp/metex/>)’

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Page 15636, line 16 and 28 (as well as later on page 15643, line 23): I suggest to capitalize ‘other’ in this sense (or to call it ‘Other Origins’) to make it more visible in the flow of the text (besides, it is capitalized in the caption of Figure 3)

Page 15636, line 27-28: suggested rephrasing: ‘Figure 3 shows all resulting trajectories assigned to China and Japan/Korea as their origins **as well as** four **example** events assigned to **Other** (Origin)’

Page 15637/15638: In general, I suggest to write that fluxes are calculated, not ‘made’.

Page 15637, line 26: What exactly does the (Marland et al, 2007) reference refer to? Is it just the updated version of the CDIAC database? Then maybe the citation should be made in the same way as (Marland, 2003) two lines before – i.e. giving the website with the version number and the last access date.

Page 15639, line 4: I would replace ‘are shown in Fig. 4a, in which the ratios are collapsed into a single year.’ by ‘are shown in Fig. 4a, plotted against time of the year.’

Page 15639, line 5: Replace ‘both events’ by ‘both types of events’

Page 15639, line 6-7: suggestion for rephrasing: ‘ O_2/CO_2 ratios for events with origin from China tend to be lower (ranging from 1.0–1.4) than those with origin from Japan/Korea (1.1–1.7).’

Page 15641, line 15-17: ‘This result suggests that the pollution events at HAT are predominantly due to FFBC fluxes’ – here the term “pollution event” already implies that these events are caused by something related to anthropogenic activity. Thus I would suggest replacing ‘pollution events’ by ‘synoptic-scale events’ or ‘short-

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term variation’.

Page 15642, line 2 – 13: Maybe you could consider presenting the results of the sensitivity test as a table rather than in the text – although there are not many number, that might be clearer. In any case, I think you should add the information on the errors of the old and new ratios to make clear whether the changes are significant.

Page 15642, line 2 – 13: As mentioned in the General comments, here (as well as in table 1), you are using the term “national O_2/CO_2 ratio”, maybe it should be clarified that this is just the fossil fuel component of the ratio.

Page 15642, line 20ff: Maybe swap the sentences – write the definition of the footprint after the first sentence, and afterwards explain what Figure 8a and b are showing (when you also go into the detailed explanation of the footprints).

Page 15642, line 23 and 25: replace ‘grid’ by ‘grid cell’

Page 15642, line 21: ‘which have small influence’

Page 15643, line 9ff: suggested rephrasing: ‘In the FLEXPART simulation, pollution events categorized by the back trajectory analysis as Japan/Korea in origin almost always contains substantial contribution of Chinese fluxes, therefore their simulated average $\Delta O_2/\Delta CO_2$ value is closer to that of China.’

Page 15644, line 9: maybe rephrase to ‘...most of the peaks associated with pollution events at HAT are **indeed** attributed to FFBC CO_2 emissions’

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