Reply to Reviewer#2

Thank you very much for your comments and suggestions on our paper.
We would like to respond to your comments from general points.

General points:

Regarding the high flow rate:
The referee raised the issue regarding the problems associated with the sample flow separation. Our O_2/N_2 measurement system requires an 8 mL/min flow rate of the sample air, which is about one thousandth of the main flow rate (8 L/min) of the sample air drawn by the diaphragm pump. As the referee pointed out, it is critical to separate the air flow without fractionation of O_2/N_2 ratio because the fractionation could easily occur at the tee junction when the flow rate between the two separated flows is large. In our O_2/N_2 measurement system, instead of tee junction, we used an originally developed flow separating system. Sample air drawn by a diaphragm pump is compressed into a 2-L spherical Pyrex-glass flask at a pressure of 0.06 MPa (relative to ambient), which is kept by using a back pressure regulator. The air sample for the O_2/N_2 measurement system is collected from the center of the spherical flask using a 1/16 inch OD stainless steel tubing at a continuous flow rate of 8 mL/min. This flow separating system considerably reduces the O_2/N_2 fractionation in comparison with the tee-junction. The details of our flow separating system were reported by Yamagishi et al. (2008). Consequently, in order to briefly state this in our paper, we have changed the first two sentences of the 2nd paragraph in section 2.1 into 'Sample air is drawn from an inlet placed on the tower at the height of 36.5 m above ground level (46.5 m above sea level) at a flow rate of about 8 L min^{-1} by using a diaphragm pump. Then, the sample air is introduced into a 2-L spherical Pyrex-glass flask at a pressure of 0.06 MPa (relative to ambient), which is kept by using a back pressure regulator. The air sample is collected from the center of the spherical flask using a 1/16 inch OD stainless steel tubing at a continuous flow rate of 8 mL min^{-1}. This air sampling system considerably reduces the fractionation effects on the O_2/N_2 ratio (Yamagishi et al., 2008), which could occur at the air inlet (Blaine et al., 2006) and the tee-junction (Stephens et al., 2007). The collected air sample is dried by passing through cold traps, and then introduced into the O_2/N_2 measurement system that includes a gas chromatograph equipped with a thermal conductivity detector (GC/TCD). Details of the sampling, analyzing and data processing methods are described elsewhere (Tohjima, 2000; Yamagishi et al., 2008).'

First point:
The referee raised the question of the manual selection of the pollution events. However, as another referee also mentioned in his/her comments, it is practically difficult to select pollution events automatically. In most cases, the correlation slopes are not sensitive to the choice of the start and end points. Therefore, uncertainty associated with the pollution peak determination is relatively small. To clearly state this, the 4th sentence of the 2nd paragraph in Section 2.2 has been changed to 'It should be noted that the start and end times of each pollution event peak are determined manually; however, the following correlation analyses are not sensitive to the choice of the start and end time.'

In order to select the pollution events, we adopted the criteria that the CO_2 peak height is larger than 4.1 ppm, the duration ranged from 12-h to 3-days, and the correlation coefficient (R) is larger than 0.8. The pollution events with |R|<0.8 were discarded because the uncertainties of such pollution events are relatively large. (The criteria is not R^2=0.8 as the referee mentioned in the comment.) For the criterion of |R|<0.8, about 25% of the pollution events were discarded. In the original manuscript, we wrote 'we eliminate about 40%'. That was our mistake, and the wrong number of '40%' has been changes to '25%' in the revised manuscript.

The referee also questioned whether our approach is applicable to the large scale estimation of regional/national emissions. Hateruma Island is a remote island, facing several countries including China, Korea, and Japan across the ocean with distances of several hundred kilometers between them. Therefore, the pollution events observed at HAT are considered to reflect the emissions from these East Asian countries without any local interference. Actually, the pollution enhancements shown in the in-situ data at HAT were so far used to roughly evaluate the national emissions of HFCs and HCFC from China, Korea, and Japan. Therefore, we consider that the O_2/CO_2 ratios at HAT could be used to constrain the national fossil fuel emissions. The problem of our approach is that the transport models were not able to adequately reproduce the contributions of the regional emissions to the observed O_2 and CO_2 changes at HAT in this study. However, we think the improvements in the model setup could resolve these problems in future. Details of the modification of the revised manuscript are described below.

In addition, the referee mentioned that the limitation of the O_2 measurements would prevent this approach from spreading widely. Yes, we agree referee's comment that setting up O_2 measurement and maintaining good data quality is still technically challenging. However, besides HAT station, NIES has been conducting in-situ observations of atmospheric O_2 at Cape Ochi-ishi on Hokkaido Island, Japan since March 2005 (Yamagishi et al., 2008), and onboard a cargo ship sailing between Japan and Australia/New Zealand since September 2007 (Yamagishi et al., in press). Therefore, we consider, these data, combined with the data at HAT, could give constraints on the fossil fuel emissions from regions/countries facing the western Pacific.

Second point:
Following the referee's suggestion that the Abstract could be shorten and re-written so as to highlight the main findings, we have rewritten the Abstract to read as:

'Pollution events extracted from the in-situ observations of atmospheric CO_2 and O_2 mixing ratios at Hateruma Island (HAT, 24°N, 124°E) during the period from October 2006 and December 2008 are examined. The air mass origins for the pollution events are categorized by using back trajectory analysis, and the oxidative ratios (OR = O_2:CO_2 molar exchange ratio) for selected pollution events are calculated. We find that there is a significant difference in the average oxidative ratios between events from China (OR = 1.14 ± 0.12, n = 25) and Japan/Korea (OR = 1.37 ± 0.15, n = 16). These values are in a good agreement with the national average oxidative ratios for the emissions from fossil fuel burning and cement production (FFBC) in China (OR_{FFBC}=1.11 ± 0.03) and

Korea/Japan (OR_{FFBC} = 1.36 ± 0.02). Compared with the observation, simulations of the atmospheric O_2 and CO_2 mixing ratios using Lagrangian particle dispersion models do a good job in reconstructing the average oxidative ratio of the pollution events originating in China but tend to underestimate for events originating in Japan/Korea. A sensitivity test suggests that the simulated atmospheric oxidative ratios at HAT are especially sensitive to changes in Chinese fuel mix.'

The LPDM and the coupled model used in this study underestimate the oxidative ratios of the pollution events from Japan/Korea region in comparison with the observations. From these results, the referee considered that the method presented here cannot be used to constrain large scale FFBC emission inventory. However, we consider that the model-observation mismatch is mainly attributed to transport problems in the model simulations. These transport problems would be solved by improvements in the model setup, for example preparation of higher spatially and temporally resolved meteorological fields as discussed in Discussion. Thus, we believe this approach could constrain the regional emissions when the transport models simulate more quantitatively accurately in future.

The reviewer suggested that we should make the following points in Introduction clear.
a) What are you planning to achieve with your study?
b) As you mention other studies on the subject what would make yours different, and why do you think it will give us a fuller picture of the studied area?
c) Do you think that the approach is a viable tool to verify the composition of countries' industrial emissions? If not, then is there room for improvement or practical solution for that?

In order to state the purpose of this study clearly, we have changed the last paragraph in Introduction as follows:

'In this study, we investigated the oxidative ratios of pollution events observed at HAT. Source regions of the individual pollution events were identified via back trajectory analysis, and the observed oxidative ratios were compared with the oxidative ratios calculated from the reported compositions of the fossil fuel types at their trajectory origins. Furthermore, in order to examine the relative impact of fossil fuel types used and the variations in the regional emission to the observed O_2 and CO_2 changes at HAT, we employed an atmospheric transport model FLEXPART that uses the Lagrangian particle dispersion scheme (Stohl et al., 1998). Based on the comparison between the observation and the model result, we examined the possibility that the observed oxidative ratios can be used as an independent mean to verify the inventories of CO_2 emissions based on the national fossil fuel mixes.'

b) As was mentioned in the manuscript, the observation at HAT often show pollution events influenced by emissions from East Asian countries. Actually, previous studies estimated the HFCs emissions from China, Japan, and Korea based on the pollution events taken from in-situ observations of HFCs at HAT (Yokouchi et al., 2006; Shirai et al., 2010). It is also revealed that the synoptic scale variations in the atmospheric CO_2 mixing ratio at HAT increased during recent decadal period, reflecting the recent rapid

increase in the fossil fuel consumption in China (Tohjima et al., 2010). In addition, there are significant differences in the ORs for the national fossil fuel mixes among these East Asian countries. According to these facts, the location of HAT is significantly unique to study the relationship between the OR for the pollution events and the regional emissions. In order to state these clearly, we have changed the third paragraph in Introduction as follows:

'The National Institute for Environmental Studies (NIES) has been measuring atmospheric O_2 and CO_2 by flask sampling at Hateruma Island (HAT, 24°N, 124°E) since July, 1997 at a frequency of several flasks per month (Tohjima et al., 2003; Tohjima et al., 2008). To capture more frequent O_2 variations, we started in-situ O_2 measurements at HAT from October 2006. Since the prevailing wind direction in the winter time is northwest due to the East Asian monsoon, the observations at HAT often show pollution events influenced by emissions from East Asian countries from late fall to early spring each year (Tohjima et al., 2002; Tohjima et al., 2010). These pollution events observed at HAT have been used to estimate the national emissions of HFCs and HCFCs from China, Korea, and Japan (Yokouchi et al., 2006; Shirai et al., 2010). Therefore, this setting of HAT gives us confidence in the unique location of the HAT observational site for analyzing the relationship between O_2 and CO_2 variations in the pollution events originating from the East Asian source regions. In fact, there is significant difference in the national average oxidative ratios for the emissions from fossil fuel burning and cement production (FFBC) coming from China (OR_{FFBC}= 1.11 ± 0.03), Japan (OR_{FFBC} = 1.37 ± 0.02) and Korea (OR_{FFBC}=1.31 ± 0.02). These oxidative ratios are calculated using the fuel mix of the respective countries taken from the CDIAC inventories for the year 2006 (Boden et al., 2010) and the oxidative ratios for the 3 main fuel types (Keeling, 1988) and the cement manufacturing (OR_{cement} = 0). It should be noted that the higher percentage of the CO_2 emissions from coal and cement production for China results in a significantly lower oxidative ratio in comparison with Japan and Korea (Fig. 1).

c): The objective of this study is to explore the possibility that the OR approach constrains the compositions of national FFBC fuel mix. As a conclusion of this study, the observation at HAT can well constrain the composition from FFBC emission from China. Although the FFBC emissions from Japan and Korea were not constrained by this approach, more improvement of the model set up could make this approach applicable to the estimation of the East Asian emissions besides China. In order to state these clearly, we have changed the last two paragraphs in Conclusion as follows:

'In order to examine how the regional FFBC emissions affect the oxidative ratios of the atmospheric pollution events observed at HAT, we simulated the observed atmospheric CO_2 and O_2 changes using the atmospheric transport model FLEXPART and the coupled model driven by O_2 and CO_2 fluxes from FFBC, TB, and the ocean. Analysis of the relative contributions of individual CO_2 fluxes to the atmospheric variations revealed that most of the peaks associated with the pollution events at HAT were indeed attributable to the FFBC CO_2 emissions. With the assigned fluxes, the transport models were able to reconstruct, with a good agreement with the observation, the average oxidative ratio of the pollution events assigned to China. Additional sensitivity analysis showed that the oxidative ratio of the pollution events originating in China reflects about 90% of the change in OR_{FFBC} for China. These results suggest that the observed OR at

HAT could be used to detect changes in the composition of fossil fuel types used in China in the future.

On the other hand, the model simulations underestimated the average OR for the Japan/Korea pollution events in comparison with the OR_{FFBC} for the Japan/Korea region. This is because the emissions from China make substantial contributions to the Japan/Korea pollution events in the model. This transport problem could be solved by using higher spatially and temporally resolved meteorological fields in the model simulation than those used in this study, which has 1°×1° grid resolution. Using higher spatially resolved FFBC flux maps might also improve the agreement between the observed and simulated oxidative ratios for the Japan/Korea pollution events.'

Minor points:

Abstract:

About the abbreviation, CDIAC: The full name of CDIAC has been written in the revised abstract.

Giving OR in the Abstract: The relevant sentence has been changed to 'These values are in a good agreement with the national average oxidative ratios for the emissions from fossil fuel burning and cement production (FFBC) in China (OR_{FFBC} = 1.11 ± 0.03) and Korea/Japan (OR_{FFBC} = 1.36 ± 0.02).'

Introduction:

Page 15633, line12: The sentence which uses the word, 'changing' has been changed to 'Recent improvements in O_2 measurement technique have enabled the detection of high-frequency changes in atmospheric O_2 mixing ratios simultaneously with that of CO_2 (Manning et al., 1999; Stephens et al., 2003; Yamagishi et al. 2008). Accordingly the oxidative ratios calculated as $-\Delta O_2/\Delta CO_2$ regression slopes for such short-term O_2 and CO_2 variations have recently been used to constrain the contributions from individual sources.'

Page 15633, line 20: The sentence including the word 'varying' has been deleted following the comment of another referee.

Page 15634, line8: The relevant sentence has been changed to 'Furthermore, in order to examine the relative impact of fossil fuel types used and the variations in the regional emission to the observed O_2 and CO_2 changes at HAT, we employed an atmospheric transport model FLEXPART that uses the Lagrangian particle dispersion scheme (Stohl et al., 1998). Based on the comparison between the observation and the model result, we examined the possibility that the observed oxidative ratios can be used as an independent mean to verify the inventories of CO_2 emissions based on the national fossil fuel mixes.'

Page 15635, line 9: 'mole fraction of' has been removed as the reviewer suggested.

Page 15635, line 22: In response to both comments from the referee and another referee, the relevant sentence starting with 'Besides these relatively long-term variations' has been changed to 'In addition, CO_2 and O_2 show short-term variations on synoptic time scales associated with pollution events, especially in late fall to early spring. In the following sections, we will focus on the analysis of this short-term component of the atmospheric signal.'

Discrepancy on 5 days and 8 days: I feel that the referee's comment concerning the periods for the backward calculations results from a misunderstanding. The period of 5 days is the length of the backward trajectories calculated by METEX and the period of 8 days is the duration for the backward plume calculation by FLEXPART.

Results and Discussion:

Page 15639, line 5: This sentence has been rewritten to read 'The oxidative ratios for all the events from both regions show large variability with a range from 1.0 to 1.7. The oxidative ratios for events with origins in China, however, tend to be lower (ranging from 1.0-1.4) than those with origins from Japan/Korea (1.1-1.7).'

Page 15639, line 7: The word, 'therefore', has been removed from the sentence.

Other countries we can see emissions from: Most of the pollution events categorized into Other correspond to the cases in which it is difficult to determine if the origin is China or Japan/Korea. A small number of events with Taiwan and Philippines origins are also included in Other pollution events. In the original manuscript, we compared the average oxidative ratio (OR) for Other origin to the average OR (1.45) obtained from the fossil fuel inventories for the global countries except China, Japan, and Korea. However, now we consider that the number of 1.45 is not appropriate for the comparison, because the origins of the observed pollution events categorized in to Other must be East Asian and South East Asian countries. The average of OR for China, Japan, Korea, Taiwan, and Philippines is 1.27 ± 0.10, which agrees with the observed OR within the uncertainties. Consequently, we have changed the relevant value of 1.45 ± 0.02 in Table 1 to the value of 1.27 ± 0.10, and enclosed it in parentheses to show the number is just for the reference. We have also added the explanation of the value, 'Average value of OR_{FFBC} for China, Japan, Korea, Taiwan, and Philippines. The uncertainty corresponds to the standard deviation (1σ)', as a footnote.

Page 15640, line 11: As the referee mentioned, the stoichiometry of the O_2 and CO_2 exchange ratios for the specific processes are fixed in the models. Actually, the uncertainties of the correlation slopes for the simulated pollution peaks are smaller than those for the observed pollution peaks as shown in **Fig. 4**. However, some pollution peaks are not well reproduced by the model simulations. In such cases, the uncertainties of the O_2/CO_2 correlation slopes are rather large probably because the relatively large oceanic O_2 and CO_2 contributions deteriorate the correlation between O_2 and CO_2 changes.

Fig.6: We have added the sentence, ‘The blue line represents a linear regression fit to the events from Japan/Korea’, in the caption of **Fig. 6**.

We have asked a native English speaker to proofread the manuscript and necessary changes have been made for grammatical mistakes and better phrasings.