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Measurement report: Method for evaluating CO_2 emission from a cement plant by atmosphere O_2/N_2 and CO_2 measurements and its applicability to the detection of CO_2 capture signals

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Abstract. Continuous observations of the atmospheric O_2/N_2 ratio and CO_2 amount fractions have been carried out at Ryori (RYO), Japan since August 2017. In these observations, the O_2:CO_2 exchange ratio (oxidative ratio (OR), $-\Delta y(O_2)\Delta\, y(CO_2)^{-1}$) has frequently been lower than expected from short-term variations in emissions from terrestrial biospheric activities and combustion of liquid, gas, and solid fuels. This finding suggests a significant effect of CO_2 emission from a cement plant located about 6 km northwest of RYO. To evaluate this effect quantitatively, we simulated CO_2 amount fractions in the area around RYO by using a fine-scale atmospheric transport model that incorporated CO_2 fluxes from terrestrial biospheric activities, fossil fuel combustion, and cement production. The simulated CO_2 amount fractions were converted to O_2 amount fractions by using the respective OR values for each of the incorporated CO_2 fluxes, and then simulated OR values were calculated from the calculated O_2 and CO_2 amount fractions. To extract the contribution of CO_2 emissions from the cement plant, we used $y(CO_2^*)$ as an indicator variable, where $y(CO_2^*)$ is a conservative variable for terrestrial biospheric activity and fossil fuel combustion obtained by simultaneous analyses of observed O_2/N_2 ratios and CO_2 amount fractions and simulated ORs. We confirmed that the observed and simulated OR values and also the $y(CO_2^*)$ values and simulated CO_2 amount fractions due only to cement production were generally consistent. These results suggest that combined measurements of O_2/N_2 ratios and CO_2 amount fractions will be useful for evaluating CO_2 capture from flue gas at carbon capture and storage (CCS) plants, which, similar to a cement plant, change CO_2 amount fractions without changing O_2 values, although CCS plants differ from cement plants in the direction of CO_2 exchange with the atmosphere.

1 Introduction

Simultaneous analyses of atmospheric O_2/N_2 ratios and CO_2 amount fractions have been used to estimate the global CO_2 budget since the early 1990s (e.g. Keeling and Shertz, 1992). Recently, these analyses have also been applied to separate the contributions of different sources to the local CO_2 budget in an urban area (Ishidoya et al., 2020; Sugawara et al., 2021). This approach uses $-O_2$:CO_2 exchange ratios (i.e. the oxidative ratio (OR), $-\Delta y(O_2)\Delta\, y(CO_2)^{-1}$) for terrestrial biospheric activities

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and fossil fuel combustion. For terrestrial biospheric O_2 and CO_2 fluxes, ORs of 1.1 or 1.05 are generally used (Severinghaus, 1995; Resplandy et al., 2019), and for the fluxes due to fossil fuel combustion, ORs of 1.95 for gaseous fuels, 1.44 for oil and other liquid fuels, 1.17 for coal and other solid fuels, and 0 for cement production are typical (Keeling, 1988). Therefore, atmospheric O_2 and CO_2 fluxes due to terrestrial biospheric activities and fossil fuel combustion (excluding cement production) vary in opposite phase.

In the cement production process, calcium carbonate is burned and calcium oxide and CO_2 are produced as follows:

$$CaCO_3 \rightarrow CaO + CO_2. \quad (1)$$

Because this chemical reaction emits CO_2 to the atmosphere without O_2 consumption, its OR is 0. It should be noted that the cement kilns are usually fired with fossil fuels, so that the overall OR for cement production is not 0. CO_2 emissions from cement production account for about 4 % of global fossil CO_2 emissions (Friedlingstein et al., 2020), and this value is included in global CO_2 budget analyses based on the atmospheric O_2/N_2 ratio (e.g. Manning and Keeling, 2006). However, because it is difficult to separate the cement production signal from CO_2 emissions due to fossil fuel combustion and terrestrial biospheric activities, no study has reported direct evidence of variations in the atmospheric CO_2 amount fraction due to cement production at the Global Atmosphere Watch (GAW) program of the World Meteorological Organization (WMO) stations. In this context, simultaneous observations of O_2/N_2 ratios and CO_2 amount fractions are expected to be useful for separating out the cement production signal owing to its characteristic OR value. Moreover, Keeling et al. (2011), who examined the possibility of verifying rates of carbon capture and storage (CCS) and direct air capture of CO_2 (DAC) by using changes in the atmospheric constituents, suggested that combined measurements of the O_2/N_2 ratio and CO_2 could powerfully constrain estimated rates.

To investigate CO_2 leak detection from a CCS site, Leeuwen and Meijer (2015) observed O_2/N_2 ratios and CO_2 from a 6-m-tall mast that was 5–15 m away from artificial CO_2 release points. They estimated that their measurement system could detect a CO_2 leak of 10^3 t a^{-1} at a location up to 500 m away from the leak point. Pak et al. (2016) monitored the air for CO_2 plumes at locations between 1 and 100 m from an artificial CO_2 release point, and collected air samples typically between 9 and 20 m from the point where the CO_2 amount fraction was 100–600 μmol mol^{-1} above ambient. They then analyzed the air samples for O_2 and CO_2 amount fractions and found much lower ORs than those expected from fossil fuel combustion and terrestrial biospheric activities. These studies support the suggestion by Keeling et al. (2011) regarding the usefulness of O_2/N_2 ratios and CO_2 measurements. As the next step to verify the usefulness of combined measurements of O_2/N_2 ratios and CO_2, their applicability to the detection of not only CO_2 leaks but also CO_2 capture from flue gas should be examined. In this regard, CCS/DAC plants remove CO_2 from the atmosphere without causing any O_2 changes, just as cement plants do, differing only in the direction of CO_2 exchange between the plant and the atmosphere. Therefore, it should be possible to evaluate the ability of combined measurements to detect a CO_2 capture signal by showing that they can be used to detect a cement production signal.

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In this paper, we present evidence of the successful detection of a cement production signal by combined measurements of O_2/N_2 ratios and CO_2 at a ground station (a designated WMO/GAW local site) located near a cement plant. We also examine the usefulness of the measurements for future detection of CCS/DAC signals by using a fine-scale 3-D atmospheric transport model to investigate the consistency between the observed signal and the simulated CO_2 emissions from the plant.

2 Methods

Atmospheric O_2/N_2 ratios and CO_2 amount fractions have been observed continuously at Ryori (RYO: 39° 2′ N, 141° 49′ E; Fig. 1), Japan, since 2017, by using a paramagnetic O_2 analyzer (POM-6E, Japan Air Liquid) and a non-dispersive infrared CO_2 analyzer (NDIR; LI-7000, LI-COR), respectively. RYO is a designated WMO/GAW station, and the Japan Meteorological Agency (JMA) has also observed CO_2, CH_4, and CO amount fractions there since 1987, 1991, and 1991, respectively (e.g. Wada et al., 2011). The CO_2, CH_4, and CO amount fraction data observed by JMA are available online at the WMO World Data Centre for Greenhouse Gases (WMO/WDCGG; https://gaw.kishou.go.jp/). A cement plant (Taiheiyo Cement Ofunato plant) is 6 km away from RYO (Fig. 1). It should be noted that the CO_2 amount fraction data posted on WDCGG have already been classified into the data for background air and those affected by local fossil fuel combustion including the cement production discussed in this study. The annual cement production at the plant is 1.966×10^6 t a^{-1} (https://www.taiheiyo-cement.co.jp/english/index.html).

The O_2/N_2 ratio is reported as $\delta(O_2/N_2)$ in per meg, where 1 per meg is 0.001 ‰:

$$\delta(O_2/N_2) = \frac{R_{\mathrm{sample}}(^{16}O^{16}O/^{14}N^{14}N)}{R_{\mathrm{standard}}(^{16}O^{16}O/^{14}N^{14}N)} - 1, \quad (2)$$

where the subscripts “sample” and “standard” indicate the sample air and the standard gas, respectively. Because O_2 amount fraction in dry air is 0.2093 to 0.2094 mol mol^{-1} (Tohjima et al., 2005; Aoki et al., 2019), the addition of 1 μmol of O_2 to 1 mol of dry air increases $\delta(O_2/N_2)$ by 4.8 per meg (= 1/0.2094). If CO_2 is converted one-for-one into O_2, it causes $\delta(O_2/N_2)$ to increase by 4.8 per meg, which is equivalent to an increase of 1 μmol mol^{-1} of O_2 for each 1 μmol mol^{-1} decrease in CO_2. Therefore, observed relative changes in $\delta(O_2/N_2)$ were converted to those in O_2 amount fraction by dividing by the ratio 4.8 per meg (μmol $mol^{-1})^{-1}$.

In this study, $\delta(O_2/N_2)$ of each air sample was measured with a paramagnetic analyzer using working standard air that had been measured against our primary standard air (Cylinder No. CRC00045; AIST-scale) using a mass spectrometer (Thermo Scientific Delta-V) (Ishidoya and Murayama, 2014). The dilution effects on the O_2 amount fraction measured by the paramagnetic analyzer were corrected experimentally, not only for the changes in the CO_2 of the sample air or standard gas measured by the NDIR but also for the changes in the Ar amount fraction of the standard gas measured by the mass spectrometer as $\delta(Ar/N_2)$. The analytical reproducibility of the $\delta(O_2/N_2)$ and CO_2 amount fraction measurements by the system

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was about 5 per meg and 0.06 μmol mol^{-1}, respectively, for 2-minute-average values. Details of the continuous measurement system used are given in Ishidoya et al. (2017). Note that we used a mass spectrometer to measure both $\delta(O_2/N_2)$ and the CO_2 amount fraction of the working standard air, whereas we determined the CO_2 amount fraction on the TU-10 scale using a gravimetrically prepared air-based CO_2 standard gas system (Nakazawa et al., 1997). However, we found that the CO_2 amount fractions observed in this study were systematically higher by about 1 μmol mol^{-1} than those observed by JMA and reported on the WMO scale, which is larger than that expected from the scale difference of about 0.2 μmol mol^{-1} between the TU-10 and WMO scales (Tsuboi et al., 2016). This discrepancy might be related to the LI-7000 NDIR used in this study because no significant difference has been found between the TU-10 and WMO scales at Minamitorishima, where a different NDIR (LI-820, LI-COR) has been used for continuous measurements of $\delta(O_2/N_2)$ and CO_2 amount fractions (Ishidoya et al., 2017). However, we found no significant difference in span sensitivities between the CO_2 amount fractions observed in this study and those observed by JMA. Therefore, the systematic difference between the observed CO_2 amount fractions and those observed by JMA does not affect the OR values, discussed in section 3, which were calculated from changes in O_2 and CO_2 amount fractions.

To calculate local transport of CO_2 around RYO, we used the National Institute of Advanced Industrial Science and Technology (AIST) Mesoscale Model (AIST-MM) fine-scale regional atmospheric transport model (Kondo et al., 2001). AIST-MM is a one-way nested model with an outer domain that covers East Japan with an approximately 10-km grid interval and an inner domain that covers an area of 120 km by 120 km near Ryori with a grid interval of approximately 1 km. The EAGrid2010-Japan emissions inventory (Fukui et al., 2014), an update of the EAGrid2000-Japan inventory (Kannari et al., 2007) to the year 2010, was used for anthropogenic CO_2 sources. Spatial resolution of EAGrid2010-Japan is approximately 1 km, and temporal resolution is monthly average of 1 hour. No further inter-annual correction of emissions is employed, but EAGrid2010-Japan considers the difference in traffic volume between weekdays and holidays. To calculate the CO_2 budget for vegetation, the NCAR Land Surface Model (Bonan, 1996) was used as a sub-model, replacing the simple function of temperature and solar insolation used in the original AIST-MM for this calculation. The cement plant source was set at the location of the plant's stack, at the effective stack height of 275 m. The CO_2 emissions from the cement plant were estimated from the clinker production capacity of the Ofunato plant in 2018 (Japan Cement Association 2020). The annual emission was calculated using the method of the Ministry of Environmental Protection (https://www.env.go.jp/earth/ondanka/ghg-mrv/methodology/material/methodology_2A1.pdf, in Japanese) as

$$E = P \times F \times D, \quad (3)$$

where E is the annual emission of CO_2 from the cement plant (t a^{-1}), P is the annual production capacity of clinker at the cement plant (t a^{-1}), F is the CO_2-to-clinker mass ratio of 0.516, and D is the cement kiln dust of 1. For initial and boundary conditions, we used GPV/MSM (grid point value of meso-scale model) meteorological data of wind, temperature, and humidity from JMA (https://www.jma.go.jp/jma/en/Activities/nwp.html).

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3 Results and discussion

From August 2017 to November 2018, $\delta(O_2/N_2)$ and CO_2 amount fractions observed at RYO varied cyclically in opposite phase to each other on timescales from several hours to seasonal (Fig. 2); however, variations in CO_2 and CO amount fractions were roughly in phase. The opposite-phase variations of $\delta(O_2/N_2)$ and CO_2 amount fractions were driven by fossil fuel combustion and terrestrial biospheric activities. In contrast, the atmospheric O_2 variation (μmol mol^{-1}) due to the air–sea exchange of O_2 is much larger than that of CO_2 on timescales shorter than 1 year because of the difference in their equilibration times between the atmosphere and the surface ocean: the equilibration time for O_2 is much shorter than that for CO_2 because of the carbonate dissociation effect on the air–sea exchange of CO_2 (Keeling et al., 1993). The in-phase variations of the CO_2 and CO amount fractions were also driven by fossil fuel combustion and biomass burning. CO:CO_2 ratios for fossil fuel combustion and biomass burning reported by past studies are about 0.01-0.04 and >0.1, respectively (e.g. Nara et al., 2011; Tohjima et al., 2014; Niwa et al., 2014). The short-term (several hours to several days) variations in CO:CO_2 ratios were about 0.01 from late autumn to early spring, but they were much smaller in summer (Fig. 2). These results suggest, therefore, that the short-term variations in $\delta(O_2/N_2)$ and CO_2 amount fractions were driven mainly by fossil fuel combustion in winter and mainly by terrestrial biospheric activities in summer. CO amount fractions also showed a seasonal cycle with a summertime minimum that is attributed to the air mass around Japan: in winter the air mass is of continental origin and in summer it is of maritime origin.

In this study, we focused on the short-term variations in $\delta(O_2/N_2)$ and the CO_2 and CO amount fractions (Fig. 2). Therefore, we subtracted 1-week average values of $\delta(O_2/N_2)$ and the CO_2 and CO amount fractions from the observed values, and examined the relationships among the residuals ($\Delta y(O_2)$, $\Delta y(CO_2)$, and Δy(CO); Fig. 3). Here, $\Delta y(O_2)$ is the equivalent value in μmol mol^{-1} converted from $\delta(O_2/N_2)$. Many of the $\Delta y(O_2)$ and $\Delta y(CO_2)$ values show the expected relationship with the OR for a composite flux from terrestrial biospheric activities and the consumption of gas, liquid, and solid fuels, similar to values observed at other Japanese sites (e.g. Minejima et al., 2012; Goto et al., 2013; Ishidoya et al., 2020). Moreover, it is clear that relationships with an OR smaller than 1.1 appear frequently, especially for data with high Δy(CO) values. Although these characteristic relationships have previously been observed only in artificial CO_2 release experiments such as those described by Leeuwen and Meijer (2015) and Pak et al. (2016), they can be interpreted as indicating a significant CO_2 flux from cement production, which has an OR value of 0. Therefore, we used the AIST-MM model to calculate atmospheric CO_2 amount fractions, with or without taking into account the CO_2 flux from the cement plant near RYO, and to convert the calculated CO_2 amount fractions to O_2 amount fractions using the respective OR values of fossil fuels and terrestrial biospheric activities. Then we compared the observed and simulated OR values.

In October 2017, short-term variations in observed CO_2 and $\delta(O_2/N_2)$ were opposite in phase, and the amplitudes (in μmol mol^{-1}) of some CO_2 variations were larger than those of the corresponding $\delta(O_2/N_2)$ variations (Fig. 4a). This result suggests an effect of cement production. Similar characteristic variations suggesting a cement production effect were also seen in the observations made at RYO in November 2017 and in February, May, and August 2018 (Fig. 4b–e). The simulated CO_2

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amount fraction, calculated from the sources and sinks in East Japan area with no background amount fraction by the AIST-MM, is also shown in Fig. 4. Comparison between the observed and simulated CO_2 amount fractions showed weak correlations: correlation coefficients were 0.41, 0.28, 0.19, 0.33, and 0.54 for October and November 2017 and February, May, and August, 2018, respectively. Therefore, the AIST-MM reproduced the general characteristics of the observed short-term variations in CO_2, but not necessarily the phase and amplitude of individual variations. The discrepancies between observed and simulated values can be attributed to the limited resolution of the model, or to problems in the parameterization of transport processes, or in the CO_2 sources/sinks incorporated into the AIST-MM.

The contribution of CO_2 amount fraction for the three components (cement production, land biospheric activities, and fossil fuel consumption other than cement production) are also shown in Fig. 4. The results demonstrate that cement production contributed significantly to the simulated CO_2 amount fraction. We examined the effect of cement production on OR values by calculating OR values by fitting regression lines to the observed and simulated O_2 and CO_2 amount fractions during successive 24-h periods (Fig. 4, bottom). For this purpose, we converted the simulated CO_2 amount fractions to O_2 amount fractions by assuming OR values of 0, 1.1, and 1.4 for cement production, terrestrial biospheric activities, and fossil fuel combustion, respectively. For comparison, we also calculated OR values for the O_2 and CO_2 amount fractions simulated without considering the contribution of cement production. Both the observed OR values and those simulated considering cement production are frequently lower than 1.1, but no OR values simulated without considering cement production are lower than 1.1. Therefore, CO_2 emissions from the cement plant must be incorporated into the transport model to reproduce the detailed variations in atmospheric O_2 and CO_2 amount fractions at RYO.

Next, we extracted signals of cement production based on the simultaneous measurements of $\delta(O_2/N_2)$ and CO_2 amount fractions. For this purpose, we use $y(CO_2^*)$ as an indicator:

$$y(CO_2^*) = \Delta y(CO_2) + \frac{X(O_2)}{\alpha_{B+F}} \Delta\delta(O_2/N_2), \quad (4)$$

where $\Delta y(CO_2)$ and $\Delta\delta(O_2/N_2)$ are the deviations of the observed CO_2 amount fractions and $\delta(O_2/N_2)$, respectively, from their monthly mean values, $X(O_2)$ (= 0.2094) is the fraction of atmospheric O_2, and α_{B+F} is the expected OR for terrestrial biospheric activities and fossil fuel combustion. The $y(CO_2^*)$ is closely related to atmospheric potential oxygen (δ(APO)), which is conserved for terrestrial biospheric activities (Stephens et al., 1998). In our previous study, we calculated δ(APO) as:

$$\delta(APO) = \delta(O_2/N_2) + \frac{\alpha_B}{X(O_2)} y(CO_2) - 2000 \times 10^{-6}, \quad (5)$$

where 2000 is an arbitrary reference (Ishidoya et al., 2022). For α_{B+F} values, we used monthly average OR values calculated from the simulated O_2 and CO_2 values without considering the contribution of cement production (Fig. 4, bottom). If there are no significant contributions from air–sea O_2 and CO_2 exchanges, then $y(CO_2^*)$ indicates the change in the atmospheric CO_2 amount fraction due only to cement production. No air–sea exchanges can be assumed if the wind field and surface ocean biological production are constant throughout the month; however, past studies have reported that $\delta(O_2/N_2)$ shows day-to-day variation due to the air–sea O_2 exchange and its atmospheric transport (e.g. Goto et al., 2017). However, changes in CO_2 amount fractions observed when the OR was lower than 1.1 occurred over periods of less than a day (Fig. 4a–e).

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Taking these findings into consideration, we derived the baseline variation in $y(CO_2^*)$, which does not include a significant contribution from cement production, as follows. First, we calculated the standard deviation (1σ) of each $y(CO_2^*)$ value from the 24-h running means of $y(CO_2^*)$. Then, we removed $y(CO_2^*)$ values greater than the 24-h running mean of $y(CO_2^*)$ + 1σ from the analyses. Finally, we recalculated the 24-h running means by using the residual $y(CO_2^*)$ values, and regarded them as the baseline variation. Accordingly, the $y(CO_2^*)$ anomaly obtained by subtracting the baseline variation from each $y(CO_2^*)$ value is considered to indicate CO_2 changes due only to the contribution of the cement production.

In October 2017, $y(CO_2^*)$ and CO amount fraction maxima at RYO appeared at the same time that the wind was blowing from the northwest (most frequently over the range of 270-300°) (https://www.data.jma.go.jp/env/data/report/data/download/atm_bg_e.html) (Fig. 5a). This result suggests that the short-term variations in $y(CO_2^*)$ were driven mainly by air masses transported from the cement plant, which is about 6 km northwest of RYO. These findings also indicate that it is possible to extract CO_2 amount fraction data from background air at RYO by selecting observed OR and CO amount fraction data. We have confirmed the present method of JMA used to select background air for the data posted on WDCGG is sufficient to exclude the effect of cement production, nevertheless the use of OR may provide an additional constraint. Note that CO is emitted during fossil fuel combustion at the cement plant to supply electricity and heat for cement production. This means CO_2 presumably as well, and the overall OR of cement production would not be 0.

To examine the consistency between the observed $y(CO_2^*)$ and simulated CO_2 emissions from the cement plant, we compared 5-h means of $y(CO_2^*)$ anomalies with changes in the CO_2 amount fraction due to the contribution of cement production as simulated by the AIST-MM (hereafter referred to as "$y(CO_2$, cement)") (Fig. 5a, bottom). The result shows that variations in the $y(CO_2^*)$ anomaly and $CO_{2cement}$ are of the same order of magnitude, although they do not necessarily occur simultaneously. This result suggests that we succeeded in using $y(CO_2^*)$ to detect a signal of CO_2 emission from the cement plant, and that this signal can be used to validate a fine-scale atmospheric transport model. In this context, Leeuwen and Meijer (2015) suggested that a CO_2 leak of 10^3 t a^{-1} is detectable at a location up to 500 m away from the leak point based on their observations of atmospheric O_2 and CO_2 amount fractions. If this relationship follows an inverse square law, a CO_2 leak of 1.44×10^5 t a^{-1} should be detectable at locations up to 6 km from the leak point. Therefore, about 10^6 t a^{-1} of the CO_2 emission from the cement plant in this study, calculated with Eq. (3), is large enough to be detected at RYO. Features during November 2017 and May and August 2018 were similar (Fig. 5b, d, e), although the short-term variations in $y(CO_2^*)$ in May 2018 (Fig. 5d) were noisier than in the other months, probably because of an effect of short-term variations in the air–sea O_2 flux due to high primary production during the spring bloom in the nearby coastal ocean (e.g. Yamagishi et al., 2008). In February 2018, however, the monthly mean $y(CO_2^*)$ anomaly was around zero (Fig. 5c), whereas $y(CO_2$, cement) was notably higher.

The monthly mean $y(CO_2^*)$ anomalies shown in Fig. 5a–e were calculated using the OR (α_{B+F}) value calculated by the AIST-MM for terrestrial biospheric activities and fossil fuel consumption excluding cement production. In Fig. 6, these $y(CO_2^*)$ anomaly values as well as those calculated using α_{B+F} values of 1.4 and 1.1 are compared with monthly mean $y(CO_2$,

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cement) values. The monthly mean $y(CO_2^*)$ anomalies were lower during autumn and winter and higher during spring and summer than the monthly mean $y(CO_2$, cement) values. We have confirmed monthly mean $y(CO_2$, cement) values were related to the occurrence of northwesterly winds (i.e. wind blowing from the cement plant). Moreover, the production of clinker at the cement plant in February 2018, when a discrepancy was observed between the $y(CO_2^*)$ anomalies and $y(CO_2$, cement), was not markedly different from the production in the other months (personal communication with Taiheiyo Cement Co.). Therefore, the discrepancy between the monthly mean $y(CO_2^*)$ anomaly and $y(CO_2$, cement) in February 2018 may be related to inadequate representation of the local transport of CO_2 by the AIST-MM due to the complicated geography around RYO. Moreover, except in February 2018, the monthly mean $y(CO_2^*)$ anomaly did not depend on the α_{B+F} value used to calculate $y(CO_2^*)$ (Fig. 6). In addition, the average monthly mean $y(CO_2^*)$ anomaly values and the average $y(CO_2$, cement) during the 5 months (right side of Fig. 6) agreed within their monthly variabilities. These results suggest that it is not necessary to use the α_{B+F} value simulated by the AIST-MM to estimate the contribution of cement production to the atmospheric CO_2 amount fraction at RYO; rather, it can be estimated from only the observed $y(CO_2^*)$ by assuming an α_{B+F} value of 1.1 or 1.4. Therefore, the observed $y(CO_2^*)$ can be used to validate monthly to annual average CO_2 fluxes from cement production simulated by a fine-scale atmospheric transport model.

$y(CO_2^*)$ is expected to be an indicator for detecting the signal of CO_2 capture from the flue gas at the cement plant. At a cement plant, CO_2 is removed from the flue gas without any O_2 changes. Therefore, if the CO_2 emitted during cement production, which is about 10^6 t a^{-1} at this plant, is removed from the flue gas, then the 5-month mean $y(CO_2^*)$ anomaly would change from 0.4 to 0 μmol mol^{-1}. Thus, a cement plant can be a useful site not only for demonstrating carbon capture from flue gas but also for monitoring its efficiency based on combined measurements of $\delta(O_2/N_2)$ and CO_2. In addition, during the future operation of a large-scale DAC plant, a negative annual mean $y(CO_2^*)$ anomaly value should be observed because a DAC plant removes CO_2 from the atmosphere without emitting O_2 to the atmosphere.

4 Summary

We analyzed atmospheric $\delta(O_2/N_2)$ and CO_2 and CO amount fraction data observed continuously at RYO to extract a CO_2 emission signal from a cement plant located about 6 km northwest of RYO. The observed $\delta(O_2/N_2)$ and CO_2 amount fractions varied cyclically in opposite phase to each other on timescales from several hours to seasonal. From the CO:CO_2 ratios, the short-term variations in $\delta(O_2/N_2)$ and CO_2 amount fraction were inferred to be driven mainly by fossil fuel combustion in winter and by terrestrial biospheric activities in summer. We found that an OR lower than 1.1 was frequently associated with short-term variations, especially when the CO amount fraction was high; this result suggests a significant effect of cement production, which has an OR of 0. We compared observed CO_2 amount fractions with those simulated by the AIST-MM for October and November 2017 and February, May, and August 2018. The general characteristics of the short-term variations in the observed CO_2 amount fraction were reproduced by the AIST-MM, although not necessarily their phases or

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amplitudes. We calculated the simulated OR values by using simulated $\delta(O_2/N_2)$ values obtained from simulated CO_2 amount fractions and OR values of 1.1, 1.4, and 0 for terrestrial biospheric activities, fossil fuel combustion, and cement production, respectively. As in the observations, simulated OR values lower than 1.1 were frequently associated with short-term variations. $y(CO_2^*)$ was calculated from the observed $\delta(O_2/N_2)$ and CO_2 amount fractions and the simulated α_{B+F} to extract the cement production signal. Variations in the $y(CO_2^*)$ anomaly relative to baseline values were generally of the same order of magnitude as CO_2 amount fraction changes due to contribution of cement production simulated by the AIST-MM ($y(CO_2$, cement)). The monthly mean $y(CO_2^*)$ anomaly averaged over the 5 months examined in this study and the 5-month average of $y(CO_2$, cement) agreed within their variabilities. These results confirm that monthly to annual average CO_2 emissions from a cement plant can be detected by using $y(CO_2^*)$, and, therefore, that a cement plant will be a useful site for demonstrating and monitoring CO_2 capture from flue gas in the future.

Data availability.

The $\delta(O_2/N_2)$ and CO_2 amount fraction data at RYO site presented in this study are included as electronic supplement to the manuscript. We will deposit the data in an appropriate data archive before the manuscript is accepted for publication.

Author contributions.

SI designed the study and drafted the manuscript. Measurements of O_2 and CO_2 amount fractions were conducted by SI, KT, and KS. KH conducted the AIST-MM simulations. NA prepared the standard gas for the O_2 measurements. KI and HM examined the results and provided feedback on the manuscript. All authors approved the final manuscript.

Competing interests.

The authors declare that they have no conflict of interest.

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390 **Figure 1: Location of the Ryori site (RYO) and the cement plant on an aerial photograph from © Google Earth. The cement plant is about 6 km northwest of RYO.**

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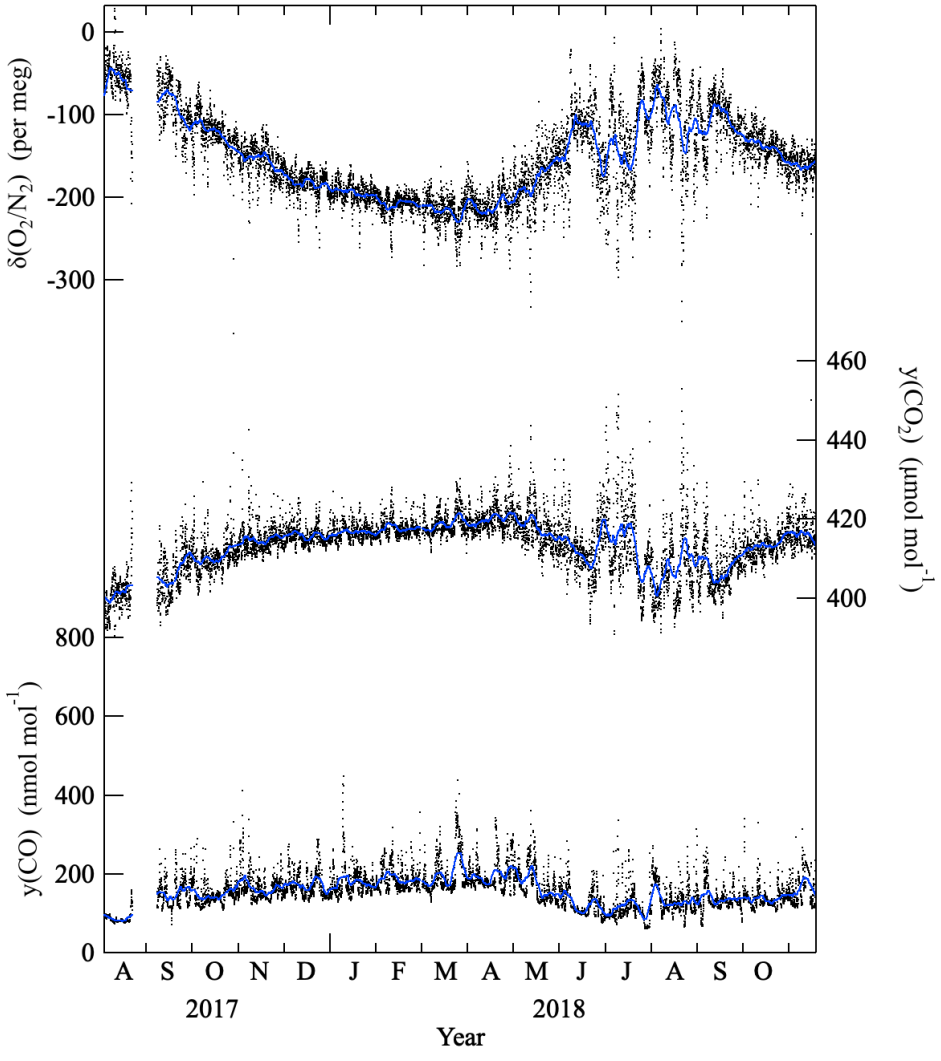

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Figure 2: δ(O_2/N_2) and CO_2 and CO amount fractions (black dots) and their 1-week average values (blue lines) observed at Ryori (RYO), Japan, from August 2017 to November 2018.

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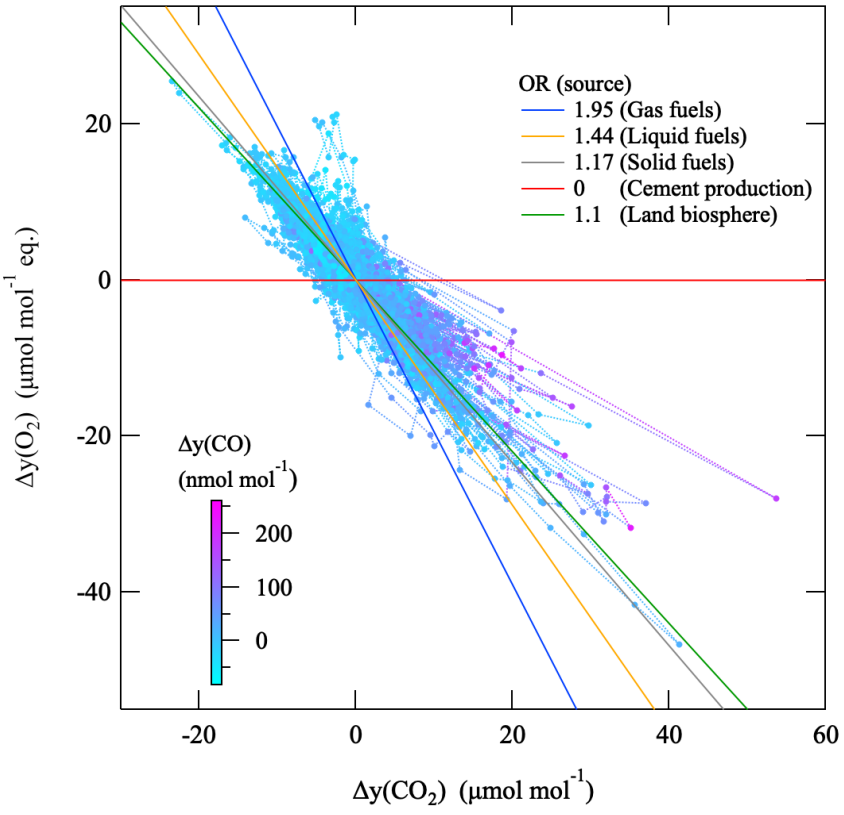

405 **Figure 3: Relationship between $\Delta y(O_2)$ and $\Delta y(CO_2)$ at RYO for the period from August 2017 to November 2018. $\Delta y(O_2)$, $\Delta y(CO_2)$, and $\Delta y(CO)$ were calculated by subtracting the 1-week mean values of $\delta(O_2/N_2)$, CO_2 and CO amount fractions from their observed values; then $\Delta\delta(O_2/N_2)$ values were converted to the equivalent $\Delta y(O_2)$. $\Delta y(CO)$ values are shown by the color scale. The plotted OR values are from Keeling (1988) and Severinghous (1995).**

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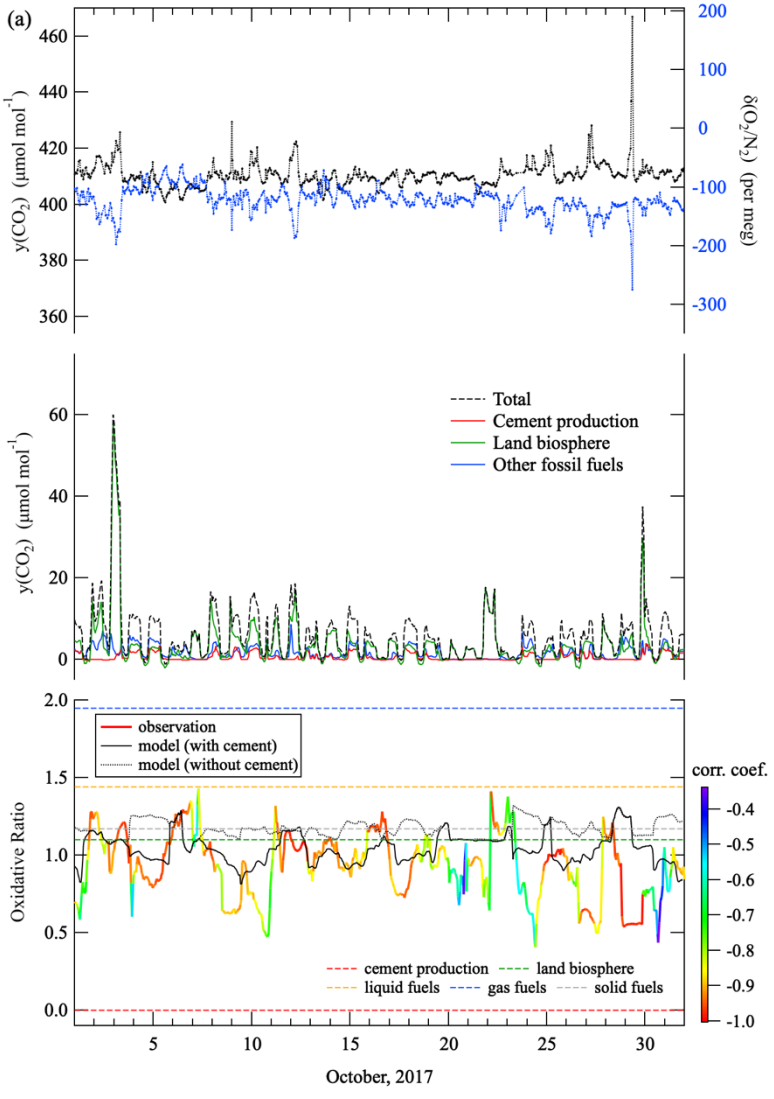

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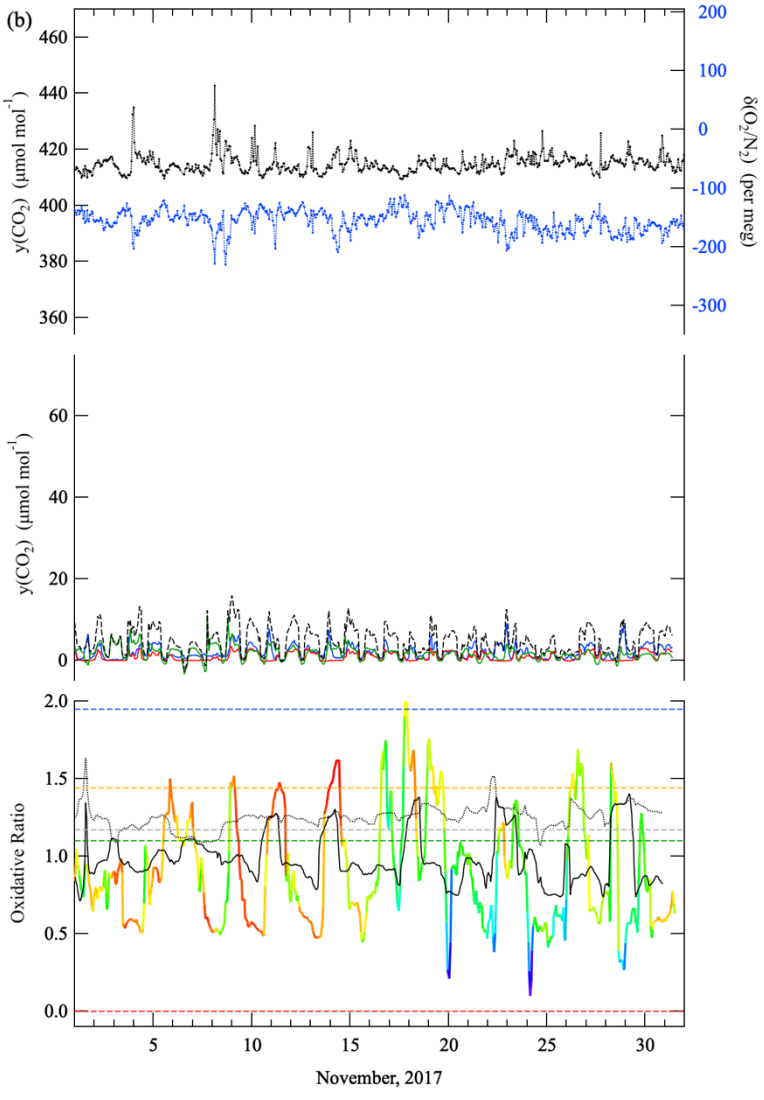

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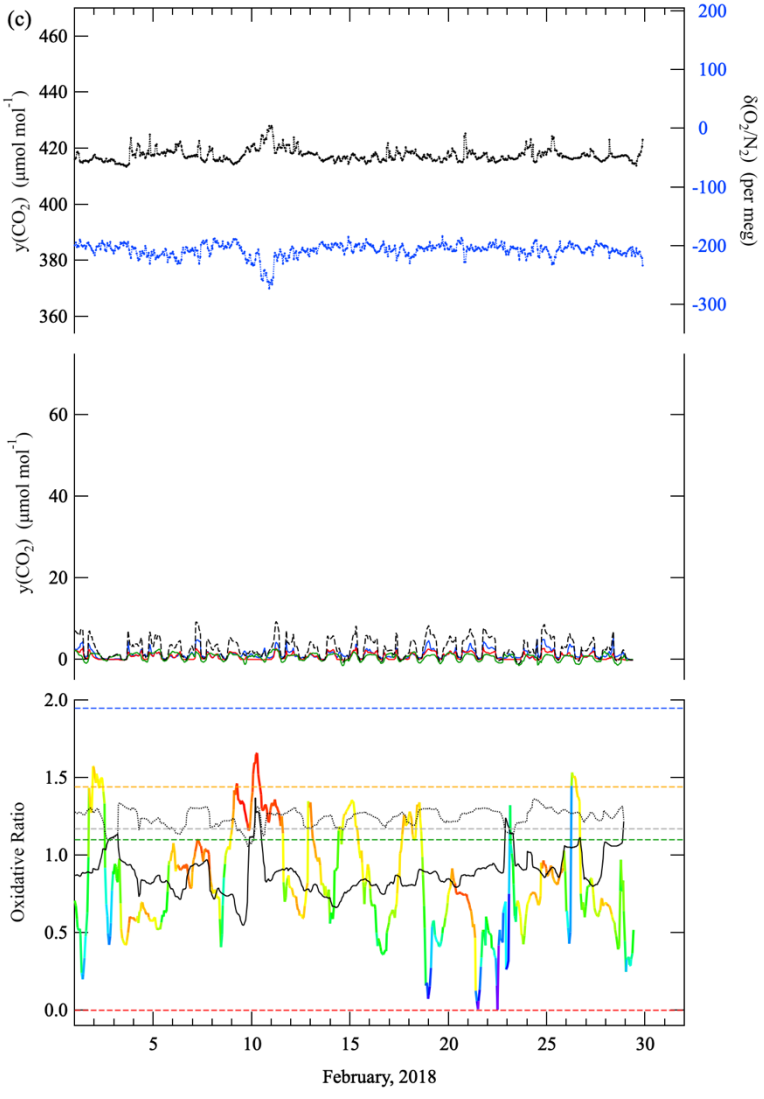

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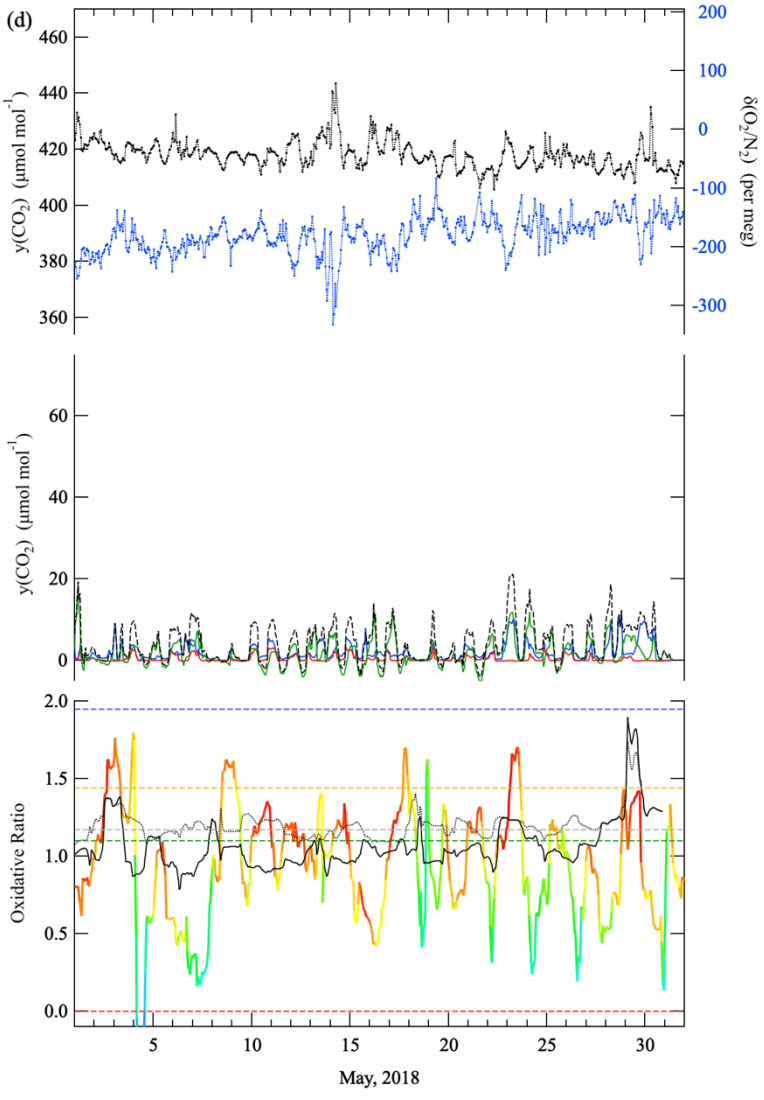

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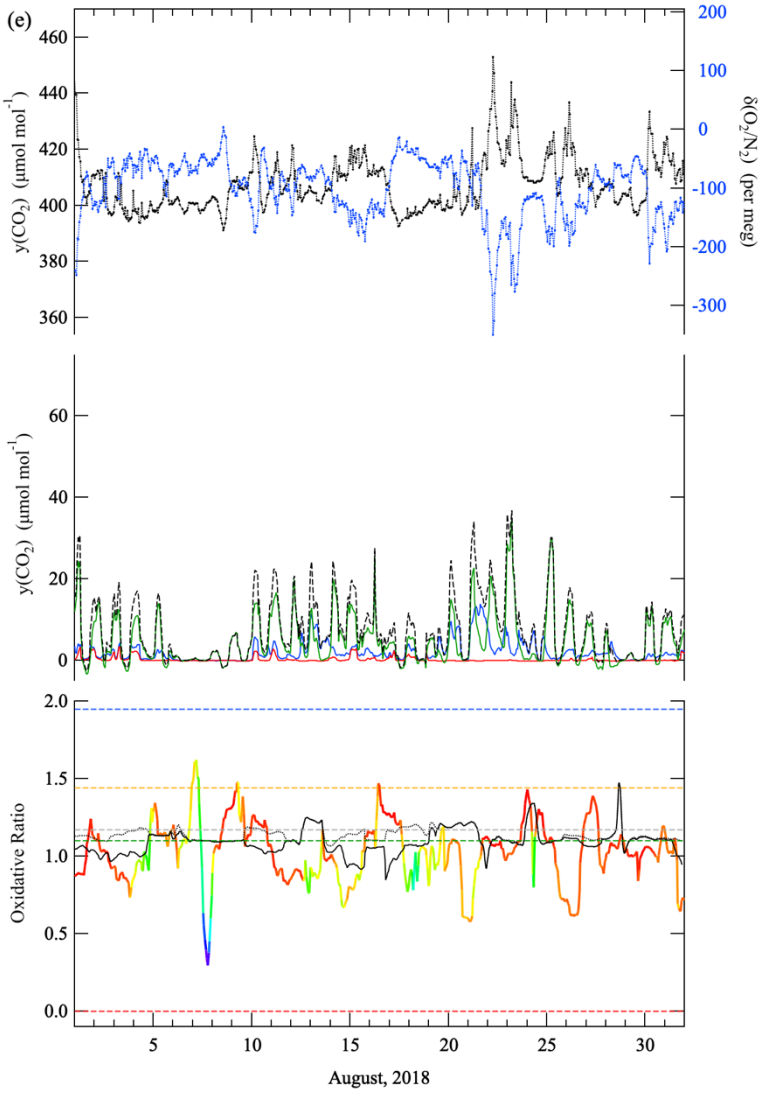

Figure 4: (a) (top) Variations in CO_2 amount fractions and $\delta(O_2/N_2)$ observed at RYO in October 2017. (middle) Variations in the total CO_2 amount fraction simulated by the AIST-MM (black dashed line, see text), and the contributions of CO_2 amount fraction for cement production (red solid line), terrestrial biospheric activities (green solid line), and fossil fuel consumption other than
430 **cement production (blue solid line). The simulated CO_2 amount fraction were calculated from the sources and sinks in East Japan area with no background amount fraction. (bottom) Variations in the oxidative ratio (OR) calculated by least-squares fitting of regression lines to the observed $\delta(O_2/N_2)$ and CO_2 values during successive 24-h periods (thick colored line, where the line color indicates the value of the correlation coefficient). The corresponding OR values calculated from the simulated O_2 and CO_2 amount fractions by the AIST-MM with and without considering the amount fraction of cement production are shown by black and gray**
435 **solid lines, respectively. Dashed horizontal lines show the expected OR values for the consumption of gas, liquid, and solid fuels (Keeling, 1988); terrestrial biospheric activities (Severinghaus, 1995); and cement production. (b) As (a), but for November 2017. (c) As (a), but for February 2018. (d) As (a), but for May 2018. (e) As (a), but for August 2018.**

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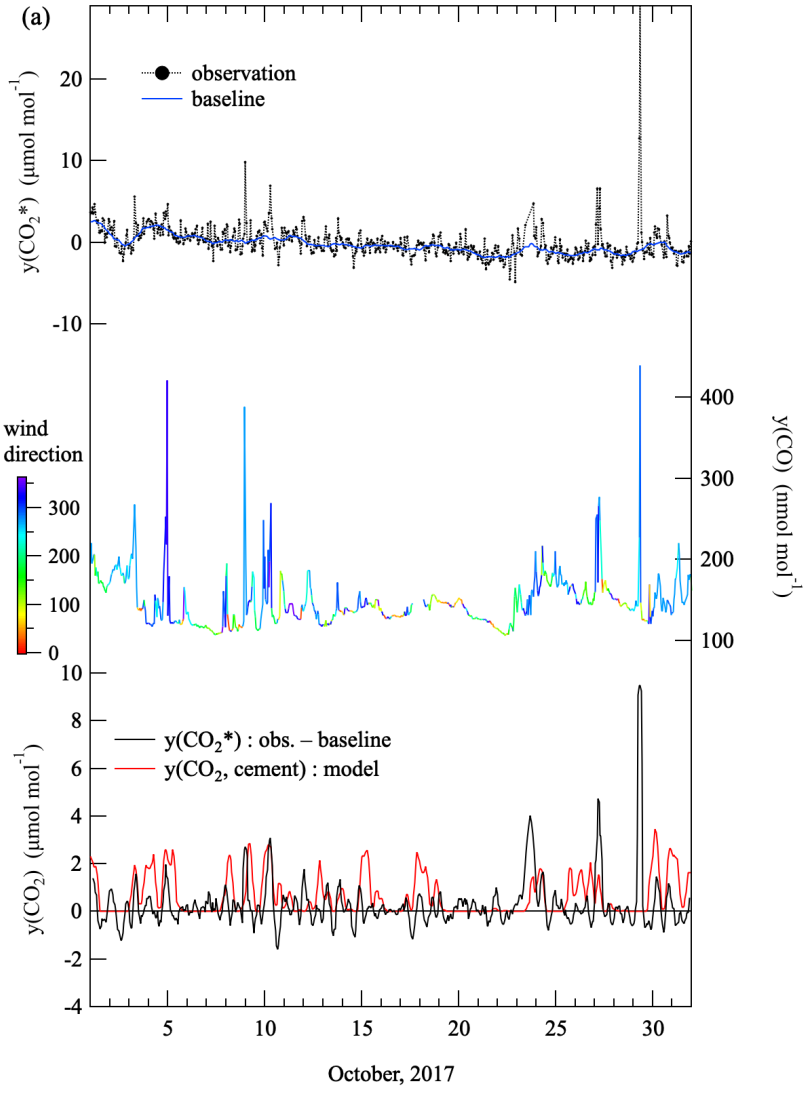

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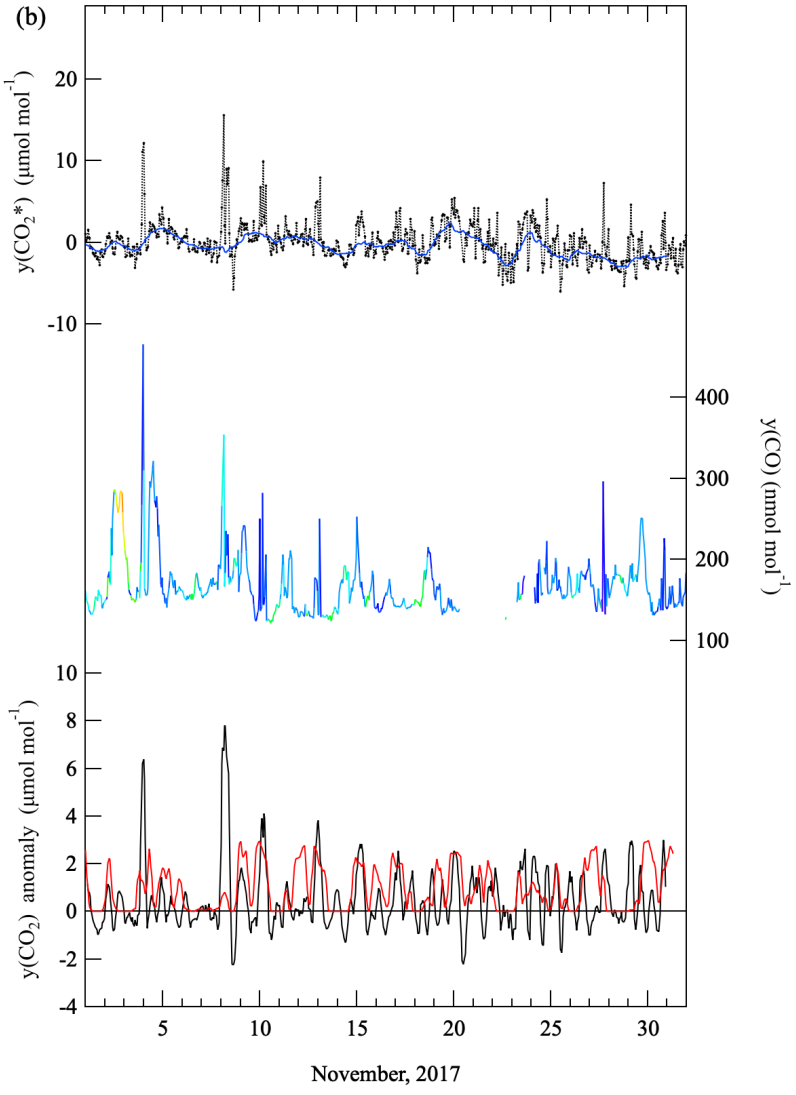

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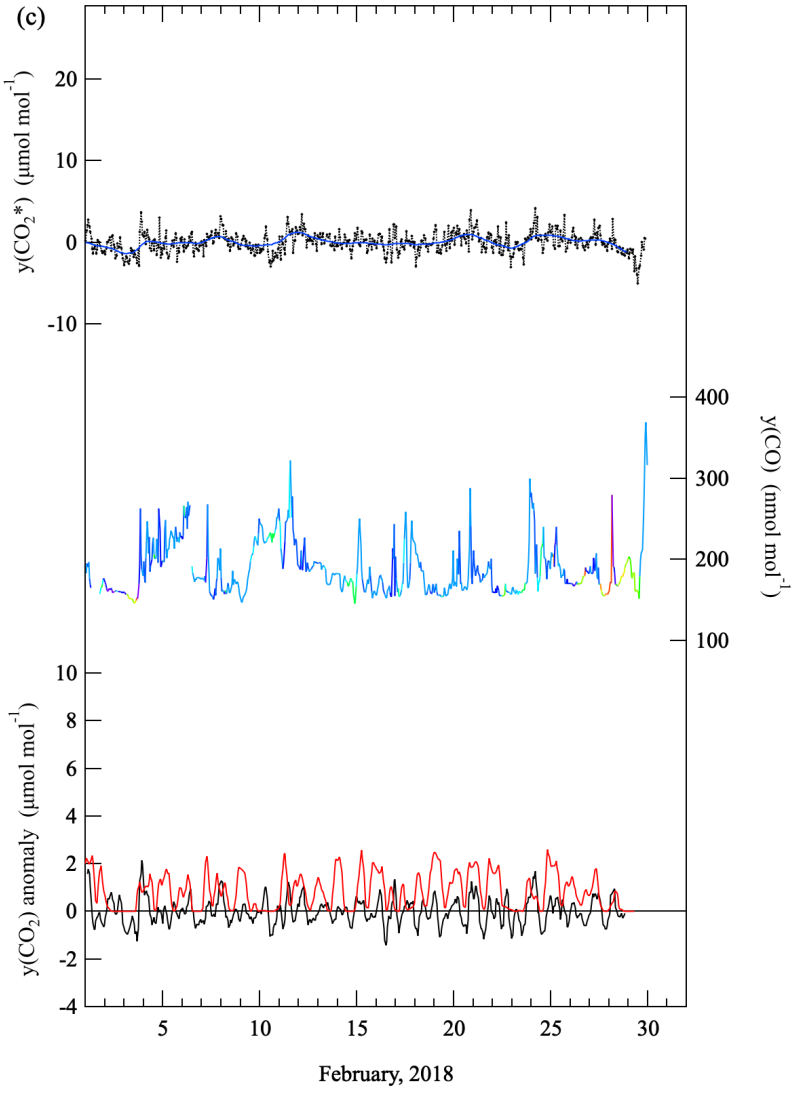

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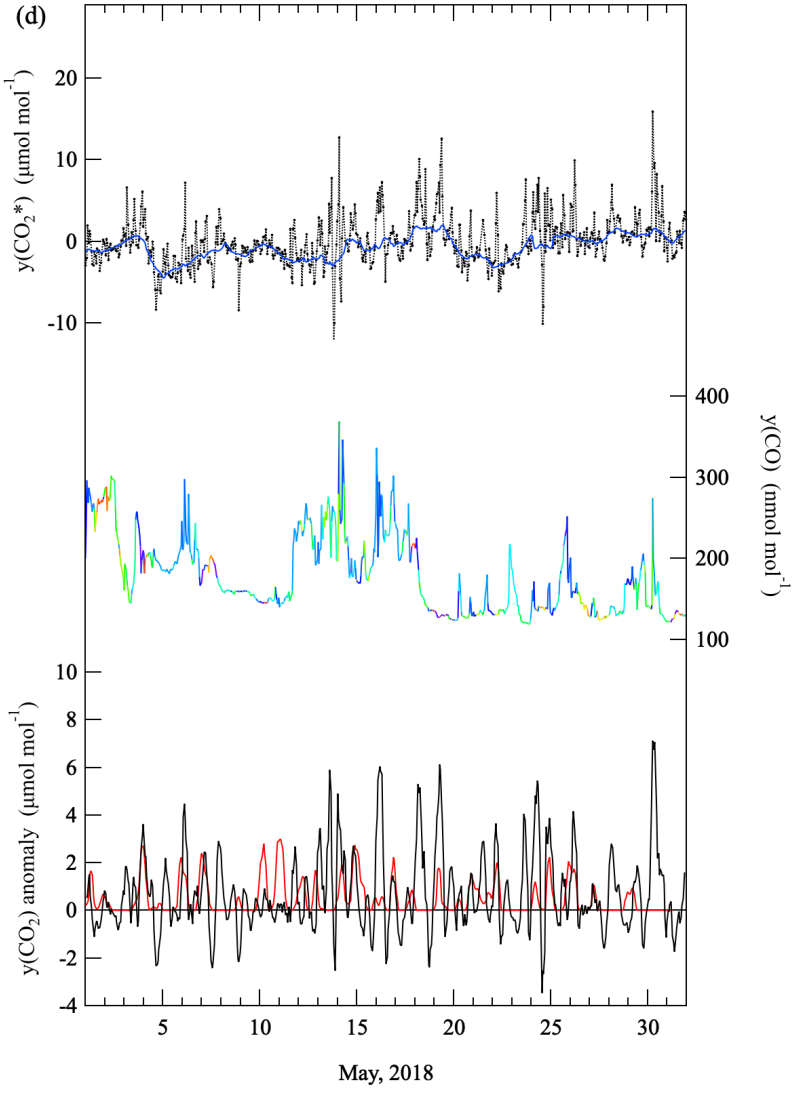

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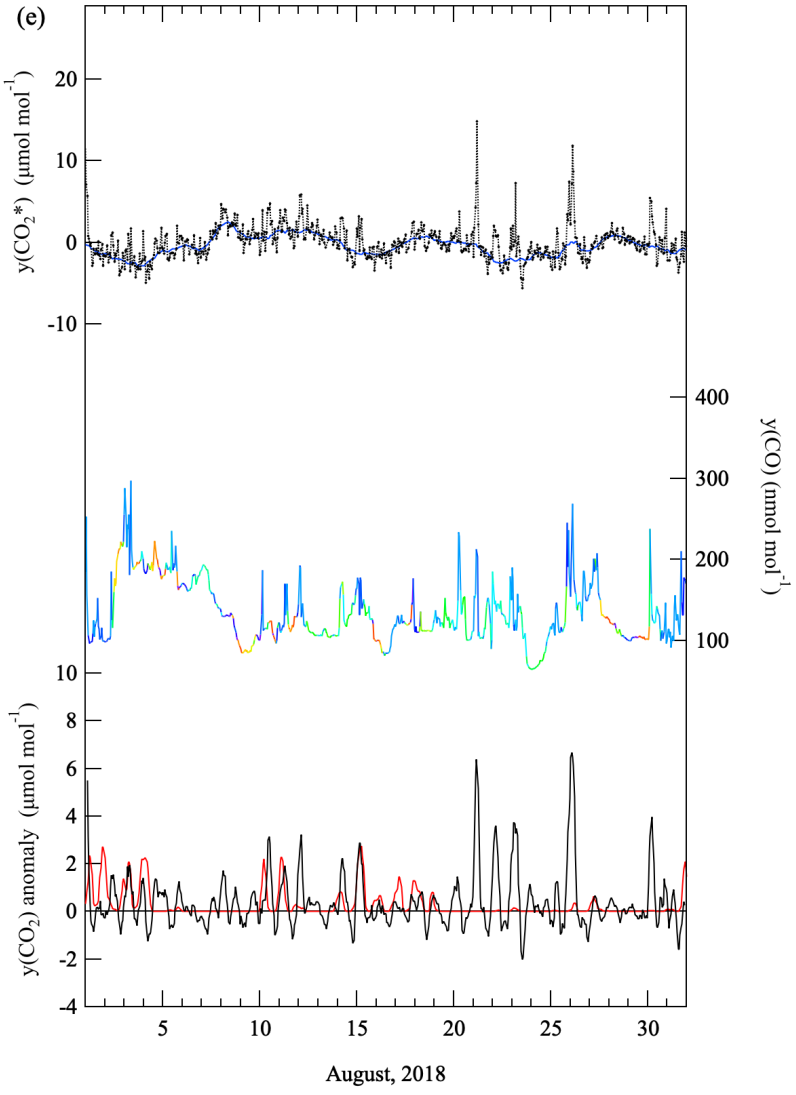

Figure 5: (a) (top) Variations in $y(CO_2^*)$ calculated from the observed CO_2 amount fractions and $\delta(O_2/N_2)$ (black filled circles) in October 2017, and the baseline variation (blue solid line). See text for the definition of $y(CO_2^*)$ and the method used to obtain the baseline variation. (middle) Variations in CO amount fractions in October 2017 and the simultaneously observed wind direction (in degrees). (bottom) Five-hour-average $y(CO_2^*)$ anomalies from the $y(CO_2^*)$ baseline variation and the corresponding variation in the CO_2 amount fraction due only to cement production ($y(CO_2$, cement)) simulated by the AIST-MM (same as the red line in the middle part of Fig. 4a). (b) As (a), but for November 2017. (c) As (a), but for February 2018. (d) As (a), but for May 2018. (e) As (a), but for August 2018.

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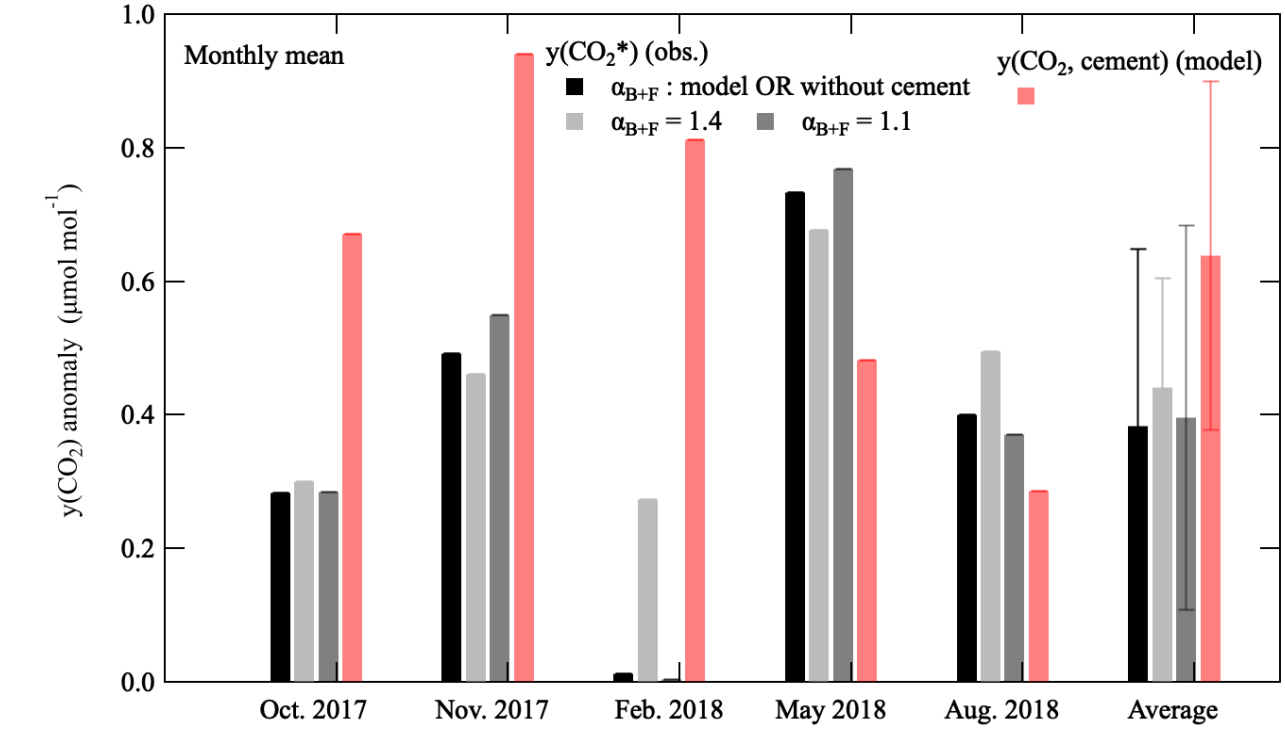

475 **Figure 6: Monthly means of $y(CO_2^*)$ anomalies, obtained using model-simulated α_{B+F} values (as in Fig. 5a–e) and α_{B+F} values of 1.4 and 1.1, and $y(CO_2$, cement). The monthly mean values averaged over the 5 months are shown at the right. Error bars indicate monthly variability (±1 σ).**