Consumption of atmospheric $\text{O}_2$ in an Urban Area of Tokyo, Japan derived from continuous observations of $\text{O}_2$ and $\text{CO}_2$ concentrations and $\text{CO}_2$ flux

Shigeyuki Ishidoya$^1$, Hirofumi Sugawara$^2$, Yukio Terao$^3$, Naoki Kaneyasu$^1$, Nobuyuki Aoki$^1$, Kazuhiro Tsuboi$^4$, and Hiroaki Kondo$^1$

$^1$National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba 305-8569, Japan
$^2$Department of Earth and Ocean Sciences, National Defense Academy of Japan, Yokosuka 239-8686, Japan
$^3$National Institute for Environmental Studies, Tsukuba 305-8506, Japan
$^4$Meteorological Research Institute, Tsukuba 305-0052, Japan

Correspondence to: Shigeyuki Ishidoya (s-ishidoya@aist.go.jp)

Abstract. In order to estimate the atmospheric $\text{O}_2$ consumption in a megacity, continuous observations of atmospheric $\text{O}_2$ and $\text{CO}_2$ concentrations and of $\text{CO}_2$ flux have been carried out simultaneously at the Yoyogi (YYG) site in middle of Tokyo, Japan since March 2016. An average $\text{O}_2$: $\text{CO}_2$ exchange ratio for net turbulent $\text{O}_2$ and $\text{CO}_2$ fluxes ($\text{OR}_F$) between the urban area and the overlying atmosphere was obtained based on an aerodynamic method using the observed $\text{O}_2$ and $\text{CO}_2$ concentrations. The yearly mean $\text{OR}_F$ was found to be 1.62, falling within the range of the average $\text{OR}$ values of liquid and gas fuels. Seasonally different diurnal $\text{OR}_F$ cycles at YYG indicated that the consumption of gas fuels was larger in the winter than that in the summer, especially in the morning and late in the evening. By using the $\text{OR}_F$ and $\text{CO}_2$ flux values, the annual mean $\text{O}_2$ consumption rate was estimated to be $-16.3 \mu\text{mol m}^{-2}\text{s}^{-1}$, which is more than 350 times larger than the global mean atmospheric $\text{O}_2$ consumption rate (about $-4 \mu\text{mol yr}^{-1}$), implying that our life in a megacity is far from sustainable from a viewpoint of the conservation of atmospheric $\text{O}_2$.

1. Introduction

Precise observation of the atmospheric $\text{O}_2$ concentration ($\text{O}_2/\text{N}_2$ ratio) has been carried out since the early 1990s to elucidate the global $\text{CO}_2$ cycle (Keeling and Shertz, 1992). The approach is based on the $\text{O}_2$: $\text{CO}_2$ exchange ratios (Oxidative Ratio; $\text{OR} = -\Delta \text{O}_2/\Delta \text{CO}_2$ mol mol$^{-1}$) for the terrestrial biospheric activities and fossil fuel combustion. The $\text{OR}$ value of 1.1 has been used widely for the terrestrial biospheric $\text{O}_2$ and $\text{CO}_2$ fluxes (Severinghaus, 1995). On the other hand, the $\text{OR}$ of 1.95 for gaseous fuels, 1.44 for oil and other liquid fuels, and 1.17 for coal or solid fuels are usually used (Keeling, 1988). Therefore, $\text{OR}$ is a useful indicator for cause(s) of the observed variations in the atmospheric $\text{O}_2$ and $\text{CO}_2$ concentrations. The atmospheric $\text{CO}_2$ concentration has been observed not only at remote sites such as Mauna Loa (19.5 °N, 155.6 °W), Hawaii, U.S.A. to capture a baseline variation in the background air (e.g. Keeling et al., 2011) but also recently in urban areas to estimate $\text{CO}_2$ emissions locally from fossil fuel combustion (e.g. Mitchell et al., 2018). For the latter purpose,
simultaneous observations of the atmospheric O\textsubscript{2} and CO\textsubscript{2} concentrations should provide important insight in separating out the respective contributions of the gaseous, liquid and solid fuels to the urban CO\textsubscript{2} emission.

Steinbach et al. (2011) estimated a global dataset of spatial and temporal variations of OR for the fossil fuel combustion using the EDGAR (Emission Database for Global Atmospheric Research) inventory and fossil fuel consumption data from the UN energy statistics. The statistically estimated OR should be validated by observed OR, however observations of the atmospheric O\textsubscript{2} concentration in urban areas are still limited (e.g. van der Laan et al., 2014; Goto et al., 2013). Moreover, simultaneous observations of the OR and CO\textsubscript{2} flux between an urban area and the overlying atmosphere have never been reported before. Observations of the CO\textsubscript{2} flux have been carried out at various urban stations such as, London, UK (Ward et al., 2013), Mexico City, Mexico (Velasco et al., 2009), Beijing, China (Song and Wang, 2012), and Tokyo, Japan (Hirano et al., 2015), allowing us to observe urban CO\textsubscript{2} emission directly in the flux footprint. Therefore, if the OR for the net turbulent O\textsubscript{2} and CO\textsubscript{2} fluxes (hereafter referred to as “OR\textsubscript{F}”) is observed, then the information can be used to separate out the contributions of the gaseous, liquid, and solid fuels, and the terrestrial biospheric activities to the observed CO\textsubscript{2} flux. From the measurements, it also becomes possible to observe the urban O\textsubscript{2} flux by multiplying the CO\textsubscript{2} flux by OR\textsubscript{F}.

In this paper, we present firstly the simultaneous observational results of the O\textsubscript{2} and CO\textsubscript{2} concentrations and the CO\textsubscript{2} flux in the urban area of Tokyo, Japan. From a relationship between the vertical gradients of the observed O\textsubscript{2} and CO\textsubscript{2} concentrations, we derive OR\textsubscript{F} based on an aerodynamic method (Yamamoto et al., 1999). The present paper follows Ishidoya et al. (2015) who reported OR\textsubscript{F} for the O\textsubscript{2} and CO\textsubscript{2} fluxes between a forest canopy and the overlying atmosphere. We also compare the observed OR\textsubscript{F} with the OR value of the overlying atmosphere above the urban canopy (hereafter referred to as “OR\textsubscript{atm}”) to highlight the characteristics of the O\textsubscript{2} and CO\textsubscript{2} exchange processes in the urban canopy air at the YYG site. Finally, we discuss the cause(s) of the urban O\textsubscript{2} flux in a megacity like Tokyo.

2. Experimental procedures

2.1 Site description

In order to observe the atmospheric O\textsubscript{2} and CO\textsubscript{2} concentrations and CO\textsubscript{2} flux between the urban area and the overlying atmosphere, the instruments were installed on a roof-top tower of Tokai University (52 m above ground, 25 m above roof) at Yoyogi (YYG; 35.66°N, 139.68°E), Tokyo, Japan. The YYG site is a mid-rise residential area and located in the northern part of Shibuya ward, Tokyo. Figure 1 shows the location of the YYG site and the flux footprints averaged for summer and winter runs, calculated by the model of Kljun et al. (2004). The main land-cover around the site is characterized by low- to mid-rise residential buildings with a mean height of 9 m. The population density in this area is 16,600 persons km\textsuperscript{-2}. At the YYG site, prevailing wind is from SW in the summer and NW in the winter. The flux footprint includes vegetated area of 9% in the summer and 2% in the winter.
2.2 Continuous measurements of the atmospheric O$_2$ and CO$_2$ concentrations and CO$_2$ flux

Observations of the atmospheric O$_2$ and CO$_2$ concentrations have been carried out at the YYG site using a continuous measurement system employing a paramagnetic O$_2$ analyzer (POM-6E, Japan Air Liquid) and a non-dispersive infrared CO$_2$ analyzer (NDIR; Li-820, LI-COR) since March 2016. The O$_2$ concentration is reported as the O$_2$/N$_2$ ratio in per meg:

$$
\delta(O_2/N_2) = \left[ \frac{(O_2/N_2)_{\text{sample}}}{(O_2/N_2)_{\text{standard}}} - 1 \right] \times 10^6 \quad (\text{eq.1})
$$

where the subscripts ‘sample’ and ‘standard’ indicate the sample air and the standard gas, respectively. Because O$_2$ is about 20.94 % of air by volume (Tohjima et al., 2005a), 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$_2$ were to be converted one-for-one into O$_2$, this would cause an increase of 4.8 per meg of $\delta$(O$_2$/N$_2$), equivalent to an increase of 1 µmol mol$^{-1}$ of O$_2$ for each 1 µmol mol$^{-1}$ decrease in CO$_2$. Therefore, the ratio of 4.8 per meg/µmol mol$^{-1}$ was used to convert the observed $\delta$(O$_2$/N$_2$) to O$_2$ concentration relative to an arbitrary reference point. In this study, $\delta$(O$_2$/N$_2$) of each air sample was determined against our primary standard air (Cylinder No. CRC00045; AIST-scale) using a mass spectrometer (Thermo Scientific Delta-V) (Ishidoya and Murayama, 2014).

In this study, sample air was taken at the tower heights of 52 m and 37 m using a diaphragm pump at a flow rate higher than 10 L min$^{-1}$. The sample air taken from 52 m and 37 m were introduced into the analyzers through a water trap cooled to $-80^\circ$C at a flow rate of 100 mL min$^{-1}$ by stabilizing the pressure to an order of 10$^{13}$ Pa, and measured for 10 minutes at each height. After 9 measurement cycles (90 minutes), high-span standard gas, prepared by adding appropriate amounts of pure O$_2$ or N$_2$ to industrially prepared CO$_2$ standard air, was introduced into the analyzers with the same flow rate and pressure as the sample air and measured for 5 minutes, and then low-span standard gas was measured by the same procedure. The dilution effects on the O$_2$ mole fraction measured by the paramagnetic analyzer due to changes in CO$_2$ and Ar of the sample air or standard gas were corrected experimentally. The analytical reproducibility of the O$_2$/N$_2$ ratio (CO$_2$ concentration) achieved by the system was about 5 and 3 per meg (0.06 and 0.04 µmol mol$^{-1}$) for 2 and 30 minute average values, respectively. The reproducibility of the O$_2$/N$_2$ ratio was equivalent to those of O$_2$ concentrations of 1.0 µmol mol$^{-1}$ for 2 minute average and 0.6 µmol mol$^{-1}$ for 30 minute average. Details of the continuous measurement system used are given in Ishidoya et al. (2017).

It should be noted that the gravimetrically prepared air-based CO$_2$ standard gas system with uncertainties of ±0.13 µmol mol$^{-1}$ on TU-10 scale (Nakazawa et al., 1991) was used to determine CO$_2$ concentration in this study. The highest concentration of the gravimetrically standard gas was about 450 µmol mol$^{-1}$, while CO$_2$ concentrations of more than 600 µmol mol$^{-1}$ were observed in this study. Therefore, we compared the NDIR-based CO$_2$ concentrations observed in this study with those observed by using Cavity Ring-Down Spectroscopy (CRDS; G2401, Picarro) on NIES-09 scale (Machida et al., 2011) at the YYG site (our unpublished data). Although the highest CO$_2$ concentration of the gravimetrically standard for the NIES-09 scale is similar to that of the TU-10 scale, the span-difference of CO$_2$ concentration between the TU-10 and NIES-09 scales
was confirmed to be within 1% for a range of 410-560 µmol mol⁻¹, as determined by applying a geometric mean regression with a correlation coefficient of 0.978 (Miller and Tans, 2003). On the other hand, the span-difference of O₂ concentration between the AIST-scale and the highly precise O₂ standard gases developed by Aoki et al. (2019) was confirmed to be within 0.2%. Therefore, the uncertainty of OR due to the span-uncertainties of O₂ and CO₂ concentrations is expected to be about 1%.

In order to observe the CO₂ flux at the YYG site, the turbulence and the turbulent fluctuation of CO₂ were observed at 52 m with a high time resolution of 10 Hz by using a sonic anemometer (WindMasterPro, Gill) and an open-path infra-red gas analyzer (LI-7500, LI-COR) since November 2012. Turbulent flux of CO₂ was calculated by the eddy correlation method using EddyPro®, (Licor) for every 30 minute period. Correlations were applied in the calculation for water-vapor density fluctuation (Webb et al., 1980) and mean vertical wind (Wilczak et al., 2001).

### 3. Results and discussion

#### 3.1 Variations in the atmospheric O₂ and CO₂ concentrations

We show the 10-minute average values of the atmospheric O₂ and CO₂ concentrations observed at the height of 52 m at YYG in Fig. 2. As seen in the figure, O₂ and CO₂ concentrations vary in opposite phase with each other on timescales ranging from several hours to seasonal cycle. In general, opposite phase variations of atmospheric O₂ and CO₂ are driven by fossil fuel combustion and terrestrial biospheric activities. On the other hand, the atmospheric O₂ variation in µmol mol⁻¹ due to the air-sea exchange of O₂ is much larger than that of CO₂ on timescales shorter than 1 year (e.g. Goto et al., 2017a; Hoshina et al., 2018); this is because the equilibration time for O₂ between the atmosphere and the surface ocean is much shorter than that for CO₂ due to the influence of the carbonate dissociation effect on the air-sea exchange of CO₂ (Keeling et al., 1993). Therefore, the opposite phase variations of O₂ and CO₂ observed in this study are attributed mainly to fossil fuel combustion and terrestrial biospheric activities. Figure 2 also shows that ΔO₂, obtained by subtracting O₂ at 41 m from that at 52 m on the tower, varies in opposite phase with the corresponding ΔCO₂. High ΔO₂ values are more frequently observed in the winter than in the summer, and short-term (several hours to days) decreases in the O₂ concentration are intense in the winter. Therefore, O₂ is consumed in the urban canopy at YYG, more so in the winter due likely to an increased usage of gas and/or liquid fuels for heating, and to a more stable stratification of surface atmosphere. The daily mean CO₂ flux from the urban area to the overlying atmosphere shown in Fig. 2 shows a seasonal cycle with a wintertime maximum, consistent with the enhancement of O₂ consumption in the urban canopy.

In this study, we focus on the short-term variations of O₂ and CO₂ for periods of several hours to days, to elucidate the O₂ and CO₂ exchange processes between the urban area and the atmosphere by examining two types of OR; one is OR\(_{\text{atm}}\) calculated from a relationship between the O₂ and CO₂ concentration values observed at 52 or 37 m, and the other one is OR\(_{\text{f}}\), for the O₂ and CO₂ fluxes between the urban area and the overlying atmosphere, calculated from a relationship between
\( \Delta O_2 \) and \( \Delta CO_2 \). The relationships of the \( O_2 \) and \( CO_2 \) fluxes with \( OR_F \) are based on the aerodynamic method of Yamamoto et al. (1999) by:

\[
F = -K \Delta O_2 / \Delta z \quad \text{(eq.2)}
\]

\[
F_C = -K \Delta CO_2 / \Delta z \quad \text{(eq.3)}
\]

\[
OR_F = -F_O / F_C = - \Delta O_2 / \Delta CO_2 \quad \text{(eq.4)}
\]

Here, \( F_O \) (\( F_C \)) (\( \mu mol \, m^{-2} \, s^{-1} \)) represents the \( O_2 \) (\( CO_2 \)) flux from the urban area to the overlaying atmosphere, \( K \) is the vertical diffusion coefficient, and \( \Delta O_2 \Delta z^{-1} \) (\( \Delta CO_2 \Delta z^{-1} \)) is the vertical concentration gradient of \( O_2 \) (\( CO_2 \)). The vertical diffusion is a sum of mass-independent eddy and mass-dependent molecular diffusion, however the effect of molecular diffusion on the observed variations of \( O_2 \) and \( CO_2 \) concentrations is generally negligible in the troposphere, whereas it is significant in the stratosphere (e.g. Ishidoya et al., 2013a). Therefore, we used the same diffusion coefficient \( K \) for \( O_2 \) and \( CO_2 \) in eqs. (2) and (3), which enabled us to estimate \( F_O \) by using the observed \( \Delta O_2 \), \( \Delta CO_2 \) and \( F_C \) as in eq. (4). In general, \( OR_{atm} \) reflects wider footprints of \( O_2 \) and \( CO_2 \) than \( OR_F \) due to horizontal atmospheric transport (Schmid, 1994). It is noted that the definitions of \( OR_F \) and \( OR_{atm} \) are similar to those of \( ER_F \) and \( ER_{atm} \), respectively, reported by Ishidoya et al. (2013b, 2015).

In order to calculate \( OR_{atm} \) for short-term variations, (1) we applied a best-fit curve consisting of the fundamental and its first harmonics (periods of 12 and 6 months) and a linear trend to the maxima (minima) values of \( O_2 \) (\( CO_2 \)) observed at 52 m during the successive 1-week periods, and regarded the best-fit curve as its baseline variation, (2) then the baseline variation of \( O_2 \) (\( CO_2 \)) concentration was subtracted from the respective \( O_2 \) (\( CO_2 \)) concentrations observed at 52 m. Figure 3 shows the baseline variations and the variations in the \( O_2 \) and \( CO_2 \) concentrations observed at Minamitorishima (MNM; 24.28°N, 153.98°E), Japan (updated from Ishidoya et al., 2017). MNM is a small and isolated coral island located 1,850 km southeast of Tokyo, Japan, and the observation site was operated by the Japan Meteorological Agency (JMA) under the Global Atmosphere Watch program of the World Meteorological Organization (WMO/GAW). The baseline variations of \( O_2 \) and \( CO_2 \) at YYG show clear seasonal cycles with peak-to-peak amplitudes of 28 and 16 \( \mu mol \, mol^{-1} \), respectively, with corresponding seasonal maximum and minimum appearing in mid August. The amplitude of the seasonal \( O_2 \) (\( CO_2 \)) cycle and the appearance of seasonal maximum (minimum) were found to be larger and earlier, respectively, than those observed at MNM, while the annual average values of the baseline concentration variations of \( O_2 \) and \( CO_2 \) at YYG did not differ significantly from those at MNM. These characteristics of the seasonal cycles and the annual average values of the baseline variations at YYG and their comparison with those at MNM are generally consistent with those observed at similar latitude over the western Pacific region (Tohjima et al., 2005b). Therefore, in spite of the fact that the YYG site is located in a megacity, the baseline variations of \( O_2 \) and \( CO_2 \) concentrations are similar to those in the background air.
3.2 $\text{O}_2$:CO$_2$ exchange ratio and $\text{O}_2$ flux between the urban area and the overlying atmosphere

Figure 4 (a) shows the relationship between all the $\Delta$O$_2$ and $\Delta$CO$_2$ values to obtain the average OR$_F$ throughout the observation period in this study. By applying a linear regression analysis to the data, the average OR$_F$ value was calculated to be 1.617±0.004 (±1σ). The relationship between the O$_2$ and CO$_2$ concentration anomalies, calculated by subtracting the respective baseline variations shown in Fig. 3 from the observed O$_2$ and CO$_2$ concentrations, is also shown in Fig. 4 (b). By applying a linear regression analysis to the data, we obtained an average OR$_{\text{atm}}$ value of 1.540±0.002 (±1σ) throughout the observation period. Both the OR$_F$ and OR$_{\text{atm}}$ values fall within the range of the average OR values of 1.44 for liquid fuels and 1.95 for gas fuels, which suggests that the short-term variations of O$_2$ and CO$_2$ concentrations at YYG site were driven mainly by a consumption of liquid and gas fuels rather than terrestrial biospheric activities of which OR is about 1.1 (Severinghaus, 1995). Under a closer inspection, the average OR$_F$ value is slightly but significantly larger than OR$_{\text{atm}}$. As mentioned above, OR$_{\text{atm}}$ is an exchange ratio for O$_2$ and CO$_2$ concentration anomalies from the baseline variations and reflects sources or sinks of O$_2$ and CO$_2$ from a wider footprint area of fossil fuel combustion and terrestrial biospheric activities than the flux footprint for OR$_F$ at YYG. Therefore, the larger average OR$_F$ value than the OR$_{\text{atm}}$ value seen in Fig. 4 suggests that a ratio of consumption of gas fuels to liquid fuels, and/or a ratio of fossil fuel combustion to terrestrial biospheric activities, is higher in the urban canopy air at YYG (represented by OR$_F$) than that in the overlying atmosphere (represented by OR$_{\text{atm}}$).

To examine the seasonal difference between the OR$_F$ and OR$_{\text{atm}}$ values, we show the OR$_F$ values calculated by applying regression lines to 1 day and 1 week successive $\Delta$O$_2$ and $\Delta$CO$_2$ values in Fig. 5. The corresponding OR$_{\text{atm}}$ values, obtained by applying regression lines to successive O$_2$ and CO$_2$ concentrations anomalies in Fig. 4 (b), are also shown. Since there is no statistically significant difference between the two (based on the uncertainties shown in the figure (±1σ)), we focus our discussion on the OR values obtained from the 1 week successive data. Clear seasonal cycles with wintertime maxima are found both in the OR$_F$ and OR$_{\text{atm}}$ values at YYG. Larger OR$_{\text{atm}}$ values in the winter than in the summer in urban areas have been reported by some past studies (e.g. van der Laan et al., 2014; Ishidoya and Murayama, 2014; Goto et al., 2013), and generally interpreted as a result of the wintertime increase and decrease of fossil fuel combustion and terrestrial biospheric activities, respectively. Biospheric activities included in the summertime and wintertime flux footprints at YYG were 9 and 2%, respectively (Hirano et al., 2015), and there was no significant solid fuel consumption, such as coal-fired power generation plant of which OR is expected to be 1.17 (Keeling, 1988), detected in the footprints. Therefore, the wintertime OR$_F$ was determined mainly by gas and liquid fuels consumption around the YYG site, given that little vegetation and weak terrestrial biospheric activities occurred in the wintertime. If we assume the wintertime OR$_F$ is determined only by gas and liquid fuels consumption, with OR values of 1.95 and 1.44, respectively, then 45% of the CO$_2$ flux during the December to February (DJF) period was driven by gas fuel consumption, with the rest attributed to liquid fuel consumption. It should be noted that the contributions of gas and liquid fuels are expected to be under- and overestimated since we have ignored the contribution from human respiration with OR values in the range of 1.0 to 1.4. The respiration quotients (the reciprocal of
OR) for carbohydrates, lipid and protein are known to be about 1.0, 0.7 and 0.8, respectively. Precise estimation of the contribution of human respiration to the urban OR will be investigated in a future study.

Figure 5 also shows that the OR$_f$ values were systematically larger than OR$_{atm}$ throughout the year, except for October 2016 and July 2017. The average OR$_f$ and OR$_{atm}$ during DJF were 1.67±0.03 and 1.63±0.02, respectively, both of which agree with the OR value of 1.65 calculated using the statistical data of fossil fuel consumption in Tokyo reported by the Agency of Natural Resources and Energy (http://www.enecho.meti.go.jp/en/), assuming OR value of 1.95, 1.44 and 1.17 for gas, liquid and solid fuels consumption, respectively (hereafter referred to as “OR$_{ff}$”). On the other hand, using the same procedure as above, the average OR$_f$ was calculated to be 1.52±0.1 for the Kanto area of about 17,000 km$^2$ that includes Tokyo. Therefore, not only OR$_f$ but also OR$_{atm}$ at YYG mainly reflected an influence of the fossil fuel consumption in Tokyo rather than that in the wider Kanto area in the wintertime. On the other hand, both the OR$_f$ and OR$_{atm}$ values in the summer were lower than OR$_{ff}$ in Tokyo (1.65), but OR$_{atm}$ was also found to be lower than OR$_{ff}$ for the Kanto area (1.52). These comparatively lower OR$_f$ and OR$_{atm}$ values than OR$_{ff}$ are attributable to the summertime terrestrial biospheric activities. The lower OR$_{atm}$ than OR$_f$ at YYG throughout the year is probably due to the higher contribution of the air mass from Kanto area to OR$_{atm}$ than OR$_f$, since the Kanto area as a whole has lower OR$_{ff}$ than for Tokyo; in addition, the south Kanto area (including Tokyo) has a larger vegetation coverage of about 50% than that in the area around YYG site.

From the observed OR$_f$ and CO$_2$ flux, we derived average diurnal cycles of the O$_2$ flux between the urban area and the overlying atmosphere for each season by using eqs. (2)-(4). Figure 6 shows the average diurnal cycles of ΔO$_2$ and ΔCO$_2$ for each season. To derive these seasonal “climatological” diurnal cycles, the observed ΔO$_2$ and ΔCO$_2$ values of each day in a season were overlaid on top of the values of other days, added up and divided by the number of days in the season. The error bars shown in Fig. 6 indicate ±1 standard error (standard deviation from the mean/square route of the data-number).

The ΔO$_2$ and ΔCO$_2$ values vary systematically in opposite phase and take positive and negative values, indicating transport of O$_2$ uptake and CO$_2$ emission signal from the urban area to the overlying atmosphere throughout the year, respectively. Daily maxima of ΔO$_2$ shown in Fig. 6 are higher in the winter than in the summer and occur in the nighttime. These characteristics would be attributable to an enhancement of the anthropogenic O$_2$ consumption in the winter, while the nighttime decrease of O$_2$ concentration would be due to the O$_2$ consumption near the surface and stable stratification of the surface atmosphere. It must be noted that the ΔCO$_2$ values in the daytime are nearly zero, while the ΔO$_2$ values are not. The intercepts of the regression lines fitted to the relationship between ΔO$_2$ and ΔCO$_2$ in Fig. 6 are 0.27, 0.41, 0.45 and 0.44 μmol mol$^{-1}$ in DJF, MAM, JJA and SON, respectively. Unfortunately, we did not fix the cause(s) of such biases yet, although it may be related, to some extent, to natural exchange processes between the urban area and the overlying atmosphere. Therefore, because of these issues, the use of OR$_f$, calculated by applying a regression line to 2-hour period values of ΔO$_2$ and ΔCO$_2$ of the climatological diurnal cycle (the number of data included in each 2-hour periods were 400 – 800, depending on the season), to determine the relationship between the O$_2$ and CO$_2$ fluxes is preferable. The OR$_f$ values plotted in Fig. 6 show diurnal cycles with daytime minima in DJF, MAM and SON while no clear cycle is found in JJA.
From 10:00 – 16:00 local time, the OR\(_F\) values are in the range of 1.44 – 1.59 in all seasons. This suggests that the dominant cause in determining the daytime OR\(_F\) is the consumption of gasoline by cars, with OR values of 1.52-1.56 (Keeling, 1988).

On the other hand, the OR\(_F\) values from 18:00 – 9:00 local time are more variable, in the range of 1.39 – 1.74, and are clearly larger in the winter than in the summer. Therefore, it is suggested that the consumption of gas fuels increases in the winter, especially in the morning and late in the evening, and that the terrestrial biospheric respiration, enhanced in the summer, makes the OR\(_F\) values smaller than that expected from liquid fuels consumption alone in JJA. The diurnal OR\(_F\) cycles are useful in identifying the causes of CO\(_2\) flux, so that the atmospheric O\(_2\) measurements will provide additional constraint on the CO\(_2\) emission analysis reported in past studies (e.g. Hirano et al., 2015).

The diurnal cycles of the observed CO\(_2\) flux and the estimated O\(_2\) flux from the urban area to the overlying atmosphere are plotted in Fig. 6. The CO\(_2\) flux shows clear diurnal cycles with two peaks for all seasons, one in the morning and the other in the evening. The shape of the diurnal CO\(_2\) flux cycle, with larger flux in the winter than in the summer, was also found in our previous study at YYG for the period 2012-2013 (Hirano et al., 2015). On the other hand, the O\(_2\) flux shows similar diurnal cycles but in opposite phase with the CO\(_2\) flux. The daily mean CO\(_2\) fluxes were 15.6 ± 0.2, 11.2 ± 0.1, 9.3 ± 0.1 and 11.5 ± 0.1 µmol m\(^{-2}\)s\(^{-1}\) in DJF, MAM, JJA and SON, respectively, while the respective daily mean O\(_2\) fluxes were -25.4 ± 0.3, -17.8 ± 0.2, -14.1±0.2 and -17.7 ± 0.2 µmol m\(^{-2}\)s\(^{-1}\). Steinbach et al. (2011) reported a global dataset of CO\(_2\) emissions and O\(_2\) uptake associated with fossil fuel combustion using the EDGAR inventory with country level information on OR, based on the fossil fuel consumption data from the UN energy statistics database. The O\(_2\) uptake around Tokyo for the year 2006 was seen from Fig. 2 in Steinbach et al. (2011) to be about e\(^{16} - e^{17}\) kgO\(_2\) km\(^{-2}\)year\(^{-1}\), which corresponds to -9 – -24 µmol m\(^{-2}\)s\(^{-1}\) of O\(_2\) flux and is consistent with those observed in this study.

It is well known that the atmospheric O\(_2\) concentration has been observed to show a secular decrease (e.g. Keeling and Manning, 2014), and the change rate was about -4 µmol yr\(^{-1}\) for the period 1996 – 2013, while the secular change rate of CO\(_2\) concentration for the period was about 2 µmol yr\(^{-1}\) (Goto et al., 2017b). The O\(_2\) change rate of -4 µmol yr\(^{-1}\) corresponds to -0.04 µmol m\(^{-2}\)s\(^{-1}\) of O\(_2\) (CO\(_2\)) flux, assuming 5.1 x 10\(^{14}\) m\(^2\) for the surface area of the earth, 5.124 x 10\(^{21}\) g for the total mass of dry air (Trenberth, 1981) and 28.97 g mol\(^{-1}\) for the mean molecular weight of dry air. Therefore, the annual mean O\(_2\) consumption rate of -16.3 µmol m\(^{-2}\)s\(^{-1}\) at YYG reported in this study is more than 350 times larger than the global mean consumption rate. If the total land surface consumes O\(_2\) with a comparable rate found at YYG and the ocean is assumed to be O\(_2\) neutral, then it would take only 70 years to reduce the atmospheric O\(_2\) concentration to 18%, causing global deficiency in oxygen for human beings. Although this is an unrealistic speculation, it does show the extent of anthropogenic consumption of atmospheric O\(_2\), and forces us to recognize the fact that our city life is not sustainable, not only in terms of CO\(_2\) emission associated with global warming but also from a viewpoint of the conservation of atmospheric O\(_2\) to survive.
4. Conclusions

Continuous simultaneous observations of atmospheric O$_2$ and CO$_2$ and CO$_2$ flux have been carried out at the YYG site, Toyo, Japan since March 2016. Sample air was taken from air intakes set at heights of 52 m and 37 m of the YYG tower, allowing us to apply an aerodynamic method by using the vertical gradients of the O$_2$ and CO$_2$ concentration measurements. We compared OR$_F$ obtained from the aerodynamic method with OR$_{atm}$, representing OR of the overlying atmosphere above the urban canopy. We found clear seasonal variations with wintertime maxima for both OR$_F$ and OR$_{atm}$, as well as slightly higher OR$_F$ than OR$_{atm}$ throughout the year. The annual mean OR$_F$ and OR$_{atm}$ were observed to be 1.62 and 1.54, respectively, falling within the range of the respective average OR values of 1.44 and 1.95 of liquid and gas fuels. Larger OR$_{atm}$ values in the winter than the summer were interpreted generally as reflecting the wintertime increase and decrease in fossil fuel combustion and terrestrial biospheric activities, respectively. The slightly lower OR$_{atm}$ than OR$_F$ in the summer was probably due to an influence of the air mass from the wider Kanto area to OR$_{atm}$ at YYG since the OR value of 1.1 for the terrestrial biospheric activities is lower than those for liquid and gas fuels consumption; in addition, the influence of the vegetation included in the flux footprints at YYG was much smaller than that in the surrounding Kanto area.

Seasonal variations were seen in the average diurnal OR$_F$ cycles, showing daytime minima in DJF, MAM and SON, while no clear diurnal cycle was distinguishable in JJA. The OR$_F$ values were more variable seasonally in the nighttime than daytime, and the nighttime OR$_F$ was clearly larger in the winter than in the summer, probably due not only to an increase in the consumption of gas fuels in winter, especially in the morning and late in the evening, but also to the enhanced terrestrial biospheric respiration in the summer. The daily mean O$_2$ flux values at YYG were about -25 and -14 µmol m$^{-2}$s$^{-1}$ in the winter and the summer, respectively. The annual mean O$_2$ flux of -16.3 µmol m$^{-2}$s$^{-1}$ was more than 350 times larger than the global mean consumption rate of atmospheric O$_2$ reported by past studies. This highlights the impact of global urbanization and the unsustainability of the dependency on fossil fuel.

Data availability.

The data at YYG site presented in this study can be accessed by contacting the corresponding author.

Author contributions.

SI designed the study and drafted the manuscript. Measurements of O$_2$ concentrations, CO$_2$ concentrations, and CO$_2$ flux were conducted by SI, SI and YT, and HS, respectively. NA prepared standard gas for the O$_2$ measurements. SI and KT conducted O$_2$ observations at MNM. HS, NK and HK examined the results and provided feedback on the manuscript. All the authors approved the final manuscript.

Competing interests.

The authors declare that they have no conflict of interest.
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References


Song, T., and Wang, Y.: Carbon dioxide fluxes from an urban area in Beijing, Atmospheric Research, 106, 139–149, 2012.


Figure 1: Upper panel: Location of the Yoyogi site (35.66°N, 139.68°E, YYG), Tokyo, Japan. Lower panel: Aerial photo from the Geospatial Information Authority of Japan around the study area at YYG. Typical flux footprints in the summer (left) and the winter (right) are also shown by black circles. Inside and outside the red circles indicate the distance of 500 m and 1000 m, respectively, from a roof-top tower of Tokai University where the observations of O$_2$ and CO$_2$ concentrations and CO$_2$ flux were carried out.
Figure 2: Variations in O$_2$ and CO$_2$ concentrations observed at the tower height of 52 m at Yoyogi, Tokyo, Japan for the period March 2016 – September 2017. The O$_2$ concentrations are expressed as deviations from the value observed at 9:58 on March 9, 2016. \( \Delta O_2 \), representing the differences calculated by subtracting the observed O$_2$ concentrations at 37 m from that at 52 m, are also shown. \( \Delta CO_2 \) are the same as \( \Delta O_2 \) but for CO$_2$ concentration. Daily mean CO$_2$ fluxes observed using the eddy correlation method are also shown, and the flux takes on positive value when the urban area emits CO$_2$ to the overlying atmosphere.
Figure 3: Baseline variations of O$_2$ and CO$_2$ concentrations at the tower height of 52 m at Yoyogi, Tokyo, Japan, represented by their best-fit curves (black solid lines) to the respective maxima and minima values during the successive 1-week periods (black dashed lines). Variations of 24 hours-averaged O$_2$ and CO$_2$ concentrations at Minamitorishima, Japan (blue dashed line) and their best-fit curves (blue solid lines) are also shown (updated from Ishidoya et al., 2017).
Figure 4: (a) Relationship between the $\Delta O_2$ and $\Delta CO_2$ shown in Fig. 2. Average OR$_F$ (see text) for the observation period, derived from the regression line fitted to the data is also shown. (b) Same as in (a) but for the deviations of $O_2$ and $CO_2$ concentrations from their baseline variations shown in Fig. 3 and the average OR$_{atm}$ (see text). OR values expected from the consumptions of gas and liquid fuels are also shown.
Figure 5: OR calculated by applying regression lines to 1 day (gray open circles) and 1 week (black closed circles) successive $\Delta$O$_2$ and $\Delta$CO$_2$ values. Also plotted are OR$_{atm}$ calculated by applying regression lines to 1-day (light red open circles) and 1-week (dark red closed circles) successive O$_2$ and CO$_2$ deviations from their baseline variations shown in Fig. 3. OR values expected from the consumptions of gas, liquid and solid fuels and land biospheric activities are also shown.
Figure 6: Plots of average diurnal cycles of ΔO₂ and ΔCO₂ for each season: December to February (back), March to May (green), June to August (blue) and September to November (red). Average diurnal cycles of OR₅, calculated by applying regression lines to the 2-hour period values of ΔO₂ and ΔCO₂, are also plotted seasonally (see text). Average diurnal cycles of the CO₂ flux observed using the eddy correlation method, and those of the O₂ flux calculated from the CO₂ flux and OR₅ values are also plotted seasonally. Error bars indicate ±1 standard error.