Diurnal variability of atmospheric O\textsubscript{2}, CO\textsubscript{2} and their exchange ratio above a boreal forest in southern Finland

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Abstract. The exchange ratio (ER) between atmospheric O\textsubscript{2} and CO\textsubscript{2} is a useful tracer on global and local scales to better understand the carbon budget. The variability of ER (in mol O\textsubscript{2} per mol CO\textsubscript{2}) between terrestrial ecosystems is not well-known, and there is no consensus on how to derive the ER signal to represent an ecosystem, as there are different approaches available, either based on concentration (ER\textsubscript{atmos}) or flux measurements (ER\textsubscript{forest}). In this study we measured atmospheric O\textsubscript{2} and CO\textsubscript{2} concentrations at two heights above the boreal forest in Hyytiälä, Finland. Such measurements of O\textsubscript{2} are unique and enable us to potentially identify which forest carbon loss and production mechanisms dominate over various hours of the day. We found that the ER\textsubscript{atmos} signal at 23 m is not representative for the forest exchange alone but is also influenced by other factors, including for example entrainment of air masses with different thermodynamic and atmospheric composition characteristics in the atmospheric boundary layer. To derive ER\textsubscript{forest} we infer O\textsubscript{2} fluxes using multiple theoretical and observation-based micro-meteorological formulations to determine the most suitable approach. Our resulting ER\textsubscript{forest} shows a distinct difference in behaviour between daytime (0.92 ± 0.17 mol/mol) and nighttime (1.03 ± 0.05 mol/mol). These insights demonstrate the diurnal variability of different ER signals above a boreal forest and we also confirmed that the signals of ER\textsubscript{atmos} and ER\textsubscript{forest} can not be used interchangeably. Therefore, we recommend measurements on multiple vertical levels to derive O\textsubscript{2} and CO\textsubscript{2} fluxes for the ER\textsubscript{forest} signal, instead of a single level time series of the concentrations for the ER\textsubscript{atmos} signal. We show that ER\textsubscript{forest} can be further split into specific signals for respiration (1.03 ± 0.05 mol/mol) and photosynthesis (0.96 ± 0.12 mol/mol). This estimation allows us to separate the Net Ecosystem Exchange (NEE) into Gross Primary Production (GPP) and Total Ecosystem Respiration (TER), giving comparable results to the more commonly used eddy covariance approach. Our study shows the potential of using atmospheric O\textsubscript{2} as an alternative method to gain new insights on the different CO\textsubscript{2} signals that contribute to the forest carbon budget.
1 Introduction

To understand how the increasing carbon dioxide (CO$_2$) levels in the atmosphere are changing our climate, we need to know the sources and sinks of CO$_2$ separately. These sources and sinks result in the global carbon budget in which the main sources are fossil fuel combustion and land-use change and the main sinks are the uptake by the land biosphere and the oceans (Friedlingstein et al., 2022). The net terrestrial biospheric sink (Net Ecosystem Exchange, NEE) results from many fluxes of which the two largest are typically Gross Primary Production (GPP) and the Total Ecosystem Respiration (TER). Knowing these gross fluxes separately will allow better estimates of the changing behaviour of the biosphere carbon sink, as GPP and TER respond differently to climate change and increasing atmospheric CO$_2$ levels.

Using additional tracers allows us to gain further insights into GPP and TER, without relying on a temperature-based function to parameterize TER as is used for Eddy Covariance (EC) measurements e.g. Reichstein et al. (2005). Additional tracers such as atmospheric O$_2$ (Keeling and Manning, 2014), and also COS, $\delta^{13}$C or $\Delta^{17}$O have the important advantage of sharing a process or pathway with CO$_2$ directly (Whelan et al., 2018; Peters et al., 2018; Koren et al., 2019; Kooijmans et al., 2021). This allows one to use numerical models to test formulations of processes, such as stomatal and mesophyl exchange, photosynthesis, pool-specific respiration, and even turbulent canopy exchange. Atmospheric O$_2$ is directly coupled to CO$_2$ in several processes through the so-called Exchange Ratio (ER) (Keeling and Manning, 2014; Manning and Keeling, 2006; Keeling et al., 1993). This ER (also sometimes referred to as Oxidative Ratio (OR) in the literature), indicates the amount of moles of O$_2$ that are exchanged per mole of CO$_2$ and gives a process-specific signature (Keeling, 1988).

On the global scale, ER has been used to derive the global oceanic CO$_2$ sink and determine the global carbon budget (Stephens et al., 1998; Rödenbeck et al., 2008; Tohjima et al., 2019). This is done by solving the atmospheric budgets of O$_2$ and CO$_2$ with the following equations:

\[
\frac{dCO_2}{dt} = F - O - B \tag{1}
\]

\[
\frac{dO_2}{dt} = -\alpha_F F + \alpha_B B + Z_{O_2} \tag{2}
\]

where F is the fossil fuel CO$_2$ emissions, O is ocean CO$_2$ uptake, B is the net land biosphere sink of CO$_2$ and $Z_{O_2}$ indicates the ocean O$_2$ outgassing. $\alpha_F$ and $\alpha_B$ indicate the ERs for fossil fuel combustion and the net land biosphere sink respectively. In these global studies simplified global average values are used for $\alpha_F$ and $\alpha_B$, where $\alpha_F$ is determined by the global mixture of fuels burned, which results in 1.38 [mol/mol] (Keeling and Manning, 2014) and $\alpha_B$ was determined by laboratory measurements and a literature study of ORs of different plant and soil materials, which resulted in 1.1 [mol/mol] (Severinghaus, 1995). Furthermore, $\alpha_B$ is also used to combine O$_2$ and CO$_2$ into Atmospheric Potential Oxygen (APO) (Stephens et al., 1998) which is used in determining the ocean carbon sink, and recently has also been shown to be a suitable tracer to detect fossil fuel emission reductions during the COVID-19 pandemic (Pickers et al., 2022). For these larger scale applications using APO
it is important to have good estimates for $\alpha_B$.

On local scales, previous studies have shown that $\alpha_B$ is not a constant value as used on the global scale, and that it shows a certain degree of temporal and spatial variability. These studies either measured ORs from elemental composition analysis (Worrall et al., 2013; Randerson et al., 2006; Gallagher et al., 2017), or derived the ER from atmospheric concentrations measurements (Battle et al., 2019; Seibt et al., 2004; van der Laan et al., 2014). By using elemental composition analysis, the OR reflects the relationship between O$_2$ and CO$_2$ over a longer time scale, of years or decades, compared to the atmospheric concentration measurements of the ER, which are on hourly and daily time scales. Both the OR and the ER based studies showed that $\alpha_B$ changes per ecosystem and over different time periods. The ER from the gas exchange experiments can furthermore be used for the separation of GPP and TER, using a specific ecosystem ER, which are determined with two alternative approaches (see Figure 1) (Seibt et al., 2004; Stephens et al., 2007; Ishidoya et al., 2013, 2015; Battle et al., 2019). The first is the ER of the atmosphere (ER$_{atmos}$), which is the ratio of the atmospheric O$_2$ and CO$_2$ concentration measurements, and the second is the ER of the forest (ER$_{forest}$), which is the ratio of the surface fluxes of O$_2$ and CO$_2$. First attempts to estimate ER$_{forest}$ were made using one-box models (Seibt et al., 2004; Ishidoya et al., 2013). More accurate estimates of ER$_{forest}$ would be based on in-situ measured O$_2$ and CO$_2$ surface fluxes, however O$_2$ currently cannot yet be measured accurately using EC techniques. Ishidoya et al. (2015) showed the first surface fluxes of O$_2$ using vertical gradients of O$_2$, an alternative technique to EC, and CO$_2$ measurements at two heights above the canopy in the surface layer in a temperate forest in Japan. Their results showed that the ER$_{forest}$ signal could be used to separate the NEE signal into GPP and TER, consistent with the separation method for EC measurements using an empirical function of air temperature.

When using O$_2$ to separately estimate GPP and TER fluxes, it is important to use the value for ER that represents ecosystem exchange. Seibt et al. (2004) showed that the signal of ER$_{atmos}$ cannot be directly linked to the exchange of carbon in the terrestrial biosphere, because in addition to the biosphere, ER$_{atmos}$ is also affected by advection, boundary layer dynamics and entrainment (Figure 1). In contrast, Ishidoya et al. (2015) found similar values for ER$_{atmos}$ and ER$_{forest}$. So far, there is no clear consensus on which signal should be used to indicate the ER of the ecosystem. Furthermore, since atmospheric O$_2$ measurements are challenging to make, only a few studies exist that measured atmospheric O$_2$ continuously above an ecosystem and that derive ER signals (Ishidoya et al., 2015; Stephens et al., 2007; Seibt et al., 2004; Battle et al., 2019). The uncertainty and spatial and temporal variability of $\alpha_B$ are therefore not well known (Manning and Keeling, 2006; Keeling and Manning, 2014), and knowledge about the difference between ER$_{forest}$ and ER$_{atmos}$, its variability across different regions and ecosystems, and how ER$_{forest}$ can be used on both the local and global scale to advance our understanding of the carbon cycle, is still limited. Therefore, more and longer in-situ time series of atmospheric O$_2$ measurements are needed and further understanding of O$_2$ and CO$_2$ exchange above and below the canopy is crucial to continue the pioneering work of Seibt et al. (2004), Stephens et al. (2007), Ishidoya et al. (2015) and Battle et al. (2019) and improve the application of the global biosphere ER, resulting in a better understanding of the carbon balance on local, regional and global scales.
Figure 1. Schematic overview of the different O\textsubscript{2}:CO\textsubscript{2} exchange ratio signals (ER), measured and analyzed in and above a forest, influenced by the different O\textsubscript{2} and CO\textsubscript{2} fluxes and meteorological processes (a), together with a more detailed look on which processes influence the different ER signals (b). (a) shows the direction of the surface fluxes during the day in the surface layer, which includes the roughness sublayer and the inertial sublayer. During the night the direction of the O\textsubscript{2} and the CO\textsubscript{2} surface fluxes are the other way around. The ER of the atmosphere (ER\textsubscript{atmos}) is determined from the change over time (\(\Delta(t)\)) in the O\textsubscript{2} and CO\textsubscript{2} concentration measurements, and the ER of the forest (ER\textsubscript{forest}) is calculated from the surface fluxes of O\textsubscript{2} and CO\textsubscript{2} which are inferred (~) from the vertical gradient (\(\Delta(z)\)). ER\textsubscript{a} represents assimilation processes and ER\textsubscript{r} represents respiration processes. (b) shows the connections between the processes, measurements, and the ERs. Dotted lines indicates smaller influences of the processes that are connected to it compared to solid lines.

The aim of this study is to improve upon existing methods to calculate ER\textsubscript{forest} and get a better comparison between how the ER\textsubscript{atmos} and ER\textsubscript{forest} signals are formed. We carried out a measurement campaign in Hyytiälä, Finland, for two short periods in spring/summer 2018 and 2019 where both O\textsubscript{2} and CO\textsubscript{2} were measured at two heights with a setup including a differential fuel cell analyser for O\textsubscript{2}. These new measurements extend the existing continuous O\textsubscript{2} records and provide us the opportunity to calculate the O\textsubscript{2} surface fluxes in a boreal forest for the first time, together with the CO\textsubscript{2} surface flux. We used our measurements to determine the relation between O\textsubscript{2} and CO\textsubscript{2} diurnal behaviour of the concentrations and the fluxes, by using either one or both measurement heights on the tower. Combining the O\textsubscript{2} and the CO\textsubscript{2} fluxes allowed us to calculate ER\textsubscript{forest}, make a comparison between the ER\textsubscript{atmos} and ER\textsubscript{forest} signals, and use ER\textsubscript{forest} to estimate GPP and TER fluxes.

In this paper, we first describe the measurement site, experimental setup and methods to derive O\textsubscript{2} fluxes and the different ER signals (Section 2). We present the measurements for the whole campaign and select a representative day to determine the
most suitable approach for deriving $O_2$ fluxes and to determine $ER_{\text{forest}}$ (Section 3). A detailed evaluation and discussion of our $ER_{\text{atmos}}$ and $ER_{\text{forest}}$ signals is given in Section 4. We finalize with our conclusion about the diurnal variability of the ER signals for a representative day of a boreal forest (Section 5).

2 Methods

To determine $ER_{\text{atmos}}$ and $ER_{\text{forest}}$, and its diurnal variability, we measured $O_2$ and $CO_2$ continuously at two heights above a boreal forest during two short campaigns at Hyytiälä. These 'OXHYGEN' (OXYGEN at HYYtiala) campaigns took place in the spring/summer of 2018 (03-Jun through 02-Aug) and 2019 (10-Jun through 17-Jul). In this section, we describe the measurement site and instrumental setup, as well as the methods used to determine the $O_2$ and $CO_2$ fluxes from the measured vertical gradient and the ER signals.

2.1 Measurement site

The measurements were made at Hyytiälä SMEAR II Forestry Station of the University of Helsinki in Finland ($61^\circ\,51'\,N, 24^\circ17'\, E, +181\,MSL$); this site is described in more detail in e.g. Hari et al. (2013). The SMEAR II station is a boreal site within the European Integrated Carbon Observation System (ICOS) network with atmospheric and ecosystem measurements. The SMEAR II station is located inside a homogeneous forest of Scots pine trees ($Pinus Sylvestris$) with a dominant canopy height of 18 m and some silver birch and aspen trees. The forest floor is covered with mosses and herbs. The soils are podzols on top of glacial till. A large lake is located close to the measurement site and has a fetch of 250 m over the dominant wind direction of $230^\circ$. The footprint of the site is mostly influenced by natural sources, with the atmospheric signal dominated by forest exchange (Carbon Portal ICOS RI, 2022). The measurement site includes several towers, including a 128m tall tower and a 23 m high walk up tower, where atmospheric variables and gas concentrations are continuously measured. The operational data from this tower are publicly available online at http://avaa.tdata.fi/web/smart/smear/. Our $O_2$ and $CO_2$ measurement setup was installed in a cabin at the bottom of the 23 m high tower, and air was sampled from aspirated inlets (Blaine et al., 2006), installed at 23 m in the smaller tower and at 125 m in the tall tower, 5m and 107m above the canopy height respectively. We used both levels to calculate the vertical gradient for the flux calculations (Section 2.3).

2.2 Experimental setup

The measurement setup is based on the instrument used in van Leeuwen and Meijer (2015), following the methods in van der Laan-Luijkx et al. (2010) and Stephens et al. (2007). $O_2$ is measured with a Sable Systems "Oxzilla II" fuel cell based instrument and $CO_2$ is measured with an ABB continuous gas analyzer "URAS26", which is a non-dispersive infrared (NDIR) photometer. The gas handling schematic is shown in Figure 2.
Figure 2. Schematic overview of the measurement setup used at Hyytiälä. The setup includes an Oxzilla O₂ fuel cell analyser and a URAS26 NDIR CO₂ analyser. The system measured air sampled from two heights of either 23 or 125 meters.

Air was pumped from either 23 or 125 metre height to the measurement system at the base of the tower. Both inlet lines were continuously flushed, where either one of the heights is measured by the system with a sample flow of around 120 ml/min and the other flushed to the room with a higher flow rate of around 2 litre per minute, which allows fast switching between the two heights. We switched between the inlets every half hour to match the Eddy Covariance (EC) measurements and to get a more stable signal of O₂. The air of the selected inlet was first cooled to -60 °C with a cryogenic cooler to remove water vapour from the air, before entering the system. Second stage drying of the air streams is done with magnesium perchlorate (Mg(ClO₄)₂) traps. The sample air was continuously measured against a reference gas (differentially for O₂, and alternatively for CO₂), and the pressure in both sample and reference line were matched to be the same using a pressure control system (MKS Instruments, types 223B, 248A and 250E for the pressure transducers, regulating valve and control system respectively). The reference and sample lines were switched every 2 minutes between the two fuel cells in the Oxzilla analyser. We measured a set of 3
The measurements of these calibration gases allowed calibration of our measurements against the international Scripps Institution of Oceanography (SIO) scale for $\delta$O$_2$/N$_2$. We did that by using cylinders that are filled in the laboratory at the University of Groningen, where they were calibrated with the primary Scripps cylinders (Nguyen et al., 2022). The O$_2$ measurements are normally expressed as $\delta$O$_2$/N$_2$ ratios in ‘per meg’ units instead of mole fraction (ppm), since O$_2$ is not a trace gas because of its high abundance of 20.95%, and therefore the mole fraction varies due to changes of other gases, such as CO$_2$ (Keeling et al., 1998). $\delta$O$_2$/N$_2$ is defined as:

$$\delta(O_2/N_2) = \left( \frac{(O_2/N_2)_{\text{sample}}}{(O_2/N_2)_{\text{reference}}} - 1 \right) \cdot 10^6 \ \text{[per meg]} \ (3)$$

For simplicity, in this paper we use the term O$_2$ instead of $\delta$O$_2$/N$_2$, and we use the term ‘concentration’ rather than ‘mole fraction’ when discussing both CO$_2$ and O$_2$. Equation 3 indicates a change compared to a reference level. Negative values therefore indicate concentrations of O$_2$ lower than the reference value. To allow comparison of changes in CO$_2$ and O$_2$ directly, we converted the units of O$_2$ from per meg to ppm equivalents (ppmEq), where a change of 1 ppm CO$_2$ corresponds to a 4.77 per meg change in O$_2$ (Tohjima et al., 2005; Kozlova and Manning, 2009).

We modified the method described in van der Laan-Luijkx et al. (2010), to calibrate the measurements. The raw CO$_2$ measurements have a frequency of one measurement per six second, the raw O$_2$ measurements have a frequency of one measurement per second and both give 1 value every 4 minutes in the form of $\Delta$CO$_2$ and $\Delta(\Delta)$O$_2$ respectively. CO$_2$ is measured on a single cell instrument, and therefore $\Delta$CO$_2$ is the difference between the 2-minute averages of the sample air (S) and the reference cylinder (R), giving (S-R). For the 2-minute averaged CO$_2$ measurements, the last 78 seconds of each 2 minute period are used. Note that for CO$_2$, the NDIR system is different compared to other systems used and therefore does not need a zero-gas (Pickers et al., 2017). O$_2$ is measured on a double cell instrument, and therefore gives a double differential signal. The $\Delta(\Delta)$O$_2$ is the difference between the 2-minute averaged difference between S and R and the 2-minute averaged difference between R and S ((S-R)-(R-S)). For the 2-minute averaged O$_2$ values, the last 100 seconds of each 2 minute period are used. In 2019, the pressure control valve was not functioning optimally. We therefore corrected the 4-minute values of $\Delta(\Delta)$O$_2$ for a deviation in the MKS pressure sensor (PMKS), by multiplying $\Delta(\Delta)$O$_2$ with 0.095*PMKS, which we derived based on the measurements of the calibration cylinders. For both CO$_2$ and O$_2$, the 4-minute values were subsequently used to calculate half hourly means, where we excluded the first 4-minute value after the heights are switched, together with the measurements that did not fall inside the boundary based on the median absolute deviation (MAD) (Rousseeuw and Verboven, 2002).

The linear calibration response functions for both O$_2$ and CO$_2$ were calculated for every measurement period of the calibration cylinders, which was about every 23 hours. For the response functions, we used a constant slope based on the mean of all the calibration slopes measured in the specific year. The y-intercept of the response functions were interpolated to the time of the measurement, based on the two calibrations bracketing the measurement time. To facilitate the comparison of the O$_2$ and
CO₂ measurements of the two heights and allow flux calculations based on the vertical gradient, we interpolated the data to one measurement for every 30 minutes for each height. Based on the target cylinders, measured during the calibration period, the stability of the long-term measurements were determined (Table 1). A different target cylinder for 2019 compared to 2018 was used, which resulted in different outcomes for the standard deviation (std) and the mean difference for these periods. The mean difference is determined by calculating the mean of the difference between the values of the target cylinder based on our own calibration and based on the declared value with calibration in Groningen. The measurement period of 2018 was also longer and therefore more points were included for the std and mean difference calculations. The measurement precision of this device compared to the recommendations of the World Meteorological Organisation (WMO) will be further discussed in section 4.1.

Table 1. The mean difference and the standard deviation (std) of the target cylinder measurements of O₂ and CO₂ for the 2018 and 2019 periods separately, together with the amount of data points used to calculated these specific values.

<table>
<thead>
<tr>
<th></th>
<th>2018 (03-06 through 01-08)</th>
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<th>2019 (16-06 through 17-07)</th>
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<tbody>
<tr>
<td></td>
<td>Std</td>
<td>Mean difference</td>
<td>Amount of points</td>
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<tr>
<td>O₂ [per meg]</td>
<td>16</td>
<td>28</td>
<td>53</td>
</tr>
<tr>
<td>CO₂ [ppm]</td>
<td>0.07</td>
<td>0.7</td>
<td>53</td>
</tr>
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2.3 Data analysis

For the analyses presented in this paper we needed representative diurnal cycles of O₂ and CO₂. We looked for a representative day in 2019 where little to no clouds were present, no unexpected behaviour in the diurnal cycles for potential temperature, specific humidity and CO₂ occurred, for example caused by advection, and where the O₂ data showed a clear difference between the two measurement heights. We used data from 2019 instead of 2018 because 2018 saw a large-scale drought in Europe, and 2019 was less extreme and closer to a typical boreal summer (Peters et al., 2020). However, no single representative day could be found in our 2019 record, where the O₂ data showed a clear negative vertical gradient during the day and positive during the night, in combination with the above-mentioned meteorological criteria. We therefore choose a sequence of days to create an aggregate day based on the average of several days, which is representative for this time of the year in Hyytiälä, following the same method used by Ishidoya et al. (2015). The main criterion was that the O₂ gradient had to be negative during the day and the negative relationship between O₂ and CO₂ concentrations at 23 m was present during the entire day. This resulted in selecting the period of 7 through 12 July 2019 to create the representative day which we used in all subsequent analyses.

For the representative day, the two O₂ : CO₂ Exchange Ratio (ER) signals, ER_{atmos} and ER_{forest}, were determined. ER_{atmos} is expressed as:

\[
ER_{atmos} = - \frac{\Delta(t)O_2}{\Delta(t)CO_2}
\]

(4)
Where both $\Delta(t)O_2$ and $\Delta(t)CO_2$ are the change in concentration over a selected time period (t). This is a unit-less quantity as it represents mol O$_2$ per mol CO$_2$. ER$_{atmos}$ was determined by the slope between the concentration of O$_2$ and CO$_2$ at the same height over a specific time period (Seibt et al., 2004; Stephens et al., 2007; Ishidoya et al., 2013; Battle et al., 2019).

The selected time periods were based on the period when O$_2$ and CO$_2$ had the highest negative correlation. Throughout the day, this could be divided into three periods when different processes dominate (Figure 1). It starts with the period during the night where the atmosphere is stable and respiration becomes the dominant surface flux (P1), and therefore the CO$_2$ concentration increases and the O$_2$ concentration decreases. Subsequently, when the sun starts to rise, the boundary layer height starts to grow and entrainment of air from the free troposphere influences the surface measurements (P2) (Vilà-Guerau de Arellano et al., 2004). Here the CO$_2$ concentration decreases rapidly and the O$_2$ concentration increases rapidly. Finally, the period starts when the effect of boundary layer dynamics and entrainment decreases and the assimilation flux becomes the most dominant (P3), here the CO$_2$ concentration decreases less rapidly and the O$_2$ concentration increases less rapidly. We calculated a ER$_{atmos}$ signal with equation 4, for the night-time (P1), the day-time (by either focusing on only P3 or both P2 and P3) and the complete day (P1 + P2 + P3). The exact boundaries of these periods have to be estimated. To be certain about the exact times that should be taken as the boundaries for each period, an atmospheric model is needed.

$$ER_{forest} = -\frac{(w'O_2')_s}{(w'CO_2')_s}$$  

(5)

Where both $(w'O_2')_s$ and $(w'CO_2')_s$ are the mean turbulent surface fluxes above the canopy of O$_2$ and CO$_2$ over a selected time period (Seibt et al., 2004; Ishidoya et al., 2015). The $w'$ in both these terms indicates the fluctuating vertical wind speed and both O$_2'$ and CO$_2'$ indicate the fluctuating concentrations of O$_2$ and CO$_2$. We derive the fluxes of O$_2$ and CO$_2$ using the vertical gradient (see next paragraph). The selected time periods for ER$_{forest}$ were chosen such that the transition periods between where the respiration flux (stable atmosphere) or the assimilation flux (well mixed atmosphere) dominate, were excluded. By excluding the transition periods, we removed the periods where the gradients of both CO$_2$ and O$_2$ were close to zero. This was done because a very small gradient makes it difficult to calculate a flux and therefore the ER$_{forest}$, and also because during this period entrainment is the most dominant process. The exact duration of the transition periods was based on the maximum and minimum of both the friction velocity and the height of 27 m ($z$) divided by the Monin Obukov Length (L). The friction velocity and ($z$/L) indicate the measure of turbulence of the atmosphere (Stull, 1988). The mean of the remaining data points of the CO$_2$ and O$_2$ flux during the stable atmosphere period was used to calculate the ER$_{forest}$ signal of the night and the mean of the remaining data points of the CO$_2$ and O$_2$ flux during the mixed atmosphere period was used to calculate the ER$_{forest}$ signal of the day. The ER$_{forest}$ for the entire day is based on the average CO$_2$ and O$_2$ flux for the entire day.

Currently, unlike for CO$_2$, the O$_2$ flux cannot be measured directly with an Eddy Covariance (EC) system. Instead, the flux can be inferred from the flux-gradient method. To calculate the flux of a certain scalar ($\phi$) with the flux-gradient method, the
following equation was used (Stull, 1988):

\[
(w'\phi')_s = -K_\phi \cdot \frac{\partial \phi}{\partial z}
\]  

(6)

Where \((w'\phi')_s\) is the surface flux, \(K\) is the exchange coefficient and \((\partial \phi/\partial z)\) is the vertical gradient of \(\phi\). To determine the \(O_2\) flux with Equation 6 \((\phi = O_2)\), the exchange coefficient of \(O_2\) \((K_{O_2})\) needs to be determined. Ishidoya et al. (2015) assumed that \(K_{O_2} = K_{CO_2}\) and determined \(K_{CO_2}\) by dividing the \(CO_2\) flux, measured with EC, by the \(CO_2\) vertical gradient between two measurement levels. However, the exchange coefficient can also be determined with other methods that for example only need two measurement heights for the vertical gradient. In this study, we explore these different options for calculating \(K_{O_2}\). The EC measurements of the \(CO_2\) flux were used as a reference, to determine the most suitable approach. The most suitable approach to infer the \(O_2\) flux is then used for both \(K_{CO_2}\) and \(K_{O_2}\). During this study we derive the surface flux in the surface layer (Figure 1) and we assume that the surface flux stays constant in this surface layer, which consists of the roughness sub-layer and the inertial sublayer.

We categorized the methods to determine the most suitable \(K\) into two groups: The observation-based approach (also called the K-theory (Stull, 1988) or the modified Bowen ratio method (Meyers et al., 1996)) and the theoretical approach (following the similarity theory (Dyer, 1974)). For the observation-based methods, the exchange coefficient (\(K\)) in equation 6 is determined by dividing a flux measured at 27 m, using an EC system, by a 3-height (16 m, 67 m and 125 m) vertical gradient of a specific scalar. Ishidoya et al. (2015) used this approach to calculate their \(O_2\) flux, using the \(CO_2\) flux and vertical gradient of two levels. Next to \(CO_2\), we also calculated \(K\) using potential temperature (\(\theta\)) for the observation-based approach. For the theoretical approach, the \(K\) in equation 6 is determined with the Monin-Obukov Similarity Theory (MOST) (Dyer, 1974), where logarithmic surface layer scaling applies for \(K\) and empirical similarity functions are used to describe the effect of atmospheric stability. In addition, we used a correction which takes into account the effect of the roughness sublayer (see Appendix for details). The SMEAR II data at 27 meter were used for the calculations with MOST. When only two heights for the gradient calculations are available, there is an option to integrate equation 6 (de Ridder, 2010). We tested both the application with and without integration in this study. We used the ICOS data, available at the SMEAR II station, for the \(K\) calculations. For the \(CO_2\) EC measurements, we used the gap-filled data to correct for the storage below the measurement height of the EC. Gap-filling was applied when the friction velocity (\(u^*\)) was below 0.4 (Kulmala et al., 2019). The Appendix gives a more elaborate explanation and provides equations of the different methods used to determine the exchange coefficients used in this study.

Finally, we select the \(K_\phi\) that produced the best \(CO_2\) flux results compared to the EC of \(CO_2\), and this \(K\) was used to calculate the \(O_2\) and \(CO_2\) fluxes, together with the vertical gradient from measurements collected during our campaigns. For our campaigns, we only have \(O_2\) and \(CO_2\) measurements at two heights (23 m and 125 m), which means that \((\partial \phi/\partial z)\) changes into \((\Delta \phi/\Delta z)\) and the gradient was calculated with finite differences.
After both the CO$_2$ and O$_2$ fluxes were determined, resulting in ER$_{forest}$, we subsequently calculated the O$_2$ : CO$_2$ exchange ratio signals for the assimilation processes (ER$_a$) and the respiration of the ecosystem (ER$_r$) with the following equations (Seibt et al., 2004; Ishidoya et al., 2015):

\[
NEE = -GPP + TER
\]  

(7)

\[
NEE \cdot ER_{forest} = -GPP \cdot ER_a + TER \cdot ER_r
\]

(8)

Where the NEE is the Net Ecosystem Exchange, GPP is the Gross Primary Production and TER is the Total Ecosystem Respiration. GPP and TER are always positive by definition, representing uptake and release by the ecosystem respectively. Therefore, the resulting negative NEE values represent carbon uptake by the ecosystem, when GPP is larger than TER. We used ICOS NEE and GPP data from EC measurements from the SMEAR II station at a level of 27 meters in the 128 m height tower. First, we assumed that nighttime NEE is equal to TER, which meant that the nighttime ER$_{forest}$ signal is equal to ER$_r$. We assumed that the processes that contributed to the ER$_r$ keep the same ratio between O$_2$ and CO$_2$ during the entire day and therefore we used a constant ER$_r$ for the entire day. Subsequently, we calculated ER$_a$, for both the entire diurnal cycle and the daytime using equation 8 with the corresponding ER$_{forest}$ and the constant ER$_r$.

By estimating ER$_r$ and ER$_a$ of this boreal forest, we created the opportunity to apply atmospheric O$_2$ measurements to separate NEE into GPP and TER (the O$_2$ method). We calculated ER$_r$ and ER$_a$ for the representative day using equations 7 and 8, and use these to calculate GPP and TER for another representative day. We selected 13 through 15 July to create a new aggregate and to calculate a new ER$_{forest}$ signal for the entire day. These three days were chosen because in 2019 they showed the clearest diurnal cycle of O$_2$ and a negative O$_2$ gradient, aside from 7 through 12 July, used above. By using the previously determined ER$_r$ and ER$_a$, and ER$_{forest}$ and NEE for the new representative day, we calculated GPP and TER from NEE for this new day. By comparing the GPP and TER fluxes of the O$_2$ method to the GPP and TER fluxes of the temperature-based function of ICOS (EC method), we could demonstrate how accurate the O$_2$ method is. Both Seibt et al. (2004) and Ishidoya et al. (2015) also applied the O$_2$ method, however both these studies used chamber measurements to first determine ER$_a$ and ER$_r$ and then used equation 7 and 8 to infer GPP and TER. Unfortunately we did not have chamber measurements of both O$_2$ and CO$_2$ available and therefore we used equation 7 and 8 to calculate ER$_a$ and ER$_r$. This means that these two equations can be used in two ways: to determine the ER$_a$ and ER$_r$ signal, or to separate NEE into GPP and TER.

3 Results

3.1 O$_2$ and CO$_2$ time series

The calibrated half hourly measurements of O$_2$ and CO$_2$ for 2018 and 2019 are shown in Figure 3, together with the vertical gradients between the two measurement heights. The O$_2$ measurements are shown here converted from per meg to ppmEq, to allow comparison of the diurnal variability for CO$_2$, and to calculate the ER signals. The differences between the 23 m and
The half hourly average O$_2$ (a) and CO$_2$ (b) concentrations at Hyytiälä for spring/summer of 2018 and 2019 for the 125 m and 23 m height levels, together with the vertical gradient ($\Delta$($z$)) between these two heights (c) for both O$_2$ and CO$_2$. The shaded area indicates the dates that were selected for the aggregate representative day, 7 through 12 July 2019. The selected days are shown in more detail for the 23 m measurements (d) and the gradients (e) for both O$_2$ and CO$_2$.

125 m measurements are observable for both CO$_2$ and O$_2$. During both campaigns in 2018 and 2019, the diurnal behaviour of the O$_2$ concentrations has a negative relationship with the CO$_2$ concentrations. This negative relationship between O$_2$ and CO$_2$ is also visible from the gradient measurements, despite the relatively high uncertainty of the O$_2$ measurements as described in Section 2.2 and further elaborated on in Section 4.1. The period 7 through 12 July 2019 shows the most clear negative relationship between the O$_2$ gradient and the CO$_2$ gradient, and also had the most suitable meteorological conditions and was therefore selected for the aggregate representative day (Section 2.3).

### 3.2 Diurnal cycles

The measurements of O$_2$ and CO$_2$ and their vertical gradient for the representative day, are shown in Figure 4. There are no measurements between 20:00 and 22:00 because this is the measurement period of the calibration cylinders each day. Note that the daylight length at Hyytiälä is long at this time of the year, with sunrise at 04:00 and sunset at 23:00. We compared our CO$_2$ observations with ICOS CO$_2$ measurements at the same height, which shows that both instruments compare well overall, with a mean different of 0.70 ± 0.65 during the period 7 trough 12 July. The comparison between the two devices was a bit difficult because of the different timing of the measurements. The diurnal cycles of O$_2$ and CO$_2$ (Figure 4a) clearly show anti-correlated behaviour between CO$_2$ and O$_2$, which is especially visible during nighttime (23:00 - 04:00) and the morning transition (05:00 - 13:00).
Figure 4. Diurnal cycles of the O$_2$ and CO$_2$ concentrations for the 23 m and 125 m height levels (a) and the vertical gradient between both levels with the uncertainty of both O$_2$ and CO$_2$ of the representative day, taken as the average values of 7 through 12 July 2019 (b). The CO$_2$ measurements of the ICOS setup are shown in (a) for comparison to the CO$_2$ setup measured during our campaigns. The shaded colors indicate the selected different periods where the most dominant processes are: stable atmosphere and respiration (00:00-04:00, P1), entrainment, boundary layer growth and assimilation (04:00-09:00, P2), convective conditions and assimilation (09:00-13:00, P3a), a remaining artefact after the pressure correction due to the instability of the MKS pressure regulator becomes visible during the convective conditions with assimilation dominating (13:00-20:00, P3b).

Figure 4 shows four different periods that can be linked to the periods to calculate ER$_{atmos}$, described in section 2.3. P1 is visible between 23:00-04:00, where respiration starts to dominate the signal and therefore the O$_2$ concentration decreases and the CO$_2$ concentration increases, in a decreasing boundary layer height dominated by thermal stratification. P2 becomes visible around 04:00 and stops around 09:00, where entrainment, the growing boundary layer and the onset of photosynthesis causes a steep increase in the O$_2$ concentration and a steep decrease in the CO$_2$ concentration. P3 can be divided into P3a and P3b and is visible between 09:00-20:00. Between 09:00-13:00 (P3a), the photosynthesis flux starts to dominate and both the O$_2$ and CO$_2$ concentration increase and decrease less rapidly. Between 13:00-20:00 (P3b) the O$_2$ concentration starts to decrease, while the assimilation flux still dominates, which is a remaining artefact that could not be corrected for with the pressure correction that we applied due to the instability of the MKS pressure regulator. The boundary of 20:00 between P3b and P1 was difficult to determine because we miss some measurements due to the calibration period and the remaining measurements around this time have a deviation caused by the pressure regulator. Measurements at both levels show this similar pattern, which is more pronounced closer to the vegetation.

The difference between the two heights results in a vertical gradient (Figure 4b). Similar to the diurnal cycle of the concentrations, the diurnal cycles of the gradients of O$_2$ and CO$_2$ also show anti-correlated behaviour. At 08:00, the CO$_2$ gradient changes from negative to positive and the O$_2$ gradient changes from positive to mostly negative, respectively representing CO$_2$ being transported downwards and O$_2$ upwards. The magnitude of the gradient depends on the degree of vertical mixing. The
sign of the gradients changes during the day, because the lowest level (23 m) is more directly influenced by forest carbon exchange compared to the highest level (125 m). Around the time of sunset, the CO$_2$ gradient changes from positive to negative and the O$_2$ gradient changes from negative to positive, because the lowest measurement level (23 m) is now influenced more by respiration processes of the forest and soils compared to the highest measurement level (125 m).

Figure 5. The O$_2$ concentration plotted against the CO$_2$ concentration for the representative day, for the 23 m level in coloured points per period representing different dominant process and the 125 m level in grey points. The dominant processes are: respiration (00:00-04:00), entrainment (04:00-09:00), assimilation (09:00-13:00), a remaining artefact after the pressure correction due to the instability of the MKS pressure regulator becomes visible (13:00-20:00). The regression lines indicate the exchange ratio of the atmosphere (ER$_\text{atmos}$) during the time with a specific dominant process.

By using equation 4, we calculated four distinctly ER$_\text{atmos}$ signals for different periods throughout the day at 23 m, and to a smaller degree at 125 m (Figure 5 and Table 3). The same periods as shown in Figure 4 are visible in Figure 5. This results in an ER$_\text{atmos}$ during the night (P1) of 1.22 ± 0.02 and two different possibilities for the ER$_\text{atmos}$ signal during daytime. By combining both P2 and P3a we get a signal of 2.28 ± 0.01 and by focusing only on P3a, which excludes the entrainment and the boundary layer dynamics, we get a signal of 1.10 ± 0.12. Last, by combining all the periods (P1, P2, P3) we get a signal for the complete day of 2.05 ± 0.03. The uncertainties given here only represent the uncertainty of the slopes from the regression lines in Figure 5. The high values for the ER$_\text{atmos}$ signal of the entire day and the daytime signal that includes entrainment and the boundary layer dynamics are not very realistic to represent an ER for the forest, and shows that we should be careful when using ER$_\text{atmos}$. This will be elaborated on in Section 4.2.

3.3 Flux calculations for CO$_2$ and O$_2$

We explored four alternative methods to derive the O$_2$ flux from the vertical gradient of the two measurement levels, as described in Section 2.3. Figure 6 shows both the theoretical and the observation-based approach that were used to calculate the
Figure 6. The CO$_2$ flux (a) calculated with different methods for the representative day, as described in Section 2.3, compared to the CO$_2$ flux of the ICOS EC measurements. (b) the comparison between the O$_2$ and CO$_2$ flux calculated using the method that gave the best results for the CO$_2$ flux calculations (using the exchange coefficient K with CO$_2$), for the representative day. The shaded colours indicate the regions that were selected for: the night signal (21:00-04:00), the day signal (09:00-17:00) and the remaining regions (04:00-09:00 and 17:00-21:00).

The CO$_2$ flux and the comparison with the ICOS EC CO$_2$ flux measurements at 27 m on the tower. By comparing these approaches to the EC measurements, we determined which method is most suitable to calculate the O$_2$ flux. The CO$_2$ flux measured by the EC system stays positive until around 05:00, when the respiration fluxes are the most dominant and the nocturnal boundary layer is shallower. After 05:00, the CO$_2$ flux of the EC system becomes negative, and the forest begins to take up CO$_2$ instead of emitting it. The assimilation fluxes increase and exceed the respiration fluxes, the boundary layer starts to grow and air with lower CO$_2$ concentrations is entrained from the free troposphere. After 20:00, the CO$_2$ flux of the EC system becomes positive again because the assimilation fluxes decrease, and the respiration signal begins to dominate again while the boundary layer height decreases. We expect to find this diurnal pattern and the sign change in our calculations of the CO$_2$ flux from the vertical gradient method as well.

First, we discuss the theoretical methods, that are indicated in Figure 6 with 'K with MOST' and 'Integrated' approach (see Section 2.3). The MOST and the Integrated method both overestimate the CO$_2$ flux during the night, between 0:00 and 05:00. The resulting CO$_2$ flux furthermore decreases and becomes negative too late in the day compared to the EC measurements. Both the CO$_2$ flux of the MOST and Integrated method evolve from a positive flux to a negative flux around 8:00. This is three hours later than the CO$_2$ flux from the EC measurements. During the day, between 08:00 and 15:00, the K with MOST method underestimates the CO$_2$ uptake and the Integrated method overestimates it. Table 2 shows that both MOST and the Integrated method have the highest mean difference and Root Mean Square Error (RMSE) compared to the observation-based
approaches. We discuss this further in section 4.3. As result of this analysis, we decided to not use the theoretical approach to calculate the O\textsubscript{2} flux.

Table 2. The mean difference and the Root Mean Square Error (RMSE) of the comparison between the CO\textsubscript{2} flux of the EC CO\textsubscript{2} flux measurements at 27 m in the tower and the CO\textsubscript{2} flux calculated with different methods for the exchange coefficient K, based on the ICOS data, and using the vertical gradient of CO\textsubscript{2} at 23 m and 125 m of our campaign data.

<table>
<thead>
<tr>
<th>Approach for K</th>
<th>Mean difference [ppm m s\textsuperscript{-1}]</th>
<th>RMSE [ppm m s\textsuperscript{-1}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Integrated</td>
<td>0.123</td>
<td>0.184</td>
</tr>
<tr>
<td>K with MOST</td>
<td>0.117</td>
<td>0.138</td>
</tr>
<tr>
<td>K with (\theta)</td>
<td>0.087</td>
<td>0.114</td>
</tr>
<tr>
<td>K with CO\textsubscript{2}</td>
<td>0.066</td>
<td>0.092</td>
</tr>
</tbody>
</table>

Secondly, we analyze the observation-based approaches, that are indicated in Figure 6 with 'K with \(\theta\)' (where K is established using potential temperature) and 'K with CO\textsubscript{2}' (where K is established using CO\textsubscript{2}). The observation-based approaches showed a better comparison with the EC observations in determining the CO\textsubscript{2} flux compared to the theoretical approach. Both the \(\theta\) and the CO\textsubscript{2} method represent satisfactorily the nocturnal CO\textsubscript{2} flux between 0:00 and 5:00. After 5:00, the fluxes calculated by both methods start to decrease and change sign around the correct time (5:00) from a positive to a negative flux. During the day between 8:00 and 15:00, both the \(\theta\) and the CO\textsubscript{2} methods underestimate the CO\textsubscript{2} flux, but not as much as the theoretical methods. Table 2 also shows that both the \(\theta\) and the CO\textsubscript{2} methods have the lowest Mean difference and RMSE. Based on the smaller mean difference and RMSE, and the direct link of CO\textsubscript{2} with O\textsubscript{2}, we decided to proceed with the method where K is calculated with the ICOS data of CO\textsubscript{2} to calculate the O\textsubscript{2} flux, instead of the ICOS \(\theta\) data. This K was then multiplied with our measured O\textsubscript{2} vertical gradient between 23 m and 125 m to finally calculate the O\textsubscript{2} flux. Section 4.3 presents a more elaborate discussion on the different methods to determine the most suitable K.

The resulting O\textsubscript{2} flux calculated with the exchange coefficient K based on the ICOS CO\textsubscript{2} data is shown in Figure 6b. The uncertainties are based on the error propagation of the standard error of the 30-minute averaged CO\textsubscript{2} and O\textsubscript{2} measurements. The daytime flux values have a high variability, but the inferred fluxes appear physically realistic and promising for one of the first attempts to calculate O\textsubscript{2} fluxes. During the night, between 0:00 and 5:00, the O\textsubscript{2} flux data has a relatively stable negative value. The O\textsubscript{2} flux is negative during the night, because the forest consumes O\textsubscript{2} for the respiration processes while CO\textsubscript{2} is released and this leads to a positive CO\textsubscript{2} flux during the night. After 5:00, the O\textsubscript{2} flux becomes positive and shows a higher variability. Overall, the O\textsubscript{2} flux is positive during the day which indicates that the forest produces O\textsubscript{2} because of the higher assimilation rate compared to the respiration. The high variability of the O\textsubscript{2} flux compared to the CO\textsubscript{2} flux, is caused by the less precise measurements of the O\textsubscript{2} vertical gradient compared to the CO\textsubscript{2} gradient (Figure 4). The measurement precision
needed to measure the difference between the two levels is very high, and therefore impacts the measurement of the gradient of O$_2$. The nighttime values of the O$_2$ flux are therefore more reliable compared to the daytime values, since the difference between the two heights is larger and therefore easier to measure due to the more stable atmospheric conditions at night.

**Figure 7.** The half-hourly exchange ratio of the forest (ER$_{\text{forest}}$) and the resulting averaged ER$_{\text{forest}}$ for the entire day (black line), the night between 21:00-4:00 (dark blue line) and the day between 9:00-17:00 (light blue line), of the representative day (a). The size of the dots indicates the size of the absolute O$_2$ flux and the shaded bands indicate the uncertainties of the different ER$_{\text{forest}}$ signals. Note that the ER$_{\text{forest}}$ lines do not match with the average of the dots in the specific time period, because the lines are based on the averaged fluxes. These different ER signals are presented in a vector diagram format with the carbon fluxes, Gross Primary Production (GPP), Total Ecosystem Respiration (TER) and Net Ecosystem Exchange (NEE), and the ER of the assimilation processes (ER$_a$) and the ER of the respiration processes (ER$_r$) (b).

By using equation 5, we find three different ER$_{\text{forest}}$ signals throughout the day (Figure 7 and Table 3). The selected time periods based on the criteria described in Section 2.3 are between 09:00-17:00 for the daytime and between 21:00-04:00 for the nighttime (Figure 6). This results in a nighttime ER$_{\text{forest}}$ signal of 1.04 ± 0.04, a daytime ER$_{\text{forest}}$ signal of 0.92 ± 0.17 and an ER$_{\text{forest}}$ signal for the entire 24 hours of 0.83 ± 0.24. Note that this 24h value is not the average of the day and night ER$_{\text{forest}}$ signals or from all the 30-minute ER$_{\text{forest}}$ signals, because we used the averaged fluxes. This means that the ER$_{\text{forest}}$ signals based on high flux values, indicated in Figure 7 with larger symbols, contribute more to the averaged ER$_{\text{forest}}$ signals compared to the lower flux values. The individual ER$_{\text{forest}}$ values of every 30-minutes show a clear difference between the day- and nighttime. The ER$_{\text{forest}}$ values during the nighttime is relatively stable. The ER$_{\text{forest}}$ values during the daytime show more variability, caused by the high variability of the O$_2$ flux during daytime (Figure 6). The uncertainty of the ER$_{\text{forest}}$ signals is determined by the propagation of the standard error of the 30-minute average O$_2$ and CO$_2$ measurements.
### 3.4 GPP and TER calculations

#### Table 3. The exchange ratio for the atmosphere (ER_{atmos}; Section 3.2), the forest (ER_{forest}; Section 3.3), and assimilation and respiration (ER_{a} and ER_{r}; section 3.3) for different time periods of the representative day. The time periods used to calculate the signals are: (09:00-13:00) for day and (23:00-04:00) for night of ER_{atmos}, and (09:00-17:00) for day and (21:00-04:00) for night of ER_{forest}, ER_{r} and ER_{a}. Note that the uncertainty for ER_{atmos} does not represent the same uncertainty as for ER_{forest}, since the first is the error of the fit, and the second is based on error propagation of the half hourly measurements.

<table>
<thead>
<tr>
<th></th>
<th>ER_{forest}</th>
<th>ER_{r}</th>
<th>ER_{a}</th>
<th>ER_{atmos}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Night</td>
<td>1.03 ± 0.05</td>
<td>1.03 ± 0.05</td>
<td>1.22 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>Day</td>
<td>0.92 ± 0.17</td>
<td>1.03 ± 0.05</td>
<td>0.96 ± 0.12</td>
<td>1.10 ± 0.12</td>
</tr>
<tr>
<td>24 hours</td>
<td>0.84 ± 0.26</td>
<td>1.03 ± 0.05</td>
<td>0.96 ± 0.11</td>
<td>2.05 ± 0.03</td>
</tr>
</tbody>
</table>

We found the ER signals for assimilation (ER_{a}) and respiration (ER_{r}) by using equation 8 (Figure 7b and Table 3). The assumption that ER_{r} stays constant throughout the day seems reasonable, because the ER_{forest} values stay stable during the night. Therefore the ER_{r} signal becomes 1.03 ± 0.05. ER_{a} of the daytime is 0.96 ± 0.11, which indicates the ER_{a} signal of the boreal forest when the surface fluxes are the highest. The ER_{a} signal of the entire diurnal cycle is 0.95 ± 0.11, which also includes the assimilation processes during sunrise and sunset. Figure 7b shows all these ER signal and how they change throughout the day, together with their carbon fluxes. ER_{a}, ER_{r} and the resulting ER_{forest} signals are more realistic compared to the ER_{atmos} signals and these differences will be further elaborated on in Sections 4.4 and 4.5.

By using equation 7 and 8 and ER_{a} and ER_{r} signals determined from the representative day, we show that the O_{2} method can be used to separate NEE into GPP and TER on any day where good simultaneous CO_{2}, O_{2} and NEE measurements are available (Figure 8). The difference between the CO_{2} fluxes determined with the O_{2} method and the EC method of both the GPP and the TER flux are around 0.01 ppm m s^{-1}, which is less that 6% of the total gross flux. The difference is relatively small which means that the O_{2} method compares well with the EC methods to separate NEE into GPP and TER. The different uncertainty bars in Figure 8) show how sensitive the O_{2} method is to the accuracy of ER_{forest}. By increasing/decreasing ER_{forest} with 0.2, the GPP estimation by the O_{2} method changes by 0.1 ppm m s^{-1} and by increasing/decreasing ER_{forest} with only 0.01, the GPP estimation changes with 0.005 ppm m s^{-1}. The effect of changing ER_{forest} on TER has the same effect on GPP. This shows that the O_{2} method is quite sensitive to ER_{forest} and should be measured accurately, with a suggested precision of around 0.05. The application of the O_{2} method will be further discussed in Section 4.5.

### 4 Discussion

We aimed to advance understanding of the O_{2} : CO_{2} exchange ratio and its diurnal variability over a boreal forest by continuously measuring both O_{2} and CO_{2} concentrations at two heights above the canopy. These measurements gave us the possibility
Figure 8. The CO$_2$ fluxes of a second representative day (13 through 15 July) for Net Ecosystem Exchange (NEE), Gross Primary Production (GPP) and Total Ecosystem Exchange (TER) based on two different methods: the EC method and the O$_2$ method. The different uncertainty bars indicate an increase/decrease of 0.2, 0.1 or 0.01 for the Exchange Ratio of the forest (ER$_{forest}$), used in the O$_2$ method.

to compare the ER$_{atmos}$ and ER$_{forest}$ signal of an aggregate representative day and compare the boreal forest signals to previous studies in different ecosystems. Our ER$_{atmos}$ signal changed between the day (2.28) and the night (1.22) and had an overall diurnal signal of 2.05. For the ER$_{forest}$ signal, we needed to determine the O$_2$ and CO$_2$ surface fluxes based on the two heights. Different flux calculating methods were compared. The O$_2$ flux was calculated with the method that resulted in the best comparison to Eddy Covariance fluxes for CO$_2$, where we found that the exchange coefficient K based on the CO$_2$ data was most suited. The resulting ER$_{forest}$ signal showed again differences between the day (0.92) and night (1.04) and the overall diurnal ER$_{forest}$ was 0.83. For these differences and variability in the ER signals, different aspects of the uncertainty have to be taken into account, on which we elaborate in the next sections.

4.1 Measurement uncertainty

Analyzing the mean difference and standard deviation of the target cylinder values between 16-06-2019 and 17-07-2019 (Table 1), we see that the values are relatively high. Previous studies that used a fuel cell analyser for continuous atmospheric O$_2$ measurements (Battle et al., 2019; Ishidoya et al., 2013; van der Laan-Luijkx et al., 2010; Popa et al., 2010; Pickers et al., 2022), achieved measurement precision of around 5 per meg. WMO recommends a maximum compatibility of 10 per meg for the world-wide O$_2$ monitoring network (Crotwell et al., 2020), which shows that our measurement precision of 19 per meg is relatively poor. This poor measurement precision could have been caused by several reasons; the O$_2$ values of the reference cylinders that were used were relatively far apart, making it more difficult to measure the values around the target cylinder value. The cabin in which the instrument and cylinders were located was not well insulated, which created unstable temperature conditions which might have affected the stability of the cylinders (Keeling et al., 2007). Our calibrations took place
during the night and therefore large temperature changes during the day might have affected daytime stability of the reference cylinder. Furthermore, tiny leakages in the setup might have influenced the measurements. Due to the relatively short period for these campaigns and remote location, it is not possible to trace back the cause of this large uncertainty. This high uncertainty resulted in a larger uncertainty of the vertical gradient of the two heights of the O\textsubscript{2} measurements. However, in this study we are mostly interested in the diurnal variability of the ER signal and differences between ER\textsubscript{atmos} and ER\textsubscript{forest} and therefore the long-term stability of the measurements are less relevant here compared to other O\textsubscript{2} studies.

To reduce the effect of the high measurement uncertainty and derive a more statistically robust signal of the vertical gradient, we created an aggregate representative day based on days with similar weather and atmospheric conditions. This representative aggregate day removes the focus from one specific day, and therefore decreases the effect of the low measurement precision. We also move away from the reality of one specific day, but rather focus on an average situation and variability of the ER signal above a boreal forest based on O\textsubscript{2} and CO\textsubscript{2} measurements at 2 levels. Given that only very few previous studies focused on deriving forest ER signals globally, our analysis helps to gain further understanding of the diurnal variability and the difference between ER\textsubscript{atmos} and ER\textsubscript{forest}, which will be discussed in the following sections.

### 4.2 ER\textsubscript{atmos} signal in comparison to previous studies

Despite the uncertainty in our measurements, there are clear differences between the slopes of O\textsubscript{2} and CO\textsubscript{2} throughout the diurnal cycle (Figure 5). Three different ER\textsubscript{atmos} signals are visible, with two signals for the day (2.28 ± 0.01 and 1.10 ± 0.12) and one for the night night (1.22 ± 0.02) slope (Table 3). Note that the uncertainty of these values is based on the slope of the fitted line in Figure 5 and does not represent the uncertainty in the stability of our measurements as indicated in Table 1. The difference between day and night values of ER\textsubscript{atmos} was expected because different processes (i.e. respiration, assimilation and entrainment) with different ER signals play a role at different times during the diurnal cycle. To exclude as much as possible the effect of entrainment and the boundary layer dynamics during the morning transition, we will from now on refer to the 1.10 value as the day ER\textsubscript{atmos} signal, which is the signal derived form period P3a. ER\textsubscript{atmos} for the complete day results in 2.05 ± 0.03.

When comparing our ER\textsubscript{atmos} signals to those from Battle et al. (2019), Ishidoya et al. (2013) and Seibt et al. (2004) (Table 4), we note several similarities but also some differences regarding the specific values of the ER\textsubscript{atmos} signals. Our daytime signal of 1.10 is similar to 1.02, 0.87 and 1.14 from the previous studies respectively, as is our nighttime signal of 1.22 compared to 1.12 (Battle et al., 2019), 1.03 (Ishidoya et al., 2013) and 1.16 (Seibt et al., 2004). However, our 24-hours ER\textsubscript{atmos} signal of 2.05 shows an unrealistically high number which clearly does not indicate the ER of the forest only. A typical ER\textsubscript{atmos} signal for a 24 hour period lies around 1, as is shown in table 4 and by Stephens et al. (2007) and Manning (2001). Our 24-hours ER\textsubscript{atmos} value includes the measurement points of the period that is influence by entrainment and boundary layer dynamics (P2), for which period we found an ER signal of 2.28. The large influence of entrainment and boundary layer dynamics made it difficult to be very precise about the specific time periods to choose for P3. Moving the selected time boundaries of P3a from 9:00 to 9:30 or from 13:00 to 12:30 leads to ER\textsubscript{atmos} values of 0.88 or 1.75 respectively. The large changes in the daytime ER\textsubscript{atmos} due to
Table 4. The different Exchange Ratio (ER) signals of previous studies, with the ER of the atmosphere (ER$_{\text{atmos}}$), the ER of the forest (ER$_{\text{forest}}$), the ER of the respiration processes (ER$_r$) and the ER of the assimilation processes (ER$_a$). The different studies are: Bat, 2019: (Battle et al., 2019), Ish, 2015: (Ishidoya et al., 2015), Ish, 2013: (Ishidoya et al., 2013), Sei, 2004: (Seibt et al., 2004).

<table>
<thead>
<tr>
<th>Study</th>
<th>ER$_{\text{atmos}}$</th>
<th>ER$_{\text{res}}$</th>
<th>ER$_{\text{forest}}$</th>
<th>ER$_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Day</td>
<td>Night</td>
<td>24 hours</td>
<td>Day</td>
</tr>
<tr>
<td>This study</td>
<td>1.10 ± 0.12</td>
<td>1.22 ± 0.02</td>
<td>2.05 ± 0.03</td>
<td>0.92 ± 0.17</td>
</tr>
<tr>
<td>Bat, 2019</td>
<td>1.02 ± 0.01</td>
<td>1.12 ± 0.01</td>
<td></td>
<td>&lt; 1.0</td>
</tr>
<tr>
<td>Ish, 2015</td>
<td>0.87 ± 0.02</td>
<td>1.03 ± 0.02</td>
<td>0.94 ± 0.01</td>
<td>≈ 0.98</td>
</tr>
<tr>
<td>Ish, 2013</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sei, 2004$^c$</td>
<td>1.01 ± 0.06</td>
<td></td>
<td></td>
<td>1.24 ± 0.06</td>
</tr>
<tr>
<td>Sei, 2004$^d$</td>
<td>1.14 ± 0.19</td>
<td>1.16 ± 0.02</td>
<td>1.03 ± 0.05</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ An ER signal is classified as ER$_{\text{atmos}}$ when the ER signal is based on one concentration measurement of O$_2$ and CO$_2$.
$^b$ An ER signal is classified as ER$_{\text{forest}}$ when the ER signal is based on surface fluxes from either an 1-box model or vertical gradient flux calculations.
$^c$ The ER signals of the location Griffin Forest of Seibt et al. (2004) are used here.
$^d$ The ER signals of the location Harvard Forest of Seibt et al. (2004) are used here.

small changes in the time boundaries, shows the high uncertainty of the daytime ER$_{\text{atmos}}$. Therefore, our measurements provide a confirmation of earlier indications (Seibt et al., 2004) that ER$_{\text{atmos}}$ is an unreliable estimate for the ER of a forest, and we recommend to use ER$_{\text{forest}}$. Instead, ER$_{\text{atmos}}$ also represents how O$_2$ and CO$_2$ are influenced by the boundary layer dynamics and entrainment (Figure 1).

For the 24-hour period, our ER$_{\text{atmos}}$ values are much higher compared to previous studies. A possible explanation could be that our study is the first to measure O$_2$ and CO$_2$ above a boreal forest. Boreal forests have different ecosystems, a colder climate and have longer days in the summer compared to the locations of the previous studies (Bonan, 2008). The measurements of Battle et al. (2019) and Ishidoya et al. (2013) were done over a deciduous forest and measurements of Seibt et al. (2004) over a needle leaf forest and mixed deciduous forest, all conducted in temperate regions. A change in the length of the day or temperature could already influence the diurnal cycles of both the O$_2$ and CO$_2$ concentrations and as a result ER$_{\text{atmos}}$ (Figure 1). A high ER$_{\text{atmos}}$ signal means the O$_2$ concentration increases more rapidly over time compared to the decrease of the CO$_2$ concentration. Further insights on the contributions of each process to ER$_{\text{atmos}}$ cannot be estimated from the measurements alone, and would require using an atmospheric model.

4.3 Uncertainties in the CO$_2$ and O$_2$ flux calculations

By comparing the theoretical and observation-based methods, we determined that the most suitable method to calculate both the CO$_2$ and O$_2$ flux was to use the observation-based method with CO$_2$ data (Section 3.3). Figure 6 and Table 2 show that the
theoretical methods (MOST and Integrated) resulted in a too late change of the CO$_2$ flux compared to the EC-measurement. This delay has been described before and is caused by the time it takes before the turbulence can mix the CO$_2$ gradient driven by stable nocturnal stratification conditions and establish the corresponding gradient (Casso-Torralba et al., 2008). When the heights of the gradient are closer together, the delay is less pronounced. However, the measurement heights used during our campaign are relatively far apart (125 m and 23 m) and the EC flux is measured at 27 m. The 125 m measurement is even located outside the surface layer during the morning transition. This made the flux-gradient method less applicable, which assumes that the surface flux stays constant in the surface layer (Dyer, 1974).

Since during our campaign we only measured at two heights, we missed information on the logarithmic profile originating from the canopy top, which resulted in an underestimation of the flux using the K with MOST. This was solved by integrating the MOST equation (‘Integrated method’). With the integrated method, the gradient is assumed to be logarithmic and the total flux increases compared to the MOST calculation (Paulson, 1970). However, with the large difference between the two measurement heights, the integrated approach still overestimated the CO$_2$ flux compared to the EC measurements during both the day and the night. Also, the delay in the timing of the sign change of the gradient cannot be solved with this Integrated method. We furthermore applied the effect of the Roughness Surface Layer (RSL) in the flux calculations of the theoretical methods, by adding an extra factor that accounts for this layer (not shown in the results) (de Ridder, 2010). The contribution of the RSL did not improve our results, because it also includes the delay of the gradient which was causing the largest deviation in the theoretical methods (Table 2).

By applying both observation-based methods, using either $\theta$ or CO$_2$ to infer the exchange coefficient K, we did not find this delay in the timing of the gradient and the observation-based methods therefore resulted in derived fluxes close to the EC measurements. Here it has to be noted that the ICOS EC measurements of CO$_2$, that we used as a benchmark for the most suitable flux calculation approach, was also used in calculating K with CO$_2$, which makes the comparison of these approaches to the CO$_2$ flux not fully independent. Most previous studies that determined fluxes based on the gradient-approach used $\theta$ to calculate K (Stull, 1988; Mayer et al., 2011; Wolf et al., 2008; Bolinius et al., 2016; Brown et al., 2020), because $\theta$ is the driver of convective turbulence. However, because O$_2$ is directly linked to CO$_2$ and our statistics (Table 2) indicated that the CO$_2$ method resulted in a better comparison to the EC fluxes, we decide to use the ICOS CO$_2$ data at 3 levels and the CO$_2$ EC measurements to calculate K. This K together with the measurements of two heights by our instrument during our campaign were used to calculate both the CO$_2$ and the O$_2$ fluxes used in our study. We also tested the impact of using only 2 vertical levels of the ICOS CO$_2$ concentrations to calculate K (not shown), which was also the case in the only previous study that derived O$_2$ fluxes. Ishidoya et al. (2015) derived O$_2$ fluxes for a temperate forest in Japan using 2 vertical levels at 18 and 27 m height for both O$_2$ and CO$_2$ concentrations. Our comparison of deriving K based on 2 vertical levels (23 m and 125 m), resulted in an underestimation of the gradient and thus an overestimation of K, and as a consequence the calculated CO$_2$ flux was overestimated. Therefore the 3 levels of ICOS CO$_2$ concentrations measurements proved to be vital in our flux calculations here. We still missed the logarithmic profile at the surface with only the two vertical campaign measurements and as a result...
slightly underestimated the final CO\textsubscript{2} and O\textsubscript{2} flux. Therefore, we recommend to always measure at at least three heights of CO\textsubscript{2} and O\textsubscript{2} inside the surface layer, when they are meant to be used for flux calculations.

Our final O\textsubscript{2} flux (Figure 6) shows a clear diurnal cycle, with the expected behaviour of negative values in the night (O\textsubscript{2} consumption for respiration) and a positive flux during the day (O\textsubscript{2} release during assimilation). The nighttime fluxes are more stable and give a clear signal due to the larger vertical gradient. K is more difficult to determine during the night because the EC measurements are less representative due to the low level of turbulence. However, the largest contributor to the uncertainty are our own O\textsubscript{2} measurements and the larger gradient allows to better establish the O\textsubscript{2} flux. The larger variability of the daytime O\textsubscript{2} fluxes is caused by the smaller gradient of the O\textsubscript{2} concentration measurements during the day (Figure 3), when the atmosphere is more well-mixed and the difference between the two heights becomes smaller. The relatively large measurement uncertainty made it difficult to measure these small difference between the two heights and increased the noise in the fluxes. The measurement noise resulted in O\textsubscript{2} gradient variations that were not tied to the CO\textsubscript{2} gradient variations and this degraded the correlation between the two fluxes. Despite this larger variability, we still find a clear diurnal behaviour, which allowed us to calculate ER\textsubscript{forest}.

### 4.4 ER\textsubscript{forest} signal compared to previous studies

Our resulting ER\textsubscript{forest} signal changes throughout the diurnal cycle, with specific daytime (0.92 ± 0.17), nighttime (1.03 ± 0.05) and overall (0.84 ± 0.26) values (Figure 7 and Table 3). The individual nighttime values show a smaller uncertainty due to the already explained effect of the larger gradient during the stable atmospheric conditions of the night. In contrast, the individual daytime values show a larger uncertainty due to the smaller gradient during the unstable atmospheric conditions of the day. We therefore used averaged values for the daytime and nighttime signals to derive the ER\textsubscript{forest} values. The daytime signal excludes the entrainment and the boundary layer dynamics during the morning transition, however these effects are still included in the overall ER\textsubscript{forest} signal.

When comparing our ER\textsubscript{forest} signals to previous studies of Seibt et al. (2004), Ishidoya et al. (2013, 2015) (Table 4) we notice that the difference between the daytime and the nighttime values that we found and the specific values of the different ER\textsubscript{forest}, have some similarities and some differences. Our results, together with Ishidoya et al. (2013, 2015) (night: 1.11 and day: 0.98) show that the ER\textsubscript{forest} signal of the nighttime is higher than the the daytime signal, whereas Seibt et al. (2004) (day: 1.24 and night: 1.01) showed the opposite behaviour. Our results is most similar to the signals of both Ishidoya et al. (2013) and Ishidoya et al. (2015), especially if we take our uncertainty range into account. When we take into account our uncertainty, the complete day signal of 0.84 ± 0.26 comes close to the globally used average ER of the biosphere of 1.1 (Severinghaus, 1995). However, the specific value suggest that the overall ER\textsubscript{forest} signal of this boreal forest lies somewhat lower than 1.1, closer to 1.0. Why the ER\textsubscript{forest} signals differ between studies could be explained with the different ER\textsubscript{a} and ER\textsubscript{r} signals, which
The ER\textsubscript{forest} and ER\textsubscript{atmos} signals are not identical, and they do therefore not represent the same information (Table 3). The ER\textsubscript{atmos} signals are higher compared to the ER\textsubscript{forest} signals, especially the 24-hour signals show a large difference. Despite the higher numbers, the day and night signals of ER\textsubscript{atmos} and ER\textsubscript{forest} show both the same pattern, where the daytime signal is lower compared to the nighttime signal. When comparing these differences to previous studies we find that not all studies find the same results. The difference between ER\textsubscript{forest} and ER\textsubscript{atmos} was not found by Ishidoya et al. (2013). In contrast, Seibt et al. (2004) found a difference between ER\textsubscript{forest} and ER\textsubscript{atmos} (Table 4). These contradicting results suggest that we should further investigate to what extent ER\textsubscript{atmos} is influenced by entrainment and boundary layer dynamics and under which conditions they can come close to ER\textsubscript{forest}. We already show that excluding the morning transition (P2) helps to improve the ER\textsubscript{atmos} signal. However, as already stated, it is difficult from the measurements alone to determine if the ER\textsubscript{atmos} signal is influenced only by the surface during this period. An Atmospheric model would therefore be needed to find how ER\textsubscript{atmos} can be derived from a single measurement height, and allow comparison to previous studies that measured at one height to determine the ER of the forest (Battle et al., 2019; van der Laan et al., 2014; Stephens et al., 2007). We are currently applying a specific mixed-layer atmospheric model to further investigate this.

### 4.5 The ER\textsubscript{a} and ER\textsubscript{r} signals

To further understand the relationship between O\textsubscript{2} and CO\textsubscript{2}, we cannot use the ER\textsubscript{forest} signal alone. To look in more detail into the processes driving the variations, we look at the exchange ratio of respiration (ER\textsubscript{r}) and assimilation (ER\textsubscript{a}). Due to lack of in-situ measurements of ER\textsubscript{a} and ER\textsubscript{r}, we calculated these numbers (Table 3 and Figure 7). ER\textsubscript{r} was taken as the ER\textsubscript{forest} night-time signal (1.03 ± 0.05), by assuming that only respiration influences the ER\textsubscript{forest} signal during the night and that the ER\textsubscript{r} signal stays constant throughout the entire day. This means that both the heterotrophic and autotrophic respiration are included in ER\textsubscript{r} and the same components are respired in the same ratios throughout the day to keep ER\textsubscript{r} a constant value. To our knowledge, potential changes of ER\textsubscript{r} throughout the day have not been studied previously, and it is therefore difficult to say how valid this assumption is. The variability of ER\textsubscript{r} between locations highly depends on the soil properties (Angert et al., 2015), which makes it difficult to compare with the few studies available (Seibt et al., 2004; Ishidoya et al., 2013) that measured ER\textsubscript{r} with chamber measurements on a brown soil. The soil in our study area is a podzol, which is characterised by a high acidity with little organic matter (Buurman and Jongmans, 2005). The OR of podzols is around 1.08 (Worrall et al., 2013) and the ER of acid soils is expected to be around this OR, because carbon cannot easily dissolve into the groundwater (Angert et al., 2015), and we therefore conclude that our ER\textsubscript{r} value of 1.04 is realistic.

We looked at two options to calculate ER\textsubscript{a}; ER\textsubscript{a} based only on the daytime measurements (between 9:00 and 17:00: 0.96 ± 0.12) and ER\textsubscript{a} based on all the measurement throughout the 24-hour period: 0.96 ± 0.11. Both numbers are close to 1, which is often assumed as a standard value for ER\textsubscript{a} (Ishidoya et al., 2015; Severinghaus, 1995). Next to that, a value of ER\textsubscript{a} close to
1 means that ammonium is used as a source for nitrogen, instead of nitrate (Bloom et al., 1989, 2012). Ammonium is indeed a larger source for nitrogen compared to nitrate in Hyytiälä (Korhonen et al., 2013). The OR of needle leaves, and plant material in general, appears to be always close to 1.0 (Jürgensen et al., 2021), which again confirms our ER_a signals. The difference between the two ER_a signals is minimal and difficult to determine with the corresponding uncertainties. The transition periods between the night and the daytime were difficult to measure, because the gradient then becomes close to zero, which means there could be a possibility that next to ER_forest, ER_a also has a diurnal cycle. To get a more detailed overview of ER_a, more precise measurements need to be done with an uncertainty that is lower than 0.1 for the ER signals. However, the similar values of ER_a for the daytime and all the measurements means that ER_a does not have a major shift because of entrainment during the morning transition and it would suggest that the morning transition is less of an issue for ER_forest than for ER_atmos.

By applying the O2 method to a new aggregate day, we showed that the O2 method gives results similar to the EC method to derive the GPP and TER fluxes (Figure 8). The EC method to separate GPP and TER fluxes, also contains uncertainties in the approach, because of the assumption to rely on a function of temperature, and should therefore not necessarily be assumed to be the ‘truth’ (Reichstein et al., 2005). Despite the uncertainty of both the O2 method and the EC method, both methods give similar results for the CO2 flux of GPP and TER. For the O2 method, the magnitude of the GPP and the TER fluxes highly depends on the ER_forest signal used and that this signal should be measured with an accuracy of around 0.05 to fall into the uncertainty range of the EC method. With such a high accuracy, the O2 method has the potential to provide an alternative method for the separation of GPP and TER without relying on the regularly used temperature-based function (EC method). Ishidoya et al. (2015) showed similar results, where the O2 method also produced GPP and TER comparable to the EC method and the magnitude of the GPP and TER fluxes highly depended on the ER_a and ER_r signals. We recommend to measure the ER_r and ER_a signals directly with chamber measurements (Seibt et al., 2004; Ishidoya et al., 2013), together with adding at least one measurement height for the O2 and CO2 concentrations below the canopy. This can help to get a better understanding of how the different signals travel from the surface towards the atmosphere and how to apply the storage correction for both the O2 and the CO2 fluxes (Aubinet et al., 2012). Despite the high dependency on the accuracy of the ER, this study showed again, as did (Ishidoya et al., 2015), that the O2 method can be used to get a better understanding of the carbon cycle. To further develop this method we need to expand the O2 measurements for longer time series and more locations, and analyze how ER_forest varies over longer time scales, which can improve the global average value of ER (α_B) of 1.1 as used in global carbon budget studies such as Manning and Keeling (2006).

5 Conclusions

By continuously measuring atmospheric O2 and CO2 concentrations at two heights above a boreal forest in Hyytiälä, Finland, we gained new insights into the diurnal variability of O2 and CO2 above a boreal forest, quantified by interpreting their Exchange Ratio (ER). We showed that the signal based on one measurement height of the O2 and CO2 concentrations (ER_atmos) is
not representative for the exchange between the forest and the atmosphere only, but instead includes other processes such as entrainment as well. To derive the ER of the forest (ER\textsubscript{forest}) specifically, we first determined the surface fluxes above the canopy of \textgreek{o}_{2} and \textgreek{c}_0\textsubscript{2} using the vertical gradient between the two measurement heights. We found that the most suitable method to calculate both the \textgreek{o}_{2} and \textgreek{c}_0\textsubscript{2} surface fluxes was to calculate the exchange coefficient based on \textgreek{c}_0\textsubscript{2} gradient calculated using three heights and on the eddy-covariance \textgreek{c}_0\textsubscript{2} flux. The ER\textsubscript{forest} signals that resulted from the ratio of the mean \textgreek{o}_{2} and \textgreek{c}_0\textsubscript{2} fluxes varied between the daytime (0.92 ± 0.17 mol/mol) and nighttime (1.03 ± 0.05 mol/mol). The different ER\textsubscript{forest} signals were composed of the ER of respiration (ER\textsubscript{r}; 1.03 ± 0.05 mol/mol) and the ER of assimilation (ER\textsubscript{a}; 0.96 ± 0.12 mol/mol).

With these findings we show improved methods to derive \textgreek{o}_{2} forest fluxes and to derive the variability in the different ER signals over a representative diurnal cycle. The ER\textsubscript{forest} signal shows a clear diurnal cycle for this boreal forest and the overall ratio is lower than 1.1 that is used in global carbon budget calculations. Finally, we show that these ER signals can be used to separate Net Ecosystem Exchange (NEE) into Gross Primary Production (GPP) and Total Ecosystem Respiration (TER).

With only a few data sets of continuous measurements of both \textgreek{o}_{2} and \textgreek{c}_0\textsubscript{2} concentrations over forests, our data set is of high importance, specifically the availability of measurements at two heights that allow calculation of \textgreek{o}_{2} and \textgreek{c}_0\textsubscript{2} fluxes. Our analyses can serve as a starting point for follow up research using coupled land surface-atmosphere models to determine the contributions and partitioning of different processes to ER\textsubscript{atmos} and ER\textsubscript{forest} signals. Further understanding of these differences will help to fully make use of the advantages atmospheric \textgreek{o}_{2} has in unraveling the different components in the carbon cycle.

Data availability. The data in this study are available from https://doi.org/10.18160/SJ3J-PD38.

Author contributions. ITL conducted the measurements and designed measurement the campaign. ITL, ERB, LNTN, PAP and ACM contributed to the design and development of the \textgreek{o}_{2} and \textgreek{c}_0\textsubscript{2} measurement setup. LNTN, BAMK, IM and TV contributed to the measurement campaigns. KAPF and ITL analyzed the measurements. KAPF, ITL, WP, JV, HAJM interpreted and discussed the methods and results. KAPF and ITL wrote the manuscript with input from all co-authors.

Competing interests. There are no competing interests.

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6 Appendix

6.1 Equations to calculate the Exchange Coefficient, K

6.1.1 Observation-based method

The gradient between three points is calculated with the following equation:

\[ \bar{\phi}(z) = a \cdot z^2 + b \cdot z + c \]  

(9)

\[ \left( \frac{\partial \bar{\phi}(z)}{\partial z} \right) = 2 \cdot a \cdot z + b \]  

(10)

Where \( z \) is the height above the displacement height (d) (d is taken as: 2/3 \cdot canopy height), \( \bar{\phi} \) is the average variable where the line is fitted through and a, b and c are the resulted fitted parameters. When only two vertical measurements are available, the gradient was determined using finite differences.

6.1.2 Theoretical approach

For the MOST method, the following equations were used (Physick and Garratt, 1995):

\[ K = \frac{\kappa \cdot z \cdot u_s}{\Phi_H \left( \frac{z}{L} \right) \phi_{rsl} \left( \frac{z}{L} \right)} \]  

(11)

Where \( \kappa = 0.4 \) and is the von Kármán constant, \( u_s \) is the friction velocity, \( \Phi_H \) indicates the stability function and \( \phi_{rsl} \) indicates the contribution of the roughness sublayer (RSL). The \( \Phi_H \) was calculated with (Dyer, 1974):

\[ \Phi_H \left( \frac{z}{L} \right) = \left( 1 - 16 \frac{z}{L} \right)^{-1/2} \quad \text{when } z/L < 0 \]  

(12)

\[ \Phi_H \left( \frac{z}{L} \right) = 1 + 5 \frac{z}{L} \quad \text{when } z/L > 0 \]  

(13)

Where \( L \) is the Obukov Length, which was based on the following equation (Dyer, 1974):

\[ L = \frac{-w'_{v}^3}{\kappa ( \theta'_v \theta'_v ) \left( w' \theta'_v \right) } \]  

(14)

Where \( \theta_v \) is the virtual potential temperature, \( w' \theta'_v \) is the virtual surface heat flux and \( g \) is the acceleration due to gravity. Because the flux was measured close to the canopy, the roughness surface layer (RSL) could become important. The RSL needs an additional length scale \( (\phi) \) and can be calculated with the following equation (de Ridder, 2010):

\[ \phi_{HRSL} \left( \frac{z}{z_s} \right) = 1 - e^{-\mu \frac{z}{z_s}} \]  

(15)
Here $z_*$ indicates the height of the RSL above the displacement height and we take that as $(2 \cdot \text{canopy height} - d)$ and $\mu$ is a constant of 0.95.

By integrating equation 6 with equation 11 for $K$, we get the following equation that was used for the Integrated method (Physick and Garratt, 1995):

$$
\phi(z_2) - \phi(z_1) = \left( \frac{w' \phi'}{\kappa \cdot u_*} \right) \left[ \ln \left( \frac{z_2}{z_1} \right) - \Psi_H \left( \frac{z_2}{L} \right) + \Psi_H \left( \frac{z_1}{L} \right) + \psi_{RSL} \left( \frac{z}{L}, \frac{z}{z_*} \right) \right]
$$

(16)

Where $\Psi_H$ are the integrated stability functions for heat and $\psi$ is the integrated function to account for the roughness sublayer (RSL) effects. $\Psi_H$ was calculated with (Paulson, 1970):

$$
\Psi_H \left( \frac{z}{L} \right) = \begin{cases} 
2 \ln \left( \frac{1 + x^2}{2} \right) & \text{when } z/L < 0 \\
-5 \frac{z}{L} & \text{when } z/L > 0 
\end{cases}
$$

(17)

(18)

The function of the integrated RSL length scale ($\psi_{RSL}$) was calculated with (de Ridder, 2010):

$$
\psi_{RSL} \left( \frac{z}{L}, \frac{z}{z_*} \right) \approx \Phi_H \left[ \left( 1 + \frac{\nu}{\mu z/z_*} \right) \frac{z}{L} \right] \frac{1}{\lambda} \ln \left( 1 + \frac{\lambda}{\mu z/z_*} \right) e^{-\mu z/z_*}
$$

(19)

Where $\nu$ and $\lambda$ are both parameters, taken as 0.5 and 1.5 respectively.
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