

An investigation into the sources of atmospheric CO₂ arriving at Weybourne Atmospheric Observatory using a multi-tracer approach

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Abstract

In order to set effective emission reduction legislation, it is crucial that the amount of CO₂ being emitted into the atmosphere is accurately known. Atmospheric measurements of CO₂ alone are inadequate to successfully separate the fluxes from the terrestrial biosphere and anthropogenic fossil fuel combustion, therefore tracers that share flux mechanisms with CO₂ are used as proxies. This study shows that the sources of CO₂ arriving at Weybourne Atmospheric Observatory (UK) can be separated using simultaneous observations of O₂, APO, δ¹³C-CO₂, CO and O₃. It was found that ffCO₂ is the dominant source of increased concentrations of CO₂, with no discernible contribution from the terrestrial biosphere. There were some discrepancies found between the fossil fuel sources indicated by the O₂:CO₂ oxidative ratios and the Keeling plot values, with the Keeling plot intercepts indicating a larger contribution from natural gas. The analysis of APO and CO observations also added confidence to the determination of these sources. This study is also a starting point for the use of O₃ as a tracer as the correlation between O₃ and O₂ was also found to be consistently strongly positive during periods of increased CO₂ concentration, thus presenting O₃ as a tracer for ffCO₂ during the winter. These results demonstrate importance of the use of a multi-tracer approach for partitioning CO₂ sources.

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Abbreviations

APO – Atmospheric Potential Oxygen

CO – Carbon monoxide

CO₂ – Carbon dioxide

ffCO₂ – Fossil fuel CO₂

GHG – Greenhouse gas

HYSPLIT - HYbrid Single Particle Lagrangian Integrated Trajectory Model

O₂ – Oxygen

O₃ – Ozone

OR – Oxidative Ratio

per meg – a dimensionless unit equivalent to 0.001 per mil

ppb – parts per billion by volume, equivalent to nmol mol⁻¹

ppm – parts per million by volume, equivalent to μmol mol⁻¹

WAO – Weybourne Atmospheric Observatory, UK

δ¹³C-CO₂ – ¹³C content of atmospheric CO₂

δ¹³C_s - ¹³C isotopic source signature

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1. Introduction

1.1 The global carbon cycle and climate change

The global carbon cycle consists of four major reservoirs: the atmosphere, the oceans, the terrestrial biosphere, and the geosphere, these reservoirs are connected by fluxes of carbon, the sizes of which are displayed in (Figure 1). The rate at which carbon is held in these reservoirs ranges from a few years for the atmosphere to decades for the terrestrial biosphere, soils and the oceans (Ciais *et al.*, 2013). The geosphere, however, is not relevant in the context of anthropogenic climate change due to a reservoir time on the scale of millennia (Ciais *et al.*, 2013).

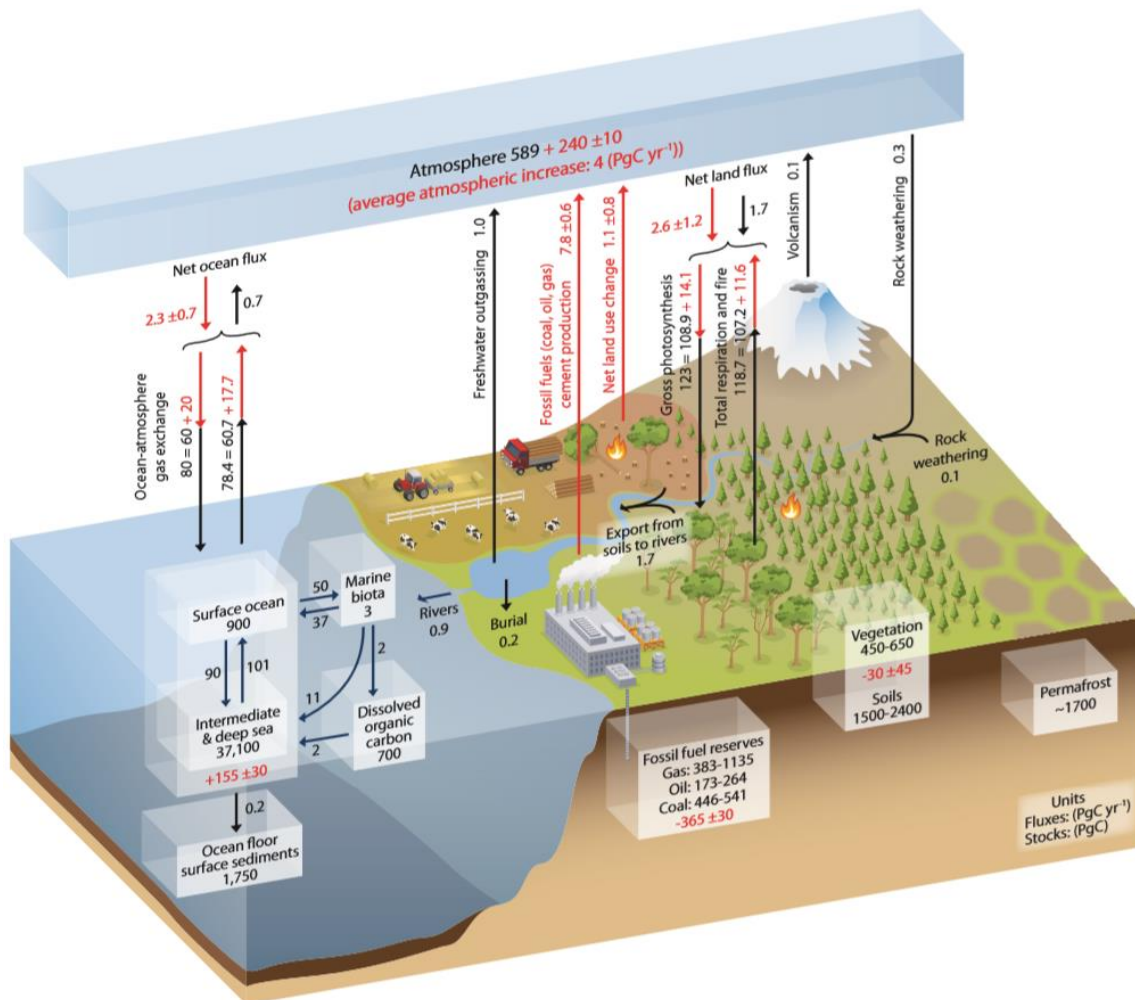


Figure 1. Simplified global carbon cycle schematic. Numbers represent reservoir mass in Pg C and annual carbon exchange fluxes in Pg C yr⁻¹. Black numbers and arrows represent reservoir sizes and fluxes prior to the Industrial Era (1750). Red arrows and numbers represent anthropogenic impacts on fluxes and reservoir sizes (averaged from 2000-2009). The blue numbers and arrows represent the interaction between ocean reservoirs (Ciais *et al.*, 2013).

Anthropogenic emissions of greenhouse gases (GHGs) resulting from fossil fuel burning and land-use change have a significant impact on this cycle through the addition of CO₂, the dominant carbon bearing trace gas, and to a lesser extent carbon monoxide (CO) and methane (CH₄) (Ciais *et al.*, 2013). Of the carbon released into the atmosphere through fossil fuel combustion approximately 56% has remained there, with the other 44% being taken up approximately equally by the oceans and terrestrial biosphere sinks (Sarmiento *et al.*, 2010). This addition of CO₂ to the atmosphere has resulted in a greenhouse effect causing the global climate to experience unequivocal rates of warming (IPCC, 2014).

The policy and scientific discussion of climate change has been framed around limiting global mean temperature increase to 2°C, relative to the pre-industrial global mean surface temperature, in order to prevent dangerous anthropogenic interference in the climate system (Meinshausen *et al.*, 2009). As such 195 nations have committed to the Paris Agreement with the intent of “holding the increase in global average temperature well below 2°C above pre-industrial level and pursuing efforts to limit the temperature increase to 1.5°C above pre-industrial levels, recognising that this would significantly reduce the risks and impacts of climate change” (UN, 2015, p.2). However, the discussion of the relationship between GHG emissions and climate targets is set within the context of the uncertainties which characterise the climate response to GHG emissions (IPCC, 2013). One of the largest uncertainties in the climate’s response to carbon emissions can be attributed to a lack of understanding of the processes involved in the global carbon cycle, as climate predictions are currently hindered by the inability to characterise feedback between a changing climate and the sources and sinks of CO₂ (Friedlingstein *et al.*, 2003; Friedlingstein *et al.*, 2014). It is the natural response of the global carbon cycle to anthropogenic emissions which will determine the relationship between emissions and atmospheric concentrations in the future, therefore increasing our understanding of the carbon cycle has significant policy importance (Rayner *et al.*, 1999).

The setting of emission reduction legislation currently relies on “bottom-up” accounting of regional and national scale GHG emissions, however, there are significant uncertainties associated with these inventories (Peylin *et al.*, 2011). In order for the legislation to be effective in reducing emissions, it is essential that these uncertainties are resolved (Weiss and Prinn, 2011). Self-reported “bottom-up” inventories, depend on emission factors being applied to local statistical data, such as fuel consumption, and scaled-up to a regional or national–scale (Nisbet and Weiss, 2010). This data extrapolation results in these reported GHG emissions and their apparent reduction being associated with uncertainties that are of the same magnitude as themselves or even larger, yet they are cited to a great degree of precision and often without uncertainties (Levin *et al.*, 2011). Furthermore, there is an incentive for nations to under-report their emissions due to the negative impacts of emissions on the climate, political pressure, and

the financial incentive from the carbon-trading market for emission reductions (Weiss and Prinn, 2011). Resultantly atmospheric observations suggest that emissions are greater than reported, often by a factor of two or more (Nisbet and Weiss, 2010). In order to independently verify the emission inventories from bottom-up methods, “top-down” atmospheric measurements of GHG concentrations are needed. Since emissions are regulated nationally or regionally, top-down estimates also need to be determined on this scale (Weiss and Prinn, 2011).

To support studies of the carbon cycle and to quantitatively determine carbon fluxes using a top-down approach, there is a global network of monitoring sites that continuously measure atmospheric CO₂ concentrations (Vardag *et al.*, 2016). High-frequency GHG measurements at regional observation stations record pollution-events where CO₂ concentrations are markedly enhanced from background CO₂ levels as a result of regional emissions, henceforth referred to as “high-CO₂ events”. These atmospheric measurements of CO₂ concentration are highly precise and provide an accurate, reliable measure of the increase of CO₂ in the atmosphere each year; however, for GHGs such as CO₂ that have natural, anthropogenic, industrial, and biogenic emissions measurements of atmospheric abundances alone are inadequate to precisely differentiate the contribution of these sources to the total atmospheric abundance (Weiss and Prinn, 2011; Vardag *et al.*, 2015). Yet, in order to provide a profound understanding of the carbon cycle processes and feedbacks there is a need to distinguish between CO₂ contributions from oceanic, biospheric, and anthropogenic sources (Vardag *et al.*, 2016).

1.2 The use of tracers to differentiate atmospheric CO₂ sources

One challenging issue associated with the atmospheric top-down approach is the attribution of emissions to specific processes. Often, the first step in this process is to distinguish between CO₂ emitted from anthropogenic activities (primarily fossil fuel combustion) and CO₂ emitted from biospheric activities; this can be achieved through the additional information provided by tracers (Lopez *et al.*, 2013). Atmospheric inversion models can then be implemented using the isolated fossil fuel CO₂ (ffCO₂) component of atmospheric concentrations in order to verify bottom-up inventories.

Tracers are gas species that can be used to provide additional information regarding the fluxes of CO₂ as they share common mechanisms with CO₂ fluxes. The use of multiple tracers allows for the separation of biospheric and anthropogenic CO₂ fluxes during high-CO₂ events, and reduces uncertainty in these fluxes (Gerbig *et al.*, 2006). In this study oxygen (O₂), Atmospheric Potential Oxygen (APO, defined in Section 2.2 below), carbon monoxide (CO), $\delta^{13}\text{C-CO}_2$ (the ¹³C content of atmospheric CO₂, defined in Section 2.4 below), and ozone (O₃) will be

investigated as tracers for CO₂ emissions, as the change in the oxidative ratio (OR) and correlation of these species with CO₂ can be used to determine the emission source. Each tracer method has its own associated limitations and uncertainties, therefore the use of multiple tracers will increase confidence in CO₂ source separation.

Back trajectories showing air-mass history can also be used in order to suggest and support conclusions of the sources of high-CO₂ events as the chemical and physical composition of an air mass is inherently related to its path through the atmosphere. Therefore, in order to obtain the maximum information from long-term time-series of composition measurements, data are often divided according to air mass history (Fleming *et al.*, 2012).

The use of multiple tracers along with meteorological parameters will therefore help to reduce uncertainty in atmospheric transport model inversions for top-down emission inventories by adding constraints to the models (Gerbig *et al.*, 2006). There is an obvious need to define efficient and reliable methods for the identification of high-CO₂ events related to local contamination sources and although tracers have been proven to be extremely useful in the determination of the sources of CO₂, their use is often neglected, either due to lack of simultaneous measurements or a pre-determined research approach (e.g. Turnbull *et al.*, 2006; Lopez *et al.*, 2013; Vardag *et al.*, 2015). Overlooking the information provided by these additional tracers as it does not fit the scope of a research project may lead to misguided conclusions, and is poor scientific practice.

1.2 Aims and objectives

This study focuses on the analyses of simultaneous and continuous indicative trace gas measurements and meteorological conditions over a 3-month time series (December 2017 – February 2018) from Weybourne Atmospheric Observatory (WAO) in order to investigate and identify the sources of CO₂ during high-CO₂ events. The large range and quantity of continuous, high-precision atmospheric observations of atmospheric gas species being collected at WAO presents a unique opportunity to investigate the sources of CO₂ arriving at the station during high-CO₂ events.

Objectives:

1. Identify high-CO₂ events during a 3-month time series at WAO.
2. Attribute the sources of CO₂ during these high-CO₂ events to an anthropogenic or biospheric source through analysis of indicative tracer species observations (O₂, APO, $\delta^{13}\text{C-CO}_2$, CO, O₃).
3. Investigate the back trajectories of air masses containing high-CO₂ concentrations to support the inference of CO₂ sources, and to illustrate the location of these sources

- 4.** Investigate the correlation between O_2 and O_3 , and the potential for O_3 to be used as a tracer for $ffCO_2$.

2. Literature Review

A key question in studies of the potential for reducing uncertainty in climate change projections is how additional observations may be used to constrain models (Cao and Jain, 2008). As discussed in the previous chapter, the use of indicative tracers, that share mechanisms with CO₂ fluxes, can assist in the separation of anthropogenic and biospheric CO₂ sources, and provide a better understanding of the carbon cycle, thus adding constraint to inversion models.

The requirements for a good tracer of CO₂ are: (1) its sources should be related in a unique way to those of CO₂, (2) it should be easily and precisely measured with a high temporal resolution, and (3) it should behave conservatively in the atmosphere or its sink mechanisms should be well understood (Gamnitzer *et al.*, 2006). This chapter will discuss the literature regarding the use of different tracers for separating the sources of observed increases in CO₂ concentrations. Each tracer has its own inherent uncertainties associated with its use to separate CO₂ sources, thus the use of multiple tracers will increase confidence determined sources.

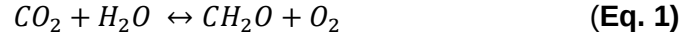
2.1 Radiocarbon

Radiocarbon (¹⁴C) observations have proven to be a nearly ideal tracer for ffCO₂ on both a regional and global scale (e.g. Manning *et al.*, 1990; Turnbull, 2006). Large concentrations of atmospheric ¹⁴C were produced by nuclear bomb testing in the 1950's and 1960's, whereas it is now only produced in small amounts from nuclear power production (Keeling, 1979). Due to its relatively short half-life of 5568 years, radiocarbon is absent in fossil fuels due to radioactive decay, whereas all other sources of CO₂ contain radiocarbon concentrations close to that of ambient air (Turnbull *et al.*, 2006; Graven and Gruber, 2011); thus the combustion of fossil fuels depletes the atmospheric ratio of ¹⁴C:¹²C (Keeling, 1979). However, measurements of the radiocarbon content of air are very expensive, and cannot be performed continuously (Gamnitzer *et al.*, 2006), with additional issues in certain regions, such as the UK, owing to interference from nuclear power plant ¹⁴C emissions (Graven and Gruber, 2011; Vogel *et al.*, 2013). Thus, a number of other proxies for tracing the sources of CO₂ are used. In this study O₂, APO, CO, δ¹³C-CO₂, and O₃ will be investigated as tracers. In the case of O₂, CO, and δ¹³C-CO₂ there have been a small number of previous studies (e.g. refer to Sections 2.2.1, 2.3, and 2.4 respectively). The use of APO is a very new method (Pickers, 2016; refer to Section 2.2.2 below) and to my knowledge, such an investigation has not been carried out using O₃.

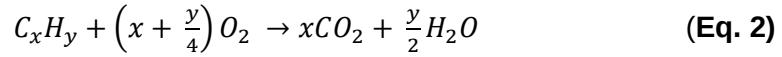
2.2 Oxygen and Atmospheric Potential Oxygen

2.2.1 Oxygen

The atmospheric concentration of O₂ and CO₂ are strongly anti-correlated. Fluxes of O₂ and CO₂ between the atmosphere and terrestrial biosphere are strongly anti-correlated due to the processes of photosynthesis and respiration (Eq. 1).



During this process, 1.1 moles of O₂ are consumed for each mole of CO₂ produced and vice versa, hence the mean global O₂:CO₂ oxidative ratio (OR) is approximately -1.1:1.0 mol mol⁻¹ (Simplified to -1.1 in this study; Severinghaus, 1995). This OR varies on both spatial and temporal scales from between -0.9 to -1.2 mol mol⁻¹ (Masiello *et al.*, 2008; Worrall *et al.*, 2013). Fluxes of CO₂ and O₂ from fossil fuel combustion are also strongly anti-correlated (Eq. 2) (Keeling and Manning, 2014).



This process has a globally weighted mean OR of -1.4:1.0 mol mol⁻¹ (simplified to -1.4 in this study), however this value can vary dependent on fuel type. Solid fuels, such as coal, have a typical OR of -1.17 mol mol⁻¹. Liquid fuels such as oil, have an OR of -1.44 mol mol⁻¹, and the OR of gases, such as natural gas, is -1.95 mol mol⁻¹ (Keeling, 1988; Steinbach *et al.*, 2011). For ocean processes, the fluxes of O₂ and CO₂ are decoupled due to inorganic reactions involving the carbonate system (Keeling and Manning, 2014). This difference in the relationship between O₂ and CO₂ for biospheric and fossil fuel fluxes mean that if the O₂:CO₂ OR during a given high-CO₂ event is known, then these sources can be separated.

2.2.2 Atmospheric Potential Oxygen

The atmospheric tracer APO was derived by Stephens *et al.*, (1998):

$$APO = \Delta O_2 + (1.1 \times \Delta CO_2) \quad (\text{Eq. 3})$$

The factor 1.1 accounts for the aforementioned O₂:CO₂ OR for terrestrial photosynthesis and respiration (Severinghaus, 1995). APO is therefore, by definition, conservative with respect to the terrestrial biosphere, so a terrestrial flux of CO₂ will have an APO:CO₂ OR of zero. Fossil fuels, however, have a depletive effect on APO due to the aforementioned higher OR of fossil fuels of around -1.4 mol mol⁻¹ (Stephens *et al.*, 1998; Keeling and Manning, 2014). Changes in APO therefore mainly reflect changes in the ocean-atmosphere exchange of O₂ and CO₂ (on seasonal and longer timescales), with a contribution from fossil fuels on both shorter and longer timescales (Pickers, 2016). APO and CO₂ are negatively correlated for fossil fuel combustion with an APO:CO₂ ratio for fossil fuel combustion ranges from -0.07 to -0.85 mol

mol⁻¹, dependent on fuel type, given that the APO:CO₂ ratio = O₂:CO₂ ratio + 1.1 (Pickers, 2016). The use of APO to investigate ffCO₂ is a very new approach, first introduced by Penelope Pickers, a recent UEA PhD graduate student, and should be less prone to bias due to fewer uncertainties in its sources and sinks (Pickers, 2016).

2.3 Carbon monoxide

CO is an atmospheric trace gas that is produced together with CO₂ as a result of incomplete combustion of fossil fuels. High atmospheric CO concentrations can therefore usually be easily traced back to local anthropogenic sources owing to the relatively short average lifetime of the CO molecule in the atmosphere of around two months (Khalil and Rasmussen, 1990). CO is therefore considered as a good tracer for polluted air masses, particularly on local and regional scales. The variations in CO have previously been used to identify and quantify ffCO₂ fluxes (e.g. Gamnitzer *et al.*, 2006; Turnbull *et al.*, 2006; Lopez *et al.*, 2013) as CO and CO₂ are evolved at specific ratios during combustion depending on fuel source and combustion efficiency (Djuricin *et al.*, 2010).

It is estimated that two thirds of CO originates from anthropogenic activities, however there are large uncertainties associated with non-fossil fuel CO sources such as biomass burning and atmospheric methane oxidation (Gamnitzer *et al.*, 2006; Seinfeld and Pandis, 2012). The major sink for CO is reaction with OH radicals; again there are large uncertainties associated with this sink, as well as minor sinks such as soil uptake and stratospheric diffusion (Gamnitzer *et al.*, 2006; Seinfeld and Pandis, 2012). The emissions ratio of CO:CO₂ associated with the combustion of fossil fuels can be offset by up to 20% due to these uncertainties in the CO sources and sinks (Gamnitzer *et al.*, 2006; Turnbull *et al.*, 2006). These uncertainties mean that although it provides a valuable indication of ffCO₂ sources, CO alone cannot be used as a reliable tracer for CO₂.

2.4 $\delta^{13}\text{C}$ -CO₂

Another approach for partitioning CO₂ sources during high-CO₂ events relies on the differences in the uptake of the most abundant carbon isotopes, ¹³C and ¹²C as atmospheric CO₂ concentrations are anti-correlated with the atmospheric ratio of ¹³C/¹²C (typically expressed as $\delta^{13}\text{C}$ -CO₂) (e.g. Yakir and Sternberg, 2000; Pataki *et al.*, 2003a; Xu *et al.*, 2017).

In general, the isotopic composition of atmospheric CO₂ is linked to the exchange between the terrestrial biosphere and the atmosphere (Figure 2). Photosynthesis and respiration impart distinct isotopic signatures to the atmosphere; during photosynthesis, terrestrial plants preferentially assimilate ¹²C-CO₂, thereby enriching the ¹³C content of the CO₂ left behind in the atmosphere (Flanagan and Ehlerger, 1998). Conversely, fossil fuels contain lower $\delta^{13}\text{C}$ -CO₂ values than the atmosphere, so anthropogenic emissions of CO₂ deplete the atmospheric

$\delta^{13}\text{C}\text{-CO}_2$ content (Vardag *et al.*, 2015). Moreover, net uptake of CO_2 between the atmosphere and oceans leaves $\delta^{13}\text{C}\text{-CO}_2$ essentially unchanged (Battle, 2000). These distinct signatures can thus be used to constrain global carbon source and sink estimates (Pataki *et al.*, 2003a). Tans (1981 in Lopez *et al.*, 2013) estimated that the release of CO_2 from anthropogenic combustion implies an average worldwide $\delta^{13}\text{C}\text{-CO}_2$ isotopic source signature for natural gas, liquid, and solid fuels of -41.0‰ , -26.5‰ , and -24.1‰ respectively. Although $\delta^{13}\text{C}\text{-CO}_2$ is particularly useful for identifying natural gas combustion, which is more depleted in $\delta^{13}\text{C}\text{-CO}_2$ than gasoline, another tracer is needed to distinguish between gasoline and respiration, which have similar isotopic sources signatures (Djuricin *et al.*, 2010).

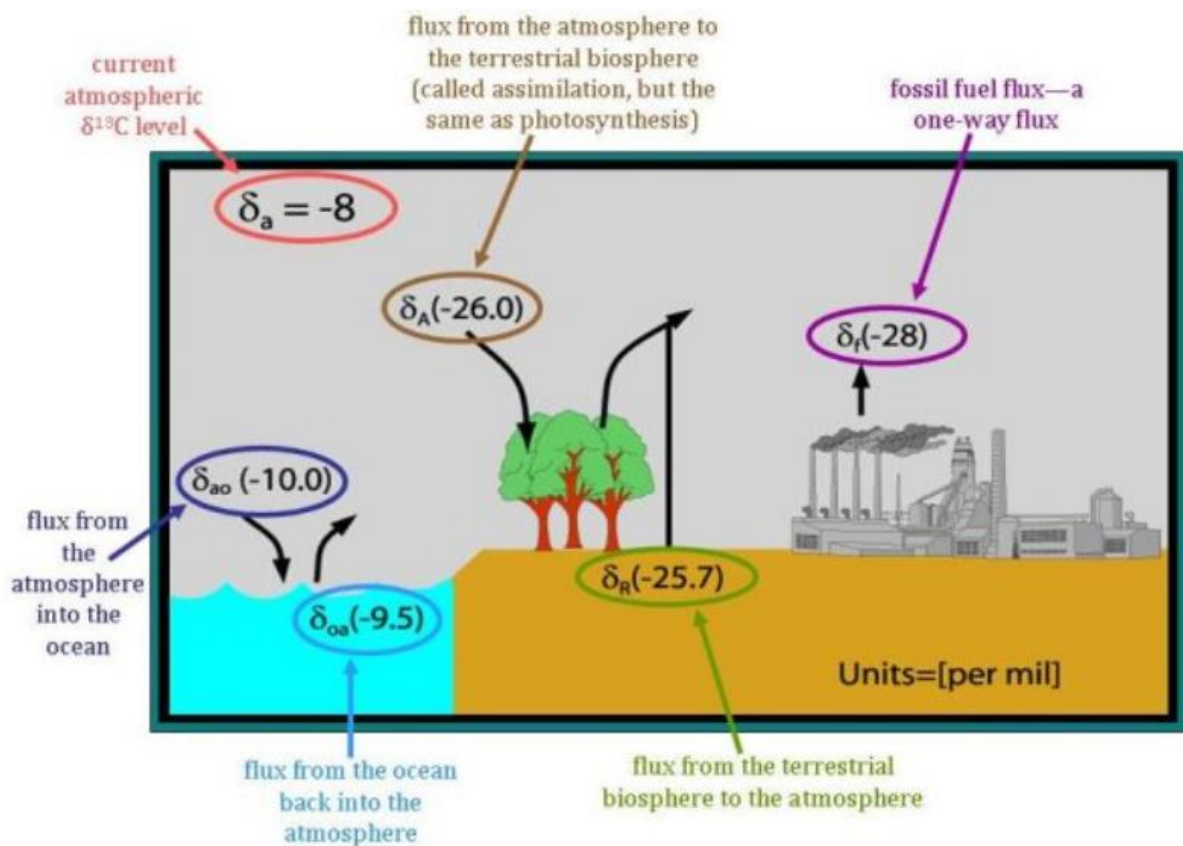


Figure 2. The $\delta^{13}\text{C}\text{-CO}_2$ values of the different fluxes from fossil fuel combustion and both into and out of the terrestrial biosphere and ocean. Note that fossil fuel flux values can vary depending on fuel type (NOAA, [No Date])

As carbon isotope ratios and CO_2 concentrations vary proportionally, with a plot of $\delta^{13}\text{C}\text{-CO}_2$ versus the inverse of the CO_2 concentration (a so-called, 'Keeling plot') it is possible to extrapolate the isotopic signature of the CO_2 source (Keeling, 1958, 1961). The basis of the Keeling plot method is conservation of mass, where the atmospheric concentration of a gas (c_a) reflects the combination of some background atmospheric concentration (c_b) and variable

amounts of that gas added or removed by sources or sinks in the ecosystem (c_s), (Eq. 4) (Pataki *et al.*, 2003a).

$$c_a = c_b + c_s \quad (\text{Eq. 4})$$

Given conservation of mass,

$$\delta^{13}C_a c_a = \delta^{13}C_b c_b + \delta^{13}C_s c_s \quad (\text{Eq. 5})$$

where $\delta^{13}C$ represents the carbon isotope ratio of each CO_2 component. Combining equations (4) and (5),

$$\delta^{13}C_a = c_b(\delta^{13}C_b - \delta^{13}C_s)\left(\frac{1}{c_a}\right) + \delta^{13}C_s \quad (\text{Eq. 6})$$

where $\delta^{13}C_s$ is the integrated value of the CO_2 sources in the ecosystem (Pataki *et al.*, 2003a).

In this approach, a linear relationship is established between $\delta^{13}C\text{-CO}_2$ and the reciprocal of the CO_2 concentration from the observed time series, with an intercept of $\delta^{13}C_s$, the isotopic source signature of the local CO_2 emissions (Eq. 6) (Yakir and Sternberg, 2000; Xu *et al.*, 2017). The value of the CO_2 concentration when y equals zero is infinite, thus this limit represents the isotopic composition of the atmosphere if all the CO_2 were due to the source (Miller and Tans, 2003). This relationship is visualised in Figure 3.

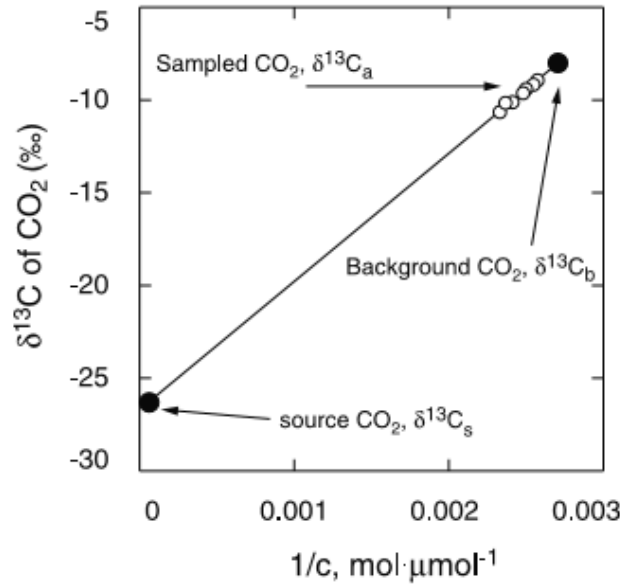
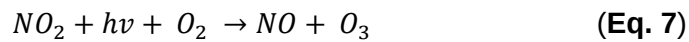


Figure 3. The Keeling plot method (Eq. 6 in text). Isotope ratios are plotted against the inverse of CO_2 concentration. The carbon isotope composition of source CO_2 ($\delta^{13}C_s$) and background atmospheric CO_2 ($\delta^{13}C_b$) are represented by black circles. The carbon isotope composition of sampled air ($\delta^{13}C_a$) is represented by open circles (Pataki *et al.*, 2003a).

2.5 Ozone

Tropospheric ozone (O_3) results from a complex combination of production, transport, chemical destruction and deposition (Ferrarese *et al.*, 2015). There are several well documented sources of tropospheric ozone, of both natural and anthropogenic origin such as transport from the stratosphere, local photochemical production from precursors (volatile organic compounds (VOCs), CO, and nitrogen oxides (NO_x) (Eq. 7)), and remote production associated with long-range transport (Chevalier *et al.*, 2007). Important sinks of ozone are local depletion by reactions with NO in the vicinity of anthropogenic NO_x emissions, as NO can quickly remove surface ozone (Eq. 8), and deposition to the ground (Hagenbjörk *et al.*, 2017).



The reactions between NO, NO_2 and O_3 in the atmosphere are theoretically a null cycle with no net production or destruction of O_3 , as the effect of Eq. 7 is the reverse of Eq.8 (Hagenbjörk *et al.*, 2017); however, the addition of NO from anthropogenic emissions disrupts this cycle. It should also be noted that although O_3 can be generated from CO oxidation, this represents a relatively minor source in many urban, suburban, and rural regions (Chameides *et al.*, 1992). In summer, the boundary layer net photochemical ozone production is linked to the photochemical oxidation of CO and hydrocarbons in the presence of NO_x , however, in other seasons, when photochemistry is less active, anthropogenic emission tend to suppress ambient ozone (Fiore *et al.*, 2002; Gilge *et al.*, 2010). A decrease in ozone concurrent with a high- CO_2 event (and decrease in O_2) would therefore indicate an anthropogenic source during the winter months (DJF). Parrish *et al.* (1998), Gilge *et al.*, (2010), and Ferrarase *et al.* (2015) attribute the cause of the negative correlation between CO_2 and O_3 to the removal of ozone by the reaction with the anthropogenic pollutant NO (Eq. 8). However, ozone has not previously been explicitly considered as a tracer for $ffCO_2$, as a result this study will present a potential tracer for $ffCO_2$, through comparison of O_3 correlations during high- CO_2 events with those of the known tracer methods discussed above.

2.6 Air mass back trajectories to support tracer analyses

In situ wind speed and wind direction measurements have been used extensively to trace the sources of air arriving at a given site, although these provide some attribution as to the source of an air mass and are useful for preliminary investigation, current science requires a better understanding (Fleming *et al.*, 2012). Interpreting air mass history and the role of transport is an important tool for interpreting atmospheric composition that is influenced by a variety of local and long range transport processes (Fleming *et al.*, 2012). Air mass back trajectories can thus be used to support the inference of CO_2 sources, and illustrate the location of these

sources. The path of an air mass through the atmosphere is intrinsically linked to its chemical and physical composition; therefore, the division of atmospheric composition observations according to air mass history allows for the extraction of more information regarding the sources of CO₂ (Fleming *et al.*, 2012).

2.7 Motivation

The discussion above acknowledges the benefits of using tracers, but also highlights the limitations from only using one tracer species. The combination of multiple high-frequency measurements of anthropogenic and isotopic tracers with meteorological conditions concurrent with CO₂ measurements for distinguishing CO₂ sources is overlooked in the current literature and can contribute to the improvement of top-down emission inventories. Therefore this study builds on the reviewed literature and addresses a gap in the literature, as well as presenting O₃ as a potential tracer for ffCO₂ during the winter.

3. Data and Methods

3.1 Weybourne Atmospheric Observatory

All atmospheric measurements were obtained from Weybourne Atmospheric Observatory (WAO) for the period December 2017 – February 2018. WAO is located on the north Norfolk coast of the UK ($52^{\circ}57'02''\text{N}$, $1^{\circ}07'19''\text{E}$, 10 m above ground level (AGL) and 20 m above sea level (ASL)), approximately 35km north west of Norwich, 170 km north east of London and 200 km east of Birmingham (Figure 4). It is part of the European Union's Integrated Carbon Observation System (ICOS) and the World Meteorological Organization's Global Atmospheric Watch programme (GAW). High-precision, high-accuracy, continuous measurements of a wide array of atmospheric gas species (including GHGs, isotopes, and reactive gases) at a fine temporal scale are funded through the UK's National Centre for Atmospheric Science (NCAS) long-term measurement programme. These measurements are suitable for accurately distinguishing terrestrial and anthropogenic CO_2 signals (Stephens *et al.*, 2000).

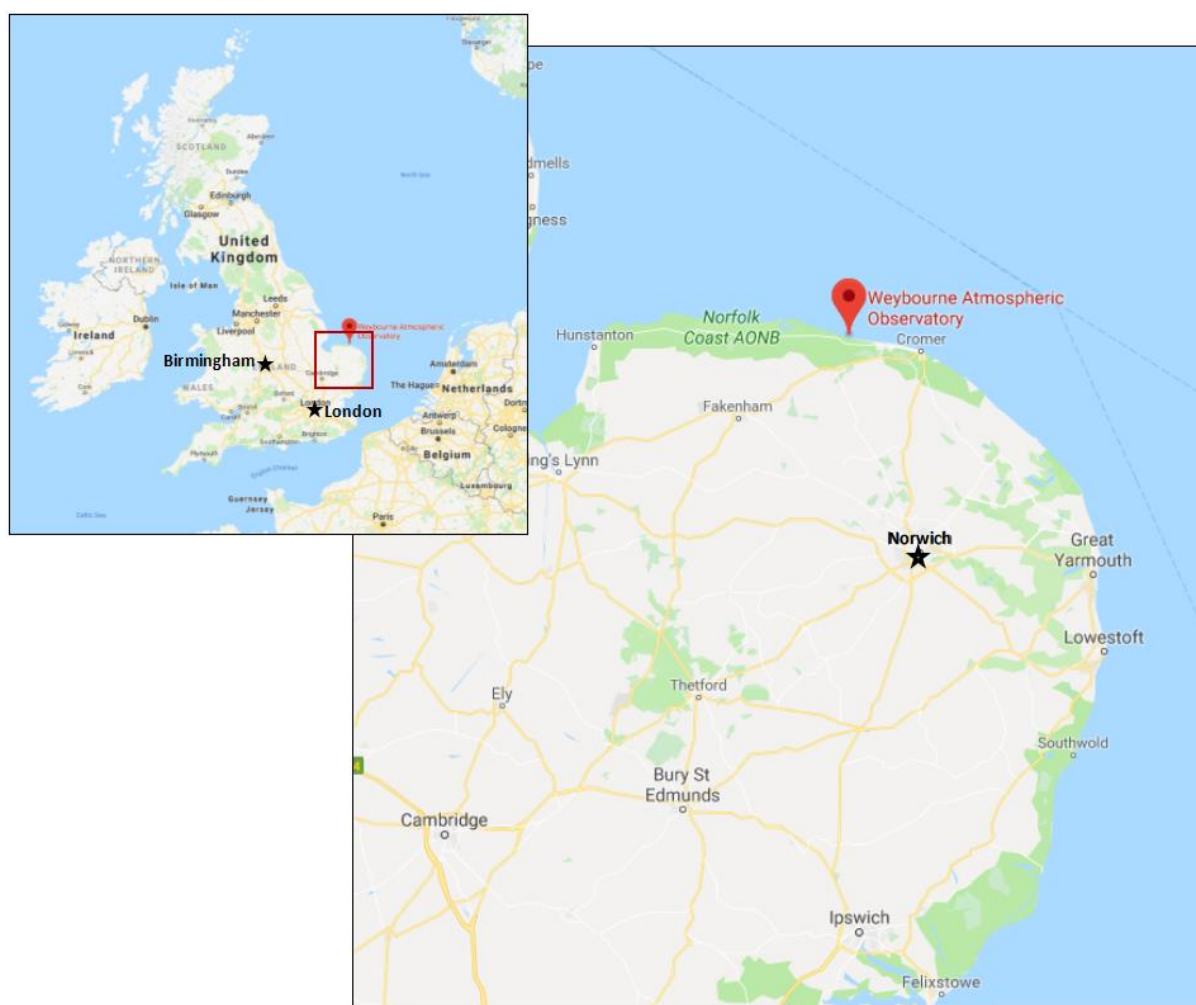


Figure 4. Location of WAO on the North Norfolk coast, UK. (Google Maps)

WAO experiences rapidly changing wind directions, with multiple influences close by, and a number of rapidly changing sources of CO₂; thus, the station is at a strategic location for experiencing a variety of air masses from a range of sources including relatively clean maritime air from the Atlantic and North Sea, and polluted continental Europe and UK air masses (Fleming *et al.*, 2012).

3.2 Datasets

All data used in the study are available from the UK Centre for Environmental Data Analysis (CEDA) and directly from Grant Forster, my supervisor and the WAO Station Manager. The observations of the species detailed in Table 1 along with wind speed and wind direction data were obtained for a three month period from December 2017 – February 2018. A three-month period was chosen, due to the large number of data observations being used, and the large number of high-CO₂ events within this period.

Table 1. Summary of the frequency of measurements at WAO for each gas species investigated. Units are explained in Section 3.2.1 below.

<i>Species</i>	<i>Unit</i>	<i>Frequency of measurements (minutes)</i>
CO ₂	ppm	2
O ₂	per meg	2
δ ¹³ C-CO ₂	per mil (‰)	1
O ₃	ppb	1
CO	ppb	5

All observations were averaged to 5 minutes (the lowest measurement frequency of any species), in order to time match the observations for analyses purposes.

N.B. the δ¹³C-CO₂ observations available at the time of this study are not final, therefore after further calibration the reported concentrations may change slightly.

3.2.1 Units of O₂ and δ¹³C-CO₂

The relative level of precision required for atmospheric O₂ measurements is very high since changes in O₂ partial pressure need to be detected to the order of 1 in 10⁶, hence changes in the partial pressure of other gases in the air will affect the O₂ measurement (Keeling and Shertz, 1992). O₂ concentrations are therefore reported on a relative scale calculated as the change in ratio of O₂ to atmospheric nitrogen (N₂) relative to a standard O₂/N₂ ratio. N₂ is much

less variable than O₂ meaning that a change in the O₂/N₂ ratio therefore mainly represents the O₂ concentration and is not sensitive to changes in other atmospheric gases (Keeling and Shertz, 1992).

$$\delta(O_2/N_2) = \left(\frac{(O_2/N_2)_{sample}}{(O_2/N_2)_{reference}} - 1 \right) \quad (\text{Eq. 9})$$

The right hand side of this equation multiplied by 10⁶ and expressed in “per meg”, a dimensionless unit equivalent to 0.0001 per mil. In these units, 4.77 per meg of δ(O₂/N₂) is equivalent to the same number of molecules as 1 ppm of a trace gas (Keeling et al., 1998). APO is also expressed in per meg units.

Similarly, the stable isotope ¹³C content of CO₂ is reported as a relative carbon isotopic ratio, due to the small changes in concentration being recorded (Keeling, 1958):

$$\delta^{13}C = \left(\frac{(^{13}C/^{12}C)_{sample}}{(^{13}C/^{12}C)_{reference}} - 1 \right) \quad (\text{Eq. 10})$$

The right hand side of this equation is then multiplied by 10³ and expressed in “per mil” units (‰).

CO₂ is expressed as parts per million (ppm), which is equivalent to μmol mol⁻¹. CO and O₃ are expressed in parts per billion (ppb) which is equivalent to nmol mol⁻¹.

3.2.2 Flagging O₂, CO₂ and APO data

There are several potential sources of uncertainty in the CO₂ and O₂ measurement system which could result in erroneous data, therefore an extensive range of diagnostic data are collected alongside the atmospheric observation such as flow rates and pressures. Data were flagged to remove periods of suspect air samples where the diagnostic plots indicated that there was a technical issue with the observations or a recalibration was occurring. These flagged data points were then removed using an R script written by Dr Penelope Pickers. This script also removed spikes and noise in the O₂ data where there was a different in values of >20 per meg between an observation and the previous and following observation.

APO values were also calculated using the aforementioned R script, using Eq. 11.

$$APO = O_2 + \left(\frac{-1.1}{0.2095} \right) \times (CO_2 - 350) \quad (\text{Eq. 11})$$

where - 1.1 is an estimate of the average O₂:CO₂ ratio for land photosynthesis or respiration, 350 is an arbitrary constant, and the factor 1/0.2095 converts CO₂ from mole fraction (ppm) to per meg units (Lueker et al., 2003).

3.3 Preliminary data analysis

The first step in investigating the sources of CO₂ during the study period was to use the plethora of functions available in the R 'openair' package (a Natural Environment Research Council project for the analysis of air pollution data) (Carslaw and Ropkins, 2011). The correlations between each gas species, wind speed, and wind direction were analysed, along with the creation of wind and pollution roses.

3.4 High-CO₂ event data selection

High-CO₂ events were first visually identified from the full time series, defined as any period where the CO₂ concentration increased significantly from the background value. The start and end time of these events was defined as at least an hour after or before the concentration deviated or returned to background level. Additionally, a prerequisite for the Keeling plot (see Section 2.3) is that the source mix needs to remain constant during each period of investigation (Figure 5a). A varying source mix is likely to occur when the wind direction, thus the footprint of the measurement site, changes which can lead to strong biases in the intercept (Figure 5b) (Vardag *et al.*, 2016).

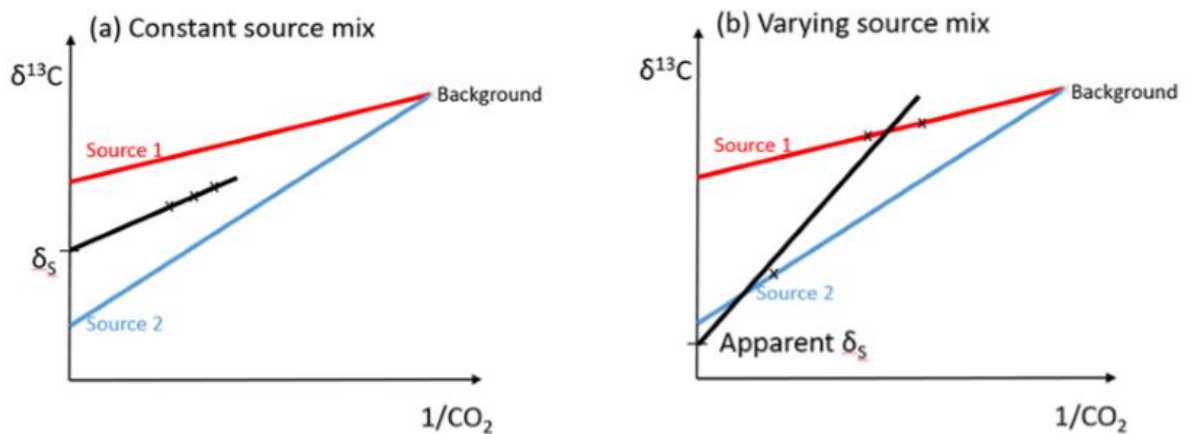


Figure 5. Regression based determination of source signature using a Keeling plot. **(a)** A constant source mix leading to correct determination of the isotopic signature. **(b)** Change of source mix during the high-CO₂ event either due to temporal change of emissions or a wind direction change leading to a biased result (Vardag *et al.*, 2016)

High-CO₂ events were therefore further categorised by a fairly consistent wind direction. For example, in Figure 6, the end of the first event ends as wind direction changes to an oceanic source, and the second event begins when the wind direction becomes fairly consistent again in order to increase the likelihood of a constant source mix. This filtering of data during the high-CO₂ events does decrease the number of data points which can be included in the analysis, but is essential in order to extract a more accurate isotopic source signature.

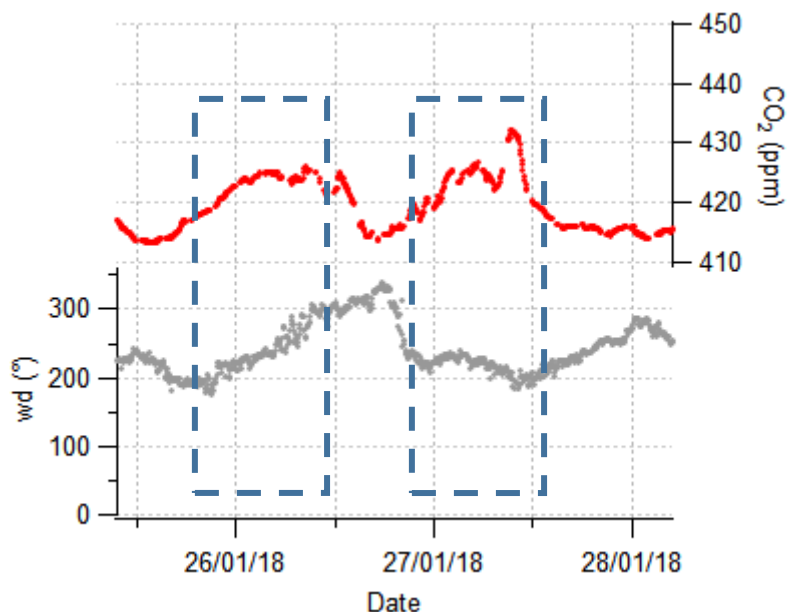


Figure 6. Example of event separation using wind speed. Dashed boxes indicate two separate event periods.

3.5 Tracer species during high-CO₂ events

In order to partition the sources of CO₂ during the high-CO₂ events, the atmospheric observations of O₂, APO, CO₂, and O₃ were first investigated. First, these observations were analysed visually, to identify the presence or absence of a simultaneous change in tracer observations during the high-CO₂ events, then the ORs and correlations were calculated.

3.5.1 Oxidative ratios

The O₂:CO₂ and APO:CO₂ ORs were computed for each high-CO₂ event using the slope of a simple least squares linear regression model.

As described in Section 3.2.1, changes in O₂ concentration are expressed as changes in the $\delta(\text{O}_2/\text{N}_2)$ ratio. Therefore, in order to present O₂ and APO in ppm equivalent units for the calculation of the OR, the $\delta(\text{O}_2/\text{N}_2)$ values were divided by 4.77. This conversion factor is due to the fact that the addition of 1 ppm of O₂ to 1 mole of dry air will increase the $\delta(\text{O}_2/\text{N}_2)$ ratio by 4.77 per meg (Keeling et al., 1998).

3.5.2 Correlations

The correlation coefficients (r) were also determined for the relationship between O₂ and CO₂, APO and CO₂, CO and CO₂, and O₃ and O₂ based on a least squares linear regression.

3.6 Keeling plots

A Keeling plot (Keeling, 1958, 1961) was produced for each identified high-CO₂ event (see Section 2.4). The isotopic source signature ($\delta^{13}\text{C}_s$) was calculated from the intercept of a least

squares linear regression between $\delta^{13}\text{C}-\text{CO}_2$ and the reciprocal of the CO_2 concentration observations. The coefficient of determination (r^2) was used to determine the suitability of the model fit. In a sensitivity analysis of the different regression approaches Zobitz *et al.* (2006) concluded that this method produces unbiased estimates of $\delta^{13}\text{C}_s$ at all ranges of CO_2 concentration and that standard error is a suitable measure of $\delta^{13}\text{C}_s$ uncertainty. An error on the intercept of greater than 2‰ indicates a varying source mix, (Vardag *et al.*, 2006), however the possibility of this was minimised by the high- CO_2 event selection procedure (Section 3.4).

3.7 Air mass back trajectory analysis

Interpreting air mass history and the role of transport is an important tool for interpreting atmospheric composition, which is influenced by a variety of local and long range transport processes (Fleming *et al.*, 2012). Therefore, once the relationships the high- CO_2 events had been identified, the origin of the air mass which contained each high- CO_2 event was computed, hence supporting the inference of CO_2 sources, and illustrating the location of these sources.

The air mass back trajectories were computed for each high- CO_2 event using the HYbrid Single-Particle Lagrangian Integrated trajectory model Version 4 (HYSPLIT_4) (<http://ready.arl.noaa.gov/HYSPLIT.php>) in 'openair'. The HYSPLIT_4 model runs a back trajectory starting every 3 hours (i.e. 00:00, 03:00, 06:00, 09:00 etc.), and was run backwards for 96-hours from the starting point of WAO (52°57'02"N, 1°07'19"E), at a start height of 10m AGL (the same height as the sample inlet). As the trajectories run every three hours, the start time nearest to that of the peak of each high- CO_2 event was used as representative of the air mass history of the entire event (e.g. an event which peaked at 5:30 was represented by the back trajectory beginning at 06:00).

The 'trajCluster' function from the 'openair' package in R was then used to group the back-trajectories for each high- CO_2 event into four clusters based on similar air mass origins. A one-way ANOVA followed by a post-hoc Tukey test was then performed in order to determine whether the determined CO_2 sources inferred from the OR and $\delta^{13}\text{C}_s$ values significantly differed between these clusters, and between the events in each cluster, at the 95% significance level.

3.7.1 Meteorological data

The HYSPLIT_4 model uses gridded meteorological data to determine simple particle trajectories, from a particular starting location and time (Draxler and Hess, 1998). The monthly meteorological files used in the back trajectories were obtained from the US National Oceanic and Atmospheric Administration (NOAA) Air Resources Library (ARL) Gridded Meteorological Data Archives reanalysis dataset (<ftp://arlftp.arlhq.noaa.gov/archives/reanalysis/>). This meteorological data has a 2.5 degree global latitude-longitude resolution.

3.8 O₂:O₃ correlation

The correlation between observations of O₃ and O₂ at WAO has been very strong (Grant Forster, personal communication, 2018). Therefore, in addition to investigating this relationship during high-CO₂ events (see Section 3.6) the correlation coefficients (r) were also calculated for each 24 hour period (00:00 $\pm$ 12 hours) using a least squares linear regression model. These 24 hour periods were then investigated in order to determine when O₃ and O₂ display strong and weak correlations. This was completed using the 'running' function from the 'gtools' package in R. The 24 hour periods with the 10 most strong positive and 10 least positive correlation periods between O₃ and O₂ were then plotted alongside the CO₂ concentrations during these periods.

4. Results and Discussion

This chapter presents the results of the analysis, their interpretation, and a discussion of their significance with comparisons drawn to the literature where possible. Firstly, the atmospheric observations of CO₂, O₂, APO, CO, $\delta^{13}\text{C-CO}_2$, and O₃ from December 2017 – February 2018 are presented, with an analysis of the overall trends and relationships between species. The identified high-CO₂ events are then presented, alongside wind speed and wind direction data. Following this, the OR of O₂:CO₂ and APO:CO₂, and correlations of CO:CO₂, and O₃:O₂ during the high-CO₂ events and indicated CO₂ sources are discussed. Next, the CO₂ sources indicated by the Keeling plot results for each high-CO₂ event (with available $\delta^{13}\text{C-CO}_2$ data) are reviewed. The 96-hour HYSPLIT back trajectories, clustered by origin, and the influence of these clusters of the CO₂ source are next discussed. Finally, the correlation between O₃ and O₂ during the entire study period is presented and interpreted with respect to the potential implications of this correlation for the use of O₃ as a tracer for ffCO₂.

4.1 Data series summary

Summary statistics for each species and wind speed after being averaged to every 5-minutes can be found in Table 2.

Table 2. Summary statistics of time-series (5-minute average).

Species	Min	Max	Range	Mean	Median	95th Percentile
CO ₂ (ppm)	408.9	450.3	41.4	417.6	415.9	430.5
O ₂ (per meg)	-989.9	-654.5	335.4	-742.0	-733.3	-690.4
APO (per meg)	-464.0	-331.5	132.5	-386.9	-387.9	-364.7
CO (ppb)	96.1	353.4	257.3	155.3	146.0	216.6
$\delta^{13}\text{C-CO}_2$ (‰)	-10.47	-8.09	2.38	-8.94	-8.80	-8.50
O ₃ (ppb)	0.28	46.82	46.54	28.11	30.60	40.50
Wind speed (m/s)	0	24.5	24.5	7.3	7.2	12.9

Figure 8 (p.26) presents the 5-minute mean wind direction, wind speed, CO₂, O₂, APO, CO, $\delta^{13}\text{C-CO}_2$, and O₃ observations at WAO from 01/12/2017 to 28/02/2018. There are gaps in each of these time-series, most noticeable between 27/12/2017 01:55 – 28/12/2017 16:15, and 10/01/2018 10:15 – 12/01/2018 10:50 for CO₂, O₂, and APO; 05/02/2018 23:20 - 07/02/2018 22:00 and 24/02/2018 15:50 – 28/02/2018 23:55 for CO; and between 21/12/2017 23:35 – 24/12/2017 14:00, 22/01/2018 10:05 – 24/01/2018 14:20, and 14/02/2018 15:05 - 28/02/2018 23:55 for $\delta^{13}\text{C-CO}_2$. These gaps in observations should not hinder the analysis due to the large quantity of remaining observations, and availability of other tracers during these gaps.

Figure 7 displays a correlation matrix of all species over the entire study period, quantitatively describing the relationships observable in Figure 8. The anti-correlation between CO₂ and O₂ is strong ($r = -0.97$), as is the anti-correlation between CO₂ and $\delta^{13}\text{C-CO}_2$ ($r = -0.96$). These relationships are to be expected, due to the anti-correlation between O₂ and CO₂ for all fossil fuel combustion and terrestrial biosphere processes (Keeling and Manning, 2014) and the depleted $\delta^{13}\text{C-CO}_2$ values of these processes compared with ambient air (Pataki *et al.*, 2003a). CO₂ is also strongly positively correlated with CO ($r = 0.89$), and O₃ with O₂ ($r = 0.79$). This strong correlation in winter between CO and CO₂ was also found by Oney *et al.* (2017) at three sites in Switzerland and is a strong suggestion that during the winter months the biospheric influence is small, and regional CO₂ is driven mainly by anthropogenic fossil fuel combustion. The decrease in O₃ with decreasing O₂ can also be ascribed to anthropogenic emissions, due to anthropogenic pollutants associated with fossil fuel combustion quickly removing surface ozone, however this relationship has not been widely discussed in the literature (See Section 4.8). CO₂ is also negatively correlated with wind speed ($r = -0.6$), indicating that higher concentrations of CO₂ occur at lower wind speeds (further discussed in Section 4.4). The wind direction was not included in this correlation plot due to it being circular data (i.e. 0 – 360°, where 0° and 359° are only 1° apart), thus the relationship between CO₂ concentrations and wind direction is discussed in Section 4.4, below through the use of wind roses.

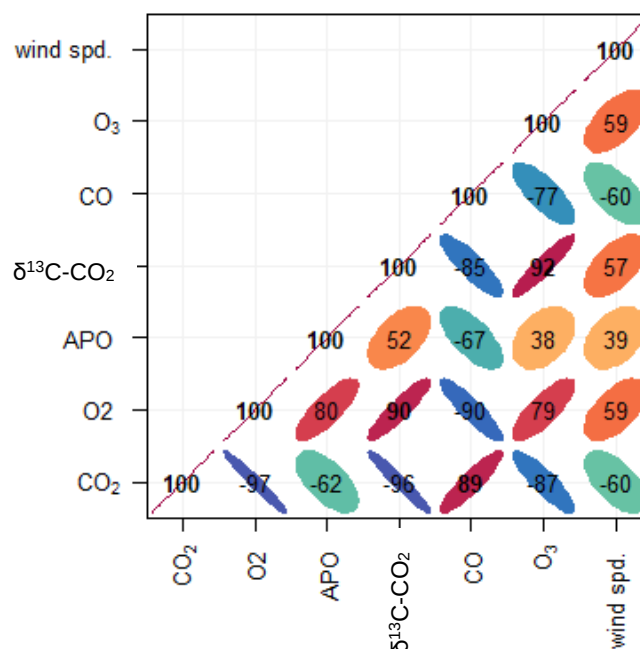


Figure 7. Correlation matrix of all observed species, and wind speed over the entire study period. The numbers indicate correlation coefficients (r) from a simple linear regression. Strong positive correlations are shaded red, strong negative correlations are shaded blue, and no correlation is shaded yellow. The ellipsoids are more circular in shape for weak correlations, and elliptical for strong correlations.

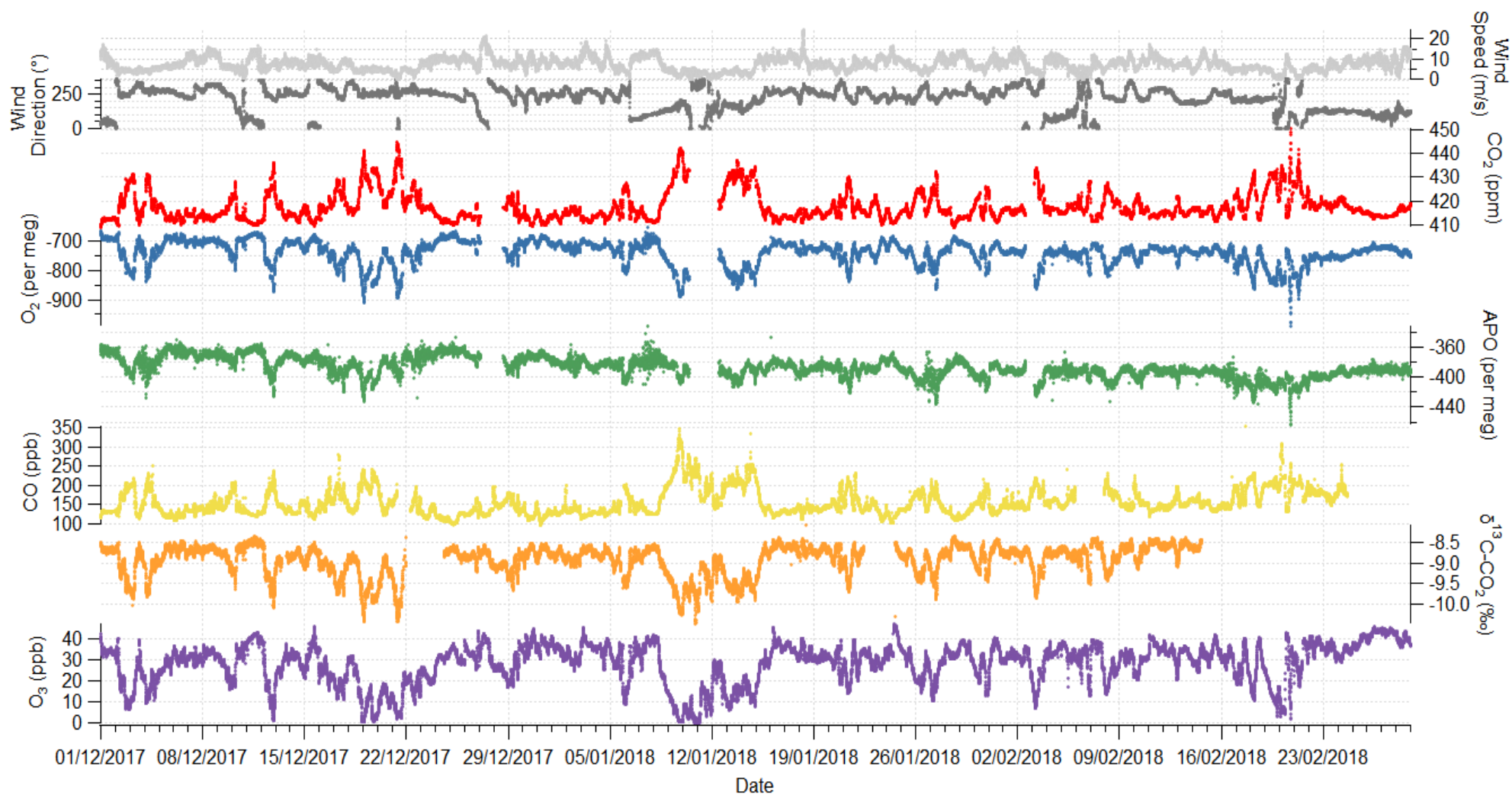


Figure 8. Wind speed, wind direction, CO₂, O₂, APO, CO, δ¹³C-CO₂, and O₃ observations at WAO from 01/12/2017 – 28/02/2018.

4.2 Diurnal cycles

Figure 9 displays the average diurnal cycles of CO_2 , O_2 , $\delta^{13}\text{C}\text{-CO}_2$, O_3 , CO , and APO for the entire study period calculated using the daily hourly mean. CO_2 and CO both experience an overnight increase in concentration, whereas the observations of O_2 , $\delta^{13}\text{C}\text{-CO}_2$ and O_3 experience an increase during daylight hours. The diurnal cycle of APO is less distinct than that of the other species with more variability throughout the day, but does display a decrease overnight. Again, there is a clear anti-correlation between CO_2 and O_2 , and CO_2 and $\delta^{13}\text{C}\text{-CO}_2$; there is also a strong correlation between O_2 and O_3 , and CO_2 and CO which can also be seen in the correlation matrix (Figure 7, Section 4.1).

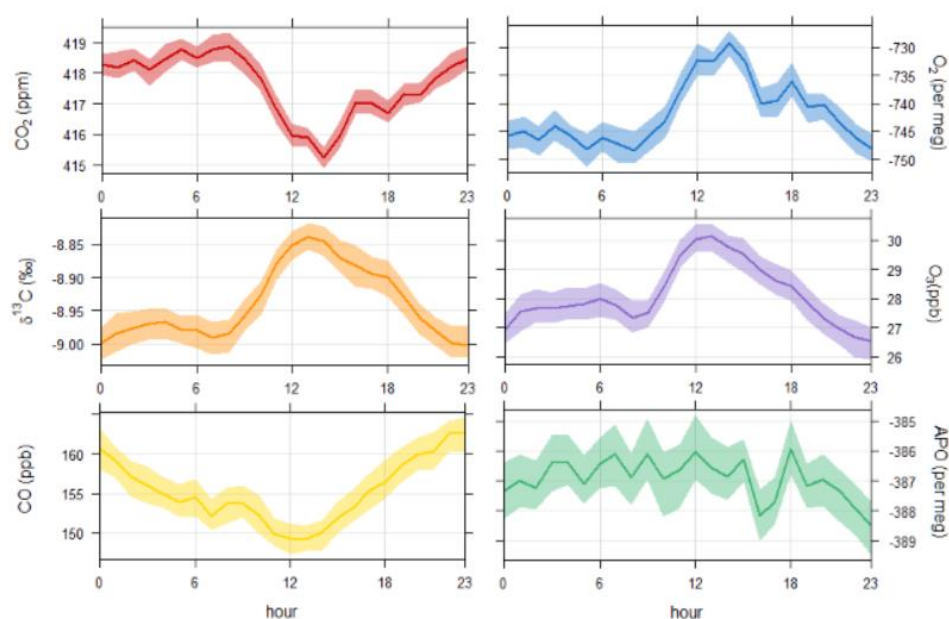


Figure 9. Diurnal variation of CO_2 , O_2 , $\delta^{13}\text{C}\text{-CO}_2$, O_3 , CO and APO with shading representing confidence intervals.

The observations at WAO are taken from a height of 10 m AGL, thus always within the well-mixed planetary boundary layer. The diurnal rectifier effect therefore has a role in the observed diurnal cycles. At night, the planetary boundary layer height is lower, meaning the volume of air it represents above the Earth's surface decreases, having the effect of increasing species concentrations within this layer as fossil fuel and respiration flux are held near the surface (Stephens *et al.*, 2000). As the sun rises, the convective vertical mixing recommences thus diluting observations over a larger air mass, photosynthesis also dominates during the day, thus increasing O_2 (Stephens *et al.*, 2000; Satar *et al.*, 2016). This phenomenon is less intense during the winter season (December – February), as the boundary layer remains lower for longer due to lower temperatures (Stephens *et al.*, 2000), and terrestrial biosphere activity is also reduced due to decreased sunlight hours, resulting in a lower amplitude of diurnal cycles. The diurnal rectifier effect influences all species, as such CO concentration also increases

overnight as the anthropogenic emissions are held near the surface, however this increase is less sustained than that of CO₂ due to the additional flux of CO₂ from the biospheric respiration. The small increase in CO concentrations observable between 8:00 - 9:00, when it is otherwise decreasing can likely be attributed to morning rush hour traffic emissions, this was also observed by Beig *et al.*, 2007 in Pune, India and by Lopez *et al.*, 2013 in Paris, France. APO does not exhibit a diurnal cycle at WAO, since the oceanic processes primarily responsible for variations in APO occur on longer timescales, so are not visible on a diurnal timescale.

4.3 High-CO₂ events

A total of 31 high-CO₂ events have been identified over the study period, the occurrence of which are highlighted in Figure 10.

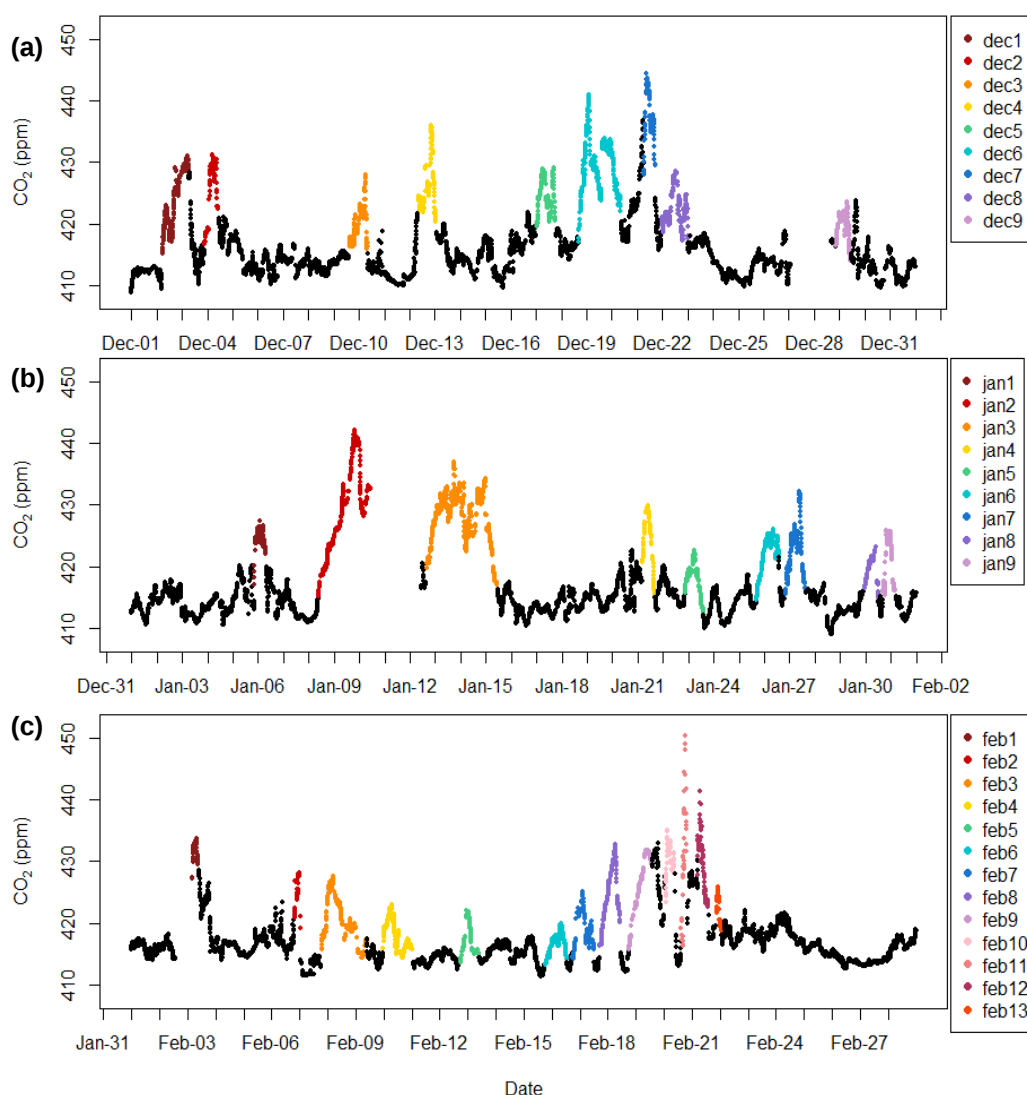


Figure 10. High-CO₂ events identified in (a) December, (b) January, and (c) February. Dec1 refers to the first event in December, dec2 to the second event and so on.

Nine high-CO₂ events have been identified in December, nine in January, and 13 in February. Due to the requirements for event selection outlined in 3.4 some of the identified events do not capture the entire increase and decrease of CO₂ observed (e.g. 'dec1'), due to a change in wind sector which implies a change in CO₂ source.

The longest high-CO₂ event identified is jan3, with a duration of 66 hours and 15 minutes; the shortest event is feb2, with a duration of 4 hours and 30 minutes. The range of CO₂ concentration also varies between the identified events, feb1 has the smallest range of 6.7 ppm and feb11 has the largest range of 34.1 ppm. Although feb2 has the smallest range of CO₂ concentrations of any identified high-CO₂ event, it does not have the lowest peak; the small range is due to a gap in observations at the beginning of the event, and a change in wind direction leading to the decrease in CO₂ not being included in the high-CO₂ event analysis. The event with the lowest peak in CO₂ concentration is feb6, with a maximum concentration of 420 ppm. For a full list of start and end times and CO₂ concentration ranges for all high-CO₂ events refer to Appendix 1.

4.4 Wind speed and direction

It is evident from Figure 11a that the dominant wind sector is during the study period, is WSW followed by W, with over 40% of observations coming from these sectors. There is very little contribution from the direction of the ocean (330° - 90°), which is a source of unpolluted air. When considering wind speed during the high-CO₂ events only (Figure 11b), there is even less influence from the ocean and over 50% of observations during these events come from the WSW and SSW. This is indicative of the transport of polluted air masses from London and industrial cities in the Midlands to WAO. Wind directions recorded at the instant a measurement is taken are not indicative of the full history of the air mass arriving at that point in time, thus the HYSPLIT back trajectories are used to provide a full history (see Section 4.7 below); however, it can be seen that there are differences in concentrations arriving from different wind directions (Figure 11c and 11d).

Overall, there is a fairly even distribution of wind speeds between 2 to 12 m/s, with fewer speeds below 2 and above 12 m/s (Figure 11a). During the high-CO₂ events, however, there are no wind speeds above the 95th percentile for the entire study period (12.9 m/s, Table 2, Section 4.1), and few observations over 8 m/s, indicating that higher CO₂ concentrations occur at lower wind speeds. This can also be seen in Figure 12c where the highest concentrations of CO₂ occur at lower wind speeds (< 5 m/s), and in Figure 12d where the highest concentrations during high-CO₂ events occur predominantly during wind speeds are less than 5 m/s. The occurrence of higher CO₂ concentrations at lower wind speeds suggests that the

observed increase high-CO₂ events are due to local events, rather than long-range transport (Gamnitzer *et al.*, 2006).

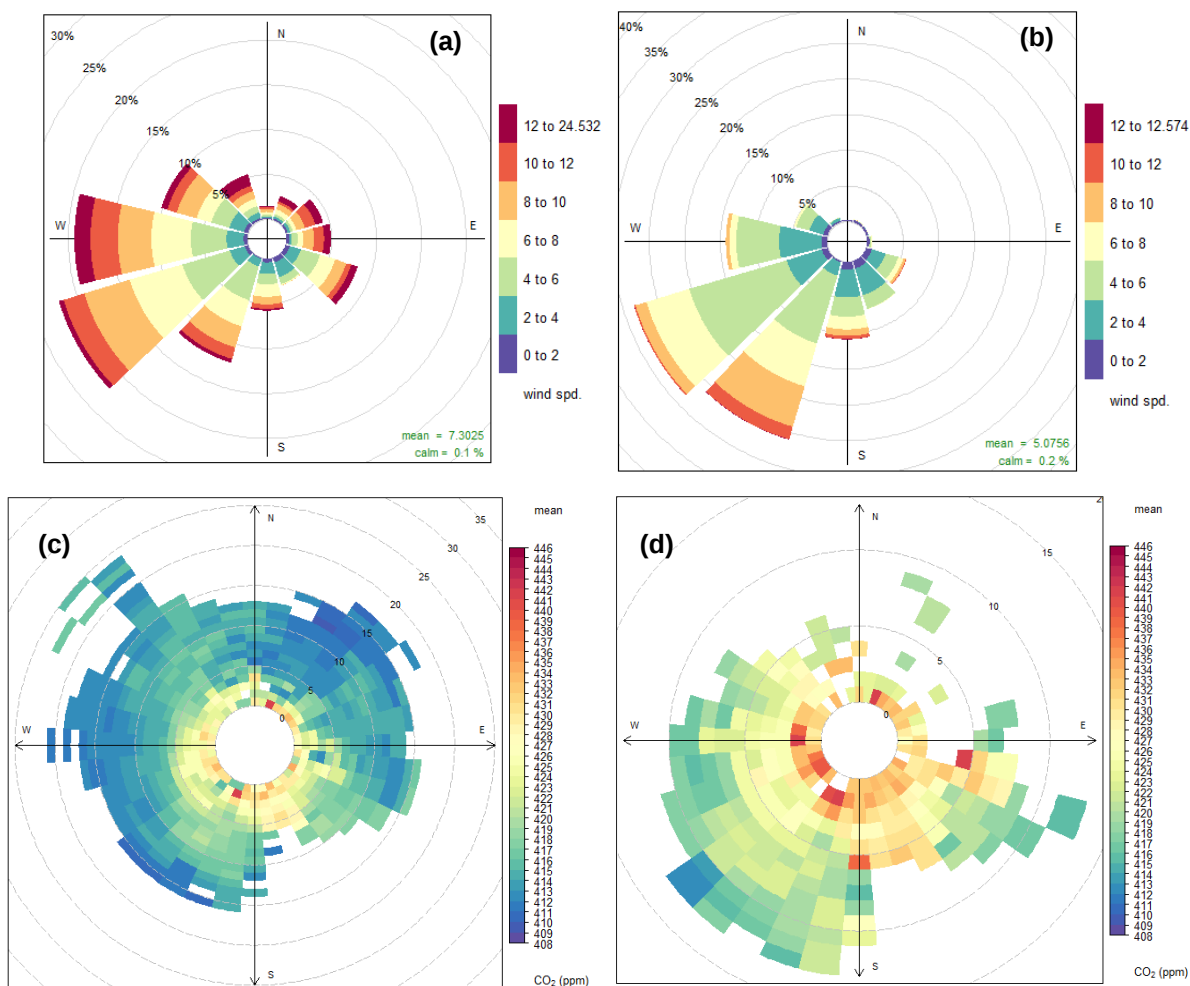


Figure 11. Wind roses displaying the frequency (%) of wind speeds experienced for each wind direction for **(a)** the entire study period and **(b)** during high-CO₂ events and Polar frequency plots displaying the mean concentration of CO₂ for **(c)** the entire study period and **(d)** during high-CO₂ events. Note the change in scale for the radial axis.

4.5 Separation of CO₂ sources using O₂, APO, CO and O₃

During each high-CO₂ event, the concurrent observations of CO, O₂, APO, and O₃ were first investigated visually. In order to quantify these relationships, and easily present the large number of events, the correlation between each species and CO₂ is described by the correlation coefficient, with the exception O₃ of which was compared to O₂ due to the strong correlation of O₂ and O₃ that has been observed at WAO (Table 3). Table 3 also presents the OR of O₂:CO₂ (Figure 12) and APO:CO₂ during each high-CO₂ event. The average molar O₂:CO₂ OR of all events is -1.40 mol mol⁻¹, the same as value cited as the global weighted

mean OR for fossil fuel combustion (Steinbach *et al.*, 2011); thus strongly indicating that these events are a result of emissions from anthropogenic combustion of fossil fuels, and not terrestrial biosphere processes. The OR does, however, have a large variability between high-CO₂ events with a range of -1.04 to -1.62 mol mol⁻¹.

Table 3. Slope and correlation coefficient from simple linear regression for the relationship between O₂ and CO₂, CO and CO₂, and O₃ and O₂ during high-CO₂ events. No CO observations were available during 'feb2'.

Event	O₂:CO₂		APO:CO₂		CO:CO₂	O₃:O₂
	<i>mol mol⁻¹</i>	<i>r</i>	<i>mol mol⁻¹</i>	<i>r</i>	<i>r</i>	<i>r</i>
<i>dec1</i>	-1.48 ± 0.01	-1.00	-0.38 ± 0.01	-0.95	0.90	0.86
<i>dec2</i>	-1.37 ± 0.05	-0.94	-0.27 ± 0.05	-0.48	0.88	0.89
<i>dec3</i>	-1.40 ± 0.02	-0.99	-0.30 ± 0.02	-0.83	0.89	0.47
<i>dec4</i>	-1.62 ± 0.02	-0.99	-0.53 ± 0.02	-0.92	0.93	0.95
<i>dec5</i>	-1.40 ± 0.04	-0.94	-0.30 ± 0.04	-0.52	0.74	0.89
<i>dec6</i>	-1.59 ± 0.01	-0.99	-0.49 ± 0.01	-0.91	0.85	0.89
<i>dec7</i>	-1.22 ± 0.02	-0.98	-0.11 ± 0.02	-0.43	0.79	0.78
<i>dec8</i>	-1.39 ± 0.03	-0.94	-0.29 ± 0.03	-0.51	0.58	0.84
<i>dec9</i>	-1.42 ± 0.02	-0.99	-0.32 ± 0.02	-0.82	0.87	0.87
<i>jan1</i>	-1.52 ± 0.03	-0.98	-0.42 ± 0.03	-0.81	0.87	0.82
<i>jan2</i>	-1.34 ± 0.01	-1.00	-0.24 ± 0.01	-0.90	0.96	0.95
<i>jan3</i>	-1.35 ± 0.01	-0.98	-0.25 ± 0.01	-0.63	0.81	0.80
<i>jan4</i>	-1.44 ± 0.03	-0.98	-0.34 ± 0.03	-0.75	0.95	0.97
<i>jan5</i>	-1.37 ± 0.02	-0.99	-0.24 ± 0.02	-0.75	0.77	0.37
<i>jan6</i>	-1.42 ± 0.01	-0.99	-0.32 ± 0.01	-0.88	0.70	0.93
<i>jan7</i>	-1.50 ± 0.04	-0.94	-0.39 ± 0.04	-0.60	0.86	0.68
<i>jan8</i>	-1.26 ± 0.03	-0.97	-0.16 ± 0.03	-0.47	0.52	0.95
<i>jan9</i>	-1.59 ± 0.03	-0.98	-0.49 ± 0.03	-0.84	0.80	0.97
<i>feb1</i>	-1.46 ± 0.04	-0.98	-0.36 ± 0.04	-0.80	0.44	0.35
<i>feb2</i>	-1.17 ± 0.02	-0.99	-0.08 ± 0.02	-0.47	-	0.86
<i>feb3</i>	-1.45 ± 0.01	-0.98	-0.35 ± 0.01	-0.80	0.92	0.91
<i>feb4</i>	-1.38 ± 0.03	-0.96	-0.28 ± 0.03	-0.56	0.58	0.91
<i>feb5</i>	-1.55 ± 0.03	-0.98	-0.45 ± 0.03	-0.82	0.82	0.83
<i>feb6</i>	-1.30 ± 0.04	-0.93	-0.20 ± 0.04	-0.38	0.64	0.89
<i>feb7</i>	-1.49 ± 0.04	-0.95	-0.39 ± 0.04	-0.63	0.61	0.80
<i>feb8</i>	-1.43 ± 0.02	-0.99	-0.33 ± 0.02	-0.85	0.61	0.96
<i>feb9</i>	-1.21 ± 0.01	-0.99	-0.10 ± 0.01	-0.52	0.84	0.97
<i>feb10</i>	-1.04 ± 0.03	-0.97	0.06 ± 0.03	0.23	0.59	0.32
<i>feb11</i>	-1.47 ± 0.01	-1.00	-0.37 ± 0.01	-0.97	0.86	0.80
<i>feb12</i>	-1.24 ± 0.01	-1.00	-0.14 ± 0.01	-0.77	0.38	0.63
<i>feb13</i>	-1.57 ± 0.03	-0.99	-0.47 ± 0.03	-0.92	0.90	0.94

The $O_2:CO_2$ OR of fossil fuel combustion is in the range of -1.17 to -2.00, depending on fuel type; solid fuels have a typical OR of -1.17 mol mol⁻¹, liquid fuels are in the range of -1.39 to -1.44 mol mol⁻¹, gasoline -1.52 to -1.56 mol mol⁻¹, and natural gas -1.83 to -2.00 mol mol⁻¹ (Keeling, 1988). These ranges are displayed in Figure 12 along with the $O_2:CO_2$ ORs obtained for each high- CO_2 event.

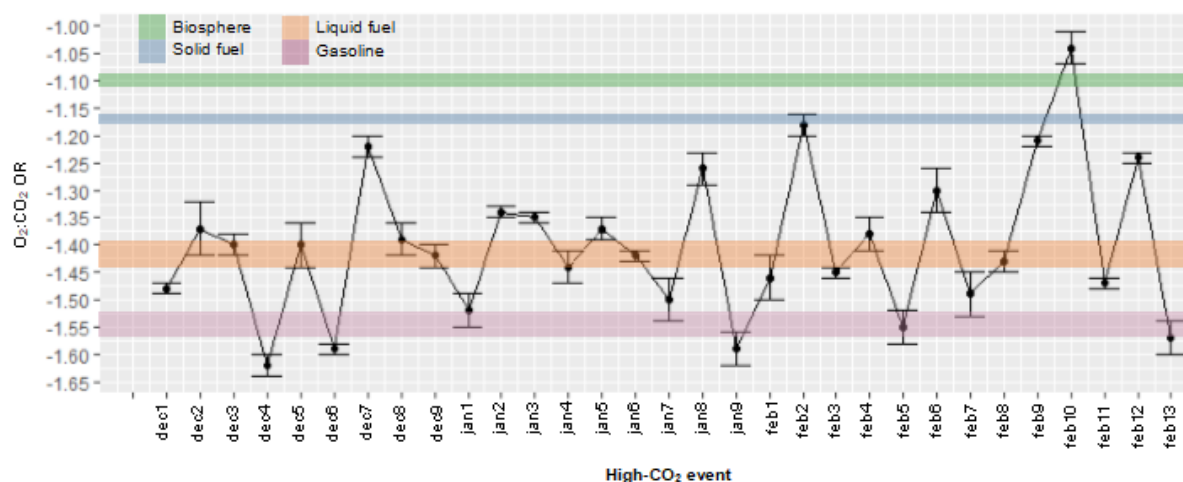


Figure 12. $O_2:CO_2$ OR ($\pm$ SE). Shaded boxes indicate the $O_2:CO_2$ OR ranges for different fuel types. Note, the range of $O_2:CO_2$ ORs for natural gas (-1.83 to -2.00) are not displayed on this scale.

The observations during the high- CO_2 events dec1 and dec2 are displayed in Figure 13. Due to the large number of events, these high- CO_2 events will be used to illustrate the process of determination of the CO_2 source for all high- CO_2 events. From Figure 13 it is evident that during the high- CO_2 events dec1 and dec2, there is a simultaneous increase in CO concentration ($r = 0.86$ and $r = 0.89$ respectively), indicating an anthropogenic origin due to CO being co-emitted with CO_2 as a result of incomplete combustion of fossil fuels (Khalil and Rasmussen, 1990). The simultaneous decrease in APO (dec1: $r = -0.95$ and dec2: $r = -0.48$ respectively) further supports this, as APO is not influenced by the terrestrial biosphere (Severinghaus, 1995). The lower correlation coefficient for dec2 than dec1 may be, in part, attributable to increased noise in the APO observations (Figure 13). Furthermore, the $O_2:CO_2$ OR for dec1 (-1.48 ± 0.01 , $r = -1.00$) and dec2 (-1.37 ± 0.05 , $r = -0.94$) indicate a ff CO_2 source. The OR of dec2 is slightly higher (less negative) to that of the range of liquid fuel, thus it is likely that the main CO_2 source during this event is liquid fuel, with a minor influence from solid fuel. Dec1 is between the range for liquid fuel and gasoline; although the event-selection requirements reduced the likelihood of a changing fuel mix, this cannot be completely removed as even in one geographic location the fuel mix can vary. Therefore it is likely that the OR obtained for dec1 is from a combined source of predominantly liquid fuel with a contribution from natural gas or gasoline lowering the $O_2:CO_2$ OR. Finally, the $O_3:O_2$ correlation is strongly positive

during these two events (dec1: $r = 0.86$; dec2 $r = 0.89$), which can likely be attributed to the removal of O_3 by NO produced during fossil fuel combustion, again indicating a ffCO₂ source.

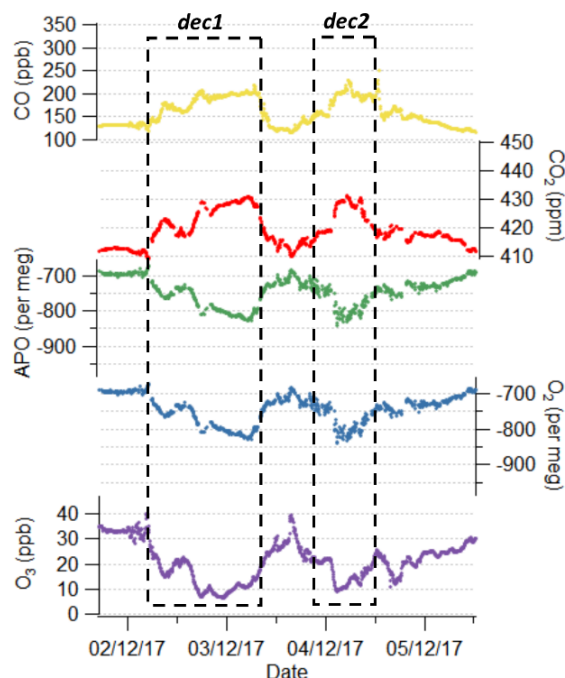


Figure 13. CO, CO₂, APO, O₂, and O₃ observations during the high-CO₂ events ‘dec1’ and ‘dec2’.

As is the case with dec1 and dec2, the O₂:CO₂ OR calculated for all high-CO₂ events, with the exception of feb10 (which is discussed in Section 4.5.1 below), are within the range of ffCO₂ ORs. Furthermore, the APO:CO₂ OR for every event, except feb10, is also within the range of ffCO₂. The concentration of CO also rises concurrently with every high-CO₂ event, indicated by a positive r value (Table 3), thus further supporting the conclusion of an anthropogenic CO₂ source, as fossil fuel combustion is a major source of CO into the atmosphere (Table 4). Satar *et al.* (2016) and Oney *et al.* (2017) also reported a strong correlation between CO and CO₂ during the winter, suggesting that the influence from biospheric fluxes are minor and regional CO₂ is dominated by collocated anthropogenic emissions of CO and CO₂.

Feb2 is the only high-CO₂ event within the O₂:CO₂ OR range of solid fuels, seven events (22.58%) are within the range of liquid fuels, and two events (6.45%) are within the OR range of gasoline combustion (Figure 12). The O₂:CO₂ ORs of the remaining events sit between the ranges of the different fuel types, there are nine events between solid and liquid fuels, seven events between liquid fuel and gasoline, and four events between gasoline and natural gas (Figure 12). Again, although the likelihood of a varying source mix was minimised during event selection, the O₂:CO₂ ORs obtained indicate a combination of fuel types. It is probable that events that sit between the ranges of differing fuel types, particularly those with an OR of less

than $-1.5 \text{ mol mol}^{-1}$ are the result of a varying source mix, with natural gas contributions reducing the observed $\text{O}_2:\text{CO}_2$ ORs. This contribution from natural gas lowering the observed $\text{O}_2:\text{CO}_2$ ORs is assumed due to the increased use of natural gas in the winter energy mix in order to meet increased energy demand for heating, with 2017 exhibiting a growth in natural gas demand in Europe (Oxford Institute for Energy Studies, 2018)..

4.5.1 Feb10 – a biospheric event?

Feb10 has an $\text{O}_2:\text{CO}_2$ OR of $-1.04 \text{ mol mol}^{-1}$, and $\text{APO}:\text{CO}_2$ OR of $0.06 \text{ mol mol}^{-1}$. The $\text{APO}:\text{CO}_2$ OR for terrestrial biosphere processes is around zero, as APO was derived to be conservative with respect to the terrestrial biosphere (Stephens *et al.*, 1998). The average global weighted $\text{O}_2:\text{CO}_2$ OR is -1.1 for all terrestrial biosphere processes (Severinghaus, 1995), however other studies have obtained values as low as that obtained for feb10 of -1.0 , -1.03 , and -1.04 (Seibt *et al.*, 2004; Masiello *et al.*, 2008; Worrall *et al.*, 2013 respectively). This event is also associated with very low wind speeds, which are also suggestive of local CO_2 flux (Figure 14a); however, the concurrent rise in CO ($r = 0.59$) raises doubts regarding the attribution of this high- CO_2 event to the biosphere, as CO production is not associated with terrestrial biosphere respiration (Stephens *et al.*, 1998). The observations from this event are presented in Figure 14b.

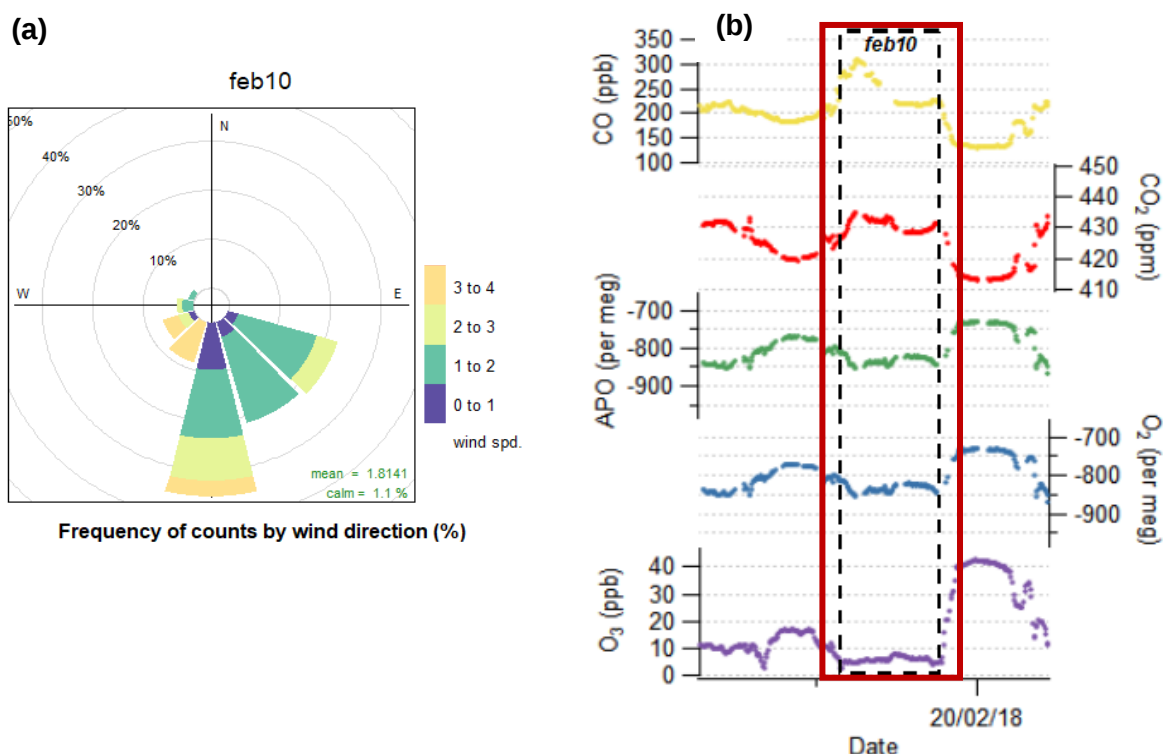


Figure 14. (a) Wind rose for feb10. **(b)** CO, CO₂, APO, O₂, and O₃ observations during the high-CO₂ event feb10. The Dashed black box indicates high-CO₂ event period and the solid red box indicates the adjusted event period capturing the entire increase and decline in CO₂ concentration.

From Figure 14b It is evident that there is a decrease in APO and O₃ during feb10, and a significant increase in the concentration of CO. The decrease in APO in particular is a clear indication that this event is not biospheric, due to APO being conservative with respect to the terrestrial biosphere (Stephens *et al.*, 1998). Due to the start and end times used in the analysis, and the shape of the event which plateaus rather than spikes, the resultant O₂:CO₂ OR is not representative of the event. When the start and end times of the event are adjusted to capture the increase and decline in CO₂ concentration (indicated by the red box in Figure 13b), rather than just the plateau, the O₂: CO₂ OR decreases to -1.21, indicative of solid fuel, with a small contribution from a fuel type with a lower O₂:CO₂ OR. It is thus, unlikely that this event is due to biospheric processes. This event illustrates the importance of a multi-tracer, as if the O₂:CO₂ OR had been investigated alone, this event may have been attributed to a biospheric source. A keeling plot could again add to the certainty in this conclusion, however no $\delta^{13}\text{C}$ -CO₂ observations are available for this period (see Section 4.6).

4.6 Separation of CO₂ sources using $\delta^{13}\text{C}$ -CO₂ – Keeling plot method

A Keeling plot was created for each high-CO₂ event (e.g. Figure 15, for all Keeling plots see Appendix 2), the results of which are summarised in Table 4. There was no $\delta^{13}\text{C}$ -CO₂ data available for the events 'dec8', 'jan5', or 'feb6' to 'feb14', thus the sources of CO₂ during these events could not be investigated through the use of a Keeling plot.

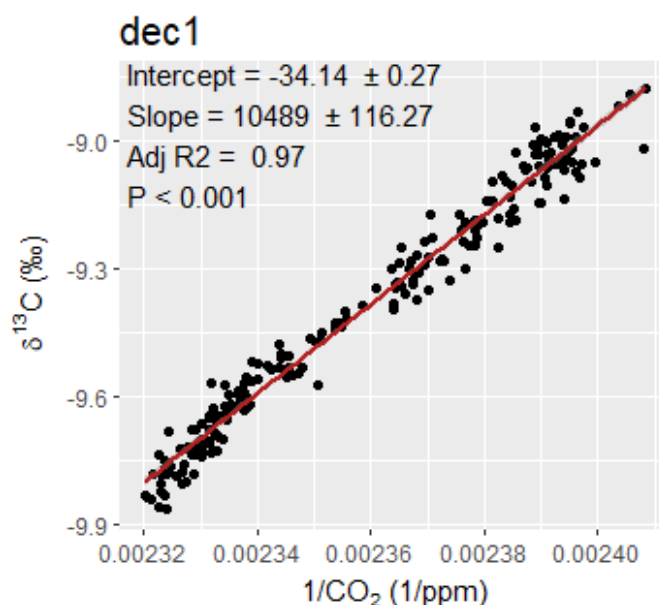


Figure 15. Keeling plot for the high-CO₂ event 'dec1'. The intercept value indicates the isotopic signature of the CO₂ source ($\delta^{13}\text{C}_s$).

The results of the Keeling plots are displayed in Figure 16 and summarised in Table 4. With the exception of jan1, feb1 and feb2, all of the Keeling plot regressions have an r^2 value greater

than 0.94, indicating a good fit. This lower r^2 value for jan1, feb1, and feb2 is likely due to a smaller number of observations being used to construct these Keeling plots resulting from the short duration and small range of CO₂ concentration during these high-CO₂ events (see Appendix 1). All linear regressions were significant ($P < 0.001$). Following Vardag *et al.* (2016) an error of the intercept of greater than 2‰ would indicate a changing source mix during the event; feb2 is the only event with an error greater than 2‰, however as previously stated, this is can be attributed to the smaller number of observations, rather than a changing source mix.

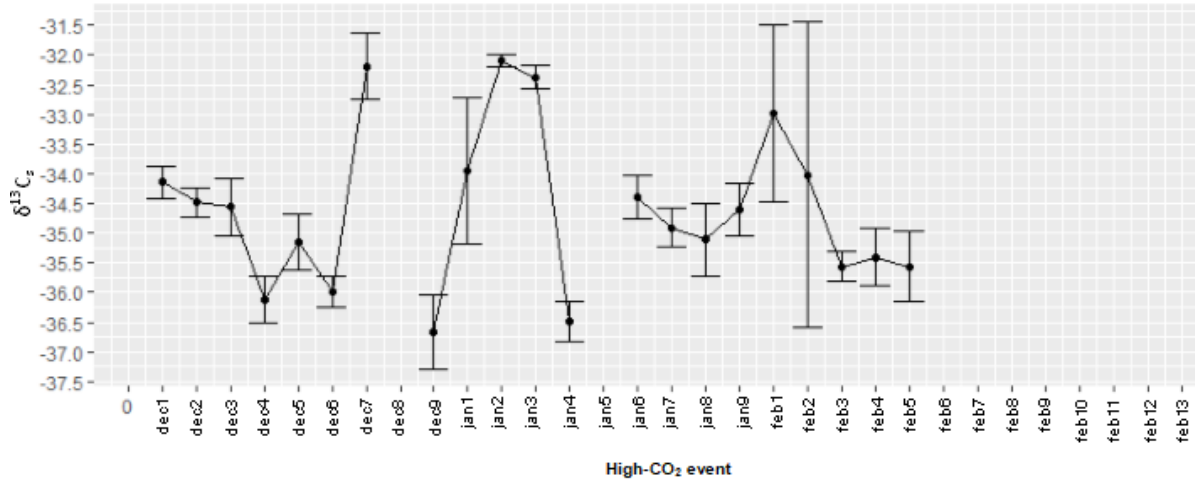


Figure 16. Isotopic source signature $\delta^{13}C_s (\pm SE)$ of all high-CO₂ events with available $\delta^{13}C$ -CO₂ observations.

Tans (1981 in Lopez *et al.*, 2013) estimated that the release of CO₂ from anthropogenic combustion implies an average worldwide $\delta^{13}C$ -CO₂ isotopic source signature for natural gas, liquid, and solid fuels of -41.0‰, -26.5‰, and -24.1‰ respectively. Additionally, in a study during winter in Paris, Lopez *et al.* (2013) reported an intercept value of -36.1 ± 2.7 ‰, and attributed this to increased natural gas combustion. The $\delta^{13}C_s$ value obtained from the Keeling plots for every high-CO₂ event are closest of that of a natural gas source, with the exception of dec7, jan2, jan3, and feb1 which are closer to that of liquid fuel (Table 4, Figure 16). As with the O₂:CO₂ OR values, it is likely that there is a varying source mix during these events, however, the depletion of the $\delta^{13}C_s$ values indicate a far greater contribution from natural gas than the O₂:CO₂ ORs. However, a natural gas source is not improbable due to the aforementioned increased usage of natural gas in Europe during winter, from increases in energy demand from heating. Bakwin and Tans (1998) also found that in winter, when the CO₂ source is dominated by fossil fuels, the isotopic source signature of high-CO₂ events is likely to be lighter (more negative) than in summer, when biological processes dominate. Pataki *et al.* (2003b) and Vardag *et al.* (2006) also reported depleted $\delta^{13}C_s$ values in the winter in

Heidelberg and Salt Lake City respectively, associated with increased combustion of natural gas.

Table 4. Intercept ($\pm$ SE), slope ($\pm$ SE), and adjusted r^2 values computed from the Keeling plot produced for each high-CO₂ event in Figure 10 with corresponding $\delta^{13}\text{C}$ -CO₂ observations available.

Event	Intercept (‰)	r^2
<i>dec1</i>	-34.14 $\pm$ 0.27	0.97
<i>dec2</i>	-34.48 $\pm$ 0.25	0.98
<i>dec3</i>	-34.56 $\pm$ 0.49	0.94
<i>dec4</i>	-36.12 $\pm$ 0.39	0.97
<i>dec5</i>	-35.15 $\pm$ 0.47	0.95
<i>dec6</i>	-35.99 $\pm$ 0.25	0.97
<i>dec7</i>	-32.19 $\pm$ 0.56	0.94
<i>dec9</i>	-36.67 $\pm$ 0.63	0.94
<i>jan1</i>	-33.95 $\pm$ 1.24	0.81
<i>jan2</i>	-32.10 $\pm$ 0.11	0.99
<i>jan3</i>	-32.37 $\pm$ 0.19	0.96
<i>jan4</i>	-36.48 $\pm$ 0.34	0.98
<i>jan6</i>	-34.40 $\pm$ 0.37	0.96
<i>jan7</i>	-34.91 $\pm$ 0.32	0.97
<i>jan8</i>	-35.11 $\pm$ 0.62	0.94
<i>jan9</i>	-34.60 $\pm$ 0.44	0.97
<i>feb1</i>	-32.98 $\pm$ 1.50	0.82
<i>feb2</i>	-34.02 $\pm$ 2.58	0.68
<i>feb3</i>	-35.56 $\pm$ 0.25	0.97
<i>feb4</i>	-35.41 $\pm$ 0.48	0.94
<i>feb5</i>	-35.56 $\pm$ 0.58	0.95

Although the attribution of the high-CO₂ events identified in this study to a natural gas source is supported by the literature, it does not correspond with the sources identified in Section 4.5 from the O₂:CO₂ OR, this is discussed in detail in Section 4.8 below.

4.7 HYSPLIT back trajectories

The air masses containing the high-CO₂ events originate from many regions. The 96-hour HYSPLIT back trajectories for each high-CO₂ event were clustered based on the origin of the air mass are displayed in Figure 17. 48.39% of events are in cluster 1 (C1) which originates from North Atlantic, Canada and Greenland, 9.68% in cluster 2 (C2) which originates from Scandinavia, 22.58% in cluster 3 (C3) originating from the Atlantic, and 19.35% in cluster 4 (C4) originating from central Europe.

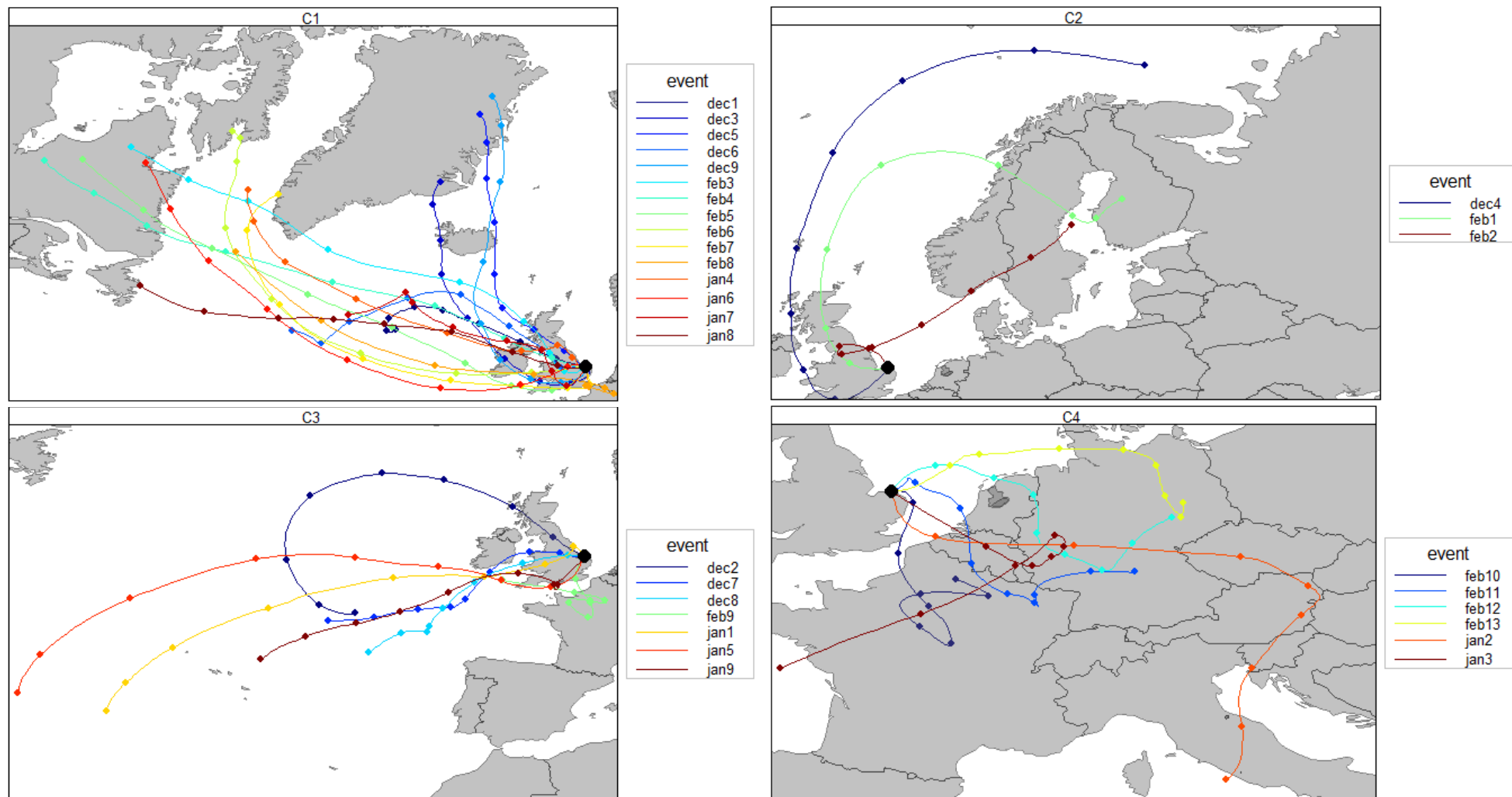


Figure 17. HYSPLIT 96-hour back trajectories for the high-CO₂ events identified in Figure 10, clustered by air mass origin. Black dot represents the location of WAO, and the dots on each back-trajectory represent 12 hours.

In order to determine the influence of air mass origin on the CO₂ source, the difference in $\delta^{13}\text{C}_s$ and OR values (Figure 18) between the clusters was analysed using a one-way ANOVA and post-hoc Tukey test. There is a significant difference between the $\delta^{13}\text{C}_s$ values of C1, C2 and C3 (Figure 18a) at the 0.95 significance level. Note that C4 only contains two events (jan2 and jan3) for $\delta^{13}\text{C}_s$ due to observation availability thus has too few observations to compare the difference with the other clusters statistically, however, from Figure 18a it can be seen that the $\delta^{13}\text{C}_s$ are substantially higher (less negative) than the other clusters.

There is no significant difference between the O₂:CO₂ OR of C1, C2, and C3, but C4 is significantly different from all other clusters different at the 0.95 significance level (Figure 18b). The lack of difference between C1, C2, and C3 may be due to the clusters representing the origin of the air mass, and not the region which it passed over. In other words, there is no difference between C1, C2 and C3 based on the origin, but all of these clusters pass over industrialised areas of the UK (Figure 17). Conversely, the O₂:CO₂ OR of C4 differs from that of the other clusters as these back trajectories show the air masses passing over the ocean before arriving at WAO, thus the O₂:CO₂ ORs of these air masses are diluted by clean ocean air (Figure 17).

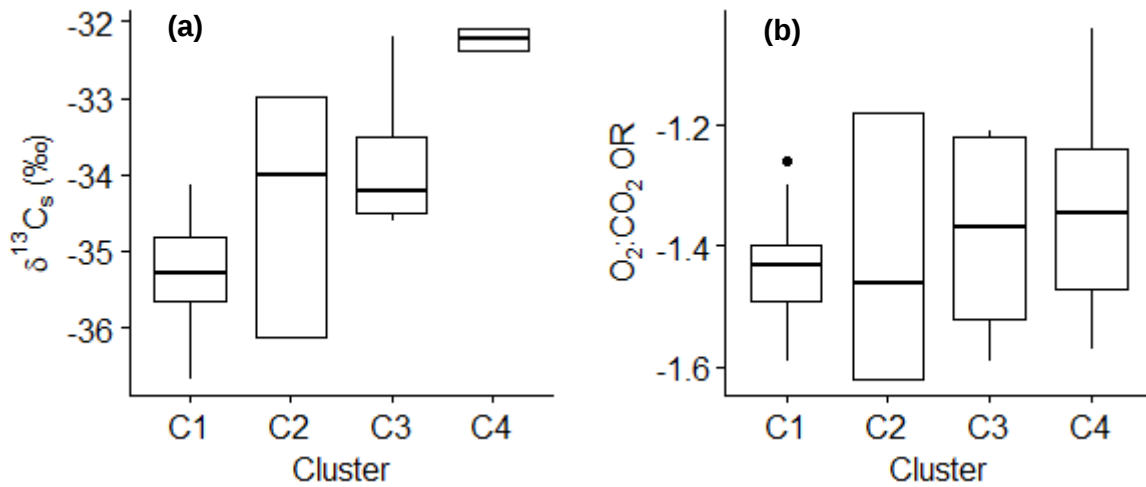


Figure 18. Box plots of (a) $\delta^{13}\text{C}_s$ and (b) O₂:CO₂ OR between HYSPLIT back trajectory clusters.

The air mass for the high-CO₂ event feb10 (discussed in Section 4.5.1 above) originated from Paris, the largest megacity in Europe, with high levels of ffCO₂ emissions (Lopez *et al.*, 2013), then continued over the English Channel, with very little residence time over the local terrestrial biosphere, further cementing the conclusion that this high-CO₂ event is not a result of terrestrial biosphere respiration. The lower O₂:CO₂ OR obtained for this event may be due to the air mass spending 24 hours over the ocean previous to arriving at WAO, as the air mass's OR is diluted by clean ocean air.

The issue with these back trajectories is that these only represents one route which the air mass could have taken, whereas in reality vertical and horizontal mixing will lead to a wide range of source locations at any one time (Ryall *et al.*, 2011). The back trajectory for the peak of the event was also used to represent the entire event, however this should not have a significant impact as a requirement of high-CO₂ event selection was a consistent wind direction.

4.8 Discrepancies between the OR and Keeling plot CO₂ sources

The discrepancy between the CO₂ sources determined by the two methods may be due to uncertainties associated with either method, or more likely a combination of both. The OR and $\delta^{13}\text{C}_s$ values obtained for each event are shown in Figure 19, not only do the values obtained from each method not indicate the same CO₂ source, but the pattern in the values over the events is also different. This section will discuss the possible explanations for these discrepancies.

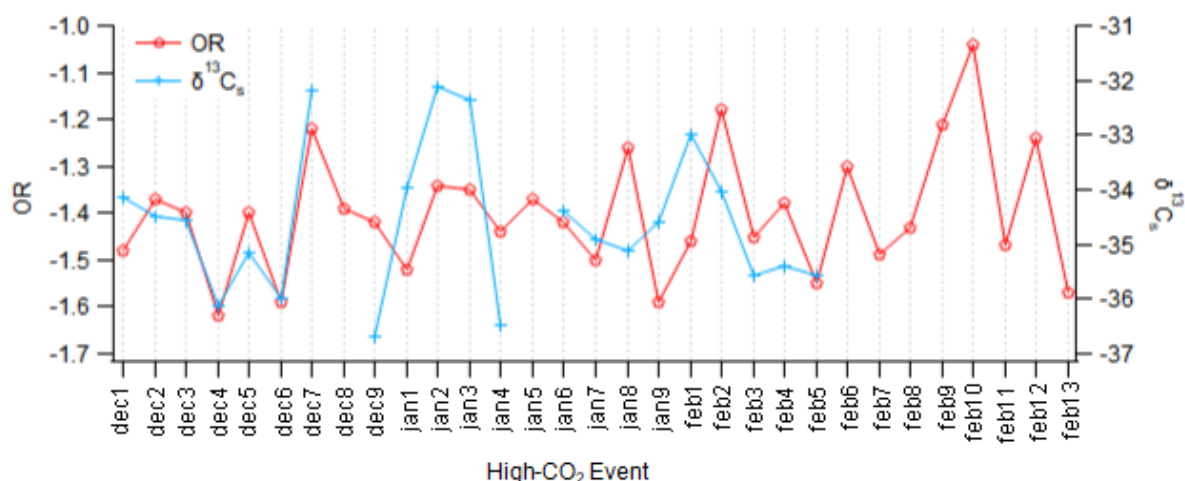


Figure 19. OR and $\delta^{13}\text{C}_s$ values for each high-CO₂ event

There are uncertainties associated with the ORs used as the ratios observed at a measurement site can vary significantly owing to changes in the emission ratios themselves prior to transportation to the measurement site, as well as changes in the atmospheric footprint of the measurement site (Picker, 2016). The composition of different fuel types also changes in both time and space, yet a global average value range from 1988 has been used. However, these are the most widely used values in the reviewed literature and the even the lowest O₂:CO₂ OR obtained in this study is 0.21 mol mol⁻¹ higher than the lower end of the range for natural gas.

The $\delta^{13}\text{C}$ -CO₂ values for different fossil fuel sources used in the analysis from Tans (1981 in Lopez *et al.*, 2013) are worldwide averages for each fuel type, that are invariant with both time

and space. However, different regions have different isotopic source signatures for fuel types, with these signatures varying over time (Andres *et al.*, 2000). This uncertainty in the isotopic source signatures hinders the straightforward determination of the source contribution (Vardag *et al.*, 2016). More recently Andres *et al.* (2000) has shown that the isotopic signature from -19 to -35‰ for liquid fuels, and from -20 to -100‰ for natural gas, dependent on geographic origin. However, Andres *et al.*, (2000) still find the global weighted average $\delta^{13}\text{C-CO}_2$ value to be -26.5‰ for liquid fuels and -44‰ for natural gas. Thus, without a regional value of $\delta^{13}\text{C-CO}_2$, the values obtained for the high- CO_2 events in this study still suggest a natural gas source.

Another potential explanation for the discrepancy between the CO_2 sources determined from the $\text{O}_2:\text{CO}_2$ ORs and the Keeling plots is the regression model used to create the Keeling plots. A least squares linear regression model was used to construct the Keeling plots, this method assumes that the independent variable ($1/\text{CO}_2$) has no errors associated with it, and that errors in the dependent variable ($\delta^{13}\text{C-CO}_2$) are unrelated to the independent variable (Zobitz *et al.*, 2006). These assumptions are not true, which may lead to bias in the model, however Zobitz *et al.*, (2006) concluded that the least squares linear regression produces unbiased estimates of $\delta^{13}\text{C}_s$ at all CO_2 concentration ranges. Pataki *et al.* (2003a) also investigated these biases in comparison with models that account for errors in both variables who found that for models with an r^2 value of greater than 0.95 intercept values produced from the different models converge. The r^2 value for the regressions of this study's high- CO_2 events is only significantly lower than 0.95 for jan1, feb1 and feb2, which as previously discussed can be attributed to the lower number of observations included, rather than the model used. The bias in models with an r^2 value of less than 0.95 from using a least square linear regression also *increased* the intercept value by up to 3‰, so would not be an explanation for the depleted values found in this study (Pataki *et al.*, 2003a). The likelihood of a varying source-mix biasing the intercept was also minimised through the event-selection process outlined in Section 3.4; this situation can also usually be identified by an error on the intercept of greater than 2‰ (Vardag *et al.*, 2016); this is only the case for one event (feb2), which was determined to be an effect of a shorter event duration. A varying source mix was, however, determined for some events, thus this may contribute towards the discrepancies found.

Due to the increased demand for heat over the winter months, and the lower $\delta^{13}\text{C}_s$ values obtained in previous studies over the winter months (e.g. Pataki *et al.*, 2003b; Vardag *et al.*, 2006; Lopez *et al.*, 2013), it is probable that a larger proportion of the high- CO_2 events are due to natural gas combustion than indicated by the $\text{O}_2:\text{CO}_2$ ORs. What can be said for certain is that all of the high- CO_2 events observed at WAO in winter can be attributed to ffCO_2 .

4.9 O₃ O₂ correlation

A strong correlation between O₂ and O₃ has been observed at WAO and can be seen during the three-month period of this study. The correlation between these species has not been discussed in the current literature for any observation site. The daily correlation (00:00 ± 12 hours) of O₂ and O₃ has been calculated over the entire study period using the correlation coefficient (r), these are displayed in Figure 20. The r values and slope of the 10 most strongly positively correlated and 10 least strongly positively correlated 24 hour periods are displayed in Table 5; there are only three periods over which O₃ and O₂ display a negative correlation.

Table 5. Correlation coefficients (r) and slope of the 10 most and 10 least positive correlation periods of O₃:O₂.

	Date	r	slope
10 Strongest Positive Correlation Periods	14/01/2018 12:00 – 15/01/2018 12:00	0.98	1.01
	18/02/2018 12:00 – 19/02/2018 12:00	0.98	1.00
	11/12/2017 12:00 – 12/12/2017 12:00	0.98	1.22
	08/01/2018 12:00 – 09/01/2018 12:00	0.98	1.11
	24/01/2018 12:00 – 25/01/2018 12:00	0.98	1.64
	12/12/2017 12:00 – 13/12/2017 12:00	0.98	0.83
	17/02/2018 12:00 – 18/02/2018 12:00	0.98	1.04
	29/01/2018 12:00 – 30/01/2018 12:00	0.97	1.03
	30/01/2018 12:00 – 31/01/2018 12:00	0.97	1.17
	21/12/2017 12:00 – 22/12/2017 12:00	0.97	0.68
10 Least Strongly Positively Correlated Periods	28/01/2018 12:00 – 29/01/2018 12:00	-0.67	-1.34
	25/12/2017 12:00 – 26/12/2017 12:00	-0.30	-0.80
	23/01/2018 12:00 – 24/01/2018 12:00	-0.16	-0.20
	31/12/2017 12:00 – 01/01/2018 12:00	0.23	0.20
	26/02/2018 12:00 – 27/02/2018 12:00	0.26	0.26
	24/02/2018 12:00 – 25/02/2018 12:00	0.34	0.31
	05/12/2017 12:00 – 06/12/2017 12:00	0.47	0.80
	22/02/2018 12:00 – 23/02/2018 12:00	0.59	0.98
	30/12/2017 12:00 – 31/12/2017 12:00	0.59	0.71
	16/01/2018 12:00 – 17/01/2018 12:00	0.60	0.68

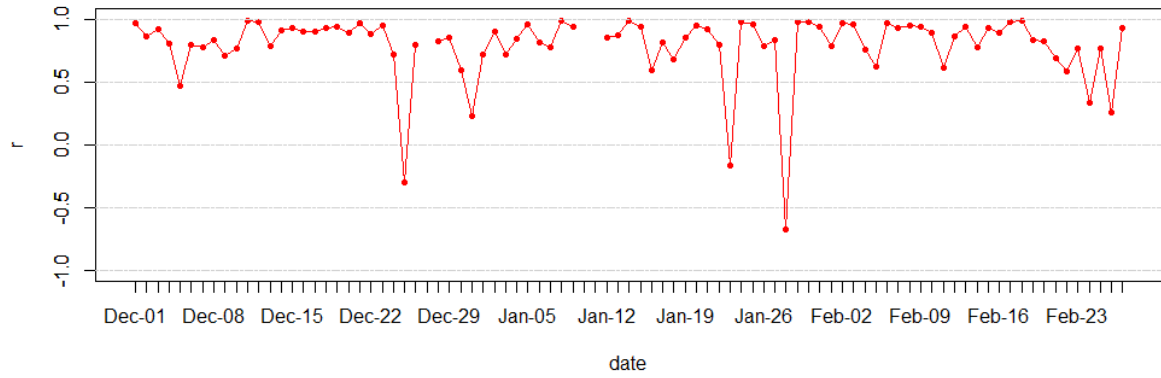


Figure 20. Correlation coefficients (r) for the relationship between O_2 and O_3 . Each point represents the correlation for a 24 hour period from 12:00 on that day until 12:00 the following.

The correlation between O_3 and O_2 is strongest during periods of elevated CO_2 , each of the periods in Table 5 occurs at time of one of the previously identified high- CO_2 events (e.g. Figure 21a, which captures the high- CO_2 event jan3). In contrast, over periods when $O_3:O_2$ correlation is low, the CO_2 is at, or close to, background level (e.g. Figure 21b). The plots for all the correlation periods in Table 5 can be found in Appendices 3 and 4 .

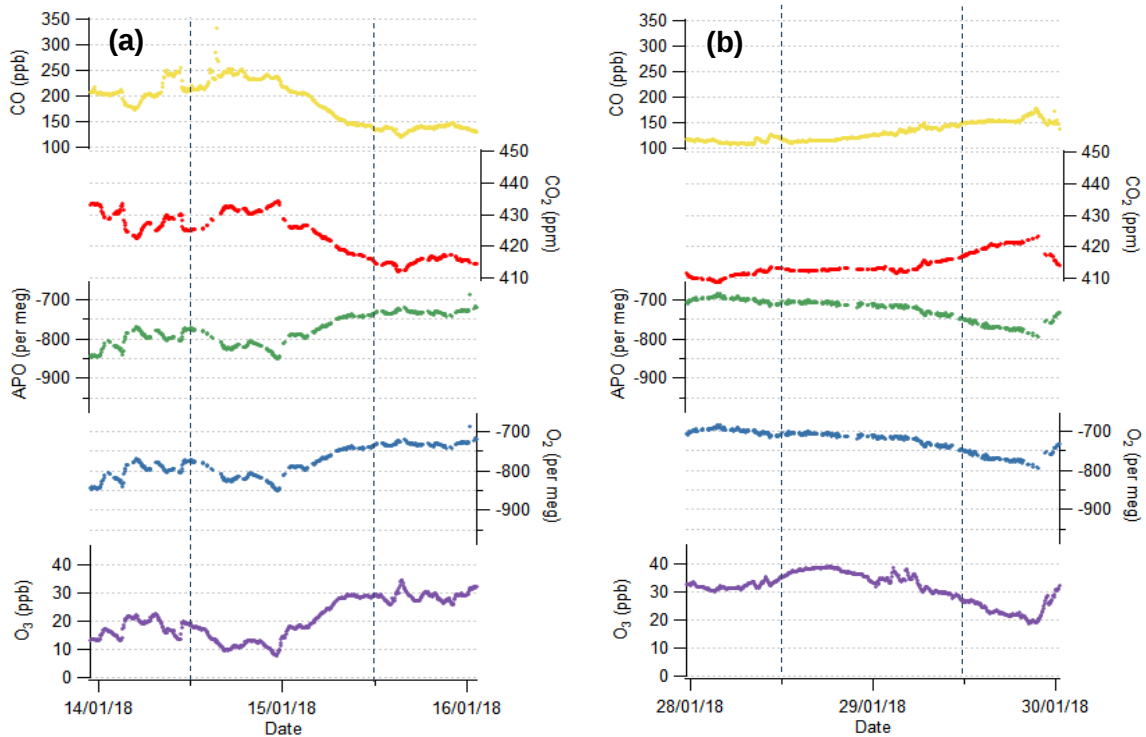


Figure 21. The 24 hour periods with (a) the strongest correlation between O_3 and O_2 observations (14/01/2018 12:00 – 15/01/2018 12:00) and (b) the weakest correlation between O_3 and O_2 observations (28/01/2018 12:00 – 29/01/2018 12:00). 24 hour period indicated by the vertical dashed lines.

The strong correlations observed between O_3 and O_2 during periods of elevated CO_2 concentrations, strongly supports the use of O_3 as a tracer for CO_2 . O_3 could be used the same way as CO, to indicate anthropogenic pollution events, due to anthropogenic emissions suppressing O_3 concentrations. This was shown also displayed in Section 4.5, where O_3 displayed high levels of correlation with O_2 during the high- CO_2 events, when CO was also increasing. Although the correlation between O_3 and O_2 was not discussed, Ferrarese *et al.* (2015) found also that O_3 minima occurred simultaneously to CO and CO_2 peaks, and credited this to anthropogenic emissions. This application of O_3 , however, may not continue into the summer months when ozone production is linked to the photochemical oxidation of CO (Fiore *et al.*, 2002), meaning that as CO is emitted along with ff CO_2 , O_3 will also increase and hence no longer display a strong correlation with O_2 .

5. Conclusion

The aim of this study was to investigate and identify the sources of CO₂ arriving at WAO during high-CO₂ events using a multi-tracer approach. This was achieved through the analysis of the O₂:CO₂ OR, observations of APO, CO and O₃, and the $\delta^{13}\text{C}$ -CO₂ isotopic source signature through the production of Keeling plots. HYSPLIT back trajectories were also created in order to determine the location of the CO₂ sources. A total of 31 high-CO₂ events were identified over the 3-month period investigated. There were some discrepancies between the ffCO₂ sources identified using the $\delta^{13}\text{C}$ -CO₂ values for the production of Keeling plots and the O₂ observations to compute O₂:CO₂ ORs which are likely caused by a combination of biases from each method. Although these discrepancies exist, it can be concluded that the identified high-CO₂ events identified at WAO between December 2017 and February 2018 were dominated by fossil fuel combustion, with little to no influence from terrestrial biosphere. The simultaneous analysis of correlations of APO and CO₂, CO and CO₂, and O₃ and O₂ also increased confidence in these conclusions, and illustrated the importance of the use of multiple tracers for the separation of CO₂ sources, particularly in the case of the high-CO₂ event feb10 which without these additional tracers may have been falsely attributed to terrestrial biosphere processes. O₃ was also presented as a tracer, with the strong positive correlation between O₂ and O₃ during the high-CO₂ events indicating a ffCO₂ source; however, the application of O₃ in this capacity may not continue into the summer months.

5.1 Scope for further research

This study has displayed the benefits of the use of a multi-tracer method when investigating the sources of CO₂ during high-CO₂ events. In addition to the tracers used in this study WAO also measures the atmospheric concentrations of $\delta^{18}\text{O}$ -CO₂, H₂, NO_x, SO₂, N₂O and CH₄. The addition of these observations to the method demonstrated in this study, would add further insight into the sources of CO₂. Additionally, ²²²Rn measurements began in spring 2018; ²²²Rn serves as a quantitative tracer for boundary layer mixing (e.g. Jacob and Prather, 1990; Williams *et al.*, 2011), thus the inclusion of these observations would reduce uncertainty regarding the effects of the diurnal rectifier effect. The investigation into the application of O₃ as a tracer for ffCO₂ should also be extended into the summer, to see if it can still be used in the same capacity. O₃ was also only investigated as an indicator of ffCO₂ sources, the application of this species as a quantitative tracer should be investigated and compared with known methods, as this could contribute towards reducing uncertainties in emission inventories.

6. References

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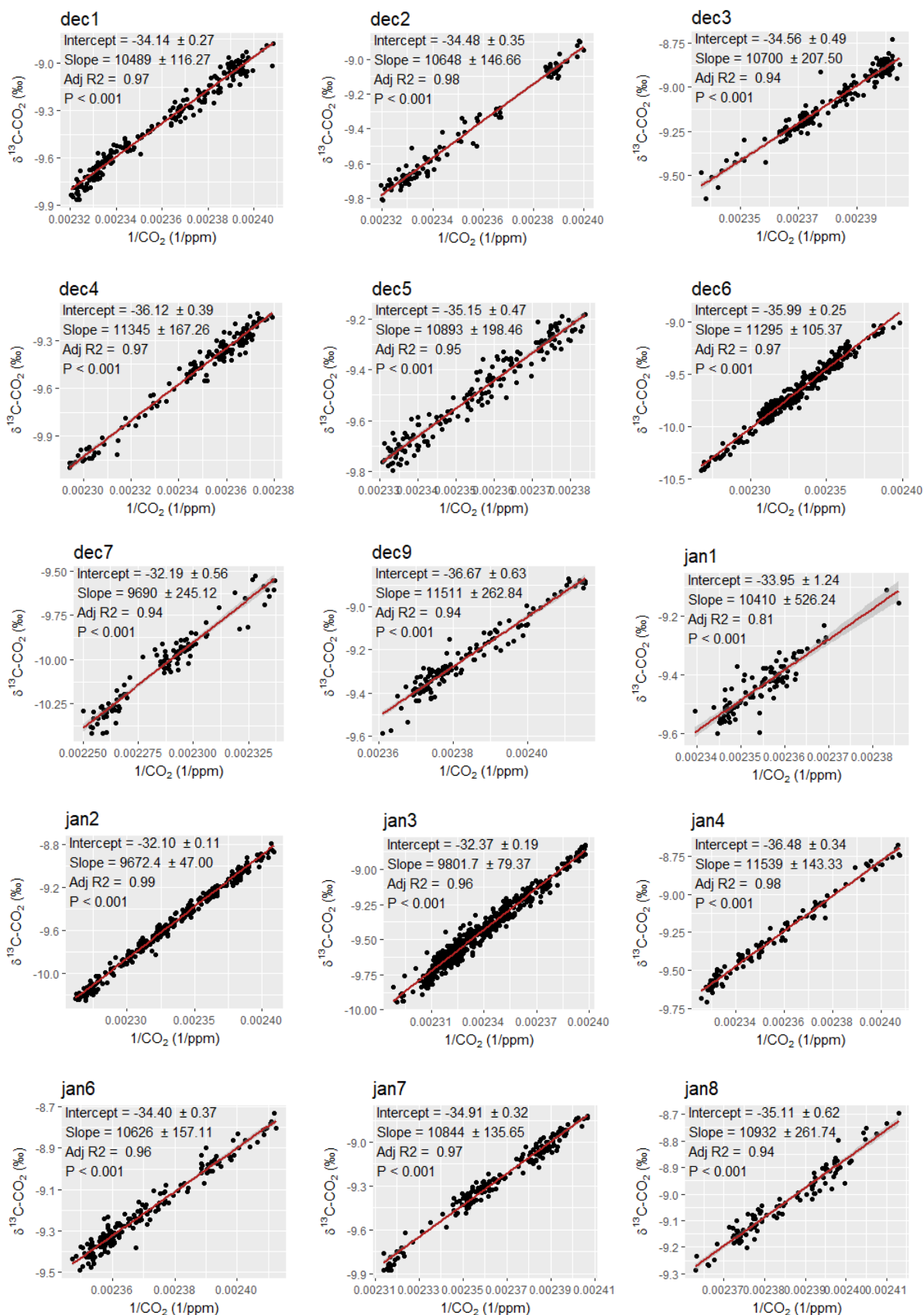
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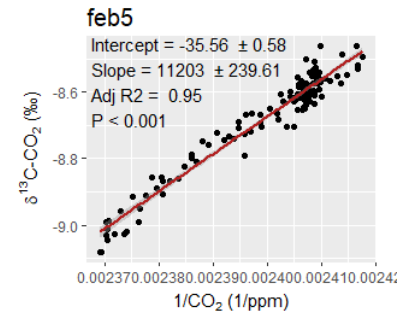
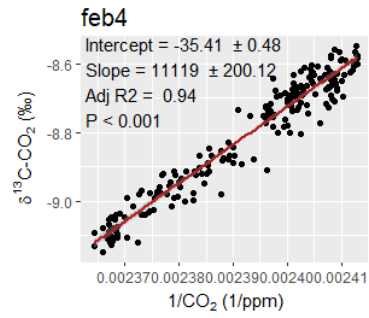
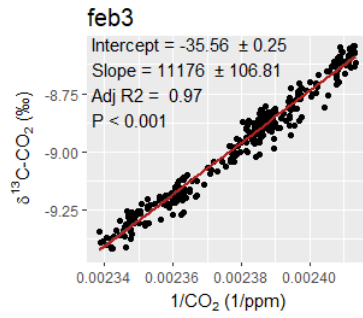
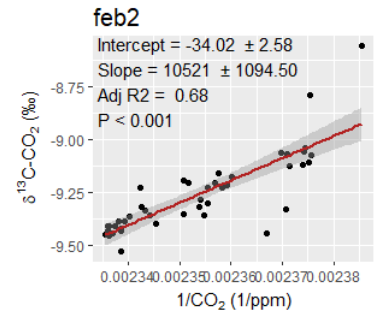
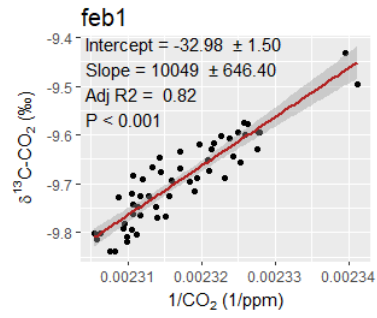
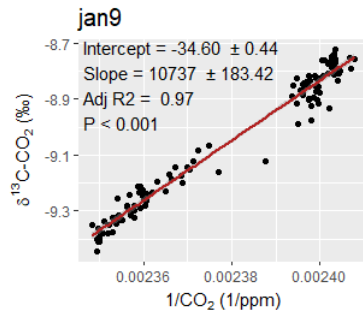
7. Appendices

Appendix 1. Start and end time, and range of CO₂ concentrations observed during each high-CO₂ event

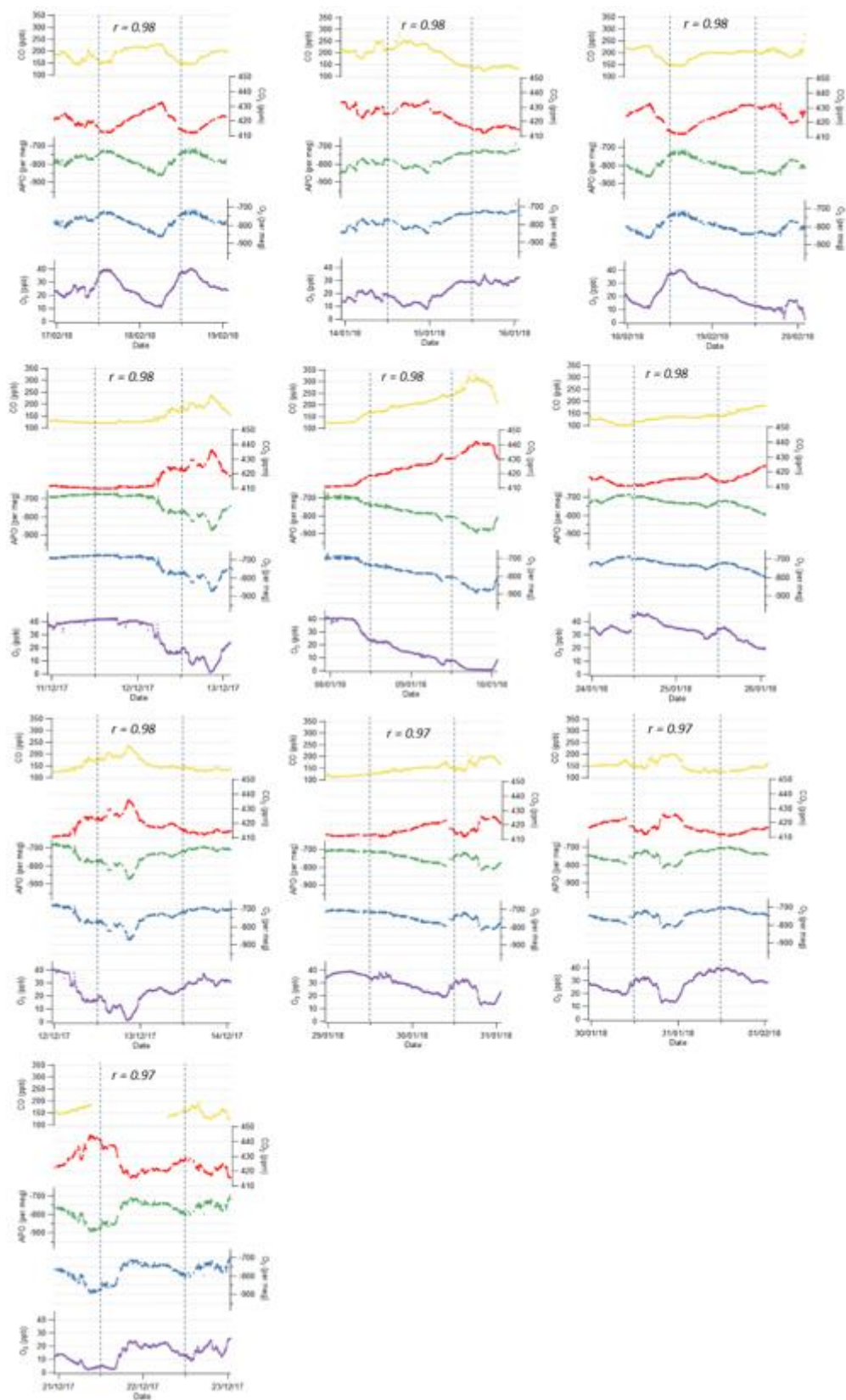
<i>Event</i>	<i>Start</i>	<i>End</i>	<i>[CO₂] range (ppm)</i>
<i>dec1</i>	02/12/2017 05:45	03/12/2017 06:35	15.8
<i>dec2</i>	03/12/2017 21:30	04/12/2017 10:10	14.4
<i>dec3</i>	09/12/2017 15:00	10/12/2017 08:00	12
<i>dec4</i>	12/12/2017 08:30	13/12/2017 01:05	15.6
<i>dec5</i>	17/12/2017 00:40	17/12/2017 18:00	9.6
<i>dec6</i>	18/12/2017 16:35	20/12/2017 08:30	24
<i>dec7</i>	21/12/2017 06:15	21/12/2017 16:50	16.5
<i>dec8</i>	21/12/2017 23:25	23/12/2017 00:05	11.3
<i>dec9</i>	28/12/2017 20:35	29/12/2017 10:35	9.5
<i>jan1</i>	05/01/2018 20:35	06/01/2018 07:45	10.3
<i>jan2</i>	08/01/2018 08:55	10/01/2018 10:10	26.9
<i>jan3</i>	12/01/2018 16:20	15/01/2018 10:35	20
<i>jan4</i>	21/01/2018 04:40	21/01/2018 16:00	14.5
<i>jan5</i>	22/01/2018 20:45	23/01/2018 14:15	10.2
<i>jan6</i>	25/01/2018 16:30	26/01/2018 13:45	11.6
<i>jan7</i>	26/01/2018 19:45	27/01/2018 15:00	16.7
<i>jan8</i>	29/01/2018 23:25	30/01/2018 12:15	8.8
<i>jan9</i>	30/01/2018 16:40	31/01/2018 04:10	10.5
<i>feb1</i>	03/02/2018 03:55	03/02/2018 10:35	6.7
<i>feb2</i>	06/02/2018 20:05	07/02/2018 00:35	8.9
<i>feb3</i>	07/02/2018 19:00	09/02/2018 09:35	13.2
<i>feb4</i>	09/02/2018 23:40	11/02/2018 00:15	8.6
<i>feb5</i>	12/02/2018 17:50	13/02/2018 09:05	8.5
<i>feb6</i>	15/02/2018 18:10	16/02/2018 12:25	6.8
<i>feb7</i>	16/02/2018 17:50	17/02/2018 11:50	10.9
<i>feb8</i>	17/02/2018 17:10	18/02/2018 10:15	16.4
<i>feb9</i>	18/02/2018 18:10	19/02/2018 13:40	16.1
<i>feb10</i>	20/02/2018 01:20	20/02/2018 09:00	11.6
<i>feb11</i>	20/02/2018 14:50	20/02/2018 19:20	34.1
<i>feb12</i>	21/02/2018 05:00	21/02/2018 14:00	18.8
<i>feb13</i>	21/02/2018 20:55	22/02/2018 01:30	7.1

Appendix 2. Keeling plots for all high-CO₂ events





Appendix 3. Species observations during the 10 24 hour periods with the strongest positive correlation between O_3 and O_2 .



Appendix 4. Species observations during 24 hour periods with the least positive correlation between O₃ and O₂.

