

**What can we learn from the analysis of a four year dataset
of atmospheric concentrations of CO₂, O₂, H₂ and CO
from the Weybourne Atmospheric Observatory?**

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I would also like to thank Dr. Zoë Fleming , NCAS Scientist, University of Leicester, for the use of the NAME dispersion model footprints.

It has been as invaluable learning experience for me, seeing the cutting edge of science at first hand and able perform analysis of previously unanalysed data. I now appreciate just how much work is required in achieving the accuracy and precision required not only to produce the atmospheric concentrations of the gases at Weybourne, but to organise and interpret the data. Above all I was made to feel welcome and part of a team. Thank you once again for the experience.

ABSTRACT

This Research Project analyses a four year dataset of carbon dioxide (CO₂) and oxygen (O₂), from Oct2007 to Dec2011 and for carbon monoxide (CO) and hydrogen (H₂) from Mar2008 to Dec2011 from the Weybourne Atmospheric Observatory, Norfolk. I observed a strongly anti-correlated seasonal cycle for CO₂ and O₂ both influenced by the terrestrial biosphere and O₂ possibly affected by oceanic influences, measured by Atmospheric Potential Oxygen (APO). CO₂ is rising at a rate of ~2.1ppm per year and O₂ is falling as a result of fossil fuel combustion. Both H₂ and CO are observed to have strong seasonal cycles with a late winter/early spring maximum. I found their cycle is approximately two months out of phase, due to a dominant soil sink for H₂ in late summer. CO₂ and H₂ show little evidence of trend, only inter-annual variability. There is little suggestion of wind direction dependency of any species until high concentrations are reached; the 99th percentile for CO₂, CO and H₂. CO and H₂ are at their highest concentrations when the wind direction is from London and the continent. CO₂ was highest in the winter, O₂ in the summer. I find evidence to suggest pollution events can be detected.

Keywords:

CO₂, O₂, CO, H₂ and APO

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1.0 INTRODUCTION:

The Earth's climate is very sensitive to atmospheric concentrations of certain gases. In particular, fossil fuel burning releases carbon dioxide (CO₂), a greenhouse gas (GHG), into the atmosphere and directly affects the Earth's temperature. At the Weybourne Atmospheric Observatory (WAO) on the north Norfolk coast, four atmospheric species associated with fossil fuel burning are measured to high precision: CO₂, oxygen (O₂), carbon monoxide (CO) and hydrogen (H₂). These datasets remain largely unanalysed, with the exception of one year of data from the H₂ dataset (Forster et al., submitted, 2012). The need to accurately monitor and study these gases continually is essential to improve understanding of their behaviour, interaction, sources and sinks. Findings may be utilised in climate modelling, to constrain uncertainty of climate feedbacks, sensitivity and prediction. Furthermore, the measurements are important for the accounting and verification of GHG emissions reported to the United Nations Framework Convention on Climate Change.

Charles Keeling published the first continuous record of high precision atmospheric CO₂ concentration in 1960 (Keeling, 1960), identifying a seasonal cycle in the northern hemisphere (NH) and a long-term increase of CO₂ concentration. Ralph Keeling established the first observations of atmospheric O₂ concentration (Keeling, 1988). Keeling and Shertz, (1992), documented a decreasing concentration and seasonal variation of O₂ in both hemispheres. Although naturally cycling via terrestrial photosynthesis and respiration, CO₂ concentration is rising and O₂ concentration is falling due to fossil fuel combustion. Today, concentrations measured at WAO, stand at ~400 ppm CO₂ and ~-560 per meg O₂. Globally there are ~109 CO₂ and fewer than 25 O₂ background monitoring stations.

It is estimated that half of anthropogenic CO₂ remains in the atmosphere (IPCC, 2007), the remainder being absorbed by the land biosphere or oceans. Precise measurements of CO₂ and O₂ can be used to quantify the terrestrial and oceanic carbon sinks (Manning and Keeling, (2006)). Precise measurements of O₂ and CO₂ have the potential to provide unique insights

into processes controlling fluxes, the atmospheric transport that distributes them and ocean biogeochemistry. Stephens et al., (1998) defined a tracer, Atmospheric Potential Oxygen (APO), $\text{APO} = \text{O}_2 + a_L \text{CO}_2$, where a_L (the oxidative ratio) is the average $\text{O}_2:\text{CO}_2$ molar exchange ratio of the terrestrial biosphere, expressed as moles of O_2 consumed per mole of CO_2 produced. APO is conservative with respect to terrestrial photosynthesis and respiration, hence changes in APO can only be caused by oceanic processes, in addition to a small long-term influence from fossil fuel combustion. Results have been used to compare against model predictions of APO (Nevison et al., 2008), to study latitudinal gradients (Stephens et al., 1998), to provide understanding of the carbon cycle and its seasonality (Bender et al., 1996 & 1998). Keeling et al., (1996) further explored regional and latitudinal differences of the CO_2 seasonal cycle, while Piao et al., (2007) considered net loss of CO_2 from northern ecosystems, resulting from winter warming.

A key term when studying APO is the oxidative ratio, α_L . Terrestrial photosynthesis and respiration is assumed to have a globally averaged oxidative ratio of 1.1 (Severinghaus, 1995), and this value is usually used for APO calculations. However, air masses may be influenced by other processes giving rise to anti-correlated changes in O_2 and CO_2 different from 1.1. Additionally, different terrestrial processes may have different oxidative ratios. Keeling, (1988) and Steinbach et al., (2011), estimated a globally averaged oxidative ratio for fossil fuel and cement production of 1.4. Keeling, (1988) estimated individual ratios for fossil fuel combustion ranging from 1.95 for natural gas, 1.44 for liquid fuel and 1.17 for coal. Work by Sirignano et al., (2010) and Steinbach et al., (2011) have identified that fluxes from the burning of fossil fuels should cause a correlative change in the $\text{O}_2:\text{CO}_2$ ratio downwind of any source and can act as a tracer for pollution. I aim to use the Weybourne dataset to identify pollution type based on oxidative ratios, reinforced with back trajectory analysis of air masses.

Fossil fuel is a major source of H_2 and CO in the troposphere. CO results from incomplete oxidation of carbon containing compounds, such as the combustion process from vehicles and industry. Most efforts to quantify the contribution of H_2 from fossil fuel combustion come from studies scaling H_2 against known inventories of CO emission (Vollmer et al., 2007). This project will provide an interpretation of in situ H_2 and CO data from WAO. Novelli et al., (1999) estimated a global average atmospheric H_2 value of 530 ppb. A background level of around 500 ppb has been recorded at WAO (Forster et al., submitted 2011). There is some uncertainty as to whether tropospheric H_2 concentration is increasing or decreasing. Grant et

al., (2010) reported stable average concentration over a 14 year period at Mace Head (Eire). CO has a background atmospheric level of about 100 ppb but can be in excess of 1000 ppb in urban areas (Singer, 1975). Seasonal and diurnal cycles have been analysed at different sites (Yver et al., (2009 and 2010); Ehhalt and Rohrer, (2009)).

Combined investigations of CO and H₂ pollution have been carried out to understand their common sources, for example at Heidelberg (Hammer et al., 2009), where diurnal variations coinciding with afternoon traffic peaks were identified. Perturbations in H₂ and CO may cause a decrease in the atmosphere's oxidizing capacity by the reduction of OH radicals and consequently increase the lifetime of methane (CH₄), a major GHG (Schultz et al., 2003). As a result, Derwent et al., (2006) classified H₂ as an important indirect GHG. Study of soil as a major sink for H₂, was examined by Simmonds et al., (2011). H₂ is also linked to increases in stratospheric water vapour leading to enhanced destruction of the protective stratospheric ozone (O₃) layer (Hauglustaine and Ehhalt, 2002). CO is also a precursor to tropospheric O₃ and is a source of CO₂.

CO has a relatively short lifetime of 1-4 months (Law and Pyle 1993), while that of H₂ is 1-2 years (Phillippe et al., 2009). Over time spans of a few days, these species may be used as a relatively inert tracer for air masses affected by recent anthropogenic emissions. Novelli et al., (1999) noted that $\Delta H_2 / \Delta CO$ ratios were higher closer to sources of pollution. The ratio has been explored further by Simmonds et al., 2011 and Grant et al., (2010). This, along with the $\Delta O_2 : \Delta CO_2$ ratio, provides further understanding of sources of pollution and potential measurement and verification of emissions.

This Research analysis, of atmospheric datasets, is vital for accurate climate prediction. Increases in CO₂ and other GHG's alters the balance of radiation emitted and absorbed by the Earth, pushing it away from equilibrium, to a warmer state. According to the Intergovernmental Panel on Climate Change (IPCC) Fourth Assessment Report (AR4) 2007, CO₂ in the atmosphere increased from a pre-industrial level of 280 ppm to 379 ppm in 2005, with an increase in global average surface temperatures of 0.74°C (1906-2005). Most of the observed increase in global average temperatures since the mid twentieth century is very likely due to the observed increase in anthropogenic greenhouse gas concentrations (IPCC, 2007). The IPCC predicts a temperature increase by 2100, varying from 1.4°C to 5.8°C, dependent on GHG emission scenario. This projects analysis of CO₂, O₂, CO and H₂ will

provide further understanding of their interaction and measurement and help constrain uncertainties in modelling and prediction.

The socio economic impact of future global temperature increases can be evaluated with greater certainty as understanding of the carbon cycle improves. The more certainty in models, the more confidence scientists should have in climate change prediction, enabling policymakers and public to make more informed decisions.

To date the UK has undertaken very little research into atmospheric GHG measurement and exploiting the potential of multi-species correlations is in its infancy. The in situ measurements at Weybourne provide an opportunity to undertake such analysis, to study interaction of species, their correlation, how they differ with air mass origin and how effectively pollution events can be detected and traced.

2.0 OBJECTIVES

I intend to present an analysis of a four year dataset of CO₂, O₂, CO and H₂ and explore three specific, related, questions:

- What can the seasonal and diurnal cycles of the four atmospheric species, tell us?
- How does the wind sector of air masses arriving at Weybourne affect the measured concentration of the four species.
- Can specific pollution events be detected from the Weybourne datasets and what do they tell us about local emissions?

3.0 METHODOLOGY

All measurements used in this project were collected at the WAO, established in 1992 and located on the north Norfolk coast of the United Kingdom at 52.95°N , 1.12°E . The Observatory is $\sim 100\text{m}$ from the sea and 16m above sea level, surrounded by open fields, in a predominantly agricultural region. The nearest settlement is Weybourne village (population ~ 518), 1km south. WAO is located approx. 35 km north-northwest of Norwich (population $\sim 132,000$), 170km north east of London, 200km east of Birmingham. (Figure 1.)



Figure 1: Location of the Weybourne Atmospheric Observatory (WAO) shown with a black star.

The WAO, provides an opportunity to study atmospheric datasets from one of only a small number of world class facilities, capable of collecting measurements to the precision and accuracy required by the World Meteorological Organization and one of only 2 such facilities in the UK.).

WAO is a coastal station and has the advantage of experiencing a clean maritime, well mixed wind sector to the north/ northwest/northeast over the sea. It is also affected by more polluted air masses from continental Europe to the east and London to the southwest.

3.1 Atmospheric measurement of CO_2 , O_2 , H_2 and CO :

Continuous measurement of species is made from air drawn down tubing with pumps from a tower, 10m above ground level. H_2 and CO analysis is performed with a Reduction Gas Analyser (RGA3, Trace Analytical, Inc, California, USA), incorporating gas chromatography resulting in eight measurements every hour (Forster et al., submitted, (2012)). O_2 analysis is

performed with a Sable Systems Oxilla II analyser with a gas handling system similar to Stephens et al., (2007), achieving very stable flow rates and pressures. Analysis of CO₂ uses a non-dispersive infrared (NDIR) Siemens Ultramat 6E Spectroscopic Analyser. Both provide fully calibrated measurements every two minutes. Rigorous calibration routines are performed on all analysers, maintaining high accuracy and precision, similar to Keeling et al., (1998). APO was calculated directly from the CO₂ and O₂ measurements using IDL scientific data visualisation software. Bespoke software automatically acquires all data and runs calibrations. All air samples are measured as a difference from a reference or ‘working tank’.

3.2 Meteorological data:

Meteorological data were obtained from a Campbell Scientific automatic meteorological station and ultrasonic anemometer (METEK GmbH Germany). Ambient temperature, relative humidity, wind speed, direction and diffuse solar irradiance are available at 10-minute time resolution.

3.3 Data preparation:

I analysed the available CO and H₂ datasets from 06Mar2008 to 31Dec2011 and those for CO₂ and O₂ from 30Oct2007 to 31Dec2011. I performed a quality control process on all 4 datasets, by removing obviously bad data and extreme outliers, with the aid of system diagnostic parameters.

The filtered data for CO₂, O₂ and APO were subject to trimming the top and bottom 25% to further eliminate outliers (Kozlova et.al., (2008)). Using bespoke “Average-O-Tron” software, averaged hourly and daily datasets were produced. Similar datasets were produced for H₂ and CO, but were not trimmed. I time-matched all atmospheric species and meteorological data using both Excel and IGOR routines. I standardized and altered time and date formats, to suit different software, for analysis.

3.4 General statistics:

I calculated the mean, median, mode, maximum, minimum, percentile values and standard deviation for each species using PASW[®] Statistics software.

3.5 The filtered data and background concentration:

I plotted the resulting concentration data using IGOR software. Background concentration was estimated using a calculated running 10 day quartile probability of 0.2 for H₂ and 0.05 for CO, CO₂ and O₂ (Barnes et al., 2003). These chosen parameters seem to best capture the estimated background concentration.

3.6 Hpspline curve fitting:

In order to examine the seasonal cycle, amplitude and longer term trends of the atmospheric species, I made use of the Scripps Institution of Oceanography 'hpspline' curve fitting program. This Fortran program uses sinusoidal harmonics to represent the seasonal cycle, polynomials to represent the long term trend and a stiff cubic spline to show interannual variability (Bacastow et al., 1985). I experimented with the number of harmonics required to produce the 'best fit' curve to the data and as a result, four were used for CO₂, O₂ and APO datasets and two for CO and H₂. The long term trend was established using the deseasonalised element of the Hpspline program. Seasonal amplitudes and 'upward and downward crossing' dates are determined from these curve fits. The significance of crossing dates is explained in the Discussion Section 5.1.1. Results were plotted using IGOR software.

3.7 Annual climatologies:

Annual climatologies are constructed from the mean monthly concentration over the dataset period. I used detrended data from the Hpspline program to calculate the monthly average for each species and standard deviation. Results were plotted using IGOR software.

3.8 Diurnal cycle:

I used the hourly averaged data from the datasets to find an overall hourly mean and standard deviation over a 24 hour period for each species. I further analysed the data to show a representative mean diurnal cycle of four periods: December, January, February (DJF); March, April, May (MAM); June, July, August (JJA); September, October, November (SON). A similar procedure was performed for the solar irradiance data available. Results were plotted using IGOR software.

3.9 Wind rose:

Meteorological data for wind direction and speed for the period 01Jan2008 to 31Dec2011 were used to produce a standard wind rose in 30° bin widths using IGOR software, to show

representative wind direction and speed over the data period. Seasonal analysis was also undertaken. The data were further analysed with Microsoft Excel to show the percentage of time the wind blew from a specific direction.

3.10 Analysis of species by wind sector:

In order to determine whether higher concentrations of the species are more likely to occur from a specific wind direction, I time-matched wind direction and species concentration, using IGOR programming. I then plotted results using the IGOR software wind rose, to show wind direction and species concentration, plotting the concentration when wind sector dependency became apparent. Data is calculated in 30° bin widths and analysed with Microsoft Excel to show the percentage of time wind blew from a specific direction at a specific concentration.

3.11 Correlation analysis: r and r^2 values:

In order to analyse any correlation between one species and another, I calculated the correlation coefficient (r) and the coefficient of determination (r^2) using Matlab script. I determined the correlations based on a non-linear least squares regression method, allowing uncertainty in both the x and y variables.

3.12 Pollution analysis:

I used peaks in CO₂ to identify where pollution events were evident. The peaks were selected from analysis of the top 99th percentile of the CO₂ data. Using $\Delta\text{O}_2:\Delta\text{CO}_2$ oxidative ratio analysis, the nature of the pollution event was analysed. Using Matlab script, the oxidative ratio was determined using the slope of the line of best fit on a correlation plot, based on the linear least squares regression method.

After removing background concentrations (Novelli et al., 1999), the $\Delta\text{H}_2:\Delta\text{CO}$ ratios were calculated for the same time period as the $\Delta\text{O}_2:\Delta\text{CO}_2$ selected events. The ratio was determined by the slope of the line of best fit on a correlation plot using linear regression analysis.

Clean air, non pollution events were identified using observation of plotted data and wind direction from a 'clean air source', taken to be between 330° and 90°, off the ocean. Similar analysis, using the $\Delta\text{O}_2:\Delta\text{CO}_2$ and $\Delta\text{H}_2:\Delta\text{CO}_2$ ratios were made.

3.13 *Back Trajectory Analysis*

I utilised back trajectory analysis from two available models to demonstrate origin of air masses arriving at Weybourne:

3.13.1 The NOAA HYSPLIT (Hybrid Single Particle Lagrangian Integrated Trajectory software) Model, using back trajectory analysis of a single particle and Lagrangian techniques, discussed in detail by Draxler and Hess, (1998). The program was run in backwards mode for 5 days from the WAO coordinates, at height of 10m above sea level.

3.13.2 The NAME (Numerical Atmospheric Modelling Environment) dispersion model (Ryall et al., 2002) , from the UK Met Office showing a 10 day back trajectory, described in Fleming et al., (In Press).

The NAME model plots are available until mid 2011.

4.0 RESULTS AND ANALYSIS OF DATA

I present my results and analysis, discussed further in Section 5.0

4.1 The datasets

The CO_2 , O_2 and APO datasets for the period 30Oct2007 to 31Dec2012 are shown in Figure 2. The gap in data from 27Oct2007 to 21Jan2008 was caused by problems obtaining calibration standards and that between 03Mar2009 and 05Aug2009 by an equipment upgrade. Other gaps in data were due to computer down time, instrumentation problems or bad calibration.

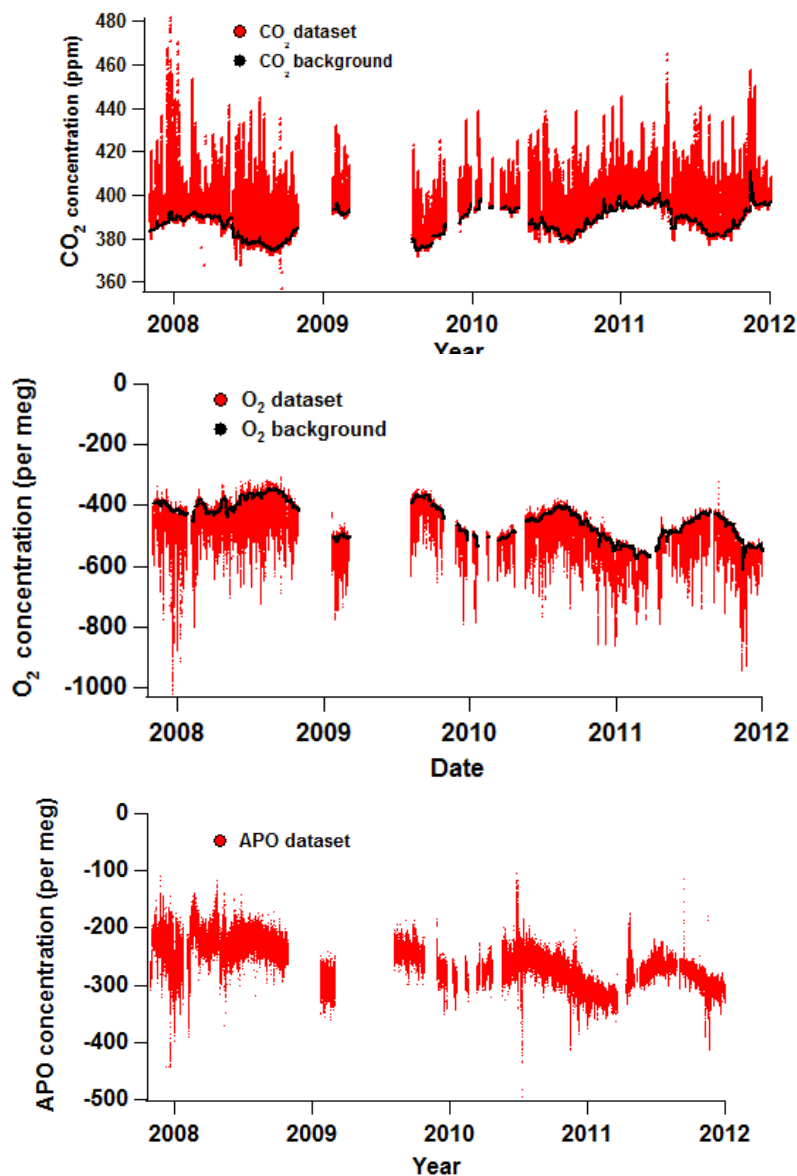


Figure 2: The CO_2 , O_2 and APO datasets. Background levels for CO_2 and O_2 are shown in black. (Not APO) Tick marks on the x axis represent 01Jan of each year in this and subsequent figures. For APO and O_2 1 per meg $\approx 4.8\text{ppm}$.

Background levels represent the estimated natural levels of species that would exist were there not any pollution events.

The time-series datasets for H_2 and CO from 06Mar2008 to 31Dec2012 are shown in figure 3. The RGA analyser was switched off between 31Mar2010 and 04Apr2011. Other gaps in the data are consistent with those outlined for the CO_2 , O_2 and APO.

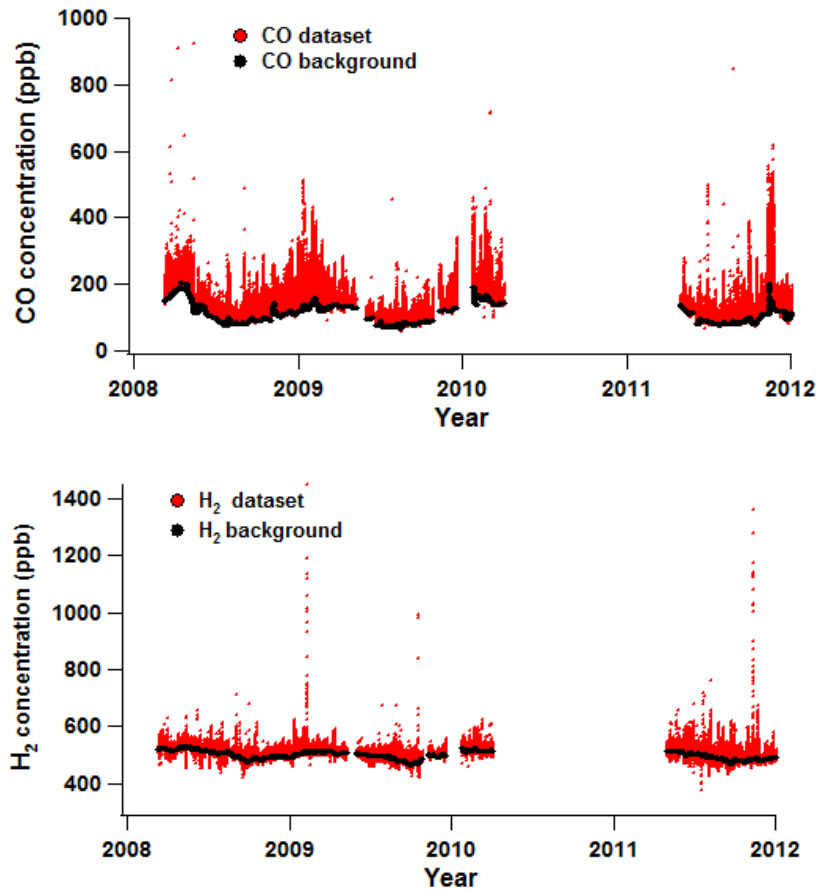


Figure 3: The CO and H_2 time series datasets, with background levels shown in black.

4.2 General observations

The H_2 and CO datasets consists of approximately 150,000 data points each, while the CO_2 , O_2 and APO datasets comprise approximately 550,000 data points each. A general statistical analysis of the datasets is shown (Table 1).

Dataset	Mean	Median	Mode	Standard Deviation	Maximum	Minimum	99th Percentile
O₂ (per meg)	-483.3	-491.9	-515.4	76.1	-304.6	-1020.5	-363.4
CO₂ (ppm)	395.4	394.5	394.5	10.0	481.4	356.9	428.7
APO (per meg)	-260.4	-262.7	-276.6	34.8	-105.1	-509.5	-182.7
CO (ppb)	141.0	130.2	105.0	53.0	935.8	55.3	325.2
H₂ (ppb)	509.8	509.9	513.4	21.2	1450	104	563.4

Table 1: General statistical analysis of the datasets.

4.3 Hpspline curve fitting

4.3.1 CO₂, O₂ and APO – Seasonal cycle and long-term trend

My results from analysis of CO₂, O₂ and APO, using the Hpspline curve fitting program showing the seasonal cycle (blue) and long-term trend (red), are illustrated in Figure 4. I found CO₂ concentration rose from 391.8ppm in Oct2007 to 400.7ppm in Dec2011, an average increase of 2.1ppm per annum. The O₂ concentration decreased from -435.8 per meg to -560.5 per meg over the same period, an average fall of ~30 per meg (~6ppm) per annum. APO has declined from -216.8 per meg to -296.7 per meg, an average fall of ~19.2 per meg (~4ppm) per annum. Detail of seasonal amplitude and mean dates of annual maximum/minimum concentration are shown in Table 2.

Species	Seasonal Amplitude – mean and yearly					Concentration	
	Mean	2008	2009	2010	2011	Mean date of maximum	Mean date of minimum
CO₂ (ppm)	15.9	14.1	17.8	15.5	16.8	01 Feb	21 Aug
O₂ (per meg)	135.2	99.9	164.5	137.8	146.0	23 Aug	28Jan
APO (per meg)	46.6	22.3	66.1	48.2	57.9	21Jan	06Aug

Table 2: CO₂, O₂ and APO Seasonal amplitude and date of maximum and minimum concentrations.

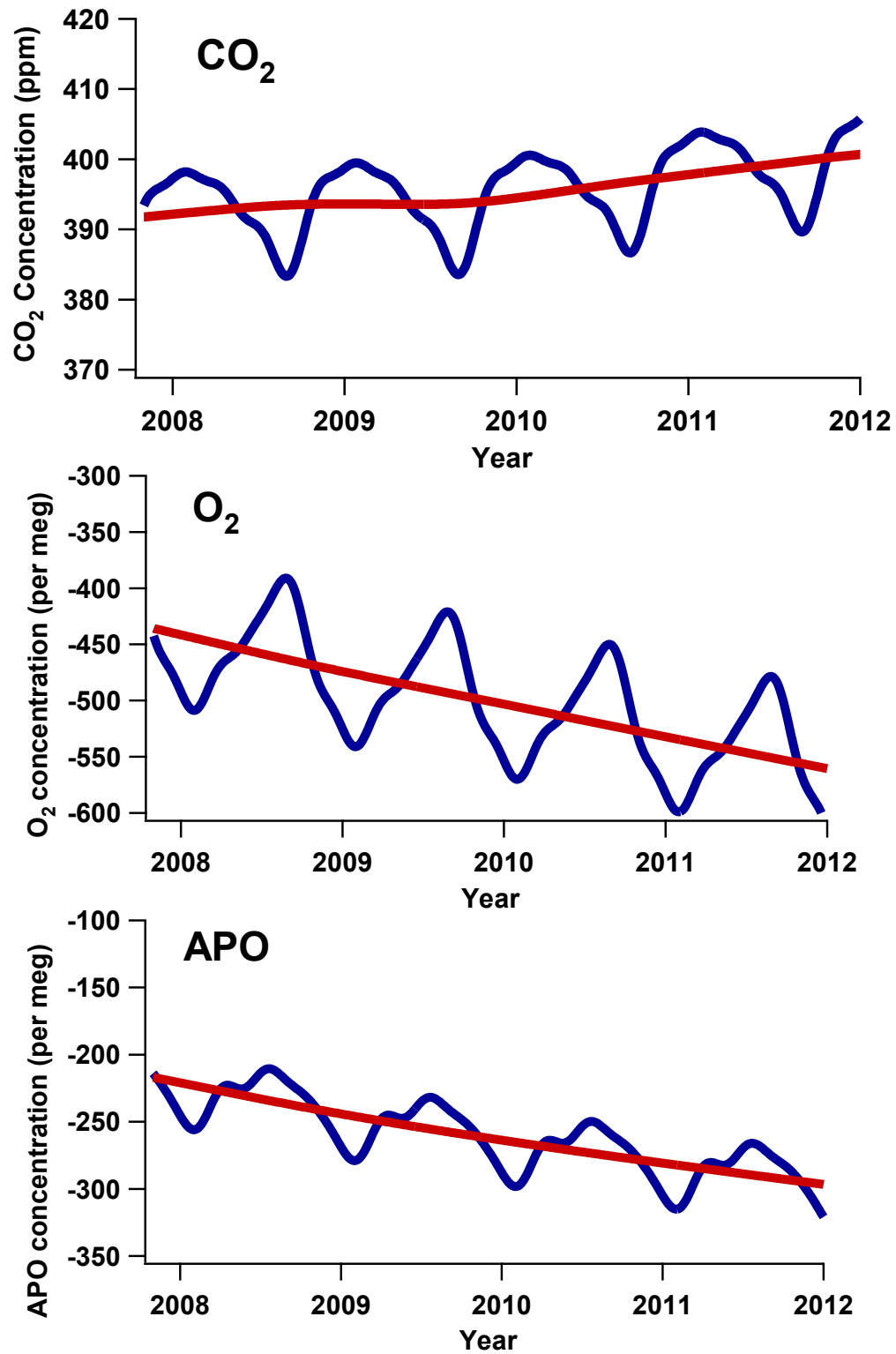


Figure 4: Seasonal cycle results of Hspline curve fitting program for CO₂, O₂ and APO .

4.3.2 CO₂ upward and downward crossing dates

The mean upward crossing date of the CO₂ dataset, determined from the Hpspline curve fits was found to be ~19Oct each year and the downward crossing date on the ~13May. The relevance of upward and downward crossing dates will be discussed in Section 5.1.2.1

4.3.3 CO and H₂ – Seasonal cycle and long-term trend

Hpspline results from analysis for CO and H₂, showing the seasonal cycle (blue) and long-term trend (red), are shown in Figure 5.

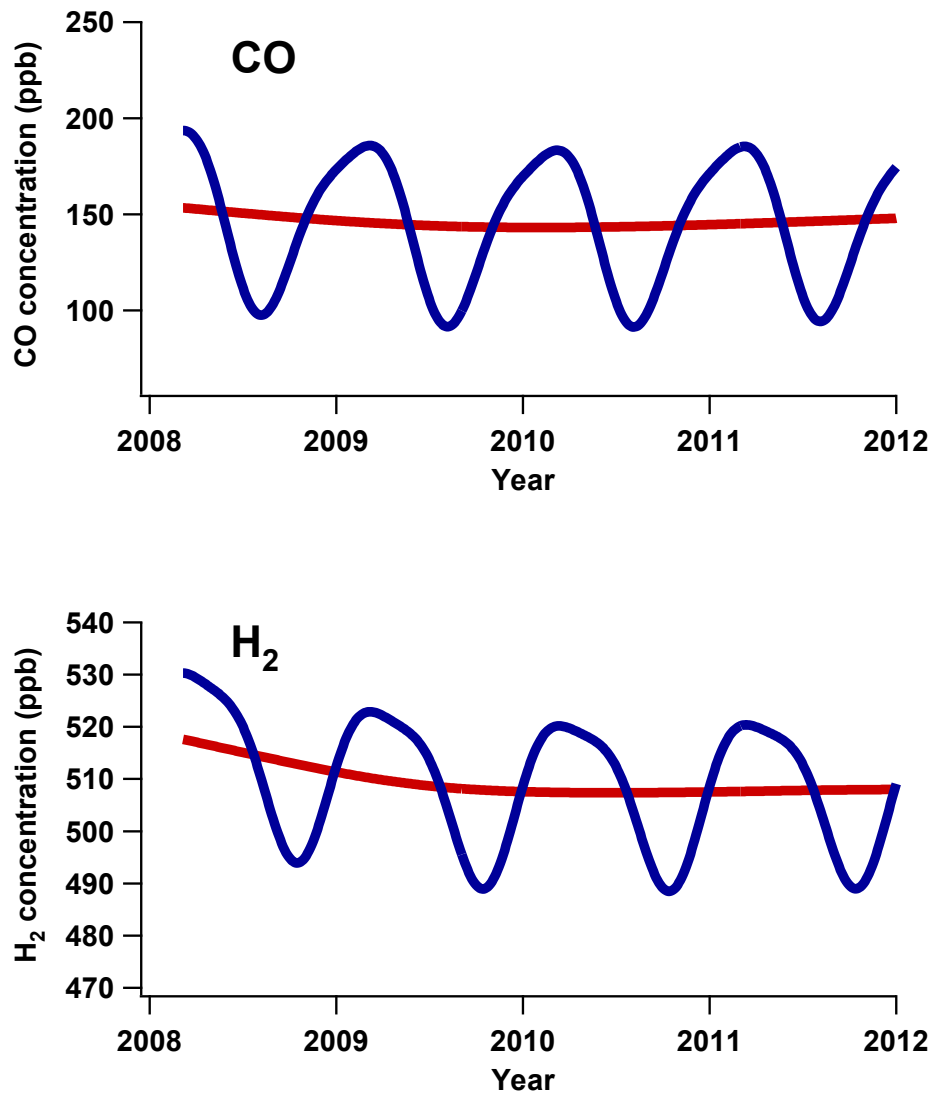


Figure 5: Seasonal cycle - results of Hspline curve fitting program for CO and H₂.

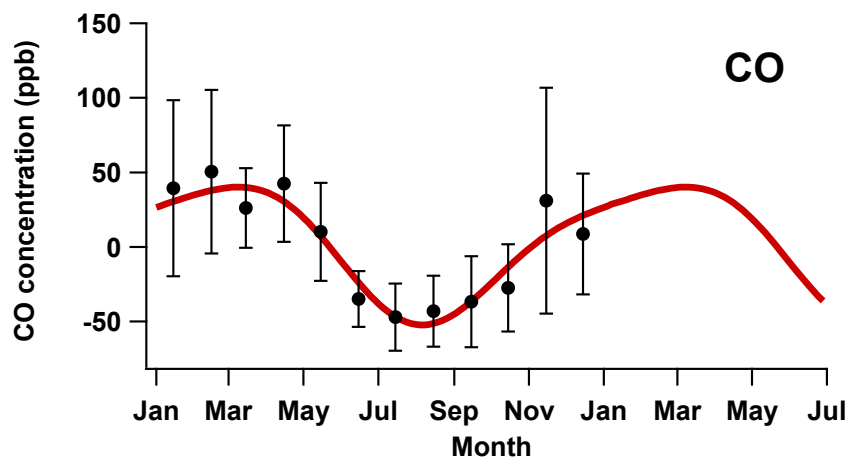
These results show that the CO long-term trend has varied from a maximum ~ 153.0 ppb in Mar2008 to a minimum of ~ 143.1 ppb in Feb2010, standing at ~ 148 ppb at the end of Dec2011. H₂ gave concentrations of ~ 517.6 ppb in Mar2008, falling to ~ 507.3 ppb in Jul2010, then remaining almost constant until the end of the dataset. The mean and yearly seasonal amplitude and mean date of annual maximum/minimum concentration for both species are shown in Table 3.

Species	Seasonal Amplitude (ppb) – mean and yearly					Concentration	
	Mean	2008	2009	2010	2011	Minimum (Date)	Maximum (Date)
CO (ppb)	92.4	94.9	91.4	105.4	86.0	02Aug	05Mar
H ₂ (ppb)	31.6	33.8	29.4	43.7	27.3	10Oct	09Mar

Table 3: Seasonal amplitude and date of maximum and minimum concentration.

4.4 Seasonal climatology

Analysis of the four-year datasets from the hpspline program revealed the seasonal climatologies for H₂ and CO, shown in red in Figure 6. The black circles show the monthly mean concentration calculated from hpspline, with error bars representing $\pm$ one sigma standard deviation of the monthly mean. Similarly, the climatologies for CO₂, O₂ and APO are shown in Figure 7. The seasonal cycle can clearly be seen, emphasised by repeating the first six months of the curve fit.



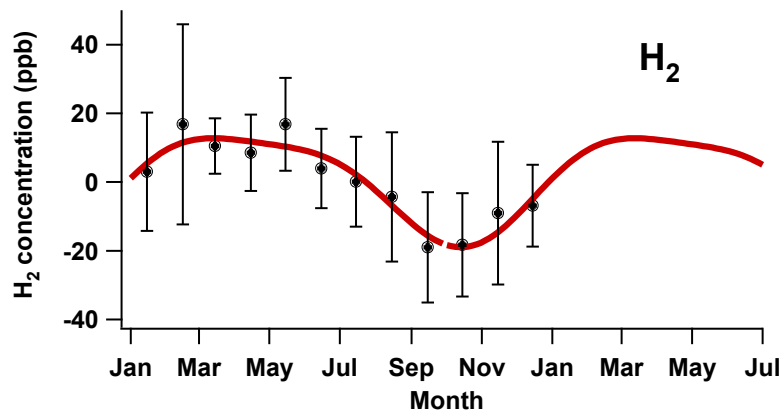


Figure 6: CO and H_2 datasets – seasonal climatology. Tick marks represent the first of the month.

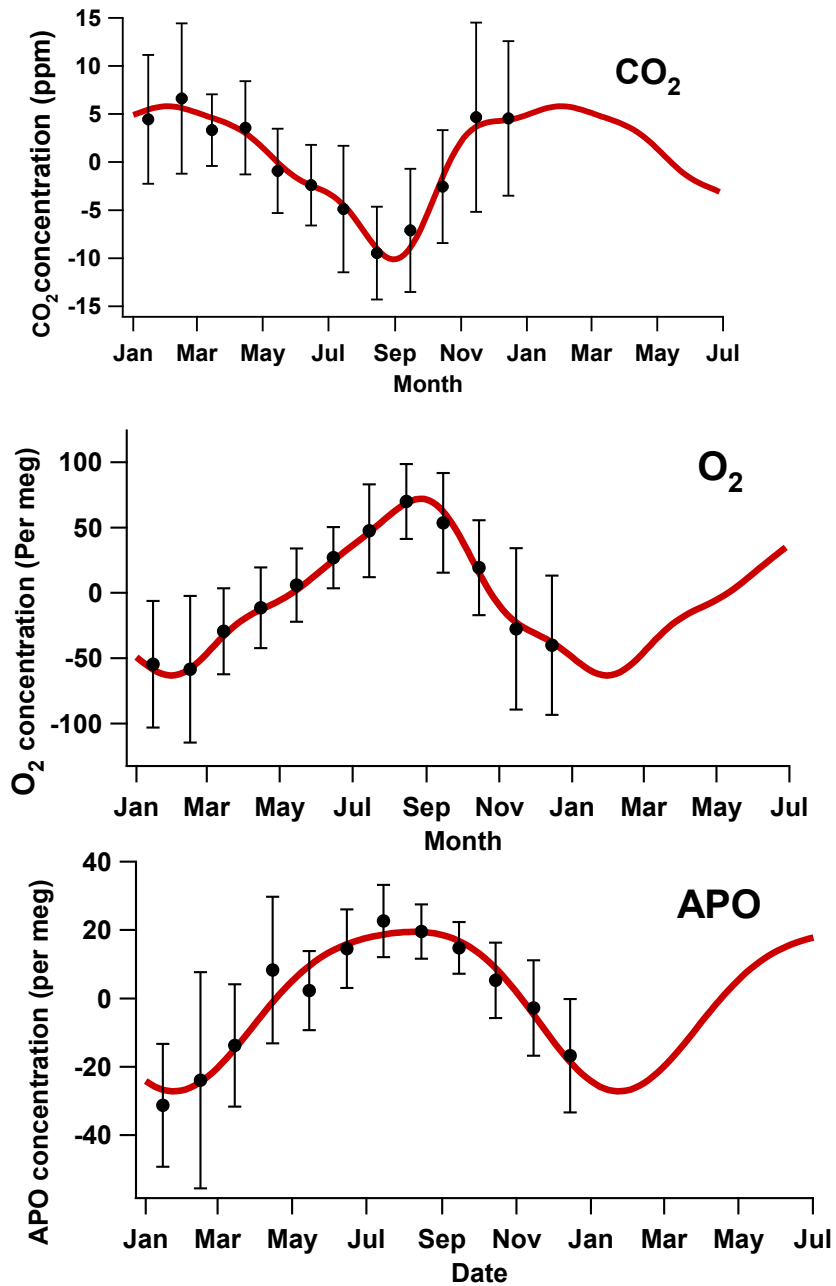


Figure 7: CO_2 , O_2 and APO datasets – seasonal climatology. Tick marks represent the first of the month.

4.5 Diurnal climatology

The diurnal cycles of the 4 species are shown in Figure 8, averaged over DJF and JJA. Error bars are omitted so that diurnal variance can be clearly illustrated, but are given in Table 4. The black line shows the mean hourly concentration and the red line shows the net hourly irradiance.

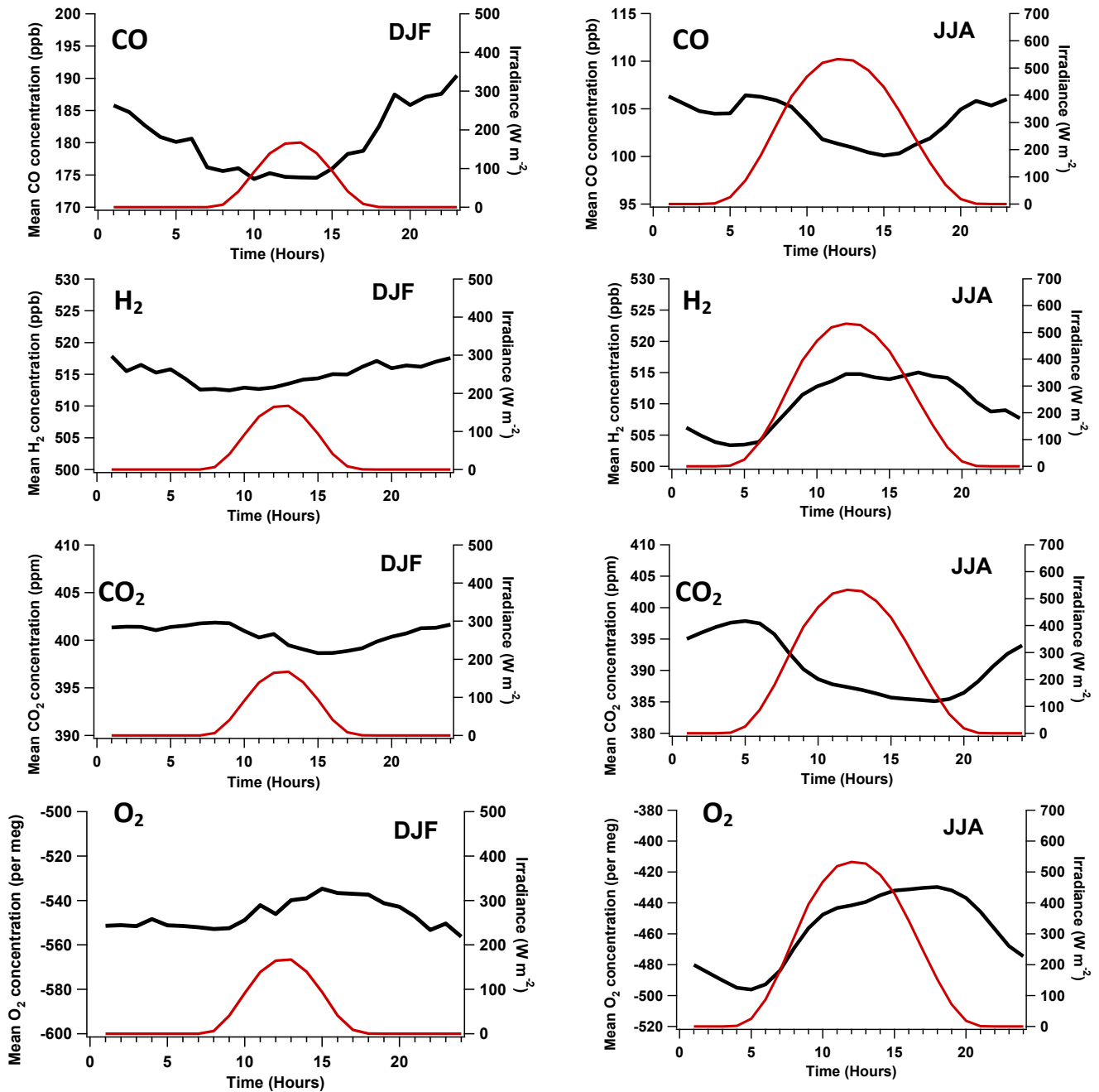


Figure 8: Diurnal climatology of species, showing concentration in black and irradiance in red.

The calculated diurnal amplitude, time of daily maximum and minimum concentration are shown for the summer (JJA) and winter (DJF) seasons in Table 4.

Species	Summer (JJA)				Winter (DJF)			
	Amplitude	Time of max. (GMT)	Time of Min. (GMT)	S.D. (mins)	Amplitude	Time of max. (GMT)	Time of min. (GMT)	S.D. (mins)
CO ₂	12.8 ppm	04:00	17:00	± 10	3.2 ppm	00:00	14:00	±10
O ₂	66.3 p.m.	17:00	04:00	±50	24.9 p.m.	14:00	00:00	±75
CO	6.3 ppb	00:00	14:00	± 22	16.0 ppm	23:00	11:00	±55
H ₂	11.7 ppb	16:00	05:00	± 12	9.1 ppb	00:00	07:00	±17

Table 4: Calculated diurnal amplitude for JJA and DJF and standard deviation.

4.6 Wind Rose

The averaged results of analysis of wind speed and direction from meteorological data at WAO for the period 30Oct2007 to 31Dec2011, are shown in the wind rose in 30° bins (Figure 9).

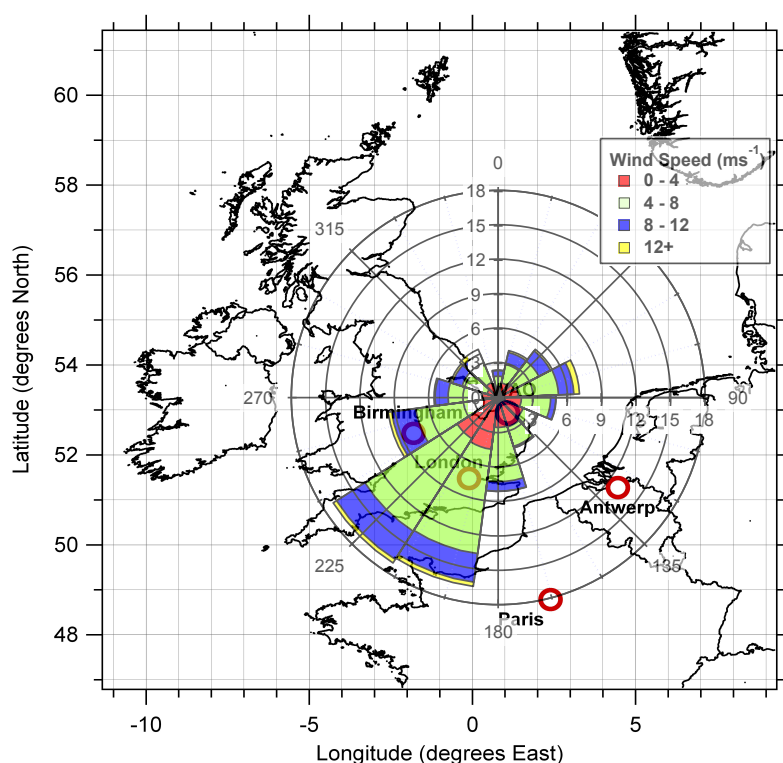


Figure 9: Wind rose plot for WAO 31Oct2007 to 31Dec2011

The wind direction for nearly half the period was from the southwest quadrant as shown in Table 5. This is true in all seasons, though slightly more in DJF at 53% and slightly less in

JJA at 47%. SON shows little difference in wind sector percentage terms from the year as a whole, but in MAM, it is notable that winds from the southwest sector drops to 42%, while winds from the northeast sector increase from 18% to 28%. For all seasons, winds from the northwest are least predominant, while winds from the southeast quadrant vary least.

Wind Sector	Bearing	Percentage
North east quadrant	0° to 89.9°	19%
South east quadrant	90.0° to 179.9°	18%
South west quadrant	180.0° to 269.9°	48%
North west quadrant	270.0° to 359.9°	15%

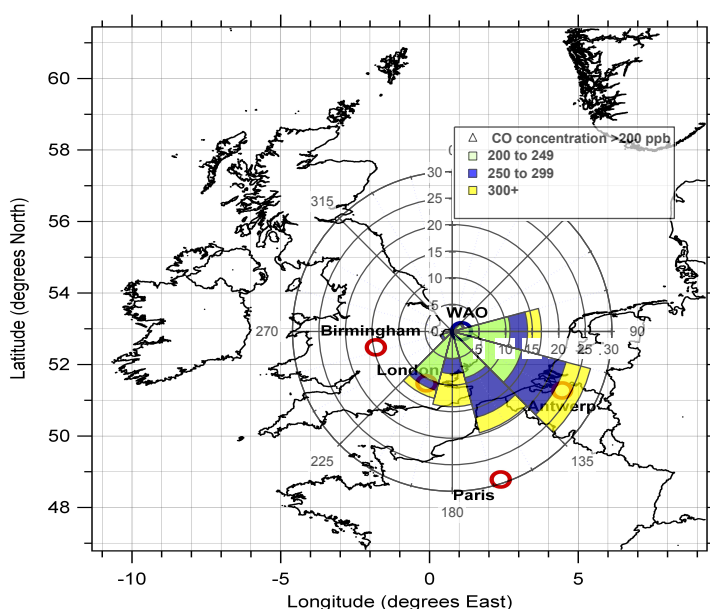
Table 5: Percentage of time the wind blew from selected directions at the WAO, 31Oct2007 to 31Dec2011.

The wind direction from the sea sector, 330° to 89.9° and from the land sector, 90.0° to 329.9°, was recorded 23% and, 77% of the time, respectively.

4.7 Analysis of species by wind sector:

Wind sector dependency for high concentration of species was examined and results shown in Figures 10 to 14. When lower concentrations of the species were plotted the plots looked similar to figure 9. For CO, H₂ and CO₂, wind dependency only became apparent above the 99th percentile, for APO, the 93rd percentile and O₂ the 70th percentile.

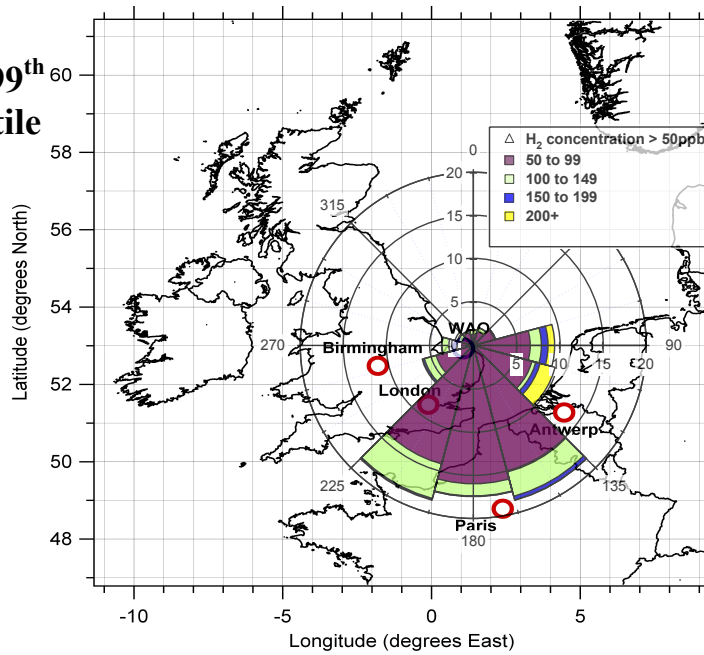
**ΔCO
above 99th
percentile**



Sector	Percentage
N.E.	8%
S.E.	54%
S.W.	27%
N.W.	1%
Sea	16%
Land	84%

Figure 10: Wind direction for CO > Δ 200ppb

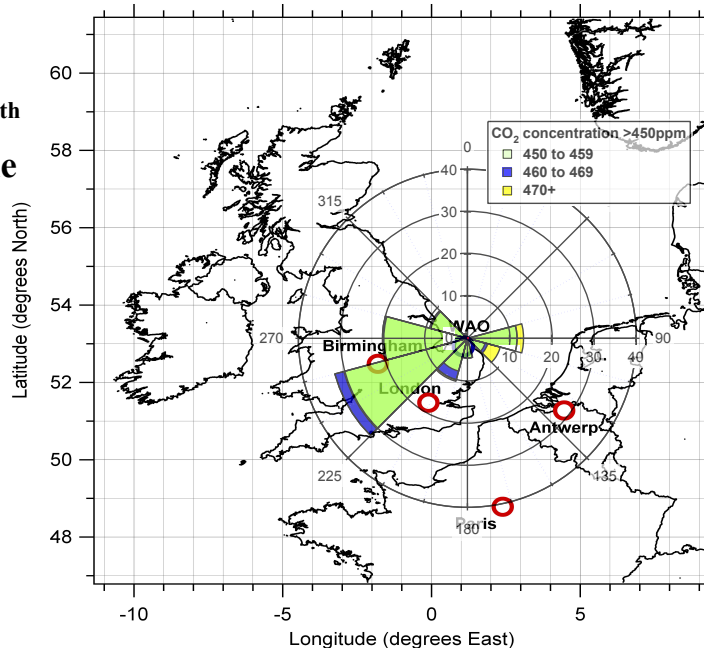
ΔH_2
above 99th
percentile



Sector	Percentage
N.E.	11%
S.E.	42%
S.W.	39%
N.W.	8%
Sea	14%
Land	86%

Figure 11: Wind direction for $\Delta H_2 > 50\text{ppb}$.

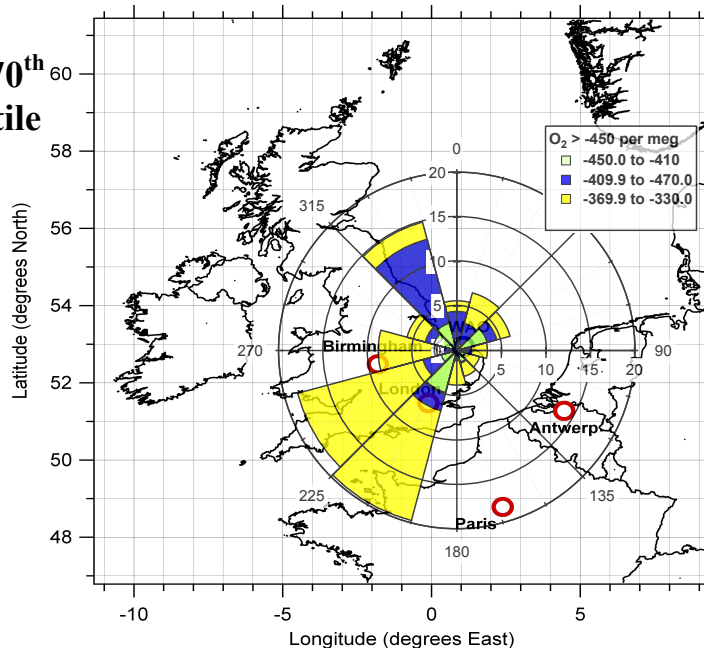
CO_2
above 99th
percentile



Sector	Percentage
N.E.	0%
S.E.	14%
S.W.	62%
N.W.	24%
Sea	0%
Land	100%

Figure 12: Wind direction for $\text{CO}_2 > 450\text{ppm}$

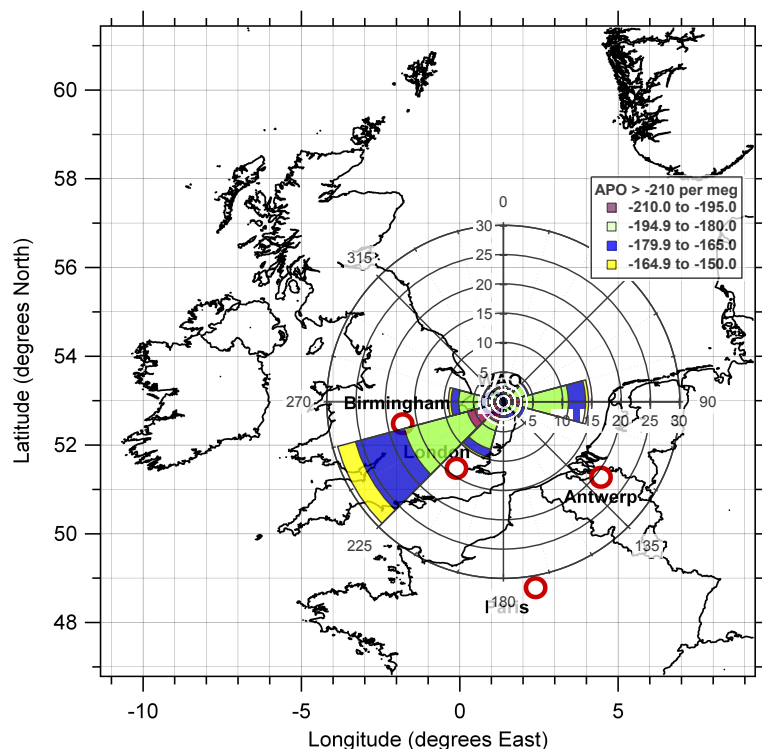
O_2
above 70th
percentile



Sector	Percentage
N.E.	20%
S.E.	15%
S.W.	52%
13	8%
Sea	22%
Land	78%

Figure 13: Wind direction for $\text{CO}_2 > 450$ per meg.

**APO
above 93rd
percentile**



Sector	Percentage
N.E.	16%
S.E.	9%
S.W.	45%
N.W.	30%
Sea	29%
Land	71%

Figure 14: Wind direction for APO above -210 per meg.

In Figures 9-14 the radial axis represents the number of data points in the given percentile and wind sector (in percent) and the colours show concentration. The percentage of time a given wind sector recorded concentrations above those stated, is shown in the Table to the right of each plot.

4. 8 Correlation analysis; r and r^2 values:

The correlation coefficient (r) and coefficient of determination (r^2), examining the correlations in concentration between pairs of species, were determined and the results shown in Table 5. An example of the correlation between CO_2 and O_2 using the non-linear least squares method, using Matlab script is shown in Figure 15.

Correlated Species	r value	r^2 value
CO_2 and O_2	-0.90	0.81
CO_2 and CO	+0.68	0.46
CO and O_2	-0.59	0.35
CO and H_2	+0.38	0.14
CO_2 and H_2	+0.13	0.02
H_2 and O_2	-0.04	0.0016

Table 5: Correlation coefficient (r) and coefficient of determination (r^2).

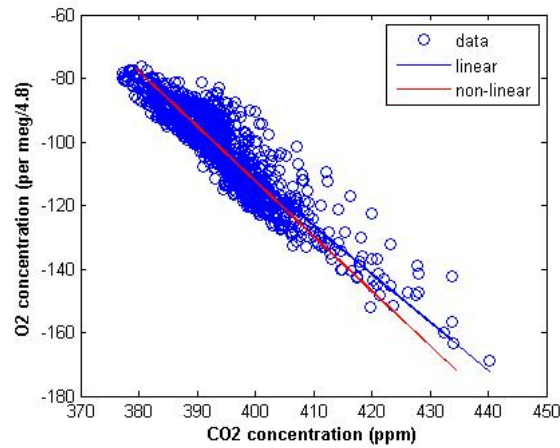


Figure 15: Determination of r^2 for CO_2 O_2 relationship. $r^2=0.81$ from non-linear fit.

4.9 Pollution analysis:

Results from analysis of data to explore the possible detection of pollution events by examining the $\text{O}_2:\text{CO}_2$ and $\Delta\text{H}_2:\Delta\text{CO}$ ratios based on a non-linear least squares regression method are shown in Table 6.

Event Date	$\text{O}_2:\text{CO}_2$	r^2	$\Delta\text{H}_2:\Delta\text{CO}$	r^2
20Dec2007	1.21	0.96	Not available	-
22Dec2007	1.90	0.89	Not available	-
26Jul2008	1.25	0.94	0.71	0.05
16Dec2009	1.44	0.87	0.90	0.34
30Dec2009 to 31Dec2009	1.83	0.80	0.38	0.18
12Jan2010 to 14Jan2010	1.44	0.96	0.19	0.16
29Jan2010 to 30Jan2010	1.40	0.97	0.38	0.18
22Feb2011	1.51	0.85	Not available	-
08Nov2011 to 09Nov 2011	1.28	0.99	0.44	0.88
13Nov2011 to 14Nov2011	1.30	0.98	0.21	0.76
Mean $\pm$ 1 S.D.	1.44$\pm$0.24		0.46$\pm$0.26	

Table 6: Date of identified pollution event and resulting $\text{O}_2:\text{CO}_2$ and $\Delta\text{H}_2:\Delta\text{CO}$ ratios. The r^2 showing the correlation between the two species are shown for the pollution events.

A further five events were analysed, using the 99th percentile of CO_2 as a guide to pollution events, but were not used as the r^2 was below 0.8.

Analysis of all $\Delta\text{H}_2:\Delta\text{CO}$ ratios for the entire dataset revealed a figure of 0.43. Excluding the large H_2 events, the figure was 0.37.

5.0 Discussion

5.1 What can the seasonal and diurnal cycles of the four atmospheric species at the WAO tell us?

5.1.1 CO₂, O₂ and APO

5.1.2.1 Seasonal cycles

A persistent decreasing trend in O₂ and APO and upward trend in CO₂ is consistent with other studies discussed in the introduction (Section1), resulting from fossil fuel burning. My analyses find background CO₂ at WAO has risen to 400.7ppm by 31Dec2011 a mean annual increase of 2.1ppm over the four years studied. This rate of increase is consistent but slightly higher than comparable studies; for example Koslova et al., (2008) recorded an annual increase of 2.02ppm from central Siberia and Sirignano et al., (2010) reported 1.7ppm both at Lutfjewad (LUT) in the Netherlands and Mace Head (MHD) (2000-2005). Anthropogenic fossil fuel emissions are increasing year on year (Peters et al. 2012), consistent with my finding.

I calculated a seasonal amplitude of 15.9ppm at WAO (Section 4.3.1), compared with values at similar latitudes of 14.4ppm (MHD) and 15.4ppm at Shetland (~60°N). The higher amplitude at WAO than MHD is most likely as it is closer to CO₂ sources. Kozlova et al., 2008, observed a 26.6ppm amplitude in central Siberia at a similar latitude to WAO. The greater amplitude reflects the continental interior biosphere and greater summertime CO₂ uptake compared to coastal sites.

The terrestrial biosphere drives the CO₂ seasonal cycle through the process of respiration and photosynthesis. The CO₂ concentration is higher in winter when respiration ($6\text{CO}_2 + 6\text{H}_2\text{O} \xrightleftharpoons{\text{light}} \text{C}_{16}\text{H}_{12}\text{O}_8$). The amplitude of CO₂ at WAO is greater than lower latitudes, such as Mauna Loa, Hawaii (MLO) ~7ppm, and Southern Hemisphere (SH) sites such as Cape Grim, Australia (CGO) ~1.2ppm, owing to the tropics and SH having little terrestrial seasonality compared to northern mid latitudes with a large landmass and deciduous forests driving a seasonal cycle. Although the amplitude of the seasonal cycle is observed to be increasing, thought to result from changes in the NH terrestrial biosphere (Piao et al. 2008), I would require a longer time series from WAO before I could make such analysis.

O₂ concentration fell an average of ~30 per meg/year and the oceanic component of O₂, APO, fell ~19.2 per meg/year (Section 4.3.1). Sirignano et al., (2010) observed a -20 per meg/year change at LUT (2000-2005). The mean seasonal O₂ amplitude at WAO of 135.2 per meg compares to MHD at 113 per meg and LUT 153 per meg (Sirignano et al., 2010), 134 per meg for the Siberia (Kozlova et al. 2008). O₂ is highest in the summer, not only due to land biotic production, but also as a result of the oceanic spring bloom in mid latitudes, releasing O₂ to the atmosphere. Warming sea temperatures generally promote the release of O₂ in the summer and cool, mixed ocean in winter promote uptake of O₂, altering atmospheric concentrations.

The mean APO seasonal amplitude at WAO of 46.6 per meg varied from 22.3 per meg to 66.1 per meg (Section 4.3.1). This compares with 95 per meg in Siberia (Kozlova et al., 2008), and Sirignano et al., (2010), reporting 44 per meg and 70 per meg for MHD and LUT respectively. The APO highlights the oceanic O₂ signal only, the maximum occurring in early August at WAO. This compares with MHD on ~27th July and Lutjewad ~16th August but is 4 months earlier than Siberia, reflecting the time it takes for the oceanic signal to propagate into the continental interior.

I found CO₂ and O₂ seasonal cycles are strongly anti-correlated (Section 4.8) and almost in phase, reflecting the stoichiometric link of the two gases. I also note the shape of the seasonal CO₂ fitted curve maxima from the WAO (Section 4.3.1) is not as broad as those from higher latitudes or colder climates, such as Siberia or Alert, Canada (80°N). Here the terrestrial biosphere is inactive for a longer over winter than WAO.

The upward and downward crossing dates are characterised by the timing of the zero crossing of the successive harmonic functions (Section 4.3.2). The downward crossing dates for CO₂ depict the spring bloom of terrestrial biosphere and had advanced by around 7 days since the early 1960's (Keeling et al., 1996), indicating a lengthening of the growing season and sequestration of carbon. My study is too short to show any trend.

Piao et al., (2008) found both photosynthesis and respiration increase during autumn warming but the increase in respiration is greater, whereas warming increases photosynthesis more than respiration in spring. Estimates show the northern terrestrial ecosystems may lose CO₂ at a rate that offsets uptake in the spring by up to 90%. This is important since if future autumn

warming is greater than spring, the ability to sequester carbon in northern ecosystems may not be as great as thought.

5.1.2.2 Diurnal cycles

The CO₂ and O₂ data show a clear anti-correlated diurnal relationship in the summer (Figure 8), reflecting the daily photosynthesis and respiration processes. The anti-correlation also appears in the winter data, but the amplitude is less, indicating the relative inactivity of the terrestrial biosphere. Summer outgassing of O₂ from the warmer sea, also results in a higher O₂ amplitude.

The timing of the diurnal maximum and minimum is 3 to 4 hours later in summer than winter. This reflects the longer daylight hours of summer, enabling photosynthesis to occur for a longer period, with greater build up of O₂ and depletion of CO₂ during the day, also resulting in greater diurnal amplitude.

5.1.3 H₂ and CO

5.1.3.1 Seasonal cycles

I observed a strong seasonal cycle for both species (Figure 6). CO displays a late winter early/spring maximum, reflecting anthropogenic emissions and summer minimum primarily resulting from reaction of CO with the OH radical, which relies on photolysis for formation. This is greater in summer when net radiation is high. The mean seasonal amplitude for the dataset is 92.4ppb, with some interannual variability (Section 4.3.3). This is higher than other studies and datasets at this latitudinal range for example, an amplitude of ~60ppb at MHD ~53°N, (2005-2009), and Jungfraujoch, Switzerland, 45ppb ~47°N (Bond et al. 2011). This may result from the WAO location and proximity to sources and sinks. For example, Jungfraujoch at high altitude and Mace Head (MHD) on the Irish Atlantic Coast are both away from major sources compared to WAO, close to London and industry in continental Europe.

I observed maximum concentrations of H₂ in late winter/early spring and minimum in late summer/early autumn. The seasonality can be mostly attributed to enzyme activity in soil, which encourages uptake of H₂. This is greater in drier, warmer conditions, usually found at the end of the summer (Lallo et al., 2008). The maximum reflects anthropogenic emissions and formation of H₂ by oxidation of methane and non-methane hydrocarbons. The summer

loss is, to a lesser extent, attributable to the reaction with OH radicals. A delayed minimum in the seasonal cycle of H₂ by approximately 2 months compared with the CO minimum is clearly seen (Figure 6), due to the H₂ soil sink maximum. This out of phase cycle results in an overall low correlation between the two species (Section 4.8).

The H₂ mean seasonal amplitude of 31.6ppb is comparable with MHD at 34ppb. Trainou recorded an amplitude of 45 ppb (Yves et al., 2010), and Jungfraujoch (Bond et al. 2010), 21ppb. This further suggests seasonality may be strongly determined by the H₂ soil sink. Jungfraujoch, at an altitude of 3471m is distant from the soil sink, resulting in dampening of amplitude, whereas the Trainou Tower appears to have a warmer, drier climate in summer, favourable to a greater soil sink and seasonal amplitude. MHD and WAO have similar climatic conditions and latitude, resulting in similar seasonal amplitude.

The CO and H₂ datasets do not show an overall long-term trend. Fluctuations in the long term trend line are likely showing intra-annual variability, reflecting possible variation in biomass burning or anthropogenic fossil fuel emission, consistent with findings (Novelli et al., (1999); Grant et al., (2010)), showing no long-term trend has been found in either species over a ~15 year period.

5.1.3.2 Diurnal cycles

CO reveals a night maximum and day minimum in both summer and winter, reflecting daytime sink by reaction with OH. The daytime minimum is later in summer than winter, owing to longer daylight hours and higher net irradiance. Night maxima occur as the OH sinks cease, but sources continue. A fall in concentration is seen after midnight in both summer and winter, possibly reflecting deposition due to the atmosphere rectifier effect (Denning et al., (1999)). Amplitude is larger in winter, reflecting greater overall CO concentration, some ~80% more than summer.

In summer, H₂ shows greater diurnal amplitude than in winter. The nighttime minimum reflects the soil sink. The daytime peak may be enhanced by photochemical formation of H₂ in summer. In winter H₂ is higher in overall concentration, but the diurnal amplitude is less, as cooler conditions are less favourable for the soil sink.

Distinct H₂ and CO₂ morning and afternoon peaks, common to studies made close to traffic sources (Hammer et al., 2009; Grant et al., 2010) are not immediately apparent in H₂. However there is some evidence of a peak in the CO data around 0700 and 2000, which warrants further investigation.

5.2 How does the wind sector of air masses arriving at Weybourne affect the measured concentration of the four species at Weybourne?

The analysis of results in Section 4.7, show winds from the southwest quadrant dominate at the WAO. Concentrations of the four species reflect this pattern. However, analysis shows that air arriving at Weybourne is more likely to be of the highest concentrations from particular directions. It is important to note the wind rose provides the wind direction recorded directly at Weybourne and does not show where the air mass had passed previously, although it may offer an indication of the general direction.

For both CO (Figure 10) and H₂ (Figure 11), the predominant wind sector recording both the highest concentrations of the gas species and most frequent occurrences are from the southeast, followed by the southwest sectors. Within the southwest sector, for both species, the greatest concentrations were recorded between 180° and 225°. This is significant since if these observations reflect the general direction of air arriving at Weybourne, then they may indicate sources of polluted air. The region upwind of WAO, between 180° and 225°, is the Greater London conurbation and the region upwind of the southeast sector is Belgium, Holland and North Germany. These are areas of major industrial production. The remaining wind sectors show relatively few instances of high concentration either species, possibly some from the Birmingham and Newcastle/Hull areas of England.

For both CO and H₂, the highest concentrations were predominantly from the landward sector, while the sea sector recorded fewer. When high concentrations from the sea were evident, back trajectories of the air masses show they had passed over areas of pollution, particularly the Benelux countries. I observed less than 1% of the highest concentrations recorded were JJA, with 60% recorded in DJF. This may reflect synoptic conditions in the winter months.

My results show CO₂ concentrations are highest when the wind blows from the land sector during the winter months (Figure 12.), indicating dominance of respiration in the terrestrial biosphere. The highest concentrations are recorded between 90° and 135°. I speculate this

may be related to pollution sources and high concentrations of CO, indeed, for the whole dataset the CO₂ and CO have an r^2 value of 0.46, showing some relationship between the species, as not all fuel is oxidised (Section 4.8).

The greatest incidences of high O₂ (Figure 13) concentrations originate from the land sector, recorded mostly in summer months. This is what I would expect from the terrestrial biosphere, with O₂ dominating the photosynthesis process. However, nearly 30% of the highest concentrations recorded are from the sea sector, suggesting ocean outgassing of O₂ in the warmer summer months. The APO rose plot shows about 22% of the highest calculation of APO coming from the sea sector, the remaining from the land. The APO relates to the oceanic signal of O₂ observed at Weybourne and shows not only a strong oceanic signal between 330° and 90°, but also a strong south-westerly component, presumably reflecting the North Atlantic influence.

5.2.1 Specific clean air event

Here I examine clean air sources from the sea sector. One particular event occurred from 10May2008-25May2008. A northerly flow dominated the period. NAME 10 day back trajectory plots (Figure 16) show the situation at 0300 on 17May2008, with a North Atlantic source of air and 2100 on 18May2008, showing an Arctic source. In both cases, the majority of the air mass had not been in contact with for land at least 5 days.

The records for the four species at Weybourne show the effect of the relatively unpolluted air, unaffected by terrestrial biosphere processes (Figure 17), with dampening of the diurnal cycle and relatively invariant concentrations for the duration of the airflow. A point of interest in the dataset is a drop in O₂ and APO concentration on 18-19May2008. This may be the result of an upwelling event, bringing O₂ depleted waters to the surface, causing a local atmospheric sink. I cannot explain this without further analysis.

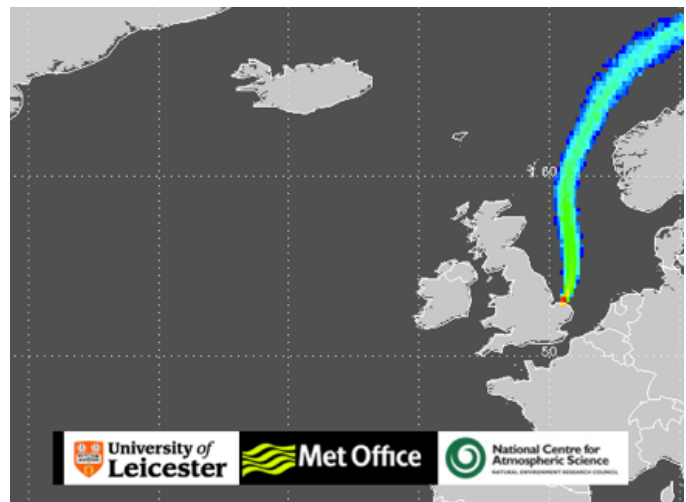
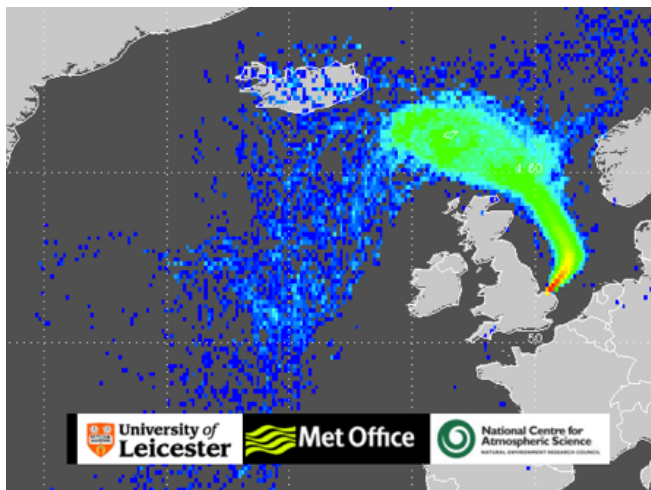


Figure 16: showing the NAME back trajectory analysis from the WAO at 0300 17May2008 (left) and at 2100hrs 18May2008 (right).

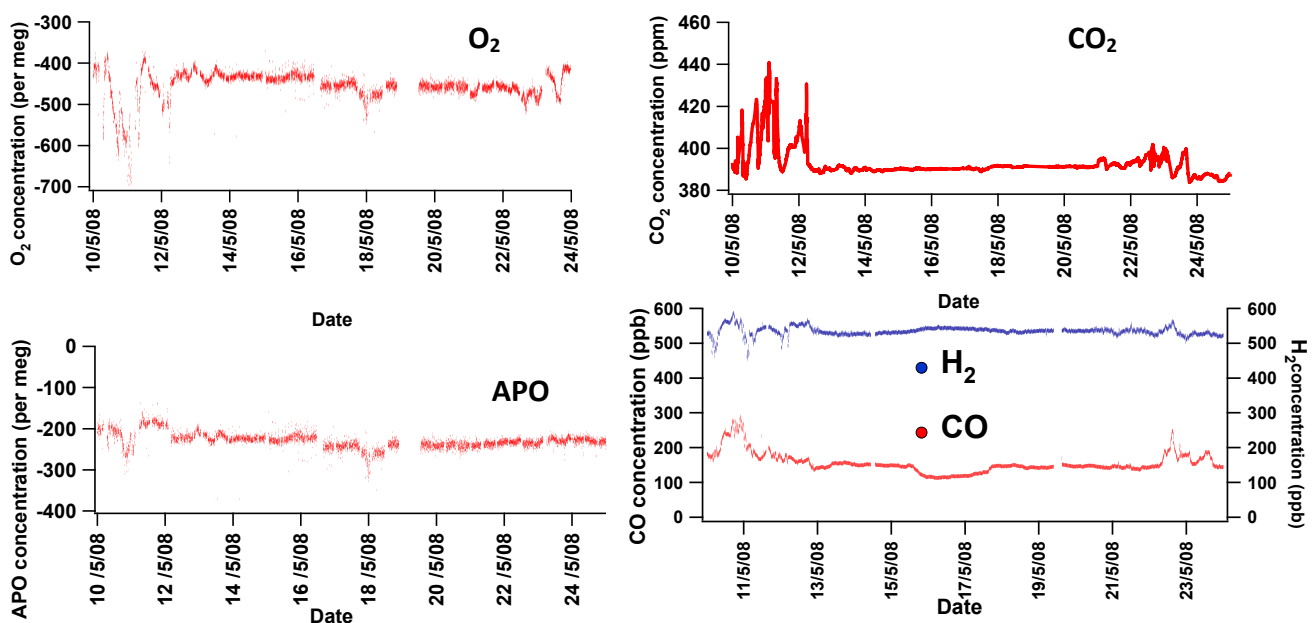


Figure 17: concentration of species at the WAO 10May2008 to 25May2008

5.3 Can specific pollution events be measured from the Weybourne datasets and what can they tell us about local emissions?

The WAO is located in a relatively remote location away from any strong local sources of pollution and is more representative of the regional scale of atmospheric environment, hence

pollution events may be identifiable. The $\Delta\text{O}_2:\Delta\text{CO}_2$ oxidative ratios derived from the observations are expected to vary between from around 1.1 (Severinghaus 1995), reflecting the biosphere processes, to around 1.4 (Keeling et al., 1988), reflecting fossil fuel combustion. The results in Table 6, do appear to reflect the expected oxidative ratio for pollution events, varying from 1.21 to 1.90, around a mean of 1.44 ± 0.24 . Whether these results can be related with any confidence to individual fossil fuel burning events, such as coal, with an oxidative ratio of 1.17, would require further analysis.

My results compare with other analyses, for example, Minejima et al., (2011) calculated the oxidative ratio at Hateruma Island, Japan of 1.0-1.7 and 1.65 at LUJ for selected pollution events. These contrast to non polluted air sources, such as the May2008 event where an oxidative ratio of ~ 6.0 was observed for the whole period. (Section 5.2).

I also observe some seasonality in these pollution events. According to Steinbach, (2011) the biospheric contributions to the oxidative ratio are expected to be greater in the summer than the winter. My results reflect this with generally higher oxidative ratios in the winter.

Using back trajectory analysis, I observed the air arriving at the WAO had passed over potentially polluted, industrial regions. There were 3 distinct regions; London to the southwest, the Netherlands/Belgium/Germany to the east and southeast and from Newcastle and Hull areas to the northwest.

A higher $\Delta\text{H}_2:\Delta\text{CO}$ ratio can indicate the relative closeness of a pollution source. For example, urban areas dominated by fossil fuel emissions from car exhausts reveal ratios between ~ 0.3 and ~ 0.6 (Steinbacher et al., 2007; Hammer et al., 2009). The Weybourne ratio for the entire dataset is 0.37. More remote sites, such as Jungfraujoch and MHD have lower $\Delta\text{H}_2:\Delta\text{CO}$ ratios of ~ 0.32 (Bond et al. 2011) and ~ 0.15 (Grant et al. 2010), respectively. My results for Weybourne would appear to be consistent with these values, being a relatively remote site, but closer to pollution sources than MHD and Jungfraujoch.

The individual $\Delta\text{H}_2:\Delta\text{CO}$ ratios (Section 4.9), time matched against the $\Delta\text{O}_2:\text{CO}_2$ oxidative ratio pollution events show a mean of 0.46 ± 0.26 , ranging from 0.19 to 0.9. The mean value would indicate identification of specific pollution events, given the elevated $\Delta\text{H}_2:\Delta\text{CO}$ ratio. However, the two events with a lower ratio, 0.19 and 0.21, require further investigation.

The overall r^2 at WAO using $\Delta H_2:\Delta CO$ ratios, for the entire dataset, was + 0.12, though slightly more elevated in the winter. This compares with an r^2 of +0.14 at Jungfraujoch (Bond et al., 2010). It is notable that 6 of the specific 7 pollution events had much higher positive correlation r^2 values, ranging from 0.16 to 0.87 (Section 4.9), indicating greater positive relationship between H_2 and CO in pollution events.

5.3.1 Specific Pollution Event

A specific pollution event of interest occurred from 08Nov2011 to 10Nov 2011. The datasets for the four species during that period are shown in Figure 18. A significant pollution peak for all species occurred around midnight on 08/09Nov2011 (Table 6). CO_2 and O_2 are strongly anti-correlated with an r^2 value of 0.99. H_2 and CO also increased at the same time by around 25 ppb and 75 ppb respectively, with an r^2 value of 0.87.

Using a 5 day back trajectory analysis from HYSPLIT, for 0000 on 09Nov 2011, it is evident the air source originated from an industrial region in the Benelux countries (Figure 18). Of particular interest is the H_2 spike to 1363ppb, the second highest in this dataset that occurred on 08Nov2011. The $\Delta H_2:\Delta CO$ ratio from 1500-1830 was 5.12. This level of H_2 concentration is normally associated with areas of high traffic in cities (Hammer et al., 2009) – unlikely at WAO.

Two other large H_2 peaks have been examined at Weybourne, Forster et al., submitted, (2012), who also used back trajectory analysis to reveal a similar source area in the Benelux countries, home to the highest two H_2 production regions in Europe at Antwerp and Zeeland. In all three cases there is no associated peak in CO_2 levels, which one might expect from the more usual type of pollution event, which occurred a few hours later. My findings lend weight to the supposition that the source of the high H_2 levels resulted from gas release from the Benelux area.

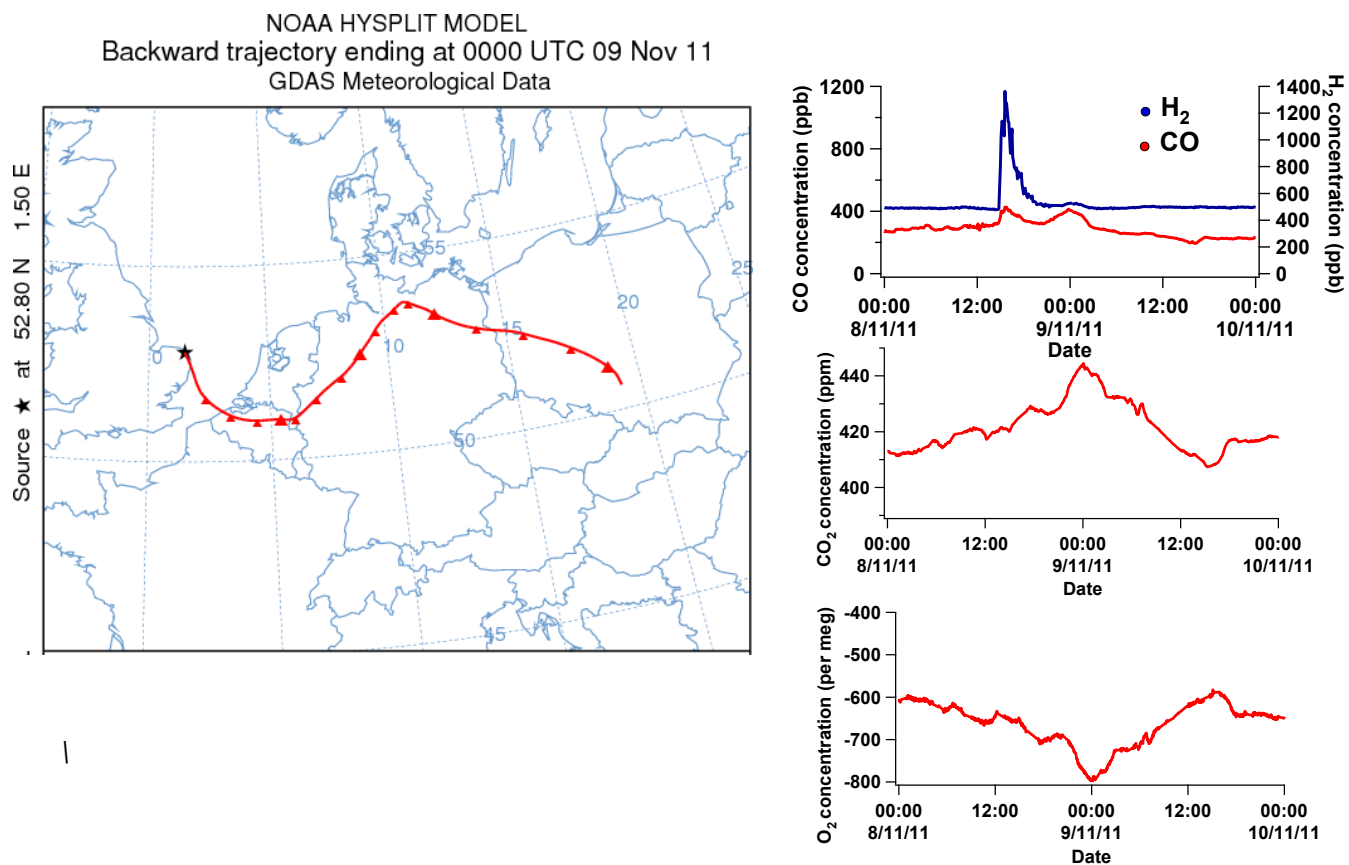


Figure 18: Pollution Event 08-09Nov2011. Back Trajectory analysis of air mass for previous 5 days arriving at WAO (left) and levels of atmospheric concentration for CO₂, O₂, H₂ and CO for 08Nov2011 to 10Nov2011 (right)

6.0 CONCLUSION

This project reports on a largely unanalysed four year dataset of atmospheric species from the WAO. I found CO₂ concentration had risen by 2.1ppm per annum to 400.7 ppm, confirming the increasing rate found in another study. O₂ concentration had fallen by 30 per meg per annum and CO and H₂ do not show any long term trend.

All species display a strong seasonal cycle, with CO₂ and O₂ anti-correlated, both influenced by the terrestrial biosphere. The seasonal amplitude of O₂ and CO₂ compares with observations in northwest Europe, reflecting the WAO's proximity to CO₂ sources. Mean amplitude of APO varied with a maximum signal occurring in early August, four months earlier than the continental interior demonstrating the time it takes for the O₂ signal to propagate the interior.

I found similar anti-correlation in the CO₂ and O₂ diurnal cycle, with smaller amplitude in winter, reflecting a less active terrestrial biosphere. The upward and downward crossing dates were determined and will be monitored as an indication for any increase or decrease in the uptake of CO₂ by the terrestrial biosphere.

CO and H₂ both show a late winter/early spring maximum. I found their cycle is approximately 2 months out of phase, due to a dominant soil sink for H₂ in late summer. CO shows a night maximum and day minimum, the OH sink.

I found the southwest wind direction dominated, with the concentrations of species recorded at Weybourne reflecting this pattern. There is little to suggest any wind dependency of any species until high concentrations are reached. CO and H₂ are at their highest concentrations when the wind direction is from London and the continent. CO₂ was highest in the winter, O₂ in the summer, reflecting the operation of the terrestrial biosphere. In addition, ~30% of the highest O₂ concentrations were recorded from the sea sector in summer, indicating outgassing of O₂ from the ocean. The APO showed influence from the Atlantic and North Sea. A clean air event was shown to dampen diurnal readings of all species.

I identified 10 pollution events using $\Delta\text{O}_2:\Delta\text{CO}_2$ oxidative ratio, having a mean ratio of 1.44 ± 0.24 , consistent with similar studies. $\Delta\text{H}_2:\Delta\text{CO}$ was used to indicate relative closeness of pollution source. The overall ratio for the dataset of 0.37, appears to be consistent with

comparable studies. When using the ratio to explore specific pollution events, the mean was similar to other studies at 0.46 ± 0.26 but with a greater range of results. I noted the $\Delta H_2 : \Delta CO$ r^2 value was greater in a pollution event.

A specific pollution event, where only H_2 had a significant spike, was observed. The air originated from Belgium, an area of H_2 production.

My project has been wide ranging, exploring and revealing what can be learned from analysis of atmospheric concentrations of CO_2 , O_2 , H_2 , and CO from Weybourne. The analysis only scratches the surface of what the datasets can tell us. Much more research is possible, particularly comparing the datasets to other atmospheric species recorded at Weybourne. I hope my analysis may provide some basis for future research.

References

- Bacastow, R.B., Keeling, C.D. and Whorf, T.P. (1985). seasonal amplitude increase in atmospheric CO₂ concentration in Moana Loa, Hawaii, 1959-1982. *Journal of Geophysical – Atmospheres*, 90 (ND6), 10529-10540.
- Barnes, D.H., Wofsy, S.C., Fehla, B.P., Gottlieb, E.W., Elikins, J.W., Dutton, G.S. and Montzka, S.A. (2003). Urban/Industrial pollution for the New York City-Washington D.C. corridor, 1996-1998: Providing independent verification of CO and PCE emissions inventories. *Journal of Geophysical Research*, 108, D6, 4185.
- Bender, M. L., Ellis, T., Tans, P. P., Francey, R. and Lowe, D (1996). Variability in the O₂/N₂ ratio of southern hemisphere air, 1991–1994: Implications for the carbon cycle, *Global Biogeochem. Cycles*, 10(1), 9–21, doi: 10.1029/95GB03295.
- Bender, M. L., Battle, M. and Keeling, R. F. (1998). The O₂ balance of the atmosphere: A tool for studying the fate of fossil-fuel CO₂. *Annual Review of Energy and the Environment*, 23, 207-223, doi: 10.1146/annurev.energy.23.1.207.
- Bond, S. W., Vollmer, M. K., Steinbacher, M., Henne, S. and Reimann, S. (2011). Atmospheric Molecular hydrogen (H₂): Observations at the high altitude site Jungfraujoch, Switzerland. *Tellus*, 63B, 64-76.
- Derwent, R., Simmonds, P., O'Doherty, S., Manning, A., Collins, W. and Stevenson, D. (2006). Global environmental impacts of the hydrogen economy. *Int J Nuclear Hydrogen Prod Appl.*, 1, 57.
- Denning, A.S., Takahashi, T. and Friedlingstein, P. (1999). Can a strong atmospheric CO₂ rectifier effect be reconciled with a 'reasonable' carbon budget? *Tellus*, 51B, 249-253.
- Draxler, R.R. and Hess, G.D. (1998). An overview of the HYSPLIT _4 modelling system for trajectories, dispersion and deposition. *Aust. Met. Mag.*, 47 (295-308).
- Ehhalt, D.H. and Rohrer, F. (2009). The tropospheric cycle of H₂: a critical review. *Tellus*, 61B, 500-535.

Fleming, Z., Monks, P.S. and Manning, A.J. (In Press). Untangling the influence of air-mass history in interpreting observed atmospheric composition. *Atmospheric Research*.

Forster, G. L., S. Emeis, Z. L. Fleming, B. J. Bandy and W. T. Sturges, A year of H₂ measurements at Weybourne Atmospheric Observatory, UK, *Tellus B*, submitted, 2012.

Grant, A., Witham, C. S., Simmonds, P. G., Manning, A. J., and O'Doherty, S. (2010). A 15 year record of high-frequency, in situ measurements of hydrogen at Mace Head, Ireland. *Atmos. Chem. Phys.*, 10, 1203-1214, doi:10.5194/acp-10-1203-2010.

Hammer, S., Vogel, F., Kaul, M. and Ingeborg, L. (2009). The H₂/CO ratio of emissions from combustion sources: comparison of top down and bottom up measurements in south west Germany. *Tellus*, 61B, 547-555.

Hauglustaine, D. A. and Ehhalt, D. H. (2002). A three-dimensional model of molecular hydrogen in the troposphere. *J. Geophys. Res.*, 107, 4330, doi:10.1029/2001JD001156.

IPCC, 2007: *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment. Report of the Intergovernmental Panel on Climate Change*: Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K.B., Tignor, M. and Miller, H.L. (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 996 pp.

Keeling, C. D. (1960). The concentration and abundances of carbon dioxide in the atmosphere. *Tellus*, 12, 2.

Keeling, R. F. (1998). *Development of an interferometric oxygen analyser for precise measurement of atmospheric O₂ mole fraction*. PhD Thesis, Harvard University, USA.

Keeling R.F., Piper S.C. and Heiman, M. (1996). Global and hemispheric CO₂ sinks deduced from changes in atmospheric O₂ concentration. *Nature* 381, 218 – 221

Keeling, R. F. (1988). Measuring Correlations between atmospheric oxygen and carbon dioxide mole fractions: A preliminary study in urban air. *Journal of Atmos. Chem.*, 7, 153-176.

Keeling, R. F. and Shertz, S. R. (1992). Seasonal and inter-annual variations in atmospheric oxygen and implications for the global carbon cycle. *Nature*, 358, 723-726.

Kozlova, E.A., Manning, A.C., Kisilyakhov, Y., Seifert, T. and Heimann, M. (2008). Seasonal, synoptic, and diurnal-scale variability of biogeochemical trace gases and O₂ from a 300m tall tower in central Siberia. *Global Biogeochemical Cycles*, 22, 4020.

Lallo, M., Aalto, T., Laurila, T. and Hatakka, J. (2008). Seasonal variations in hydrogen deposition to boreal forest soil in Southern Finland. *Geophysical Research Letters*, 25, 4, 1-4.

Law, K. S. and Pyle, J. A. (1993). Modelling trace gas budgets in the troposphere, 1. Ozone and odd nitrogen; 2. CH₄ and CO. *J. Geophys. Res.*, 98, 18377-18412.

Manning, A. C. and Keeling, R. F. (2006). Global Oceanic and land biotic carbon sinks from the Scripps atmospheric oxygen flask sampling network. *Tellus*, 58B, 95–116.

Minejima, C., Kubo, M., Tohjima, Y., Yamaguchi, H., Koyama, Y., Maysyutov, S., Kita, K. and Mukai, M. (2011). Analysis of $\Delta\text{O}_2 / \Delta\text{CO}_2$ ratios for the pollution events observed at Hateruma Island, Japan. *Atmos. Chem. Phys. Discuss.*, 11, 15631-15657.

Nevison, C. D., Mahowald, N. M., Doney, S. C., Lima, I.D. and Cassar, N. (2008). Impact of variable air-sea O₂ and CO₂ fluxes on atmospheric potential oxygen and land-ocean carbon sink partitioning, *Biogeosciences*, 5, 875-889.

Novelli, P.C., Lang, P.M., Masarie, K.A., Hurst, D.F., Myers, R. and Elkins J.W. (1999). molecular hydrogen in the troposphere: Global distribution budget. *Journal of Geophysical Research*, 104, 30427 – 30444.

Peters, G.P., Marland, G., Le Quéré, C., Boden, T., Canadell, J.G. and Raupach, M.R. (2011). Rapid growth in CO₂ emissions after 2008-2009 global financial crisis. *Nature Climate Change*, 2, 2-4.

Philippe, C., Poissant, L. and Villemur, R. (2009). Tropospheric H₂ budget and the response of its soil uptake under the changing environment. *Science of the Total Environment*, 407, 1809-1823.

Piao, S., Clais, P., Friedlingstein, P., et al. (2008). Net carbon dioxide losses of northern ecosystems in response to autumn warming. *Nature*, 451, 49-52.

Ryall, D.B., Derwent R.G., Manning A.J., Simmonds, P.G. and O'Doherty, S. (2001). Estimating source regions of European emissions of trace gases from observations at Mace Head. *Atmospheric Measurement*, 35, 14, 2507-2523.

Schultz, M. G., Diehl, T., Brasseur, G. P. and Zittel, W. (2003). Air pollution and climate-forcing impacts of a global hydrogen economy. *Science (New York, N.Y)*
doi:10.1126/science.1089527.

Severinghaus, J. P. (1995). *Studies of the terrestrial O₂ and Carbon Cycles in sand dune gases and in Biosphere 2. PhD Thesis*. University of California, San Diego, USA.

Simmonds, P. G., Derwent, R. G., Manning, A. J., Grant, A., O'Doherty, S. and Spain, T. G. (2011). Estimation of hydrogen deposition velocities from 1995-2008 at Mace Head, Ireland using a simple box model and concurrent ozone depositions. *Tellus*, 63B, 40-51.

Singer, S. F. (1975). *The Changing Global Environment*, Dordrecht: D. Reidel Publishing Company. P 90.

Sirignano, C., Neubert, R. E. M., Rodenbeck, C. and Meijer, H. A. J. (2010). Atmospheric Oxygen and Carbon Dioxide observations from two European coastal stations 2000-2005: Continental influence, trend changes and APO climatology. *Atmos. Chem. Phys.*, 10, 1599-1615.

Steinbach, J., Enhancing the usability of atmospheric oxygen measurements through emission source characterization and airborne measurements, Ph. D. thesis, Friedrich Schiller Universität Jena, Jena, Germany, 2010.

Steinbach, J., Gerbig, C., Rodenbeck, C., Karstens, U., Minejima, C. and Mukai, H. (2011). The CO₂ release and Oxygen uptake from Fossil Fuel Emission Estimate (COFFEE) dataset: effects from varying oxidative ratios. *Atmos. Chem. Phys* 11 6855-2011.

Steinbacher, M., Fischer, a, Vollmer, M., Buchmann, B., Reimann, S. and Hueglin, C. (2007). Perennial observations of molecular hydrogen (H₂) at a suburban site in Switzerland, *Atmospheric Environment*, 47, 10, 2111-2124

Stephens, B. B., Keeling, R. F., Heimann, M., Six, K. D., Murnane, R. and Caldeira, K. (1998). Testing global ocean carbon cycle models using measurements of atmospheric O₂ and CO₂ concentration, *Global Biogeochemical Cycles*, 12, 213-230.

Stephens, B. B., Bawkin, P. S., Tans, P. P., Teclaw, R. M. and Baumann, D. D. (2007). Application of a differential fuel cell analyzer for measuring atmospheric oxygen variations. *American Meteorological Society* 24 82-94. doi:10.1175/JTECH1959.1.

Vollmer, M. K., Juergens, N., Steinbacher, M., Reimann, S, Weilenmann M. and Buchmann, B. (2007). Road vehicle emissions of molecular hydrogen (H₂) from a tunnel study. *Atmos. Environ.*, 41, 8355–83.

Yver, C., Schmidt, M., Bousquet, P., Zarhorowski, W. and Ramonet, M. (2009). Estimation of the molecular hydrogen soil uptake and traffic emissions at a suburban site near Paris through hydrogen, carbon monoxide and radon -222 semicontinuous measurements. *Journal of Geophysical research*, 114, D18304.

Yver, C., Schmidt, M., Bousquet, P. and Ramonet, M. (2010). Measurements of molecular hydrogen and carbon monoxide on the Trainou tall tower. *Tellus B*, 63,1, 52-63.
DOI: 10.1111/j.1600-0889.2010.00520.x