Source and meteorological influences on air quality (CO, CH₄ & CO₂) at a Southern Hemisphere urban site

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HIGHLIGHTS

• In situ measurements (2011–2014) at a chemically interesting site in Australia.
• Background CO is influenced by Australian and transported biomass burning.
• A negative trend in CO is attributed to reduction in northeast Australian fire.
• Ozone production is associated with anticyclonic meteorology.

ABSTRACT

Wollongong, Australia is an urban site at the intersection of anthropogenic, biomass burning, biogenic and marine sources of atmospheric trace gases. The location offers a valuable opportunity to study drivers of atmospheric composition in the Southern Hemisphere. Here, a record of surface carbon monoxide (CO), methane (CH₄) and carbon dioxide (CO₂) was measured with an in situ Fourier transform infrared trace gas analyser between April 2011 and August 2014. Clean air was found to arrive at Wollongong in approximately 10% of air masses. Biomass burning influence was evident in the average annual cycle of clean air CO during austral spring. A significant negative short-term trend was found in clean air CO (−1.5 nmol mol⁻¹ a⁻¹), driven by a reduction in northern Australian biomass burning. Significant short-term positive trends in clean air CH₄ (5.4 nmol mol⁻¹ a⁻¹) and CO₂ (1.9 μmol mol⁻¹ a⁻¹) were consistent with the long-term global average trends. Polluted Wollongong air was investigated using wind-direction/wind-speed clustering, which revealed major influence from local urban and industrial sources from the south. High values of CH₄ with anthropogenic ∆CH₄/∆CO₂ enhancement ratio signatures, originated from the northwest, in the direction of local coal mining. A pollution climatology was developed for the region using back trajectory analysis and ∆O₃/∆CO enhancement ratios. Ozone production environments in austral spring and summer were associated with anticyclonic meteorology on the east coast of Australia, while ozone depletion environments in autumn and winter were associated with continental transport, or fast moving trajectories from southern latitudes. This implies the need to consider meteorological conditions when developing policies for controlling air quality.

1. Introduction

Carbon monoxide (CO), methane (CH₄), carbon dioxide (CO₂) and ozone (O₃) have important roles in air quality and/or climate. The World Health Organization (2014) has estimated that in 2012,
3.7 million premature deaths occurred worldwide due to outdoor air pollution. Outdoor air pollution particularly affects the urban atmosphere, and with the percentage of population living in urban areas projected to rise to 70% by 2050 (United Nations, 2012), poor air quality is set to affect more people. Additionally, the rise in population and associated energy consumption has led to a rise in anthropogenic greenhouse gas emissions. Understanding the relative contributions from anthropogenic and natural, local and transported sources is imperative for making realistic decisions about reducing the human impact on our health and climate.

With a lifetime of several months, CO can be used to track local and regional air pollution, biomass burning and oxidation processes (Weinstock, 1969; Edwards et al., 2006a). CO is mainly lost by reaction with the OH radical, the most abundant cleaning agent in the atmosphere (Logan et al., 1981; Holloway et al., 2000; Duncan et al., 2007). Through reaction with OH, CO abundance affects the self-cleaning ability of the atmosphere and consequently the decay of other climate and health relevant gases. CO directly affects the self-cleaning ability of the atmosphere and consequently the decay of other climate and health relevant gases. CO is directly a product of incomplete combustion such as biomass burning and fossil fuel use, important sources for local and regional air pollution. On average in the Southern Hemisphere, over 50% of atmospheric CO is indirectly sourced from oxidation of CH4 and volatile organic compounds (VOCs) (Logan et al., 1981). CO is an important atmospheric trace gas, itself being a toxic molecule, and also involved in producing harmful tropospheric ozone.

The relative atmospheric abundance of O3 to CO can be used as an indicator of ozone production environment. Positive O3–CO correlations and regression slopes (ΔO3/ΔCO enhancement ratios) are associated with ozone production while negative correlations are associated with ozone removal by chemistry or deposition and/or stratospheric subsidence (Fishman and Seiler, 1983; Parrish et al., 1993, 2000). Historically, O3–CO correlation studies using in situ measurements have focused on continental air, for example pollution from North America reaching the North Atlantic (e.g. Parrish et al., 1998) or Asian outflow affecting North America (e.g. Price et al., 2004). Biomass burning plumes from South America have also been a target of previous research (e.g. Andreae et al., 1994). There has been limited analysis of in situ O3–CO correlation in Australia, with the body of research comprising an aircraft study in 1999 (Takegawa et al., 2003) and a ship–borne study in 2006 (Nara et al., 2011), both campaign-style studies focused on remote northern Australia, distant from populous regions.

Trace gases CO2 and CH4 are major targets in climate research. Increasing human use of fossil fuels, a source for both these gases, has been the main driver of their increasing global abundance (Hartmann et al., 2013). CH4 is also anthropogenically produced from agriculture. Natural sources of CH4 include wetlands and biomass burning. Similar to CO, CH4 abundance influences the atmospheric cleansing capacity via the main loss reaction with OH (Mikaloff-Fletcher et al., 2004; Hartmann et al., 2013). Natural sources of CO2 include biomass burning and oxidation of natural VOCs. Globally, approximately 1/4 of the anthropogenically produced CO2 is taken up by each of the terrestrial biosphere and the oceans. The terrestrial biosphere is a net sink for CO2 due to the balance between photosynthesis and respiration fluxes, and there is net ocean uptake due to CO2 dissolving in water (Ciais et al., 2013).

A majority of air quality studies in Australia have focused on remote areas to learn about well-mixed air, because the Southern Hemisphere is an ideal location to study background conditions in comparison to the Northern Hemisphere (e.g. Fisher et al., 2015). Those that have studied polluted air masses tend to have been campaign based and focus on the influence of biomass burning (e.g. Paton-Walsh et al., 2012).

Wollongong is at the intersection of anthropogenic, biomass burning, biogenic, and marine sources of atmospheric trace gases, and presents a valuable opportunity for studying the interaction of different sources. Recently, the MUMBA campaign (Measurements of Urban, Marine and Biogenic Air) in Wollongong (Paton-Walsh et al., 2013) deployed a suite of instruments measuring atmospheric properties, to study different source interactions. The multi-year measurements investigated in this paper will provide context for campaigns like MUMBA and will help researchers assess whether air quality was typical during campaign periods.

This study aims to characterise the drivers of atmospheric composition for a complex urban Southern Hemisphere site and its relationship to two remote sites, one clean background site representative of the Southern Ocean — Cape Grim — and one site in the tropical north with strong biomass burning influences — Cape Ferguson. We present new semi-continuous measurements at Wollongong of in situ CO, CO2 and CH4 that are traceable to global calibration scales. While the Wollongong site in Australia has a long record of atmospheric column measurements through the programs Network for the Detection of Atmospheric Composition Change (NDACC, http://www.ndsc.ncep.noaa.gov/) and Total Carbon Column Observing Network (TCCON, http://www.tccon.caltech.edu/), this is the first published record of multi-year in situ measurements from the site (Section 3.1). Wollongong clean air is separated from polluted air using statistical techniques (Section 3.2) and subsequently examined using average annual cycles and short-term trend analysis. Annual cycles of CO and CO2 are interpreted using tagged tracer modelling experiments. Wollongong CO and CH4 measurements are studied with wind speed—wind direction cluster analysis, targeting conditions of polluted air (Section 3.3). Enhancement ratios of ΔO3/ΔCO combined with trajectory analysis are used to determine the pollution climatology at Wollongong.

2. Material and methods

2.1. Site description

The Wollongong measurement site is operated by the Centre for Atmospheric Chemistry (CAC, http://smah.uow.edu.au/cac) and is located at the University of Wollongong (UOW, 34.406° S, 150.879° E, 30 masl), Australia (Fig. 1, inset). Prevailing winds during spring and summer are from the northeast, associated with sea-breezes. During autumn and winter, the prevailing wind direction is southwest. UOW experiences local, regional, and long-distance influences on atmospheric composition. The UOW site, Wollongong, and surrounds are displayed in Fig. 1, shown with major local sources of atmospheric trace gases. Urban sources are local, from Wollongong city, as well as transported from Sydney, the largest Australian city approximately 60 km to the north of UOW (population 4.3 million in 2011, Australian Bureau of Statistics (2011)). A major motorway flanks the UOW site to the north and east. Local industry also significantly affects the local atmosphere: steelmaking facilities are located to the south at Port Kembla; coal mining, and related activities are located to the north and west. Biogenic emissions and local bushfires frequently impact the site, with large forested areas such as the Royal National Park to the north and water catchment areas to the west. Agriculture exists to the southwest of the Wollongong urban extent. Local topography — a 500 m escarpment — combined with sea-breezes frequently creates inversion meteorology, which assists in pollution build-up (Bryant, 1982).

2.2. In situ FTIR instrumentation

Atmospheric datasets of CO, CH4 and CO2 were developed by combining records from two in situ Fourier Transform InfraRed
The in situ FTIR instrument was comprised of a low spectral resolution Bruker IR-spectrometers at UOW. The combined record spans April 2011—August 2014 (http://dx.doi.org/10.1594/PANGAEA.848263). The in situ FTIR instrument was first developed at UOW by Esler et al. (2000) and Griffith and Galle (2000) and has been most recently described in Griffith et al. (2012). Briefly, the in situ FTIR spectrometers are comprised of a low spectral resolution Bruker IRTCube (1 cm⁻¹ resolution), with a thermoelectrically-cooled Mercury Cadmium Telluride (MCT) detector. The infrared (IR) source is modulated through a CaF₂ beamsplitter in a Michelson interferometer, before being reflected through an atmospheric sample within a White cell (White, 1942) to produce a folded path length of 24 m.

Trace gas mole fractions were retrieved over four broad spectral regions (2097–2242, 2150–2310, 3001–3150, and 3520–3775 cm⁻¹) using the non-linear least-squares program MALT (Multiple Atmospheric Layer Transmission, Griffith, 1996, Griffith et al., 2012). MALT iteratively improves a simulated transmittance spectrum, initialised with estimates of absorbing trace gas amounts, reference spectral lines from the HITRAN database (Rothman et al., 2013) and measured infrared line shape and measured parameters such as temperature and pressure. Instruments sampled ambient air continuously throughout the day. Daily instrument running procedures are detailed in Appendix A.

2.2.1. Cross-sensitivity, calibration and uncertainty

While instruments 1 and 2 are functionally identical, cross-sensitivity to parameters such as pressure and flow are unique to each instrument and were determined using a set of experiments as described in Hammer et al. (2013). A complete list of cross-sensitivity factors used here can be found in Buchholz (2014). Cross-sensitivity correction typically results in adjusting measured values by less than 1%.

Calibration to account for systematic uncertainty was achieved by measuring air from three tanks held at three different constant compositions. Reference tanks were provided by CSIRO Global Atmospheric Sampling Laboratory (GASLAB) with mole fractions measured relative to working standards on WMO-GAW scales and traceable to the relevant primary standards for all species (Griffith et al., 2011). Reference trace gas values are listed in Appendix A. Table A2. Monthly calibration of the FTIR instruments was performed as recommended by Hammer et al. (2013). Linear regression was used to determined calibration constants (slope: Cal_fit and intercept: Cal_int). Mean calibration values were applied to the ambient record during stable instrument periods (for a complete list of stable instrument periods and corresponding calibration constants, see Appendix A, Tables A3 and A4).

Adjustment to the previous calibration method included accounting for drift in tank CO composition, a well-known issue (Novelli et al., 2003; Zellweger et al., 2009). Drift in tank CO occurs due to oxidation of volatile organics within the tank atmosphere, additionally from the release of adsorbed CO from internal metal surfaces of the tank over time. Here, drift could be determined for two reference tanks that were replaced during the measurement period (UAN20101231 and UAN991072), as they had been measured by GASLAB both at the beginning and end of their lifetime with differing values for CO. Drift in CO was assumed to be linear and was determined to be 1.5 nmol mol⁻¹ a⁻¹ for UAN20101231 and 0.3 nmol mol⁻¹ a⁻¹ for UAN991072. Drift values were subsequently applied in calibration calculations. Other reference tanks had not received a second analysis by GASLAB, and therefore were assumed to have constant composition, an assumption which will need to be reviewed in future analyses.

Dataset uncertainty was the combined uncertainty of each processing step and was calculated for the ensembles of ambient air records, rather than for each individual measurement. Uncertainties in the records were determined for several instrumental regimes, defined by major changes in the instruments such as relocation or laser replacement. Regimes are defined in Appendix A, Tables A3 and A4. Details of the uncertainty analysis can be found in Buchholz (2014). Absolute and relative dataset uncertainties are recorded in Table 1.

2.3. Meteorological data

Wind vector and wind speed were recorded at UOW using a Davis weather station (Davis Wireless Vantage Pro2), averaged to 10-min time resolution. Wind vectors were converted to wind direction prior to analysis.

Back trajectories were calculated with the HYSPLIT model (Hybrid Single Particle Lagrangian Integrated Trajectory model, http://ready.arl.noaa.gov/HYSPLIT.php, Draxler and Hess, 1998), using the Global NOAA-NCEP (National Oceanic and Atmospheric Administration-National Centers for Environmental Prediction) meteorological reanalysis fields at 2.5° horizontal resolution. Trajectories were calculated backwards from a 10 m arrival height at Wollongong and for arrival times at every 3 h (00:00, 03:00, 06:00, 09:00, 12:00, 15:00, 18:00 and 21:00 local time) for each day of 2011 through to 2014. Total back trajectory duration was 96 h (4 days), in 1 h time steps. The uncertainty in backward trajectories increases relative to the distance back in time, with position errors generally being 20% of the distance travelled (Stohl, 1998). Uncertainties were minimised by combining trajectories to produce an ensemble.
2.4. Complementary data

Trace gas values from monthly flask data taken at the Cape Ferguson station (19.283°S, 147.050°E) and the Cape Grim baseline station (40.683°S, 144.689°E) were used as Southern Hemisphere comparison datasets (CSIRO, 2014a,b). These datasets were obtained prior to filtering to remove polluted sources. The Cape Grim record was stringently controlled by CSIRO to collect air samples only originating from the Southern Ocean. In CSIRO datasets, CO was measured by gas chromatography with a mercury oxide reduction gas detector; CO2 and CH4 were measured by gas chromatography with a flame ionisation detector (FID). Analytical techniques are detailed in Francey et al. (1996) and measurement uncertainty described in Francey et al. (2003). CO is reported relative to a CSIRO scale, which is scale to the derived by NOAA/CMDL (Novelli et al., 1998, 2003). CH4 is reported on the NOAA04 scale and CO2 on the WMOX2007 scale (Dlugokencky et al., 2005). These scales match those used for the FTIR UOW datasets. Cape Grim CO dataset was only available to June 2014, while CH4 and CO2 spanned the same time period as UOW. Cape Ferguson datasets for each species were only available to December 2013.

To complement cluster analysis (Section 2.6.3.), O3 and NO2 data from the NSW OEH (Office of Environment and Heritage (2013)), Gipps St, Wollongong city station were combined with the UOW in situ FTIR record. Ozone and NO2 measurements were obtained as hourly averages. Although the OEH site is approximately 2 km southeast of UOW, these data can help in the interpretation of source contribution to UOW data due to hourly time averaging resulting in representation of a wider spatial area. Ozone was measured using ultraviolet spectroscopy (Australian Standard 3580.6.1, 1990), and NO2 using chemiluminescence with a selective converter (Australian Standard 3580.5.1, 2011).

2.4.1. Defining a baseline

Background trace gas values were statistically separated from polluted values using a local regression method. A background threshold was determined using REBS (Robust Extraction of Baseline Signal), available in the IDPmisc R package (Ruckstuhl et al., 2009, 2012). Ruckstuhl et al. (2012) found the REBS method produced similar baseline selection for CO when compared to commonly used methods such as “smooth curve fit” (Thoning et al., 1989; Novelli et al., 1998, 2003) and AGAGE (Advanced Global Atmospheric Gases Experiment, described in O’Doherty et al., 2001). REBS assumes that long-term trends and seasonal contributions vary slowly relative to local sources. REBS determined a background envelope with least-squares regression on a “local neighbourhood” of data (approximately representing one month), smoothed with a tricube weighting function. Values below the background envelope were classed as background values.

2.5. Tagged model simulations

To interpret the influence of sources on the average background seasonal cycles at our measurement sites, we performed tagged simulations of CO and CO2 with the 3-D global chemical transport model GEOS-Chem (http://geos-chem.org/, Bey et al., 2001). Input emission files for biomass burning (GFEDv3, van der Werf et al., 2010) were not available for the same years as the measurements. The latest available emissions consequently dictated the three-year time period that was simulated: 2009–2011. Simulations were averaged over three years to reduce the impact of interannual variability on the comparisons. Biomass burning emissions were taken as monthly average GFEDv3 and biofuel emissions were from Yevich and Logan (2003). The model was driven by NASA GEOS-5 meteorological reanalysis, in 2° × 2.5° resolution and 47 vertical layers. Transport was performed in 15 min timestep intervals, while emissions and chemistry were performed every 60 min for CO and 30 min for CO2. The two simulations used here are decoupled and have different development histories. The latest available versions were used at the time of modelling, which was v9-01-03 for CO and v8-03-02 for CO2.

CO: GEOS-Chem used for simulating CO (Duncan et al., 2007) included non-local planetary boundary layer (PBL) mixing. CO was tagged by different emissions sectors and by source region. Source regions used in the tagged run are displayed in Appendix B, Fig. B1. Biogenic emissions were determined using the Model of Emissions of Gases and Aerosols from Nature (MEGAN v2.1, Guenther et al., 2012). Default anthropogenic emissions of CO were from EDGAR 3.2-FT2000 inventory (Emissions Database for Global Atmospheric Research, Olivier et al., 2005), overwritten by regional emission in the Northern Hemisphere, as described in Fisher et al. (2010). Biogenic emissions were reduced by 10%. The main loss mechanism of CO is through photochemical oxidation with OH, which was calculated in GEOS-Chem using saved monthly mean OH fields from a v9-01-03 full-chemistry simulation. A diurnal cycle based on the cosine of the solar zenith angle was imposed on the monthly mean OH fields. Differences between CO in a full chemistry run using online OH and the offline run using monthly mean OH (with diurnal variation) were less than 1% at the surface. Chemically produced CO was also taken from saved 3-D fields of a full-chemistry simulation.

CO2: Tagged CO2 was modelled with a spin-up period of 8 years, first implemented in GEOS-Chem by Sutherland (2004) with updates described in Nassar et al. (2010). Monthly fossil fuels were from Andres et al. (2011) scaled for years after 2006 (Nassar et al., 2010); ocean exchange from Takahashi et al. (2009); the biosphere described by CASA balanced terrestrial exchange (Carnegie-Ames-Stanford-Approach, Olsen and Randerson, 2004) and net annual terrestrial exchange determined from TransCom 3 climatology (Baker et al., 2006; Nassar et al., 2010). The ICOADS ship emissions were also implemented (International Comprehensive Ocean-Atmosphere Data Set, Corbett, 2003) with applied trends determined from Endresen et al. (2007). Additional options for aviation and chemical sources were not used. CO2 was tagged based on flux sector.

2.6. Analysis methodology

2.6.1. Defining a baseline

Background trace gas values were statistically separated from polluted values using a local regression method. A background threshold was determined using REBS (Robust Extraction of Baseline Signal), available in the IDPmisc R package (Ruckstuhl et al., 2009, 2012). Ruckstuhl et al. (2012) found the REBS method produced similar baseline selection for CO when compared to commonly used methods such as “smooth curve fit” (Thoning et al., 1989; Novelli et al., 1998, 2003) and AGAGE (Advanced Global Atmospheric Gases Experiment, described in O’Doherty et al., 2001). REBS assumes that long-term trends and seasonal contributions vary slowly relative to local sources. REBS determined a background envelope with least-squares regression on a “local neighbourhood” of data (approximately representing one month), smoothed with a tricube weighting function. Values below the background envelope were classed as background values.
optimal number of clusters was consistently two in all seasons for group variance for trace gas values. For CO, the optimal number of clusters was based on minimising within-source contributions. Known sources were from the Port Kembla industrial area to avoid the direct sampling of fresh pollution from known local sources. Potential build up due to local sources under low turbulence conditions were also removed (speeds <0.4 m s⁻¹).

2.6.2. Short-term trend analysis

Trends were calculated using the “TheilSen” function, supplied in the OpenAir R package (Carslaw and Ropkins, 2012). The Theil-Sen function applies bootstrap resampling methods and uses non-parametric techniques based on Theil (1950) and Sen (1968) to determine trends in timeseries data. The method calculates slopes between all pairs of points in a dataset and the median of all these slopes is the Theil-Sen estimate of the trend. Confidence intervals and an estimate of statistical significance were also calculated. Prior to trend analysis, datasets were deseasonalised by first linearly interpolating missing data then applying the loess-based seasonal decomposition R function, “stl”.

2.6.3. Clustering

Cluster analysis was performed using wind speed, wind direction and concentration k-means clustering (Carslaw and Beever, 2013). An advantage of k-means analysis is that it is robust to outliers. The k-means methodology groups data around a user-defined k number of randomly chosen initial centroid points. Remaining dataset values were grouped with the closest centroid. Once the entire dataset was assigned into groups, new centroids were calculated and grouping performed again around the new centroids. This process was iterated until the centroids were stable. Clustering was performed for a range of k groups (2–12), on the seasonally separated, hour-averaged UOW CO and CH₄ datasets. The optimal number of clusters was based on minimising within group variance for trace gas values. For CO, the optimal number of clusters varied between 4 and 6, depending on the season. The optimal number of clusters was consistently two in all seasons for CH₄, therefore the entire dataset was separated into two clusters.

3. Results and discussion

3.1. Trace gas time series

Time series of ambient CO, CH₄, and CO₂, measured at UOW between April 2011 and August 2014 are shown in Fig. 2. Analysis of measurement overlap times determined no significant bias existed between the two instruments. All three trace gases exhibit large enhancements above baseline values. For a closer look at the baseline region, see Appendix B, Fig. B2. Trace gas statistical properties are summarised in Table 2.

Mean CO at UOW (124.45 nmol mol⁻¹) is substantially higher than Southern Hemisphere typical background (40–60 nmol mol⁻¹, Blunden and Arndt, 2014), indicating UOW is influenced by a number of local CO sources. Mean values at UOW for longer lived trace gases CH₄ (1887 nmol mol⁻¹) and CO₂ (401.8 μmol mol⁻¹) are also higher than Southern Hemisphere background (CH₄: average ~1735 nmol mol⁻¹, Fraser et al., 2011; CO₂ Antarctica: 393 μmol mol⁻¹, Sun et al., 2014). UOW “clean air” records were determined to understand the drivers of background composition.

3.2. Wollongong clean air

Wind direction and wind speed restriction aimed at filtering for clean air reduced the UOW record to 30% of the original 10-min averaged FTIR record. Subsequent REBS application on the restricted datasets resulted in clean air datasets, with 14%, 13% and 6.5% of the original number of data points remaining for CO, CH₄ and CO₂, respectively. Therefore in general, clean air arrives at UOW in approximately 10% of air masses.

Clean air datasets (UOWCA) were compared with background records at two other Australian sites: Cape Grim (CGO) and Cape Ferguson (CFA). Datasets were compared directly as all were calibrated to the same scales. Although CSIRO used a different method to extract background values at CGO and CFA, the REBS baseline extraction has been shown to produce similar results to other methods (Ruckstuhl et al., 2012), allowing comparison of all three datasets. Additionally, while Cape Grim can be affected by outflow from Melbourne (~200 km north of CGO, Dunse et al. (2005)) or biomass burning from the continent (Lawson et al., 2015), the CGO record selects stringently for background air, with flask sampling only performed during strong baseline conditions when air originates from the Southern Ocean. Therefore, CGO may be thought of as representing a point in the Southern Ocean.

Statistical differences between sites (Table 2) can be explained by station proximity to trace gas sources combined with transport and trace gas lifetime. The continental sites CFA and UOWCA are closer to local and regional sources from natural origins, such as biomass burning and biogenic emissions, compared to CGO. As a result, continental sites generally have higher values, as is seen for mean CO and CH₄. The tagged CO simulation showed Australian biomass burning sources contributed the most to mean surface mole fraction of CO at CFA (9%), followed by Wollongong (3%), and relatively little at CGO (1%).

Additionally, of the three sites, UOW is closest to the largest Australian city, Sydney. While the UOWCA dataset is filtered to avoid directly sampling urban pollution, atmospheric mixing would ensure Sydney urban influence on the regional background, thereby affecting the magnitudes of all three trace gases for UOWCA. In contrast, the other two stations are distant from large urban sources, Cape Ferguson in north Queensland and Cape Grim being representative of the Southern Ocean. Therefore, the UOWCA record is the most influenced by anthropogenic sources. Model results found Australian anthropogenic CO contributed the most to mean surface mole fraction at Wollongong (7%), with much less contribution at CFA (3%) and CGO (3%).

3.2.1. Annual cycles

Average annual cycles were determined for de-trended UOWCA, CGO and CFA datasets (Fig. 3). For each trace gas, differences between sites vary depending on month, which implies a difference in source and sink characteristics at each location.

At all three sites, CO and CH₄ show approximately sinusoidal seasonal cycles (Fig. 3(a) and (b)), driven by a combination of the OH sink with sources. The main loss mechanism for CO and CH₄ is through reaction with photochemically produced OH radicals. Production of OH is maximised in summer (Novelli et al., 1998), therefore, a maximum in the OH sink drives the summer minima in CO and CH₄. Overlaid on the cycle induced by OH is the seasonality of source contributions.

GEOS-Chem tagged tracer studies of CO were used to identify source contributions. Absolute magnitudes cannot be
quantitatively compared between measurements and model values because different time periods were available (see Section 2.5). However, we used the model to understand seasonality in the regional background, which is not expected to change over the timescales investigated here. A regional background was defined by an average of model output over a 8 by 10°C14 region around each station. In order to avoid possible influence from Melbourne, Cape Grim was taken to be a point to the southwest of the station, resulting in an average over a region of the Southern Ocean. It is common to compare modelled Southern Ocean to the Cape Grim record to replicate baseline conditions, for example as used in Fisher et al. (2015). February 2009 was removed from annual cycle calculations due to unusually high biomass burning in southeast Australia (Paton-Walsh et al., 2012), not covered in the measurement period here. The modelled and measured average annual cycles at each station are compared in Appendix B, Fig. B3. Modelled annual cycles adequately simulated the measured annual cycles, allowing further analysis of modelled sources. The contribution from each CO source type to average annual cycles at each station is shown in Fig. 4. Each source-specific annual cycle intrinsically includes loss processes.

Modelled results show that the main contributor to CO seasonality at Cape Ferguson and Wollongong is from biomass burning sources, modulated by sink processes. Approximate biomass burning source contribution to the seasonal amplitude is 30 nmol mol–1 for Cape Ferguson and 10 nmol mol–1 for Wollongong. Biomass burning is also a major contributor to the seasonal cycle at Cape Grim, with a seasonal amplitude of approximately 8 nmol mol–1. However, other sources contribute comparatively to the annual cycle at Cape Grim, meaning this site reflects a mixture of sources, as expected from a baseline station. Transported Southern Hemisphere biomass burning CO contributes equally at Cape Ferguson and Wollongong, and it is only the stronger influence from Australian biomass burning at Cape Ferguson that drives a larger amplitude. Wollongong experiences more contribution from Australian burning in February–May than Cape Ferguson. Cape Grim is the least affected by Australian biomass burning. Anthropogenic sources from Australia contribute the most at

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<td>CO2 μmol mol–1</td>
<td>UOW</td>
<td>401.8</td>
<td>398.5</td>
<td>377.9</td>
<td>501.5</td>
<td>397.2</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>UOWCA</td>
<td>394.0</td>
<td>394.3</td>
<td>388.5</td>
<td>394.9</td>
<td>394.9</td>
<td>2.1</td>
</tr>
<tr>
<td></td>
<td>CFA</td>
<td>391.2</td>
<td>391.5</td>
<td>386.5</td>
<td>395.6</td>
<td>395.6</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Datasets analysed were Wollongong 10 min average (UOW, 34.4°S, 150.9°E), Wollongong clean air 10 min average (UOWCA), month average Cape Ferguson (CFA, 19.3°S, 147.1°E) and month average Cape Grim (CGO, 40.7°S, 144.7°E). Means are significantly different to CGO (p < 0.001), except for CFA CO2 and CH4.

Records span April 2011–August 2014, with exceptions due to data availability: the CGO CO record, which ends in June 2014, and all CFA records, which end in December 2013.
Wollongong. Mixing of anthropogenic CO from the Northern Hemisphere is approximately the same at all stations, and contributes on average about 2 nmol mol\(^{-1}\).

These results are consistent with other studies that have found that the characteristic spring maximum in CO (August–October) is associated with peak Southern Hemisphere biomass burning (Edwards et al., 2006b). Northern Australian burning also peaks in spring (Craig et al., 2002), responsible for the larger magnitude in springtime CO at the northern-most site, CFA.

The model overestimates CO in February at UOW and CFA (Appendix B, Fig. B3 (a) and (b)), which may be due to different years being modelled than measured, consequently modelling different biomass burning from highly variable east-coast fires. Additionally, secondary VOC oxidation contributes in February, so...
VOC oxidation may also be overestimated in the model. The model underestimates the CFA shoulder in May–August (Appendix B, Fig. B3 (a)), which suggests an underestimation or missing source. Early Australian biomass burning may be underestimated, as CFA shows a shoulder in this modelled source from May–August. Alternatively, a possible explanation for this underestimation at CFA is detailed in the CH4 annual cycle section below.

CH4 has been intensively studied at these three sites by Fraser et al. (2011) using tagged GEOS-Chem simulations. They found modelled CH4 at Wollongong was dominated by coal, animals, and landfill fluxes; at Cape Grim by animals, landfills, and ocean; and at Cape Ferguson by coal, animals and wetlands. The timing of the seasonal cycle for wetland CH4 tracer at Cape Ferguson in Fraser et al. (2011) coincides with the annual cycle bump seen in May–July for CFA (Fig. 3(b)), suggesting wetland emissions are the likely cause. Deutscher et al. (2010) also found that north Australian wetlands contribute significantly to CH4 sources during the wet season. Through oxidation, the northern Australian wetland source of CH4 would also contribute to the shoulder seen in CO measurements at CFA (Fig. 3(a)). However, GEOS-Chem does not reproduce the measured shoulder, suggesting inaccurate wetland emissions are the cause of underestimation (Appendix B, Fig. B3(a)). Chemically produced CO in the tagged CO simulation was taken from a full chemistry model run, which included specified CH4. GEOS-Chem full chemistry CH4 is averaged over large latitudinal bands, and determined from surface observations taken at Global Monitoring Division background sites, distant from the north Australian wetlands. Oxidation of the modelled CH4 to CO will also be driven by the latitudinal bands. Therefore, the tagged CO simulation used here would not have correctly captured the contribution from north Australian wetlands, particularly important for sites close to these emission sources such as CFA.

Annual cycles for CO2 are markedly different between sites (Fig. 3(c)), suggesting major differences in flux contributions. GEOS-Chem tagged CO2 tracer results (2009–2011) were also averaged over an 8 by 10° region around each station. A comparison of normalised measured and modelled annual cycles is shown in Appendix B, Fig. B4. Although modelled cycles are timed slightly differently to measurements, the relative differences between stations are captured, with bimodal behaviour at Cape Ferguson and a shifted phase of Wollongong to Cape Grim. Also, measured and modelled seasonal amplitudes are approximately equivalent: modelled $A_{\text{sec}}$: 2.2, measured 2.1 μmol mol$^{-1}$ for Cape Ferguson; modelled 1.8, measured 1.3 μmol mol$^{-1}$ for Wollongong; and modelled 0.7, measured 1.2 μmol mol$^{-1}$ for Cape Grim. Therefore modelled results may be used to further interpret the annual cycles at each station. The contributions from each flux type to average seasonality are shown in Fig. 5. Seasonality has been normalised by the mean of each flux-type, due to the large differences in magnitude between fluxes.

Model results show the main driver of CO2 annual cycle at CFA and UOW is biospheric uptake (Fig. 5(a) and (b)). Biomass burning is also a significant contributor to surface annual cycle at Cape Ferguson. The Cape Grim annual cycle is a combination of the seasonality of all sources, as expected for a well-mixed baseline site. These results are consistent with Deutscher et al. (2014), who used tagged tracer studies to show annual cycles of column-averaged CO2 in Australasia were dominated by the biosphere. CFA is similar to the tropical site Darwin in Deutscher et al. (2014), who explain the bimodal seasonality at Darwin CO2 as a combination of transported Northern Hemisphere biogenic drawdown, with tropical biogenic drawdown. They also found a smaller, but significant influence to the column from Southern Hemisphere biomass burning.

Timing of the total CO2 annual cycles is shifted in the model compared to measurements at all three sites (Appendix B, Fig. B4). This suggests the main driver of biospheric uptake may be mis-timed either due to emissions or transport errors. Without regional decomposition it is unclear whether the NH and/or the Australian biosphere fluxes are mis-timed.

Comparing sites, the measured UOWCA CO2 annual cycle summer peak is shifted in phase from the CGO cycle, which is replicated...
in model results. Modelled CO$_2$ (Fig. 5(b)) indicates the Wollongong cycle is mainly driven by biogenic drawdown. Photosynthesis is both light and water-limited in the arid Australian climate (Eamus et al., 2001), meaning a drop in photosynthesis occurs over much of the continent during the dry summer periods. Baldocchi (2008) found the largest drawdown of CO$_2$ in Australian semi-arid regions occurred during the winter months, consistent with the result in Fig. 5(b). Additionally, fire has been found to change savanna regions from carbon sinks into net carbon sources, as respiration outweights photosynthesis in new growth (Beringer et al., 2015). This suggests the Australian interior savanna region would become a carbon source following the spring burning season. Therefore, it is hypothesised that the Australian biosphere is the main driver of the CO$_2$ annual cycle seen at Wollongong.

3.2.2. Short-term variability

A negative trend was found in CO for both UOWCA and CFA (Table 3). The trend for UOWCA was $-1.5$ nmol mol$^{-1}$ a$^{-1}$ with a 95 percent confidence interval of $-2.2$ to $-0.45$ nmol mol$^{-1}$ a$^{-1}$. A stronger negative trend in CO was seen for CFA, at $-4.9$ [95% CI: $-6.2$ to $-3.6$] nmol mol$^{-1}$ a$^{-1}$. CO$_2$ did not have a significant trend for CO. Fisher et al. (2015) have also found no significant trend in surface measurements of CO at Cape Grim between 1991 and 2011.

Compared to CGO, UOWCA and CFA are located closer to changing sources of CO. The approximately two-month lifetime of CO, combined with atmospheric mixing required to reach CGO, would become a carbon source following the spring burning season (Fig. 6). Surface measurements have a dependence on wind speed and wind direction. The UOW dataset within each bin. The result was a surface of mean mole fraction, Generalized Additive Model was used to calculate mean values for CO$_2$ and CH$_4$. These studies all include upper tropospheric CO that may have diluted the surface trends. Surface data show stronger trends than column-averaged data due to the proximity to changing sources. For example, Novelli et al. (1998) used surface CO measurements from the National Oceanic and Atmospheric Administration, Earth System Research Laboratory, Global Monitoring Division (NOAA/ESRL/GMD) between 1990 and 1995 and found Southern Hemisphere trends of $-3.0$ % a$^{-1}$ relative to 1991 levels.

Zeng et al. (2012) suggested the main driver of the trend in Southern Hemisphere column CO was a decline in CO industrial and urban emissions. While this may be the cause of long-term trends in column data, it does not adequately explain the trend in surface CO found here, as a stronger trend was found in background air at CFA than for clean air at UOWCA. CFA is further from the regional influence of industry and urban areas than Wollongong, so CFA experiences an overall lower contribution from anthropogenic sources, as determined from annual cycle analysis (Section 3.2.1). Therefore, CFA would capture less contribution from any trend in anthropogenic emissions than UOWCA.

Positive trends in CH$_4$ and CO$_2$ were found at all sites. The UOWCA short-term trend values for CH$_4$ and CO$_2$ are consistent with IPCC mean global long-term trends in observations. The trend for UOWCA CH$_4$ is 5.4 [95% CI: 3.8, 6.4] nmol mol$^{-1}$ a$^{-1}$, compared to the IPCC trend of approximately 6 nmol mol$^{-1}$ a$^{-1}$ between 2007 through 2011 (Hartmann et al., 2013). The trend in UOWCA CO$_2$ is 1.9 [95% CI: 1.8, 2.1] nmol mol$^{-1}$ a$^{-1}$ and the IPCC trend since 2001 is 2.0 ± 0.3 nmol mol$^{-1}$ a$^{-1}$ (Hartmann et al., 2013). This indicates that enough clean air can be isolated at Wollongong to determine globally relevant trends in CO$_2$ and CH$_4$.

3.3. Air quality and cluster analysis

Polluted air masses were investigated by analysing mole fraction relationship to wind speed and wind direction. The UOW dataset was filtered to remove wind speeds below 0.4 ms$^{-1}$. Seasonal bivariate polar plots were produced from hour-averaged UOW CO and an annual bivariate polar plot was produced for CH$_4$, following the method described in Carslaw and Beevers (2013). Briefly, the trace gas was grouped by 30 wind speed and 10° wind sector bins. A Generalized Additive Model was used to calculate mean values within each bin. The result was a surface of mean mole fraction plotted against wind speed and wind direction, centred at UOW.

Seasonal bivariate polar plots of atmospheric CO demonstrate that mean CO varies with wind speed and wind direction in each season (Fig. 6). Surface measurements have a dependence on boundary layer mixing, where stable conditions under a contracted boundary layer encourage build up of emissions from local sources. The record was therefore filtered against low wind speeds (defined here as <0.4 ms$^{-1}$) in order to remove stable meteorological
Table 4  
UOW cluster-specific mean CO, enhancement ratios $\Delta O_3/\Delta CO$, $\Delta CO/\Delta CO_2$ and mean NO$_2$.  

<table>
<thead>
<tr>
<th>Season</th>
<th>Cluster (# values)</th>
<th>Mean CO ($\sigma$) nmol mol$^{-1}$</th>
<th>$\Delta O_3/\Delta CO$</th>
<th>$\Delta CO/\Delta CO_2$</th>
<th>Mean NO$_2$ nmol mol$^{-1}$</th>
<th>Mean wind direction and land use type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spring (SON)</td>
<td>1 (488)</td>
<td>86 (44)</td>
<td>6.03 (r:0.4)</td>
<td>5.4</td>
<td>SW to W, escarpment/forest</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2 (158)</td>
<td>185 (143)</td>
<td>25.0 (r:0.6)</td>
<td>6.6</td>
<td>S, local urban &amp; industry</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3 (1256)</td>
<td>146 (110)</td>
<td>0.26 (r:0.2)*</td>
<td>8.89 (r:0.4)</td>
<td>8.0</td>
<td>NE to SE, ocean &amp; local urban</td>
</tr>
<tr>
<td></td>
<td>4 (96)</td>
<td>110 (40)</td>
<td>0.22 (r:0.3)</td>
<td>11.24 (r:0.7)</td>
<td>3.6</td>
<td>NE to E, ocean &amp; transported urban</td>
</tr>
<tr>
<td></td>
<td>5 (183)</td>
<td>143 (133)</td>
<td>8.62 (r:0.3)</td>
<td>7.9</td>
<td>N to NW, transported urban</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6 (35)</td>
<td>90 (61)</td>
<td>15.6 (r:0.7)</td>
<td>3.9</td>
<td>NW, escarpment/forest</td>
<td></td>
</tr>
<tr>
<td>Summer (DJF)</td>
<td>1 (206)</td>
<td>86 (65)</td>
<td>9.60 (r:0.5)</td>
<td>5.9</td>
<td>SW, escarpment/forest</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2 (217)</td>
<td>143 (115)</td>
<td>20.3 (r:0.4)</td>
<td>6.1</td>
<td>S, local urban &amp; industry</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3 (279)</td>
<td>81 (54)</td>
<td>11.0 (r:0.6)</td>
<td>2.4</td>
<td>E to SE, ocean</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4 (332)</td>
<td>80 (21)</td>
<td>6.32 (r:0.7)</td>
<td>2.3</td>
<td>NE, ocean &amp; transported urban</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5 (1263)</td>
<td>112 (91)</td>
<td>7.15 (r:0.4)</td>
<td>6.2</td>
<td>N to NW transported &amp; local urban</td>
<td></td>
</tr>
<tr>
<td>Autumn (MAM)</td>
<td>1 (803)</td>
<td>73 (31)</td>
<td>-0.55 (r: -0.3)</td>
<td>-</td>
<td>5.5</td>
<td>NW to SW, escarpment/forest</td>
</tr>
<tr>
<td></td>
<td>2 (1024)</td>
<td>124 (77)</td>
<td>6.15 (r:0.3)</td>
<td>9.1</td>
<td>S, local urban &amp; industry</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3 (679)</td>
<td>99 (48)</td>
<td>-0.72 (r: -0.2)</td>
<td>5.13 (r:0.3)</td>
<td>8.0</td>
<td>NW to E, local &amp; transported urban</td>
</tr>
<tr>
<td>Winter (JJA)</td>
<td>1 (894)</td>
<td>79 (28)</td>
<td>-0.46 (r: -0.3)</td>
<td>7.32 (r:0.6)</td>
<td>4.5</td>
<td>SW to W, escarpment/forest</td>
</tr>
<tr>
<td></td>
<td>2 (105)</td>
<td>176 (143)</td>
<td>25.2 (r:0.7)</td>
<td>11</td>
<td>S, local urban &amp; industry</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3 (404)</td>
<td>107 (57)</td>
<td>-0.44 (r: -0.2)</td>
<td>13.9 (r:0.5)</td>
<td>8.6</td>
<td>SE, ocean</td>
</tr>
<tr>
<td></td>
<td>4 (1385)</td>
<td>139 (76)</td>
<td>-0.53 (r: -0.2)</td>
<td>8.26 (r:0.5)</td>
<td>11</td>
<td>N to NE local &amp; transported urban</td>
</tr>
<tr>
<td></td>
<td>5 (702)</td>
<td>78 (27)</td>
<td>-0.54 (r: -0.4)</td>
<td>6.51 (r:0.5)</td>
<td>5.4</td>
<td>NW to N, escarpment/forest</td>
</tr>
<tr>
<td></td>
<td>6 (52)</td>
<td>66 (11)</td>
<td>-0.24 (r: -0.5)</td>
<td>1.9</td>
<td>NW, escarpment/forest</td>
<td></td>
</tr>
</tbody>
</table>

Cluster numbers match the numbering in Fig. 6. Enhancement ratios were determined using ranged major axis (RMA) and are recorded where $|r| > 0.2$ and/or $p < 0.01$. Units of $\Delta O_3/\Delta CO$ are nmol mol$^{-1}$ O$_3$ per nmol mol$^{-1}$ CO. Units of $\Delta CO/\Delta CO_2$ are nmol mol$^{-1}$ CO per $\mu$mol mol$^{-1}$ CO$_2$.

* 2 outliers (CO < 1000) were removed from the record to avoid skewing of results.

High CO is measured at UOW in all seasons when winds originate from the south to southwest direction with wind speeds less than 3 ms$^{-1}$ (Fig. 6). Sources from this direction are local urban pollution associated with the centre of Wollongong city and the steelworks at Port Kembla. Enhanced CO at UOW also occurs in air originating from the north to northeast direction. Sources of CO from the north at lower wind speeds (e.g. spring at speeds <2 ms$^{-1}$) are likely due to pollution from the adjacent motorway; while faster wind speeds (e.g. spring from the north at speeds >2 ms$^{-1}$) are likely associated with a plume of Sydney urban outflow. Lowest mole fractions occurred in autumn, which is consistent with the background annual cycle (Section 3.2.1).

Features of the bivariate polar plots of CO were investigated using cluster analysis. Clusters are indicated in Fig. 6 by grey outlines and are numbered. Minimising within group variance of CO determined the optimal number of clusters for each season. Winter and spring had the highest number of optimal clusters, 6, while summer produced 5 clusters, and autumn had 4 clusters. Consistent clusters between seasons are those containing high CO to the south (Cluster 2 in all seasons) and those containing low CO to the west/southwest (Cluster 1 in all seasons).

Table 4 summarises the properties of each cluster, including mean CO, mean NO$_2$, and $\Delta O_3/\Delta CO$ and $\Delta CO/\Delta CO_2$ enhancement ratios from correlation analysis. Enhancement ratios ($\Delta Y/\Delta X$) were calculated using the ‘scatter technique’ described in Parrish et al. (1993), where a linear fit is applied to a plot of one trace gas, Y, against the other, X. The slope of the line is the enhancement ratio ($\Delta Y/\Delta X$). Here, enhancement ratios were recorded only if correlation existed between trace gases, defined as $r \geq 0.2$, $p \leq 0.01$. Ranged major axis fitting (RMA, Legendre and Legendre, 1998) was used to perform linear regression between tracers for each cluster, accounting for uncertainty in both variables.

Enhancement ratio analysis of $\Delta O_3/\Delta CO$ can indicate environments of O$_3$ production (positive) or O$_3$ destruction and/or deposition (negative) (Fishman and Seiler, 1983; Parrish et al., 1993). Here, $\Delta O_3/\Delta CO$ gave qualitative insight into the atmospheric oxidation environment in the Wollongong region. A quantitative analysis of O$_3$ production is more complicated due to differing background amounts, and was not pursued.
In all seasons, Cluster 2 receives fresh pollution, as evidenced by high mean CO, high mean NO2 and large ΔCO/ΔCO2 ratios (Table 4). Fresh pollution plumes have had little time to undergo ozone production, therefore no significant ΔO3/ΔCO was observed.

Negative ΔO3/ΔCO in autumn and winter indicates the Wollongong atmosphere is an ozone destruction/deposition/subsidence environment during these seasons. In contrast, positive ΔO3/ΔCO during spring and summer implies that ozone production occurs. Ozone is produced photochemically from VOCs and NOx. Spring and summer experience enhanced incoming solar radiation and higher emissions of biogenic VOCs, relative to autumn and winter. In Wollongong, this enhanced incoming solar radiation combined with local and regional urban pollution, large sources of VOCs and NOx, produces ozone. Additionally, the peak biomass burning season in the Southern Hemisphere occurs during austral spring (Edwards et al., 2006b; Craig et al., 2002), and O3 is photochemically produced in the aged biomass burning plume (Jaffe and Wigder, 2012). Therefore, ozone production environments during austral spring are likely a combination of transported smoke plumes and urban pollution plumes.

Results found here are in agreement with Voulgarakis et al. (2011), who showed positive ΔO3/ΔCO around the east coast of Australia during austral summer and negative correlations during austral winter in a global study using the TES satellite instrument. Results here also agree with a global study using OMI/AIRS satellite products from 2008 (Kim et al., 2013), which investigated seasonal ΔO3/ΔCO in the free troposphere and found summer (DJF) gave positive correlations localised around the east Australian coast, while autumn (MAM) gave negative correlations across the bottom half of Australia. They did not calculate enhancement ratios below 30° S in winter due to data limitations. This agreement between Wollongong in situ and the spatially averaged satellite correlations from summer to winter suggests the Wollongong ozone production environment is representative of a wider region in the free troposphere. In contrast, while spring results from Kim et al. (2013) showed a large latitudinal band (0°–40° S) of strong positive correlation over much of the Southern Hemisphere, the region around eastern Australia gave negative correlations, thus disagreeing with surface correlations found here. This may mean Wollongong in situ correlations are more representative of local surface conditions in spring.

The polar bivariate plot for CH4 is consistent between seasons, therefore the plot for the whole dataset is shown (Fig. 7). High CH4 originates from the north to northwest, the direction of transported urban and coal mining sources. Cluster analysis found 2 distinct clusters for CH4. Cluster specific mean CH4, mean NO2 and enhancement ratios of CH4 relative to CO and CO2 are listed in Table 5. Cluster 2 shows high mean CH4, high mean NO2 and larger enhancement ratios than Cluster 1. Cluster 2 ΔCH4/ΔCO2 enhancement ratios are higher than ratios previously found for anthropogenic air masses (reference value in Table 5). The higher values are likely due to Wollongong being located close to coal seams and related mining. Annual cycles for each cluster (Appendix B, Fig. B5) show that Cluster 2 produced a maximum in June–July, coinciding with maximum coal use for energy production in austral winter. These results are supported by Fraser et al. (2011), who found coal mining made the largest contribution (60%) above background CH4 conditions at Wollongong. In contrast, Cluster 1 produces an annual maximum indicative of background CH4.

### 3.3.1. Pollution climatology

Back-trajectories were used to determine meteorological influence on the ΔO3/ΔCO separated into seasonal CO clusters at Wollongong. Mean trajectories were determined for each cluster and are shown in Appendix B, Fig. B6, with selected clusters also in Fig. 8. Back trajectories were combined with atmospheric data of each cluster before gridded frequency maps and Concentration Weighted Trajectory (CWT) plots were calculated (Fig. 8). Gridded frequencies describe the number of unique trajectories passing through a particular grid square, providing an overview of spatial contribution to Wollongong atmospheric measurements. However, frequency maps do not determine where high pollution originates. To determine contribution to high CO at Wollongong, the CWT method was applied (Seibert et al., 1994). CWT used a gridded domain and tracked trajectory residence time in each grid box prior to arrival at Wollongong, in combination with the arrival value of CO. High values over certain grid cells indicate that when a trajectory passed over that area, it often led to high atmospheric CO at Wollongong.

As discussed in the previous section, photochemistry and higher local sources are likely the main cause of the differences between winter Cluster 4 and spring Cluster 3, which display similar

---

### Table 5

<table>
<thead>
<tr>
<th>Cluster (# values)</th>
<th>Mean CH4 nmol mol⁻¹</th>
<th>ΔCH4/ΔCO</th>
<th>ΔCH4/ΔCO2</th>
<th>Mean NO2 nmol mol⁻¹</th>
<th>Mean wind direction and land use type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (7817)</td>
<td>1817</td>
<td>2.2 (r:0.3)</td>
<td>19 (r:0.4)</td>
<td>6.1</td>
<td>NNE to NW, ocean, urban, escarpment</td>
</tr>
<tr>
<td>2 (2801)</td>
<td>2027</td>
<td>13 (r:0.2)</td>
<td>61 (r:0.3)</td>
<td>9.7</td>
<td>NW to NNE, transported urban &amp; coal mining</td>
</tr>
</tbody>
</table>

Cluster numbers match the numbering in Fig. 7. Enhancement ratios were determined using ranged major axis (RMA) and are recorded where |r| ≥ 0.2 and/or p = 0.01. Units of ΔCH4/ΔCO are nmol mol⁻¹ CH4 per nmol mol⁻¹ CO. Units of ΔCH4/ΔCO2 are nmol mol⁻¹ CH4 per μmol mol⁻¹ CO2.
meteorological patterns (Appendix B, Fig. B6) and similar mean CO and ΔCO/ΔCO₂ (Table 4), but have different ozone production environments. The CWT plot of spring Cluster 3 (Fig. 8(c)) shows high CO is sourced from a large area around southeast Australia, reflecting the higher amounts generally present at this time of year from transported and regional biomass burning.

In addition to photochemical influence, meteorology can influence ozone production environments at Wollongong. Positive ΔO₃/ΔCO enhancement ratios at UOW were frequently associated with slow moving trajectories possessing anticyclonic behaviour. For example, summer Cluster 4 has a positive ΔO₃/ΔCO with intermediate mean CO, but low levels of NO₂, probably lost during photochemical production of O₃. Fig. 8(d) shows back trajectories associated with summer Cluster 4 have mean anticyclonic behaviour. The resulting probability map (Fig. 8(e)) indicates trajectories had a high probability of originating from low latitudes and east of the continent. The concentration weighted trajectory (CWT) analysis indicates areas of most probable spatial source of CO to UOW measurements.

Meteorology also appears to influence ozone destruction/depocent. Ozone destruction was found to be associated with faster moving trajectories that originate from the south (e.g. autumn Cluster 1, Fig. 8(g)). These faster moving trajectories also tended to originate from higher altitudes. For example, negative ΔO₃/ΔCO was found for autumn and winter clusters 1 and was
associated with mean trajectories originating from higher altitudes, compared with equivalent spring and summer clusters 1, which showed lower altitude origins and no correlation (Fig. 9). The negative correlation in winter and autumn clusters 1 is therefore most likely due to transport and subsidence of air with higher O3 and lower CO.

The ozone destruction environments are also associated with trajectories that originate in the west and travel over the continent (e.g. winter Cluster 5, Fig. 8(j)). The winter Cluster 5 probability map (Fig. 8(k)) indicates a high probability that trajectories have travelled from inland regions, and the CWT plot shows main CO biospheric influence. We postulate that the summer peak in CO2 at UOW is due to the influence of water-limited biospheric drawdown on the continent during summer. Tracer modelling CO2 experiments tagged by region would be valuable to quantitatively determine how the Australian biosphere is affecting the seasonal cycle at Wollongong.

A short-term negative trend was found in clean air CO at UOW, with Cape Ferguson background experiencing a more negative trend than UOW clean air. The negative trend in CO was attributed to a negative trend in fire over northeast Australia during the same time period, hence the stronger trend at Cape Ferguson than UOW. Other areas of the Southern Hemisphere that could contribute to transported sources of CO saw no trend in fires. Backward Lagrangian and tagged tracer analysis over the same time-period would help quantify which sources are contributing to the decline in CO. Short-term positive trends in UOW clean air values of CH4 and CO2 were consistent with the global average long-term trends for these gases reported by the IPCC. These trace gases at UOW could therefore be used to follow globally relevant trends, in background values. Long-term measurements at this site will be able to determine globally relevant changes in greenhouse gases and pollution.

Polluted air was investigated with seasonal cluster analysis, and determined high CO pollution originated from the southern direction in all seasons. Clusters from the south were likely influenced by a combination of local urban and industrial sources. High CO was also transported from the north/northeast in winter and spring, indicating influences from local and Sydney pollution. A cluster of high CH4 from the northwest coal mining direction had higher ΔCH4/ΔCO2 enhancement ratios than previously found for anthropogenic air.

The autumn and winter Wollongong atmosphere supports ozone destruction (negative ΔO3/ΔCO correlations) while spring and summer show ozone production (positive ΔO3/ΔCO correlations). Trajectory analysis indicated that at UOW, ozone production environments are often associated with slower moving, anticyclonic trajectories that spend more time close to the ground and east of the continent before arriving at UOW. Aged pollution gives rise to positive ΔO3/ΔCO in spring and summer, driven by enhanced photochemistry. The anticyclonic behaviour traps local and Sydney urban pollution over the eastern coastal region, providing an ideal environment for photochemical ozone production in the recirculated pollution plume. In contrast, ozone destruction environments correspond with fast trajectories from the west over the continent, or from southern trajectories. Meteorological conditions should therefore be taken into account when developing policies for controlling air quality.

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