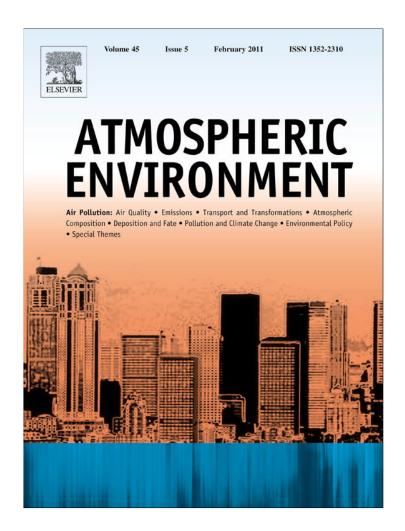
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# Measurements of carbon dioxide in an Oregon metropolitan region

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#### ABSTRACT

Ambient concentrations of atmospheric carbon dioxide ( $CO_2$ ) are reported for the Portland, Oregon (USA) metropolitan region for the late July through December, 2009 period. Three stationary locations were established: a downtown location on the campus of Portland State University; a residential site in southeast Portland; and a rural station on Sauvie Island, located ~30 km northwest of Portland in the Columbia River Gorge. Continuous measurements of  $CO_2$  at each site average 403–408 ppm and show considerable variability at each site (360–610 ppm) due to  $CO_2$  sources, sinks and meteorological variability. Within this variability, a marked 20–30 ppm diurnal cycle is observed due to photosynthetic activity and variations in the planetary boundary layer. In-city  $CO_2$  concentrations are on average enhanced by 5–6 ppm over the Sauvie Island site during upgorge wind conditions, a difference which is greatest in the afternoon. Measurements of the  $^{13}C/^{12}C$  ratio of  $CO_2$  in downtown Portland are significantly depleted in  $^{13}C$  relative to  $^{12}C$  compared with background air and suggest that regional  $CO_2$  is dominated by petroleum sources (75–80%). High degrees of relationship between  $CO_2$  variability and primary air pollutants  $CO_3$  and  $CO_3$  in dominated by the Oregon Department of Environmental Quality at the Southeast Portland location, corroborate this finding and illustrate the importance of traffic emissions on elevated ambient  $CO_2$  concentrations.

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## 1. Introduction

Metropolitan regions are responsible for a large fraction of anthropogenic carbon dioxide ( $CO_2$ ) emissions globally (Andres et al., 2010). Urban centers, in particular, are dense in population and support extensive commercial activity resulting in high rates of fossil fuel consumption in energy and transportation sectors. The apportionment by fuel source in cities varies widely around the world depending on regional petroleum, natural gas, and coal use (Decker et al., 2000).

Due to a lack of federal regulatory framework in the United States, a patchwork of regional and statewide approaches to reducing  $\mathrm{CO}_2$  emissions has emerged. The City of Portland, Oregon together with Multnomah County established itself as an early frontier in this regard by creating greenhouse gas emissions inventories in 1990 and adopting a regional plan to reduce emissions in 1993. The most recent work-product of this effort is a Climate Action Plan, released in 2009, which details an ambitious proposal to decrease greenhouse gas emissions by 40% below 1990 levels by 2030 and 80% below by 2050 (Adams et al., 2009).

The Portland Metropolitan region, located in the Columbia River Gorge, is the most populous region in Oregon. Greenhouse gas (GHG) emissions inventories for Multnomah County (population  $\sim$ 710 k, Proehl, 2008) estimate 2008 emissions to be 8.5 million metric tons CO<sub>2</sub> equivalent (MMTCO<sub>2-e</sub>), of which CO<sub>2</sub> is the dominant source (Adams et al., 2009). The County accounts for  $\sim$ 14% of Oregon statewide GHG emissions (Duncan et al., 2009). Despite this large fraction of state GHG, per capita emissions in the Multnomah County are 12 MTCO<sub>2-e</sub>, which are lower than the statewide average of 17 MTCO<sub>2-e</sub>. Recent emissions inventories suggest that County-wide GHG emissions are near 1990 levels, despite a 22% growth in population (Proehl, 2008). This contrasts with the US National GHG emissions, which have grown  $\sim$ 14% since 1990 (EPA, 2010). Despite these efforts, there has been no validation of either emissions inventories in the Portland metropolitan region or their trends in time

A number of studies in the past decade have characterized  $CO_2$  concentrations and fluxes in urban areas, most of which can be attributed to fossil sources (George et al., 2007; Grimmond et al., 2002; Idso et al., 2001; Newman et al., 2008; Pataki et al., 2009; Velasco et al., 2005). These studies make progress towards better understanding urban  $CO_2$  sources and ultimately improving emissions inventories. Prior to this study, little work has taken place in cities of the northwestern United States. Yet this region warrants comparison because its fossil fuel intensity may be lower than

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other regions of the United States due to efforts in urban planning as well as the benefit of a relatively moderate climate. Here, we report methods and first results of a study to characterize  $\rm CO_2$  variability and its  $^{13}\rm C$  isotopic composition in Portland, Oregon. We focus this paper on measurements from three regional monitoring stations in the metropolitan area during the months of July through December, 2009.

#### 2. Methods

#### 2.1. Study area

The Columbia Gorge is one of the windiest areas in the northwest due to the unique topography as the only near-sea level gap through the Cascade Mountains. The consistently strong winds have attracted significant investment in wind energy and is the reason the Columbia Gorge is one of the premier windsurfing locations in the continental United States. During Summer months and into Fall months upgorge winds dominate due to a strong east—west temperature gradient across the Cascade Range. In the Portland region, mean wind direction during this time of year is dominated by northwesterlies. In Winter months a reversal in east—west temperature and density gradients cause the wind direction to shift direction to downgorge. These Winter easterlies are regularly enhanced by synoptic scale pressure differences which set up a condition for downgradient movement of air through the Columbia Gorge known as "gap flow" (Sharp and Mass, 2004).

In this study, we exploit this climatic feature of the Columbia Gorge by establishing one rural and two in-city sites to monitor CO<sub>2</sub> concentrations. In mid-Summer 2009, three sites were established: Sauvie Island ~30 km northwest of Portland (SIS, 45.77°N, 122.77°W, 6 m); downtown Portland on the campus of Portland State University (PSU, 45.51°N, 122.69°W, 63 m); and southeast residential Portland (SEL, 45.50°N, 122.60°W, 75 m) (Fig. 1). Working in collaboration with Oregon Department of Environmental Quality (DEQ) two of the three sites are in DEQ shelters for the ongoing regional air quality monitoring program (SIS and SEL). The northwesterlies dominant during Summer and early Fall months, establish the Sauvie Island site as directly upwind of Portland and a model location to monitor GHG concentrations in incoming air to the metropolitan region. Elevated levels of GHGs within the metropolitan region can be attributed to sources, most of which are anthropogenic.

#### 2.2. Instrumentation

All three sites are equipped with a Li-Cor infrared gas analyzer (model 840) which measures  $CO_2$  and  $H_2O$  concentrations at 4 Hz, smoothed with a 20-s moving average, which we sample at 1 min intervals. Ambient air is sampled at 0.5 l min<sup>-1</sup> through 6.35 mm (0.25") tubing (PFA or Synflex) from an inlet that is located at least 1 m above roof level at each of the sites. Ambient air is drawn into the optical cell of the Li-Cor analyzer using a KNF diaphragm pump (Model NMP830). Data are collected and stored on a Campbell

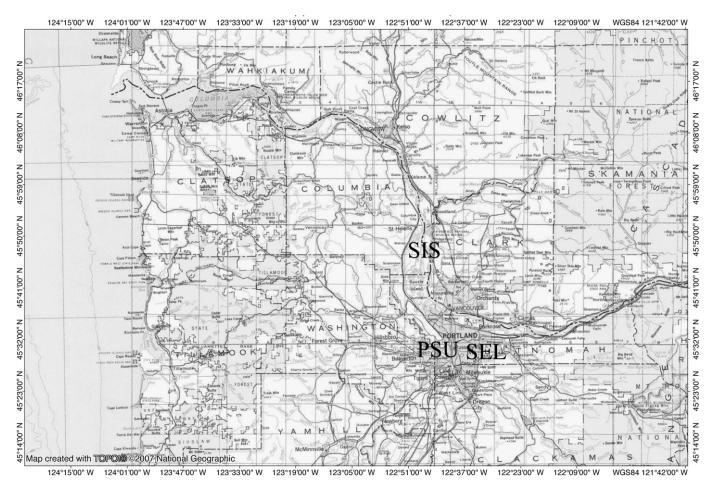


Fig. 1. Map showing the location of the Portland metropolitan region in the Columbia River Gorge. Sampling locations for this study are indicated: Sauvie Island (SIS, 45.77°N, 122.77°W, 6 m elevation), Portland State University (PSU, 45.51°N, 122.69°W, 63 m elevation), Southeast Portland (SEL, 45.50°N, 122.60°W, 75 m elevation).

Scientific Datalogger (Model CR1000). At SIS and SEL, instrumentation is housed inside single story temperature controlled DEQ shelters alongside air quality instruments. At PSU, instruments operate in a laboratory on the second floor of Science Building 2. At the PSU site, we are also equipped with a Picarro  $^{13}\text{C}-\text{CO}_2$  analyzer (Model G1101-i) which measures the  $^{13}\text{C}/^{12}\text{C}$  isotope ratio of CO<sub>2</sub> and atmospheric CO<sub>2</sub> concentration. Data is acquired every 5–10 s and processed from this instrument at 5 min averaged intervals for statistical purposes.

Li-Cor  $CO_2$  instruments are calibrated weekly with high pressure aluminum cylinders containing  $CO_2$  gas mixtures in ultrapure air from Scott-Marrin Inc. The weekly calibration procedure includes a zero using ultra-high purity  $N_2$ , a span measurement using a 511 ppm  $CO_2$  mixture, and a near-ambient 393 ppm  $CO_2$  mixture. The calibration scale is based on a  $394 \pm 4$  ppm gas mixture which is NIST-Traceable to SRM 1672a (355 ppm). Instrumental drift, checked prior to recalibration, is typically <1 ppm per week. Precision of measurement of the Li-Cor analyzer is <1 ppm averaged over a 1 min interval. The  $H_2O$  channel of the Li-Cor instruments are calibrated using a dew point generator;  $CO_2$  values are corrected for dilution and band broadening due to  $H_2O$  vapor.

At PSU, calibration of the <sup>13</sup>C-CO<sub>2</sub> analyzer is automated and occurs once every 12 h using a high pressure cylinder of calibrated whole air on a timer-controlled valve manifold. Measurements of the <sup>13</sup>C/<sup>12</sup>C ratio of atmospheric CO<sub>2</sub> are expressed in parts per thousand (or 'per-mil') using the delta notation  $(\delta)$  relative to the VPDB scale, where  $\delta^{13} C = [(^{1\overline{3}}C/^{12}C)_{sample}/(^{13}C/^{12}C)_{VPDB} - 1] \times 1000$ as established by the International Atomic Energy Agency (IAEA) in Vienna, Austria (Coplen, 1995). Isotopic calibration of the Picarro instrument is based on dual inlet isotope ratio mass spectrometry using a suite of three gas phase 1-L CO2 reference gases acquired from Oztech Trading LLC ( $\delta^{13}$ C -3.60%, -40.68%, and -47.54%versus VPDB). These were calibrated independently at PSU using NBS 19 (SRM 8544,  $\delta^{13}$ C +1.95% versus VPDB). Uncertainty of calibration is better than  $\pm 0.02\%$  for  $\delta^{13}\text{C}.$  The high pressure whole air cylinder used for the Picarro instrument ( $\delta^{13}$ C -9.85% versus VPDB) was calibrated using techniques described previously (Schauer et al., 2005). Precision of measurement for the Picarro  $^{13}$ C–CO<sub>2</sub> analyzer is better than 0.5% averaged over 5 min intervals. Instrumental drift between calibrations is typically less than 0.5%. A second analysis of CO<sub>2</sub> concentrations at PSU was also possible using the Picarro analyzer, which has a precision of <50 ppb over 5 min intervals. The Picarro and Li-Cor instruments were in agreement for  $CO_2$  concentrations ( $r^2 = 0.92$ ).

Long term monitoring stations SEL and SIS are maintained by Oregon DEQ for studying regional air pollution. Standard

meteorological data is available at both sites (i.e., temperature, barometric pressure, humidity, wind speed, wind direction, and solar radiation). Air monitoring at SEL includes a full suite of measurements including CO, NO, NO<sub>2</sub>, O<sub>3</sub>, and PM<sub>10</sub> and PM<sub>2.5</sub>. Meteorology and air quality is typically measured on the Science Building 2 rooftop at PSU. However, this capability has been temporarily interrupted as a result of a building remodel. For meteorology at PSU, nearby data from the downtown Portland DEQ site is used, located  $\sim 1$  km from PSU (45.52°N, 122.67°W, 13 m).

### 3. Results and discussion

#### 3.1. Measurements of CO<sub>2</sub> concentrations

Continuous measurements of CO $_2$  were recorded from our three station network July 22 through December 31, 2009 at 1 min intervals (Fig. 2). Measurements at PSU were initiated earliest (July 13), followed by SEL (July 18) and SIS (July 22). Short breaks in the data result from instrument calibration and longer periods from instrument and data storage failures. One minute CO $_2$  concentrations were passed through a  $6\sigma$  filter to remove irregular spikes in the data. This analysis preserved >99.9% of all raw data. Hour means were calculated from filtered data on the half-hour mark. Considerable variability is observed in hourly means at each site, which ranges 360-610 ppm. Over the measurement period, the sites averaged  $408 \pm 24$  ppm,  $407 \pm 30$  ppm, and  $403 \pm 25$  ppm at PSU, SEL, and SIS, respectively ( $\pm 1\sigma$ ).

Several features are notable in the resulting dataset. First, the two urban Portland sites (PSU and SEL) are typically and on average higher in CO<sub>2</sub> concentration than the rural SIS site, commonly by several ppm or more. This is due to sources of CO<sub>2</sub> in the Portland metropolitan region, primarily the combustion of petroleum in motor vehicles and natural gas and petroleum for heating and industrial processes. To quantify the enhancement of CO2 concentrations in urban Portland, we use the upgorge feature of air flow in the region. Over the measurement period, wind speed at SIS averaged 2.3  $\pm$  1.5 m s<sup>-1</sup> and was dominated by a northwesterly-northerly direction (Fig. 3). Selecting hourly CO2 data with a 270–360° wind component at SIS we calculate hourly differences in coincident CO2 concentrations between in-city sites (PSU and SEL) and the upwind SIS site ( $\Delta CO_2$ ). The distributions of these analyses are shown as histograms in Fig. 4; both results show a significant enhancement of in-city concentrations over the upwind site with 79% of hourly averages higher in-city during upgorge wind conditions. The mean difference between PSU and SIS was 5.1  $\pm$  1.4 ppm (95% confidence interval, p value <0.001), the

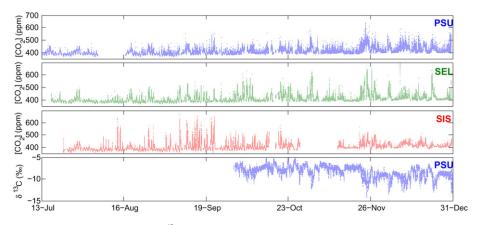


Fig. 2. Time series of 1 min  $CO_2$  concentrations and 5 min mean  $\delta^{13}C$  of  $CO_2$  measured at PSU (blue), SEL (green), and SIS (red) between July 13 and December 31, 2009. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

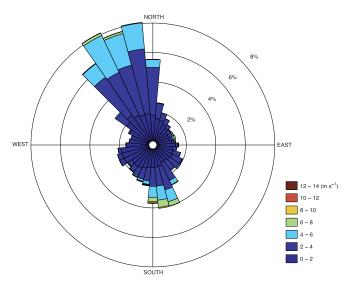
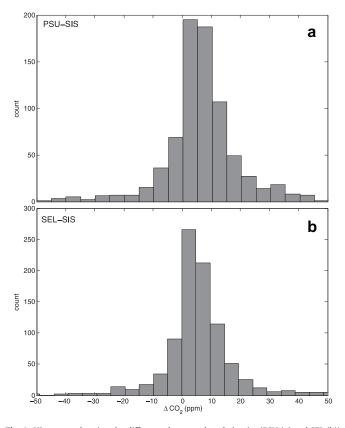


Fig. 3. Windrose at SIS showing meteorological features of the Columbia River Gorge.

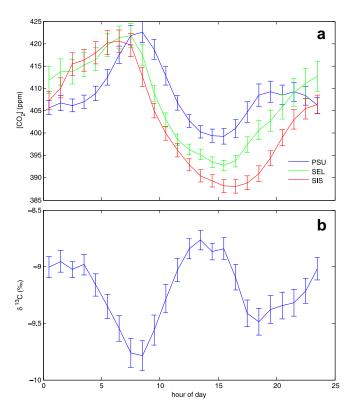
difference between SEL and SIS was  $5.5\pm1.5$  ppm (95% CI, p value <0.001). The difference between in-city and rural area  $CO_2$  concentrations for Portland is on the low end compared to studies in other urban centers, which typically are 30–100 ppm above outlying areas (George et al., 2007; Idso et al., 2001; Newman et al., 2008). This may result from the relatively high rate of ventilation for the Portland metropolitan region.



**Fig. 4.** Histogram showing the difference between hourly in-city (PSU (a) and SEL (b)) and upwind (SIS)  $CO_2$  concentrations ( $\Delta CO_2$ ) selected for a westerly to northerly wind vector (270–360°). Coefficients of skewness and kurtosis indicate distributions have slight left-skews and are heavy-tailed from normal.

Differences between week and weekend concentrations are also found at all three sites; weekday mean concentrations are  $4.0\pm0.2$  ppm,  $2.8\pm0.3$  and  $1.3\pm0.3$  (95% CI, p value <0.001) higher than weekend mean concentrations at PSU, SEL, and SIS respectively. This finding for PSU and SEL is consistent with increases in weekday traffic volume in the region and consistent with previous observations in cities (Gratani and Varone, 2005). The existence of a smaller but significant difference between week and weekend CO<sub>2</sub> concentrations at SIS may be due to increases in traffic volume in the larger metropolitan region or to periods when SIS is downwind of the Portland region. Similar differences have been observed in remote and semi-remote locations (Thoning et al., 1989).

There is a 20–30 ppm diurnal cycle in CO<sub>2</sub> observed at all three sites in the hourly data (Fig. 5a). Highest concentrations occur in the early morning hours (5-8am, local time) and lowest concentrations occur in the afternoon (3–5pm). This feature is driven by a combination of biological activity (photosynthesis and respiration) and variations in the planetary boundary layer height (Thoning et al., 1989). The two urban sites have 5–10 ppm higher concentrations than SIS during the daytime when anthropogenic sources are most significant. PSU, located in downtown Portland, experiences higher daytime concentrations than either SEL or SIS on the average. The difference between PSU and SIS is greatest in late afternoon, ~ 15 ppm. In contrast, early morning concentrations are comparable at SIS and SEL and lower at PSU by 5-10 ppm. The causes of lower early morning concentrations in downtown Portland are not known but could relate to a smaller local plant respiration source or a weakening of stratification and thickening of the nocturnal boundary layer due to the urban heat island effect (Fan and Sailor, 2005; Martilli, 2002). As a result of higher afternoon concentrations



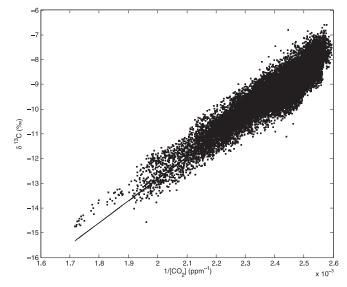
**Fig. 5.** Mean diurnal cycle of  $CO_2$  concentration (a) and  $\delta^{13}C$  of  $CO_2$  (b) at PSU (blue), SEL (green), and SIS (red) over the measurement periods (July—December, 2009). Data are 1 h means centered around the half hour; error bars are the standard error of hourly means. Time is Pacific Standard Time (UTC-8). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

and lower evening concentrations, PSU experiences the smallest amplitude diurnal cycle of the three sites (23 ppm). The largest amplitude diurnal cycle is at SIS (32 ppm). Notably, though the diurnal cycle in CO2 at all sites are in-phase, the SIS and SEL sites are more alike in sinusoidal behavior. In particular, the diurnal cycle at PSU has a strong first harmonic in the signal which is apparent as a later rise in CO<sub>2</sub> in the early morning hours and an afternoon rise in  $CO_2$  to approximately steady state levels between  $\sim$ 6pm and 3am. Spectral analysis of both 1 h and 1 min data, reveals a unique frequency at PSU of two cycles per day of near equal magnitude to the fundamental (one cycle per day). We speculate that this occurrence may be largely due the importance of traffic sources in and near downtown Portland which have peak volumes typically centered around 7-8am and 5pm from rush hour (data from Portland Regional Transportation Archive Listing (PORTAL): http://portal.its.pdx.edu/ portal2.1/index.php/highways). When differentiated by week and weekend, the two cycle per day spectral feature at PSU is unchanged in week data (large compared with fundamental) whereas the two cycle per day feature in weekend data is small (i.e., comparable with harmonic contribution at other sites).

To our knowledge, there is only one previous study with which to compare our results in the Portland metropolitan region (Khalil and Rasmussen, 2004). In that work, authors compared carbon dioxide concentrations in discrete flask samples collected in the Portland region with those collected at a coastal site (Cape Meares, Oregon, 45.48°N, 123.97°W, 30 m) and found an enhancement of  $\sim\!3\%$ . When we compare mean values observed in our work with boundary layer CO<sub>2</sub> observations made at Trinidad Head, California (41.05°N, 124.15°W), a coastal site operated by the NOAA Earth System Research Laboratory Global Monitoring Division, we find our in-city values higher by  $\sim\!6\%$  on average (C. Sweeney, Personal Communication).

# 3.2. The isotopic composition of CO<sub>2</sub>

Measurements of the  ${}^{13}C/{}^{12}C$  isotope ratio of CO<sub>2</sub> began October 1, 2009 at PSU. Five minute averages from the Picarro instrument are shown in Fig. 2d alongside  $CO_2$  concentration time series (as  $\delta^{13}C$ ). These data are further degraded to hourly averages of  $\delta^{13}C$  of  $CO_2$ which vary between -7 and -15% with an average of  $-9.2 \pm 1.0\%$  $(1\sigma, n = 2184)$ . The mean value is significantly lower than the  $\delta^{13}$ C of CO<sub>2</sub> of clean coastal air at this latitude and time of year which ranges -8.0 to -9.0% relative to VPDB (White and Vaughn, 2009). The depletion of <sup>13</sup>C relative to <sup>12</sup>C in CO<sub>2</sub> is the result of regional CO<sub>2</sub> sources. Two fossil sources, in particular, have isotopic signatures which can cause this effect; petroleum has a  $\delta^{13}$ C  $\sim -28\%$  and natural gas has a  $\delta^{13}$ C  $\sim -40\%$  versus VPDB (Pataki et al., 2006). The relationship between  $\delta^{13}$ C and inverse CO<sub>2</sub> concentration ("Keeling" plot") can provide some constraint on the partitioning between these sources. Fig. 6 shows the high degree of correlation between 5 min averaged values of  $\delta^{13}$ C and  $1/\text{CO}_2$  ( $r^2 = 0.85$ ); least squares regression of these data, considering errors in both variables, results in a y-intercept value of  $-30.5~\pm~0.2\%_{o}$  versus VPDB (95% CI). Considering anthropogenic sources alone, petroleum and natural gas sources account for 80% and 20% of the CO<sub>2</sub> source, respectively. An important caveat in this analysis is that it neglects biogenic sources of respiration, which have a  $\delta^{13} \text{C} \sim -25\%$  for C3 plants which are dominant respiration sources in the region. To address this bias, we selected data for daytime hours, when plant respiration is lowest and anthropogenic sources are at the greatest. This analysis resulted in a y-intercept value of  $-31.0 \pm 0.2\%$  versus VPDB (95% CI), which corresponds to a 75/25 split between petroleum and natural gas. Excluding electricity which is generated outside the metropolitan region, petroleum sources (including oil-based heating fuel) in Multnomah County are thought to be responsible for



**Fig. 6.** The relationship between  $\delta^{13}C$  of CO<sub>2</sub> and inverse concentration (1/[CO<sub>2</sub>]) for 5 min mean values at PSU. The y-intercept is  $-30.5\pm0.2\%$  versus VPDB (95% confidence interval) and correlation coefficient ( $r^2$ ) is 0.85.

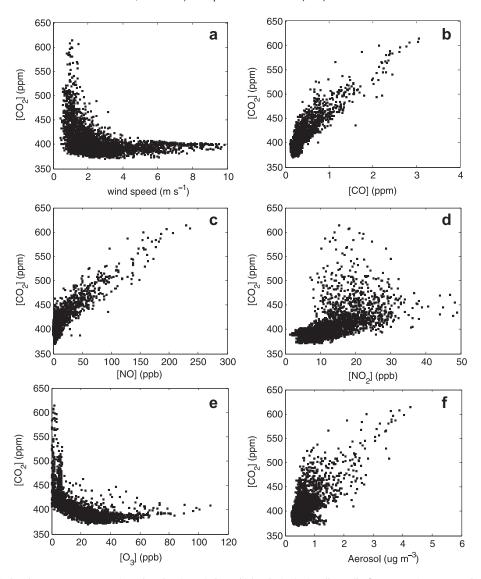
 $\sim$ 67% of CO<sub>2</sub> emissions based on emissions inventories (Adams et al., 2009). Petroleum sources may be lower in emissions inventories compared with our estimates due to traffic into Multnomah County fueled from gasoline stations located outside the county because emissions inventories are based on fuel sales. In contrast, natural gas sources are non-mobile and better defined in space.

The diurnal cycle in  $\delta^{13}$ C of CO<sub>2</sub> at PSU is also apparent in hourly averaged data (Fig. 5b). It is in anti-phase with CO<sub>2</sub> concentrations with lowest values (most  $^{13}$ C depleted) occurring in early morning ( $\sim$ 7–9am) and highest values (most  $^{13}$ C enriched) occurring in afternoon (12–4pm). As with CO<sub>2</sub> concentration, this effect is driven by both biological processes and boundary layer meteorology. The first harmonic observed in the CO<sub>2</sub> diurnal cycle is also apparent in the  $\delta^{13}$ C results. These observations of  $\delta^{13}$ C of CO<sub>2</sub> show potential to identify temporal trends in CO<sub>2</sub> concentration. For example, the dramatic drop in  $\delta^{13}$ C value at  $\sim$ 5pm (Fig. 5b) coincides with a corresponding rise in CO<sub>2</sub> concentration (Fig. 5a) at PSU and is further evidence of a petroleum source (depleted in  $^{13}$ C) intensifying at this time of day.

#### 3.3. Ancillary measurements

Co-location of our Li-Cor  $CO_2$  instruments at Oregon DEQ regional air quality stations allows the examination of relationships between  $CO_2$  concentrations and both meteorological variables and air pollutants. These can help to identify primary drivers of variability in  $CO_2$  in the Portland metropolitan region. Variations in  $CO_2$  concentrations with hourly averaged wind speed and with several criteria air pollutants observed at SEL are shown in Fig. 7.

At low wind speeds  $(0-2 \text{ m s}^{-1})$   $CO_2$  concentrations display considerable variability up to 610 ppm due to variations in sources, sinks, and dynamical processes (Fig. 7a). The relationship between  $CO_2$  and wind speed approaches an asymptotic value near 400 ppm at wind speeds above 2 m s<sup>-1</sup> as ventilation is sufficient that the enhancement above  $CO_2$  background concentrations due to urban sources is not significant and concentrations are <410 ppm. Relationships of  $CO_2$  with additional meteorological variables were not highly correlated ( $r^2 < 0.6$ ). Primary pollutants carbon monoxide



**Fig. 7.** Variability observed in hourly mean  $CO_2$  concentrations plotted against wind speed (a) and criteria air pollutant (b-f) concentrations measured at SEL. Primary pollutants  $CO_2$  (b,  $r^2 = 0.80$ ) and  $CO_3$  (c,  $CO_4$ ) are highly correlated with  $CO_2$ ; secondary pollutants  $CO_3$  (d,  $CO_4$ ) and  $CO_3$  (e,  $CO_4$ ) and aerosols (f,  $CO_4$ ) have lower degrees of correlation.

(CO) and nitric oxide (NO) show strong correlations with CO2 variability at SEL (Fig. 7b and c,  $r^2 = 0.80$  and 0.77, respectively). Both CO and NO are produced by the internal combustion engine and the strength of these correlations shows the importance of automotive sources on CO<sub>2</sub> concentrations in the Portland region. This finding is consistent with both  $\delta^{13}C$  observations and with emissions inventories which place transportation as the leading regional source of CO<sub>2</sub>. Correlations with secondary air pollutants tend to be weaker. Though NO<sub>2</sub> and O<sub>3</sub> are linked to mobile sources, they are dependent on photochemical processes which are unrelated to CO<sub>2</sub> sources. As a result, the correlation between variability of CO<sub>2</sub> and NO<sub>2</sub> in ambient air is weaker (Fig. 7d,  $r^2 = 0.29$ ) and CO<sub>2</sub> and O<sub>3</sub> are bifurcated due to day-night differences (Fig. 7e,  $r^2 = 0.36$ ). Finally, aerosols show only a medium degree of correlation with  $CO_2$  (Fig. 7f,  $r^2 = 0.52$ ). Though particulates are generated during combustion of automotive fuels, there appear to be other significant controlling variables for aerosols in the Portland metropolitan region, which include industrial processes, non-road equipment, wood burning, and secondary organic aerosol.

# 4. Conclusions

Analysis of continuous ambient CO2 concentrations at three locations in the Portland, Oregon metropolitan region during the period July 13-December 31, 2009 provides a first accounting for mean behavior and variability of CO2 levels in the region due to anthropogenic and natural sources. On average, we observe a 20-30 ppm diurnal cycle in CO<sub>2</sub> concentration with highest concentrations in early morning and lowest concentrations in late afternoon as a result of biological activity and planetary boundary layer dynamics. Urban CO2 sources result in enhanced concentrations of CO<sub>2</sub> at PSU and SEL over SIS during the daytime. At night into early morning, CO2 concentrations at SEL and SIS are closely matched whereas PSU displays lower concentrations. PSU also displays somewhat unusual behavior consistent with a strong contribution from the first harmonic. The diurnal cycle in  $\delta^{13}$ C of CO<sub>2</sub> measured at PSU is in anti-phase with CO<sub>2</sub> concentrations with lowest values in the early morning and highest values in the afternoon.

Based on coincident analyses at in-city and SIS locations, we find that CO<sub>2</sub> concentrations are enhanced in the city of Portland by an average of 5–6 ppm over incoming air due to regional sources. The sources of CO<sub>2</sub> in the region appear to be dominated by mobile automotive sources based on the carbon isotopic composition ( $\delta^{13}$ C) of CO<sub>2</sub> which shows a source value near -31% relative to VPDB, providing a split of 75–80% petroleum and 20–25% natural gas sources, when ignoring biogenic sources. Strong correlations with primary automotive pollutants NO and CO support the assertion that this sector drives much of the variability in CO<sub>2</sub>.

Data resulting from this ongoing work are useful to better understand regional sources of CO<sub>2</sub> and their changes in time. The straightforward approach presented here using continuous monitoring of upwind and in-city CO<sub>2</sub> concentrations is effective for quantifying the enhancement in CO<sub>2</sub> levels due to regional sources in mid-sized cities. Additional monitoring stations or mobile field campaigns would be useful to better characterize spatial dimensions of this urban CO<sub>2</sub> enhancement. Finally, long-standing time series will be particularly useful for measuring changes in regional CO<sub>2</sub> sources in time responding to regional approaches to reduce GHG emissions. Accompanying these datasets, fine resolution gridded inventories in time and space and chemical transport models will be useful for quantitatively testing carbon emissions inventories at regional scales.

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