Atmospheric CO_2 in the coastal marine boundary layer: observations and implications

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Abstract

Substantial variation in near surface atmospheric carbon dioxide (CO_2) mixing ratios observed offshore over the Gulf of Maine are documented and examined within the context of efforts to estimate and monitor the air-sea exchange of CO_2 along coastal margins. Using the Mauna Loa Observatory (MLO) monthly average observations as a reference, it is shown that marine atmospheric boundary layer CO_2 times series data, collected in our region from an offshore island, buoy, and ship indicate several clear features: frequent occurrence of mixing ratios exceeding MLO by 20-40 parts per million (ppmv), a systematic summertime diurnal cycle with peak-to-peak magnitude of more than 20 ppmv, and stronger signal excursions nearer to the coast - although 30 ppmv excess levels have been recorded as far as 80-90 km offshore. University of New Hampshire (UNH) AIRMAP Observing Stations located 24 km inland and 10 km offshore are used to show that the diurnal variability is primarily associated with the seaward advection of low-altitude trace gases from forested New England and that this temporal signal is mostly attributed to the seasonal terrestrial photosynthesis and respiration cycle combined with prevailing summertime boundary layer characteristics. Additional frequent positive-going perturbations come via synoptic air mass advection where increased carbon monoxide levels are also observed. Little of the measured variability at the daily-to-weekly time scale is attributed to oceanic CO_2 variations and attendant air-sea exchange. Implications to ongoing and future coastal CO_2 air-sea flux measurement programs include potential systematic error in air-sea flux estimates and informing sampling strategies for short and long term trace gas field studies in coastal settings.

1.0 Introduction

Accurate monitoring and prediction of the rise in atmospheric carbon dioxide gas levels and of the oceanic uptake of this gas are prominent goals within the climate research community. One area where uncertainty remains in the global budget for CO_2 rise is the amount of air-sea gas exchange that takes place throughout the coastal zones of the ocean. The continental margins represent a relatively small component in the ocean surface area, yet they contain the most bio-chemically dynamic, productive, and unpredictable oceanic ecosystems including regions of upwelling and river plumes (Gattuso et al., 1998). Above the ocean surface, trace gases in the coastal atmospheric marine boundary layer may also exhibit more variability than that predicted by open ocean (or background) level atmospheric trace gas models or observations because these parcels will often represent the complex horizontal and vertical mixing of maritime and continental air masses. The most fundamental driver of the flux of CO_2 between the ocean and atmosphere is the disequilibrium between the carbon dioxide partial pressures within the ocean and atmospheric boundary layers. While measurement and prediction of waterside CO_2 levels receives the bulk of attention in this research area, this paper is concerned with the variability of near-surface atmospheric CO_2, its sampling, and potential impacts in the area of ocean-atmosphere mass flux studies in the coastal margins.

Technological and programmatic evolutions have led to a growing number of observational data sets containing near-surface seawater and atmospheric CO2 mixing ratio data across the ocean and its near shore regions. One dataset feature observed in numerous coastal water field campaigns is the occasional or frequent occurrence of significantly elevated levels of atmospheric CO2 (Leinweber et al., 2003; Worthy et al., 2003; personal comms., C. Sweeney and R. Wanninkhof), where the airside mixing ratio values extend well above monthly mean estimates of well-mixed free troposphere background levels obtained from stations such as NOAA's Mauna Loa Observatory (MLO). The observed signals have in some cases been flagged out in analyses or considered erroneous, and in others attributed to air mass advection to the observation point from continental sources. In all cases, if one were not sampling the air along with the in-water CO2 levels, application of the common assumption that the near-surface marine boundary layer atmospheric level can be well-approximated by the Mauna Loa background free troposphere CO2 mixing ratio (e.g. Bakker et al., 2001; Degrandpre et al., 2002; McNeil et al., 2006; Salisbury et al., 2006) may lead to a substantial error in the air-sea disequilibrium term.

While this airside assumption may sometimes be required due to the fact that only submerged in-water CO2 sampling or infrequent atmospheric sampling is available, it is important to address and/or bound this uncertainty and questions surrounding this type of atmospheric signal variability within gas exchange studies. Are these events so infrequent or of small enough magnitude or temporal duration that they can be considered noise in air-sea flux estimation and prediction work? Is atmospheric variability random about its mean value and in its time-varying content such that any effect on the air-sea concentration disequilibrium cancels out? What sampling time interval is adequate for

field measurement purposes and how far offshore do the effects persist? As importantly, what are the sources or controls of the observed atmospheric variability? These are some of the questions addressed here. The objectives of this study are to document and assess variability in atmospheric marine boundary layer CO2 for our measurement site, and to assess potential impacts upon ocean-atmosphere gas exchange estimates as well upon observational programs designed to monitor and to improve flux estimation parameterization. The study is motivated by and presents a series of high quality CO2 measurements recently collected in the western Gulf of Maine (NW Atlantic) east of Portsmouth, NH, U.S. These data come from two offshore observing stations and shipboard cruise data, and are augmented by a nearby inland trace gas observing node. Details follow on the measurement methods, results focusing on observed atmospheric CO2 signals in the Gulf, and discussion of their controls and impact within air-sea flux estimation activities.

2.0 Observational Methods

Three offshore and one inland data collection subsystems provide the near-surface atmospheric CO_2 measurements used in the study. First is the University of New Hampshire's AIRMAP observing station on Appledore Island (AI), ME (42.97N, 70.62W), located 12 km E from the coast of NH at the Shoals Marine Laboratory as shown in Fig. 1. Sampling for CO_2 has occurred here in summer months 2004-2006, operating in a continuous time series mode with data recorded at 1 min intervals. Ambient air is drawn from a 5.1 cm i.d. Teflon manifold located atop a World War II-era lookout tower 36 m above sea level (asl). An infrared gas analyzer (Li-7000, Li-Cor Biogeosciences, Inc., Lincoln, NB) samples the air at 0.5 liters per minute (lpm). The Li-7000 is automatically zeroed with Ultra High Purity Nitrogen (UHP N_2) every 12 hours and is calibrated every 14 hours with a standard (Scott-Marrin, Inc., Riverside, CA). Calibration standards range between 370 and 400 ppmv ± 1% and are on the system approximately one year.

The second site provides data measured onboard a 1.9 m discus buoy moored 7 km northeast of the Appledore Island tower and 12 km offshore (43.01N, 70.55W). Water depth at the buoy is 63 m. The autonomous CO_2 data collection system on the buoy is a joint collaboration between UNH and NOAA's Pacific Marine Environmental Laboratory (PMEL). Buoy measurements of atmospheric and surface layer oceanic CO_2 are collected every two hours using an automated equilibrator-based gas collection system and an infrared gas analyzer (Li-820, Li-Cor Biogeosciences, Inc., Lincoln, NB) based on the approach of Friederich et al. (1995). The height of the atmospheric intake is 1.5 m asl and the depth of the water intake is 0.6 m. Calibration is performed immediately prior to these measurements using a CO_2 calibration span tank calibrated with standards from NOAA/ESRL. This paper uses buoy data collected in summer 2006, where on board processing provides data of preliminary quality. Absolute values may change slightly (typically less than 1 %) due to future post-buoy recovery reprocessing, but the precision and accuracy are sufficient for present objectives.

Monthly R/V Gulf Challenger shipboard transects of this same coastal Gulf of Maine region provide the third marine data source and one that adds information on cross shore spatial variations. A continuous sampling of atmospheric CO_2 is drawn from a Teflon-lined bow intake at a height of 3 m asl. An infrared gas analyzer (Li-840, Li-Cor Biogeosciences, Inc., Lincoln, NB) with custom built sample water vapor removal loop (Nafion filter with N_2 gas) is used to measure dry CO_2 at a 0.1 lpm flow rate. Prior to implementing this continuous mode atmospheric data in 2006, the airside measurements were acquired periodically over a 3-5 min measurement period during cruises from the same bow intake using a similar IR-based system (Salisbury et al., 2006). Calibration procedures and standards are akin to those used at the AIRMAP site, excepting that the CO_2 standard gas span tank used on the ship is nominally 820 ppmv. Monthly Challenger cross shore transects provide data from 3 to 80 km offshore, with the ship passing north of the Appledore site on an ESE heading (Figure 1) and returning the same day on a reverse course. Data processing filters out any possible ship exhaust contamination influencing the atmospheric CO_2 mixing ratio estimates. Measurements from twenty-one cruises between May 2004 and June 2006 were used to support this study.

The inland atmospheric CO_2 measurement site for this study lies 31 km to the east of AI at the AIRMAP observing station Thompson Farm (TF, 43.11N, 70.95W, see Figure 1) in Durham, New Hampshire. It is an active corn farm surrounded by a mixed temperate forest. Continuous measurement of atmospheric CO_2 (1 min sample rate) at TF began in February, 2002. Here, ambient air is subsampled at 0.5 liters lpm from a 10 cm diameter PFA Teflon lined manifold which runs up the side of a 12 m tower. Sample air is pulled through the main manifold at a rate of 700 lpm. Measurement and calibration of ambient CO_2 is performed as described for Appledore Island.

In addition to CO_2, we also present measurements of carbon monoxide (CO) measured at both Thompson Farm and Appledore Island. If covariance is high between observed CO and CO_2 increases then anthropogenic sources are likely as will be discussed below. A Thermo Environmental Instruments model 48CTl was extensively modified to measure CO. Details of the instrument calibration and zeroing procedure can be found in Mao and Talbot (2004).

Ancillary meteorological data used in the study come from the AIRMAP AI and TF stations where wind speed and direction are continuously logged. An air mass back trajectory model is also employed to determine likely air mass source regions. The model used here is the HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) model from the NOAA Air Resources Laboratory (Draxler and Hess, 1998).

We also make use of CO_2 monthly time series data collected from NOAA's Mauna Loa Observatory (MLO). These data represent a well-established benchmark for monthly CO_2 observations in the Northern Hemisphere for the mid-to-upper level tropospheric mixing ratio. And one that is often cited and utilized in oceanic air-sea flux studies to provide the near-surface atmospheric CO2 mixing ratio estimate when those data are not measured directly (e.g. Bakker et al., 2001; Degrandpre et al., 2002; McNeil et al., 2006;

Salisbury et al., 2006**).** The MLO values do differ slightly from a global monthly estimate for this study's latitude (43N) obtained from the data-assimilating model of the NOAA Earth System Resource Laboratory (ESRL), the differences are of the order of a few ppm and the seasonal trends follow MLO as well. This level of difference between the two products does not impact study findings and we use the monthly MLO data as the benchmark reference level for assessing variability in the coastal New England atmospheric observations.

3.0 Results

3.1 Coastal site atmospheric CO_2 observations

Time series atmospheric CO_2 mixing ratio data (in parts per million per volume (ppmv)) at Appledore Island (OFFSHORE) and Thompson Farm (INLAND) are shown in Fig. 2 for a 14 day period in summer 2005. As noted above, we use the Mauna Loa monthly average data as a reference or baseline for assessing regional variability in space and time. Focus on the offshore station shows that the 30 m altitude CO_2 levels often deviate 10-20 ppmv above and below the monthly average Mauna Loa (MLO) value for July 2005. Moreover, there is a systematic temporal pattern that coincides with the daily solar cycle with maximum levels typically occurring near 0500 hours local (0900 UTC) time.

The inland station data, 31 km to the west, show even larger signal excursions away from the fixed MLO value, particularly the positive going levels that often extend above 500 ppmv in Fig. 2. Moreover, it is clear that the offshore and inland temporal variations are highly correlated – a diel cycle signal is also apparent at the inland site. Offshore-vs-inland comparisons show the average amplitude of the diurnal signal excursions for the summer of 2005 was consistently smaller at Appledore Island (27 ppmv) than at Thompson Farm (77 ppmv). However, the offshore-inshore amplitude difference was not the same with respect to the time of day. The minimum observed values at Thompson Farm were, on average, 4.5 ppmv below those observed at Appledore Island. In contrast, the average inland versus offshore difference in daily maximum CO_2 was +70 ppmv. Fig. 2 data also indicate a systematic time shift between the diel signatures observed inland and offshore. This lag time between the offshore and inland site CO_2 mixing ratio maxima (early morning) was calculated to be 100 minutes while the average time lag between observed the minima (late-day) was 170 min, about 3 hr.

At the beginning of the time series shown in Fig. 2 we observe no significant diel variation in the Appledore Island CO_2 mixing ratios. This is likely due to the predominance of onshore NNE marine flow from July 7 through July 10 as indicated by the wind barbs. The Thompson Farm site data for this period show a small diel signal enhanced CO_2 above the Appledore site likely due to CO_2 sources between the island and the inland sampling site situated in a forested region.

The data of Fig. 2 were collected in boreal summer. While we do not yet have a full year of offshore AI site measurements, Fig. 3 presents a full year at the inland TF site data to provide an annual cycle perspective for the region. The monthly mean TF CO_2 mixing ratio was consistently higher than MLO over the entire year. The largest observed

difference between these two sites (TF and MLO) occurred in the fall (~20 ppmv). The smallest differences took place in the late winter/early spring period (~8 ppmv). The highest variability in CO_2 mixing ratios at Thompson Farm was observed during the photosynthetically active season with large diurnal oscillations observed almost daily. The largest TF site maximum and minimum CO_2 levels coincided with the local May - September growing season where the TF site minima consistently fall below the MLO values consistent with photosynthetic drawdown. During this period there was also a clear diurnal signal as seen in Fig. 2.

Diel periodicity at the inland site was mostly absent in the fall and winter months. Nonetheless, large positive perturbations in CO_2 were also observed in these seasons (e.g. see Fig. 3 at 1 Feb 2005). The increases do not have a corresponding daily sub-MLO minimum as in the summer and the magnitude of the spikes were lower on average than for the summer months but still of the order of 50-70 ppmv above background. The high CO_2 events that occurred in the winter were typically correlated with increased carbon monoxide (CO) measured at the same location (see the gray curve in Fig. 3). CO is emitted during the combustion process and is widely considered to be a robust tracer of industrial and domestic biomass burning. Fig. 4 presents a scatter plot of coincident TF CO and CO_2 observations for the winter period from January 1 through March 31, 2005. Correlation between the concentration changes for these two gases was remarkably high with a 100 ppbv change in CO leading to a 15 ppmv change in CO_2. This correlation has been observed at Thompson Farm each winter since measurements of carbon dioxide began in the winter of 2002 and is also seen at the island site.

The almost constant occurrence of a summertime diurnal signal offshore at the AI site was somewhat unexpected because if the offshore signal is indeed terrestrial or continental in origin, then one would predict that onshore winds would tend to provide maritime flow free of these land influences. As discussed above, onshore maritime flow with corresponding quiescent (or well-mixed free tropospheric) atmospheric CO2, is occasionally observed such as in Fig. 2. This case is, however, the exception within our summertime observations across three years of sampling. Summertime wind observations for this study region suggest that onshore flow is indeed rare for these months. Hourly wind records from the NDBC IOS weather station, located 1 km from Appledore Island, show that flow from the maritime quadrant (NE through to SE) occurs only 15% of the time in the May-September period for the years 2004-2006. Moreover, the remaining wind flow comes from forested New England, a directional extent that spans more than 180 deg. from the south, CW through to northeastern Maine. Thus while marine boundary layer winds and turbulence dynamics are a certain influence on the observed CO_2 mixing ratio, the data from this site suggest that proximity to forested New England to the west is one likely \predominant or prevalent atmospheric trace gas control.

The strong correlation between the inland and offshore time series data in Figs. 2-4 suggests a terrestrially-influenced marine boundary layer exists from shore out to at least 10 km, the Appledore Island offshore distance. Monthly shipboard cross-shore transects in this region (see Figure 1) offer a spatial view that extends 80-90 km offshore to address the issue of how far out to sea these signals may persist.

Bow intake (altitude 3 m asl) CO_2 data from three R/V Gulf Challenger cruise dates are shown in Fig. 5 to illustrate three differing observed scenarios. The 22 March 2006 (Figure 5a) data represent roughly fifty percent of the sampling days where there is very little space or time dynamics in observed CO2. On this day the standard deviation of measured atmospheric CO_2 for the entire cruise was 1.60 ppmv. The dynamic range of a well-mixed day is typically less than 6 ppmv and an increase of 5-10 ppmv near the coast is not uncommon. However, similar to the Fig. 2 Appledore Island data, there are days with much greater variability. These usually occur in the summer months. During the outgoing leg of the transect on the morning of 18 July 2006, a strong negative offshore gradient of 55 ppmv was observed and extended from the coast to 25 km offshore (Figure 5b). As the day progressed, levels of CO_2 dropped and became more uniform. Also, beyond about 25 km from shore the data are quite uniform and consistent with other data from well-mixed days. The temporal decrease in these observations agreed with the mixing ratios measured at Appledore Island (data not shown). As a last illustration, Fig 5c shows data from 16 June 2004 where substantially elevated mixing ratios of CO_2 were observed out to 80 km offshore. On this day, moderate winds (5-7 m s^{-1}) had been blowing from the west for 10 hours prior to and during the cruise. Overall, the largest at-sea atmospheric level observed within the shipboard data archive is 462 ppmv, observed 50 km offshore in July of 2004 in still-air stagnant boundary layer conditions.

3.2 In-water CO_2 observations

Another potential factor controlling atmospheric CO_2 variations such as that seen in Figs. 2-5 is air-sea exchange, where high mass flux between the two reservoirs might imprint near-surface airside measurements. Fig. 6 presents one week of coincident oceanic and atmospheric measurements at the UNH/NOAA CO_2 buoy (15 km offshore, see Fig. 1) to evaluate this possibility. Mixing ratios of CO_2 in the atmosphere ranged between 370 and 440 ppmv. A clear diurnal variation in the atmospheric CO_2 was observed with amplitudes ranging from 25 to 50 ppmv, quite similar to that seen in Fig. 2. For this period shown in Fig. 6, the in-water CO_2 mixing ratios were always lower than the atmospheric level, thus continuous mass flux from the air to the ocean would be occurring and drawing down the atmospheric pool. Moreover, unlike the temporal atmospheric variation, the in-water mixing ratio increased by nearly 15% over the first 36-hour time period and then leveled off. There was in-water temporal variability at the diel scale in oceanic data, but the time-dependent signature shows no correlation with the atmospheric data. Also note that the peak-to-peak amplitude of in-water variations at the diel time scale was significantly less. These changes are most likely attributed to ocean surface skin layer temperature dynamics. Together, these observations suggest that air-sea flux is not a significant control on the strong daily airside CO_2 mixing ratio perturbations seen at the site.

4.0 Discussion

Offshore atmospheric CO_2 measurements collected in the Western Gulf of Maine present evidence of significant spatial and temporal variability in the concentration of near surface atmospheric CO_2 levels. Results shown also point to information pertaining to source of these variations and a first-order sense for the magnitude, time, and space scales of the variations. A brief discussion of these controls and study implications for air-sea gas exchange studies follows.

4.1 Controls on enhanced CO_2 offshore

The observations from Appledore Island and the buoy, 12 and 15 km offshore of New England, respectively, suggest the variability in atmospheric CO_2 over this coastal ocean is ubiquitous and often systematic. An analysis of a suite of trace gases measured during the summer of 2004 by Chen et al. (2006) support the hypothesis that the Appledore Island site is impacted predominantly by advection of continental air masses previously influenced by terrestrial biogenic and recent anthropogenic emissions. Other researchers have observed enhanced CO_2 levels at sea under offshore flow conditions (Worthy et al., 2003; Leinweber et al., 2003) on both coasts of North America. The close coupling of summertime diurnal patterns between Appledore Island and Thompson Farm, located inland and 30 km to the west of the island, provides strong observational support for this continental influence (Fig. 2). The primary source for the observed summertime maximum CO_2 in the Western Gulf of Maine is the advection of low-level air, enhanced in CO_2. This enhancement is due to a combination of a stable nighttime boundary layer on land in combination with terrestrial respiration [*Crill*, 1991; *Bubier et al.*, 2003] and local combustion sources of CO_2 [Figure 4;; *Talbot et al.*, 2005]. The minimum CO_2 mixing ratios observed at Appledore Island were 4.5 ppmv higher on average than those at Thompson Farm. These offshore minimums are likely the result of advection of air masses depleted in CO_2 through photosynthesis on the continent [*Bubier et al.*, 2003; Worthy et al., 2003]. These diel signals will then be diluted and/or blocked from the offshore sites as determined by wind flow patterns. In New England, we find that offshore flow is common in the summer period and thus a significant remnant of the terrestrial signature is advected to sea on a regular basis.

This conceptual model of coastal atmospheric CO_2 mixing ratio dynamics driven by terrestrial biota and local meteorology was probably a realistic one before large-scale use of fossil-based fuel combustion, but observations also show that the picture is now complicated by anthropogenic impacts. These are likely to occur throughout the year and can drive offshore maritime atmospheric CO_2 levels upwards by 40-80 ppmv (Fig. 4). Our preliminary evaluation of these occurrences using back trajectory analyses finds that the majority of measurable events have sources to the W and SW in U.S., regions with large population and coal-fueled electricity generation plants. This is consistent with air quality studies for this region reported recently (Worthy et al., 2003; Chen et al., 2006) as well as New England's well recognized fate as the tail pipe of North America.

These findings are in accord with the substantially larger and more exacting air pollution and marine meteorological study efforts that have taken place in New England waters over the past decade (Angevine et al., 1996; Angevine et al., 2006). According to these

studies a shallow, stable boundary layer forms in almost offshore flow cases in the summertime for this region attribute in large part, though not solely, to the significant land-to-ocean temperature gradient where the Gulf waters are often 10-15 degrees C cooler than the adjoining coast. This stable layer was found to be ubiquitous in space and time, often extending 10s of km offshore

Oceanic-driven control (via air-sea mass flux) of the large observed diurnal atmospheric CO_2 mixing ratios in this study was not expected, but the possibility was examined. Observations from Appledore Island under shoreward flow conditions show no diel signature, which is consistent with a well-mixed marine boundary layer that imposes much lower atmospheric variability of CO_2 , nominally less than 3 ppmv over 12-24 hour periods. Moreover, coincident air and sea CO_2 measurements of Fig. 5 show that air-sea exchange attributed to oceanic surface layer pCO_2 diurnal variability is not the source driving the observed 20-40 ppmv atmospheric levels (Fig. 6).

4.2 Implications for coastal air-sea exchange of CO_2

A central study objective is to provide observations to help bound the range and characteristics one will encounter in near-surface atmospheric CO_2 mixing ratios at a coastal site. While the observations at this Western Gulf of Maine site reflect its local wind patterns, the advection from neighboring terrestrial ecosystems and from distant corridors passing along pollutants and increased trace gas levels, we now derive conclusions from the observations that should pertain to other coastal air-sea CO_2 exchange research and monitoring efforts going on within the North American Carbon Program efforts.

A working model for CO_2 gas transfer at the air-sea interface (McGillis and Wanninkhof, 2006) is

$$F_{CO2} = k * S * [C_{air} - C_{aq}] \qquad (1)$$

where F_{CO2} is the flux (mmol C m^{-2} day^{-1}); k is the transfer velocity (m hr^{-1}); S is the solubility of CO_2, a function of water temperature and salinity; and the air and sea concentrations (C_{air} and C_{aq}) are those at the atmosphere-ocean interface. For this paper, we assume the surface skin and bulk fluid (air and water) depths are in thermal equilibrium and move S outside of the brackets. Thus the air-sea difference drives the estimate for flux.

Field studies dealing with CO_2 fluxes typically focus either on estimation of the annual or episodic carbon flux due to air-sea exchange, or on refinement of the model approach for estimating the gas transfer velocity k. This study's implication related to the former objective primarily involves how to estimate airside CO_2 for application in Eq. 1. If one has coincident air and oceanic CO_2 observations then this study suggests that the sampling interval should be less than 3 hours, in effect short enough to capture atmospheric temporal variations. At minimum, it should be understood that significant aliasing could take place if only one daily air sample is collected at a standard time of

day. Our buoy data can provide some guidance on the bounds of such systematic error (Fig. 7). The sea-air CO_2 difference for July through September 2006 show that oceanic levels generally exceed the atmosphere, leading to a positive flux. A three-day running mean was applied to the atmospheric data to ameliorate the observed diurnal signal effect (the center curve in Fig. 7 represents the value of delta CO_2 with this filter). The traces above and below the mean represent estimates obtained if we use the local three-day minimum or maximum CO_2 value (i.e. the envelope of the time series). The observed range about the mean then provides estimated bounds for expected summertime diurnal atmospheric effects on the air sea difference at this site, and also a sense of systematic air-sea exchange error that could occur if fixed time daily sampling is used. For example, routine afternoon (18 UTC) sampling would tend to sample at the minimum atmospheric levels and thus the upper curve on Fig. 7 resulting in a systematic overestimate of the disequilibrium.

In looking at these data we then suggest that to estimate the air-sea difference when atmospheric data are unavailable, the optimal approach appears to be use of the data-assimilating tropospheric CO2 mixing ratio model of NOAA/ESRL - a model that enfolds the monthly NOAA CO_2 flask sample data collection efforts. The analysis of data presented in Fig. 7 can provide some bounds for the percentage uncertainty that one might expect when using this atmospheric estimate to obtain the flux over the period of hours to days. It is important to point out that, for our New England site, the significance of these near shore atmospheric dynamics to annual average coastal margin fluxes appears to be small (O μatm) as long as systematic daily aliasing is avoided. Table 1 provides a calculation of the estimated error in CO_2 air-sea flux attributed to this type of monthly approximation in the atmospheric value in lieu of hourly data. The monthly calculations are performed using the CO_2 buoy data (2 hour time step) and corresponding wind speed measurements from nearby NDBC station IOSN3 with measured winds adjusted to 10 m and neutral boundary layer stability. These results are primarily for summer to fall period in our region. They do not rule out the possibility that accurate and high temporal resolution atmospheric CO_2 concentration data may be critical when the annual or seasonal air-sea CO_2 flux budget for a region can depend strongly on short-term storm events (cf. Memery et al., 2002).

Regarding spatial variability, recall that the island and buoy observations are taken at sites within 15 km of the coast and the land-advected CO_2 signals appear to lessen offshore in much of our shipboard sampling. The spatial shipboard transect data of Fig. 5b suggest that our 10 and 12 km island and buoy stations are often located within a near shore coastal air shed mixing regime that may not prevail further offshore. A 10-20 km cross shore length scale for advected land-ocean boundary layer mixing is consistent with that observed for turbulence profiles in recent field experiments off North Carolina (Vickers et al., 2001; Sun et al., 2000). However, as noted above, extensive recent marine meteorological field experiments (Angevine et al., 2004 and 2006) in the summertime Gulf of Maine suggests that the enhanced near surface trace gas levels advected from shore are typically trapped in a stable shallow boundary layer that is ubiquitous and extends well past this 10-15 km distance, consistent with our observations

of 16 June 2004 in Fig. 5. Overall, what does appear to be certain is that one can not assume that CO_2 fall be within 5-10 ppmv of Mauna Loa estimates on any given day.

Arguably, the most significant point to make is in relation to near shore (e.g. coastal tower or buoy site) eddy correlation flux or deliberate tracer studies directed at improved determination and parameterization of the transfer velocity. These studies often focus their attention on fluxes occurring over a short time span of hours to days (e.g. Zhang et al., 2006; McNeil et al., 2006) to evaluate processes affecting *k* such as steep fetch-limited wind waves, wave breaking, subsurface turbulence, or the effects of slicks. In these cases, one wishes for the interfacial disequilibrium between the air and sea carbon pools to hold static or be well-behaved to constrain the far right hand side of Eq. 1. It is important to realize that dynamics in the air-sea gas disequilibrium associated with advective atmospheric CO_2 could compete strongly with *k* in controlling the measured fluxes, and thus need to be considered accordingly in experiment design and implementation.

5.0 Conclusions

This note provides data showing substantial *O*(20-40 ppmv) variability in the near surface values of the atmospheric CO2 mixing ratio in coastal waters east of New England in the Gulf of Maine. We attribute these dynamics primarily to advection of continental air from the south, west, or north on the prevailing winds. In summer months, the sign of these variations about the monthly Northern Hemisphere global monthly tropospheric estimate (MLO) alternates on a diurnal time cycle that is closely correlated with the adjoining day-night cycle of the continental terrestrial Northeastern US ecosystem (the AIRMAP Thompson Farm site) to the west. In particular, we often see nearly one-to-one correspondence between these offshore island and inland sites that are separated by 35 km. More sporadic but equally large perturbations are attributed to the synoptic flow of anthropogenic fuel-combustion sources throughout the year, air traveling from local sources as well as distances as far away as 1000 km, and tagged as such using a combination of CO_2 and CO measurements. In all cases, the local meteorological boundary layer dynamics also enter into the air mass dilution and subsequent offshore transport and mixing observed in the mixing ratio data. The findings agree well with those observed in recent regional air pollution studies (Angevine et al., 2006; Chen et al., 2007) where more exhaustive marine boundary layer and trace gas observations, and meteorological modeling indicate that shallow stable summertime boundary layer formation and maintenance is common for these Gulf of Maine waters.

The central motivation for this study was to assess the impact of such variability upon coastal zone air-sea carbon dioxide gas flux studies. On this point we make the following conclusions. For coastal margins, the near-surface atmospheric CO2 mixing ratio levels may often exhibit temporal dynamics and magnitudes that span days and 20-40 ppmv, respectively. Thus the atmospheric dynamics will often compete with oceanic surface layer variability in controlling the air-to-sea CO2 disequilibrium concentration factor that drives CO2 flux across the interface. For our region however, these airside dynamics only affected the monthly averaged fluxes at the 1-4% level. This despite a chronic

diurnal variation in the airside values for most of the summertime period. The implication is that the air and sea side CO_2 levels are largely decorrelated at this hourly time scale and the diurnal variability is averaging itself out over the month. This error did increase to 23% in the month of October indicating that collection and analysis of the full annual cycle observations are required to assess the possibility that a systematic bias in the air-sea flux may result from the always positive multi-day wintertime pulses of CO_2 associated with anthropogenic sources advected to our region from the west. These numbers are for our particular study site, but similar atmospheric perturbations have been observed and cited elsewhere and thus similar considerations may be warranted to bound the uncertainty associated when estimating the surface-level atmospheric CO_2 across space and/or time to develop carbon flux estimates for a region. Similarly, the potential for episodic multi-day events of increased atmospheric levels due to land-to-ocean advection processes is one that may require consideration in short-duration field study campaigns of gas transfer velocity and/or large mass flux events such as those associated with large storms or short-term upwelling events.

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6.0 References

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Figure Captions

Figure 1. Map of sampling locations and cruises in the Western Gulf of Maine region. The Appledore Island site is located within the Isles of Shoals. Scale of the map is roughly 80 km by 80 km.

Figure 2. Hourly averaged mixing ratios of CO_2 from Thompson Farm (gray circles) and Appledore Island (black circles) for 7 July through 21 July 2005. The line indicates monthly averaged measurements from the Mauna Loa Observatory. Above the gas data is a stick plot of the near-surface (10 m) wind vector derived from the NNBC IOSN3 site 1 mile SE of Appledore. Wind direction is from the NE at the start of the time period.

Figure 3. Hourly and 30 day averaged mixing ratios of CO_2 (black lower trace) and CO (gray upper trace) from Thompson Farm (INLAND) for the full year 2005. Monthly mean CO_2 from Mauna Loa Observatory is the black dashed line.

Figure 4. Hourly averaged atmospheric CO plotted against CO_2 data from Thompson Farm for the wintertime months of Nov. 2004 through to March 2005.

Figure 5a, b and c: Cross shore Gulf of Maine atmospheric CO_2 measurements collected from the R/V Gulf Challenger for a) March 22, 2006, b) July 18, 2006 and c) June 16, 2004. All panels contain the corresponding monthly mean CO_2 measured at Mauna Loa Observatory. Panels (a) and (b) are data smoothed with a running 2 min. filter while (c) shows discrete measurements made prior to implementation of a continuous sampling system.

Figure 6. One week of atmospheric (black) and inwater (gray) CO_2 mixing ratios, collected every 2 hours, from the UNH/PMEL coastal CO_2 buoy located 12 km offshore of Portsmouth NH.

Figure 7. Summer 2006 CO_2 sea-air difference calculations derived from the coastal CO_2 buoy measurements. A 72-hour running filter (uniform weighting) was used to smooth the atmospheric data prior to the difference calculation. The three traces represent the concentration difference obtained using atmospheric estimates derived from the 72-hour minimum (gray), the 72-hour maximum (dashed), and the 72-hour average (black) of the raw atmospheric CO_2 mixing ratio data.

Extra figures not likely to be included in the paper:

Figure x. Spectral analysis of CO2 data at the buoy
Spectral analysis of the air and sea data for a 30 day summertime period indicates that both signals exhibit a clear 24 hour cycle within this span, but the magnitude of the airside spectral density at this frequency is 10 times greater than for the water.

Figure y. Sample frequency of the atmospheric signal

Figure z. Average diurnal CO_2 mixing ratios observed at Appledore Island and Thompson Farm during the summer 2005.

Table 1 Air-sea flux estimates for month long averaging periods using the CO2 buoy data set and hourly wind speed measurements as well as the MLO estimate for the atmospheric level.

Month (2006)	Air-sea flux*, *in situ* (mmol/m^2/yr)	Air-sea flux*, using Mauna Loa atmospheric data (mmol/m^2/yr)	Percentage difference (%)
June	- 1.64	- 1.57	+ 04
July	+ 0.27	+ 0.27	+ 01
August	+ 0.99	+ 0.95	- 04
September	+ 0.28	+ 0.30	- 04
October	+ 0.45	+ 0.55	+ 23

* Fluxes were estimated using hourly buoy wind, sea surface temperature, and sea surface salinity data along with the gas transfer algorithm of Wanninkhof (1992). Column *in situ* uses the in-water and atmospheric pCO2 measurements directly from the buoy while Mauna Loa monthly pCO2 data are substituted for the latter in the following column. Positive values indicate flux from the ocean to the atmosphere.

Figure 1

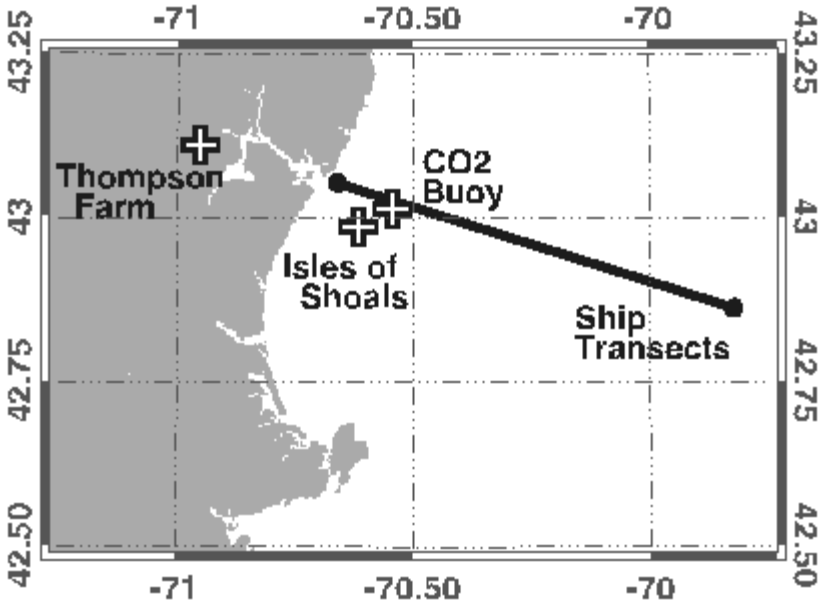

-71
-70.50
-70
43.25
43
42.75
42.50
Thompson Farm
CO2 Buoy
Isles of Shoals
Ship Transects

Figure 2

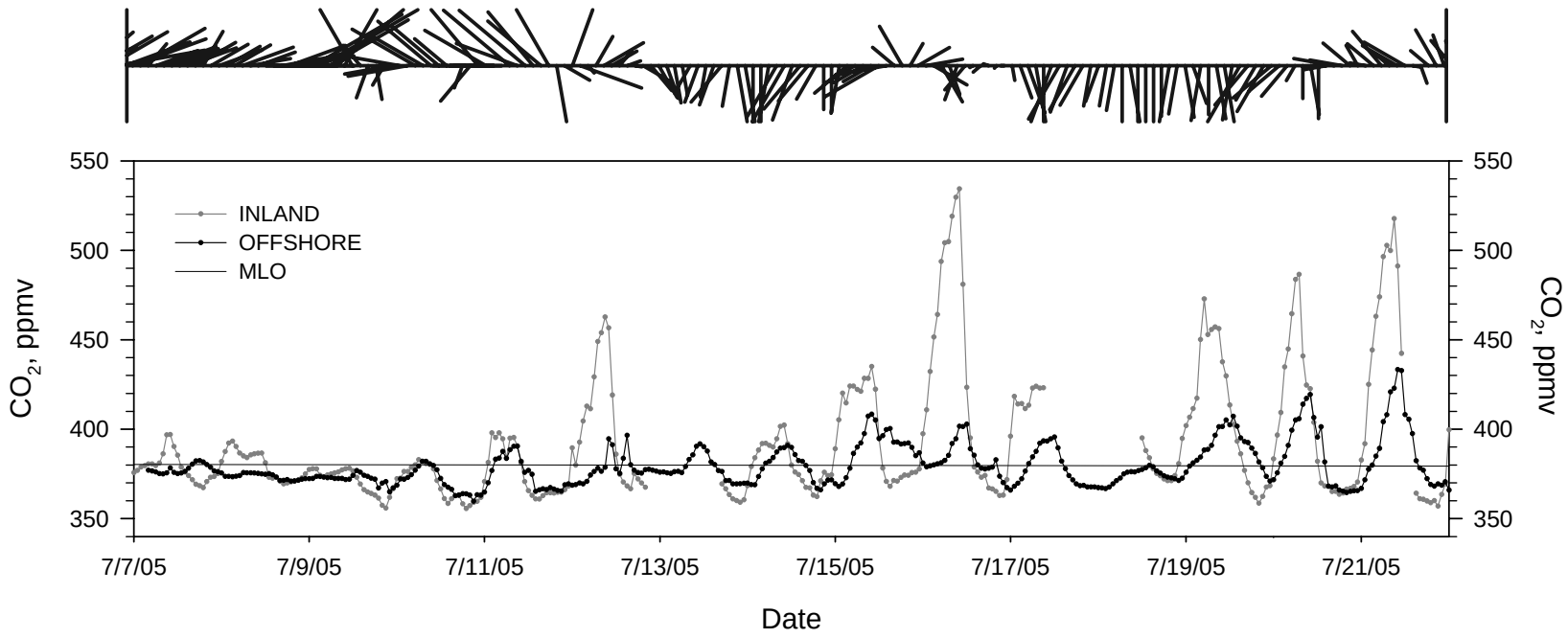

INLAND
OFFSHORE
MLO
550
500
450
400
350
CO2, ppmv
7/7/05
7/9/05
7/11/05
7/13/05
7/15/05
7/17/05
7/19/05
7/21/05
Date

Figure 3

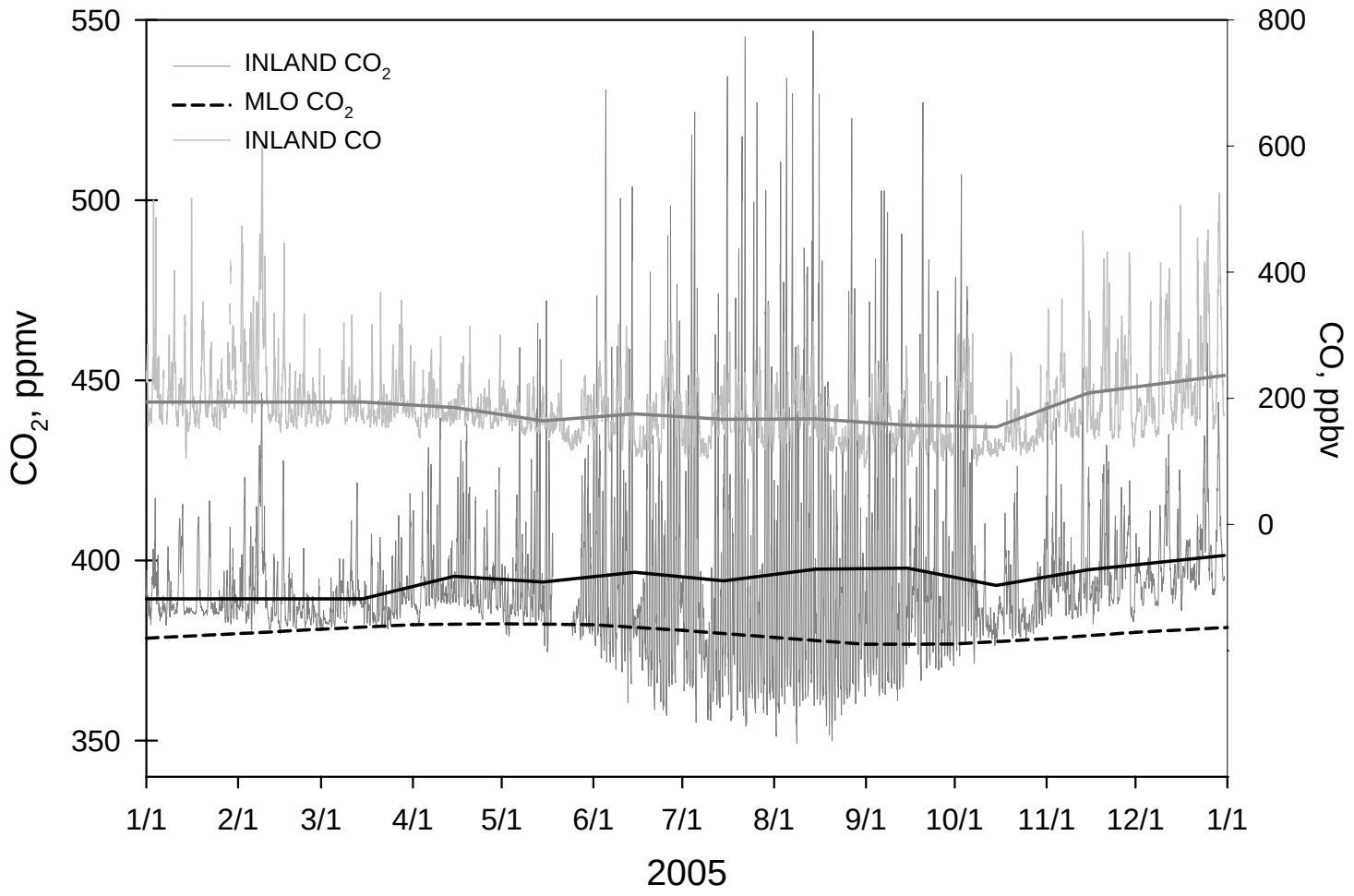

INLAND CO_2
MLO CO_2
INLAND CO
CO_2, ppmv
CO, ppbv
550
500
450
400
350
800
600
400
200
0
1/1
2/1
3/1
4/1
5/1
6/1
7/1
8/1
9/1
10/1
11/1
12/1
1/1
2005

Figure 4

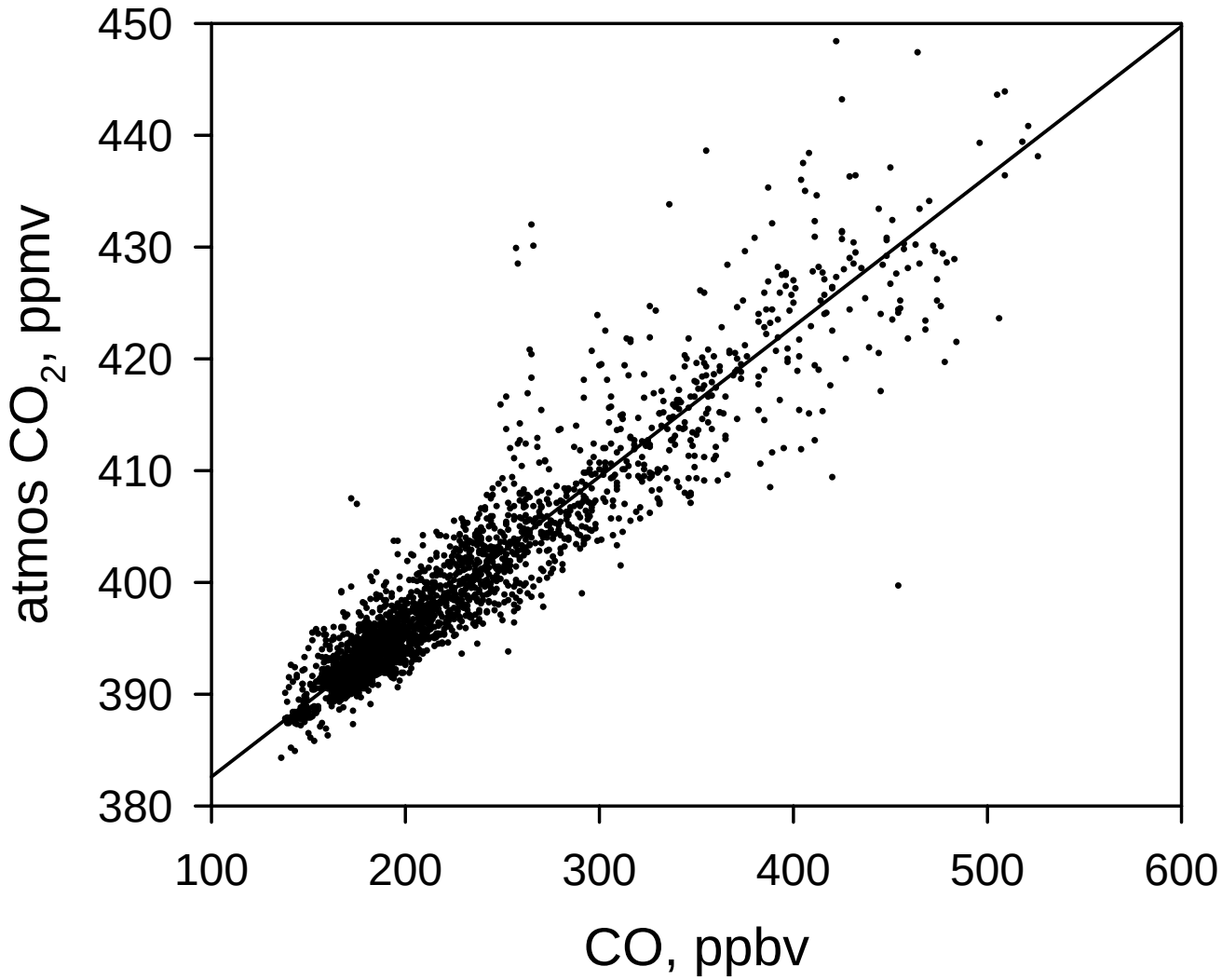

450
440
430
420
410
400
390
380
atmos CO_2, ppmv
100
200
300
400
500
600
CO, ppbv

Figure 5

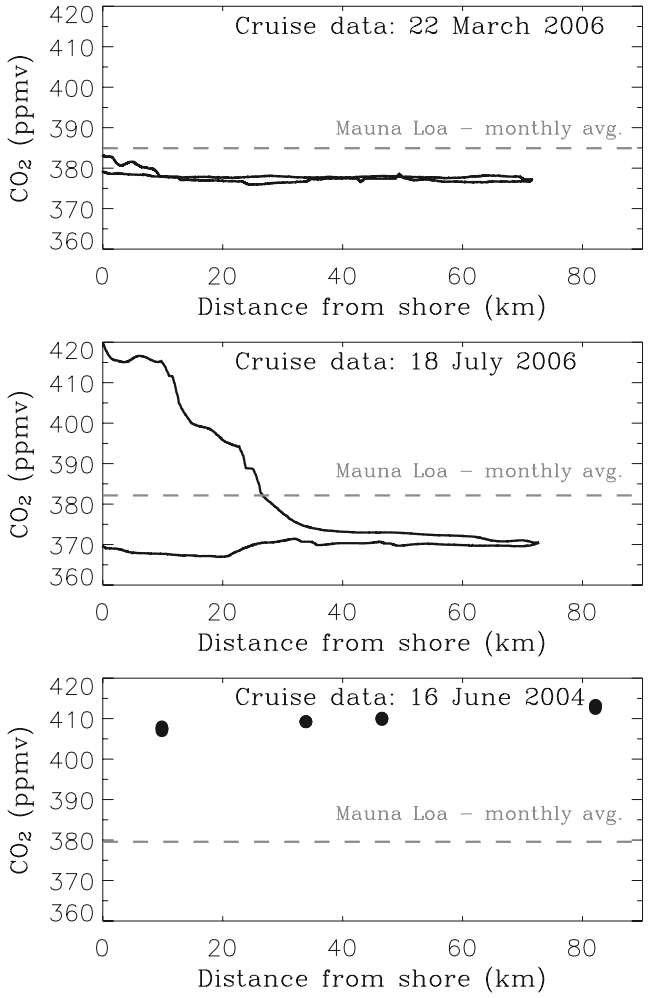

Cruise data: 22 March 2006
Mauna Loa – monthly avg.
Cruise data: 18 July 2006
Mauna Loa – monthly avg.
Cruise data: 16 June 2004
Mauna Loa – monthly avg.
CO2 (ppmv)
Distance from shore (km)
420
410
400
390
380
370
360
0
20
40
60
80

Figure 6

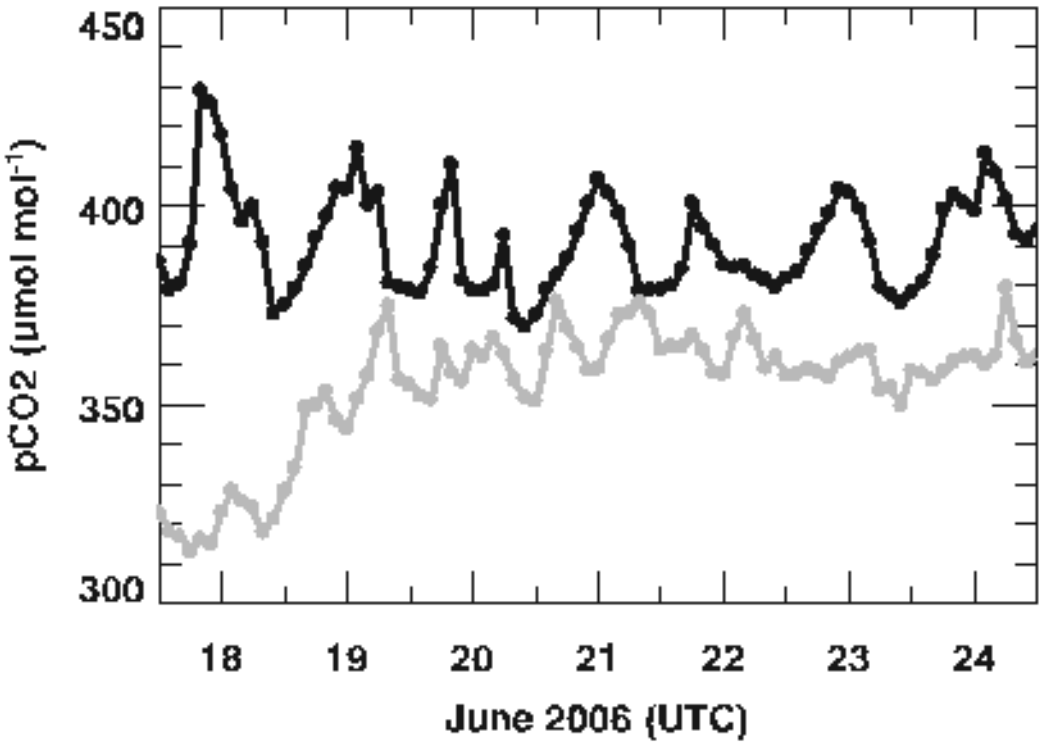


Figure 7

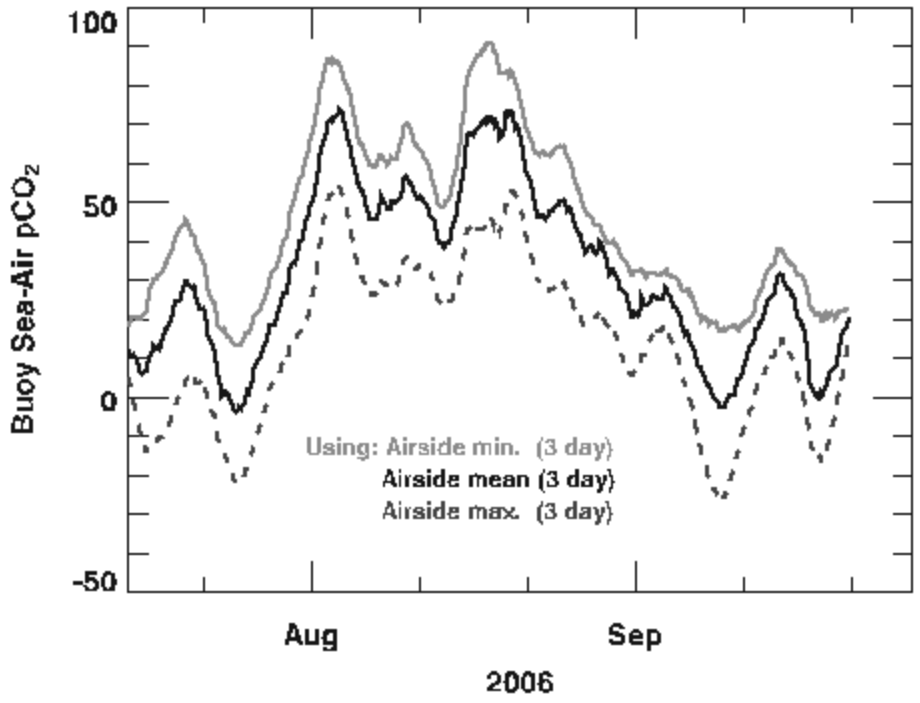

100
50
0
-50
Buoy Sea-Air pCO2
Using: Airside min. (3 day)
Airside mean (3 day)
Airside max. (3 day)
Aug
Sep
2006

Figure x

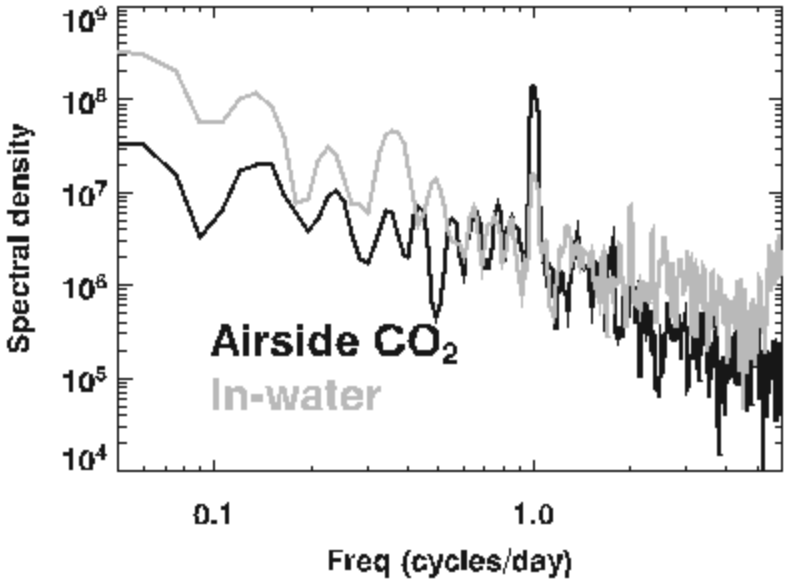

Spectral density
10^9
10^8
10^7
10^6
10^5
10^4
Airside CO_2
In-water
0.1
1.0
Freq (cycles/day)

Figure y

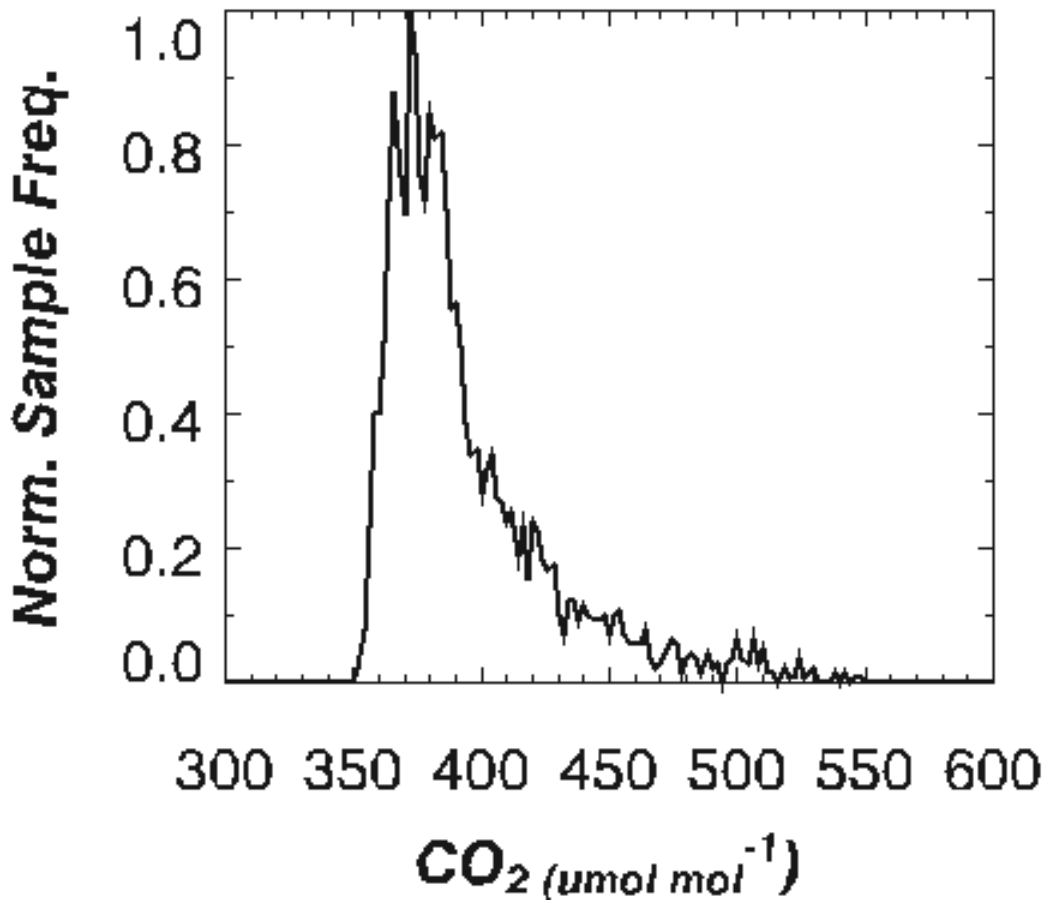
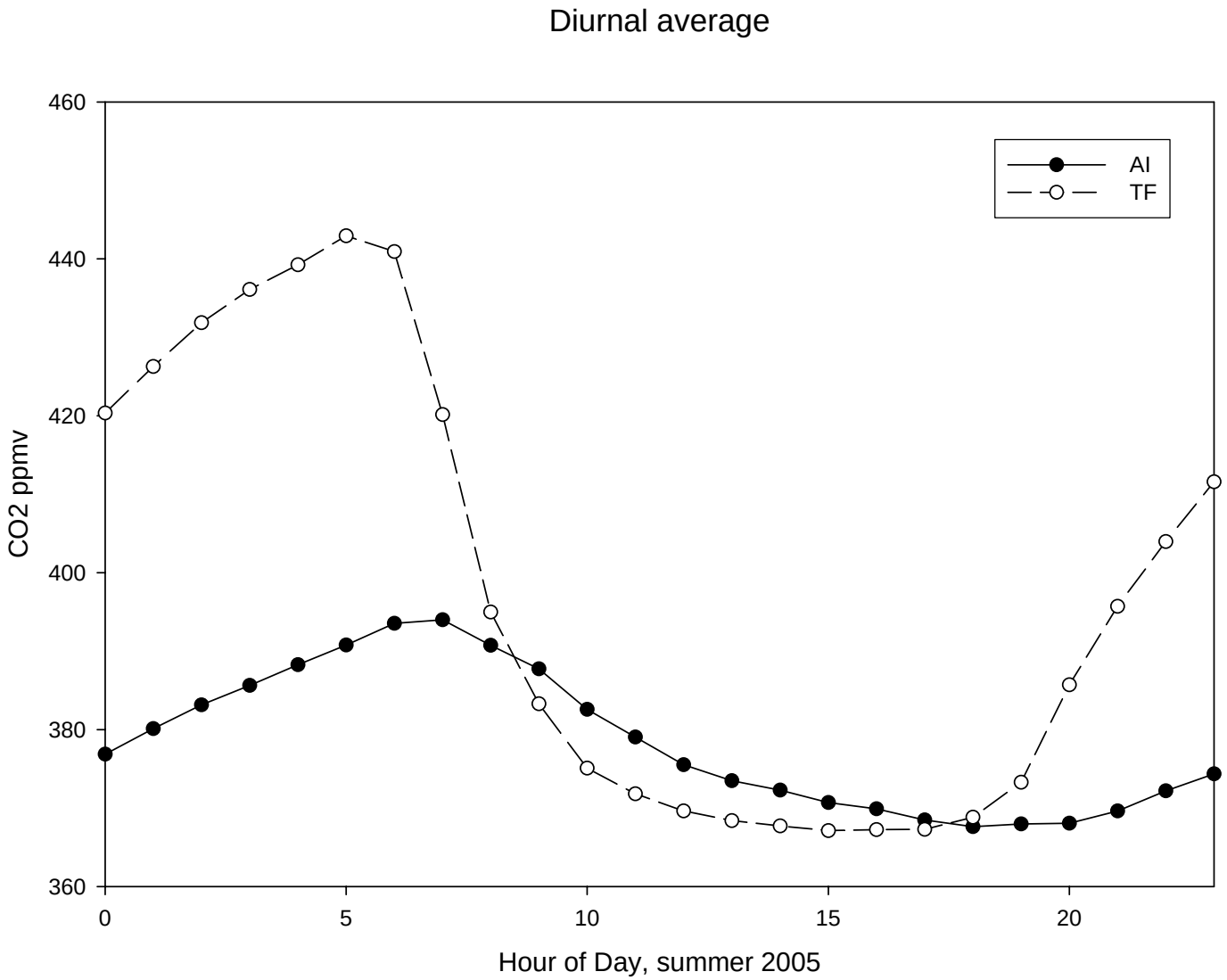

Norm. Sample Freq.
1.0
0.8
0.6
0.4
0.2
0.0
300 350 400 450 500 550 600
CO2 (umol mol-1)

Figure z


Diurnal average
460
440
420
400
380
360
CO2 ppmv
0
5
10
15
20
Hour of Day, summer 2005
AI
TF