Temporal and spatial dynamics of CO₂ air-sea flux in the Gulf of Maine

The exchange of CO₂ between the atmosphere and ocean is recognized as a key regulator, which buffers the contemporary rise of levels of this greenhouse gas in Earth’s atmosphere. Many recent and ongoing observation and modeling investigations have focused on the precise estimation, monitoring, and prediction of this exchange in the open ocean [cf. Takahashi et al., 2009; Doney et al., 2009]. Developing these same capabilities for the coastal ocean represents an important topic of research because elevated rates of biologically mediated carbon cycling and land-ocean carbon input underscore the point that marginal shelf regions hold the greatest potential to significantly modify present and future global ocean CO₂ fluxes. One hurdle to clarifying the role of the coast within global air-sea flux budgets and models is the fact that the gas exchange and its controls typically exhibit larger magnitudes and are more dynamic in both space and time for coasts than for the open ocean. Field observations conducted in many marginal shelf areas are helping to address this issue and are now of the breadth where synthesis activities have been undertaken [e.g., Cai et al., 2006; Chen and Borges, 2009; Chavez and Takahashi, 2007]. However, these works indicate that reported data are often subject to large uncertainties due to limited sampling, and that more long-term, high-resolution oceanic CO₂ observations are needed in coastal settings to assess uncertainty, to provide the data needed to confront models, and to characterize key controlling processes.

The motivations for the present study are twofold. First, we wish to document the annual and seasonal cycle of CO₂ air-sea exchange in the Gulf of Maine, a marginal sea at temperate latitudes that is important to the North American coastal ocean carbon (C) budget, due to its extensive productivity and land-to-ocean C transport. The physical, biological, and chemical oceanography of this region has been...
studied for decades [Bigelow, 1924; Riley, 1957; Brooks, 1985; Townsend, 1991], yet few measurements of inorganic C and surface water CO$_2$ exist [cf. Chavez and Takahashi, 2007; Salisbury et al., 2009]. Seasonal stratification and high primary productivity rates in the Gulf of Maine [O’Reilly and Busch, 1984; Balch et al., 2008] might imply that this region acts as an atmospheric C sink, yet the region’s significant riverine C input, coupled with significant physical controls tied to temperature, tidal, and wind dynamics, leaves source versus sink status as an open issue. Clearly, an estimate of the air-sea CO$_2$ flux is a required, but unresolved, component in C budget closure for the Gulf of Maine and along the northern U.S. seaboard, augmenting recent efforts by DeGrandpre et al. [2002] and Jiang et al. [2008].

Second, we wish to examine the magnitude of variability observed in space and time within the setting of this biophysically dynamic coastal ocean, particularly with respect to aqueous CO$_2$. There are logistical limitations in any observational effort and a key question in coastal biochemical studies is how much information is missing or in error when one neglects temporal or spatial under sampling. Two recent examples dealing with this question are found in the works of Schiettecatte et al. [2007] and Jiang et al. [2008]. To address this issue, one ideally needs to oversample in space and time and do this over a long time period to observe multiple realizations of key processes and time scales. Few field programs are able to accomplish such measurements [cf. Friederich et al., 2002; Bates, 2001; Keeling et al., 2004], and most are not in coastal waters.

This paper presents observations from a multiyear time series study within the western Gulf of Maine with the dual objectives of (1) characterizing the air-sea CO$_2$ flux for this biome and (2) assessing this exchange and surface ocean CO$_2$ dynamics at space scales of 2–100 km and time scales from hours to years within the Gulf of Maine. To support our analyses, monthly shipboard flow-through data are combined with meteorological and CO$_2$ data taken hourly at a fixed station. We present measurements from repeat sampling for the period 2004–2008, evaluate and quantify measurement uncertainty associated with terms in the air-sea exchange equation, and then document and discuss the observationally informed CO$_2$ gas exchange results for this region. The study focus is primarily on this flux rather than the evaluation of the processes controlling oceanic CO$_2$, which are addressed elsewhere [Salisbury et al., 2009] and will be studied in subsequent investigations.

2. Methods

2.1. Study Site

The Gulf of Maine (GOM) is a marginal sea bounded by Cape Cod to the south and Nova Scotia to the east (Figure 1, inset). Physical characteristics include a large semidiurnal tide, a persistent counter clockwise gyre circulation with several distinct coastal currents [Pettigrew et al., 2005], an uneven coastline and bathymetry with a predominately mud and gravel bottom, and large seasonal freshwater inflow [Salisbury et al., 2008]. It is separated from the open

Figure 1. Map of the study region including the station locations for two UNH monthly shipboard measurement transects, the cross shore Wilkinson Basin (WB) and alongshore coastal (CT) transects, as well as a moored time series MAPCO2 buoy and a long-term atmospheric CO$_2$ observation site (Appledore Island at 70°40′W). Hourly meteorological data are available from the indicated wind observing nodes including NDBC IOSN3, 44005, and 44030. The CO$_2$ buoy is located at station WB2, while the farthest WB station to the east is WB7 located in the deep (>300 m) Wilkinson Basin. The inset figure shows the U.S. east coast down to Cape Hatteras NC in the south, our measurement region (crosshatch) and a dashed line bounding the seasonally stratified portion of the Gulf of Maine.
Atlantic by Georges and Browns Banks, and much of the seasonal to interannual circulation control is attributed to variations in shelf-sea exchange through the narrow Northeast Channel and fresher coastal source waters from along the Scotian shelf [e.g., Townsend, 1991; Pringle, 2006]. The region as a whole is well known for its high gross productivity [Townsend et al., 2006] and extensive commercial fishing activities. The Western Gulf of Maine (WGOM), our study domain shown in Figure 1, lies within a seasonally-stratified portion of the GOM [Pettigrew et al., 2005] where heat and buoyancy fluxes exceed tidal and wind-driven mixing forces from roughly March to November each year. This domain is also regularly impacted by local and distant river runoff from April to July of each year, with a resulting increase in buoyancy flux and coastal current velocities [Geyer et al., 2004; Salisbury et al., 2008] and decrease in surface water residence times [Manning et al., 2009]. In general, coastal upwelling and downwelling length scales are \( O(10-20 \, \text{km}) \) and durations are 2–4 days. For the sake of comparison with other studies and regional C budgets, we assume that our study site is representative of the seasonally stratified Gulf of Maine [Bisagni, 2003], an area of roughly \( 10^4 \, \text{km}^2 \), comprising 55% of the GOM (see dashed line on Figure 1, inset). The surface area associated with inner (0–20 m), middle (20–50 m), and outer (>50 m) shelf depths within this domain are respectively. This portion of the GOM thus represents a deeper bathymetric profile than for the shallower and sloping NW Atlantic shelves to the south [DeGrandpre et al., 2002; Jiang et al., 2008].

2.2. Methods and Materials

[7] A monthly shipboard Western GOM measurement program was initiated in 2004 to develop baseline data supporting improved ecosystem description and monitoring. Ocean surface layer \( \text{CO}_2 \) was measured from 2004 to 2008 as part of this program. The R/V Gulf Challenger was used to collect data on the two single-day transects shown in Figure 1. The primary (ca) monthly line runs across shore, roughly 80 km west to east, and ends at Wilkinson Basin (WB). The secondary Coastal Transect (CT) was taken seasonally alongshore north to the large Kennebec-Androscoggin river estuary. Discrete water samples and vertical profiler measurements were routinely taken at stations along these transects as marked in Figure 1. The cross-shore WB line is the focus of this study, in part because an array of nearby oceanic and meteorological observations is available to support this and other studies. As noted in Figure 1, the second WB station (WB2) from the coast lies roughly along the 50 m isobath and less than 15 km from two long-term buoys (GoMOOS 44030 and UNH \( \text{CO}_2 \)), a long-term NDBC meteorological station (IOSN3), and the UNH AIRMAP atmospheric trace gas measurement tower on Appledore Island. Station WB2 is within 2 km of the UNH \( \text{CO}_2 \) buoy, and data from these two sites are combined in this study. For comparison with previous shelf studies we have divided the WB line data into inner, middle, and outer shelf sections. Only the innermost station (WB1) at 20 m can match the typical inner shelf definition as the depth reaches 50 m just 5 km from the coast. The composite data set used here includes 59 WB and 26 CT cruises.

[8] Measurements of \( \text{CO}_2 \) and other ancillary parameters needed to address the air-sea flux have been assembled from several sources. A monthly time series of sea surface (water intake at 0.7 m) temperature and salinity (Seabird SBE45), atmospheric pressure (Vaisala), and surface water and atmospheric \( \text{CO}_2 \) molar fraction \( (x_{\text{CO}}) \) were all measured by a continuously operated shipboard flow-through system, with data recorded at 1 Hz and then postprocessed to 20 s sample output. For oceanic \( \text{CO}_2 \), the water was pumped to an equilibrator, similar to that described by Wanninkhof and Thoning [1993], but consisting of three Plexiglas chambers instead of a single chamber. Measured differences between intake and equilibrator water temperature were negligible, as were pressure differences between ambient and equilibrator pressures. Equilibrated air was drawn out of the third chamber, while ambient air was drawn into the first chamber and passed through the second and third chambers, equilibrating with the pumped water supply at each step. Equilibrated air was drawn at 100 mL/min through tubing containing a Nation selectively permeable membrane (Perma Pure, Toms River, NJ) with a counterflowing stream of dry nitrogen to remove water vapor from the sample gas stream. After drying, the sample was pumped to a nondispersive infrared gas analyzer (Li-cor, LI-6262, or LI-840) to measure the \( x_{\text{CO}_2} \) of the sample stream. The analyzer was calibrated several times per day with pure nitrogen (0 ppm \( \text{CO}_2 \)) and a gas mixture of 832 ppm \( \text{CO}_2 \) (Scott-Marin, Riverside, CA). Correction of all \( \text{CO}_2 \) study data for water vapor pressure and sea surface temperature and conversion between \( \text{CO}_2 \) and the fugacity of carbon dioxide (\( f_{\text{CO}_2} \)) were carried out according to standard methods [Dickson et al., 2007]. Atmospheric \( x_{\text{CO}_2} \) was either periodically (2004–2005) or continuously (2006 to present) measured while the ship was underway. Ambient air was drawn from the ship’s bow through a length of Teflon tubing, dried, and pumped into an NDIR analyzer as described above. Precision of resulting \( f_{\text{CO}_2} \) measurements is estimated at \( \pm 3 \, \mu \text{Atm} \).

[9] The UNH \( \text{CO}_2 \) buoy near station WB2 provides data recorded onboard a 1.9 m discus buoy moored 7 km northeast of the Appledore Island tower and 12 km offshore (43.01°N, 70.55°W). Water depth at the buoy is 65 m. Operation of the buoy’s autonomous \( \text{CO}_2 \) data collection system (MAPCO2) is a joint collaboration between UNH and NOAA’s Pacific Marine Environmental Laboratory. Buoy measurements of atmospheric and surface layer oceanic \( \text{CO}_2 \) are collected every 2 h (2006) or 3 h (2007 to present) using an automated equilibrator-based gas collection system and an NDIR gas analyzer (Li-820, Li-Cor) based on the approach of Friederich et al. [1995]. The height of the atmospheric intake is 1.5 m above sea level (asl), and the depth of the water intake is 0.6 m. Calibration is performed immediately prior to these measurements using a soda lime (CaCO\(_3\)) reservoir for zero \( \text{CO}_2 \) reference and \( \text{CO}_2 \) span tank (500 ppm) calibrated with standards at NOAA/ESRL. Field validations indicate the accuracy of this \( \text{CO}_2 \) measurement system is better than 3 ppmv [Shellito et al., 2008].

[10] Continuous fast rate \( x\text{CO}_2 \) measurements are available for several extended time periods between 2004 and 2008 from atop the AIRMAP tower 36 m asl on Appledore Island. Data are collected at 1 Hz and averaged to 0.5 h periods. Ambient air is drawn from a 5.1 cm i.d. Teflon manifold into an NDIR analyzer (Li-7000, Li-Cor). The analyzer is...
automatically zeroed with ultrahigh purity nitrogen every 241 h and calibrated every 14 h with a range of standards 242 (Scott-Marrin, Inc., Riverside, CA). Calibration standards 243 range between 370 and 400 ppmv ± 1% and are used in the 244 system for approximately 1 year. Agreement between the 245 buoy MAPC2 atmospheric xCO2 data, and this AIRMAP 246 station is observed to be ±1.7 ppmv [Shellito et al., 2008]. 247 [11] Continuous hourly wind speed and sea state mea- 248 surements for 2004–2008 are produced from a composite of 249 the surrounding meteorological stations available near the 250 WB line. The primary source of wind speed data is buoy, 252 ISOS3, located near Appledore Island, for the inner and 253 middle shore segments. For the offshore end of the WB line 254 data, we use buoy N44005, located NE of WB7 (see 255 Figure 1). Two wind values are used because we find a 256 slightly elevated wind speed offshore (on average +0.5 m/s). 257 However, we note that the linear correlation coefficient 258 between five long-term meteorological stations across the 259 region (IOS3, 44029, 44030, 44007, 44009, and 44005) 260 exceeds an $R^2$ of 0.95, affirming that winds are nearly uni- 261 form over our roughly 150 by 150 km measurement domain. 262 All wind speeds are converted from the observed value to a 263 neutral stability wind speed at 10 m asl using the Toga-Coare 264 3.0 bulk flux algorithm [Fairall et al., 2003] including use 265 of hourly water and air temperature, pressure, and relative 266 humidity measurements.

267 2.3. Air-Sea Fluxes and CO2 Disequilibrium 268 Computations 269 [12] All air-sea CO2 flux ($F$) values are estimated using 270 a commonly employed parameterization based on a gas 271 transfer velocity ($k$) and the disequilibrium between dissolved 272 CO2 gas concentrations, [CO2], across the surficial air-sea 273 boundary layer. Formulations are given as

$$F = k_w k_0 (f_{CO2} - f_{CO2}_{atm})$$

where $k_w$ is the aqueous (aq) phase gas solubility given as

274 function of salinity and temperature [Weiss, 1974], atmo-

275 spheric CO2 carries the (atm) subscript, Sc is the Schmidt 276 number [Wanninkhof, 1992], and gas transfer velocity sub-

scripts 6xx and w refer to wind-related models produced in 278 the literature at values of 600 or 660. Following the work 279 of Jiang et al. [2008], we produce hourly estimates for $k_w$

280 (and $F$) using five candidate $k_{6xx}$ algorithms [Wanninkhof, 281 1992; Nightingale et al., 2000; Wanninkhof and Mc Gillis, 283 1999; Mc Gillis et al., 2004; Ho et al., 2006]. All models

284 are formulated with a quadratic or cubic dependence and

285 implemented with the buoy-derived 10 m neutral stability

286 wind speed.

287 3. Results 288 3.1. Time Series Observations 289 [13] Monthly and hourly measurements at station WB2 for 290 the 5 year period from 2004 to 2008 are shown in Figure 2 291 to provide an overall view of temporal dynamics for the 292 parameters involved in regional CO2 air-sea flux computa-

293 tions. Similar variation in all observations is found across the 294 measurement transects shown in Figure 1.

[14] Seasonal change in the hydrographic cycle can be 295 observed in Figure 2c where sea surface temperature (SST) 296 values range from 3 to 5°C in late March to 18–20°C in late 297 August. Surface salinity in this region is quite fresh, with a 298 mean value near 31.4 psu, and also variable at the monthly 299 scale. For comparison, the GOM as a whole has a mean 300 salinity near 32.3 psu, and the adjoining NW Atlantic shelf 301 break is roughly 33.5 psu. Values during the spring period 302 of April–June, when river flow is typically high due to snowmelt 303 and rainfall, often drop to 28–29 psu at stations WB1–WB3. 304 Both the SST and SSS curves represent a linear interpolation 305 between monthly samples obtained within 5 km of WB2 on 306 the sampling dates indicated by symbols in Figure 2a. The 307 water column here is seasonally stratified [e.g., Bisagni, 308 2003] and the approximate date of the spring mixed layer 309 formation and fall breakdown can be determined by the 310 intersection of the SST and SSS curves during these seasons.

[15] The wind speed and sea state data in Figure 2d re-

present the hourly wind speed ($U$) observations as well as 312 weekly averaged $U$ and SSWH. A pattern of increased wind 313 speed from November to April in each year coincides with 314 winter cooling below roughly 10°C, mixed layer deepening 315 (offshore), and desalination (inshore). The lowest wind 316 speeds occur in middle late summer, coincident with the 317 warmest SST. The sea state data typically follow $U$ closely 318 at the weekly to monthly time scale, in part because the GOM 319 typically experiences only weak swell from the NW Atlantic, 320 and thus, the sea state is characterized by wind-driven. Some 321 cross-shore variation in SSWH under strong W and NW winds 322 may be expected, but for this multiyear study, we present only 323 SSWH data taken from station 44030 near WB2.

[16] Figure 2a provides monthly shipboard $f_{CO2}$ mea-

surements, along with a trace indicating linear interpolation 327 to hourly values as well as 2 or 3 hourly buoy data when 328 available. A repeatable seasonal cycle is apparent, with a 329 minimum of 200–250 µAtm seen in most spring periods and 330 an annual maximum of 400–500 µAtm observed in late fall 331 to early winter. Summertime values consistently reside near 332 400 µAtm. Typically, the $f_{CO2}$ measurements taken by 333 the buoy at a finer time resolution do not deviate more than 10– 334 20 µAtm from the ship-based $f_{CO2}$ measurements; however, 335 there are notable periods with deviations exceeding 50 µAtm.

[17] Ship-based atmospheric $fCO2$ measurements, also 337 roughly once per month, are shown in Figure 2b on the same 338 scale as the ocean data. In this case, we present the median 339 value for the entire daily cruise in an attempt to filter out observed variability. The trace in Figure 2b does not represent a linear interpolation but rather a time-varying 340 $fCO2$ model developed using the hourly buoy and AIRMAP 341 station data near WB2, as shown in Figure 3. Recently, sev-

eral authors [Padin et al., 2007; Perez et al., 2001; Jiang et al., 344 2008] have shown that atmospheric boundary layer 345 CO2 in the coastal zone frequently exhibits 5–20 µAtm var-

iability at diel to multiday time scales. The data compiled in 346 Figure 3 indicate that near our site this magnitude can be even 347 greater and is O(20–40 µAtm) throughout the summer. While 348 not shown, the largest values occur early in the morning near 349 500–700 AM local time, which we attribute to a routinely 350 occurring shallow nocturnal boundary layer [Zhou et al., 351 2005]. Summertime afternoon values (when our ship mea-

surements typically occur) fall below the daily average value 352 due to terrestrial photosynthesis and advected continental air.

4 of 14

MARINERS' INC., RIVERSIDE, CA). CALIBRATION STANDARDS RANGEBETWEEN 370 AND 400PPMV ±1%AND ARE USED IN THE SYSTEM FOR APPROXIMATELY 1 YEAR. AGREEMENT BETWEEN THE B UOY MAPC2 ATMOSPHERIC XCO2 DATA, AND THIS AIRMAP STATION IS OBSERVED TO BE ±1.7PPMV [SHELLITO ET AL., 2008]. (SCOTT-MARRIN, INC., RIVERSIDE, CA). CALIBRATION STANDARDS RANGE BETWEEN 370 AND 400PPMV ±1% AND ARE USED IN THE SYSTEM FOR APPROXIMATELY 1 YEAR. AGREEMENT BETWEEN THE BUOY MAPC2 ATMOSPHERIC XCO2 DATA, AND THIS AIRMAP STATION IS OBSERVED TO BE ±1.7PPMV [SHELLITO ET AL., 2008].
In the mean value and at a seasonal scale, Figure 3 indicates the local data significantly depart from the Mauna Loa atmospheric measurements often used as a Northern Hemisphere atmospheric reference in air-sea flux studies [e.g., Bakker et al., 2001; DeGrandpre et al., 2002; McNeil et al., 2006; Salisbury et al., 2008]. For this study, we choose to create an hourly estimate following the approach of Padin et al. [2007] where we develop a second-order harmonic fit to the observations in Figure 3 to produce a model covering the entire 2004–2008 period and given as

\[
x_{\text{CO}_2}(t) = a_0 + a_1 t / dy + a_2 \sin((t - b_1)\phi) + a_3 \sin^2((t - b_2)\phi),
\]

where \(\phi = 2\pi / dy\), \(dy = 365.25\) (days of year), and \(a = [382, 2.1, -9.05, 1.10]\) and \(b = [138, -82]\). Because observed atmospheric variations tend to be random about the weekly mean, the use of the model is considered a superior choice to linear interpolation [Padin et al., 2007] of once per month ship-based values. For example, we find that monthly cruise data in Figure 3 sometimes fall 5–20 ppmv from this mean.

Hourly \(\text{CO}_2\) flux and \(\Delta f\text{CO}_2\) time series for the entire 5 year period are given in Figure 4, along with an annually repeating \(\Delta f\text{CO}_2\) climatology that we produce using an average over the 5 year period. Note that for any further 5 year averages involving ship data (not wind speed or \(k_w\)) the average is produced using data from days 107 to 365. Our time series began on day 107 in 2004 and thus days 1–107 represent a 4 year average. The seasonal cycle of ocean surface \(\text{CO}_2\) seen in Figure 2 is reflected in Figure 4a with apparent spring \(\Delta f\text{CO}_2\) drawdown occurring between days 100 and 200. The \(\text{CO}_2\) hourly flux time series in Figure 4b shows a strong qualitative correspondence with the seasonal \(\Delta f\text{CO}_2\) cycle, Figure 3. Data from the AIRMAP Appledore Island (30 min) site or the UNH \(\text{CO}_2\) buoy (bihourly) are given over a multiyear period along with shipboard daily median samples (solid circle) and flask sample data from Sable Island Nova Scotia (diamond). The thicker solid trace is weekly averaged \(x_{\text{CO}_2}\) from the hourly stations. The vertical gray bars represent weekly minima and maxima in the hourly estimates. Also shown is the time varying \(x_{\text{CO}_2}\) model fit to the multiyear hourly data set (thin solid) and the monthly observations from Mauna Loa Hawaii station data (dashed trace).
as is somewhat expected from the equation (1). Hourly flux measurements indicate significant minima and maxima associated with high-wind events following the chosen $k_w$ algorithm [Wanninkhof, 1992], with the flux magnitude exceeding 4 mmol m$^{-2}$ h$^{-1}$ on numerous occasions. Year-to-year variability is observed in both panels, with $\Delta$CO$_2$ data at times deviating from the climatology by values greater than 100 $\mu$Atm. Interannual differences in the extent and magnitude of spring influx and fall to winter efflux periods are seen in the flux time series.

[19] A monthly view of the annual air-sea flux cycle at WB2 is given in Figure 5 along corresponding controls, $\Delta$CO$_2$ and $k_w$. Data for the full period average, as well as the individual years 2005 and 2007, are shown to document both the mean seasonal cycle as well as years that deviate most strongly from this mean. The thickest traces in each panel provide the climatologies and seasonal cycles already seen in Figures 2 and 4. It is now apparent that $\Delta$CO$_2$ and the flux are effectively in phase. The periods with highest gas transfer velocity coincide with the positive $\Delta$CO$_2$ periods and thus accentuate the source of CO$_2$ to the atmosphere in the late fall to winter. The two individual years (2005 and 2007) generally follow the longer-term average, but there are also substantial monthly differences, especially during late fall and into winter. Estimates of the measurement standard deviation, computed over each monthlong period, are provided as a

![Figure 4](image_url)

Figure 4. (a) Time series of observed sea-air CO$_2$ difference (symbols) and hourly interpolated data (dashed) at station WB2 as well as a repeating annual climatology (solid) produced from the 2004–2008 average at WB2. (b) The hourly flux is produced for the same period using hourly NDBC wind data and the gas transfer model of Wanninkhof [1992]. Note that days 001–107 fluxes in 2004 are produced using the $\Delta$CO$_2$ climatology rather than observations.

![Figure 5](image_url)

Figure 5. Monthly averaged estimates of (a) CO$_2$ flux, (b) $\Delta$CO$_2$, and (c) transfer velocity at WB2. Data show years 2005 (dark) and 2007 (light gray), depicted from a moving 30 day average over the hourly data, as well as the 5 year average (thickest trace). Error bars are one standard deviation over the monthly averaged results for the 5 year period and provide one measure of interannual dynamics in each month. Net annual flux values are provided in Figure 5a.
The annual estimate uncertainty as discussed in the text. The straight gray line for the entire period at $F = 0.38 \text{ mol m}^{-2} \text{ yr}^{-1}$ represents the region-wide 5 year average flux.

412 measure of year-to-year variation. Smallest error bars coincide with summer months and the lowest $\Delta f/CO_2$ and $k_w$. While the 5 year net annual flux (Figure 5a) shows station WB2 to be a net CO$_2$ source of $+0.32 \text{ mol m}^{-2} \text{ yr}^{-1}$, years 2005 and 2007 differ from this value by a significant amount, with year 2005 being a relatively strong sink (i.e., negative flux).

419 [20] The net annual flux in each year, and for different cross-shelf subsections, is shown in Figure 6 with values provided in Table 1. In all but three instances, the data indicate a positive flux (export of CO$_2$ to the atmosphere). Year 2006 appears to be in net balance region wide, while year 2005 is the anomalous case indicating a sink on the inner and middle shelf regions. Similar year-to-year variation for all stations indicates the three shelf subregions generally agree with each other at an annual scale to better than $0.5 \text{ mol m}^{-2} \text{ yr}^{-1}$. The inner shelf does consistently exhibit the largest positive flux values. The estimated uncertainty for these annual averages is $0.26 \text{ mol m}^{-2} \text{ yr}^{-1}$ and is shown on Figure 6 in the lower right corner.

432 3.2. Spatial Variability

433 [21] The net annual flux values shown in Figure 6 also provide a first measure of the spatial variability observed cross-shore on the WB monthly transects. As shown in Figure 1, the data collection extends from shore to roughly 80 km east into the GOM at Wilkinson Basin, where depths exceed 300 m. We produce flux estimates for inner (0–50 m depth), middle (50–100 m), and outer (>100 m) shelf segments of the WB line following methodologies from previous marginal shelf air–sea flux studies [DeGrandpre et al., 2002; Jiang et al., 2008]. Note that the bottom in the GOM drops off quickly (>60 m at 10 km from shore) and does not slope smoothly along the WB line, and thus, our segments and locale are not ideal representations of this type of division. For this study, we assume the wind speed (and $k_w$) are spatially uniform over the roughly 100 km$^2$ region. Therefore, most spatial variation in the computed fluxes comes from variation in $\Delta f/CO_2$, with a change due to SST and salinity small enough to be negligible. Therefore, the oceanic $f/CO_2$ data are used as a surrogate for describing observed spatial flux variability on a given day.

434 [22] Cross-shore variation of daily $f/CO_2$ for several months and in two different years is presented in Figure 7. The traces represent a 2 km along-track smoothing of shipboard flow-through data, averaged at 20 s intervals, that typically has resolution below 100 m. January and July data indicate that $f/CO_2$ varies less than 25 $\mu$Atm across the entire 80 km transect, with a smoothly varying change at the 40–80 km length scale. Similar behavior is seen for April 2008 and October 2005 transects. The two most variable transects show a 115 $\mu$Atm increase on the inner shelf in October 2008 and a 140 $\mu$Atm increase on the outer shelf for April 2005. These two largest values are still a factor of 2 lower than the seasonal $pCO_2$ signal observed from April to October. Overall, the data typically show variations of less than 5 $\mu$Atm occurring at spatial scales shorter than 10 km.

435 [23] A multiyear average of monthly $f/CO_2$ for the inner, middle, and outer shelf segments is given in Figure 8. As in Figure 6 and Table 1, the three estimates agree to better than 20 $\mu$Atm in most months and present very similar seasonal

### Table 1. Annual and Multiyear Sea-Air CO$_2$ Flux Estimates for the Study Region

<table>
<thead>
<tr>
<th>Year</th>
<th>Inner</th>
<th>Middle</th>
<th>Outer</th>
<th>Region</th>
</tr>
</thead>
<tbody>
<tr>
<td>2004</td>
<td>0.91</td>
<td>0.51</td>
<td>0.75</td>
<td>0.74/0.68</td>
</tr>
<tr>
<td>2005</td>
<td>0.31</td>
<td>0.75</td>
<td>0.15</td>
<td>0.09/0.10</td>
</tr>
<tr>
<td>2006</td>
<td>0.38</td>
<td>0.14</td>
<td>0.02</td>
<td>0.05/0.05</td>
</tr>
<tr>
<td>2007</td>
<td>1.37</td>
<td>1.34</td>
<td>0.60</td>
<td>0.71/0.65</td>
</tr>
<tr>
<td>2008</td>
<td>1.07</td>
<td>0.35</td>
<td>0.47</td>
<td>0.49/0.46</td>
</tr>
<tr>
<td>5 Year</td>
<td>0.81</td>
<td>0.32</td>
<td>0.35</td>
<td>0.38/0.35</td>
</tr>
</tbody>
</table>

*With units mol m$^{-2}$ yr$^{-1}$ and with positive values being a source to the atmosphere. Estimates for the inner, middle, and outer shelf as well as a weighted average representing the seasonally stratified Gulf of Maine are provided.

*The second values are derived from an ensemble average of fluxes separately estimated using the five $k_w$ algorithms discussed in section 2.

All other values utilize Wanninkhof [1992].
cycles. One indicator of interannual variability for each month and segment is provided using the standard deviation calculated over all years, which shows a similar level of variation at the three locations. Observed alongshore \(fCO_2\) variation, measured along roughly the 50–60 m isobath on seasonal CT transects (see Figure 1), is presented in Figure 9. The middle 40–50 km of this transect is farther from the coast and river plumes, and in this transect segment, we see variation below 20–40 \(\mu\)Atm on most days. Data nearer the 0–10 and 60–80 km ends of the legs represent areas near the Piscataqua and Kennebec estuaries where more variability is expected due to salinity, temperature, and carbon dynamics [Salisbury et al., 2009]. Only in April 2007 does one observe a strong alongshore \(fCO_2\) gradient with a magnitude of 120 \(\mu\)Atm and lowest values in the south toward the WB transect line. This is not uncommon in the April–May period when local riverine input is greatest.

### 3.3. Air-Sea Flux Estimate Uncertainties

It is difficult to accurately quantify the level of uncertainty to apply to monthly and annual air-sea flux estimates for a site or region, especially in coastal waters. While the \(\Delta fCO_2\) measurement accuracy may be high, one does not have complete coverage in either space or time. Nor is there a definitive method or parameterization for the gas transfer velocity [Wanninkhof et al., 2009]. Here the error estimation conventions applied in numerous coastal studies are taken into account [e.g., DeGrandpre et al., 2002; Friederich et al., 2002; Schiettecatte et al., 2007; Kuss et al., 2006], with a particular emphasis given to the approach of Jiang et al. [2008]. We take a similar root mean square uncertainty approach to pose the potential error for a given monthly flux estimate as

\[
\varepsilon F_{CO_2} = F \left[ \varepsilon_{kw}^2 + \varepsilon_{fCO_2}^2 + \varepsilon_{fCO_{aqeous}}^2 \right],
\]

where \(\varepsilon\) is the relative standard error associated with \(k_w\), the Weiss solubility assumption is assumed negligible in equation (1), and the latter two terms reflect measurement and sampling uncertainties (including relative error due to space and time interpolation) in the hourly air and sea \(fCO_2\) values used to produce the fluxes. These error terms are assumed to be uncorrelated. As in the work of Jiang et al. [2008] and other works [e.g., Wanninkhof et al., 2009; Olsen et al., 2005], the relative error of the gas transfer velocity is taken to be 12%, including potential random error in the wind measurements. Following Jiang et al. [2008], we evaluated the flux obtained using the five algorithms listed in section 2 at flux averaging periods of hours to years. The differences amongst flux estimates are typically below 10% at the monthly scale and less than 3% at the annual scale, consistent with what is observed in Table 2 of their study. As one attempt to summarize the impact and difference between choice of...
Figure 10. One year of ship and buoy-derived observations of (top) ΔfCO₂ and (bottom) CO₂ sea-to-air flux derived from hourly data sets at station WB2. Buoy ΔfCO₂ observations are at a 3 h time step, while the monthly ship measurement times are indicated by large symbols on the top. The difference between fluxes is shown at hourly time step (Figure 10, bottom) along with monthly smoothed flux estimates as indicated.

4. Discussion

[28] The first objective of this observational program is to provide the first regional air-sea CO₂ flux characterization. A second is to establish a long-term coastal ocean CO₂ time series with temporal and spatial sampling resolution sufficient to shed new light on potentially unresolved dynamics and processes. As with the open ocean time series projects such as HOTS, BATS, and Carioca, these coastal data can help inform state-of-the-art ocean measurement and modeling efforts, as well as to help answer a common question in coastal CO₂ studies: What are we missing? We address these issues with our data sets with the understanding that not all variability in fCO₂ observed at 5–10 km length scales (see Figures 6 and 8) indicates that temporal dynamics dominate the error term fC₀₂aqueous in equation (3). A yearlong comparison of the ship and mooring-based estimates of fCO₂ and the derived flux at site WB2 is shown in Figure 10. The hourly wind (and kₜ) data used to estimate the flux were identical, and thus, all differences come from ΔfCO₂. The results indicate hourly flux differences can be very large, at times exceeding the monthly mean values. Mooring data in the spring of 2007 show that [cal] monthly ship sampling missed significant CO₂ drawdown events at the 5–15 daytime scale. As a result, 25%–50% errors in the monthly fluxes are observed in April and May. On average, over a 22 month ship and buoy data evaluation at WB2, we find the monthly fCO₂ error due to temporal sampling is 16%. This factor will dominate fC₀₂aqueous and equation (3). Applying the overall rms error estimation model to monthly data sets for 2004–2008 yields an average monthly flux uncertainty of ±0.43 mol m⁻² yr⁻¹. This monthly number is similar to that obtained by Jiang et al. [2008] for the SAB.

[27] If one assumes successive monthly sampling errors are independent and uses the central limit theorem to derive the annual and five-year uncertainty, then standard error (SE = standard deviation/N) estimates become ±0.12 and ±0.05 mol m⁻² yr⁻¹, respectively. However, the flux differences shown in Figure 10, especially in spring, indicate the potential for substantial systematic error over an annual period, at least in 2007–2008. For that period the mooring-derived net annual flux is +0.01 mol m⁻² yr⁻¹ while the ship-derived value is 0.43 mol m⁻² yr⁻¹. This annual difference is of the order of our monthly standard error and significantly outside ±0.12 mol m⁻² yr⁻¹. Thus, it is likely that monthly samples in the time series are not independent. One measure of this is seen in the computed temporal decorrelation (e-folding) time scale for the ocean fCO₂ buoy data at WB2. This time scale is roughly 45 days (a similar result is obtained using an autocorrelation evaluation of either hourly buoy data over 22 months or the 60 month monthly time series). Thus, there is a need to obtain an effective number of independent samples N*. N* can be derived from the actual sample number N and the lag-1 or first-order autocorrelation value ρ as suggested by World Meteorological Organization [1966] with N* = N(1 − ρ)/(1 + ρ). In our case, the lag 1 month lag ρ = 0.55, N* = 3, and the average annual uncertainty for our study becomes ±0.26 mol m⁻² yr⁻¹. This is the uncertainty (SE) level for net annual fluxes in Table 1 and shown on Figure 6.

522 gas transfer model, the bottom row in Table 1 provides the 523 regional annual fluxes obtained using our chosen standard 524 gas transfer algorithm [Wanninkhof, 1992] and that obtained 525 using the ensemble of the five algorithms. The difference is at 526 the second digit in the annual values. The atmospheric CO₂ 527 data of Figure 3, sampled at high temporal resolution, illustrate that observed deviations from our hourly fCO₂a m model 529 estimates of equation (2) may often be significantly larger 530 than the Jiang et al. [2008] atmospheric error estimate of 531 ±6 μAtm estimated for the South Atlantic Bight. However, 532 the computed monthly deviation between equation (2) and 533 buoy-measured values over 20 months at buoy station WB2 534 yield a maximum error of 4 μAtm and a monthly standard 535 error of 2 μAtm. We make the assumption that spatial vari- 536 ation impacts at a monthly scale are of this order. Combining 537 these findings with a ±3 μAtm atmospheric CO₂ measure- 538 ment error, we conservatively prescribe 3% for the second 539 error term above.

540 [26] For coastal sites in particular, error due to under- 541 sampling the aqueous fCO₂ in a monthly or seasonal mea- 542 surement program is a certain and potentially large source of 543 error in flux calculations. As in most studies, the fCO₂ 544 interpolation of monthly data used for Figure 4 and Table 1 545 assumes well-predicted behavior between ship measure- 546 ment visits. However, most studies must either neglect an 547 estimate of error due to this assumption or develop an ad hoc 548 accounting because no data exist to resolve the issue. In this 549 study, monthly shipboard data collection next to the mooring 550 at WB2 permits sampling error assessment at one location. As 551 part of this approach, we assume that the limited spatial
complexity in the observations and controlling coastal pro-
cesses, especially at finer space and time scales, are included.  

4.1. CO₂ Air-Sea Flux Dynamics and Net Annual  

Values  

A first conclusion, drawn from inspection of spatial  
and temporal data in Figures 7 and 9, is that regional hori-
zontal gradients in ocean /CO₂ (and CO₂ flux) are typically  
small relative to seasonal time scale /CO₂ variations. The data  
indicate that surface water /CO₂ spatial variability in both  
cross-shore and alongshore directions from the WB2 middle  
shelf site is O(10–20 μAtm) on most occasions, while the  
peak-to-peak seasonal range is 150–200 μAtm. The observed  
spatial scale of /CO₂ gradients is typically longer than 20 km,  
especially for the cross-shore measurements (Figure 7). Such  
a large scale agrees with recent Gulf of Maine investigations  
[e.g., Balch et al., 2004] where the relative homogeneity is  
attributed to mixing by energetic tidal and wind stress forcing  
during daily to weekly time scales. Table 1 does indicate  
a small but consistent efflux increase for the inner shelf (depth  
< 20 m), a tidally mixed zone of limited area that lies within  
5–10 km from shore in the Gulf of Maine. The elevated near  
shore values are also consistent with results observed to our  
South [Boehme et al., 1998; DeGrandpre et al., 2002]. Other-
wise, we observe middle and outer shelf annual flux esti-
mates that are statistically equivalent (Table 1 and Figure 6),  
and that the monthly and seasonal /CO₂ observations for  
inner, middle, and outer cross-shelf locations are also in near  
agreement (Figure 8; see also Figure 4 in Salisbury et al.  
[2009]). These conclusions rely on the assumption that  
ocean /CO₂ dynamics reflect air-sea flux dynamics, since  
observed spatial variations in hourly winds (and hence kₑ) are  
small. Moreover, the multiyear data of Figure 4 indicates that  
spatial variation in /CO₂ and flux data will be greater in the  
30–45 day spring and fall periods, when the mixed layer is in  
transition [see also Salisbury et al., 2009]. Overall, given the  
similarity between stations along the WB transect out to the  
deep Wilkinson Basin end point, we assume that time series  
results near the CO₂ buoy site (station WB2) in 60 m of water  
can be considered as reasonably representative of the sea-
sonally stratified Gulf of Maine, an area that encompasses  
most of the Gulf with the largest exceptions being the Bay of  
Fundy and Georges Bank. A fuller validation of this last  
assumption awaits data from ongoing and future observa-
tional efforts.  

The multiyear time series results of Figures 1, 4 and 5  
document fairly consistent annual patterns in flux, Δ/CO₂,  
wind speed (and gas transfer velocity), while Figures 5a and  
5b demonstrate a high temporal correlation between the flux  
and Δ/CO₂ data. This is not unexpected given equation (1)  
and the data in Figures 5b and 5c. The 5 year average flux  
in Figure 5a indicates a near sinusoid where the Gulf of Maine  
generally spends half the year (February to July) removing  
CO₂ from the atmosphere and the other half (August to  
February) releasing it. As seen in Figures 1 and 5, the  
strongest winds and gas transfer velocities coincide with  
the months of ocean-to-atmosphere CO₂ release, and at the  
5 year time scale, this factor helps tip the balance toward the  
overall +0.38 mol m⁻² yr⁻¹ flux value. As some confirmation,  
if one computes the fluxes using only the mean 2004–2008  
wind speed (U = 6.7 m s⁻¹), the 5 year flux values in Table 1  
shift downward by an average of 0.35 mol m⁻² yr⁻¹. This  
implies that with steady winds and all other factors and  
feedbacks unchanged, the air-sea exchange would have been in  
net balance.  

Across the region and in an annual net sense, the area  
acted as a net source of +0.38 ± 0.2 mol m⁻² yr⁻¹ over the  
period 2004–2008. Our long-term program provides data (see  
Figures 5 and 6) illustrating that while 3 of 5 years effectively  
might match this 5 year average (WB2 is +0.32 in Figure 5a),  
years 2005 and 2007 differed substantially, 2007 being a  
substantially larger source (WB2 is +1.34) and 2005 as a net  
CO₂ sink (WB2 is −0.75). Thus, collecting data in only 1 year  
may skew conclusions related to net annual source versus  
sink status. An estimate for the net carbon (C) import or  
export through the interface over the seasonally stratified  
Gulf of Maine is made using an area of roughly 10 × 10⁴ km²  
[Bisagni, 2003; Townsend, 1991]. In this case, the y axis of  
Figure 6 will span from −1.8 to +1.8 Mt C yr⁻¹, net annual  
fluxes across the stations, and time period range from  
−0.75 to +1.4 Mt C yr⁻¹. The multiyear average for the entire  
area is +0.45 ± 0.3 Mt C yr⁻¹.  

How do these results compare with neighboring  
coastal sites and other reported data? While there are no  
previous studies dedicated to CO₂ flux estimates in the Gulf  
of Maine, a recent and extensive compilation of coastal ocean  
data [Chavez and Takahashi, 2007] did provide an estimate of  
NW Atlantic flux of −1 ± 2 mol m⁻² yr⁻¹ for our approximate  
study latitude, 42°N (see their Figure 15.4). Their value is  
based on a limited number of cruises over the period of 1979–  
2004, with only one cruise within the Gulf of Maine and the  
rest along the shelf break or along Georges Bank. The present  
study’s multiyear and single-year estimates all lie within their  
±2 mol m⁻² yr⁻¹ range of uncertainty, but there is an obvious  
sink versus source discrepancy when compared with our  
+0.38 mol m⁻² yr⁻¹ multiyear estimate and an absolute differ-
ence near 1.4 mol m⁻² yr⁻¹. Comparing study observations  
(Table 1 and Figure 5) with shelf regions to the immediate  
south shows a similar contrast where the Gulf of Maine,  
despite its large known rate of gross biological productivity,  
most often acts as a net CO₂ source, whereas sink levels of  
−0.7 to −1.6 mol m⁻² yr⁻¹ (+0.5) [DeGrandpre et al., 2002;  
Boehme et al., 1998] and −0.48 (±0.21) mol m⁻² yr⁻¹ [Jiang  
et al., 2008] are reported for the Middle Atlantic (MAB) and  
South Atlantic Bight (SAB) regions, respectively. On the  
basis, in part, of the data from these cited studies, the  
Chavez and Takahashi [2007] compilation indicates that CO₂ flux  
values transition from C source to sink as one moves from  
south to north along the U.S. Atlantic coast. However, use of  
data exclusively from the studies focused on the SAB, MAB,  
and GoM would seem to indicate a more complex and per-
haps reversed picture along the U.S. NW Atlantic shelf. On a  
global synthesis level, the status of the GoM as a source is  
also somewhat in contrast with the Chen and Borges [2009]  
compilation of about 60 marginal sea/continental shelf mea-
surement sites where the global norm shows these areas to  
be a net sink. In yet another contrast, their sampling of mar-
ginal seas shows that these sites generally absorb CO₂ from  
the atmosphere in the autumn and winter, whereas this is a  
period of efflux in the Gulf of Maine. We next compare the  
observed GoM seasonal /CO₂ cycle with neighboring SAB  
and MAB results using an approach similar to recent studies  
in the North Sea [Thomas et al., 2005].
reflects not only biologically mediated \( \Delta CO_2 \) decline below the atmospheric \( CO_{2\text{Atm}} \) and \( MAB \) indicating close agreement to one another, [2006, 2007]. Here the assumption is that one can subtraction from the value on a fixed reference day where is given as control ratio than the \( SAB \) and \( MAB \) section, see also \( CO_2 \) to observed values, respectively. Typical station annual mean control is change due to its known isocline input of low DIC and TA waters. Simulated \( CO_2 \) (\( \Delta CO_2 \)) in seawater. The effect of all other processes is termed the biological (BIO) perturbation and can be estimated from the residual gained using the 752 observed and annual mean SST and \( fCO_2 \). This BIO term reflects not only biologically mediated \( CO_2 \) change, but other 753 perturbing factors including advection, air-sea loss, and riverine input of low DIC and TA waters. Simulated \( CO_2 \) time series reflecting temperature and BIO controls are given as

\[
fCO_2(T) = fCO_2_{\text{new}} e^{\left(0.0423(SST_{\text{new}} - SST_{\text{old}})\right)}
\]

757 and

\[
fCO_2_{\text{BIO}}(t) = fCO_2_{\text{obs}} e^{(0.0423(SST_{\text{obs}} - SST_{\text{new}}))},
\]

758 where subscripts \( m \) and \( obs \) refer to annual mean and 759 observed values, respectively. Typical station annual mean 760 values are 10°C and 383 \( \mu \text{Atm} \) for SST and \( fCO_2 \), respectively. To assess these controlling factors over a 1 year period 762 in regions of seasonal stratification, one can derive a set of 763 residual time series (\( \delta fCO_2_{\text{BIO}}, \delta fCO_2_{\text{T}}, \), and \( \delta fCO_{\text{2obs}} \)) by 764 subtraction from the value on a fixed reference day where 765 well-mixed surface layer conditions are observed [Schiettecatte 766 et al., 2006]. For the Gulf of Maine, this day is taken as 767 15 February, and \( \delta fCO_2_{\text{T}} \) is given as

\[
\delta fCO_2(T) = fCO_2(T) - fCO_{2\text{T}|_{\text{day 45}}}
\]

768 Results for all three variables and two example years (2005 769 and 2006) are shown in Figure 12. If the magnitude of \( \delta fCO_2_{\text{T}} \) exceeds \( \delta fCO_{\text{BIO}} \) (i.e., the ratio is greater than 1), then temperature is the greater control. This is not the case for the western GoM in late March and into summer, where the BIO term is seen to match or exceed \( T \) for both years presented (and for the other three not shown). In the latter half of the year, both terms are of similar magnitude. Thus, solubility is typically in competition with other controls throughout the year in the Gulf of Maine. By contrast, Jiang et al. [2008] reported a nearly 1:1 correlation between water temperature and \( fCO_2 \) dynamics in the SAB (their Figure 10) and conclude that the dominant \( fCO_2 \) control is \( T \). Similarly, a temperature-dominated result was seen in the MAB [DeGrandpre et al., 2002]. The competing BIO \( fCO_2 \) control within our region is not unexpected [cf. Salisbury et al., 2009] because photosynthetic production is known to greatly exceed that in the SAB and MAB in both magnitude and persistence [Townsend et al., 2006]. But the results do highlight the finding that even though this coastal site exhibits a much larger BIO: \( T \) control ratio than the SAB and MAB and one rightly expects a large annual phytoplankton drawdown (sink) of \( CO_2 \), the net annual air-sea flux still yields a \( CO_2 \) export to the atmosphere. Our working explanation for this finding is that, to first order, the annual surface ocean \( fCO_2 \) cycle in the GoM follows the observed variation of surface nitrate in the region for the seasonally stratified water column [cf. Bisagni, 2003; Townsend, 1991]. Put most simply, a strong surface water \( fCO_2 \) decline below the atmospheric level occurs each spring-to-summer due to phytoplankton production and riverine impacts, while a nearly corresponding increase above atmospheric levels occurs in middle-to-late autumn and into winter associated with destratification and upward mixing of carbon-replete deeper water. Perturbations attributed to temperature (solubility), air-sea flux, and net community production processes act throughout the year with the net result seen in Figures 5 and 10.
4.2. Findings Related to Sampling of Temporal CO₂ Variations

The daily variability of CO₂ in the atmosphere shown in Figure 3 reveals a complexity that is difficult to quantify using infrequent shipboard measurements; however, this complexity can have a potentially large impact upon the fluxes computed under equation (1). When examining flux modifications due to the recurring diel and seasonal variations in atmospheric CO₂ seen in Figure 3, however, we find limited net impacts (<2%), similar to the comprehensive study of Padin et al. [2007]. The variability is attributed to advected continental airflow and, similar to Padin et al. and Leinweber et al. [2009], we find the air mass often reflects regional signatures such as daily terrestrial photosynthesis in spring and summer and 2–3 day pollution events (also evident in coincident carbon monoxide data not shown) collected on Appledore Island throughout the year. These Gulf of Maine daily CO₂ perturbations generally average out over sufficient time scales, and thus, a least squares harmonic model fit to our data (equation (2)) is adequate for use in monthly and longer-term flux estimates. However, at shorter time scales of hours to weeks, one should avoid a sampling program that collects atmospheric data at a single fixed local time of day, especially in the summer. Such data, without adjustment for unobserved diel variations, will almost certainly bias flux study results conducted over nearly any time scale longer than 3–6 h in this region.

Regarding ocean surface layer fCO₂, the combination of hourly and long-term monthly time series data permit us to resolve several features: the fCO₂ decorrelation time scale is roughly 45 days, M2 tidal dynamics are of second order (see Figure 10), and that episodic variations inside of 30 days can impact monthly derived flux estimates at O(20–50%) in the spring and fall, with a lesser impact in other times of the year.

The effect of such unresolved variations on annual estimates (see Figure 10 and accompanying text) led to significant systematic error of O(4.0 mol m⁻² yr⁻¹) in our example case. As pointed out in at least three recent studies [cf. Jiang et al., 2008; Schiettecatte et al., 2006, 2007], deriving net annual flux estimates over a coastal region in 1 year and then later revisiting that site in another sampling campaign can lead to differences well beyond 0.4 mol m⁻² yr⁻¹. These studies attribute differences to a variety of sources, with one being unresolved short-scale temporal variation in ocean fCO₂ as we illustrate in data from April and May 2007 (Figure 10). But our multiyear results in Figure 6 also point to the likelihood that geophysical variability at interannual time scales is also substantial, at least in this region. Both factors corroborate the need to conservatively assign flux estimate uncertainties in coastal data synthesis efforts, particularly for studies having only one year of results (e.g., from four to six cruises), as well as the need to establish long-term monitoring in regions of particular interest. The relative dominance of temporal versus spatial factors observed with respect to air-sea exchange in the Gulf of Maine suggests that a limited network of moorings may serve to monitor this region’s air-sea gas flux with relatively high accuracy. This suggestion is tempered by the need to assess spatial and temporal dynamics nearer to the eastern Gulf that is strongly coupled to the Bay of Fundy and M2 tidal mixing and similarly for the large and shallow Georges Bank region to the south.

As a final point, we return to the topic of interannual variability. Figures 5 and 6 suggest substantial annual flux anomalies for years 2005 and 2007. By inspection of Figure 5 and use of equation (1), it is apparent that the deviations are largely due to perturbations in fCO₂ and not seasonal gas transfer (wind) changes in those years. Figure 13 shows the seasonal flux anomaly (units of mol m⁻² yr⁻¹) computed over the 2004–2008 period at WB2. While this paper has shown that greatest observed short-scale variation in ocean fCO₂ occurs here in the spring and fall, Figure 13 indicates that the largest observed seasonal flux anomalies, especially in 2005 and 2007, occurred in winter (January to March) and this is the season dominating the interannual differences in our data collection to date. Future work will thus include a focus on this winter period and its possible preconditioning by interannual variations in fall destratification, early winter storm mixing, heat flux events, and biochemistry below the mixed layer.

5. Summary

Multiyear shipboard fCO₂ data and air-sea flux estimates in the Gulf of Maine for the period 2004–2008 indicate that this marginal sea coastal region acted as a net source of CO₂ to the atmosphere of +0.38 ± 0.26 mol m⁻² yr⁻¹. A strong seasonal cycle in both ΔCO₂ and the air-sea flux is observed, with a large springtime sink offset by a large fall-to-winter efflux. A significant part of this regions’ net source status is explained by the coincidence of highest winds and above atmospheric fCO₂ in the winter months. Observed spatial variations were found to be of second order compared to temporal dynamics, and our observations are considered to scale to about 40% of the Gulf of Maine. On average and under this scaling assumption, this region delivered roughly 0.4 MTC (TgC) to the atmosphere per year. Interannual variability in the flux is observed at a level of 0.5 mol m⁻² yr⁻¹, with 2005 being the only year found to be a sink (−0.1 mol m⁻² yr⁻¹). Bihourly MAPCO2 time series measurements are used to show that multi-monthly cruise data can under sample fCO₂ dynamics in this system. The ship versus buoy data...
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Bisagni, J. J. (2003). Seasonal variability of nitrate supply and potential uptake in the Gulf of Maine and Georges Bank regions to the south. Combined ship and buoy measurements continue into 2010 and are being used in several process control studies aimed at empirical and numerical prediction to better understand inorganic carbon dynamics within this system at differing time scales. Moreover, the air-sea flux for adjoining Bay of Fundy and Georges Bank regions will likely act quite differently than for the seasonally stratified waters surrounding our site. Thus, an accounting for the full Gulf of Maine will require an expanded sampling and modeling effort. A final general conclusion is that the complexity gained with increased resolution and extended time series data suggests both caution in data interpretation with respect to statistical confidence in the observations under study and the potential for improved understanding and definition of cycling in this region.