Primary production and eddy correlation measurements of CO_2 exchange over an intertidal estuary

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[1] Field measurements by eddy correlation indicate an average CO_2 uptake of 1.9 g C m^{-2} d^{-1} by the intertidal Wadden Sea estuary in spring 2008. The flux did not show a dependency on the tide and fluxes during high and low tide were comparable. We hypothesize that biological production in the water column and in microbial mats that cover sediments lead to an undersaturation of CO_2 that is strong enough to support the observed fluxes. The total carbon uptake by this intertidal estuary from day of the year 101–168 is estimated to be −1.7 Tg C. Extrapolation of this flux over three months in spring suggests that the uptake of CO_2 by this estuary over this period is comparable to 24% of the yearly carbon flux over the North Sea and the European estuaries. **Citation:** Zemmelink, H. J., H. A. Slagter, C. van Slooten, J. Snoek, B. Heusinkveld, J. Elbers, N. J. Bink, W. Klaassen, C. J. M. Philippart, and H. J. W. de Baar (2009), Primary production and eddy correlation measurements of CO_2 exchange over an intertidal estuary, *Geophys. Res. Lett.*, *36*, L19606, doi:10.1029/2009GL039285.

[2] Coastal seas play a key role in the global carbon cycle by linking the terrestrial, oceanic and atmospheric carbon reservoirs. Recent studies highlighted the significance of continental shelves in the global carbon cycle and in particular for the budgets of CO_2 [*Tsunogai et al.*, 1999; *Frankignoulle and Borges*, 2001; *Cai et al.*, 2003; *Thomas et al.*, 2004, 2005]. The concentrations, temporal changes and spatial variations of total dissolved inorganic carbon (DIC), alkalinity (TA) and the partial pressure of CO_2 in surface water (pCO_{2w}) provide crucial data for how these systems function at the biogeochemical level. Current estimates suggest that within coastal systems the estuaries emit about 0.3–0.4 PgC yr^{-1}; largely balancing the estimated CO_2 sink associated with marginal seas of about 0.45 PgC yr^{-1} [*Borges*, 2005]. The annual emission of European estuaries is estimated to range from 10 to 20 Tg C yr^{-1} [*Ciais et al.*, 2008] close to the annual uptake by the North Sea of −10.3 Tg C yr^{-1} [*Thomas et al.*, 2004]. However, current European studies of marine carbon budgets largely neglect fluxes over the intertidal Wadden Sea estuary, one of the largest intertidal estuaries in the world, lying off the coast of North Western Europe. Here, we present data on EC-based CO_2 fluxes measured in spring 2008 over the Wadden Sea estuary.

[3] Exchange of CO_2 with the atmosphere is usually based on (i) floating flux chambers [*Frankignoulle et al.*, 1998] or on (ii) pCO_2 values in surface water versus air values that are estimated from equilibrators that measure pCO_2w or (iii) assessed indirectly from measurements of DIC and TA in subsurface water. Fluxes (F) are subsequently calculated from the product of the air-water concentration disequilibrium (ΔpCO_2) and a kinetic parameter, the transfer velocity (k), which quantifies the rate at which the gas crosses the air-water interface, $F = k\ \alpha \Delta pCO_2$, where α is the solubility coefficient of CO_2 [e.g., *Borges*, 2005]. Measuring ΔpCO_2 is comparatively straightforward. However, the current measurement techniques only supply discrete samples. Although these discrete measurements give good insight in processes that determine fluxes, they cannot detect temporal and spatial variability of gas concentrations that are required for accurate estimates of fluxes. This is especially relevant in highly dynamic systems such as estuaries.

[4] Even when CO_2 concentrations in the water column are fairly well known, it remains difficult to calculate fluxes because the transfer velocity across the water surface is highly uncertain [e.g., *Upstill-Goddard*, 2006]. Hence, the accuracy of calculated fluxes is generally limited by the ability to adequately resolve the transfer velocity. Typically k is constrained by turbulence and commonly parameterized as a function of wind speed and temperature alone; despite the acknowledged role of several other environmental parameters such as waves, biological productivity and surface films that are not related to wind speed [*Watson and Orr*, 2003; *Calleja et al.*, 2005].

[5] This is especially relevant to shallow coastal areas where gas exchange is also controlled by tides: tidal-driven rather than wind-driven turbulence could determine fluxes from the water [*Raymond and Cole*, 2001; *Zappa et al.*, 2007]. In addition, tidal pressure waves and surface heating during low tides potentially influence gas exchange from tidal flats. Moreover, tidal flats are often not taken into account in current flux estimates from estuaries with intertidal habitats. This in spite of the fact that they are thought to function as suboxic, fluidized bed reactors which promote efficient degradation and respiration of organic materials [*Aller*, 1998], resulting in substantial respiration rates [*Middelburg et al.*, 2005].

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[6] An alternative approach to quantifying gas exchange is to measure it directly, precluding the need for information on k and ΔC separately. Recent studies have demonstrated that direct measurements of CO_2 flux by the micrometeorological technique eddy correlation (EC) can be used to study processes that determine fluxes [*Zappa et al.*, 2007] and can constrain the magnitude of fluxes of CO_2 (and other trace gas) to the atmosphere in the marine environment [e.g., *Zemmelink et al.*, 2006, 2008]. EC (in combination with pCO_2w) is regarded to be capable of elucidating the relationship between gas exchange and underlying environmental and ecosystem parameters, on time scales short enough to resolve short term temporal (diurnal, seasonal) variability; relevant to highly dynamic intertidal systems such as the Wadden Sea.

[7] The surface area of the Wadden Sea extends to 13,500 km^2, of which 2/3 emerges during low tide. This study is conducted at the island of Griend (53°15′05″N, 5°15′15″E), a small (0.2 Km^2) island centrally located in the western part of the Wadden Sea. The island is surrounded by tidal flats and tidal channels that are in the fetch of the ten meter high EC tower from which fluxes are measured in this study. Sediments near the island mainly consist of sand (grain size > 62 μm) with an increasing silt fraction (grain size < 62 μm) with distance from the island. Dry falling finer sediments near the island are covered with well developed microbial mats that support dense communities of bacteria and photosynthetically active algae.

[8] The flux of CO_2 was measured by EC which is considered to be the most direct technique for measuring gas fluxes [*Fairaill et al.*, 2000], since it utilizes the covariance of scalar concentrations (or mixing ratios) and vertical wind velocity. EC requires measurements at a sufficient rate (10–20 Hz) to adequately capture all turbulence frequencies contributing to the flux. The EC system (Wittich and Visser, Inc.) was powered through solar panels and included an R350 three-axis sonic anemometer (Gill instruments, UK) and an open-path infrared CO_2/H_2O analyzer (Li-7500, Li-COR, USA). Data acquisition and postprocessing were based on EC measurement protocols set by the integrated project CarboEurope: an assessment of the European terrestrial carbon balance [*Aubinet et al.*, 2000]. We used the Alteddy software that was developed at Alterra institute (Wageningen University, the Netherlands). Postprocessing of the data included coordinate rotation followed by the application of the *Webb et al.* [1980] corrections to determine the latent (LE) and sensible (H) heat fluxes from the measured mean covariances of vertical wind speed with sonic temperature and with water vapor density. For CO_2 the flux (F_{CO2}) is subsequently calculated by:

$$F_{CO2} = \overline{w'\rho'_{co2}} + \overline{\mu}_{co2}\left(w'\rho'_{H2O} + \frac{\overline{\rho}}{\overline{T}}\overline{w'T'}\right) \approx \overline{w'\rho'_{co2}} + \overline{\mu}_{co2}(LE + H),$$

where, w is the vertical wind, ρ_{CO2} is the CO_2 density, μ_{CO2} is the mixing ratio relative to dry air, ρ_{H2O} is the H_2O density, ρ is the air density, T is the temperature. Overbars denote averaged values; primes denote deviations from the average. The relative importance of the density correction depends strongly on the average ambient mixing ratio μ_{CO2}. Since the ambient CO_2 concentration is generally large compared to the eddy flux, the relative correction can have the same order of magnitude as the eddy flux. Next density-corrected CO_2 fluxes were computed with an averaging period of 30 min. Fluxes are indicated according to the micrometeorological convention, i.e., negative when directed downward.

[9] Fluxes from dry-falling sediments and surface waters were also measured by discrete sampling methods: flux chambers and ΔpCO_2 measurements. Flux chambers with a volume of 0.25 m^3 were made of UV-transparent Polymethylmethacrylate and in a closed circuit connected to a Licor 7000. Head space air in the flux chamber was pumped through the system at a rate of 2.5 liter per minute providing fluxes over short (ten minutes) time scales. The partial pressure of CO_2 in the water (pCO_{2w}) was derived from DIC and TA measurements. Analysis of DIC was performed by means of the coulometric method, TA was determined with an automated potentiometric titration using a combined DIC/Alkalinity analyzer system (Vindta 3C, Marianda, Germany). Accuracy of DIC and TA measurements was set by using certified reference material obtained from Prof. A. Dickson (Scripps Institution of Oceanography). Three replicates were determined for each sample and CRM with a precision better than 2 μmol kg^{-1}. Fluxes were calculated following $F = k\ \alpha\ \Delta pCO_2$. The transfer velocity k was determined by using the wind dependency parameterization for spot measurements as proposed by *Wanninkhof* [1992].

[10] The seasonal cycle of Chlorophyll-a in the Wadden Sea always shows the highest values in April to June, in association with a spring peak in diatoms followed by a *Phaeocystis* bloom [*Cadée and Hegeman*, 2002]. During this season a net fixation of carbon through photosynthesis can be expected. Indeed, a relative uptake of carbon was measured during our study. The daily flux as measured by EC showed a pronounced diurnal signal with mid day fluxes around -2.7 g C m^{-2} d^{-1} sometimes exceeding -5 g C m^{-2} d^{-1} just after mid day. In the night, when CO_2 is produced through respiration, the flux decreased to an average of -0.57 g C m^{-2} d^{-1} (Figure 1a; in order to present more detail only the fluxes are shown for day of the year 114–121 and 162–168. Overall fluxes from day of the year 101 till 168 show a similar diurnal variation and amplitude). The EC-fluxes are in close agreement with primary production rates of 1.6 g C m^{-2} d^{-1} (Table 1) that are obtained from laboratory incubations as part of an ongoing time series study of phytoplankton dynamics in the Marsdiep tidal inlet (53°00′11″N; 4°47′40″E) of the Wadden Sea [*Cadée and Hegeman*, 1974, 2002; *Philippart et al.*, 2007].

[11] We estimate the uncertainty of covariance measurements in this study in the order of 10%. However, it is difficult to give an estimate of the uncertainty of the flux without independent measurements in the field. The total of random errors, however, is less than 50%. This can be seen from consecutive measurements that should cluster together since they are conducted during similar meteorological conditions. There are, however, some outliers that can not be readily accounted for and that might be caused by measurements in the exhaust of ships that pass the island. The contribution of these outliers to the averaged flux is small by averaging over many individual values of F_{CO2} together.

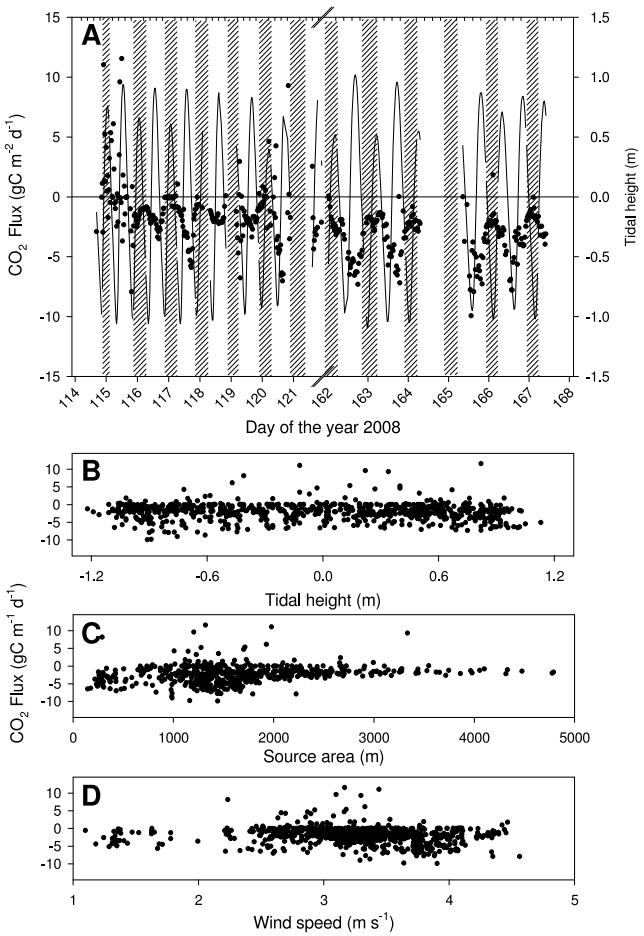

Figure 1. (a) Turbulent CO_2 flux (g C m^{-2} d^{-1}) over the Intertidal Wadden Sea estuary as measured by eddy correlation from day of the year (2008) 114–122 and from 162–168 (here, only a selection of the data is presented so that more details can be seen in the plots. Fluxes and their diurnal variation are similar during the whole study period). Shaded areas represent night time. The solid black line is the tidal height (m). (b) CO_2 flux (g C m^{-2} d^{-1}) as a function of tidal height (m). (c) CO_2 flux (g C m^{-2} d^{-1}) as function of the extend of the area around the meteorological tower that supports 80% of the flux (source area, m during low tides the sediments emerge from the water till a distance of at least 3000 m). (d) CO_2 flux (g C m^{-2} d^{-1}) as function of wind speed (m s^{-1}).

[12] During low tide the emerging sediments around the meteorological tower are within the source area of the measured flux. Surprisingly, CO_2 fluxes did not show a dependence on the tidal height or on scale of the source area within the uncertainty of the measurements (Figures 1b and 1c and Table 2). A linear regression analysis of the absolute CO_2 flux versus tidal height T (m) and source area S (m) resulted in: $F_{CO2} = -0.9T - 2.0$ ($R^2 = 0.02$) and $F_{CO2} = -6$ 10-4S $- 2.5$ ($R^2 = 0.06$), respectively. The uptake of carbon during incoming tide at day time was on average -2.7 (± 2.0) g C m^{-2} d^{-1}, not different from fluxes of -2.3 (± 1.9) g C m^{-2} d^{-1} that were measured during outgoing tide. Also fluxes measured at high tide and low tide during the day did not differ (-2.9 (± 2.3) and -3.2 (± 1.9) g C m^{-2} d^{-1}, respectively). Fluxes measured during the night were smaller and in some cases positive: averages ranged from -0.1 (± 2) to -1.0 (± 0.7) g C m^{-2} d^{-1} during the tidal cycle (Table 2).

[13] Measurements with flux chambers over tidal flats in the source area of the EC system are in agreement with EC measurements showing a day time carbon uptake of -8.1 (± 5.1) g C m^{-2} d^{-1}, decreasing to 0.5 (± 1.2) g C m^{-2} d^{-1} during the night. Flux chamber studies show that fluxes can be highly variable and dependent on sediment type and cover; with day time fluxes over fine sediments higher than over coarse sediments (-12.6 g C m^{-2} d^{-1} and -3.6 g C m^{-2} d^{-1}, respectively). In addition, *Spilmont et al.* [2007] show in a recent publication that the variability of intertidal benthic community production is correlated to light and the tidal cycle; where maximum production (up to 8 g C m^{-2} d^{-1}, in August) occurred just before and after immersion with water. Unfortunately, our limited number of flux chamber measurements does not allow such a detailed study, but this will be conducted in the near future.

[14] In the water pCO_2 tended to decrease in the course of spring with average pCO_{2w} values of 244 ± 67 μatm (n = 8, T_w = 11°C; late April), 202 ± 84 μatm (n = 12, T_w = 13°C; mid May) and 193 ± 95 μatm (n = 7, T_w = 15°C) in early June. pCO_{2w} showed a clear diurnal cycle, with values near 140 μatm during the day and near 280 μatm during the night (averaged over the three months, Table 1). The flux computed from pCO_2 measurements and the wind speed parameterization of gas transfer was at least an order of magnitude lower than the flux measured by EC (Table 2). While the above mentioned parameterization of *Wanninkhof* [1992] is most commonly used for the open ocean, where wind stress is the dominant factor affecting turbulence at the water surface, the EC measurements over the Wadden Sea estuary did not reveal a correlation between gas flux and wind speed U (m s^{-1}) within the uncertainty of the measurements: $F_{CO2} = 0.29U + 1.5$ ($R^2 = 0.008$, Figure 1d). Other parameterizations exist for estuaries that might better represent cases where wind forcing and tidal current together generate transfer velocities [*Raymond and Cole*, 2001; *Borges et al.*, 2004]. It is, however, difficult to find a common parameterization that fits all estuaries. Individual systems will have unique (tidal) currents that affect turbulence in the water column. In an intertidal system such as the Wadden Sea macro-scale bottom roughness will even further enhance turbulence and transfer velocities [*Moog and Jirka*, 1999a, 1999b; *Tokoro et al.*, 2008]. It is theoretically possible to derive transfer velocities from $k = F/(\alpha\ \Delta pCO_2)$, where

Table 1. Primary Production Rates Derived From Laboratory Incubations[a]

	2002	2003	2004	2005	2006	2007	2008	Avg	Std
April	0.29	1.60		2.22	0.47	1.53	0.85	1.16	0.75
May	0.35	1.11	1.00	2.59	1.86	1.19	2.85	1.56	0.91
June	3.88	0.61	2.54	2.72	1.23	1.47	3.01	2.21	1.15

[a]Primary production rates, g C m^{-2} d^{-1}. Samples were obtained from the Marsdiep tidal inlet of the Wadden Sea.

Table 2. Average and Standard Deviations of Partial Pressure CO_2 in the Water and of CO_2 Flux Derived from Eddy Correlation, Flux Chambers and the Partial Pressure Difference of CO_2 Between the Water and Atmosphere at Different Phases During the Tidal Cycle[a]

	Average pCO_2 (μatm)		CO_2 Flux (g C m^{-2} d^{-1})	
	Day	Night	Day	Night
EC- Incoming tide			−2.7 (±2.0)	−0.9 (±1.2)
EC- Outgoing tide			−2.3 (±1.9)	−1.0 (±0.7)
EC- High tide			−2.9 (±2.3)	−0.1 (±2.0)
EC- Low tide			−3.2 (±1.9)	−0.3 (±1.4)
Flux chamber Coarse sediment			−3.6 (±2.3) n = 12	−0.0 (±1.0), n = 12
Flux chamber Fine sediment			−12.6 (±1.9) n = 11	−1.0 (±1.1), n = 12
pCO_{2w} high tide	145 (±34) n = 7	275 (±12) n = 7	0.1 (±0.02) n = 7	0.06 (±0.02) n = 7
pCO_{2w} low tide	137 (±32) n = 7	286 (±17) n = 6	0.2 (±0.05) n = 7	0.08 (±0.04) n = 6

[a]Partial pressure CO_2, μatm; CO_2 flux, g C m^{-2} d^{-1}. Fluxes derived from pCO_{2w} are based on the wind speed parameterization as proposed by *Wanninkhof* [1992] using wind speeds between 3 and 6 m s^{-1}.

the flux is measured by EC. These transfer velocities would include all factors that control gas exchange in the source area of the EC system. Following this approach an average ΔpCO2 of 208 μatm (n = 27, April through June) and the EC reported flux measurements suggest a gas transfer velocity of ≈100 cm/hr which is two to 5 times higher then observed for the Scheldt, Thames, or Rhine [*Abril and Borges*, 2004] and more than ten times greater then expected from common wind speed parameterizations [e.g., *Wanninkhof*, 1992].

[15] However, the limited number of samples for pCO_{2w} measurements that were taken during this study can not reflect the heterogeneity of surface water pCO_2. Consequently pCO_{2w} values obtained through this study can not be used to derive a reliable "Wadden Sea transfer velocity". Such a parameterization would require high resolution measurements of pCO_{2w} in the source area of the EC tower. Where pCO_{2w} is ideally measured near the water surface where gas exchange and planktonic metabolism control air sea CO_2 disequilibria.

[16] Fluxes over the Wadden Sea are in the same order of magnitude as EC-derived fluxes over forests and grasslands [e.g., *Mauder et al.*, 2008]. In contrast, the average flux measured from April through June (day of the year 101 untill 168) of −1.93 g C m^{-2} d^{-1} is an order of magnitude larger than fluxes that have been calculated from continuous underway pCO_2 measurements in nearby European coastal zones. Estimated uptakes of carbon by the Scheldt estuary in May 2001–2004 do not exceed −0.4 g C m^{-2} d^{-1} [*Borges et al.*, 2008]. In addition, continuous underway measurements of pCO_{2w} in the North Sea showed that this basin formed a sink for CO_2 in May 2002 with fluxes that ranged from near 0 to −0.12 g C m^{-2} d^{-1} in the southern North Sea up to a flux of −0.50 g C m^{-2} d^{-1} in the northern North Sea. Part of this discrepancy might be due to the fact that these flux estimates are based on wind speed parameterizations.

[17] In the source area of the meteorological tower at Griend the total carbon uptake from day of the year 101 untill 168 was 129 g C m^{-2}. Assuming that the surface area around Griend is representative for the heterogeneity found in the whole Wadden Sea and that EC integrates fluxes over heterogenic surfaces and over relevant meteorological conditions; the total carbon uptake by the Wadden Sea from day of the year 101 untill 168 would be −1.7 Tg C. If this flux is carried by primary production and if primary production remains relatively constant from April through June (as can be hypothesized from our measurements and the time series study presented in Table 2) the total uptake in spring amounts to −2.4 Tg C. However, one can not assume that this carbon is going to remain in the Wadden Sea: part of this carbon will be transported to the North Sea and/or might return to the inorganic carbon pool and atmosphere later in the year.

[18] From a study conducted in 2001/2002 the CO_2 uptake by the North Sea is estimated at −10.3 Tg C yr^{-1} [*Thomas et al.*, 2004], in addition recent studies indicate that European Estuaries emit 10 to 20 Tg C yr^{-1} to the atmosphere [*Ciais et al.*, 2008]. This indicates that the estimated spring flux over and into the Wadden Sea is significant beyond the local scale as it compares to 24% of the annual flux over various marine systems of Europe. However, all of these estimates are crude since they are based on local, non-continuous measurements of carbon budgets that are upscaled to larger regions and even to different ecosystems. Such estimates inevitably neglect *in situ* variability and complexity of processes underlying CO_2 production and consumption. The accuracy of current carbon budgets is limited by the ability to resolve the temporal and spatial heterogeneity of surface conditions and concentrations of CO_2. Field-based continuous long term *in situ* measurements of exchange of CO_2 with the atmosphere is possible with EC. When supplemented with measurements of dissolved inorganic carbon and alkalinity one is able to quantify sinks and sources of CO_2 in estuaries as needed to truly understand the role of these systems in the global carbon cycle.

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