# Distribution of surface carbon dioxide and air-sea exchange in the English Channel and adjacent areas

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[1] In the present paper we report the distribution of the partial pressure of  $CO_2$  ( $pCO_2$ ) in surface waters along 13 transects in the English Channel, covering the four seasons. The spatial and temporal variability of  $pCO_2$  is controlled by a complex combination of primary production (from May to June), degradation of organic matter, temperature change, and freshwater inputs. Preliminary air-sea  $CO_2$  exchange computations suggest that the Channel is not a major sink of atmospheric  $CO_2$  and is probably neutral from the point of view of atmospheric coupling. This is mainly related to a relatively low export and/or burial of organic carbon and intense benthic calcification. *INDEX TERMS:* 4219 Oceanography: General: Continental shelf processes; 4243 Oceanography: General: Marginal and semienclosed seas; 4805 Oceanography: Biological and Chemical: Biogeochemical cycles (1615); 4806 Oceanography: Biological and Chemical: Carbon cycling; 4820 Oceanography: Biological and Chemical: Gases; *KEYWORDS:* English Channel, coastal,  $CO_2$ , air-sea exchange, benthic calcification

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#### 1. Introduction

[2] The role of the coastal sea in the global carbon cycle is the subject of a long-lived controversy [Walsh et al., 1981; Smith and Hollibaugh, 1993; Alongi, 1998; Wollast, 1998]. The prevailing question is whether the coastal sea is net heterotrophic or net autotrophic. The corollary to this question is whether the coastal sea is a net source or sink of atmospheric CO<sub>2</sub>. These questions have been approached with various methods, for instance, the budget of the carbon fluxes across the continental shelf margin [e.g., Wollast, 1998] and the compilation of available data of gross primary production and total respiration in various ecosystems [Smith and Hollibaugh, 1993; Gattuso et al., 1998]. However, these studies yield different and sometimes contradictory conclusions due to the complexity and heterogeneity of the carbon fluxes in the numerous contrasted ecosystems of the coastal sea, that are not fully described by the relatively sparse available data sets.

[3] The most direct approach to determine if a given ecosystem is a net source or sink of atmospheric CO<sub>2</sub> is to measure the air-sea gradient of CO<sub>2</sub> with an adequate temporal and spatial resolution to allow the integration of the computed fluxes on an annual basis. This approach has been successfully applied in open ocean studies [e.g., *Takahashi et al.*, 1995] but it has seldom been applied in coastal ecosystems. *Tsunogai et al.* [1999] showed that the East China Sea is a net sink of atmospheric CO<sub>2</sub>, characterized by strong net annual air-sea fluxes of CO<sub>2</sub> ranging between -3.3 and -7.7 mmol C m<sup>-2</sup> d<sup>-1</sup>. These results led *Tsunogai et al.* [1999] to formulate the concept of the

"continental shelf pump," i.e., a net influx between 0.5 and 1.0 Gt C  $yr^{-1}$  if these air-sea fluxes are extrapolated to the worldwide continental shelf surface area. Frankignoulle and Borges [2001] found similar values of net annual airsea CO<sub>2</sub> fluxes in the Gulf of Biscay, that extrapolated to the surface area of the Northern European continental shelf give an additional net influx of atmospheric CO<sub>2</sub> of about 45% compared to the one proposed by Takahashi et al. [1995] for the open North Atlantic Ocean. On the other hand, Borges and Frankignoulle [2002a] showed that the plume of the river Scheldt in the Southern Bight of the North Sea is a net source of atmospheric  $CO_2$  ranging between +3.0 and +5.2 mmol C m<sup>-2</sup> d<sup>-1</sup>. Frankignoulle et al. [1998] showed that European inner estuaries are characterized by high positive air-sea CO<sub>2</sub> fluxes converging to a value of +170 mmol C  $m^{-2} d^{-1}$ . Last, in upwelling systems, *Goyet et al.* [1998] reported a CO<sub>2</sub> evasion of +2.5 mmol C  $m^{-2} d^{-1}$  off the Omani coast, while Borges and Frankignoulle [2002b] found off the Galician coast a net annual atmospheric  $CO_2$  uptake ranging between -3.5 and -7.0 mmol C  $m^{-2}$  d<sup>-1</sup>. This wide range of flux values illustrates the complexity of coastal ecosystems and emphasizes the need of high spatiotemporal resolution data sets of dissolved inorganic carbon (DIC) and  $pCO_2$  to allow a better estimation of the air-sea fluxes of  $CO_2$  in the coastal sea on a global basis.

[4] The English Channel is relatively shallow (<100 m, cf. Figure 1), characterized by a strong tidal range (3-9 m) and intense tidal currents [maximum speeds between 0.5 and 2.0 m s<sup>-1</sup>, *Reid et al.*, 1993]. Under average wind and tidal conditions, the flow of water is eastward [*Salomon and Breton*, 1993] (cf. Figure 1) so that the channel can be considered as a pathway between the North Atlantic and the North Sea, receiving lateral inputs from 76 estuaries and

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**Figure 1.** Map of the study site showing the bathymetry [adapted from *Reid et al.*, 1993] and the residual flow under average meteorological and tide conditions [adapted from *Salomon and Breton*, 1993].

rivers along the French and English coastlines. The freshwater inputs along the French coast create a thermohaline front located less than 20 km away from the coast and extending from the Bay of Seine up to the Dover Strait [e.g., Brylinski et al., 1996]. The less-saline water trapped between the coast and the thermohaline front corresponds to the plume of the rivers Seine and Somme and is called the "coastal flow." The energy dissipation from the tidal currents maintains, all year round, the water column vertically mixed in the shallower Eastern Channel and in the Western Channel along French coast. During summer, the water column is thermally stratified in the Western Channel along the English coast. Within the frontal structure (Ushant front) separating the well-mixed and the stratified waters, high phytoplanktonic biomass has been frequently observed [e.g., Pingree et al., 1979; Jordan and Joint, 1984].

[5] From processes such as river inputs, high primary production, and frontal structures, intense spatial and temporal variability of DIC can be expected [*Mackenzie*, 1991]. While there is a fairly large amount of information on physical, biological, and chemical processes in the English Channel, little data on DIC have been reported in the channel and to our knowledge only those of *Frankignoulle et al.* [1996a, 1996b] that show a seasonal  $pCO_2$  variability in the range of 225–460 µatm (May 1994 and September 1993, respectively) related to both primary production and river inputs. The aim of the present work is to further investigate  $pCO_2$  dynamics and variability, and attempt to establish a budget of air-sea exchange of  $CO_2$  in order to characterize the English Channel in the atmospheric  $CO_2$  source and sink context.

## 2. Material and Methods

[6] Data presented in this paper were obtained on board the R/V *Belgica* and the RRS *Charles Darwin* during nine cruises (Figure 2). Underway parameters (seawater  $pCO_2$ , dissolved oxygen, salinity, and in situ temperature) were sampled with a frequency of 1 min from the seawater supply of the ship (pump inlet at a depth of 2.5 m). A nondispersive infrared gas analyzer (Li-cor<sup>®</sup>, LI-6262) was used to meas-

ure  $pCO_2$  in wet air equilibrated with seawater. Before 1998,  $pCO_2$  was measured in equilibrated air dried with Drierite<sup>®</sup> and the data were converted into wet air using the algorithms proposed by *Department of Energy* [1994]. The Li-cor<sup>®</sup> was calibrated daily using three dry gas standards: pure nitrogen (0.0 ppm; Air Liquide Belgium) and two gas mixtures with a CO<sub>2</sub> mole fraction of 351.0 ppm (Air Liquide Belgium), and 360.5 ppm (National Oceanic and Atmospheric Administration). The temperature at the outlet of the equilibrator was monitored with a platinum resistance thermometer (PT100, METROHM<sup>®</sup>) with an accuracy of  $\pm 0.05^{\circ}$ C and the pCO<sub>2</sub> values are corrected for the temperature difference between in situ seawater and water in the equilibrator, using the algorithm proposed by Copin-Mon*tégut* [1988]. The accuracy of the  $pCO_2$  measurement by equilibration is estimated to be  $\pm 3 \mu atm$  (cumulative errors of temperature correction and instrument calibration). For the detailed description and quality control of the equilibrator system, refer to the work of Frankignoulle et al. [2001]. In 1999, a second Li-cor was used to measure atmospheric  $pCO_2$  sampled at the bow of the ship at approximately 10 m height. The accuracy of the atmospheric  $pCO_2$  measurements is estimated to be  $\pm 0.5$  µatm. During the March 1995 cruise, the  $pCO_2$  data were computed from underway measurements of pH (sampling frequency of 1 min, data not shown) and total alkalinity (TAlk) discrete samples (data not shown). The measurement of pH was carried out using a Ross type combination electrode  $(ORION^{\text{(B)}})$ , calibrated on the Total Hydrogen Ion Concentration Scale (mol kg SW<sup>-1</sup>), using the Tris and AMP buffers proposed by Dickson [1993]. The reproducibility of the pH measurements is estimated to be  $\pm 0.004$ . TAlk was determined using the classical Gran electrotitration method, on 100 ml GF/F filtered samples. The precision of TAlk measurements performed on board is  $\pm 4 \mu mol kg^{-1}$ . The computation of pCO2 was performed using the dissociation constants of carbonic acid of Roy et al. [1993], the borate molality obtained from the Culkin [1965] ratio to salinity, the dissociation constant of boric acid by Dickson [1990], and the carbon dioxide solubility coefficient of Weiss [1974]. The accuracy of the  $pCO_2$  values computed from the pH-TAlk couple is estimated to be  $\pm 10 \mu$ atm. Due to the small range of variation of salinity and TAlk values during the March 1995 cruise, no significant relationship was found between these parameters, so that the TAlk values (about one sample per degree of longitude) were interpolated linearly to obtain values every minute and compute  $pCO_2$  values. The uncertainty on TAlk introduced by the linear interpolation is estimated to be  $\pm 5~\mu mol~kg^{-1}$  that adds an error of  $\pm 1 \mu$ atm to the pCO<sub>2</sub> computation. Underway dissolved oxygen was measured using a galvanic electrode (Kent<sup>w</sup>) calibrated, every 3 hours, from discrete samples. Discrete samples of dissolved oxygen were measured by the Winkler method using a potentiometric endpoint determination, with an estimated accuracy of  $\pm 2 \mu mol kg^{-1}$  $(\pm 0.8\%$  of saturation level). The calibration of the galvanic electrode adds an uncertainty of  $\pm 1.5~\mu mol~kg^{-1}~(\dot{\pm 0.6}\%$  of saturation level) on the underway  $O_2$  data. The oxygen saturation level (%O<sub>2</sub>) is computed from the observed concentration of dissolved  $O_2$  and the concentration of  $O_2$ at saturation calculated according to Benson and Krause [1984]. The concentration of chlorophyll a (Chl a) and



**Figure 2.** Ship track of cruises. Symbols correspond to the position of discrete samples of chlorophyll *a*. Dates correspond to the full duration of the cruises. The specific dates of transects are shown in Figures 3-5.

pheopigments were determined from GF/F filtered samples by the fluorimetric method [*Arar and Collins*, 1997] and before 1997 by the spectrophotometric method [*Lorenzen and Jeffrey*, 1978], with a precision of  $\pm 4\%$ . Active chlorophyll is calculated from the concentration of Chl *a* and pheopigments (pheo) according to the formula: Chl *a*/(Chl *a* + pheo). This ratio gives an indication of the state of phytoplanktonic development: one for pristine phytoplanktonic cells and zero for detritus. Salinity and in situ temperature were measured using a SeaBird<sup>®</sup>21 thermosalinograph (Belgica) and a Falmouth Scientific Instruments<sup>®</sup> thermosalinograph (Charles Darwin), with an estimated accuracy of  $\pm 0.05$  and  $\pm 0.01^{\circ}$ C, respectively.

[7] The flux of CO<sub>2</sub> across the air-sea interface (*F* in mmol C m<sup>-2</sup> d<sup>-1</sup>) is commonly expressed as  $F = \alpha K \Delta p \text{CO}_2$ , where  $\alpha$  is the solubility coefficient of CO<sub>2</sub> (mmol C m<sup>-3</sup>  $\mu$ atm<sup>-1</sup>), *K* is exchange coefficient (m d<sup>-1</sup>), and  $\Delta p \text{CO}_2$  is the air-sea gradient ( $\mu$ atm). We used the values of atmospheric  $p \text{CO}_2$  from the Mace Head site (53°33'N 9°00'W, southern Ireland) from the National Oceanic and Atmospheric Administration/Climate Monitor-ing and Diagnostics Laboratory/Carbon Cycle Greenhouse

Gases Group (NOAA/CMDL/CCGG) air sampling network (available at http://www.cmdl.noaa.gov/) and the K-wind relationship recently proposed by Nightingale et al. [2000]. This algorithm is based on a dual tracer experiment in the Southern Bight of the North Sea that is similar to the English Channel from the point of view of physical characteristics (shallow, well-mixed water column and high tidal currents). We computed K from daily values of geostrophic wind speed to cover the full annual cycle. Also, wind speed is highly variable at the timescale of a week, thus the use of ship-borne data introduces a bias in the flux computation. The data were computed at 50.0°N 6.0°W by the Pacific Fisheries Environmental Laboratory (PFEL) from synoptic pressure fields produced by the Fleet Numerical Meteorology and Oceanography Centre (FNMOC). The seawater  $pCO_2$  data set includes the data of *Frankignoulle et al.* [1996a, 1996b] and comprises data from 1992 to 1999. The atmospheric  $CO_2$  mole fraction ( $xCO_2$ ) at the Mace Head site has increased by 12.4 ppm between 1992 and 1999, at an average growth rate of  $1.8 \pm 0.1$  ppm yr<sup>-1</sup>. Hence to compute the air-sea gradient of pCO2 from a consistent single-year (1997) atmospheric  $pCO_2$  signal, the seawater

**9** - 4

CO<sub>2</sub> mole fraction data were corrected according to the following equation:

$$xCO_{2 \text{ sea } 1997} = xCO_{2 \text{ sea } 199i} + (xCO_{2 \text{ air } 1997} - xCO_{2 \text{ air } 199i}),$$

where  $xCO_{2sea 1997}$  is the CO<sub>2</sub> mole fraction in seawater fitted to 1997,  $xCO_{2sea 199i}$  is the CO<sub>2</sub> mole fraction in seawater from a given year,  $xCO_{2air 1997}$  is the atmospheric CO<sub>2</sub> mole fraction in 1997, and  $xCO_{2air 199i}$  is the atmospheric CO<sub>2</sub> mole fraction for a given year.

#### 3. Results and Discussion

#### 3.1. Spatial and Temporal Variability of pCO<sub>2</sub>

# 3.1.1. Longitudinal Variability

[8] Figures 3–5 show underway data obtained along 13 transects, covering the Southern Bight of the North Sea, the English Channel, and the Armorican Shelf. At 3.5°W, the English Channel is separated into eastern and western parts, based on the average extension during summer of the stratified waters according to *Reid et al.* [1993].

# 3.1.1.1. Southern Bight of the North Sea

[9] In the Southern Bight of the North Sea, two distinct systems were sampled. The segment of the transects where a sharp salinity variation is systematically observed corresponds to the plume of the river Scheldt that extends from 3.2 to on average  $2.7^{\circ}E$  (±0.3, standard deviation: std). Within the Scheldt plume, the maximal observed  $pCO_2$ value is 740 µatm (late September 1995, Figure 5c) and the minimal value is 300 µatm (June 1997, Figure 3e). The amplitude of the spatial  $pCO_2$  variation is  $\sim 230 \mu atm$  for all cruises, however, CO<sub>2</sub> undersaturation is seldom observed. For all cruises, O<sub>2</sub> undersaturation is observed and the distribution of %O<sub>2</sub> generally mirrors the one of pCO<sub>2</sub> (e.g., Figures 3h and 4f) showing that biological activity is largely responsible for the  $pCO_2$  dynamics in the Scheldt plume. A more detailed analysis of DIC dynamics was given by Borges and Frankignoulle [1999, 2002a] who show that the  $pCO_2$  spatial and seasonal variability is controlled by: (1) the input of DIC from the Scheldt inner estuary; (2) mixing with offshore saline water; (3) the seasonal cycle of primary production; (4) the net heterotrophic status of the Scheldt plume fueled by organic carbon inputs from the inner estuary and the Belgian coast.

[10] In the region of the Southern Bight of the North Sea extending from 2.7°E to the Dover Strait (1.58°E), the average salinity for all transects is 34.7 (±0.2 std) with a maximum value of 35.25. This shows that this region is, to some extent, influenced by river inputs. The amplitude of the spatial variations of  $pCO_2$  is smaller than in the Scheldt plume ( $\sim$ 80 µatm), and the maximal and minimal values are 480 µatm (late September 1995, Figure 5c) and 240 µatm (May 1997, Figure 3c), respectively. In this region, CO<sub>2</sub> undersaturation is observed in May and June (Figures 3c, 3e, and 4a), near CO<sub>2</sub> equilibrium in July 1997 (Figures 3g and 4c) and distinct CO<sub>2</sub> oversaturation in July 1998, September, and November (Figures 4c, 4e, 4g, 5a, 5c, 5e, and 5g). Along some transects, the %O<sub>2</sub> distribution roughly mirrors the pCO<sub>2</sub> one, as in June 1997, July 1998, and early September 1999 (Figures 3f, 4d, and 4f), but this is not the case for all transects. Thus biological activity is not always the dominant process of the  $pCO_2/O_2$  dynamics. The time

required for the equilibration of  $O_2$  is much shorter than  $CO_2$ and this can explain, for instance, the strong  $CO_2$  undersaturation observed in May 1997 associated with near- $O_2$ equilibrium conditions (Figures 3c and 3d). Indeed, in the Southern Bight of the North Sea, by late May, the spring phytoplankton bloom is declining quickly [e.g., *Lancelot et al.*, 1998], so that  $O_2$  rapidly comes to equilibrium while the  $CO_2$  undersaturation remains.

# 3.1.1.2. Eastern English Channel

[11] In the eastern English Channel, salinity increases regularly westward in July 1997, July 1998, and early and late September 1999 (Figures 3g, 4c, 4e, and 4g, respectively). Along other transects, in the region extending from 1.5°E to 1.5°W, salinity is distinctly lower than in the rest of the Eastern Channel, as in May 1997, June 1997, and June 1998 (Figures 3c, 3e, and 4a, respectively). This is due to the fact that, in the English Channel, about 73% of the freshwater is discharged between 1.5°E and 1.5°W and mainly by the river Seine [based on the work of Reid et al., 1993]. Along some transects, a marked salinity decrease (on average of  $\sim$ 1) can be observed as in March 1995, early and late September 1995, early and late November 1998, and January 1998 (Figures 3a, 5a, 5c, 5e, and 5g, respectively). For the March 1995 transect (Figure 3a), the salinity signal is related to the coastal flow (cf. section 1). For the transects in September 1995 and January 1998 (Figures 5a and 5g, respectively), the salinity signal is related to the plume of the Solent, and for the remaining transects, it is due to plume of the Seine that is deflected westward by the residual current (cf. Figure 1).

[12] For all transects, a slight  $pCO_2$  increase (~20 µatm) is associated with these salinity decreases, however, this is more well marked for the March 1995 and September 1995 transects (~50 and ~100 µatm, Figures 3a and 5a, respectively). During spring and summer, primary production controls the latitudinal  $pCO_2$  distribution as shown by the fact that O<sub>2</sub> is significantly oversaturated, and furthermore, the distribution of  $\%O_2$  mirrors the one of  $pCO_2$  as along the transects of May 1997, June 1997, July 1997, and June 1998 (Figures 3c and 3d, 3e and 3f, 3g and 3h, and 4a and 4b, respectively). For the other transects,  $\%O_2$  is close to atmospheric equilibrium except for the early and late September 1995 transects (significant O<sub>2</sub> undersaturation). This would suggest that there are distinct periods of net heterotrophy that induce significant O2 undersaturation associated with CO<sub>2</sub> oversaturation as discussed in more detail in section 3.1.3. Also, the CO<sub>2</sub> oversaturation generally observed with near-O2 equilibrium conditions could be in some cases related to the thermodynamic effect on equilibrium constants associated with temperature increase, as along both transects of September 1999 (Figures 4e and 4f, and 4g and 4h). It is uneasy to check this hypothesis from the present data set because of probable interannual variability. However, temperature in early September 1999 is on average 2.5°C higher than in July 1998 and the  $pCO_2$ distributions are clearly different (Figures 4c and 4e). The average value of  $pCO_2$  normalized to a constant temperature of 17°C is 387 (±15, std)  $\mu atm$  in July 1998, a value relatively close to 404 (±19, std) µatm in early September 1999, while average  $pCO_2$  values at in situ temperature are 355 ( $\pm 12$ , std) and 410 ( $\pm 20$ , std)  $\mu$ atm for the same transects, respectively. If the transect of July 1998 is



**Figure 3.** Distribution of salinity, temperature, seawater  $pCO_2$  (µatm), and oxygen saturation level (%) along four transects in the English Channel in March 1995, May 1997, June 1997, and July 1997. The horizontal dotted line corresponds to atmospheric  $pCO_2$  from Mace Head. SBNS, EC, WC, and AS are four hydrological regions: Southern Bight of the North Sea, eastern English Channel, western English Channel, and Armorican Shelf, respectively. S and T stand for salinity and temperature, respectively. In May 1997 (plot C), seawater  $pCO_2$  data were lost between 3.2° and 2.5°E due to equipment failure.

considered representative of the conditions during the same period in 1999, then the water temperature increase from July to early September could explain in part the  $CO_2$  oversaturation observed along the early September 1999 transect.

**3.1.1.3. Western English Channel and Armorican Shelf** [13] Although underway parameters in the western English Channel in most cases follow the same trends as those of the eastern channel, one major difference is the presence of very sharp temperature gradients during the warm period of the year that are obvious along the transect of early

September 1999 (Figure 4f). Similar thermal gradients are observed over the Armorican Shelf and are caused by the same physical process, so both regions are discussed together.

[14] We observe sharp temperature gradients because the ship crossed (in some cases several times) the Ushant front that is generally created between the warm and stratified northern waters and the colder permanently well-mixed southern waters of the Eastern Channel [e.g., *Pingree et al.*, 1979]. This is the case in June 1997, June 1998, and July 1997 (Figures 3h, 4b, and 4h, respectively). However,



**Figure 4.** Distribution of salinity, temperature, seawater  $pCO_2$  (µatm), and oxygen saturation level (%) along four transects in the English Channel in June 1998, July 1998, and early and mid-September 1999. The horizontal dotted line corresponds to atmospheric  $pCO_2$  from Mace Head. The abbreviations SBNS, EC, WC, AS, S, and T are defined in legend of Figure 3. For clarity, the temperature in plot (f) is not on the same scale as in the other figures.

in some cases, there is a front between recently destratified waters and stratified waters. Indeed, *Sournia et al.* [1990] propose that the front is "eroded" during spring tides and stratification redevelops during neap tides. This seems to be the case in late September 1995 and 1999 (Figures 5c and 4h, respectively). Indeed, the destratified water in the eastern channel is cooler than both the still stratified water over the Armorican Shelf and the well-mixed waters of western channel (that gained heat during summer and thus also warmer). This could hold true, however, not as conspicuous for July 1998 and mid-September 1995 (Figures 4d and 5b, respectively).

[15] The temperature variations observed during the early September 1999 transect (Figure 4f) are very irregular because the ship crossed several times the frontal structure established between the destratified and the stratified waters. Very low  $pCO_2$  and high %O<sub>2</sub> values are associated with the warmer waters of both the western channel and the Armorican Shelf (the transect continued westward and at  $6.25^{\circ}W pCO_2$  increased to  $350 \mu$ atm and %O<sub>2</sub> decreased to 103% and thereafter both remained stable). This strongly suggests high DIC fixation by phytoplankton in the warmer waters of the frontal structure. Furthermore, underway fluorescence data (not shown) follow closely the %O<sub>2</sub>



**Figure 5.** Distribution of salinity, temperature, seawater  $pCO_2$  (µatm), and oxygen saturation level (%) along four transects in the English Channel in September 1995, January 1998, and November 1998. The horizontal dotted line corresponds to atmospheric  $pCO_2$  from Mace Head, except for the September 1999 transects when we measured atmospheric  $pCO_2$ . The abbreviations SBNS, EC, WC, AS, S, and T are defined in legend of Figure 3. The vertical dashed lines in plots (a) and (b) delimit the Solent.

signal and discrete Chl *a* values (not shown) in the warmer waters of the western channel are much higher (~8.5 µg  $l^{-1}$ ) than the colder waters (~1.5 µg  $l^{-1}$ ) and the adjacent eastern channel (~0.7 µg  $l^{-1}$ ). High Chl *a* values in the stratified waters adjacent to the Ushant front have been frequently reported [e.g., *Jordan and Joint*, 1984]. *Pingree et al.* [1979] attribute this to enhanced primary production related to both favorable light conditions (i.e., stratification) and nutrient availability supplied by eddies of well-mixed water that cross the front. *Sournia et al.* [1990] hypothesize that the enhanced primary production is associated with the waters that regularly stratify and mix as a function of the neap and spring tide cycle, creating optimal growth conditions. However, *Sournia et al.* [1990] also argue that the high Chl *a* values could be simply due to passive accumulation of phytoplankton cells by convergence. This hypothesis does not seem to hold true at least in the case of the early September 1999 transect, since the extremely high  $%O_2$  values strongly suggest active phytoplankton growth.

[16] The thermal frontal structures are also observed in all transects carried out in June, July, and September (Figures 3f, 3h, 4b, 4d, 4h, 5b, and 5d) although not as salient as in early September 1999. Lower  $pCO_2$  values (and in most



**Figure 6.** Property-property plots of temperature (°C) versus salinity,  $pCO_2$  (µatm) versus salinity, and  $pCO_2$  (µatm) versus temperature (°C) from the two transects carried out in November 1998 (Figure 5). The symbols correspond to the different water masses identified (see text). The line in plot (c) corresponds to the theoretical evolution of  $pCO_2$  with temperature change in a water parcel with an initial  $pCO_2$  of 369 µatm at 13°C (computed from the *Copin-Montégut* [1988] relationship).

cases higher %O<sub>2</sub> values) associated with the warmer waters are observed in both Armorican Shelf and the eastern English Channel in June 1997, June 1998, late September 1999, mid-September 1995 (Figures 3e, 4a, 4h, and 5a, respectively) or only in the Armorican Shelf as in July 1997, July 1998, and September 1995 (Figures 3g, 4c, and 5c, respectively).

# 3.1.2. Latitudinal Variability

[17] It is difficult to apprehend the potential latitudinal variability of  $pCO_2$  and other parameters from the linear transects analyzed in the previous section. However, the

two transects carried out in November 1998 (Figures 5e and 5g) can give some insight into this variability. Indeed,  $pCO_2$  in early November is significantly higher (390 (±3, std) µatm) than in late November (371 (±5, std) µatm). This difference is most probably not related to a temporal change in biological activity since the transects were carried out within 9 days. The most probable explanation is that different water masses with specific  $pCO_2$  signals were sampled along each transect. We plotted in Figure 6 various property-property plots to check this hypothesis. The *T-S* diagram shows that four different water masses were

sampled during the two transects (Figure 6a). Three water masses located close to the French coast are related to freshwater input as shown by the good relationship between temperature and salinity. The fourth water mass was sampled close to the English coast and in the middle of the channel, and seems unaffected by river inputs as shown by the relatively high and constant salinity (around 35.25  $(\pm 0.03, \text{ std})$ ) despite a wide range of temperature values (~1.7°C). The  $pCO_2$  values of the three water masses affected by river inputs are well correlated against salinity indicating the input of CO<sub>2</sub>-rich river waters (Figure 6b). The two water masses observed in the vicinity of the Bay of Seine are indistinguishable on the  $pCO_2$  versus salinity plots but are clearly distinct from the water mass observed close to the French coast in proximity of the Somme River. As expected, the  $pCO_2$  in the three water masses influenced by the river inputs are well correlated to temperature (Figure 6c). The  $pCO_2$  values of the water mass from the middle of the channel show a fairly good correlation with temperature. Furthermore, most of the data points fall around the theoretical evolution of  $pCO_2$  with temperature change alone, indicating that the variation of water temperature can explain, to some extent, the variations of  $pCO_2$  in the water mass of the channel unaffected by river inputs. Thus the lower  $pCO_2$  values along the late November 1998 transect (Figure 5g) are, to a large extent, related to the lower temperature  $(13.1 (\pm 0.4, \text{ std})^{\circ}\text{C}$ , Figure 5h) than along the early November 1998 transect  $(14.0 (\pm 0.2, \text{ std})^{\circ}\text{C},$ Figures 5e and 5f).

#### 3.1.3. Seasonal Variability

[18] To investigate the processes controlling the seasonal variability of  $pCO_2$ , the relevant parameters for a given transect were averaged from 1.5°E to 5.2°W (Figure 7). The data obtained by Frankignoulle et al. [1996a, 1996b] were also included to allow full annual coverage. The seasonal evolutions of  $pCO_2$  and  $%O_2$  are consistent, strongly suggesting that photosynthesis and respiration control the annual cycle of  $pCO_2$  (Figures 7a and 7b). In winter (January, March, and November), the surface waters of the channel are slightly oversaturated in CO<sub>2</sub> and undersaturated in O<sub>2</sub> showing the effect of moderate degradation processes. In April, there is a slight increase of %O<sub>2</sub> and Chl a (Figure 7c) with the onset of the spring phytoplankton bloom [e.g., Jordan and Joint, 1984; L'Helguen et al., 1996]. In May, June, and July, there is a marked decrease in the  $pCO_2$  values associated with an increase in  $O_2$  while surface Chl *a* concentrations remain relatively high. The seasonal minimum of  $pCO_2$  is in summer rather than in spring because the permanently well-mixed waters characterize most of the channel. According to L'Helguen et al. [1996], phytoplankton growth in the well-mixed waters of the channel is not limited by nutrient availability due to the absence of vertical stratification and the seasonal maximum of primary production is related to the maximum of light availability in June/July. In September, there is a marked increase in  $pCO_2$  associated with a decrease in %O2. The %O2 data point in brackets corresponds to the early September 1999 transect (Figure 4f) and does not seem to fit the seasonal trend because the extremely high  $%O_2$  values measured at the Ushant front bias the average value, since O<sub>2</sub> was close to saturation in the eastern channel. The Chl a concentrations remain relatively high



**Figure 7.** Seasonal cycle of average values of  $pCO_2$  (µatm), oxygen saturation level (%), chlorophyll a (µg l<sup>-1</sup>, circles), and active chlorophyll (small squares). The transect data were averaged from 1.5°E to 5.2°W (data from the Southern Bight of the North Sea and the Armorican Shelf were excluded). Open symbols correspond to data by *Frankignoulle et al.* [1996a, 1996b], while solid symbols correspond to data from Figures 3 to 5. The dotted line in plot (a) corresponds to the atmospheric  $pCO_2$  seasonal cycle at Mace Head based on the interpolation of the 1997 fortnightly data points. See text for brackets in plot (b). The seawater  $pCO_2$  data were fitted to 1997 (see section 2). The position of the chlorophyll *a* samples is shown in Figure 2.

although the decrease of active chlorophyll suggests that the phytoplankton cells are not pristine and are in the course of degradation. Enhanced degradation of organic matter during fall associated with high  $pCO_2$  values has also been described in the adjacent Southern Bight of the North Sea by *Borges and Frankignoulle* [2002a] in relation to the decline of phytoplanktonic activity. In October,  $pCO_2$ 



**Figure 8.** Evolution of salinity, temperature (°C), and  $pCO_2$  (µatm) at a fixed station (48.85°N 1.28°W: cross in the map of Figure 6) from 14 (2028 UT) to 15 (1346 UT) November 1998. The shaded area corresponds to nighttime. LT and HT stand for low tide and high tide, respectively.

rapidly decreases while  $\text{\%O}_2$  increases showing the diminution of the degradation processes and the combined effect of air-sea exchange and temperature decrease (shown in Figure 9b).

## 3.1.4. Daily Variability

[19] Strong daily variations of  $pCO_2$  have been reported in both open oceanic and coastal waters that are related to temperature change [e.g., *Goyet and Peltzer*, 1997] and/or biological activity [e.g., *Robertson et al.*, 1993], with significant impact on air-sea CO<sub>2</sub> exchanges. Data can be obtained from a fixed station approach [e.g., *Bakker et al.*, 1996] or in a Lagrangian mode [e.g., *Robertson et al.*, 1993]. The evolution of salinity, temperature, and  $pCO_2$ during 17 hours at a fixed station in the vicinity of the Bay of Seine in November 1998 is shown in Figure 8. The evolution of salinity and temperature clearly follows a periodical signal related to the displacement of different water masses during the tidal cycle as also reported in the Southern Bight of the North Sea by *Bakker et al.* [1996] and *Borges and Frankignoulle* [1999]. The evolution of  $pCO_2$  also shows a clear periodical signal that closely matches the one of salinity with the highest  $pCO_2$  values associated with the lowest salinities. The periodical  $pCO_2$  signal is inconsistent with the one expected from the diel cycle of photosynthesis/respiration. For instance, the lowest  $pCO_2$  values were observed at dawn when the highest  $pCO_2$  values are normally observed in a system where the daily variations of DIC are mainly controlled by the diel biological cycle [e.g., *Robertson et al.*, 1993; *Borges and Frankignoulle*, 2001]. We can conclude that in the English Channel the tidal cycle has a major impact on the daily variability of  $pCO_2$  and that a Lagrangian approach should be envisaged to study the potential impact of the diel biological cycle on  $pCO_2$ .

#### 3.2. Air-Sea CO<sub>2</sub> Exchanges

[20] Figure 9d shows an example of air-sea  $CO_2$  flux computation using daily values of interpolated air-sea gradient of  $pCO_2$  (Figure 9a, based on data from Figure 7), geostrophic wind speed in 1997 (Figure 9c), and interpolated water temperature (Figure 9b). The range of variation of the daily values of the flux is high ~10 mmol C m<sup>-2</sup> d<sup>-1</sup> and the maximal absolute value (-36 mmol C m<sup>-2</sup> d<sup>-1</sup>) is observed in late July due to the combination of strong air-sea gradient (-36  $\mu$ atm) and high wind speeds (16.9 m s<sup>-1</sup>). The highest flux data do not necessarily correspond to the highest air-sea gradient as shown by the similar flux values in late August and mid-September although the air-sea gradient increases by a factor of almost 2.

[21] The air-sea  $CO_2$  fluxes were computed with wind speed data from different years and integrated annually (Table 1). On first analysis, the English Channel seems to be, on an annual scale, a net source of atmospheric CO<sub>2</sub> of about + 0.9 mmol C m<sup>-2</sup> d<sup>-1</sup> although the flux is not significantly different from zero. The uncertainty of the flux computation was estimated by assuming a  $\pm 5\%$  error on wind speed data, and a  $\pm 6.5 \,\mu$  atm error on the air-sea CO<sub>2</sub> gradient (the data of Frankignoulle et al. [1996a, 1996b] are computed from pH and TAlk so that we estimate the overall error on the interpolated seawater  $pCO_2$  to  $\pm 6.0$  µatm and we assume an error on atmospheric  $pCO_2$  of  $\pm 0.5$  µatm). We carried out a similar error analysis on CO2 flux computations in the Galician upwelling system and found that the uncertainty on wind speed represented about 80% of the total error [Borges and Frankignoulle, 2002b]. However, in the present computations, the uncertainty on wind speed represents about 16% of the total error because in the channel the annually integrated air-sea gradient of  $pCO_2$  is close to zero ( $\Delta pCO_2 = +5 \mu atm$ ) while in the Galician upwelling system it is highly significant ( $\Delta p CO_2$  $\sim -25$  µatm). Air-sea CO<sub>2</sub> fluxes were also computed using other K-wind relationships (not shown) and the annually integrated net flux based on Nightingale et al. [2000] corresponds to an average of 134, 78, and 67% of the one computed from the formulation of Liss and Merlivat [1986], Wanninkhof [1992], and Wanninkhof and McGillis [1999], respectively. However, considering the relatively large uncertainty on the calculations, the flux values computed from any of these relationships are not significantly different. Last, the flux values computed with the wind speed data sets from different years are not significantly



**Figure 9.** Seasonal evolution of daily values of (a) air-sea gradient of  $pCO_2$  (µatm) based on interpolated seawater and atmospheric  $pCO_2$  data from Figure 7, (b) water temperature (°C), (c) geostrophic wind speed (m s<sup>-1</sup>) in 1997 at 50.0°N 6.0°W, (d) air-sea CO<sub>2</sub> flux computed from the data in plots Figures 9a, 9b, and 9c, using the CO<sub>2</sub> exchange coefficient formulated by *Nightingale et al.* [2000], the Schmidt number according to *Wanninkhof* [1992], and the CO<sub>2</sub> solubility coefficient according to *Weiss* [1974]. In Figure 9b, open symbols correspond to data from *Frankignoulle et al.* [1996a, 1996b], while solid symbols correspond to data from Figures 3 to 5.

different and the standard deviation on the average value  $(\pm 0.2 \text{ mmol m}^{-2} \text{ d}^{-1})$  is much smaller than the estimated error on the computation.

[22] Atmospheric  $pCO_2$  in coastal areas is known to be influenced by nearby land leading to an increase up to 30 µatm of the uncontaminated signal, introducing an additional uncertainty in the flux computations that is difficult to account for because of high dependency on wind direction and intensity [Friederich et al., 1995; Bakker et al., 1996; Borges and Frankignoulle, 2001, 2002c]. We only measured atmospheric  $pCO_2$  along the two transects of September 1999 (Figures 4e and 4g). The atmospheric mole fraction values are stable at the entrance of the channel (between  $6^{\circ}$  and  $5^{\circ}$ W): 362.8 (±0.7) and 364.9 (±0.8) ppm, for the early and late September 1999 transects, respectively (the uncertainty includes the standard deviation on the mean and estimated experimental error  $\pm 0.5$  ppm). The atmospheric  $xCO_2$  values increase toward the Dover Strait, in a relatively regular manner, to reach maximal values of 375 ppm for both transects. Atmospheric  $xCO_2$  at the Mace Head site was 360 ( $\pm 0.3$ , std) and 361 ( $\pm 1.8$ , std) ppm during each of the two transects.

[23] We computed the air-sea CO<sub>2</sub> fluxes assuming a minimal and maximal atmospheric xCO<sub>2</sub> increase of 1 and 15 ppm, giving annually integrated air-sea CO<sub>2</sub> flux values in the channel that are positive and negative, respectively (Table 1). However, in both cases, the flux values are not significantly different from zero. The average atmospheric xCO<sub>2</sub> excess for the channel in relation to the Mace Head site data is for both transects 6 (±1, std) ppm, so that the air-sea flux values computed assuming an intermediate increase of 8 ppm are probably the most reliable and would suggest

that the channel is neutral from the point of view of atmospheric coupling.

# 3.3. Why is the English Channel Not a Significant Sink of Atmospheric CO<sub>2</sub>?

[24] Although the status of the English Channel as a source or a sink of atmospheric  $CO_2$  is not resolved, we can at least conclude that it is not a significant sink of atmospheric  $CO_2$ . Recently published studies of marginal continental shelves [Boehme et al., 1998; Tsunogai et al., 1999; Frankignoulle and Borges, 2001; Borges and Frankignoulle, 2002b] and semienclosed coastal systems [Thomas and Schneider, 1999; Borges and Frankignoulle, 2002a] show that both air-sea  $CO_2$  gradient and computed fluxes

 Table 1. Net Annually Integrated Air-Sea Fluxes in the English Channel<sup>a</sup>

	$\begin{array}{c} \Delta p \text{CO}_2, \\ \text{mmol} \\ \text{C} \text{ m}^{-2} \text{ d}^{-1} \end{array}$	$\Delta p \text{CO}_2 + 1,$ mmol C m <sup>-2</sup> d <sup>-1</sup>	$\Delta p \text{CO}_2 + 8,$ mmol C m <sup>-2</sup> d <sup>-1</sup>	$\frac{\Delta p \text{CO}_2 + 15}{\text{mmol}}$ $\text{C m}^{-2} \text{d}^{-1}$
1995 1996 1997	$\begin{array}{c} 1.4 \pm 1.5 \\ 1.4 \pm 1.7 \\ 0.9 \pm 1.6 \end{array}$	$\begin{array}{c} 1.2 \pm 1.5 \\ 1.2 \pm 1.6 \\ 0.7 \pm 1.6 \end{array}$	$\begin{array}{c} -0.1 \pm 1.3 \\ -0.2 \pm 1.5 \\ -0.8 \pm 1.5 \end{array}$	$\begin{array}{c} -1.3 \pm 1.5 \\ -1.5 \pm 1.7 \\ -2.0 \pm 1.8 \end{array}$
1998 1999 Average	$\begin{array}{c} 1.5 \pm 1.9 \\ 1.4 \pm 1.8 \\ 1.3 \pm 1.7 \end{array}$	$\begin{array}{c} 1.3 \pm 1.8 \\ 1.1 \pm 1.7 \\ 1.1 \pm 1.6 \end{array}$	$\begin{array}{c} -0.3 \pm 1.7 \\ -0.4 \pm 1.6 \\ -0.4 \pm 1.5 \end{array}$	$\begin{array}{c} -1.8 \pm 1.9 \\ -1.8 \pm 1.8 \\ -1.7 \pm 1.7 \end{array}$

<sup>a</sup>Computed from the data in Figures 9a and 9b, the CO<sub>2</sub> exchange coefficient formulated by *Nightingale et al.* [2000], the Schmidt number according to *Wanninkhof* [1992], the CO<sub>2</sub> solubility coefficient according to *Weiss* [1974], and daily geostrophic wind speeds from 1995 to 1999 at 50°N 6°W, assuming an increase of 1, 8, and 15 ppm of the atmospheric *x*CO<sub>2</sub> data from Mace Head. The uncertainty on the flux computation was estimated assuming an error of  $\pm$ 5% on wind speed and  $\pm$ 6.5 µatm on the air-sea gradient of *p*CO<sub>2</sub>.

are highly significant ( $\sim$ -5 mmol C m<sup>-2</sup> d<sup>-1</sup>). It is difficult to explain why this is not the case for the channel because to our knowledge there is no published comprehensive carbon budget for this area, however, the sparse carbon flux data found in literature can give us some clues.

[25] One of the main processes that determines if a system acts as a source or sink of atmospheric CO<sub>2</sub> is the net ecosystem production (NEP) that corresponds to gross primary production minus total respiration, including both pelagic and benthic components. If NEP is positive, then such a system exports and/or stores organic carbon and is potentially a sink for atmospheric CO<sub>2</sub>. Estimating NEP is a difficult task considering the numerous processes that must experimentally be determined, but it can be approximated by new primary production (for a discussion on the conceptual differences between NEP and new primary production refer to the work of *Thomas et al.* [1999] and references therein). New primary production is the fraction of net primary production fueled by an external input of nitrate (as opposed to regenerated primary production based on ammonia and urea) and supplies the organic carbon made available for export and/or storage. Based on the N-assimilation annual rates reported by Le Corre et al. [1996] and L'Helguen et al. [1996], and assuming a Redfieldian elemental molar ratio of organic carbon (106C:16N), new primary production in the well-mixed waters of the channel is estimated to be 1.6 mmol  $C m^{-2} d^{-1}$  on an annual basis. Furthermore, Maguer et al. [1998] estimate that between 25 and 35% of nitrate in the channel is made available through nitrification. As noted by Wollast [1998], nitrate regenerated in coastal sediments through nitrification does not constitute an external input and leads to an overestimation of new primary production based on NO3<sup>-</sup> assimilation experiments. Hence new primary production in the channel is  $\sim 1.0 \text{ mmol C} \text{ m}^{-2} \text{ d}^{-1}$ that is considerably lower than the average value given by *Wollast* [1998] of 9.1 mmol C m<sup>-2</sup> d<sup>-1</sup> for worldwide continental shelves. Moreover, new primary production in the channel is lower than the rates of exported/buried organic matter in the adjacent Southern Bight of the North Sea [Wollast, 1998] and Gulf of Biscay [Wollast and Chou, 2001]: 4.8 and 6.8 mmol C m<sup>-2</sup> d<sup>-1</sup>, respectively.

[26] In some coastal ecosystems such as coral reefs, calcification can have a significant impact on CO<sub>2</sub> air-sea exchange [e.g., Gattuso et al., 1993]. Migné et al. [1998] estimate the calcification rate of the brittle star Ophiothrix fragilis population at the vicinity of the Dover Strait to 18.6 mmol CaCO<sub>3</sub> m<sup>-2</sup> d<sup>-1</sup>. This leads to the release of CO<sub>2</sub> into the surrounding water and potentially further transfer to the atmosphere at an annually integrated rate of 13.2 mmol C m<sup>-2</sup> d<sup>-1</sup>. Considering that the areal extent of the brittle star population is 5400 km<sup>2</sup> in the Eastern Channel, the minimal potential CO<sub>2</sub> emission from benthic calcification is 0.86 mmol C m<sup>-2</sup> d<sup>-1</sup> for the entire English Channel  $(82.6 \times 10^3 \text{ km}^2)$ . Furthermore, extensive coccolithophorid blooms have been reported in the western English Channel [Garcia-Soto et al., 1995], although to our knowledge annual pelagic calcification rates have not been published.

[27] Last, the transfer of DIC and organic carbon from inner estuaries to the adjacent coastal area can lead to significant air-sea CO<sub>2</sub> emissions [e.g., *Borges and Frankignoulle*, 1999, 2002a]. Little data are available concerning carbon fluxes from rivers or estuaries to the channel, except the flux of total organic carbon from the river Seine to the channel that amounts to  $27.4 \times 10^6$  mol C d<sup>-1</sup> [Cossa et al., 1994; Bodineau et al., 1999]. If we assume that all of this organic carbon is respired, then it would produce a potential  $CO_2$  emission for the entire channel of 0.33 mmol C m<sup>-2</sup> d<sup>-1</sup>. According to *Kempe et al.* [1991], about 57.1  $\times$  10<sup>6</sup> mol C  $d^{-1}$  of terrestrial organic carbon enter the Seine, so that approximately  $29.7 \times 10^6$  mol C d<sup>-1</sup> are respired in the estuary. If we assume arbitrarily that 75% of the produced DIC is lost to the atmosphere within the Seine itself, then  $7.4 \times 10^6$  mol C d<sup>-1</sup> of the DIC produced in the estuary would be transferred to the adjacent coastal area leading to a potential CO<sub>2</sub> emission for the entire channel of 0.09 mmol C m<sup>-2</sup> d<sup>-1</sup>. Kempe et al. [1991] also estimate that 102.5  $\times$  $10^6$  mol C d<sup>-1</sup> of terrestrial DIC are introduced into the Seine estuary. However, is not possible to calculate how much of this terrestrial DIC is transferred from the Seine to the channel and further exchanged with the atmosphere. However, considering that 43% of the total freshwater input to the channel is delivered by the Seine, we can conclude that the impact of river inputs on air-sea CO<sub>2</sub> exchange is smaller but still significant compared to new primary production and benthic calcification.

## 4. Conclusions

[28] In the present work, we discuss the distribution of surface  $pCO_2$  along 13 transects obtained during 9 cruises and covering the 4 seasons. The main processes controlling the distribution of  $pCO_2$  in the surface waters of the channel are primary production that strongly decreases  $pCO_2$  values from May to June when light availability is highest and the degradation of organic matter that seems to be particularly intense during fall. From the present data set it is difficult to determine the contribution of water temperature changes to the seasonal cycle of  $pCO_2$ , however, we hypothesize that it could be significant in late summer.

[29] The CO<sub>2</sub> air-sea fluxes were computed from our data set combined to the one by *Frankignoulle et al.* [1996a, 1996b]. In spite of a large seasonal signal in seawater pCO<sub>2</sub>, the integrated air-sea gradient of CO<sub>2</sub> is close to zero. Furthermore, the computations are biased by the increase of atmospheric pCO<sub>2</sub> related to the presence of nearby land that is difficult to account for. We suggest that the English Channel is close to a neutral state in relation to atmospheric CO<sub>2</sub> fluxes, as opposed to midlatitude marginal continental shelves studied so far that are significant sinks of atmospheric CO<sub>2</sub>. This can be explained by the fact that NEP is relatively low in the channel and of the same order of magnitude as the rate of CO<sub>2</sub> released by benthic calcification, while the contribution of carbon inputs from rivers is smaller but significant.

[30] The  $CO_2$  air-sea fluxes we computed for the channel should be considered as preliminary. Indeed, the data were mostly obtained along transects through the middle of the channel and do not take into account the latitudinal gradients that are apparent in studies dealing with other chemical and biological parameters [e.g., *Jordan and Joint*, 1984; *Brylinski et al.*, 1996]. Our data set shows some of the potential latitudinal variability in the distribution of  $pCO_2$  as for instance in November 1998 in relation to the presence of different water masses, temperature change, and freshwater inputs, and in late August 1999 in relation to tidal frontal structures. Finally, from the present data set it is difficult to work out the potential importance of the variability of  $pCO_2$  at interannual and daily scales. The study of the effects of diel biological cycles should be approached with a Lagrangian mode because the daily variability of  $pCO_2$  is strongly modulated by the tidal cycle based on a fixed station approach.

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