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## Distribution of inorganic carbon and related parameters in surface seawater of the English Channel during spring 1994

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### Abstract

The complete CO<sub>2</sub> system, dissolved oxygen, nutrients and chlorophyll concentrations, fluorescence, salinity and temperature of surface seawater have been determined in the English Channel and the Southern Bight of the North Sea during Spring 1994. As already mentioned in a previous study, this area is characterized by important spatial and temporal variations of the considered set of parameters. This paper focuses on the distribution of the homogeneous buffer factor [ $\beta = \text{dln}(p\text{CO}_2)/\text{dln}(\text{TCO}_2)$ ]. It is shown that this parameter is a useful tool for identifying processes that mainly affect the CO<sub>2</sub> distribution, such as primary production or water mass mixing, even in such a complex area.

### 1. Introduction

Field data on the distribution of marine inorganic carbon species are needed in order to assess the effective role of the oceans in the global carbon cycle. In particular, the coastal zone is the site of specific processes (upwelling, river input, tidal mixing, important and diverse biological activity) which could induce large disequilibrium conditions with respect to the atmosphere and associated intense air–sea CO<sub>2</sub> exchanges (MacKenzie et al., 1991, Wollast, 1991). Also, continental shelves are sites where primary production

may reach levels of 25% of total oceanic production (Walsh, 1988, see also Walsh, 1991).

Because primary production results in a decrease of seawater CO<sub>2</sub> partial pressure, air–sea CO<sub>2</sub> exchange in shelf areas is a fundamental process which could have a significant impact on the global oceanic carbon cycle.

However, field data on surface seawater  $p\text{CO}_2$  in coastal seas are very sparse. For the European Atlantic shelf, the only available sets of data are those of Pegler and Kempe (1988) and Kempe and Pegler (1991) who calculated the surface  $p\text{CO}_2$  distribution in the North Sea from potentiometric determinations of total alkalinity and total inorganic carbon, and of Hoppema (1993). These authors present  $p\text{CO}_2$  values ranging from about 100 to 600 ppmv, providing evidence for a

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large range in coastal water quality. Frankignoulle et al. (1995) provide the first set of  $\text{CO}_2$  data collected in the English Channel in 1992 and 1993 and also document large variations in the distribution of surface water  $p\text{CO}_2$ , especially for the eastern part of the Channel, which is influenced by river inputs mainly from the Seine and the Scheldt river systems. These preliminary results suggested that further investigations should be made in this area to assess the relative importance of various processes, such as primary production and water mass mixing, on the  $\text{CO}_2$  distribution. This paper presents a new set of marine inorganic carbon data recently obtained in the English Channel and in the Southern Bight of the North Sea.

## 2. Material and methods

Data presented here have been obtained during cruise 94/12 of the R.V. *Belgica* in April–May 1994. Two transects were carried out through the Channel, one from the Belgian coast to the Gulf of Biscay on 11–13 April and the other one on the way back on 4–5 May. Previous data obtained for this area (Frankignoulle et al., 1995) were collected while crossing the Channel along the French and English coasts, while those discussed in this paper were obtained during a research cruise in the middle of the Channel (Fig. 1).

Total inorganic carbon ( $T\text{CO}_2$ ) was calculated from experimental determinations of pH and to-

tal alkalinity ( $TALK$ ). The later is obtained from the classical Gran electrotitration on 100 ml GF/C filtered samples. The  $TALK$  calculation was made with corrections for fluoride and sulphate according to Hansson and Jagner (1973). The precision was determined to be 0.1% ( $2 \mu\text{eq} \cdot \text{kg}^{-1}$ ) under laboratory condition and using pure carbonate standard solutions. The reproducibility at sea on seawater samples is  $4 \mu\text{eq} \cdot \text{kg}^{-1}$ .

pH was measured using a Ross combination electrode (Orion), calibrated using Tris buffer as proposed by Dickson (1993) on the total proton scale [pH(SWS)]. The reproducibility of the pH measurement is 0.2 mV, which corresponds to 0.004 pH unit.

The complete  $\text{CO}_2$  system speciation is calculated according to the pH(SWS) scale (total proton,  $\text{mol} \cdot \text{kg}^{-1}$ ) using the  $\text{CO}_2$  acidity constants from Goyet and Poisson (1989), the  $\text{CO}_2$  solubility coefficient from Weiss (1974), and the borate acidity constant from Hansson (1973). The total borate molality is calculated using the Culkin (1965) ratio to salinity. The error in the calculation of  $p\text{CO}_2$ , calculated from pH and  $TALK$  uncertainties, is 8 ppm.

Salinity, temperature, pH, oxygen, nutrients and fluorescence were measured on a continuous time basis (sampling frequency of 1 minute) using a fully computerized acquisition system connected to the subsurface (–2 m) seawater pump of the ship. Nitrate and dissolved silicate were measured using the automated method described in Elskens and Elskens (1989), with detection limits of  $0.1 \mu\text{M}$  and  $0.5 \mu\text{M}$ , respectively.

Dissolved oxygen was measured using a polarographic electrode (Kent). Discrete samples were regularly collected for calibration purposes, as well as for alkalinity and chlorophyll a determinations. Calibration of the dissolved oxygen probe was made according to the classical Winkler method, using a potentiometric electrode and Gran plots (Anderson et al., 1992) for the determination of the equivalence point. The oxygen saturation level was calculated according to the algorithm proposed by Benson and Krause (1984). Salinity and temperature were measured using a SEABIRD SBE25 system.

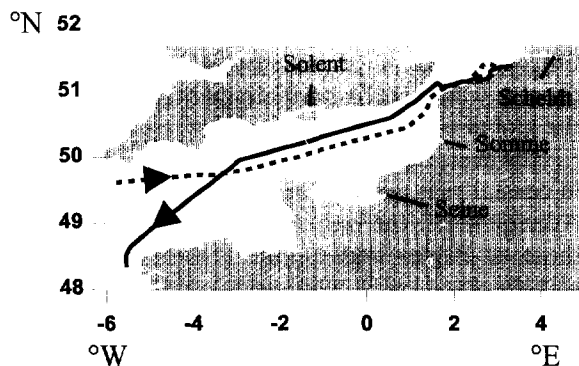


Fig. 1. Cruise tracks for the two transects through the Channel (filled black line: 11–13 April 1994; dotted line: 4–5 May 1994).

Fluorescence data were obtained from a TURNER fluorimeter. Unfortunately, this instrument was not calibrated during the cruise but it was checked to display a linear response to the chlorophyll a content in seawater. For this reason, fluorescence data are expressed as *relative* values. Chlorophyll a and pheopigment concentrations were determined using the spectrophotometric method described by Lorenzen and Jeffrey (1978).

### 3. Results and discussion

Two major conclusions were drawn from the previous sets of CO<sub>2</sub> data collected in the same area in 1992 and 1993 (Frankignoulle et al., 1995):

–The Southern Bight of the North Sea, widely influenced by the Scheldt, is characterized by important spatial and temporal variability in the distribution of CO<sub>2</sub>. The pCO<sub>2</sub> level in surface water can vary from about 100 up to 700 ppm, partly due to tidal processes.

–in the Channel itself, the distribution of pCO<sub>2</sub> seems mostly related to the chl. *a* concentration, in spite of the complex hydrodynamics of the area. However, when river input is a dominant process (e.g. September 1993), this relationship is not observed. Each area, under the influence of river input, displays CO<sub>2</sub> levels which depend upon the chemical characteristics of the river: the Seine induces low pCO<sub>2</sub> in surface water (down to about 200 ppm), while the Scheldt has an opposite effect (up to 700 ppm).

Data discussed in this paper were obtained in 1994 during two transects carried out in the middle of the Channel (Fig. 1). Salinity, temperature, oxygen, fluorescence and chlorophyll data are shown in Fig. 2.

The salinity distribution shows that the Scheldt river input is of importance, because salinity values fall below 30 east of 3°E (Belgian coast). The temperature profiles, obtained 3 weeks apart, were quite different, and the warming between transects ranged from a few tenths of degrees at the western end to about 4 degrees off the Belgian coast.

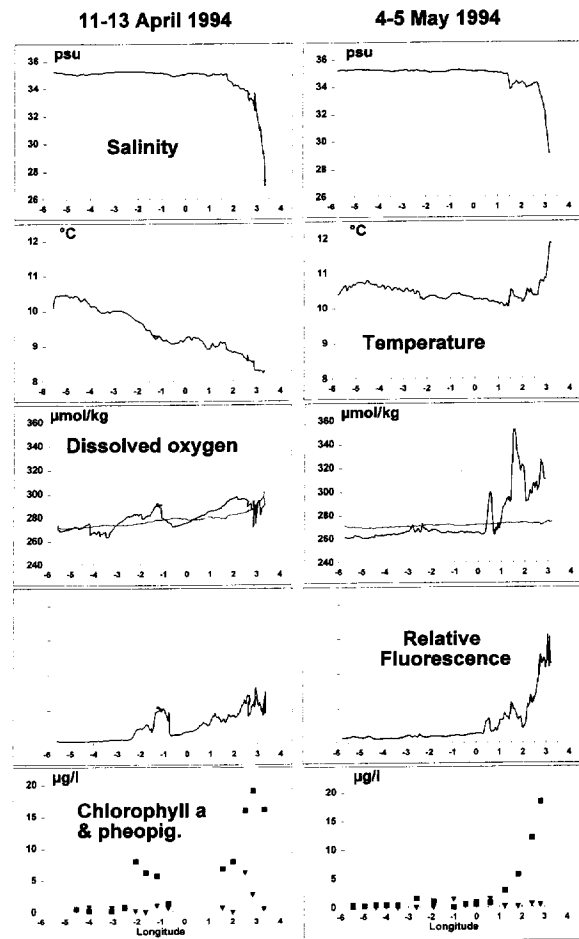


Fig. 2. Data set obtained during transects through the Channel. Left and right columns correspond, respectively, to the April and May transects. On the oxygen graphs, the thin line indicates the saturation level. On the chlorophyll graphs, squares and triangles are related, respectively, to chlorophyll and pheopigment concentrations.

During both transects, dissolved oxygen, fluorescence and chlorophyll a concentrations were well correlated in the Channel. During the first transect, the whole area was characterized by an undersaturation in dissolved oxygen. A peak in O<sub>2</sub> was detected around 1.2°W, which could have been induced by an input of nutrient-rich water from the Solent. During the second transect, an important but local peak of oxygen (about 130% saturation) was observed at 1.5°E, in an increasing gradient of both fluorescence and chlorophyll.

This area (from 1 to 3°E) is under the influence of three important rivers (Seine, Somme and Scheldt), and each of them could have had a different impact on the dissolved oxygen distribution. The Scheldt is known to carry water with very high nutrient concentrations (Wollast, 1989) but undersaturated with respect to oxygen. This is in agreement with the observed high chlorophyll level (20  $\mu\text{g/l}$ ) and the corresponding slight oxygen oversaturation (105-110%) in the region influenced by the Scheldt. In the area from 0 to 2°E, the apparent discrepancy between fluorescence and chlorophyll a profiles could be due to the low spatial resolution of discrete chlorophyll sampling, as suggested by the good correlation between the continuous measurements of both oxygen and fluorescence.

Fig. 3 illustrates the horizontal distribution pattern of nitrate and dissolved silicate during the May transect. Both nitrate and silicate profiles are clearly related, with relatively high concentrations observed between 6°W and Greenwich. A large decrease in nutrient concentrations is observed at 0.5°E and from 1 to 2 °E, corre-

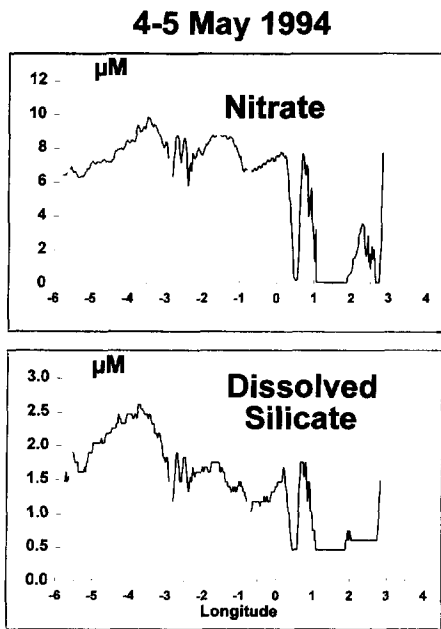


Fig. 3. Nitrate and dissolved silicate data obtained through the Channel during the May transect.

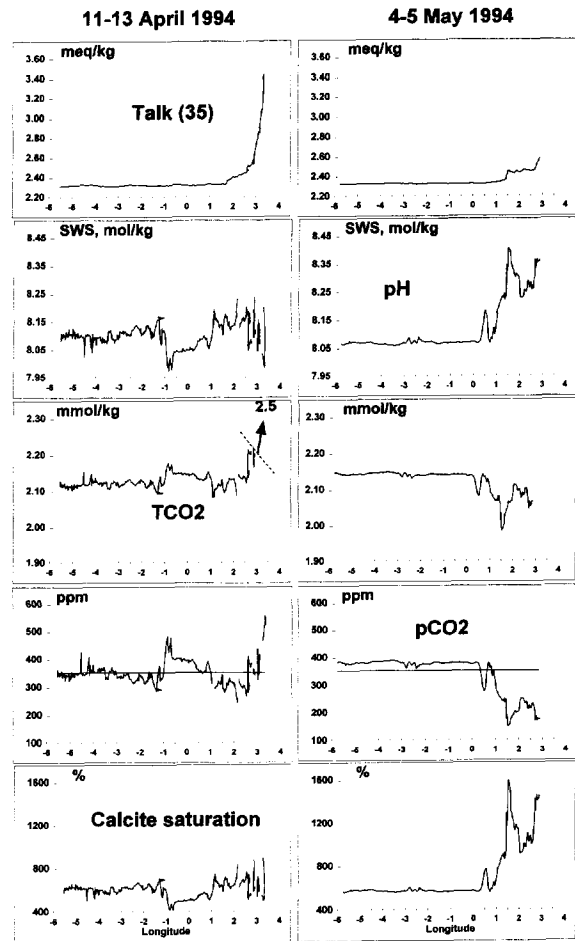


Fig. 4. Inorganic carbon data set obtained during transects through the Channel. Left and right columns correspond, respectively, to the April and May transects.

sponding to pH and O<sub>2</sub> peaks and to a strong fluorescence signal. These observations suggest important primary production rates in this area. However, the nutrient peaks observed between 0.5 and 1°E are likely due to the influence of Baie de Somme waters, as also suggested by the local decrease of salinity (about 1). At 3°E, nutrient concentrations increase again due to the influence of the Scheldt estuary (see also salinity and temperature profiles).

Fig. 4 shows the set of parameters related to inorganic carbon speciation. Total alkalinity, normalized to 35 salinity [*TALK* (35)], displays a

constant value around 2.35 meq/kg in the whole Channel and a very sharp increase along the Belgian coast (up to about 3.5 meq/kg) due to the influence of Scheldt waters (Wollast, 1989; Frankignoulle et al., 1992,1995). Unfortunately, for technical reasons, no CO<sub>2</sub> data are available for the second transect farther east than 2.9°E.

pH profiles are in excellent agreement with those of oxygen, especially during the second transect when large variations in both parameters were observed. At 1.5°E, the 120% oxygen peak corresponds to a pH as high as 8.4, causing surface waters to be 1600% oversaturated with respect to calcite.

pCO<sub>2</sub> profiles are very different between the two transects. In April, surface water off the Belgian coast is highly oversaturated with respect to CO<sub>2</sub> (up to 550 ppm), in spite of a relatively high chlorophyll concentration (20 μg/l). Of course pCO<sub>2</sub> profile is mainly driven by pH one and high CO<sub>2</sub> oversaturation is observed together with high alkalinity values. The Channel is slightly undersaturated between 1 and 2°30'E, oversaturated between 1°W and 1°E, and then roughly at equilibrium between 1 and 6°W. In May, waters in the area between 1 and 3 °E are clearly undersaturated but the remainder of the Channel is slightly oversaturated. Processes that can lead to changes in surface seawater pCO<sub>2</sub> in the area are: –primary organic production decreases pCO<sub>2</sub> as a result of dissolved CO<sub>2</sub> uptake for organic carbon metabolism. Respiration has the opposite effect; –calcification (or carbonate precipitation) increases pCO<sub>2</sub> as a result of chemical equilibria involved in carbonate (or bicarbonate) fixation; –an increase of temperature produces an increase in pCO<sub>2</sub> resulting from the change in the values of equilibrium constants as a function of temperature; –river input can produce large pCO<sub>2</sub> changes which are mainly determined by the physico-chemical properties of the river.

These processes can occur simultaneously (e.g. photosynthesizing carbonate-secreting plankton such as coccolithophorids) with different relative intensity and the resulting CO<sub>2</sub> distribution, therefore, can be difficult to interpret. From field data collected in 1992 and 1993, Frankignoulle et al. (1995) suggested that in the area under the

influence of the Scheldt, the river input of CO<sub>2</sub>-oversaturated water is so important that chlorophyll should exceed 20 μg/l to induce undersaturation in surface waters. It appears from the present data set that this conclusion was not valid for 1994: in May and April, chlorophyll was about 20 μg/l in the vicinity of 3°E, but pCO<sub>2</sub> did change from oversaturation (400 to 550 ppm) during the first transect to about 200 ppm during the second. It is worth noting that fluorescence, in the same area, is nearly 3 times higher during the May transect. Brunet et al. (1992) also observed discrepancies between spectrophotometrically determined chlorophyll and fluorescence data obtained in the Channel. While the spectrophotometric method is mostly sensitive to chl. *a* and phaeopigments, the fluorescence method can be influenced by external parameters such as turbidity, which is an important variable in the area.

A convenient parameter which can be used to discuss processes responsible for marine inorganic carbon variations is the homogenous buffer factor,  $\beta$ , defined by:

$$\beta = \left( \frac{\Delta p\text{CO}_2}{p\text{CO}_2} \right) \cdot \left( \frac{\Delta T\text{CO}_2}{T\text{CO}_2} \right)^{-1} = \frac{d\ln p\text{CO}_2}{d\ln T\text{CO}_2}$$

While  $\beta$  value is obviously a function of physico-chemical conditions (i.e. pH, *Talk*, salinity and temperature, see e.g. Sundquist and Plummer, 1981), it also depends on processes that induce modifications in the CO<sub>2</sub> system speciation, namely uptake/release of carbonate, bicarbonate and dissolved CO<sub>2</sub> (Frankignoulle, 1994). When dissolved CO<sub>2</sub> is the inorganic species involved in the carbon exchange (e.g. air–sea exchange), this buffer factor is the well known REVELLE factor. Its value is about 12 for average seawater conditions. If processes other than the uptake or release of dissolved CO<sub>2</sub> occur,  $\beta$  can have a different value. Frankignoulle (1994) recently proposed a relationship which allows calculation of the  $\beta$  value when organic and inorganic carbon metabolism occurs simultaneously ( $\beta = -7.02 + 0.186 \times \%C_{\text{org}}$ , where  $\%C_{\text{org}}$  is the percentage of carbon uptake for organic metabolism). Pure carbonate precipitation would induce a  $\beta$

Table 1

The homogenous buffer factors obtained by plotting  $\ln(p\text{CO}_2)$  vs.  $\ln(\text{TCO}_2)$ .  $p\text{CO}_2$  has been normalized to 10°C. (cf. Fig. 5)

The homogenous buffer factor ( $\beta = d\ln p\text{CO}_2 / d\ln \text{TCO}_2$ )

	6°W → 1.3°E (A)	1.3°E → 3°E (B)	> 3°E (C)
April 1994	12.9 ( $r^2 = 0.92$ , $n = 328$ )	5.8 ( $r^2 = 0.78$ , $n = 83$ )	5.4 ( $r^2 = 0.93$ , $n = 18$ )
May 1994	13.1 ( $r^2 = 0.98$ , $n = 338$ )	8.1 ( $r^2 = 0.74$ , $n = 95$ )	/

value of about  $-7$ , whereas a 50% value for carbon uptake in inorganic metabolism would give a rise to a  $\beta$  value of about 2.3. Thus, the buffer factor has a wide range of values depending on the inorganic species involved in the  $\text{CO}_2$  dynamics.

The data set presented here allows us to estimate  $\beta$  values using the slope of a plot of  $\ln(p\text{CO}_2)$  vs.  $\ln(\text{TCO}_2)$ . Robertson et al. (1994) recently used this approach to study a coccolithophore bloom in the North Atlantic, and they showed that the slope so obtained suggests a 50% uptake for organic metabolism in this ecosystem.

Fig. 4 illustrates results obtained using our data set from the two Channel transects (see also Table 1). To take into account the temperature effect on  $p\text{CO}_2$ , these data were normalized to 10°C, using the algorithm proposed by Copin-Montegut (1988). The results obtained show that the area investigated can be divided into 3 parts in terms of the calculated buffer factor:

–Almost the whole Channel, from 6°W to 1.3°E, is characterized by an excellent linear relationship (line A, Fig. 5) for  $\ln(p\text{CO}_2)$  vs.  $\ln(\text{TCO}_2)$ . The slope,  $\beta$ , is calculated to be 12.9 ( $r^2 = 0.92$ ) during the first transect and 13.1 ( $r^2 = 0.98$ ) during the second (Table 1). These values are very close to the expected theoretical value ( $\beta = 11.6$ , with  $S = 35.3$ ,  $t = 10^\circ\text{C}$ ,  $p\text{CO}_2 = 355$  ppm and  $TALK = 2.35$  meq/kg), calculated assuming that dissolved  $\text{CO}_2$  is the only inorganic species involved in  $\text{CO}_2$  dynamics. This observation clearly indicates that total inorganic carbon variations measured in this area are mainly driven by changes in the dissolved  $\text{CO}_2$  level, e.g. air–sea  $\text{CO}_2$  exchanges and/or organic matter production/degradation, without any associated calcification or calcium carbonate precipitation.

–The area included between 1.3°E and 3°E (line B, Fig. 5), as well as that along the Belgian coast ( $\beta = 5.4$ , line C Fig. 5, longitude  $> 3^\circ\text{E}$ ), yields  $\beta$  values which are lower ( $\beta = 5.8$  and 8.1)

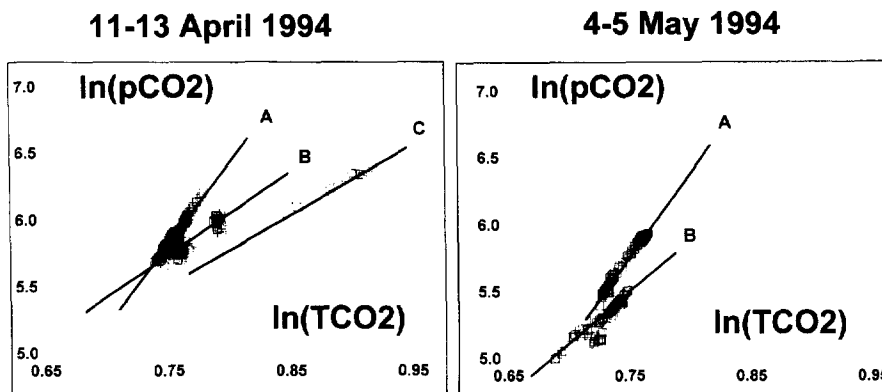


Fig. 5. Plots of  $\ln p\text{CO}_2$  vs.  $\ln \text{TCO}_2$  to obtain the homogeneous buffer factors. Left and right figures correspond respectively to the April and May transects through the Channel. See text and Table 1 for geographical significance of regression lines A, B and C.

during the first transect. The linear correlation coefficients are excellent ( $r^2$ , respectively, equal to 0.78, 0.93 and 0.74). As stated previously, this area is under the influence of riverine inputs from the Seine, Somme and Scheldt. Fig. 2 clearly shows that the normalized alkalinity [ $TALK(35)$ ] starts to increase strongly from about 1.5°E to 3°E indicating an input of water with high dissolved carbonate content. As discussed by several authors (Salomon et al. (1993), Chou and Wollast (1993), Frankignoulle et al., 1995), this observation is probably explained by the fact that Scheldt water, which is high in  $TALK$ , can reach the eastern entry of the Channel. The calculated  $\beta$  values (around 5.5 for the April transect and 8.4 for the transect in May) result from both organic matter production and chemical mixing between seawater and the alkalinity-rich, Scheldt estuarine water. The significantly higher  $\beta$  values obtained in May are probably due to a higher organic production rate, as suggested by oxygen and pH profiles, which tends to mask the input of alkalinity-rich water. This conclusion also suggests that, in spite of the very high calcite oversaturation level observed in May, calcium carbonate is not an important process involved in the  $CO_2$  dynamics.

#### 4. Conclusions

Our data confirm the main chemical and biological features previously obtained in this area of the English Channel. Important spatial and temporal variability in properties induced by both biological production and river input characterizes the area. In our approach, we used the homogeneous buffer factor ( $\beta$ ) to discuss processes responsible for the observed  $CO_2$  distribution. Plotting  $\ln(pCO_2)$  vs.  $\ln(TCO_2)$  yields excellent linear relationships, even in such a complex system, which allow us to divide the region oceanographically on the basis of calculated  $\beta$  values. Nearly the whole Channel is characterized by a  $\beta$  value which is very near the one expected when dissolved  $CO_2$  is the only species involved in  $CO_2$  dynamics (air–sea exchanges, organic production without calcification). The area in-

cluded between 1.3°E and 3°E yields a low  $\beta$  value resulting from both organic production and water mass mixing in the estuarine region.

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