

## 2. Uptake of CO<sub>2</sub> by the North Sea in interaction with plankton blooms

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### Abstract

The processes of uptake and increase of CO<sub>2</sub> in the entire North Sea are investigated by a combination of various field observations and biological-chemical modeling, also providing some assessments of shifts of the chemical composition of seawater.

The project has produced the following major results:

1. observational time series database of CO<sub>2</sub> and plankton distributions and CO<sub>2</sub> air/sea exchange fluxes,
2. observational database of CO<sub>2</sub> datasets collected during dedicated cruises,
3. integrated modeling of North Sea carbon cycle including air/sea CO<sub>2</sub> fluxes, estuarine exchanges, and exchanges with the Atlantic Ocean,
4. annual air/sea CO<sub>2</sub> flux estimates show that the North Sea is a strong net sink for uptake of CO<sub>2</sub> from the atmosphere. The “biological pump” combines with deep waters exchange with the North Atlantic in an overall “continental shelf pump” for drawdown of CO<sub>2</sub> from the atmosphere.

## **i. Problem**

Due to combustion of fossil fuels and some other human activities large amounts of carbondioxide ( $\text{CO}_2$ ) are emitted in the atmosphere. More than half of the extra  $\text{CO}_2$  remains airborne causing a steady increase of the partial pressure of  $\text{CO}_2$  in the atmosphere. Seas and oceans take up another large portion (about 40 %) of the emitted  $\text{CO}_2$ . This uptake is partly by strictly physical-chemical processes, partly by biological fixation in photosynthesis by phytoplankton in the sea. Overall, the pool of dissolved  $\text{CO}_2$  in seawater is increasing and the ensuing shifts in the chemical composition of seawater are a cause of concern with regards to conceivable effects on marine biota. One major shift is a general decrease of the hydroxide ion ( $\text{OH}^-$ ), in other words the seawater becomes less alkaline (Van Santen, 2007; De Baar, 2008).

## **ii. Objectives**

The overall aim is to quantify changes in  $\text{CO}_2$  uptake by the North Sea via plankton blooms by means of field measurements, and to quantify the role of climate change by ecosystem modelling.

## **iii. General Methodology**

This research program on the North Sea carbon cycle is in the fortunate situation to rely on a previously collected comprehensive basinwide data set collected during cruises in four seasons (Thomas et al., 2004, 2005a; Bozec, 2005; Bozec et al., 2005, 2006). The North Sea has been sampled repeatedly in 1-month cruises (8/2001, 11/2001, 2/2002, 5/2002) taking some 23,000 surface water values of  $p\text{CO}_2$  and occupying each time 97 stations for sampling the complete water column for the  $\text{CO}_2$  system and a suite of 20 other parameters. In addition a summer cruise was performed in 2005. All five cruises were aboard RV Pelagia of Royal NIOZ. Two more basinwide summer cruises in summers of 2005 and 2008, integrated simulation modeling of the carbon cycle of the North Sea, and time series observations of atmospheric  $\text{CO}_2$  at a fixed position, all leading to a suite of estimates of the air/sea  $\text{CO}_2$  gas exchange rate.

In all four seasons it was found there is a strong North-South transition in the entire North Sea coinciding with the transition at the Frisian Front from shallow waters (<50 m depth) in the southern part of the North Sea to deeper waters in the northern North Sea. In contrast, the gradients in east-west direction are modest. This distinct transition at the Frisian Front is also comprised in the Netherlands Continental Platform (NCP) jurisdictional part of the North Sea.

The strong North-South trends led us to design a long term multi-year observational program through all seasons along the North-South transect from Bergen (Norway) to IJmuiden (The Netherlands) in a collaborative program between the universities of Bergen (Norway) and Groningen and the Royal NIOZ, with additional subsidy support in context of the EU Integrated project CARBOOCEAN (2005-2009). During several years data was collected of  $p\text{CO}_2$  in sea surface and air by a Voluntary Observing Ship (VOS) the TransCarrier sailing between Bergen (Norway) and IJmuiden (The Netherlands). At the start of the project the TransCarrier had a weekly track with triangular shape from Bergen to IJmuiden to Immingham (England) to Bergen. However sometimes the track was changed and as a result the most continuous long term set of observations is in the North-South direction from Bergen to IJmuiden and back again.

Towards the first interpretation (Omar et al., 2010) of the first three years 2005-2007 this Bergen-IJmuiden transect database of TransCarrier has been combined with data of an East-West VOS line aboard the Nuka Arctica of Royal Arctic Lines with the scientific program of pCO<sub>2</sub> and ancillary measurements by A. Olsen of the University of Bergen. Moreover the pCO<sub>2</sub> and ancillary data of the above mentioned five Pelagia cruises were included, as well as pCO<sub>2</sub> data calculated from some 'ancient' NIOZ cruises in 1987 aboard the vessels Aurelia and Holland.

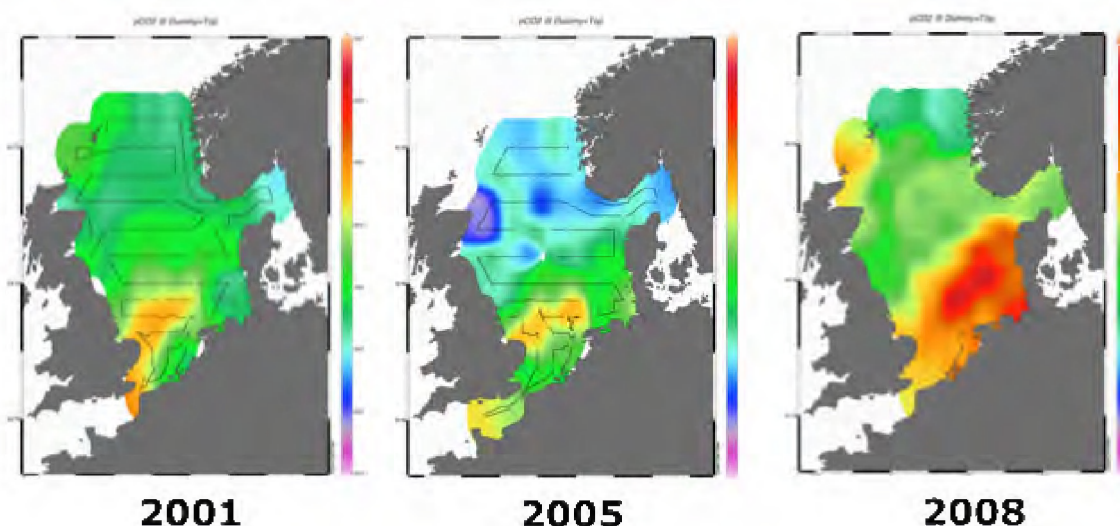
#### **iv. General Results**

By normalization of the pCO<sub>2</sub> as function of the atmospheric pCO<sub>2</sub> in anyone given year, a composite of the pCO<sub>2</sub> trends during every month of the annual cycle was constructed. From this one clearly observes a strong pCO<sub>2</sub> minimum in the spring time due to intensive CO<sub>2</sub> uptake by photosynthesis of phytoplankton. Budget assessments of this biological CO<sub>2</sub> sink term are consistent with the abundance of phytoplankton biomass derived from SEAWIFS satellite observations of chlorophyll color of the sea surface.

Alternatively when looking at the increasing trend of pCO<sub>2</sub> over the years, here also including some very 'ancient' data of 1970, one finds that the pCO<sub>2</sub> in surface waters of the northern North Sea increases with  $61 \pm 33 \cdot 10^{-6}$  atm. over 40 years, more or less tracking the atmospheric CO<sub>2</sub> increase ( $\sim 1.6 \cdot 10^{-6}$  atm/yr observed at Mauna Loa) in agreement also with our recently published community estimate of pCO<sub>2</sub> growth rate in North Atlantic surface waters (Takahashi et al., 2009). This emphasizes that waters originating of the North Atlantic are compatible with the northern North Sea (Thomas et al., 2007). However, this consistency with open Atlantic Ocean trends should not be extrapolated to the shallow southern North Sea (Schiettecatte et al., 2007). Here the Alkalinity effect tends to cause perturbations, this is due to anaerobic alkalinity generation within anoxic sediments notably of the Wadden Sea (Thomas et al., 2009).

#### **Observational database of CO<sub>2</sub> datasets collected during cruises**

The very large and comprehensive database collected aboard of the PELAGIA from 19 August to 11 September 2008 is completed and stored at the central Data Management Group (DMG) of NIOZ. This latest basinwide North Sea dataset continues from previously collected similar large datasets in the summer of 2005 and the summer of 2001, as well as the similar datasets for three other seasons autumn, winter and spring in 2001-2002. When comparing the consecutive summers of 2001, 2005 and 2008 in the below Figure C-2.1 one notices differences between years but also the distinct North-South gradients.

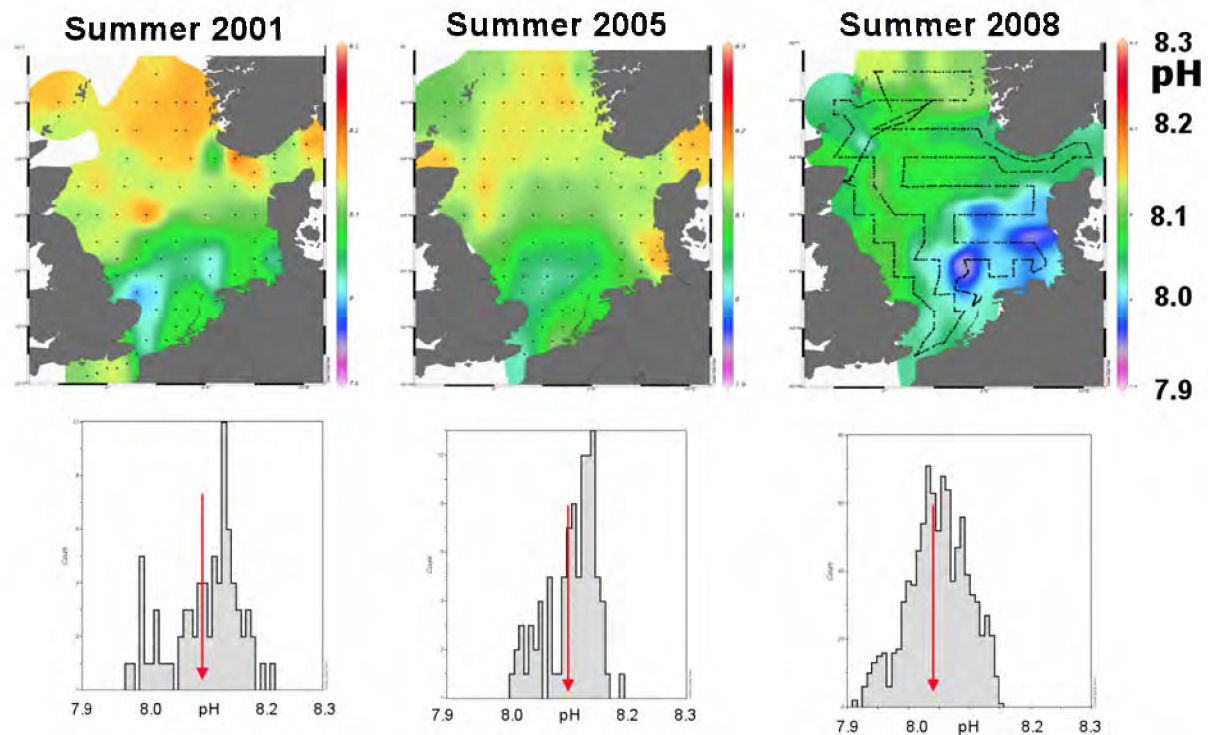


**Fig. C-2.1:** Summer values of delta- $p\text{CO}_2$  in surface waters of the North Sea in years 2001, 2005 and 2008 (Salt et al., 2011).

When comparing the corresponding pH values in surface waters over these same years, there is an observed decrease of pH in the 2001-2005-2008 intervals. This is consistent with but stronger than the predicted world ocean trend of increasing ocean acidification due to uptake of anthropogenic  $\text{CO}_2$  in seawater. The larger pH decrease of 0.06 unit between 2005 and 2008 as compared with 0.01 unit between 2001 and 2005 is in the expected direction because the increasing  $\text{CO}_2$  content is known to cause a decreasing general buffer capacity of seawater. Otherwise the pH trend is stronger than predicted for the open oceans, where the more intense dynamics of biological production and decomposition in coastal seas (Thomas et al., 2004), as well as interactions with estuaries and underlying sediments play a role.

The latest summer cruise in 2008 was an improvement over the previous cruises in the sense that all four measurable parameters  $p\text{CO}_2$ , DIC, pH and Alkalinity of the  $\text{CO}_2$  system in seawater were measured directly. Given the fact that in natural oceanic waters one needs to measure only two distinct parameters and then can calculate the others, one is able to verify internal consistency of the dataset. For example from measured DIC and Alkalinity one may calculate the  $p\text{CO}_2$  value and compare this with the actual measured  $p\text{CO}_2$  value. Having done such systematic intercomparisons of internal consistency we found some intriguing trends. Briefly, in the central northern North Sea there is excellent internal consistency between all four parameters. Quite remarkably when approaching either Britain to the west or Wadden Sea and Kattegat to the east, deviations become apparent. We are currently assessing possible causes. Firstly this may be due to pH calibration issues. Secondly this may partly be due to the Alkalinity effect emanating from shallow sediments (Thomas et al., 2009). Alternatively or complementary the Dissolved Organic Carbon moieties in nearshore waters may also interfere with the inorganic  $\text{CO}_2$  system, notably the determination of the measured Alkalinity values. Thirdly river inflows with variable compositions of dissolved salt content of the river water, may interfere with the general law of constant proportionality of seasalt (Dittmar, 1884) in the oceans. In other words deviations of this Law of Dittmar in coastal waters may, or may not, affect the calculations of the  $\text{CO}_2$  system variables which rely on the measured salinity of the seawater sample as one of the input variables.

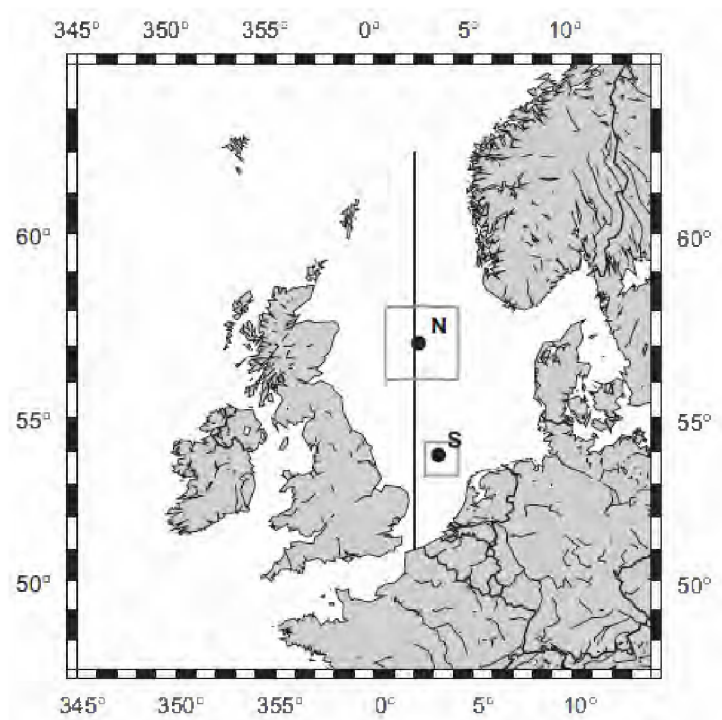
The findings of the summer 2008 cruise have been worked out into three different draft manuscripts by Lesley Salt in context of the preparation of her PhD thesis.



**Fig. C-2.2:** Summer values of pH in surface waters during consecutive summer cruises in 2001, 2005 and 2008. The lower graphs show the ranges of pH values for these same years. The average values of pH are indicated by the red arrows, with a decreasing trend of 0.01 pH unit between 2001 and 2005 and 0.06 pH unit between 2005 and 2008. Given the wide range of pH values in every of the three years, the average decreasing trend is of only modest significance thus far.

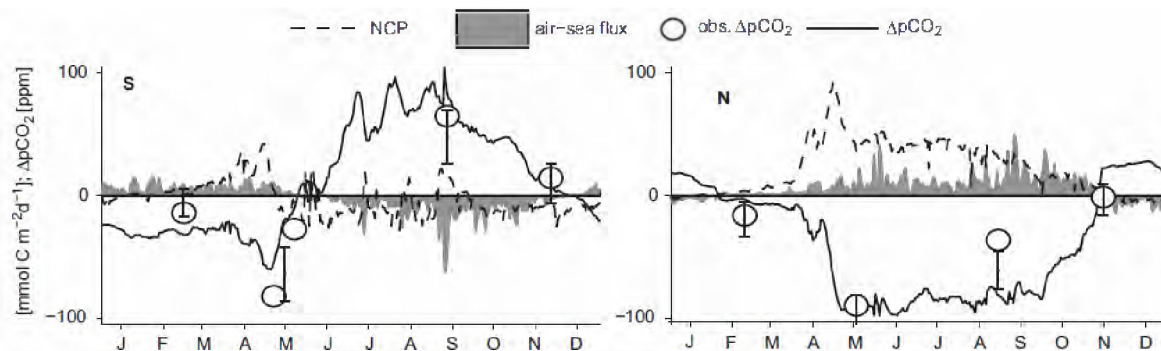
### Integrated modeling of North Sea carbon cycle

The datasets as mentioned above have been utilized as reference framework for basinwide computer simulation modeling of the carbon cycle within the North Sea (Prowe et al., 2009). The modeling integrates the key physical, chemical and biological processes and interactions in the water column extending from the shallow ~50m vertically well-mixed deep southern North Sea and the deeper vertically layered northern North Sea. The mechanisms driving the air–sea exchange of carbondioxide ( $\text{CO}_2$ ) in the North Sea are investigated using the three-dimensional coupled physical–biogeochemical model. We validate our simulations using field data and identify the controls of the air–sea  $\text{CO}_2$  flux for two locations representative for the North Sea’s biogeochemical provinces. In the seasonally stratified northern region, net



**Fig. C-2.3:** Chart of the model domain including the North Sea. Within the model (Prowe et al., 2009) the section along  $2^{\circ}\text{E}$  is used to illustrate the strong north-south trends largely coinciding with the transition from deep northern North Sea to shallow southern North Sea. The regions N and S are used as representative examples of these two regimes in the below Figure C-2.4.

$\text{CO}_2$  uptake is high ( $2.06 \text{ mol.m}^{-2}\text{a}^{-1}$ ) due to high net community production (NCP) in the surface water. Overflow production releasing semi-labile dissolved organic carbon needs to be considered for a realistic simulation of the low dissolved inorganic carbon (DIC) concentrations observed during summer. This biologically driven carbon drawdown overrules the temperature-driven rise in  $\text{CO}_2$  partial pressure ( $p \text{ CO}_2$ ) during the productive season. In contrast, the permanently mixed southern region is a weak net  $\text{CO}_2$  source ( $0.78 \text{ mol.m}^{-2}\text{a}^{-1}$ ). NCP is generally low except for the spring bloom because remineralization parallels primary production. Here, the  $p\text{CO}_2$  appears to be controlled by temperature.



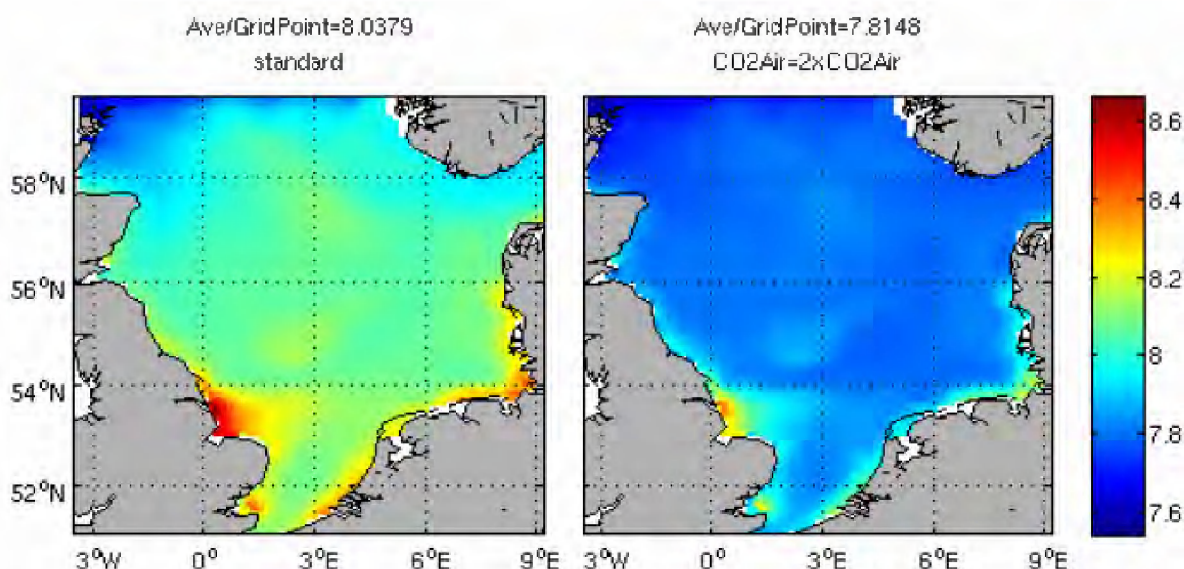
**Fig. C-2.4:** The annual cycle of model-derived air-sea flux of CO<sub>2</sub> based on model-derived delta pCO<sub>2</sub> and Net Community Production (NCP). Also shown is the observed delta pCO<sub>2</sub> throughout the seasons of the year. Left graph is for southern region S in the shallow southern North Sea (see Fig. C-2.3) which is vertically mixed throughout almost the whole year. Right graph is for the northern region N in the deep northern North Sea (see Fig. C-2.3) where in large part of spring-summer-autumn there is strong vertical stratification of surface waters well distinct from deep waters.

### Modelling Climate Change: doubling of the p CO<sub>2</sub> concentration in the atmosphere

The ERSEM-model is applied to forecast the effect of doubling the pCO<sub>2</sub> concentration of the atmosphere on the pH of the North-Sea ecosystem. For the possibility to apply the GETM-ERSEM to model changes with respect to the dynamics of dissolved inorganic carbon (DIC) the following additions are implemented:

- routine which describes the DIC-speciation (CO<sub>2</sub>, HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>) as controlled by Alkalinity, salinity, temperature, nutrients and pH. This routine is public-domain available at <http://www.ipsl.jussieu.fr/OCMIP/phase2/simulations/Abiotic/HOWTO-Abiotic.html>.
- separate routines for the pelagic and benthic systems which describe processes which modify alkalinity such as nitrification, denitrification and anaerobic mineralization, re oxidation of anoxic constituents (e.g. sulphide).
- separate routines for the pelagic and benthic system which describe processes which modify the DIC-dynamics such as light induced primary production, oxic respiration, chemical induced primary production (nitrification) and anoxic respiration.





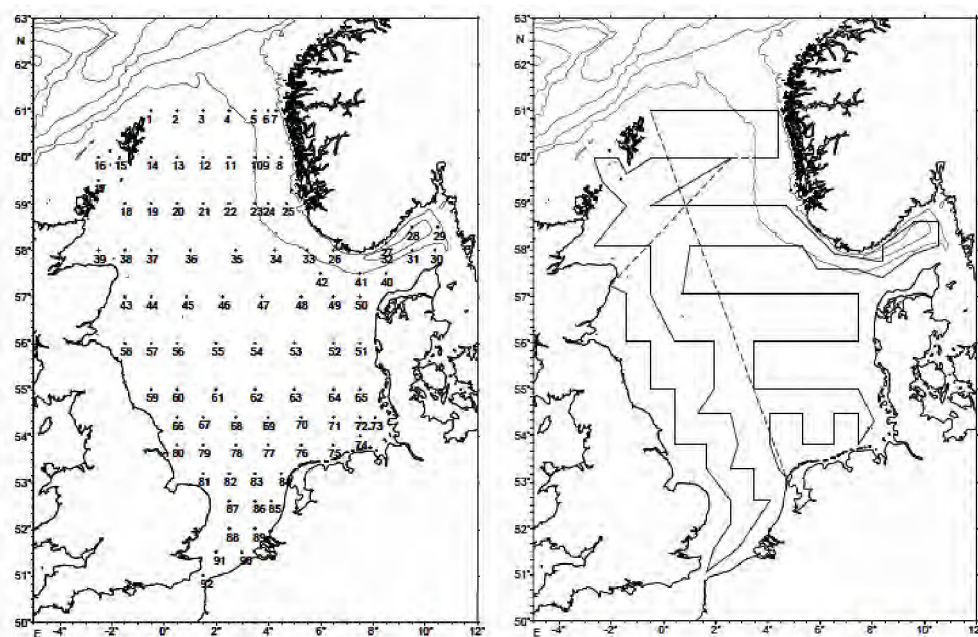
**Fig. C-2.5:** Comparison of two model simulations at modern  $p\text{CO}_2$  and double  $p\text{CO}_2$  in the air expected at about the end of this century (IPCC, 2007). The ensuing annual average values of pH are decreasing but comparatively less than the actually observed average decrease of pH over 3 years time intervals in Figure C-2.3. However the latter observed average decrease is not significant due to the large natural variability in the observed data.

A two-year run is made to verify the consequences of a change of  $\text{CO}_2$  in the atmosphere. In this run only this forcing is changed. It is assumed further that a higher  $\text{CO}_2$  concentration in the water has no direct effect on the primary production. This assumption is based on the fact that the most limiting process in a cell is the transfer of inorganic carbon to organic carbon. The uptake capacity of a cell to take up  $\text{CO}_2$  and/or  $\text{HCO}_3^-$  at the prevailing pH conditions is such that it will not be a controlling factor for the primary production. If we look to the whole North Sea (Fig. C-2.5) and to the pH averaged over the whole year we see a difference of maximally 0.2 units on the pH-scale.

Please notice that in this modeling run the pH is always greater than 7, implying that the seawater is and will remain alkaline, i.e. the major change being a decrease of the  $\text{OH}^-$  ion that however will remain more abundant than its counterpart  $\text{H}^+$  in the well known water equilibrium  $[\text{H}^+][\text{OH}^-]=10^{-14}$ . Thus the seawater will not become acidic ( $[\text{H}^+]>10^{-7}$  hence  $\text{pH}<7$ ) and the popular phrase 'Ocean Acidification' is somewhat of a misnomer.

When comparing the model simulation (Fig. C-2.5) with the observations (Fig. C-2.3) there appear to be discrepancies. Notably the decrease of pH over three years intervals of observations (Fig. C-2.3) is admittedly not significant due to large variability, yet appears much stronger than the model simulation (Fig. C-2.5) would suggest. These inconsistencies are not well understood yet partly ascribed to effects of Alkalinity changes due to interactions of the seawater in the North Sea with the adjacent Wadden Sea (Thomas et al., 2009a) and the biogeochemical reactions in the underlying sediments. These unresolved questions will now be addressed in a new project 'Dynamics of acidification in the North Sea: documentation and attribution' that has started in year 2010.





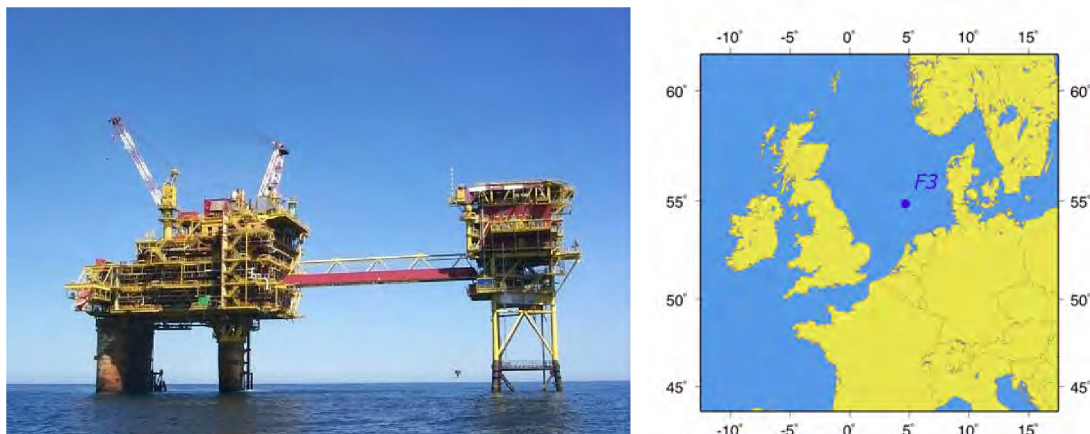
**Fig. C-2.6:** Left is station grid of the summer 2008 cruise, identical to station grids of the preceding cruises in 2001-2002 and 2005. At each station all four variables  $p\text{CO}_2$ , DIC, Alkalinity and pH were determined at 12 depths. Right is the cruise track from station to station in 2008, underway there was semi-continuous measurements of  $p\text{CO}_2$  in surface waters plus ancillary data (S, T, wind velocity). Please refer also to Figures C-2.1 and C-2.2, Salt et al., 2011).

### Annual air/sea $\text{CO}_2$ flux estimates

The flux estimations have been addressed in several ways. Firstly for all the basinwide cruises in four seasons of 2001-2002 and summers of 2005 and 2008 (Fig. C-2.6) large datasets of air/sea  $\text{CO}_2$  gas exchange fluxes have been produced. Underway along the cruise track (Fig. C-2.6, right hand graph) there was semi-continuous measurements of  $p\text{CO}_2$  in surface waters plus ancillary data (S, T, wind velocity). In combination with once every two hours  $p\text{CO}_2$  values in the air this provides an overall about 20,000 data points of delta  $p\text{CO}_2$ . In combination with the air-sea gas exchange coefficient parameterized as function of the measured wind velocity this yields about 20,000 estimates of air/sea  $\text{CO}_2$  gas exchange rates. Similarly datasets of about 20,000 values of air/sea gas exchange rates are available for the previous five cruises in four seasons of 2001-2002 and summer 2005. One is aware that the empirical parameterization of  $\text{CO}_2$  gas exchange rate coefficient as function of wind velocity is not perfect, therefore we are also working on a more direct quantification by eddy correlation (Zemmelink et al., 2009).

Secondly we obtained atmospheric time series observations at the F3 Platform (Luijkx et al., 2009; Van der Laan-Luijkx, 2010). This atmospheric measurement site F3 (Fig. C-2.7) is situated ( $54^\circ 51' \text{N}$ ,  $4^\circ 44' \text{E}$ ) in the central North Sea, close to cruise station 63 (Fig. C-2.6 left graph). The closest land (The Netherlands) is located 200 km away from the measurement station. It is therefore an ideal location for measuring atmospheric background concentrations and studying air-sea interaction of  $\text{CO}_2$  and partitioning of  $\text{CO}_2$  emissions between the land biosphere and oceans. The data from this measurement station are a valuable contribution to the existing European data sets of atmospheric  $\text{O}_2$  and  $\text{CO}_2$ , since only few atmospheric measurements

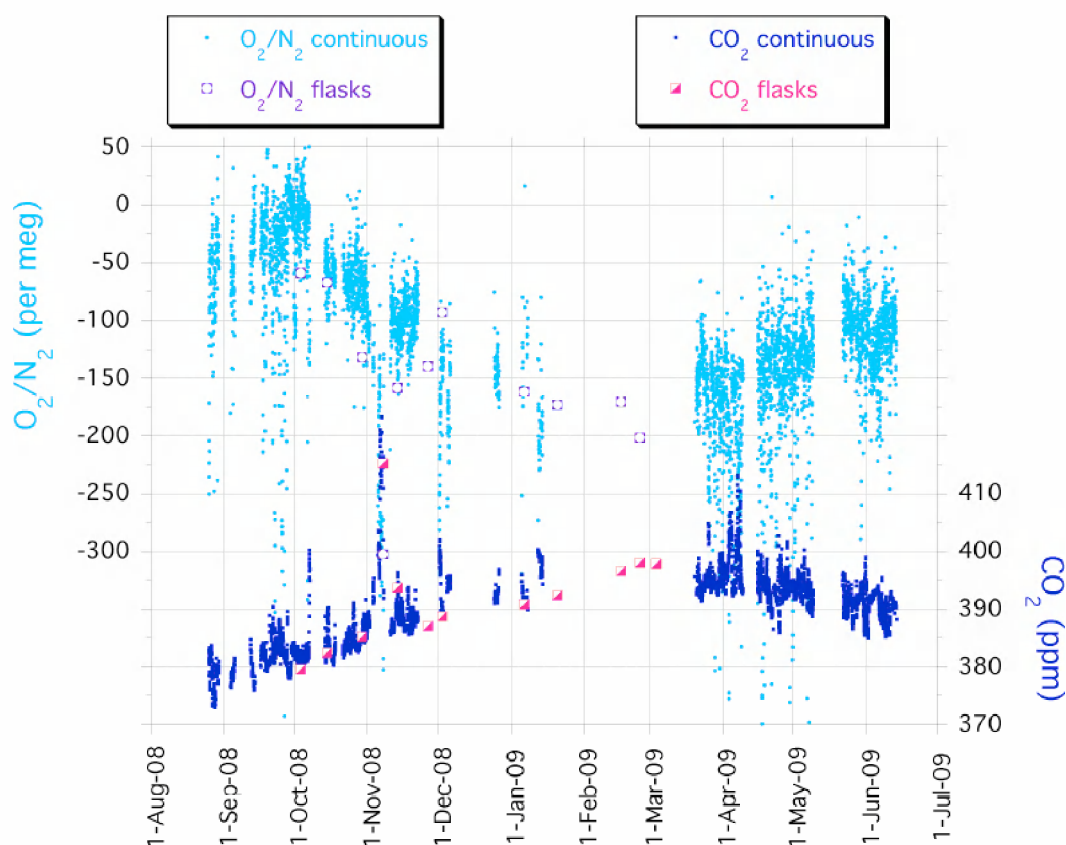
stations exist that are equipped to measure atmospheric  $O_2$  continuously. Moreover, this station is the first sea based atmospheric measurement station with on-site continuous  $O_2$  and  $CO_2$  measurements.



**Fig. C-2.7:** The F3 platform (left graph) consisting of the larger actual production platform and the smaller accomodation platform, and its location (right graph) in the central North Sea.

As the prevailing wind direction is south-west, potential leakages or fires are blown away from the accommodation platform. The ideal situation for atmospheric measurements is therefore on the south-west corner of the accommodation platform. This is where the air-inlet of the measurement system is situated. The air inlet is on the topmost deck, which is around 50 meters above sea level.

Next to the atmospheric  $pCO_2$  values, the additional data of atmospheric  $O_2/N_2$  ratio values and trends does provide fundamental constraints to discriminate the  $CO_2$  exchange between the air and on the one hand the sea and on the other hand the land (Van der Laan-Luijkx, 2010). The continuous measurements for delta  $O_2/N_2$  and  $CO_2$  have been started at the end of August 2008. Flask samples have been collected on a weekly basis, generally during well-mixed atmospheric conditions and preferred wind direction, i.e. between south and west. Figure C-2.8 shows the combined first data from the F3 platform for continuous and flask measurements between August 2008 and June 2009. Although the measurements do not yet cover an entire year, the amplitude of the seasonal cycle can be estimated. In this section only the peak-trough difference will be discussed, which we call the amplitude in the rest of the text. The seasonal amplitude for  $CO_2$  is about 16 ppm. For delta  $O_2/N_2$  a single harmonic fit of the data yields an amplitude of about 110 per meg. When looking at the data however, this is likely to be too small, and an estimate by the eye would produce about 150 per meg.



**Fig. C-2.8:** Observations at the F3 platform for the period August 2008 through June 2009. The continuous measurements of delta  $O_2/N_2$  (small light circles) and  $CO_2$  (small dark squares) were performed with the Oxzilla/CarboCap setup as described by Van der Laan-Luijkx (2010). The data points are half-hourly averages and include all measurements. Also shown are measurements of flask samples (open symbols). Both y-axes have been adjusted so that their ranges are nearly the same on a molar basis. Although the measurements do not yet cover an entire year, the amplitude of the seasonal cycle of delta  $O_2/N_2$  can be estimated. The seasonal amplitudes are about 150 per meg for delta  $O_2/N_2$  and 16 ppm for  $CO_2$ .

For  $CO_2$  the seasonal amplitude compares well to the marine boundary layer reference from the same latitude from the GLOBALVIEW- $CO_2$  (2008) database with an amplitude of 15 ppm. Both  $O_2$  and  $CO_2$  amplitudes can be compared to the observations at other stations at similar latitudes. For station Lutjewad (53°24'N, 6°21'E) at the coast of the WaddenSea in the Netherlands the seasonal amplitude of  $CO_2$  is 14 ppm (Van der Laan-Luijkx, 2010). This value is based on continuous measurements. For both Lutjewad and Mace Head, Ireland (53°20'N, 9°54'W), flask data show a seasonal amplitude of 153 and 102 per meg for delta  $O_2/N_2$  and 16 and 14 ppm for  $CO_2$  respectively.

Thirdly in the simulation model by Prowe et al. (2009) as illustrated in the above Figure C-2.4 we have estimated the annual cycle of the air/sea  $CO_2$  gas exchange in the North Sea. As shown the validity of the modeling simulation derived delta p $CO_2$  is verified versus the observed delta p $CO_2$  in the cruises.

In summary there is the combination of three distinct approaches to assess air/sea gas exchange of CO<sub>2</sub> in the North Sea:

- (i) large datasets of gas exchange rates obtained from shipboard measurements of delta pCO<sub>2</sub> and wind velocity in the context of thus far six basinwide cruises;
- (ii) annual cycle dataset of atmospheric CO<sub>2</sub> and delta O<sub>2</sub>/N<sub>2</sub> at F3 platform from which the CO<sub>2</sub> exchange between air and sea or land respectively, is assessed;
- (iii) integrated simulation modeling of the carbon cycle in the North Sea including estimates of the air/sea exchange rate in the seasons.

## **v. Future Work**

The research is continued with a new granted project entitled 'Dynamics of acidification in the North Sea: documentation and attribution. This will comprise the next summer survey cruise scheduled in September 2011, as a continuation of the once every three years summer cruises in 2002, 2005 and 2008. By comparison over these 3-years intervals we observe increasing CO<sub>2</sub> contents of the seawater and related chemical changes. Moreover additional focus will be on exchanges with surface sediments and the adjacent intertidal Wadden Sea, notably towards assessing perceived changes of Alkalinity in the water column of the North Sea.

## **vi. Acknowledgements**

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- Netherlands LOICZ Program, Focus III 'Carbon and other cycles in the coastal zone'; grant entitled: 'Budgeting of carbon and related nutrient pools and fluxes in the North Sea employing a coupled hydrodynamic ecosystem model' (2002-2005; ALW/NWO project number 014.27.001)
- two grant entitled: 'The continental shelf pump; a pilot study in the North Sea' (2001-2005; ALW/NWO project number 810.33.004 and 810.33.007)
- grant entitled: 'CO<sub>2</sub> Buffering Capacity of the North Sea' (2008-2012; ALW/NWO project number 817.01.004);
- investment grant entitled: 'Observation Facility of the Oceans in a High-CO<sub>2</sub> World' (2005; ALW/NWO project number 834.05.005);
- grant entitled 'Dynamics of acidification in the North Sea: documentation and attribution' (2010-2013; ALW/NWO ZKO NorthSea project number 839.10.500)
- the EU CARBOCEAN Integrated Project ([www.carbocean.org](http://www.carbocean.org)) in 2005-2009 with subsidy support to Royal NIOZ and to University of Groningen;
- the subsidy of the 'Klimaat voor Ruimte' program ([http://www.senternovem.nl/bsik/projecten/hoogwaardig\\_ruimtegebruik/klimaat\\_voor\\_ruimte.aspBSIK](http://www.senternovem.nl/bsik/projecten/hoogwaardig_ruimtegebruik/klimaat_voor_ruimte.aspBSIK)); subproject Climate related shifts in the Netherlands Continental Platform ecosystem, and consequences for future spatial planning.

- the company SeaTrans AS for availability of the commercial vessel Transcarrier as a Voluntary Observing Ship platform;
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