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The carbonate system in the North Sea: Sensitivity and model validation

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ABSTRACT

The ocean plays an important role in regulating the climate, acting as a sink for carbon dioxide, perturbing the carbonate system and resulting in a slow decrease of seawater pH.

Understanding the dynamics of the carbonate system in shelf sea regions is necessary to evaluate the impact of Ocean Acidification (OA) in these societally important ecosystems. Complex hydrodynamic and ecosystem coupled models provide a method of capturing the significant heterogeneity of these areas. However rigorous validation is essential to properly assess the reliability of such models. The coupled model POLCOMS–ERSEM has been implemented in the North Western European shelf with a new parameterization for alkalinity explicitly accounting for riverine inputs and the influence of biological processes. The model has been validated in a like with like comparison with North Sea data from the CANOBA dataset. The model shows good to reasonable agreement for the principal variables, physical (temperature and salinity), biogeochemical (nutrients) and carbonate system (dissolved inorganic carbon and total alkalinity), but simulation of the derived variables, pH and pCO_2, are not yet fully satisfactory. This high uncertainty is attributed mostly to riverine forcing and primary production. This study suggests that the model is a useful tool to provide information on Ocean Acidification scenarios, but uncertainty on pH and pCO_2 needs to be reduced, particularly when impacts of OA on ecosystem functions are included in the model systems.

1. Introduction

In the last 10 years a significant body of marine and climate research has shown that the increase in atmospheric CO_2 concentration is causing not only the well-known phenomenon of global warming, but is also leading to a change in the oceanic carbonate system termed Ocean Acidification (OA) resulting in, amongst other changes, a decrease of pH (Caldeira and Wickett, 2003).

Oceans are indeed a significant sink for anthropogenic CO_2, having absorbed about 48% of the anthropogenic emissions throughout the industrial era (Sabine et al., 2004) and will continue to absorb a significant proportion of future emissions. Adding CO_2 to seawater disrupts the carbonate system, leading to an increase in free CO_2/carbonic acid and the bicarbonate ion concentration while decreasing the carbonate ion, pH and carbonate saturation states (Zeebe and Wolf-Gradow, 2001). All of these have implications for a range of biological and chemical processes like calcification, primary production and reproduction (Blackford, 2010; Doney et al., 2009; Fabry et al., 2008; Pörtner, 2008; Society, 2005). This general trend predicted by chemical models has been confirmed by several long term observational data sets such as the Hawaiian Ocean Time series (HOT/ALOHA, Dore et al., 2009), the Bermuda Atlantic Time series Studies (BATS, Bates, 2007) and the European Station for Time Series in the Ocean (ESTOC, Santana-Casiano et al., 2007) where a consistent decrease of about 0.02 pH units in the last 20 years has been observed.

Several models have been implemented to forecast the future state of the carbonate system under different emission scenarios (Feely et al., 2009; Orr et al., 2005): depending on the scenarios and the structure of the model, they consistently predict a decrease of surface pH on the global ocean of about 0.3–0.4 pH units by 2100, corresponding to a decrease of about 40–50% of carbonate ions in the seawater. Global oceanic models show significant spatial variability with the Polar regions, in particular the Arctic, exhibiting more vulnerability because of temperature effects (Steinacher et al., 2009).

Even higher spatial and temporal variability can be observed in shelf seas and reef systems (Blackford and Gilbert, 2007; Santos et al., 2010; Thomas et al., 2004) as a result of several concurrent processes. Primary productivity is often high in these areas leading to a large drawdown of dissolved inorganic carbon (DIC, the sum of CO_2, bicarbonate and carbonate ions) and consequent rise of pH (Thomas et al., 2005). Due to the shallow depth, benthic processes can also significantly affect the pelagic carbon cycle and alkalinity (Thomas et al.,

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2009). Finally terrestrial inputs, in particular from rivers, can inject significant loads of DIC and total alkalinity (TA) into coastal systems strongly driving the carbonate system (Borges and Gypens, 2010; Gypens et al., 2011).

Simulating all these processes in requisite detail in a biogeochemical model is a significant challenge and requires a relatively complex coupled hydrodynamic–ecosystem–carbonate model.

Given the high variability in the physical, chemical and biological dynamics of the shelf seas and the relative complexity of these models, it is particularly important to rigorously validate such a model to prove the ability to reproduce the major patterns of variability if not the exact values of the different variables. Such validation is needed before using the model to forecast future scenarios in order to quantify and attribute the sources of uncertainty in such simulations.

Validation of complex ecosystem models is a non-trivial task. The first limitation is data availability: validating a complex ecosystem model on a large domain (like the North-Western European Shelf) requires a set of seasonal vertically resolved profiles of physical, chemical and biological variables covering the geographical extent of the whole domain. These datasets should cover an annual cycle to check the ability of the model to reproduce seasonal dynamics, several years to assess the reproduction of interannual variability and decadal scales to assess the presence of long term trends. Unfortunately no dataset meets all of these criteria, with a general trade-off between frequency and spatial coverage, while long term data is extremely rare. Merging the databases from different sampling programmes is not necessarily straightforward because of the mismatch in the type of variable measured, the analytical methods used and observational accuracy.

A second important limit is the spatial and temporal scale mismatch. Observed data are representative of a portion of water surrounding the few litres sampled whose dimension depends on the characteristic length scale of the local turbulent process. Oceanic models have a much more coarse spatial resolution and their output usually consists of temporal averages at daily time scale or longer.

A third issue, specific for the carbonate system, is the potential for mismatch between the generally accepted theoretical derivations of the carbonate system as used in models (e.g. Robbins et al. (2010)) and ‘over-constrained’ observational data sets. Four variables of the carbonate system are determinable in natural systems: DIC, TA, pH and pCO_2. Theoretically, knowledge of any pair allows the derivation of the other members. However over-constrained carbonate system data sets have shown significant discrepancies when observed values have been compared with derived values calculated from a subset of the measured variables (Dickson and Millero, 1987; Hoppe et al., 2010; McElligott et al., 1998; Millero et al., 2002). Consequently, for example, pH derived from observed DIC and TA may differ significantly from directly observed pH. The reason for this mismatch is undefined, potentially residing on the theoretical calculations of the equilibrium constants, observational inaccuracy or a conceptual understanding, in particular of alkalinity (Kim and Lee, 2009). This places limitations on the skill achievable by a model. The model system uses DIC and TA as its ‘master’ carbonate system variables; these are the only two available for dynamic models. The pair of master variables determines the minimum uncertainty achievable in the estimate of the derived carbonate system variables. With this choice, the uncertainty in pH and pCO_2 estimates will be larger than with other pairs (Millero et al., 1993), while estimates of carbonate ion concentration (and then saturation state) will be more precise (Dickson, 2010).

In this work, we assess the skill of an improved version of the coupled hydrodynamic–ecosystem–carbonate system model POLCOMS–ERSEM (Blackford et al., 2004; Holt and James, 2001) in comparison to the CANOBA dataset (Thomas et al., 2004) which provides a seasonally, spatially and vertically resolved data set of the key carbonate system variables over one annual cycle.

Initially we analyse the consistency of the observed carbonate system with theoretical derivations of the carbonate system. This provides an estimate of the observational uncertainty and the limitations on model accuracy. Secondly, an improved dynamic alkalinity module is presented. Compared to earlier versions (Blackford and Gilbert, 2007), riverine alkalinity is now explicitly taken into account as well as the influence of ERSEM's biological processes on alkalinity. The new model is used to simulate the North-Western European Shelf over the period 2001–2002, concurrent with observations. The validation of the main biogeochemical variables is shown, with a particular focus on the carbonate system. The error in the modelled carbonate system is analysed where possible identifying the processes responsible for the inaccuracy. Finally some suggestions are provided for further model improvement and on how to reduce the uncertainty in the carbonate system, in particular when projecting the state of the carbonate system under future climate scenarios.

2. Materials and methods

2.1. Data source, analysis and uncertainty

The CANOBA project (CArbon and nutrient cycling in the NOrth Sea and the BAltic Sea) provided a comprehensive dataset ideal for 3D model validation over a seasonal cycle. It includes vertically resolved measures of physical (Temperature, Salinity) and chemical (Nutrients, dissolved oxygen, DIC, TA and pH) variables repeated seasonally in a set of stations spread over the entire North Sea from summer 2001 to spring 2002. Partial pressure of CO_2 has been measured with an underway system sampling water every minute during all four cruises. The uncertainty associated with the carbonate system parameter measurements is significantly lower than 0.5% ($\varepsilon_{DIC} = 3$ mmol kg^{-1}, $\varepsilon_{TA} = 1.5$ μmol kg^{-1}, $\varepsilon_{pCO2} = 1$μatm (Thomas et al., 2007).

To assess the magnitude of the discrepancies between the CANOBA dataset and theoretical calculations, pH and pCO_2 have been calculated from the observed TA and DIC and compared with the observed value: this also provides a reference value for the model validation metrics. Additionally, the sensitivity of the derived variables to DIC and TA has been tested by analysing how the calculated pH and pCO_2 vary in response to changes in DIC or TA starting from a reference point ($T = 15$ °C, $S = 35$ PSU, DIC = 2100 μmol kg^{-1}, TA = 2350 μmol kg^{-1}). This provides a useful insight to interpret the model validation.

All the calculations to solve the carbonate system from observed data have been made using the CO2sys software (Lewis and Wallace, 1998), following OCMIP recommendations for the set of constants, i.e. using the Weiss (1974) formulation of Henry's constant for CO_2, the dissociation constants for carbonic acid defined by Millero (1995) using the refit of Mehrbach et al. (1973), and the borate dissociation constant from Millero (1995) using data from Dickson (1990). This is consistent with the scheme used within the dynamic model, except that here pH is expressed in the total scale for consistency with the dataset.

2.2. Model description

The model used is the coupled hydrodynamic–ecosystem model POLCOMS–ERSEM.

POLCOMS is a 3D baroclinic circulation model (Holt and James, 2001; Proctor and James, 1996). It is a primitive equation finite difference model using the “Piecewise Parabolic Method” advection scheme and the Mellor–Yamada level 2.5 turbulence closure to calculate viscosity and diffusivities. The model domain (Fig. 1) spans from 40°N to 65°N and from 20°W to 13°E, with a horizontal resolution of approximately 12 km and depth resolved into 42 s-coordinate layers. The model is forced by ERA40 meteorological data, and the model uses simulations from a 1 degree global ocean reanalysis (Smith and Haines, 2009) as boundary conditions. See Holt et al. (2009) and Wakelin et al. (2009) for further details of this configuration and its forcing. Light