Validation of a marine primary production model for the North Sea using in-situ data

First steps towards recalibration of the 3D ecological model GEM

MSc Thesis

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Abstract

Over the last century, the North Sea experiences eutrophication in its coastal zones due to elevated nutrient loads from rivers (Neal et al. 2000). In several studies, observed changes in phytoplankton biomass in the North Sea have been coupled to an increase in anthropogenic nutrient loadings (Vermaat et al. 2008; Los et al. 2008; Blauw et al. 2010). Elevated phytoplankton primary production rates can locally lead to harmful situations such as a rapid increase of a phytoplankton population, called a ‘bloom’ (Peperzak and Poelman, 2008). The link between nutrients and phytoplankton primary production rates is not always straightforward. Especially in coastal waters, modelling of ecosystems provide a challenge in terms of physics, biogeochemistry and ecology as large fluctuations and strong spatial gradients exist in the salinity, suspended matter concentrations, nutrient concentrations and phytoplankton biomass. Computer models prove a valuable tool to further examine the driving forces of phytoplankton growth in the North Sea. In this study, validation results of a Generic Ecological Model (GEM) with regard to the prediction of phytoplankton growth and nitrate, phosphate and silicate concentrations in the North Sea are presented. Up till present, mainly measurements from the Dutch water authority Rijkswaterstaat were used for the validation and calibration of GEM, focussing on the prediction of nutrient and chlorophyll-a concentrations in the Dutch Exclusive Economic Zone (EEZ). It is not known how GEM performs when tested using a larger dataset, covering the entire North Sea. Possible causes of errors in modelled nutrient concentrations are identified and suggestions for the improvement of model fit in the Dutch EEZ are given. The GEM model shows a negative bias of modelled chlorophyll-a concentrations with respect to observations in most regions of the North Sea. In the Dutch EEZ, this is because the initialisation of the spring bloom is predicted 2-4 weeks too late. This can be due the fact that the residual flow through the Strait of Dover is being underestimated, leading to high concentrations of DOC in the Dutch coastal zone. Nutrient concentrations are generally being overestimated, which is likely to be partly due to an underestimation of the residual flow through the Strait of Dover. Modelled nutrient concentrations can be improved by recalibration several parameters related to biochemical processes. The sensitivity of the model to the parameters is strongly region dependent. Therefore, they would need to be adjusted regionally. Generally, the model is most sensitive to sediment related parameters in coastal regions and to water column related parameters in offshore regions.

Preface

This thesis has been submitted to the Faculty of Geosciences at Utrecht University in partial fulfilment of the requirements for the degree Master of Science in Sustainable Development (specialization: Integrated Coastal Zone Management).

The study was done at Deltares, an institute for applied research in the field of water, subsurface and infrastructure. The thesis was part of the COBIOS project that aims to integrate satellite products and ecological models into an operational information service on high biomass blooms in Europe's coastal waters, and the VECTORS project, that aims to improve our understanding of how environmental and anthropogenic factors are impacting marine ecosystems now and how they will do so in the future.

It was a pleasure to perform this research at Deltares. I'd like to thank Ghada El Serafy, Willem Stolte and Hans Los for their support and useful feedback. Many thanks also to Ghada El Serafy for providing me the opportunity to present and discuss my work at the 45th International Liege Colloquium on Ocean Dynamics. Furthermore, I'd like to express my gratitude to Maarten Eppinga for his help in structuring the research and critical analysis. Also, I'd like to thank Sandra Gaytan Aguilar for her technical support. Lastly, I'd like to express my gratitude to Dana Stuparu for her support, and the other students at Deltares who made my stay very pleasant.

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1 Introduction

1.1 Background and relevance

Over the last century, the North Sea experiences eutrophication in its coastal zones originating from elevated riverine nutrient loads (Neal et al. 2000). In several studies, observed changes in phytoplankton biomass in the North Sea have been coupled to anthropogenic nutrient loadings (Vermaat et al. 2008; Los et al. 2008; Blauw et al. 2010). Elevated primary production rates can locally lead to harmful situations such as the occurrence of phytoplankton blooms, a rapid increase of a phytoplankton population (Peperzak and Poelman, 2008). The effects of phytoplankton blooms range from nuisance to beach recreation caused by foam accumulation or toxicity of the phytoplankton, to shellfish and fish mortality due to local oxygen depletion in so called 'dead zones' (Peperzak and Poelman, 2008). In the latter case, the blooms are considered harmful algal blooms (HABs) (Peperzak, 2003). Not only in the North Sea, but worldwide phytoplankton blooms cause substantial ecological and economic damage to marine systems (Paerl and Huisman, 2008).

In the period 1930-1980 riverine nutrient inputs in the North Sea have increased significantly, which can be attributed to the introduction of fertilizers (De Jonge et al. 2002). In the 1990's, policy measures to reduce domestic and industrial point sources of nitrogen and phosphorus came into effect, which led to a reduction of North Sea nutrient loadings (Vermaat et al. 2008). As a consequence, in the period 1985-2000 phosphate loads of the German and Danish rivers flowing into the North Sea were halved and nitrate loads were reduced by 40% (OSPAR Commission 2003b). In the Marsdiep tidal inlet, phosphate concentrations have also decreased since the 1980's. However, in the year 2000 nitrate concentrations were still twice as high as they were in the 1970's. After the 1990's algal growth has slightly decreased in the area, indicating that the North Sea is becoming less eutrophic (Cadée et al. 2002).

Computer models prove a valuable tool to examine the driving forces of phytoplankton growth in the North Sea, as they take many of the factors on which the occurrence of phytoplankton growth may depend into account and allow for a large scale analysis. These models vary in their grid resolution and complexity with regard to the description of water quality and ecological processes (Skogen and Soiland, 1998; Allen et al. 2001; Luyten et al. 1999; Lancelot et al. 1995, 2000, 2005; Lacroix et al. 2007). In most models a set of differential equations is solved, in which phytoplankton growth is dependent on resource availability. In this study a Generic Ecological Model (GEM) is used to model primary production in the Southern North Sea. The GEM model has originally been developed at Deltares, a research institute in the Netherlands, and has been under constant development over the past 20 years (Los et al. 2008; Los et al. 2010).

Clearly, the link between nutrient concentrations and phytoplankton primary production rates is not always straightforward. Especially in coastal waters, modelling of ecosystems provide a challenge in terms of physics, biogeochemistry and ecology. Large fluctuations and strong spatial gradients exist in salinity, suspended matter concentrations, nutrient concentrations and phytoplankton biomass. These fluctuations, along with benthic-pelagic interactions and light attenuation have proven to be difficult to replicate in models (Blauw et al. 2009). Given the complexity of the system and the importance of nutrients for primary production rates, further analysis of the mechanisms determining nutrient concentrations in the entire North Sea is required. As growing anthropogenic stress on coastal ecosystems exists and as legislative agreements demand to control and reduce undesirable ecosystem changes, the GEM model can provide a powerful tool to increase our knowledge of the dynamics and driving forces of coastal ecosystems. The study is therefore closely linked to one of the key research themes of the Copernicus Institute: gaining insight into how ecosystem components are affected by human induced changes, how those components interact and why this is important for sustainability.

1.2 Problem definition

Up till present, mainly measurements from the Dutch water authority Rijkswaterstaat were used for the validation and calibration of GEM, focussing on the prediction of nutrient and chlorophyll-a concentrations in the Dutch Exclusive Economic Zone (EEZ). It is not known how GEM performs when tested using a larger dataset in which data from different sources are combined, covering the entire North Sea. Furthermore, the study is performed using a new version of the model that contains updates regarding the precision of the model and biochemical process formulations.
In this study, several datasets that cover a large part of the North Sea will be used to validate modelled nutrient and chlorophyll-a concentrations in GEM for the period 2003-2007. Subsequently, possible causes of errors in modelled nutrient concentrations will be identified. These causes can be related to different factors, including hydrodynamics, loadings and boundary settings and biochemical processes. Subsequently, possible improvements in hydrodynamics, loadings and boundary settings and biochemical process parameters will be identified and tested. To summarize, to following questions will be answered:

-How well does GEM predict nutrient and chlorophyll-a concentrations with respect to in situ measurements in different regions of the North Sea for the period 2003-2007?

-Are observed errors in modelled nutrient concentrations with respect to in situ measurements due to errors in hydrodynamics, loadings and boundary settings or model processes?

-How can modelled nutrient concentrations in the North Sea most effectively be improved?

2 Methodology

In order to evaluate model performance of an ecological model of the North Sea and identify possible errors, it is necessary to have basic knowledge of the hydrography of the North Sea. In section 2.1.1 a brief description of the hydrography of the North Sea is provided. In addition, more detailed knowledge is required in the nutrient chemistry of the North Sea and nutrient cycling within the ecosystem. An overview of the biological and chemical processes that determine nutrient concentrations present in the water column is given in section 2.1.2.
An overview of the translation of these processes as they occur in reality to the GEM model is provided in section 2.2. A description of the datasets used for model validation is given in section 2.3, including an analysis of possible differences between the datasets due to, for example, measurement techniques. In section 2.4 a plan of analysis is provided, followed by a description of the statistical methods applied in section 2.5.

2.1 The North Sea

The North Sea is a dynamic coastal sea where different physical, biochemical and ecological factors play a role in determining nutrient concentrations present. In this section a brief overview is provided of the hydrography and nutrient chemistry of the North Sea.

2.1.1 Hydrography

The North Sea is a shallow shelf area, which widens and deepens from approximately 30 m in the south towards 200 m in the northwest (Otto et al. 1990). The water budget of the North Sea is mainly determined by water in- and outflow from the North Atlantic. The hydrodynamics are being dominated by the tidal motion, which is among other factors responsible for the anti-clockwise residual current entering the North Sea at its northern boundary (Otto et al. 1990). By winds and tides the water column remains well mixed in the shallow eastern part of the North Sea throughout the entire year (Van Beusekom et al. 2009). Parts of the central and northern North Sea regularly become temperature stratified in summer. In the coastal regions, periods with high river outflow may lead to a density gradient in the water column, called salinity stratification (Otto et al. 1990). The tidal current restricts the northward flow of the continental long shore current. Therefore, riverine influence is highest along the south eastern coast. In the central and northern part of the North Sea, water masses mainly consist of water from the Atlantic Ocean (Los et al. in prep).

2.1.2 Nutrient chemistry

External nutrient loads

Nutrients enter the North Sea through the English Channel, the North Atlantic, rivers and atmospheric deposition. The North Atlantic inflow contributes 70-75% of the nitrogen and 81-82% of the phosphorus loads to the North Sea. The residual current originating from the North Atlantic that enters the North Sea at its northern boundary is nutrient-depleted in the surface layer in summer, while nutrient concentrations in the deeper layers are much higher (Brockmann et al., 1990). The contribution of the English Channel remains to be investigated; total nitrogen loads were estimated by Brockmann et al. (1990) to be 5-8% and the phosphorus loads 5-6%, whereas Sydow et al. (1990) estimated these percentages to be twice as high. Rivers comprise 12-17% of the total nitrogen load and 8-11% of the total phosphorus load to the North Sea. In the continental coastal waters the contribution of the English Channel and rivers is dominating (Peeters et al. 1993). The contribution of atmospheric deposition to nutrient loads of the North Sea is small for all nutrients except nitrogen (Prospero et al. 1996). No exact numbers were found in literature.

River loads vary depending on the season, being highest in winter and lowest in summer when nutrient uptake by phytoplankton is eminent. Phosphorus concentrations fluctuate the least, silicate concentrations the most and nitrate concentrations are considered to be intermediate (Figure 1) (Klein & van Buuren, 1992). In spring and summer, silicate concentrations are low due to low river discharges during that period and uptake of silicate by freshwater diatoms in the river basins. Silicate concentrations can be fully depleted by diatoms, as nitrogen and phosphorus concentrations are generally high in the river basins that flow into the North Sea (Peeters et al. 1993).

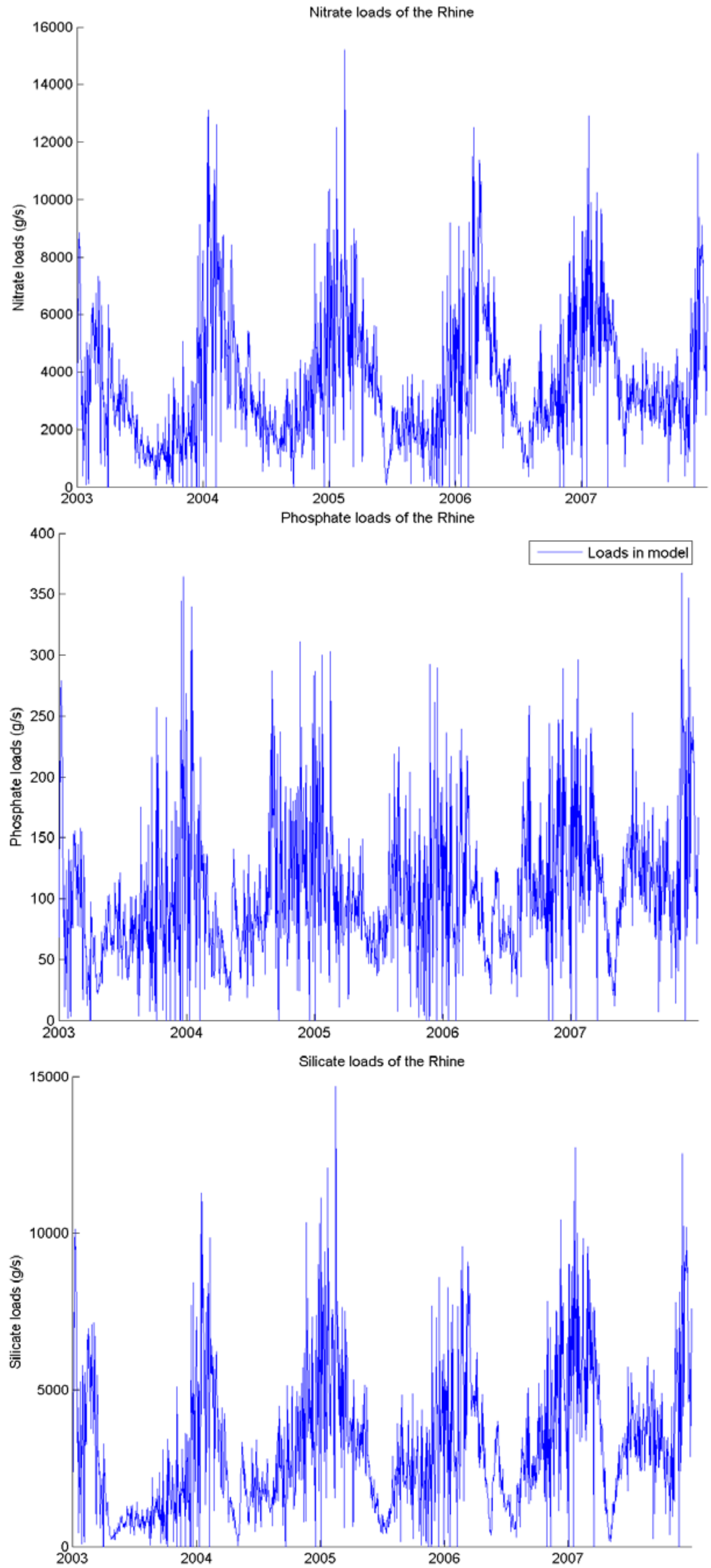


Figure 1. Nitrate, phosphate and silicate loads of the Rhine to the North Sea for the period 2003-2007.

The role of nutrients in the North Sea ecosystem

Generally, nutrient concentrations are lowest in the central North Sea and show an increasing gradient towards the continental coast, due to a higher influence of nutrient-rich river water (Figure 2) (Van Beusekom et al. 2009).

In spring, nutrient concentrations mainly decline due to uptake by phytoplankton. Phytoplankton growth starts to increase quickly as soon as light availability reaches a critical level, inducing a spring bloom. These blooms can occur already in January or February in areas off the Dutch west coast or on the Dogger Bank in the central North Sea, where the turbidity of the water is relatively low. In the coastal areas, where the turbidity is higher, the spring bloom is highly influenced by light availability and develops from April onwards. Phytoplankton blooms can deplete nutrients in the mixed layer within a couple of days. Nutrient ratios and availability are important factors in determining the size and species composition of the spring bloom (Van Beusekom et al. 2009). Nutrient elements are taken up by phytoplankton at a relatively constant C:N:P:Si ratio of 106:16:1:18 in coastal areas, the 'Redfield' ratio (Redfield et al. 1963).

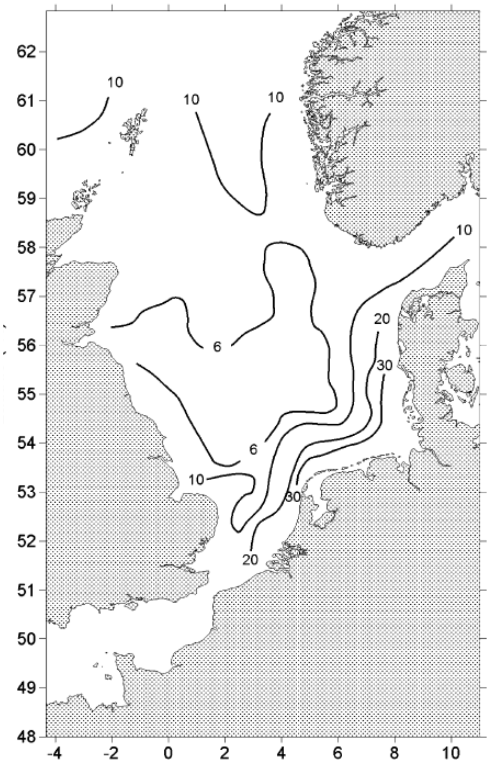


Figure 2. Distribution of winter nitrate (µM) concentrations in the North Sea. Phophate and silicate concentrations show a similar pattern (figure from Van Beusekom et al. 2009).

Generally, spring blooms appear in two phases in the North Sea. The first phase is dominated by diatoms and is limited by the availability of silicate. Subsequently, the bloom becomes dominated by flagellates (mainly *Phaeocystis* sp.*),* which are limited by the availability of nitrate and/ or phosphate.

When phytoplankton dies, a large part of the nutrients that were incorporated in the biomass settles and can subsequently be stored in the benthic pool (Figure 3)(1). Another part of the nutrients is grazed upon by zooplankton or zoobenthos and is subsequently being remineralised (2). Remineralisation rates differ per nutrient. Ammonia and phosphate are being mineralized very quickly, while mineralisation rates of silicate are low as the silicate is incorporated in the silica shells of diatoms. Autolysis of phytoplankton will result in production of organic nutrients as well. Part of these nutrients is being released as easily degradable organic matter, which is almost immediately converted into inorganic substances. The majority of the remaining dead organic matter (DOM) is converted into inorganic species via microbial decomposition (3). A small part of the DOM is transformed into humic and fulvic substances that are highly resistant to decomposition.

In the water column the most active cycling of nutrients is found. However, according to Brockmann et al (1989), large fractions of nutrients taken up by phytoplankton originate from sediments (5). For example, in the western Wadden Sea, 16-50% of the phosphorus stored in sediments is biologically available. The amount of phosphorus stored in sediments seems to accumulate in winter. When temperatures rise in spring, the phosphorus is remobilised from the sediment as the adsorption capacity decreases (Brockmann et al. 1990).

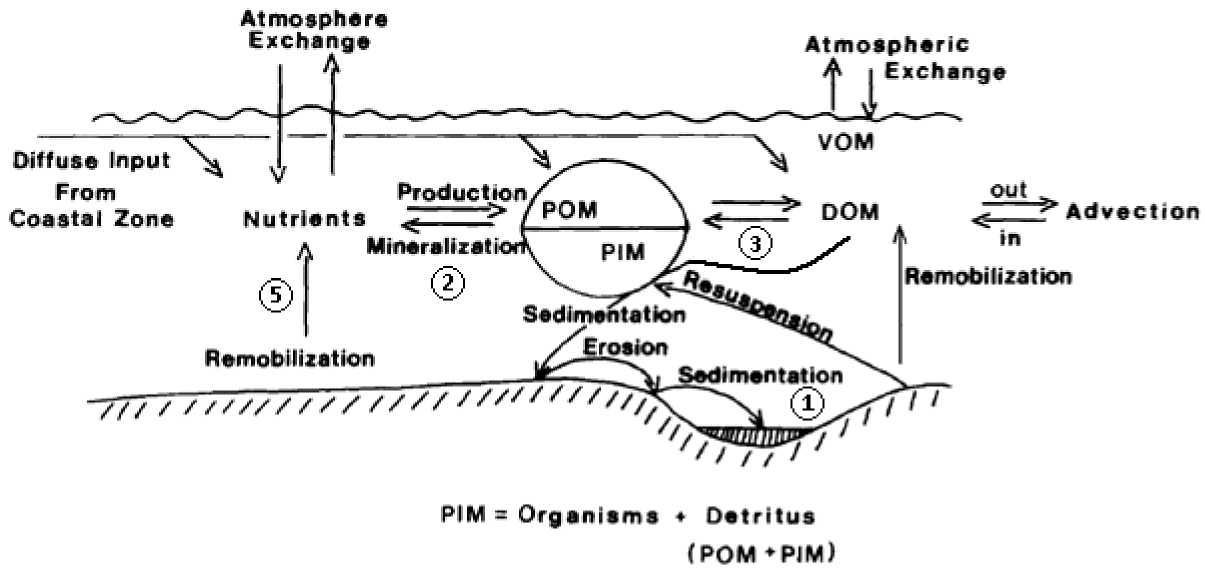


Figure 3. Schematic overview of nutrient fluxes between different compartments in a marine environment. POM = particulate organic matter, PIM = particulate inorganic matter, DOM = dissolved organic matter and VOM = volatile organic matter (adapted from Brockmann

Nitrogen is present in sea water as ammonium, nitrite, nitrate, urea, amino acids and many other organic compounds. Phytoplankton prefers nitrogen in the order: ammonium, urea, nitrite, and nitrate. Some phytoplankton species can also use organic nitrogen as source. Denitrification and nitrogen fixation act as potentially important sink and source terms in the marine nitrogen budget (Peeters et al. 1993). Ammonium is being formed via the mineralisation of organic nitrogen, which is subsequently converted to nitrate via nitrification. In the nitrification process, nitrate is formed via the biological oxidation of ammonia with oxygen to nitrite and further to nitrate. Nitrification occurs in two steps: first, ammonium is oxidized to nitrite by ammonium oxidizing bacteria; second, nitrite is oxidized by nitrite- oxidizing bacteria (Eq. 1).

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O \qquad \text{Eq.1}$$

When oxygen concentrations in the water are low, bacteria can use nitrate as a source of oxygen. In this process of denitrification, nitrate is being converted to gaseous nitrogen compounds (Eq. 2). In ecosystems with well oxygenated waters denitrification is mainly confined to the sediment. Denitrification rates are dependent on local sediment characteristics and the concentration of nitrate present. Denitrification rates in the North Sea are high in autumn, when a large amount of dead organic matter is being remineralized. The loss of nitrogen via denitrification is estimated to be 10-20% of the annual nitrogen load of the North Sea.

$$NO_3^- + H^+ \rightarrow 0.5N_2 + 1.25O_2 + 0.5H_2O \qquad \text{Eq. 2}$$

In the process, nitrate is reduced into elementary nitrogen, which may leave the water system as gaseous nitrogen.

Silicate is an important limiting nutrient for diatoms, as it is being used for the formation of its cell wall. Silicon is only available to phytoplankton in the form of dissolved silicate. The pool of dissolved silicate is gradually replenished by slow dissolution of opal silicate, the residue of the silicate skeletons of diatoms (Van Beusekom et al. 2009).

2.2 The GEM model

The GEM model has originally been developed at Deltares and has been under constant development over the past 20 years. GEM is one of several large-scale 3D ecosystem models applied to the North Sea (Skogen and Soiland, 1998; Allen et al. 2001; Luyten et al. 1999; Lancelot et al. 1995, 2000, 2005; Lacroix et al. 2007). In this section, a short description of the model is provided focussing on the different processes related to nutrients, the model grid, nutrient loadings and the hydrodynamics model used.

2.2.1 Model description

GEM is a generic model that can be applied to fresh, transitional as well as coastal waters to calculate primary production, chlorophyll-a concentrations and phytoplankton species composition (Los et al., 2008). It supports one-, two- and three-dimensional model schematisations. The GEM model has two main tasks. First, it calculates the transport of substances in the water column as a function of advective and dispersive transport, using a standard advection-dispersion equation. Second, it calculates water quality and ecological processes that affect state variable concentrations (Blauw et al. 2009). The processes that cause the concentration of substances to change are related to oxygen production and consumption (Figure 4)(1), nutrient uptake and release (2), mineralisation of organic matter (3) and algae growth and mortality (4). Algae growth and mortality is being calculated as a function of light and nutrient availability. Competition exists between different functional groups of phytoplankton, which means that the total net production is being optimised under certain constraints. These constraints are posed on growth, mortality, light and nutrient uptake. The latter is determined by the available resources. The GEM model includes complete cycles for oxygen and the nutrients phosphate, nitrate and silicate that can typically be limiting for algae. A closed mass balance exists for the nutrients, while the availability of inorganic carbon is unlimited (Los et al. 2008). An overview of all processes included is provided in Figure 4.

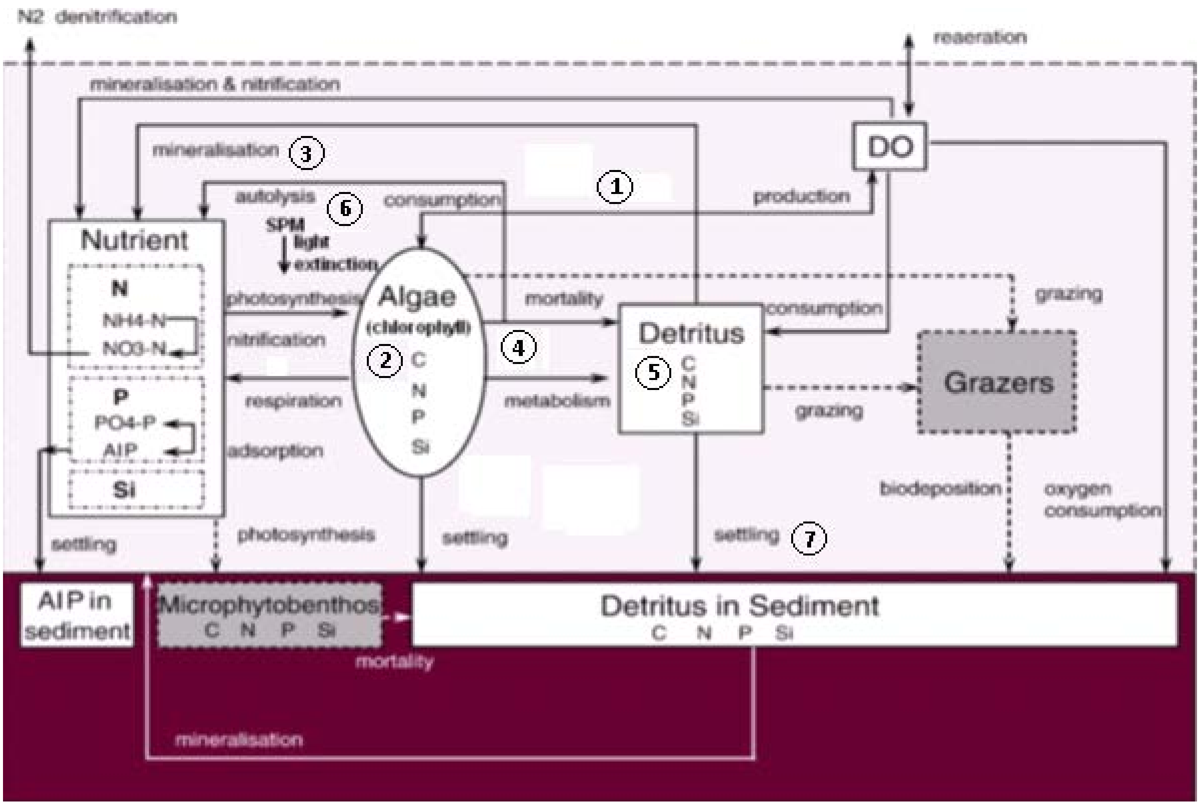


Figure 4. Scheme of state variables and processes included in GEM (from Los et al. 2008).

In GEM, the nutrient cycle consists of three major pools: dissolved inorganic nutrients that are taken up by primary producers (2), living organic matter (4) and dead organic matter (5). Nutrients become available when primary producers are being grazed upon or die. In a process called autolysis, part of the nutrients is released as dissolved inorganic nutrients (6). The remaining part is released as dissolved or particulate dead organic matter. Microbial decomposition of the DOM leads to the release of the nutrients back to their dissolved inorganic form (3). Particulate organic matter can settle to the sediment, which can cause the nutrients to become entrapped (7). The organic matter will then continue to decompose, which may eventually lead to the release of nutrients back to the water column. Primary producers living on the sediment can fix dissolved inorganic nutrients into living organic matter from the sediment. Phosphate can temporarily be removed from the system via adsorption to sediments. No mass balance exists for nutrients in the pore waters of the sediment. Fluxes of nutrients to the upper layer of the sediment only occur via sorption to inorganic material or the incorporation of nutrients in organic matter. Nutrients that are being released via mineralisation of detritus from the sediment are released directly in the water column. Nutrients can be removed from the system by the burial of organic material from the upper layer of the sediment to a second, deeper layer.

Nutrient concentrations are thus being determined by different sources, including boundary conditions, loads, atmospheric deposition, and sinks such as denitrification and uptake by phytoplankton. Lastly, the transport velocities of nutrients play an important role in determining nutrient concentrations at a certain location. The mass balances for the nutrients (NO3, NH4, PO4 and Si) are:

oxygen available. The constant background rate is equal to zero when a critically low temperature or a critically high dissolved oxygen concentration (0.02 g/m^3) is reached.

$R = k0 + k \times fni \times fox$

The burial process is generally unknown for marine ecosystems, which makes it an important calibration parameter (Blauw et al. 2009).

2.2.2 The model grid

In the Dutch coastal zone concentration gradients of nutrients, chlorophyll-a and suspended matter can be very steep. Therefore, the predefined ZUNO coarse grid with a variable grid cell size will be applied to the model. The cells have a minimum size of 1 km^2 in the coastal zone and a maximum of 100 km^2 in the north-west part of the modelled area (Figure 5) (Los et al., 2008). The grid consists of twelve vertical layers, where the thickness of each layer is dependent on the total depth of the water column. Near the bed and the surface, the layer thickness comprises about 4% of the local water depth. At mid-depth, the layer thickness is about 20% of the local water depth (Los et al., 2008).

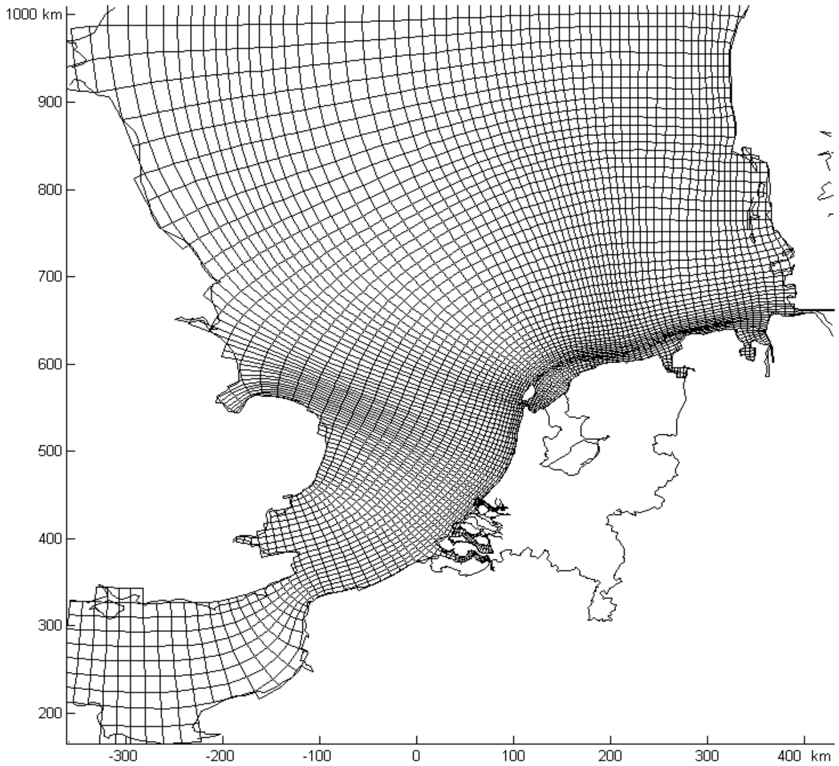


Figure 5. The ZUNO Coarse grid.

2.2.3 Hydrodynamics

The GEM model is coupled to the hydrodynamics model Delft3D-FLOW. The boundary conditions of the hydrodynamics model have been derived from a larger scale hydrodynamics model which covers the entire Continental Shelf. Boundary conditions were calibrated with measurements of several parameters, including river discharges, salinities and temperatures (Los, Villars et al. 2008).

2.2.4 Loads

The main Belgian, Dutch, German, French and UK rivers that flow into the North Sea are included in GEM. The river loads are included as point sources of nutrients and were based on a database from the Centre for Environment, Fisheries and Aquaculture Science (CEFAS, UK).For technical reasons, the freshwater is being discharged at the surface layer. The effect of this is generally very small, as the coastal waters of the North Sea are usually well mixed (Keetels et al., 2012).

Measurements of river discharge are available per day for most rivers, while measurements of nutrient concentrations are available per week (Los and Blaas, 2010).

2.3 Model validation

Before a model can be used for gaining insight into a system or forecasting, it is necessary to validate the model. Model validation is in this context defined as testing whether the model produces outputs that fall within a satisfactory range of accuracy with regard to the intended applications of the model. In the past, the GEM model has been validated various times using measurements from water quality and ecology monitoring stations located in the Dutch EEZ. Los et al. (2008) validated modelled nutrient concentrations for the period 1981-1994 using 27 sampling stations in the Dutch region of the North Sea. To indicate the goodness of fit of the model the OSPAR cost function was used, which is the sum of the absolute deviations of the model values from measured values, normalised by the deviations of the observations (Table 1). At most sampling stations, model performance was rated as 'good' to 'very good'.

Table 1. Cost function results for GEM for five substances: nitrate (NO3), phosphate (PO4), silicate (SiO2), chlorophyll-a and the salinity (table adapted from Los et al. (2008)).

Substance	**Very good** (0-1)	**Good** (1-2)	**Reasonable** (2-3)	**Poor** > **3**
NO_3	6	11	6	4
PO_4	2	15	5	5
SiO_2	25	1	1	1
Chlorophyll-a	22	2	3	0
Salinity	4	17	5	1

Los and Blaas (2010) created target plots, which display the difference between modelled values and measurements in terms of the bias, normalised by the standard deviation of the measurements, and the unbiased root-mean-squared difference (Figure 6). The radial distance from the origin represents the total root-mean-square difference (RMSD). A model result with an RMSD >1 can be considered poor, while the model reproduces the annual mean of observations well when the RMSD < 1. In addition, an RMSD < 1 indicates that model values correlate positively with measurements. A further explanation of the interpretation of target diagrams is provided in section 2.5. It can be observed that the annual mean of nutrients and chlorophyll-a is reproduced well by the model.

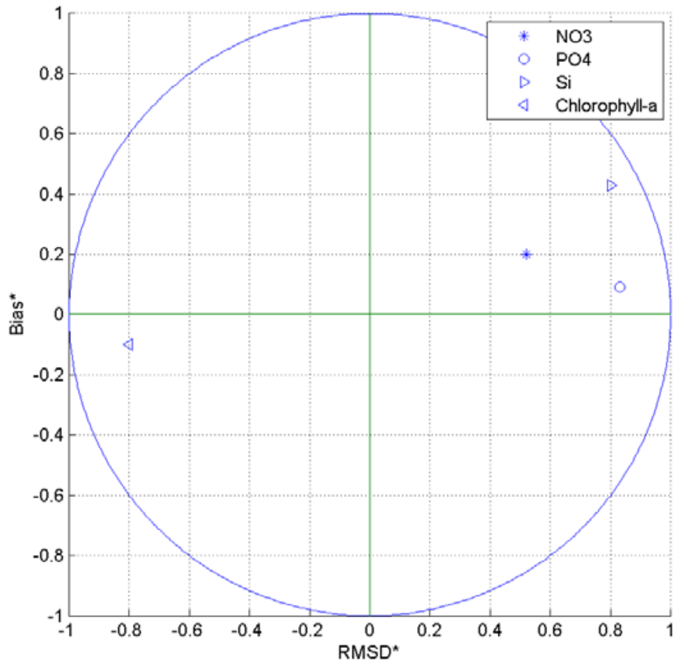


Figure 6. Target plot of modelled nutrient concentrations at six sample stations in the Dutch region of the North Sea in 2003 (adapted from Los and Blaas (2010)).

Up till present validations have mainly focused on model performance in the Dutch EEZ. In this study, model performance with regard to several water quality parameters for the entire North Sea will be tested. To evaluate the accuracy of the model, model predictions were compared to in situ measurements.

In this study, observations were considered to represent the 'true state' of the system. However, it's important to keep in mind that measurements deviate from the true state of the system as well, due to uncertainties that arise in measurement techniques and low quantity of the data. The quality of the measurements will be tested by comparing the medians of the datasets at matching time and locations (section 2.3.2). In this way, it will be tested whether differences arise in measured values between datasets due to measurement techniques. If this is not the case, the datasets will be merged in order to increase the quantity of the data and therefore to decrease uncertainty.

2.3.1 Datasets

Three datasets will be used for the validation of different variables, namely from 1) the Dutch water agency Rijkswaterstaat (RWS), 2) the Management Unit of the North Sea Mathematical Models and the Scheldt estuary (MUMM) that is part of the Royal Belgian Institute of Natural Sciences, and 3) the International Council for the Exploration of the Seas (ICES).

For the validation of river nutrient loads, a database from the European Environment Agency on the status and quality of Europe's rivers, lakes and coastal waters, 'Waterbase', will be used.

The RWS database contains measurements of stations located in the Dutch region of the North Sea, whereas the MUMM dataset contains measurements from stations in Belgian waters. The RWS and MUMM databases mainly contain data from the surface layer. The RWS stations are visited by survey vessels every 2-4 weeks, randomly timed regarding the tidal cycle and always under relatively calm weather conditions (Los and Blaas, 2010). The MUMM monitoring stations are only visited 1-5 times per year.

The ICES database contains data of the entire North Sea obtained from many different sources, measured at monitoring stations as well as data obtained during cruises. On several locations, measurements have been performed at different depths.

2.3.2 Data integration

The years 2003-2007 were chosen as time frame, as validation of nutrient concentrations has not been performed extensively for this time period yet. The statistics, described in mode detail in section 2.5, will be calculated for the entire time period considered. In situ measurements will be compared to model values closest in time. The GEM model will be run producing an output every three hours, ensuring that model values are never more than 1,5 hours deviated from measured values. In this way, possible fluctuations in nutrient concentrations due to tidal movement are taken into account. The North Sea has a lunar-dominated semi-diurnal tide with a period of 12 hours and 25.2 minutes. Statistics will be calculated per OSPAR region, as defined by the Convention for the protection of the marine Environment of the North-East Atlantic (the 'OSPAR' convention) (Figure 7). Only model values from locations for which a corresponding measurement is available will be considered.

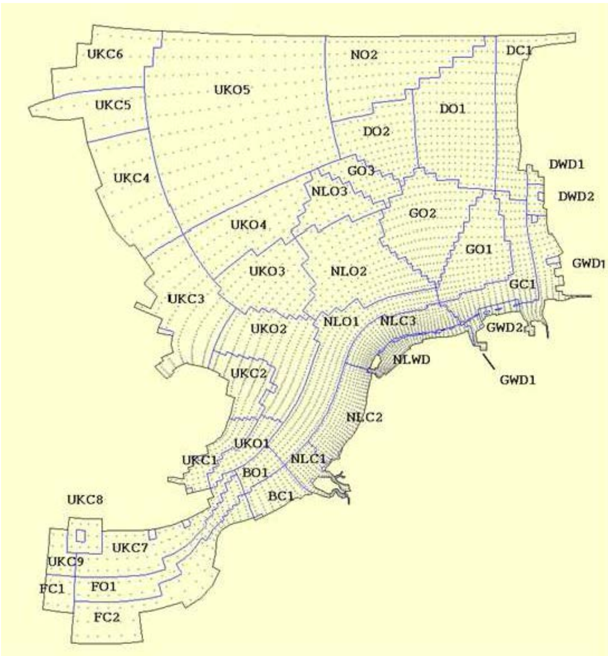


Figure 7. OSPAR regions in the southern North Sea. To each region, a code is assigned; the first one or two letters refer to the country owning the area, while the last letter indicates whether the region is considered 'coastal' (C) or 'offshore' (O).

Closer inspection of the RWS dataset versus the ICES dataset showed that all data points performed by RWS are included in the ICES dataset. Therefore, the RWS dataset was excluded from the analysis. The ICES dataset does contain measurements performed in the Belgian region of the North Sea that are not included in the MUMM dataset. In order to check whether differences in the measured values exist, for example due to different measurement techniques applied, the distribution of the measured values in both datasets in the BC1 OSPAR region were compared. BC1 is the region where the majority of the MUMM measurements were performed. Data points were selected from the months January – April, November and December, as for these months measurements were included in both datasets. Phosphate measurements performed by MUMM are all included in the ICES dataset.

In order to determine the appropriate statistical tool for comparing both datasets, the datasets were first tested for normality using a normal probability plot. The data is plotted against a theoretical normal distribution, such that the data points should approximately display a straight line.

(Figure 9, right column). This is mainly due to the fact that there is a natural limit on the values that can occur, leading to a relatively large amount of values close to zero and a decreasing frequency as values become higher (Figure 9, left figures). Therefore, a non parametric test, the Mann-Whitney U test, was used to determine whether the medians of the datasets are different. According to the test, the medians of nitrate measurements in both datasets are equal (Table 2). However, the silicate measurements of the datasets have a different median. However, based on the low size of the silicate datasets and the fact that measurements of both datasets were not taken at exactly the same time (Figure 8) , the datasets were merged without further corrections.

Table 2. Mann-Whitney U test results.

Region	Nutrient	Dataset	Medians	Difference	U	P-value
BC1	NO_3	ICES	0.2311	No	107206	0.2367
		MUMM	0.2731			
	SiO_2	ICES	0.2486	Yes	5065	0.013
		MUMM	0.1298			

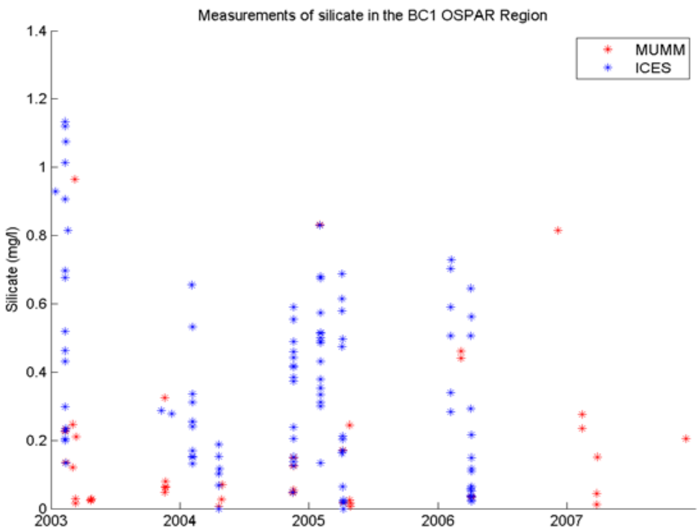


Figure 8. Measurements of silicate in the BC1 OSPAR region from the MUMM (red) and ICES (blue) dataset for January - April, November and December.

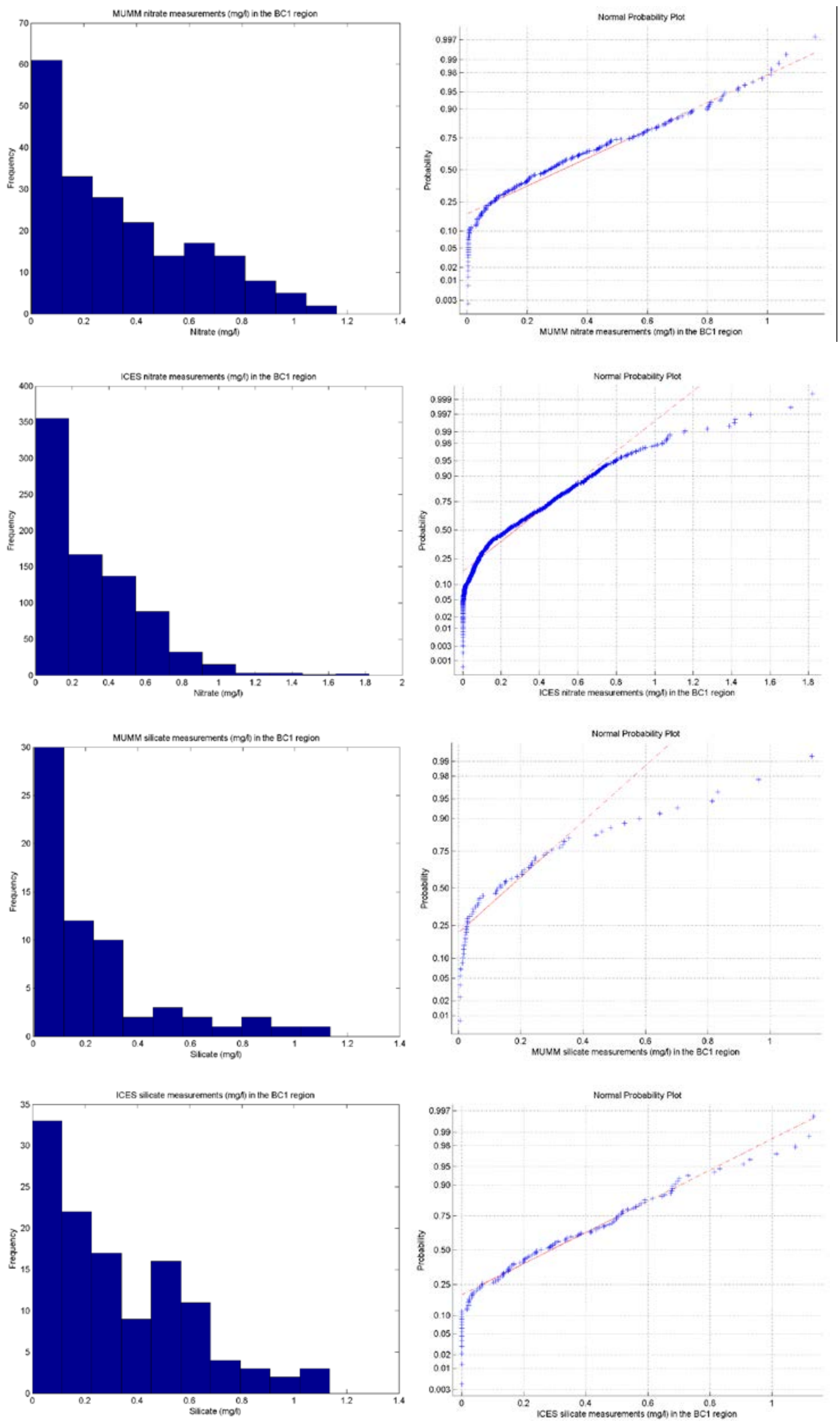


Figure 9. Histograms and normal probability plots for measured nitrate (upper figures) and silicate (lower figures) concentrations from the ICES and MUMM dataset in the BC1 OSPAR region.

As in coastal areas most phytoplankton growth occurs in the upper layers of the water column, the validation focusses on the upper 15 meters of the water column. An overview of data availability per OSPAR region is provided in Table 3. Only regions where more than 20 measurements were available during the period 2003-2007 were considered. The boundary was chosen in order to exclude the regions for which only few measurements were available and a comparison to the model would not be insightful.

Table 3. Data frequency for each nutrient in the 0-15 m depth zone per OSPAR region for 2003-2007.

Number of measurements							
	Nitrate	**Phospha-te**	**Silicate**	**Salinity**	**Oxygen**	**Tempe-rature**	**Chloro-phyll-a**
'BC1'	294	105	365	126	184	128	51
'BO1'	2	0	4	1	6	1	0
'DO1'	184	185	184	283	561	284	0
'DO2'	7	0	7	9	397	9	0
'DC1'	248	153	216	354	395	354	0
'FC2'	4	0	18	4	23	4	0
'FO1'	3	0	6	7	11	7	0
'GC1'	147	82	147	720	1209	776	0
'GO1'	160	75	160	194	1023	194	41
'GO2'	107	63	107	135	775	135	0
'GO3'	9	0	9	15	257	15	0
'NLO1'	152	31	157	167	222	167	89
'NLO2'	204	16	204	209	362	209	156
'NLO3'	2	0	2	2	108	2	0
'NLC1'	148	39	369	174	188	174	69
'NLC2'	351	47	351	362	452	362	255
'NLC3'	144	15	178	151	244	151	102
'UKC1'	2	6	2	19	38	19	0
'UKC2'	0	0	0	1	12	1	0
'UKC3'	2	0	2	14	60	14	0
'UKC4'	2	0	2	3	76	3	0
'UKC5'	2	0	2	20	47	20	0
'UKC6'	2	0	0	29	20	29	0
'UKC7'	2	2	8	12	8	12	0
'UKC8'	0	1	0	3	1	3	0
'UKC9'	1	0	0	2	5	2	0
'UKO1'	0	6	23	14	13	14	0
'UKO2'	4	0	4	8	45	8	0
'UKO3'	2	0	2	6	139	6	0
'UKO4'	54	3	54	59	198	59	40
'UKO5'	15	0	15	51	346	51	0
'NO2'	6	4	6	27	270	27	0

2.4 Plan of analysis

2.4.1 Chlorophyll-a

Chlorophyll-a is considered an important indicator for the presence of phytoplankton in marine waters (Vermaat et al. 2008). In GEM, chlorophyll-a concentrations are derived from the biomass of phytoplankton present by a fixed species dependent C : chlorophyll-a ratio. The use of this ratio causes uncertainty in the model, as in reality the C : chlorophyll-a ratio highly varies depending on environmental conditions. For example, under low light conditions the amount of chlorophyll-a in phytoplankton is relatively high, while under light saturated conditions the amount of chlorophyll-a present in phytoplankton is relatively low (Kaiser et al. 2011). However, the advantage of using chlorophyll-a for the validation is that the variable is easy to measure. Chlorophyll-a concentrations in GEM have been validated extensively for the Dutch EEZ using in situ measurements and remote sensing images. The model performs 'good' to 'very good' according to the OSPAR cost function (Los, Villars et al. 2008; Lannoy, de C. 2012).

An important objective of the GEM model is the prediction the spring bloom. The ability of the model to capture the initialisation of the bloom was assessed by comparing in situ measurements available for chlorophyll-a to modelled values at the corresponding time and location. As most chlorophyll-a measurements were performed in January, February and March, which corresponds to the period in which the spring bloom occurs, these months for 2003-2007 were taken as time frame. For each OSPAR region and within the time frame, the measurements and corresponding modelled value were taken, which were used to calculate one value for the RMSD* and the bias* per region. Model performance of the different regions will be summarized in a target plot.

2.4.2 Nutrients

The nutrients considered for validation are nitrate, phosphate and silicate. The ability of the model to capture the annual mean of the nutrients will be assessed using target plots and visual inspection of time series of average modelled nutrient concentrations per OSPAR region with respect to measurements. Depending on the results of the validation, one or several focus regions will be selected for further analysis.

Errors in modelled nutrient concentrations can originate from different sources, including:

1) Hydrodynamics
2) Loads and boundary settings
3) Biochemical processes

Hydrodynamics, loads and boundary settings

Errors in the salinity can reveal model errors in transport of water masses. The salinity is closely related to the concentration of chlorine in water and is hardly influenced by biological or chemical interactions. Furthermore, little transfer of salinity across the air-sea and sea-bottom interfaces occurs. It is thus a conservative quantity, mainly transported by advection and diffusion processes and is therefore a good tracer of water masses, as each water mass has its typical salinity value (Lacroix et al. 2004). Water from the Atlantic Ocean has a salinity of about 35.5 practical psu. Water entering the North Sea from the English Channel can be identified by a tongue of water with salinities higher than 34.75 psu. The salinities of freshwater run-off are lower with minimum values of 29-30 psu (Van Beusekom et al. 2009).

Some of the sources of error related to hydrodynamics, loads and boundary settings will be ruled out by looking at a composition matrix obtained from labelling experiments (Los et al. in prep). The contribution of different sources to the total nutrient concentration present at a certain location has been analyzed for every OSPAR region in the year 2002 (Figure 10). A distinction was made between nutrient sources throughout the entire year and only in winter. Nutrient uptake by phytoplankton is very low in winter, which provides the opportunity to determine the share of river loads to total nutrient concentrations. The study shows that in the north-western part of the model area total dissolved inorganic nitrogen (DIN) and total phosphorus concentrations largely originate from the North-Atlantic Ocean. In the south-eastern part of the North Sea nutrients largely originate from river discharges and the English Channel. The contribution of the English Channel to nutrient concentrations is quite high along the French coast (>50%) and decreases towards the north, while the share of river loads increases. For example, in the German Bight river loads make up more about 80% of the nutrient sources.

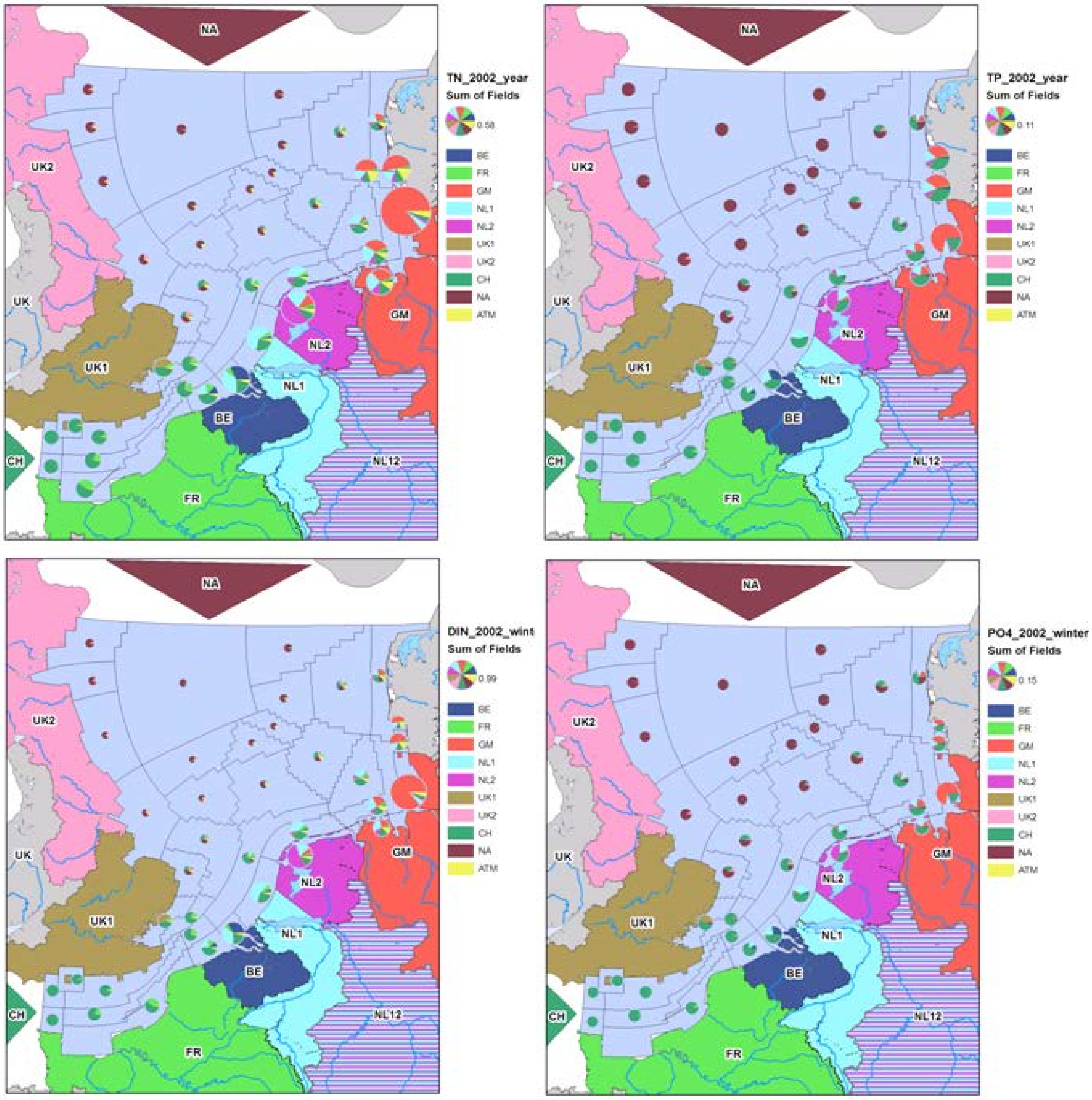


Figure 10. Relative contribution of different sources to the total nitrogen, phosphorus throughout the entire year 2002 and DIN and phosphate concentrations in the winter of 2002 respectively (figure from Los et al. (in prep)).

Using the composition matrix, possible error sources in different regions such as river loads and volume fluxes can be validated.
River loads will be checked using the original CEFAS dataset that was used to construct the loads included in the model. This dataset was chosen as it is the most extensive dataset available for river

loads, and can therefore provide the most reliable indication whether loads are included correctly in the model. By comparing the original CEFAS data with the model input, conversion or interpolation errors can be ruled out.
The residual flow through the Strait of Dover will be validated as the English Channel provides an important source of nutrients in the entire eastern North Sea coast. The residual flow is the net transport of water across a certain boundary over a certain period of time. The residual flow across the Strait of Dover will be derived from the cumulative discharge calculated in Delft3D-FLOW, which is given as an output daily. Due to various factors, including changes in local meteorological conditions and tidal forcing, the daily cumulative discharge can be either positive or negative. By adding up all these cumulative discharges for an entire year, the yearly residual flow is given. There are no frequent measurements of the residual flow available for the Strait of Dover, as the variable cannot be measured directly but needs to be derived from e.g. radioactive tracers combined with transport models. The residual flow remains relatively constant in the long term, as it is mainly dependent on tides and winds (Gerritsen et al. 2000). Therefore, modelled residual flows were validated using studies performed before the period 2003-2007.

Biochemical processes

Subsequently, variables related to biochemical processes will be validated and it will be evaluated whether the adjustment of different parameters related to biochemical processes can improve model fit with respect to in situ measurements of nutrients. Parameters related to the burial of detritus, the mineralisation of nitrogen and silicate, denitrification and nitrification rates will be considered. Furthermore, as mineralisation rates are temperature dependent, it is important that the ambient water temperature is included correctly in the simulation. The correctness of the temperature used for the model runs was tested by making target plots for each OSPAR region, which is further explained in section 2.5.
Another important variable is the oxygen concentration, as it partly determines nitrification and denitrification rates (section 2.1.2). In addition, oxygen depletion can lead to mortality of fish and benthic invertebrates when dissolved oxygen levels fall below 5 g/m^3. Oxygen depletion due to the decomposition of large phytoplankton blooms occurs frequently in the central North Sea, where the water column regularly becomes stratified due to vertical temperature gradients. During stratification, the oxygen that is consumed for the decomposition of organic matter cannot be replenished from the atmosphere by reaeration. Oxygen concentrations start rising again when reaeration becomes larger than oxygen consumption. This might occur when the level of vertical mixing increases or when less organic matter is available for decomposition (Kaiser et al. 2011). The variable was validated by making target plots for each OSPAR region.

The parameters listed above will be used to perform a sensitivity analysis, in order to identify parameters that could be adjusted to achieve increased model performance with respect to in situ measurements. The parameters will be varied by increasing or lowering the parameter by 10%, 20%, 40%, 60% and 80%, depending on the desired direction of change that resulted from the validation (Table 4). The GEM model is deterministic, meaning that the model always gives the exact same output using one set of initial conditions. Therefore, the model will be run once for each different parameter setting.

Table 4. Overview of the parameters that will be adjusted in the given range in order to improve model fit regarding nitrate, phosphate and/ or silicate.

Nutrient	Parameter	Range from (current value)	Range to (+/- 80%)

As the sediment-related parameters needed a spin-up time of 1-2 years, all runs including the default run will be performed using a spin-up of two years. Model fit was expressed in the RMSE of modelled nutrient concentrations with respect to observed values within the different OSPAR regions. To illustrate differences between regions in model sensitivity to the different parameter settings, an overview will be provided of the change in RMSE after an 80% change of all parameters. Furthermore, using target pots the response of the different OSPAR regions to the parameter adjustments that are optimal for the selected focus regions.

2.5 Statistical methods

The difference between modelled and observed values can be expressed in various quantitative metrics. Besides traditional metrics such as the root mean square error, target plots will be made.

The times at which observations were performed will be rounded to a three hour scale. As measurements at different depths are available, model performance will be tested in the 0-15 m depth zone, which is located above the mixing depth and is therefore assumed to be well mixed.

The root mean squared error (RMSE) will be used as a measure of the size of difference between modelled and measured values. Using the RMSE, negative errors cannot cancel out positive errors. The closer the RMSE gets to zero, the better the model fit. RMSE values were calculated according to the following formula:

$$\mathrm{RMSE} = \sqrt{\frac{\sum_{i=1}^{n}(M_i - O_i)^2}{n}}$$

Target plots will be made in order to provide summary information about how the normalized bias and unbiased RMSD each contribute to the magnitude of the total Root-Mean-Square Difference (RMSD).

The normalized unbiased root mean square difference will be calculated using the following formula:

where,

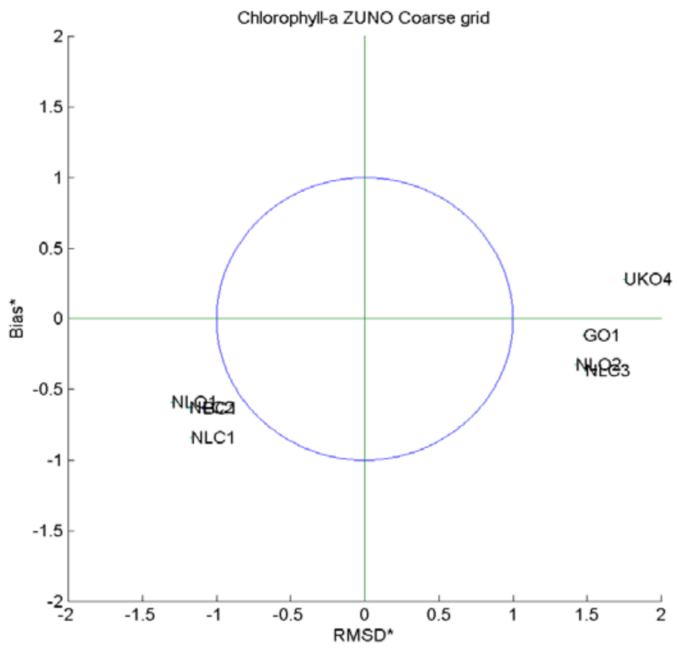
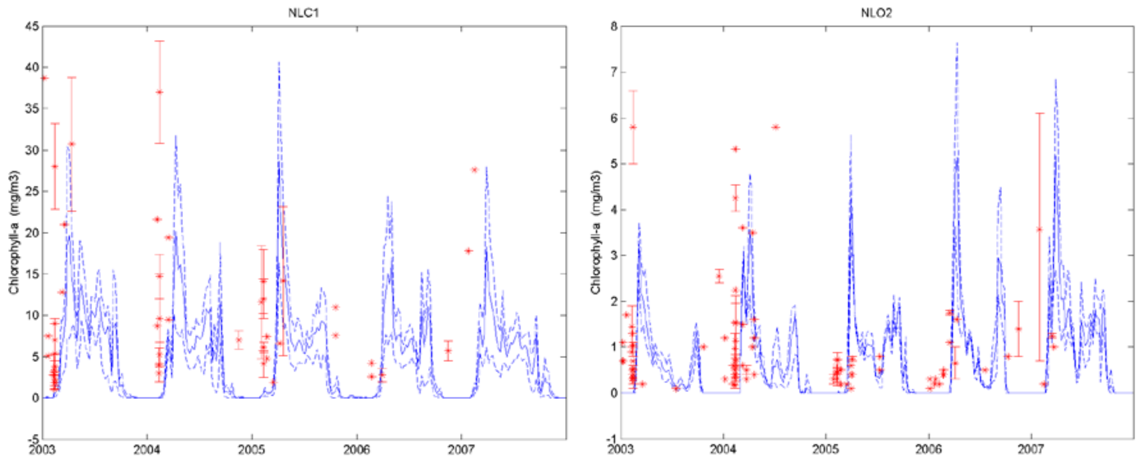


Figure 11. Target plot of model performance with regard to chlorophyll-a for different OSPAR regions in the period 2003-2007in the 0-15 m depth zone.

The underestimation of modelled chlorophyll-a concentrations is most pronounced in the Dutch and Belgian coastal zone. In the Dutch coastal zone, this is mostly due to the initialisation of the spring bloom being 2-4 weeks too late in spring (Figure 12).



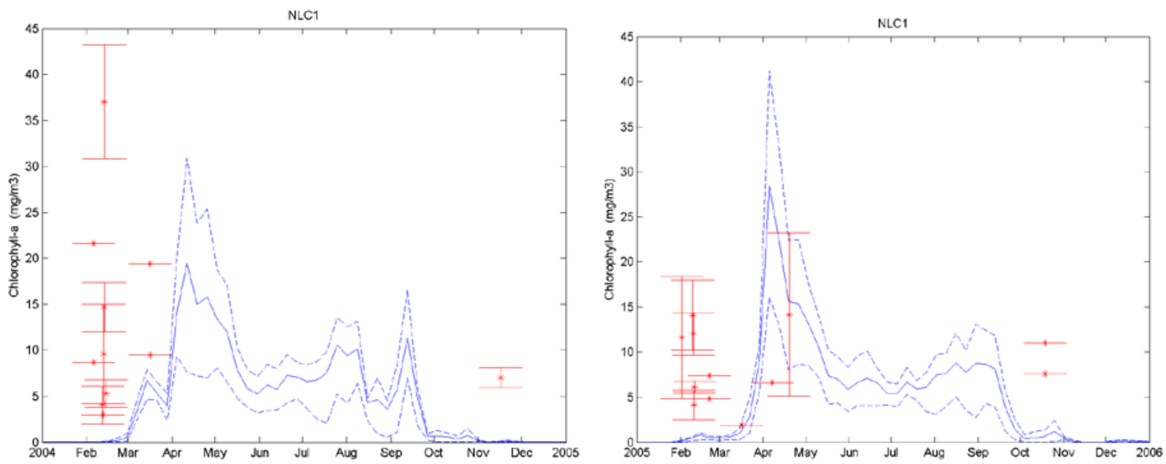


Figure 12. Average modeled (blue) and observed (red) chlorophyll-a concentrations in the NLC1 and NLO2 OSPAR region for the entire model period (upper figures) and for 2004 and 3005 (NLC1). The dashed lines picture the maximum and minimum weekly medians of modelled chlorophyll-a concentrations.

In the Belgian coastal area, no error can be observed in the timing of the initialisation of the spring bloom. The bias seems to be more closely related to the height of the peaks (Figure 13).

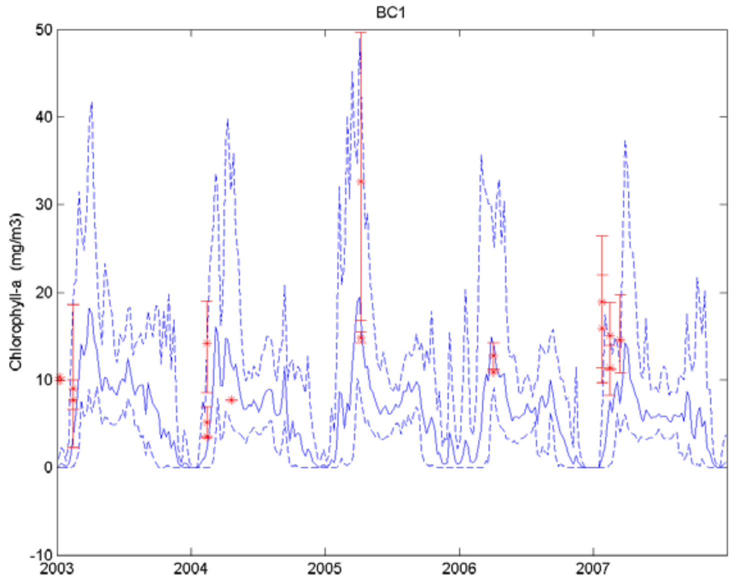


Figure 13. Average modeled (blue) and observed (red) chlorophyll-a concentrations in the BC1 OSPAR region for 2003-2007. The dashed lines picture the maximum and minimum weekly medians of modeled chlorophyll-a concentrations.

In the UKO4 region , a small positive bias is observed. In the years 2003, 2004 and 2005 the initialisation of the spring bloom is being captured well by the model (Figure 14). The positive bias observed in the model is mostly due to the spring blooms peaks being higher than observations: up to 7 mg/m^3, while observations generally display concentrations of about 1 mg/m^3 except for 2003 and 2004, where peaks up till 4 mg/m^3 were measured. However, it has to be kept in mind that the data frequency is quite low. Therefore, the possibility that spring bloom peaks have not been measured due to the low measurement frequency cannot be excluded. The size of the spring bloom has previously been assessed by comparing modelled chlorophyll-a concentrations to satellite images of the Dutch

EEZ (Lannoy, 2012). According to Lannoy (2012) the height of the spring bloom peak is generally being underestimated in coastal areas, but overestimated in offshore regions.

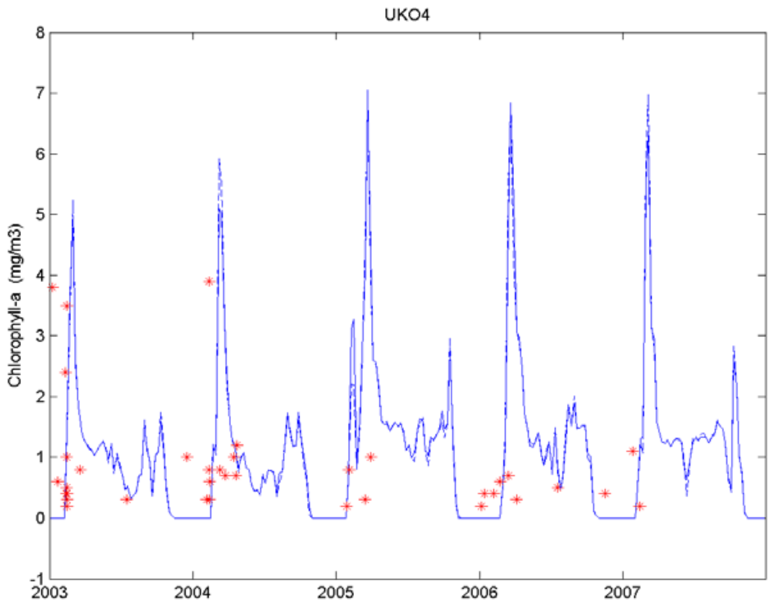


Figure 14. Average modeled (blue) and observed (red) chlorophyll-a concentrations in the UKO4 OSPAR region for 2003-2007. The dashed lines picture the maximum and minimum weekly medians of modeled chlorophyll-a concentrations.

In coastal areas, the initialisation of the spring bloom is mostly determined by the availability of light, as nutrients are available in high concentrations during this time of the year. Errors in the timing of the spring bloom could therefore be due to the amount of suspended particulate matter in the water column being too high, increasing light extinction and therefore the photosynthetically active radiation available for phytoplankton growth. An overestimation of the amount of suspended particulate matter can be due to an overestimation of riverine influence, as river inflow comes along with high amounts of suspended particulate matter.

Nutrient concentrations mostly determine the size of the phytoplankton blooms. In order to examine whether the observed error could be due to errors in modelled nutrient concentrations, nitrate, phosphate and silicate concentrations were validated for the coastal and offshore regions for which in situ measurements were available.

3.2 Validation nutrient concentrations

Nitrate concentrations are being captured quite well by the model, as the RMSD* is close to or below 1 for nearly all OSPAR regions (Figure 15,a). Considering the model bias, it can be observed that nitrate concentrations tend to be overestimated in most regions of the North Sea. In region BC1, nitrate concentrations are somewhat being underestimated.

The RMSD* of modelled phosphate concentrations is close to 1 in most coastal regions (Figure 15,b). In all offshore regions a positive bias is observed, which is most pronounced in region UKO4 and DO1. However, it has to be kept in mind that absolute phosphate concentrations are low in these regions throughout the entire year as the phosphate mainly originates from the English Channel or the Atlantic Ocean. Therefore, the observed error is likely to result from incorrect boundary conditions at the northern or southern boundary of the model grid or an error in biochemical processes.

Silicate concentrations are being modelled quite well in all regions, except region NLO1 where a strong positive bias is observed (Figure 15, c). This can be due to an overestimation of influence from the Rhine, or an error in biochemical processes. Furthermore, it can be observed that in general, silicate concentrations tend to be slightly overestimated in most regions of the North Sea.

In the regions NLC2 and NLO1, concentrations of nitrate, phosphate as well as silicate are somewhat being overestimated (Figure 15,Figure 16). This indicates that in these regions nutrient loads from rivers or dispersal of nutrient-rich freshwater are not included well in the model. Furthermore, a process related to the amount of organic matter present in the area or the release of nutrients from organic matter could cause the observed error.

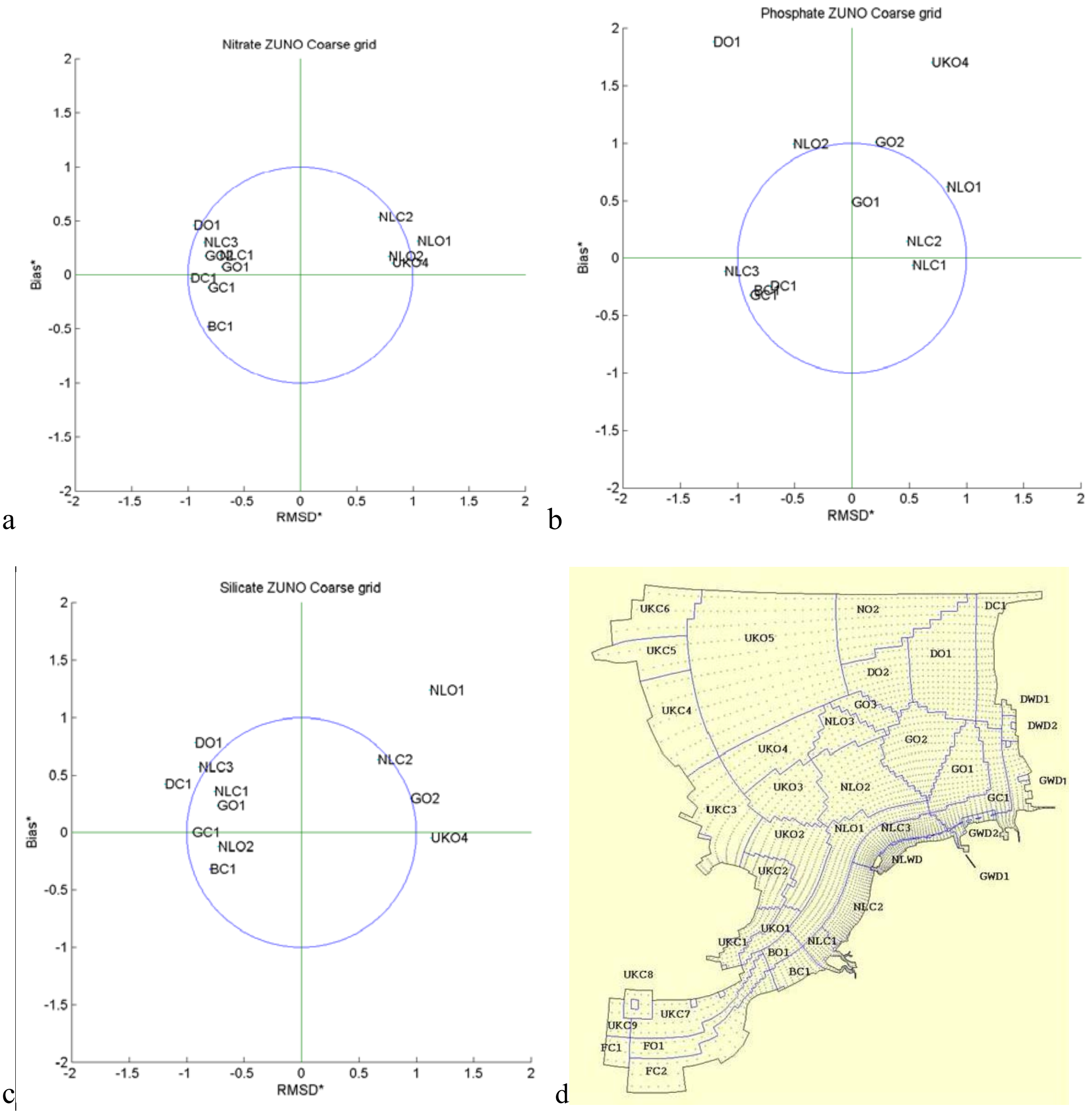


Figure 15. Target plots of model performance with regard nitrate (a), phosphate (b) and silicate (c) for different OSPAR regions (d) in the period 2003-2007 in the 0-15 m depth zone.

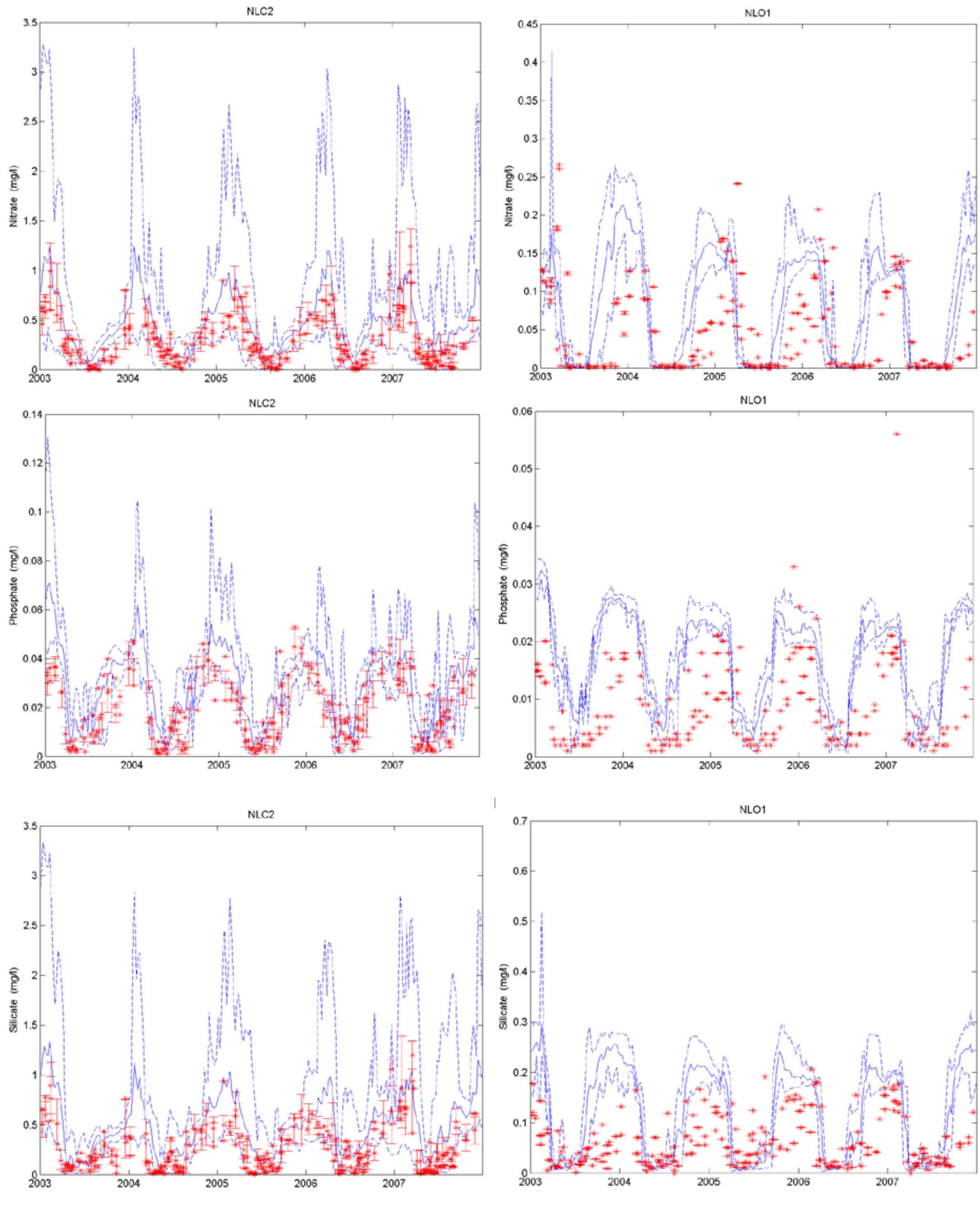


Figure 16. Average modeled (blue) and observed (red) nitrate, phosphate and silicate concentrations in the NLC2 (left) and NLO1 (right) OSPAR regions. The dashed lines picture the maximum and minimum weekly medians of modeled nutrient concentrations.

3.3 Identification of model errors

Considering the time available for the research, the focus regarding the identification of model errors is on the Dutch coastal zone. As discussed previously, errors in modeled nutrient concentrations can result from errors in hydrodynamics, loads and boundary conditions or biochemical processes.

Therefore, the hydrodynamics and loadings of the model are considered first. Subsequently, it is evaluated whether parameter settings related to biochemical processes can be improved.

3.3.1 Hydrodynamics

The salinity is an important indicator of how well freshwater dispersal is being captured by the model. The salinity is being modeled well in most regions, but is underestimated in the Belgian and most of the Dutch OSPAR regions, both near the coast and offshore (Figure 17). Underestimation of the salinity in region NLC2 and NLO1 possibly coincides with the overestimation of nutrient concentrations observed, as salinity is usually negatively correlated with nutrient concentrations in marine coastal regions (Kaiser et al. 2011).

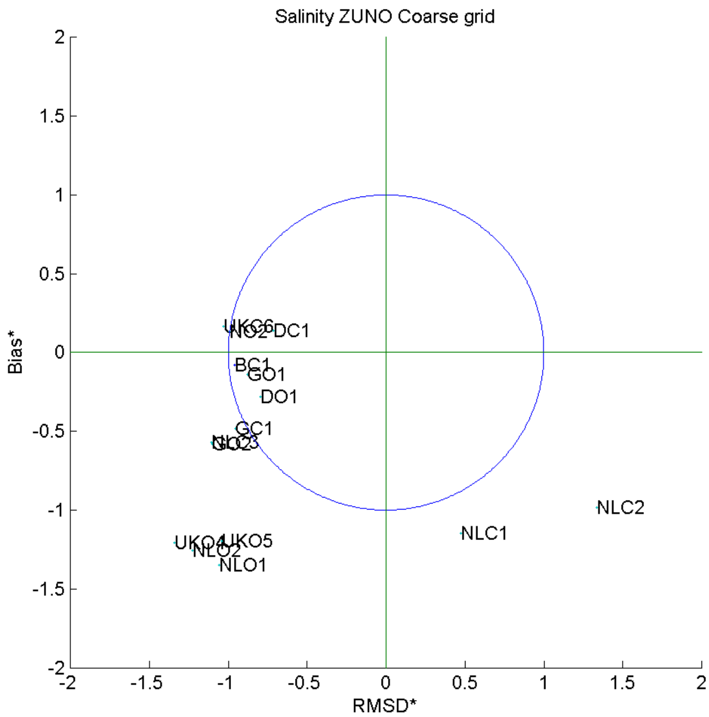
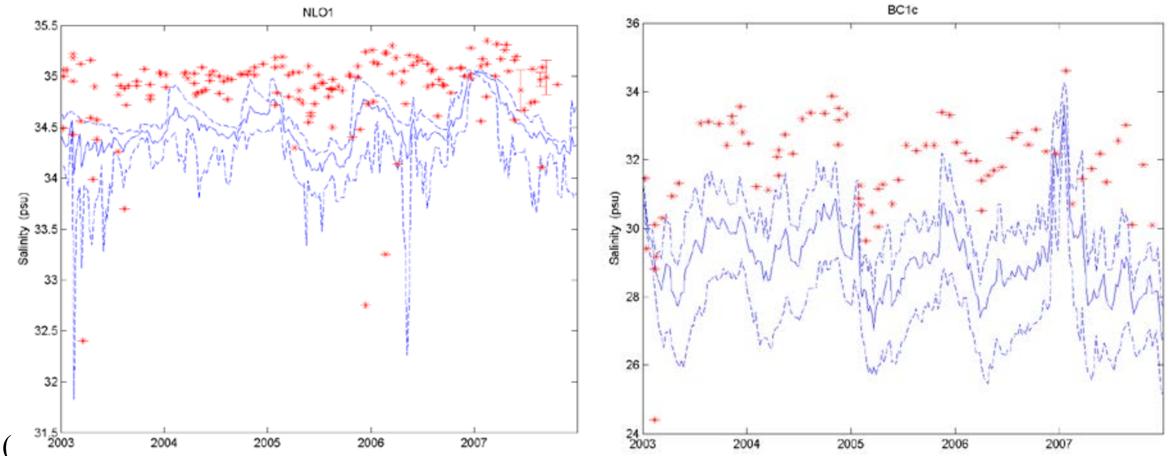


Figure 17. Target plot of model performance with regard to the salinity for different OSPAR regions in the period 2003-2007 in the 0-15 m depth zone.

The observed error in the Belgian and Dutch regions could be due to an error in volume fluxes entering the North Sea from the south through the English Channel, or an error in the influx or dispersal of freshwater.

The former hypothesis is supported by the fact that the salinity in the offshore part of region BC1 (> 30 km offshore) is being underestimated, as well as offshore in the Dutch EEZ



(

Figure 18).

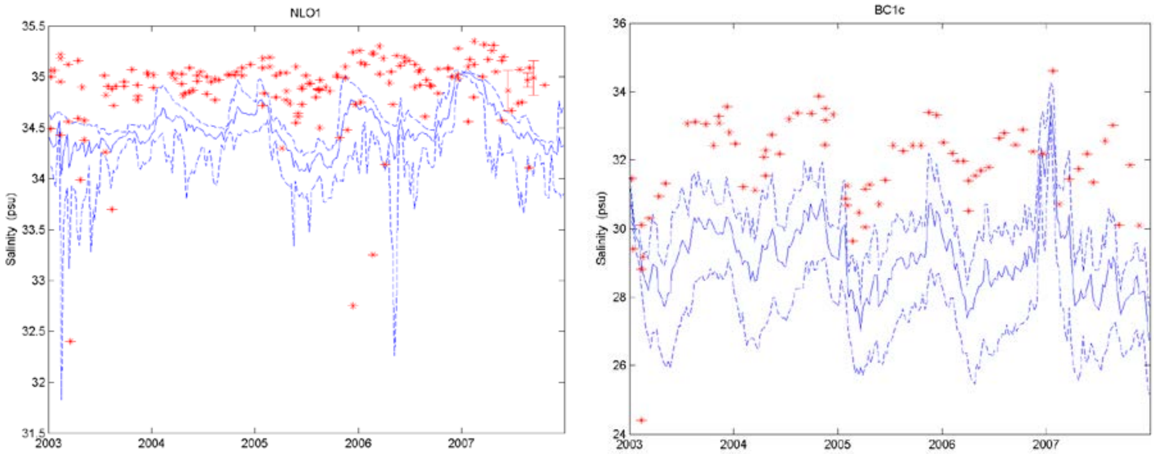


Figure 18. Average modeled (blue) and observed (red) salinities in the NLO1 and BC1c region, which is the part of the BC1 region located > 30 km offshore. The dashed lines picture the maximum and minimum weekly medians of modeled salinities.

To examine whether the cause of the error in modeled salinities in the offshore Belgian and Dutch coastal areas is due to an error in volume fluxes entering the North Sea from the south, the residual flows through the Strait of Dover were validated (for methodology, see section 2.4.2). The residual flow is always a positive number, indicating that there is a net transport of water from the English Channel into the North Sea. The modelled residual flow shows a high interannual variability, ranging from 57.078-106.860 m^3 / s for the period 2003-2007 (Figure 19).
Various calculations of the residual flow through the Strait of Dover can be found in literature. Over the period 1983-1991 an average annual flow of 114000 m^3 / s was determined using radioactive tracers discharged at La Hague cape, located at the French coast of the English Channel (Salomon et al. 1993). The interannual variability of the calculated residual flows was quite low, ranging from about 100.000-150.000 m^3 / s. For the period between January-July in 1988 residual flows through the Strait of Dover were estimated to be 97.000-195.000 based on radiotracer distributions (du Bois et al. 1995). In 1990-1991 year-long measurements were performed using a shore-based high frequency radar and an mounted acoustic Doppler current profiler, resulting in an estimate of a net flow into the North Sea of 94.000 m^3/s (Prandle, 1996).

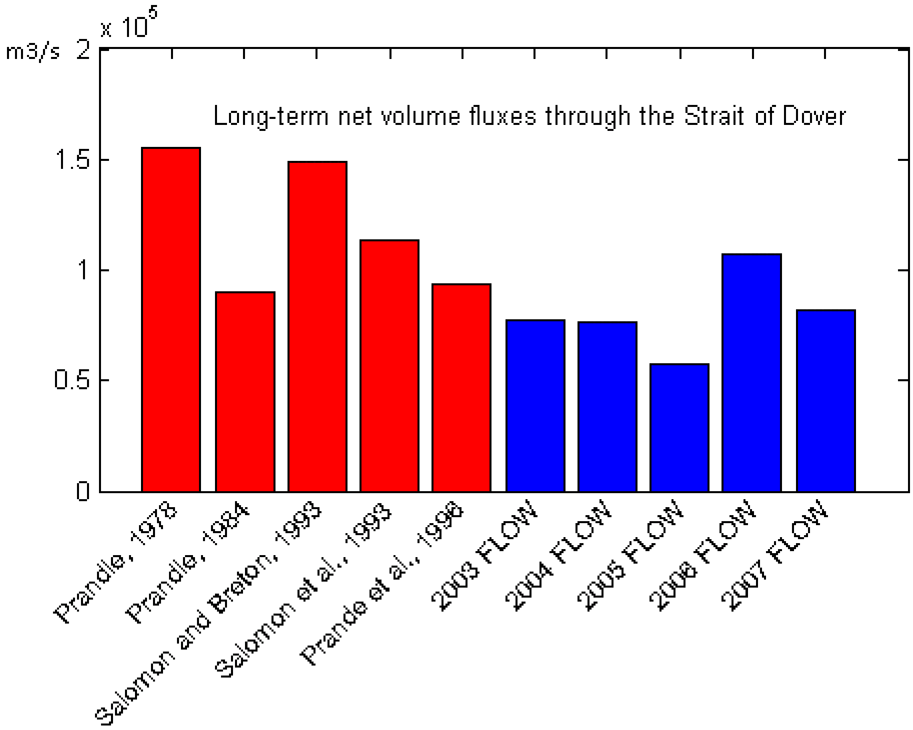


Figure 19. Long-term modelled volume fluxes through the Strait of Dover from literature (red) and modelled by FLOW (blue) (adapted from Gerritsen et al. 2000).

This indicates that the volume fluxes in the model are somewhat low, possibly causing the salinity to be lower in the offshore Belgian and Dutch coastal areas. However, increasing the residual flow through the Strait of Dover is out of the scope of this study, as it concerns the underlying FLOW model.

3.3.2 River loadings

A second cause of the salinity being too low in the offshore Belgian and Dutch coastal areas could be an overestimation of riverine influence in the area. In the Belgian coastal area salinities are being modeled well near shore (Figure 21). This indicates that river discharges from the Rhine and Scheldt that flow into the area are included correctly in the model.

The salinity is being underestimated in region NLC1 and NLC2 (Figure 17,Figure 20). This gives an indication that river inflow into the regions is being overestimated.

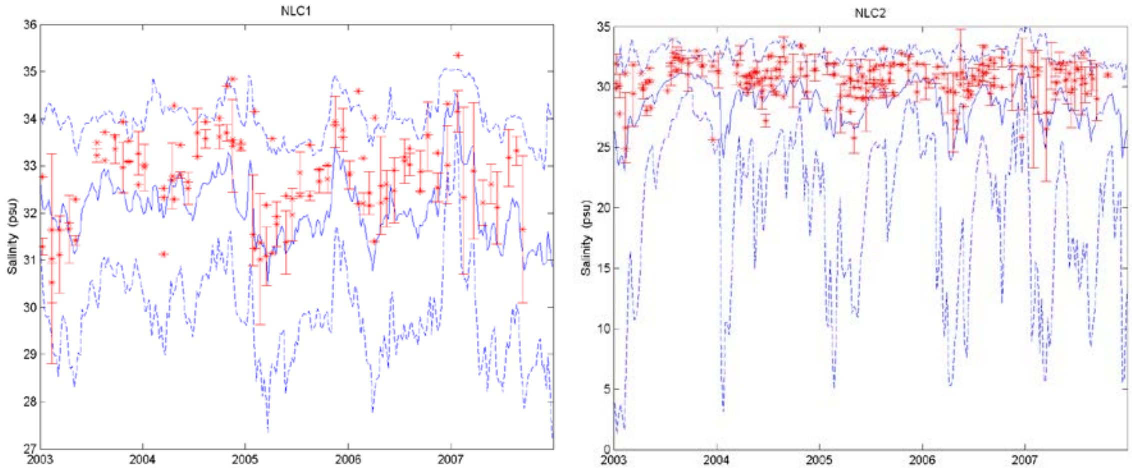


Figure 20. Average modeled (blue) and observed (red) salinities in the NLC1 and NLC2 OSPAR region. The dashed lines picture the maximum and minimum weekly medians of modeled salinities.

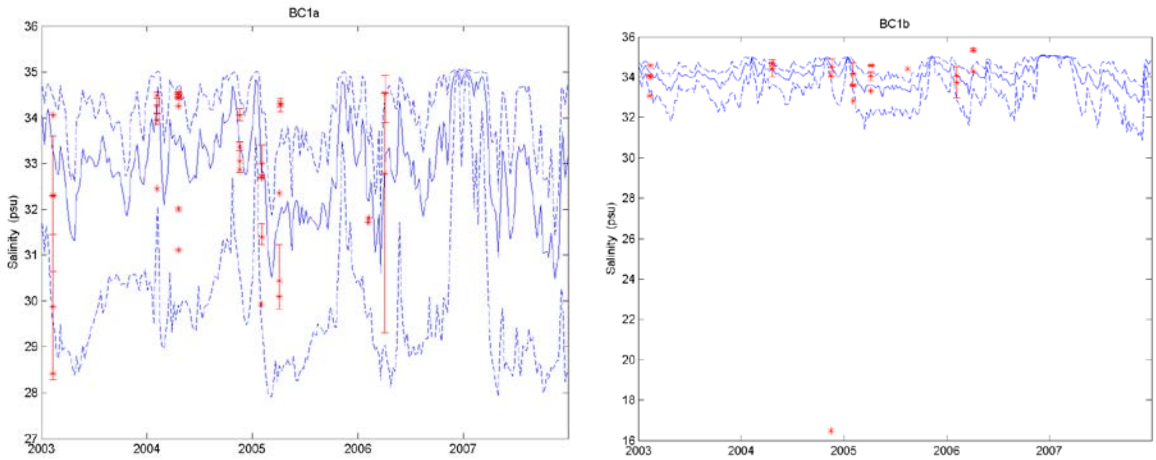


Figure 21. Average modeled (blue) and observed (red) salinities near the Scheldt estuary (BC1a) and 0-30 km from the shore (BC1b). The dashed lines picture the maximum and minimum weekly medians of modeled nutrient concentrations.

However, the river loads and discharges into the North Sea have been validated extensively in previous studies (Meuwese, 2007). The Waterbase dataset that was used to include the loads in GEM, is the largest dataset available of river loads. As a double check, the original data was compared to the loads in the model input file in order to ensure that no errors arose due to conversion mistakes. Plotting time series of the loads as included in the dataset against the loads in the model input file, showed that no mistakes have been made in the unit conversions (Appendix). Therefore, the observed error likely results partly from low volume fluxes through the Strait of Dover. However, within the scope of this study it is not possible to adjust these volume fluxes, as running the hydrodynamic model and matching the output with the GEM model is very time consuming.

3.3.3 Biochemical processes

Validation temperature

Lastly, model errors might result from parameter settings related to biochemical processes.
As discussed in section 2.2.1, mineralization rates are temperature dependent. Therefore, it is crucial that ambient water temperatures are included in the model correctly. Water temperatures in the upper

15 meters of the water column were validated using measurements from ICES. In all OSPAR regions, the ambient water temperature corresponds well with measurements (Figure 22). Therefore, observed errors in modeled nutrient concentrations are not likely to result from an under- or overestimation of modeled water temperatures. In region UKO1 temperatures are somewhat being underestimated. However, little measurements of nutrients were available for this region, which means that no clear link can be made between the error in the modeled temperatures in the region and possible errors in modeled nutrient concentrations.

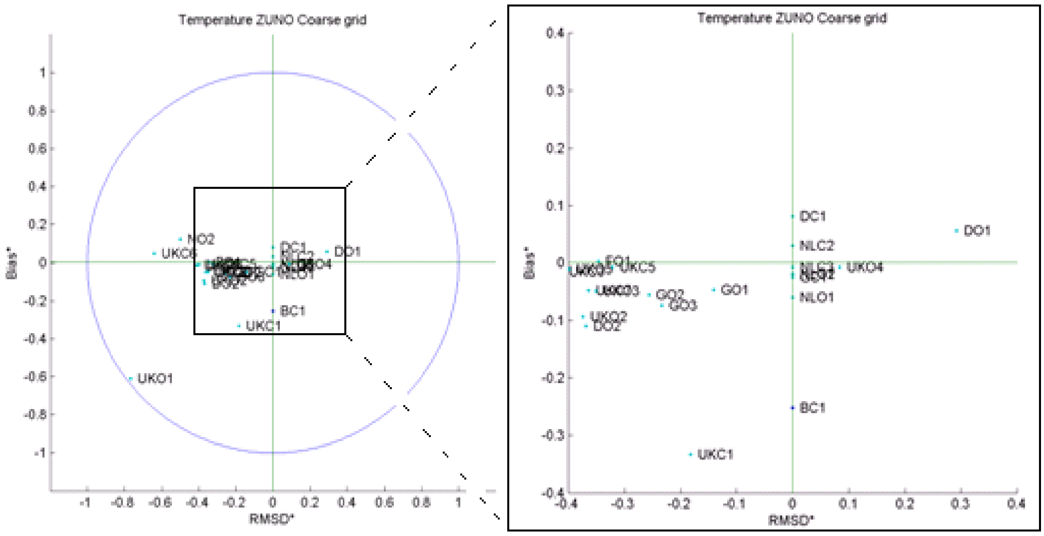
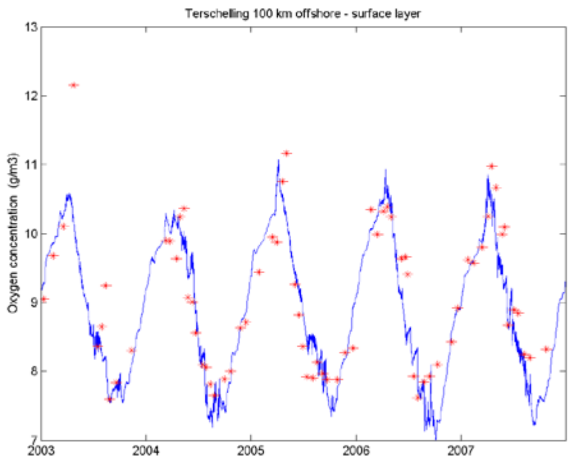


Figure 22. Target plots of model performance with regard to the temperature for different OSPAR regions in the period 2003-2007 in the 0-15 m depth zone.

Validation oxygen concentrations

Oxygen concentrations in the upper 15 meters of the water column are being captured well by the model (Figure 23). Modeled oxygen concentrations in every OSPAR region are within the RMSD* < 1 marker. However, the model does not capture oxygen depletion events of the bottom layer. Time series of different monitoring stations in the central North Sea show that in the years 2004-2007, no oxygen depletion events have occurred. However, during the summer of 2003 measured dissolved oxygen concentrations dropped until about 3 g/m^3, which is almost the concentration where mortality of marine organisms starts occurring, while modeled values didn't reach lower values than about 7



g/m^3 (

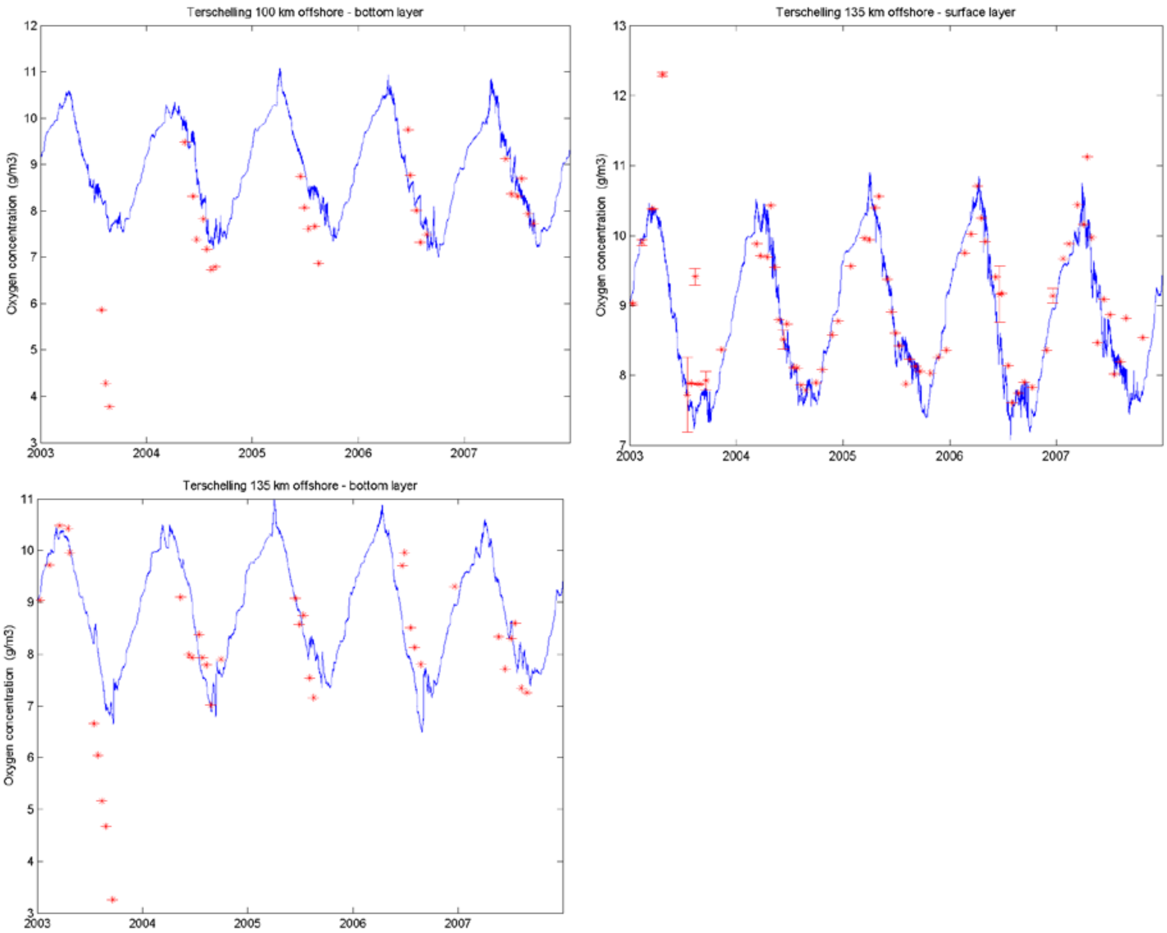


Figure 24).

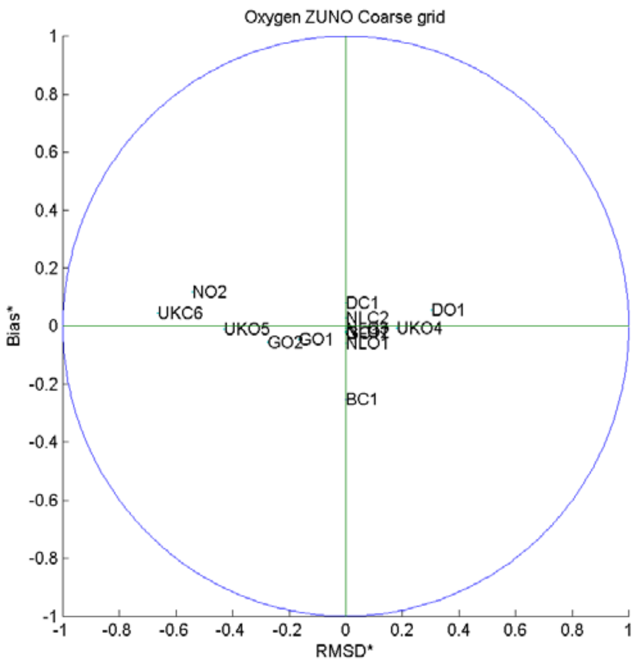


Figure 23. Target plots of model performance with regard to the oxygen concentration for different OSPAR regions in the period 2003-2007in the 0-15 m depth zone.

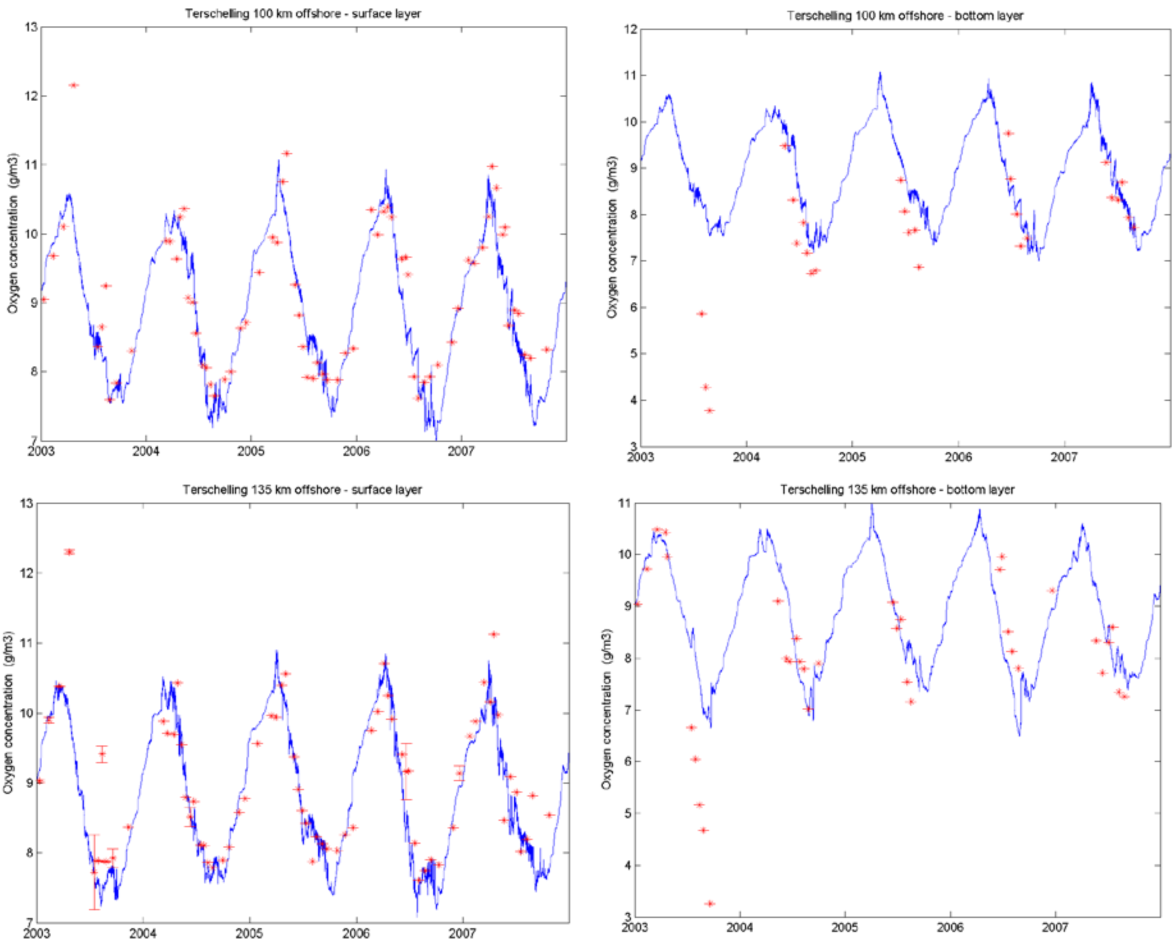


Figure 24. Modelled and observed dissolved oxygen concentrations in the surface layer and bottom layer of the stations Terschelling 100 and 135 km offshore

A vertical depth profile of monitoring station Terschelling 135 km offshore in the summer of 2003 shows that dissolved oxygen concentrations start to decrease below the thermocline at about 22 m depth (Figure 25). However, modeled values remain at about 8 g/m^3.

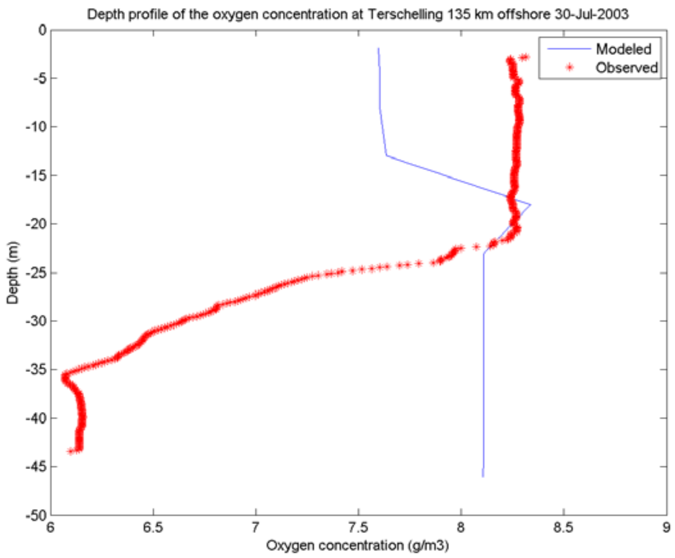


Figure 25. Depth profile of the dissolved oxygen concentration at Terschelling 135 km offshore at July 30th 2003.

From measurements at station Terschellingen 175 km offshore it can be observed that the model does capture small vertical gradients in oxygen concentrations (Figure 26).

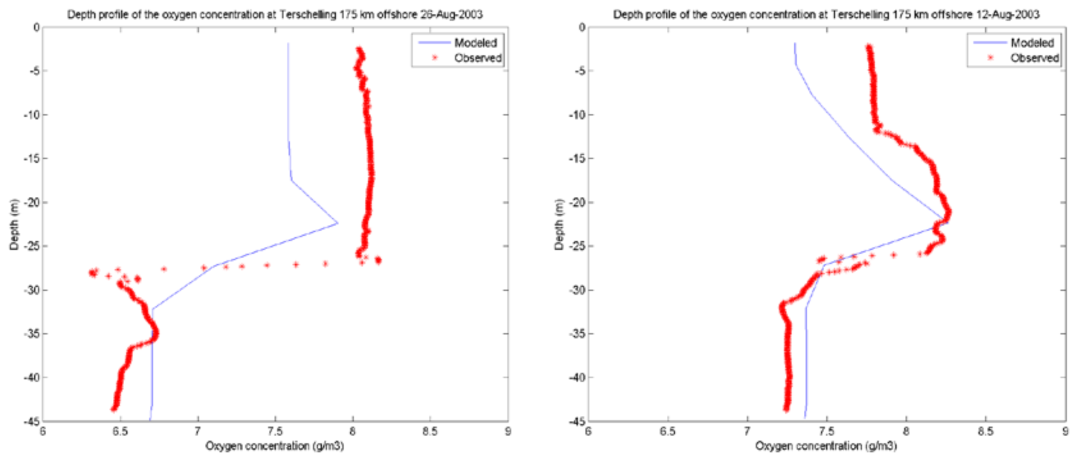


Figure 26. Depth profiles of the dissolved oxygen concentration at Terschelling 175 km offshore at August 12th and 26th 2003.

Due to time limitations, no further research is performed in analyzing the causes of the fact that the model does not capture severe oxygen depletion events. However, one simulation was performed where the vertical dispersion of substances in the model was reduced extremely. Namely, it is known that from earlier studies that vertical mixing is being overestimated by the model in the central North Sea (Los, F.J., personal communication). However, reducing the vertical dispersion of substances did not lead to a drop in oxygen concentrations in the bottom, as was expected based on the limited reaeration that would occur. Instead, oxygen concentrations increased across the entire water column, with a peak at the mixed layer depth. This might occur as a consequence of an increase of light availability in the photosynthetically active layer, due to the lower degree of mixing. The observed error is discussed further in section 4.

As both the temperature and oxygen concentrations are being modeled well in the 0-15 m zone of the water column, the different parameters as discussed in section 2.4.2 were varied in order to improve modeled nutrient concentrations. Due to time limitations, the analysis focused on improving modeled nutrient concentrations in the Dutch EEZ as this is an area where economic activity is high. However, the effect of varying the parameters on other OSPAR regions will be discussed briefly as well.

3.4 Sensitivity analysis

Validation of modeled nutrient concentrations showed that nitrate and silicate concentrations are generally being overestimated in the Dutch regions of the North Sea. Concentrations of phosphate being modeled well or slightly overestimated in these regions. Likely, this can partly be explained by the relatively low residual flows through the Strait of Dover, which is discussed in more detail in section 4. However, the model makes use of several parameters of which the exact values are not known, as they are not all being measured in situ. In addition, due to the simplification of processes in the model in comparison with reality, model parameter values do likely not reflect process rates exactly as observed in reality. Therefore, the parameters can be adjusted in order to fit modeled nutrient concentrations in the water column with measurements.

3.4.1 Nitrate concentrations

Nitrate concentrations in the water column can be adjusted by varying several parameters: the burial rate of organic matter into the upper layer (S1) of the sediment, the denitrification rate in the water column and sediment, respectively, the mineralization rate of nitrogen in the water column and sediment, respectively, and the nitrification rate (see section 2.4.2).

The sensitivity of the model for the different parameters is clearly region dependent, which can be observed from the change in RMSE of modeled nitrate concentrations with respect to observations if the parameters are adjusted by 80% (

Table 5). In Appendix 5.2 the gradual change in RMSE is visualized per region. Generally, in coastal regions the model is most sensitive to adjustments in the denitrification rate in the sediment.

Table 5. **Percentage change in RMSE after an 80% increase or decrease of the different parameters. The values in bold indicate the parameter change to which the model was most sensitive in each region.**

Region type	Region name	% Change of RMSE					
		Burial rate for layer S1	**Denitrification rate in layer S1**	**Mineralisation rate in layer S1**	**Mineralisation rate in the water column**	**Denitrification rate in the water column**	**Nitrification rate**
Coastal	'BC1'	1,7	**23,4**	-0,3	8,1	10,5	2,3
	'DC1'	-1,2	**16,1**	2,5	10,9	7,1	-3,1
	'GC1'	4,3	**24,1**	1,1	6,2	9,9	9,3
	'NLC1'	-3,9	-4,1	-11,2	**-14,5**	-5,8	-8,1
	'NLC2'	-3,1	**-8,8**	-5,3	-6,7	-5,0	-6,9
	'NLC3'	-4,2	-14,3	-15,2	**-22,3**	-10,0	-9,1
Offshore	'DO1'	-16,1	-13,3	**-18,2**	-11,8	-15,6	-16,3
	'GO1'	-6,9	-0,6	**-12,5**	-5,7	-1,7	-7,4
	'GO2'	-9,9	-8,8	**-13,5**	-2,3	-8,0	-3,1
	'NLO1'	-12,5	-12,6	-18,8	-24,9	-12,1	**-33,4**
	'NLO2'	-8,1	-5,2	-6,9	-17,8	-6,4	**-27,5**
	'UKO4'	-4,0	-5,8	-0,1	**-14,7**	-7,6	-11,7

Likely, the higher sensitivity of the model to the denitrification rate in the sediment in coastal regions can be explained by the higher amount of detritus available in the upper layer of the sediment compared to offshore regions (Figure 27). Namely, denitrification rates are dependent on concentrations of ammonium available that are being released via the mineralisation of detritus. The denitrification rate in the water column has a lower impact on modelled nitrate concentrations, due to the higher oxygen concentrations present that inhibit the denitrification process.
In region NLC1, the model is more sensitive to adjustments in the mineralisation rate in both the water column and the sediment than the burial rate. Likely, this is due to the fact that region NLC1 is a very dynamic region where the Rhine flows into the North Sea. Therefore, the amount of detritus present in the upper layer of the sediment is relatively low in the region(Figure 27).

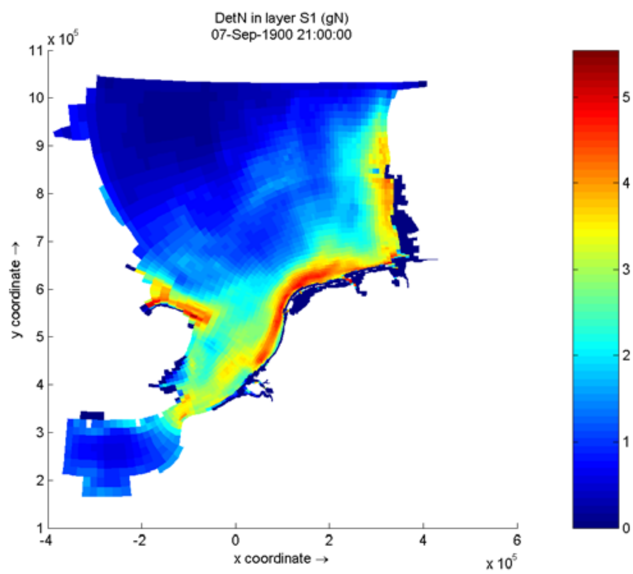


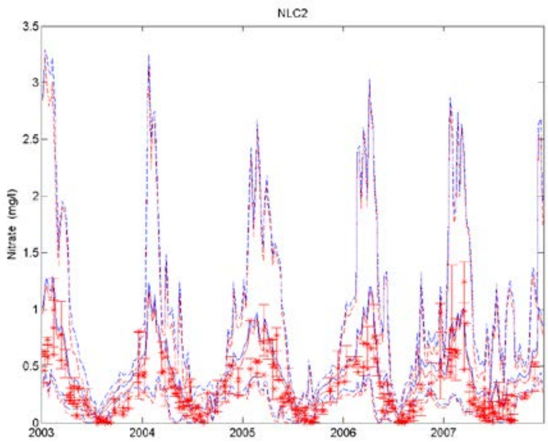
Figure 27. Amount of nitrogen incorporated in detritus in the upper layer of the sediment.

In the offshore regions where hardly any detritus is present in the sediment (NLO2 and UKO4), the model is most sensitive to adjustments in parameters related to the water column: the mineralisation and nitrification rate (

Table 5). In the offshore regions DO1, GO1, GO2 and NLO1, located in the eastern part of the North Sea where still a considerable amount of detritus is present in the upper sediment layer, the model is most sensitive to changes in the mineralization rate in layer S1.
In region NLC1 and NLC3 the RMSE can most effectively be reduced by decreasing the mineralisation rate in the water column.

The Dutch EEZ
As discussed in section 3.3.3, parameters were varied with the primary goal of improving modeled nutrient concentrations in the Dutch EEZ. All parameter adjustments lead to an improvement of modeled nitrate concentrations in region NLC2, as they lead to a lower concentration of nitrate in the water column, reducing the overestimation of the model with respect to observations (

Table 5). In region NLC2, the model is most sensitive to adjustment of the denitrification rate in the upper layer of the sediment. An adjustment of 80% of the parameter leads to a reduction of the RMSE of modeled nitrate concentrations with respect to in situ measurements of 8,8% (.



b.

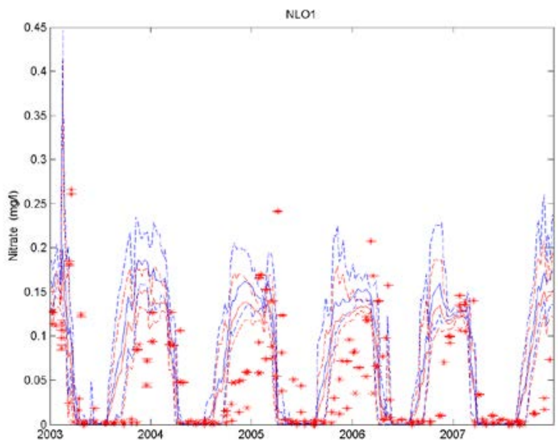


Figure 28).

Increasing the denitrification rate decreases nitrate concentrations in the water column and generally causes the position of the regions in the target plot to move downwards (Figure 29). In the regions located above the x-axis, nitrate concentrations were being overestimated in the default model set-up. Therefore, elevating the denitrification rate generally improves model fit for these regions. Even though the parameter is sediment related, adjustment can also improve modeled nitrate concentrations in offshore regions. In the NLO1 region, an 80% reduction of the parameter reduces the RMSE of modeled nitrate concentrations with 12,6% (

Table 5,Figure 29).

However, in some regions model bias was already low, and increasing the denitrification rate by 80% would cause the model to show a negative bias instead. In the regions GO1, NLC1 and UKO4 the denitrification would therefore need to be adjusted only by about 10%, 40% and 20%, respectively. In the regions located below the x-axis, nitrate concentrations were already underestimated by the model. Lowering nitrate concentrations in the water column therefore logically increases the negative model bias. As denitrification rates were already set to zero in the default model set-up, another parameter, such as the mineralisation rate in the water column, needs to be adjusted in order to improve model fit in these regions.

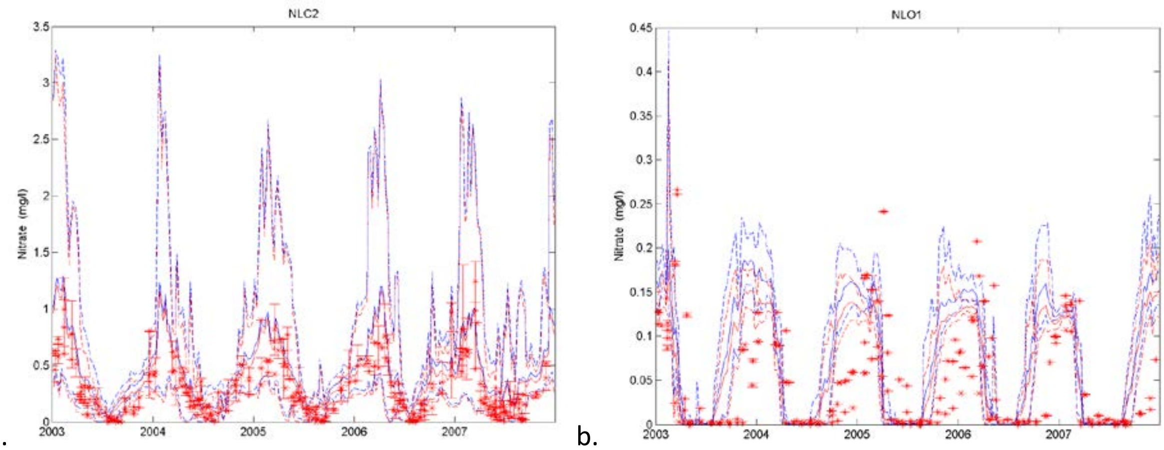


Figure 28. Average modelled nitrate concentrations from the standard model run (blue) and a reduction fo 80% of the denitrification rate in layer S1 (red). The dashed lines picture the maximum and minimum weekly medians of modeled nutrient concentrations.

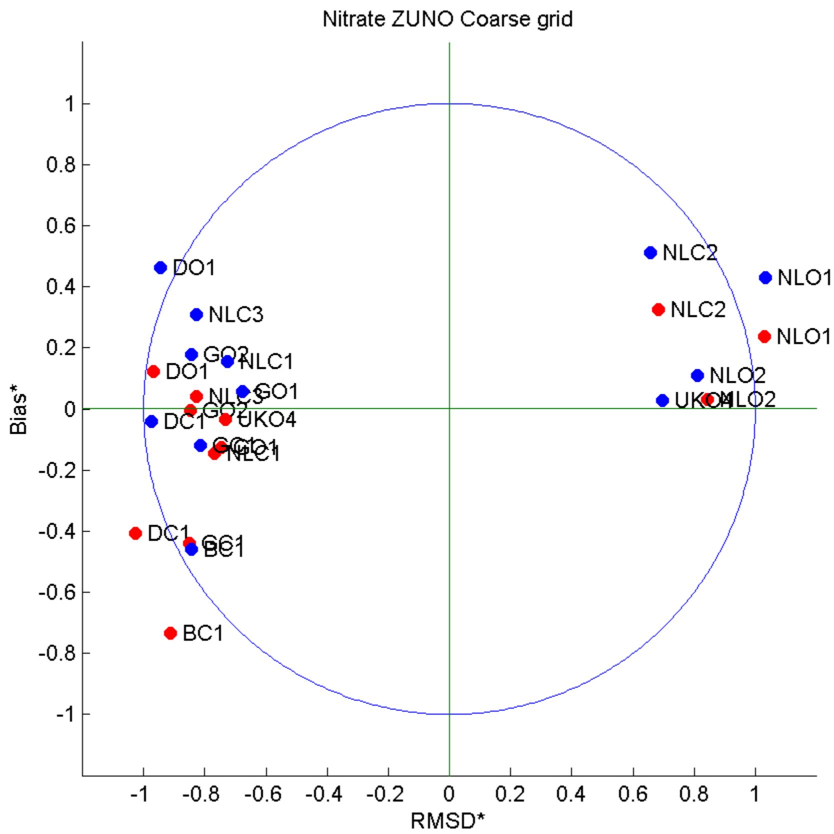


Figure 29. Target plot of modelled nitrate concentrations in different OSPAR regions for the default model run (blue) and a reduction of 80% of the denitrification rate in the upper layer of the sediment.

3.4.2 Phosphate concentrations

Phosphate concentrations in the water column are adjusted by varying the following parameters: the burial rate of organic matter into the upper layer (S1) of the sediment, the mineralisation rate in the water column and the mineralisation rate in the sediment (section 2.4.2).

Among the coastal regions, the sensitivity of the model to the different parameters is strongly region dependent. In region NLC2 and NLC3 the model is most sensitive to adjustment of the burial rate. In other coastal regions, phosphate concentrations in the water column can most effectively be recalibrated by adjusting the mineralization rate in the water column or sediment. Altering any of the parameters by 80% has only a small effect on the RMSE of modeled phosphate concentrations in the regions BC1, NLC2 and NLC3 (Table 6). Here, transport of nutrients and river loads likely play a more dominant role in determining local phosphate concentrations.
As was observed in the sensitivity analysis of nitrogen related parameters, the model is most sensitive to adjustment of the mineralisation rate in the water column in the dynamic region NLC1.

In offshore regions, the model is generally most sensitive to adjustments in the mineralisation rate in the water column. In the regions NLO2 and UKO4, where only little amounts of detritus are present in the upper layer of the sediment (Figure 30), the sensitivity of the model for the mineralization rate in the water column is highest. In regions where a considerable amount of detritus is present in the sediment, all three parameters can improve modeled phosphate concentrations in the water column.

Table 6.Percentage change in RMSE after an 80% increase or decrease of the different parameters. The values in bold indicate the parameter change to which the model was most sensitive in each region.

Region type	**Region name**			
		Burial rate for layer S1	Mineralisa-tion rate in layer S1	Mineralisa-tion rate in the water column
Coastal	'BC1'	0,6	0,97	**1,4**
	'DC1'	18,0	**32,3**	29,7
	'GC1'	15,3	**27,8**	24,1
	'NLC1'	4,4	14,3	**22,0**
	'NLC2'	**-6,5**	-1,4	-2,4
	'NLC3'	**-3,1**	-2,1	-2,1
Offshore	'DO1'	**-31,7**	-29,6	-30,4
	'GO1'	**-22,9**	-20,6	-17,9
	'GO2'	-23,5	-18,3	**-35,9**
	'NLO1'	-16,2	-19,1	**-21,0**
	'NLO2'	-11,3	-17,9	**-47,7**
	'UKO4'	-8,0	-12,5	**-40,7**

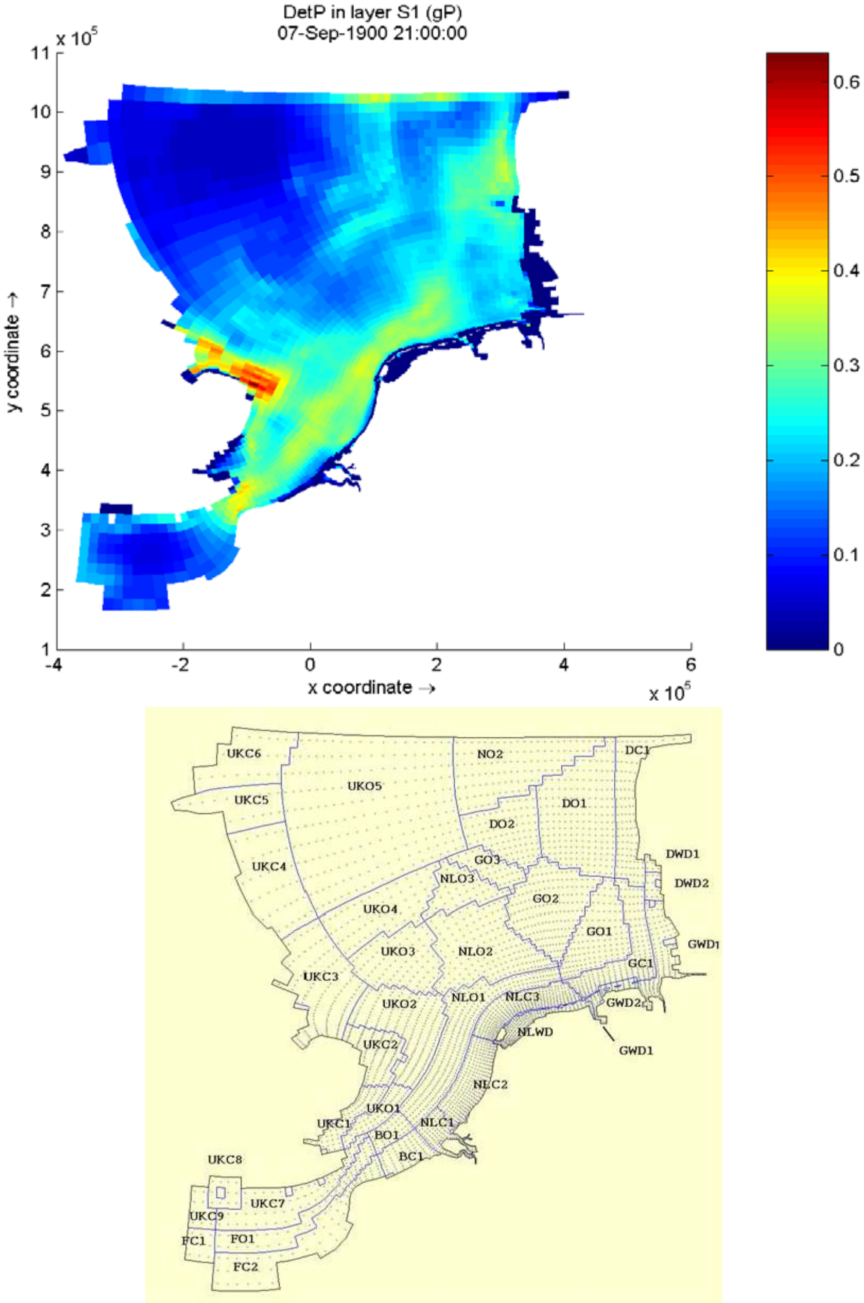
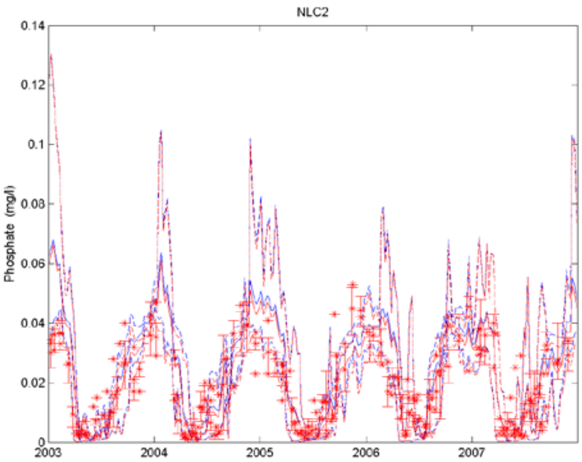


Figure 30. Amount of phosphorus incorporated in detritus in the upper layer of the sediment

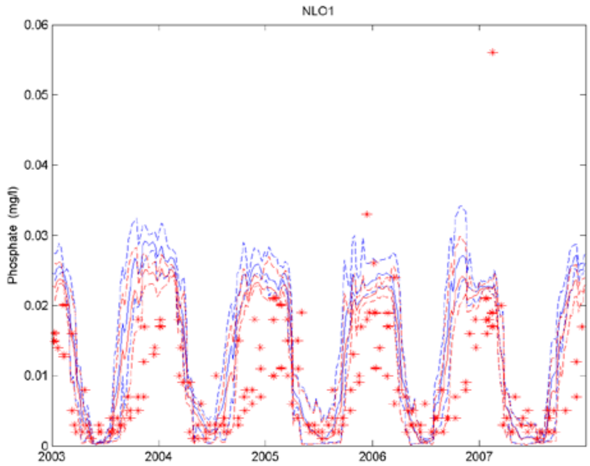
The Dutch EEZ

All parameter adjustments can improve model fit with regard to phosphate concentrations in region NLC2. However, the model is most sensitive to adjustments in the burial rate (Table 1).

Elevating the burial rate of organic matter to the upper layer of the sediment, reduces the RMSE of modeled phosphate concentrations by 6,5%. Average modeled phosphate concentrations in the region become lower and are better fitting with observations


NLC2
Phosphate (mg/l)
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
2003
2004
2005
2006
2007

(


NLO1
Phosphate (mg/l)
0.06
0.05
0.04
0.03
0.02
0.01
0
2003
2004
2005
2006
2007

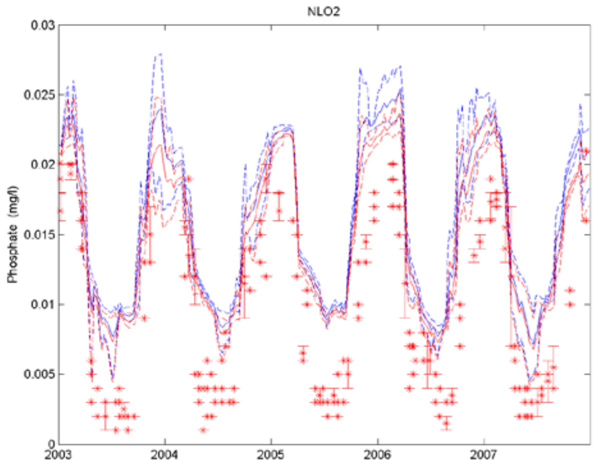

NLO2
Phosphate (mg/l)
0.03
0.025
0.02
0.015
0.01
0.005
0
2003
2004
2005
2006
2007

Figure 31).

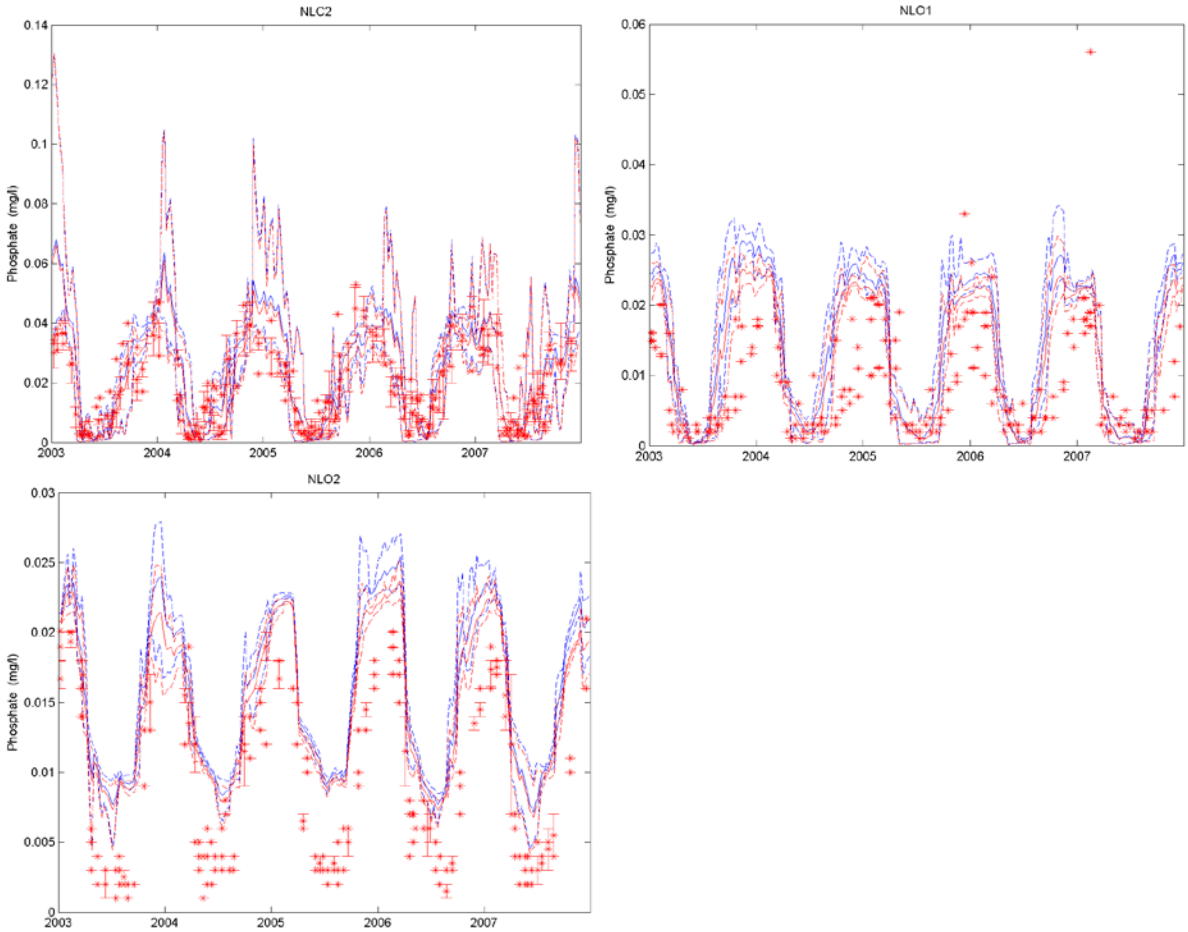


Figure 31. Average modelled phosphate concentrations from the standard model run (blue) and a reduction of 80% of the burial rate in layer S1 (red). The dashed lines picture the maximum and minimum weekly medians of modeled phosphate concentrations.

In the majority of the North Sea regions phosphate concentrations are being overestimated by the model. Increasing the burial rate of organic matter therefore improves model fit in most regions, which are located above the x-axis (Figure 32). In the regions BC1, DC1, GC1, NLC1 and NLC3 phosphate concentrations were underestimated by the model. Therefore, elevating the burial rate only increases the model bias.

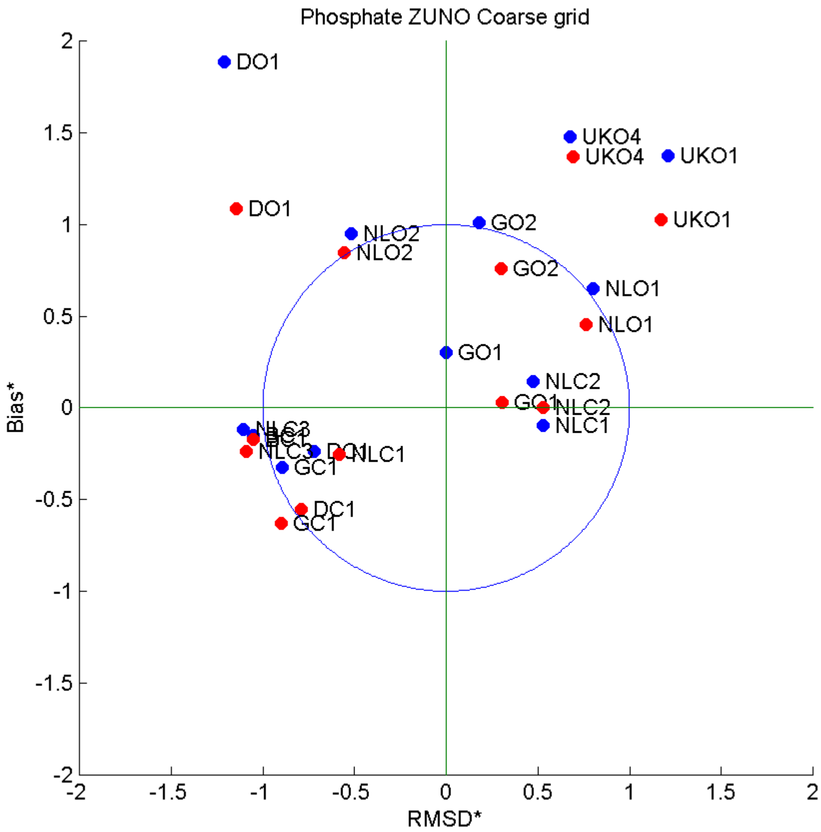


Figure 32. Target plot of modelled phosphate concentrations in different OSPAR regions for the default model run (blue) and a reduction of 80% of the burial rate in the upper layer of the sediment.

In order to improve model fit in the regions located below the x-axis, the burial rate would need to be varied regionally.

3.4.3 Silicate concentrations

Silicate concentrations in the water column can be changed by adjusting several parameters. The following parameters were varied: the burial rate of organic matter into the upper layer (S1) of the sediment and the mineralisation rate in the water column and sediment.

In all regions the model is most sensitive to changes in the mineralisation rate in the water column (Table 7). This indicates that most siliceous skeletal material is being recycled there instead of settling to the bottom first.

Table 7. Percentage change in the RMSE after an 80% increase or decrease of the different parameters. The values in bold indicate the parameter change to which the model was most sensitive in each region.

Region type	Region name	Burial rate for layer S1	Mineralisation rate in layer S1	Mineralisation rate in the water column
Coastal	'BC1'	1,7	0,9	**12,3**
	'DC1'	-0,7	-7,5	**-27,0**
	'GC1'	4,3	-3,8	**-4,9**
	'NLC1'	-2,5	-6,0	**-16,9**
	'NLC2'	-1,8	-2,4	**-9,9**
	'NLC3'	-4,9	-9,8	**-27,3**
Offshore	'DO1'	-12,9	-7,2	**-29,0**
	'GO1'	-4,2	-9,0	**-16,9**
	'GO2'	-6,5	-3,7	**-14,8**
	'NLO1'	-8,0	-8,0	**-44,2**
	'NLO2'	0,1	0,6	**30,1**
	'UKO4'	-1,2	0,1	**-4,3**

In the Dutch OSPAR regions, modelled silicate concentrations can also be improved most effectively by reducing the mineralisation rate of organic material in the water column. It can be observed that adjusting the parameter improves model fit with respect to observations (Figure 33).

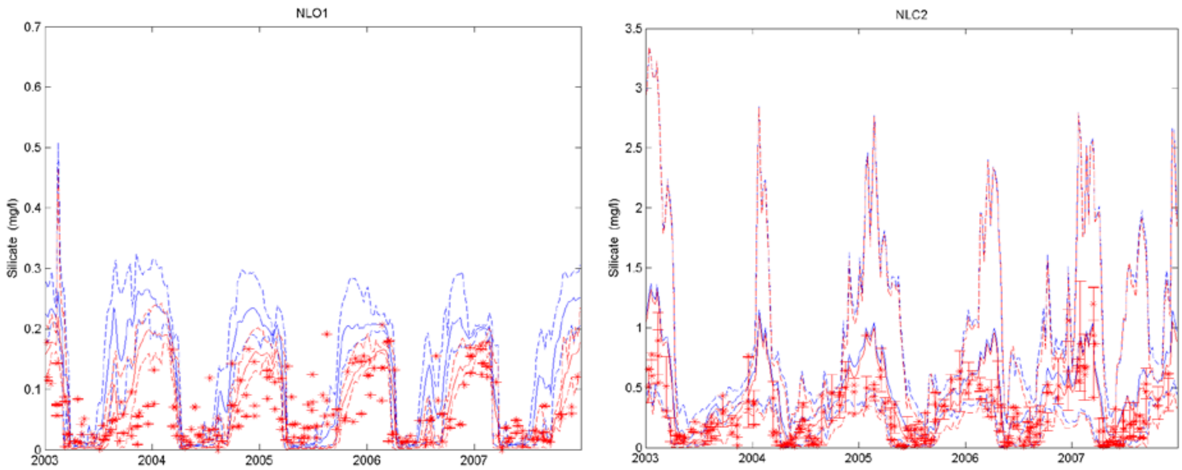


Figure 33. Average modelled silicate concentrations from the standard model run (blue) and a reduction of 80% of the mineralisation rate in the water column (red lines). The dashed lines picture the maximum and minimum weekly medians of modeled silicate concentrations.

Reducing the mineralisation rate in the water column reduces the bias of the model in most regions of the North Sea, as silicate concentrations tend to be overestimated in the default model (Figure 34). However, in the regions BC1 and NLO2 silicate concentrations were already being underestimated and therefore, the mineralisation rate in the water column would have to be adjusted in the opposite direction in order to improve model fit.

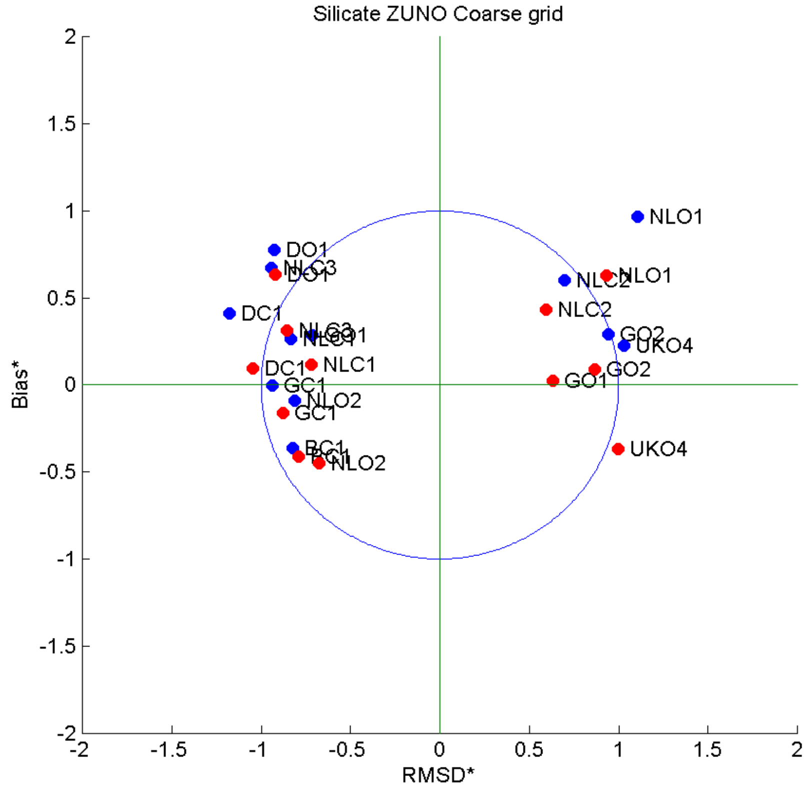


Figure 34. Target plot of modelled silicate concentrations in different OSPAR regions for the default model run (blue) and a reduction of 60% of the burial rate in the upper layer of the sediment.

4 Conclusions and Discussion

In this study, validation results of the GEM model with regard to the prediction of phytoplankton growth and nutrient concentrations are presented. Furthermore, possible causes of errors in modelled nutrient concentrations are identified and suggestions for improvement in the Dutch EEZ are given.

The GEM model shows a negative bias of modelled chlorophyll-a concentrations with respect to observations. In the Dutch EEZ, the GEM model generally predicts the initialisation of the spring bloom 2-4 too late. Likely, this error is not related to model performance with regard to nutrient concentrations present, as nutrients are available in high concentrations during this time of the year. In coastal regions, temperature and light availability are the main limiting factors for phytoplankton growth in spring (Kaiser et al., 2011).

Nutrient concentrations are generally predicted well by the model, as the RMSD* is < 1 in most regions of the North Sea. However, it can be observed that in offshore regions phosphate and silicate concentrations are generally being overestimated. Furthermore, nutrient concentrations can be further improved in the Dutch regions NLC2 and NLO1, where concentrations of all nutrients considered are being overestimated by the model.

The observed error in modelled nutrient concentrations in the Dutch EEZ is not likely to result from an error in river loads, as they have been validated extensively in previous studies (Meuwese, 2007). However, volume fluxes through the Strait of Dover are significantly below the long-term average in the considered time period. In FLOW, the yearly residual flow is in the range of 57.078-81.811 m^3/s for the considered time period, except for the year 2006 where the yearly residual flow is 106.860 m^3/s. Residual flows calculated in earlier studies are within the range of 94.000-150.000 m^3/s and

therefore significantly higher. This likely causes the riverine influence in the Dutch EEZ to be overestimated by the model, as freshwater is flushed away to a lesser extent along with the long shore current. Therefore, the residence time of the freshwater increases, leading to an underestimation of the salinity and an overestimation of nutrient concentrations in the area. Indeed, the salinity in the Dutch OSPAR regions NLC1, NLC2, NLO1 and NLO2 is being underestimated by 1-1.4 psu. Furthermore, in the Belgian BC1 region > 30 km offshore the salinity is being underestimated by about 2 psu. The relatively low volume fluxes likely contribute to the observed overestimation of nutrient concentrations in the Dutch EEZ.
In addition, freshwater generally contains relatively large amounts of DOC, whereas marine water as a rule contains only very small amounts of these substances. DOC makes a significant contribution to the extinction of light in the water column. As a consequence, a negative linear correlation exists between the salinity and DOC (Brockmann et al., 1990). This empirical relationship is included in the light extinction process in GEM. An underestimation of the salinity in the model can therefore cause the onset of the spring bloom to be too late, as the amount of dissolved humic acids is being overestimated, leading to higher light extinction. Along with the water temperature light availability is an important limiting factor in coastal areas. Therefore, this likely explains part of the observed error in the onset of the spring bloom. If less light is available, the onset of the spring bloom will be delayed until the sun is higher in the sky and light intensity is enough for a bloom to be initiated.

Increasing the residual flow through the Strait of Dover is out of the scope of this study, as it concerns the underlying FLOW model. However, it is recommended to run simulations of GEM with about 50-100% higher residual flows through the Strait of Dover. This will likely improve modelled nutrient concentrations in the Dutch EEZ. However, this will likely lead to an underestimation of nutrient concentrations in the Belgian EEZ, as it will reduce riverine influence in the area. This implicates that nutrient concentrations in the Belgian EEZ are currently predicted right for the wrong reasons. This is very likely, as in the Belgian coastal area submerged sand banks and a shallow region offshore of the mouth of the Scheldt estuary modify the tidal residual current, resulting in a clockwise residual gyre that transports water from the Scheldt south-westward and then offshore (Lacroix et al., 2004). This means that the residence time of the water is higher in reality than currently included in the model. Improving the hydrodynamics in the area would lead to higher nutrient concentrations present, which could balance out an increase of the offshore residual flow. Further research is required on the hydrodynamic processes that occur in region BC1, in order to gain further insight in chemical and biological distributions in the area. COHERENS is a 3D hydrodynamic model of the area that is replicating salinities well in the Belgian coastal zone (X. Desmit, personal communication). It is recommended to align the FLOW model with COHERENS in order to improve modelled hydrodynamics in the area.

Water temperatures and dissolved oxygen concentrations are replicated well by the GEM model. However, it needs to be highlighted that the model is not able to capture oxygen depletion events in the deeper layers of the central North Sea. This could be due to an underestimation of the degree of stratification in the water column by the FLOW model. However, decreasing the vertical dispersion of substances did not improve modelled dissolved oxygen concentrations in the water column (section 3.3.3). Therefore, it is recommended to further examine the mechanisms behind oxygen depletion events in the central North Sea. Namely, under certain conditions benthic fauna starts to show unusual behaviour when oxygen levels drop below 2 ml O_2/l, such as abandoning their shelters. They subsequently become available for epibenthic predators, increasing the energy flow to higher trophic levels. Oxygen levels below 0.5 ml O_2/l can result in mass mortality of fish and benthic invertebrates (Kaiser et al., 2011). Prediction of these events is desirable in order to be able to protect the diverse

benthic fauna present on the oyster ground in the central North Sea.
Due to time limitations the temperature and oxygen concentrations in the deeper layers of the model have not been validated for the entire North Sea. It is recommended to do so in the future, as many sediment related processes are directly or indirectly coupled to the temperature or oxygen concentrations in the upper layer of the sediment.

The sensitivity analysis of the nitrogen and phosphorus related parameters shows that in coastal regions the model is most sensitive to sediment-related parameters. Regarding nitrogen related parameters, the model is most sensitive to adjustment of the denitrification rate in the sediment in coastal regions. To improve modelled phosphate concentrations in coastal regions, it is most effective to adjust the burial rate of organic matter or the mineralisation rate in the sediment. This can be explained by the fact that in coastal regions high amounts of detritus are available in the upper layer of the sediment. The high sensitivity of the model to sediment-related parameters in coastal regions shows that the nutrients released from the detritus via mineralisation contribute significantly to the total nutrient concentrations present in the water column.
Regarding silicate related parameters, it is observed that the model is most sensitive to adjustment of the mineralisation rate in the water column. This indicates that most siliceous skeletal material is being recycled there instead of settling to the bottom first.
Genrally, in offshore regions where little amounts of detritus are present in the upper layer of the sediment, the model is most sensitive to the mineralisation rate in the water column. In offshore regions where still a considerable amount of detritus is present, mainly the regions DC1 and GC1, the model is sensitive to sediment related parameters as well.

In order to improve modelled nitrate concentrations in the Dutch regions NLC2 and NLO1, the denitrification rate in the upper layer of the sediment can be elevated by 80%. Model fit with regard to modelled phosphate concentrations in the region can be improved by increasing the burial rate of organic matter by 80%. To improve model fit regarding silicate concentrations in the regions, the mineralisation rate in the water column can be reduced by 80%.
Adjusting the burial rate of organic matter would affect concentrations of all nutrients. Therefore, another option would be to increase the burial rate in combination with other parameters. It is recommended to further explore how the errors of modelled nutrient concentrations with respect to measurements can be reduced by adjusting different parameters simultaneously. As the sensitivity of the model with respect to the different parameters varies regionally, the adjustment of multiple parameters simultaneously likely leads to a better model fit than when only one parameter is varied. In addition, as model performance regarding nitrate, phosphate and silicate concentrations varies regionally it is inevitable to adjust parameters regionally in order to improve modelled nutrient concentrations in the entire North Sea. For example, in regions where nitrate concentrations were only slightly being overestimated (GO1, NLC1 and UKO4), the denitrification rate would need to be adjusted by only 10-40%. In other regions, the denitrification could be elevated more extremely.

5 Appendices

5.1 Appendix 1 River loads Scheldt and Rhine river

5.1.1 River loads from the Scheldt

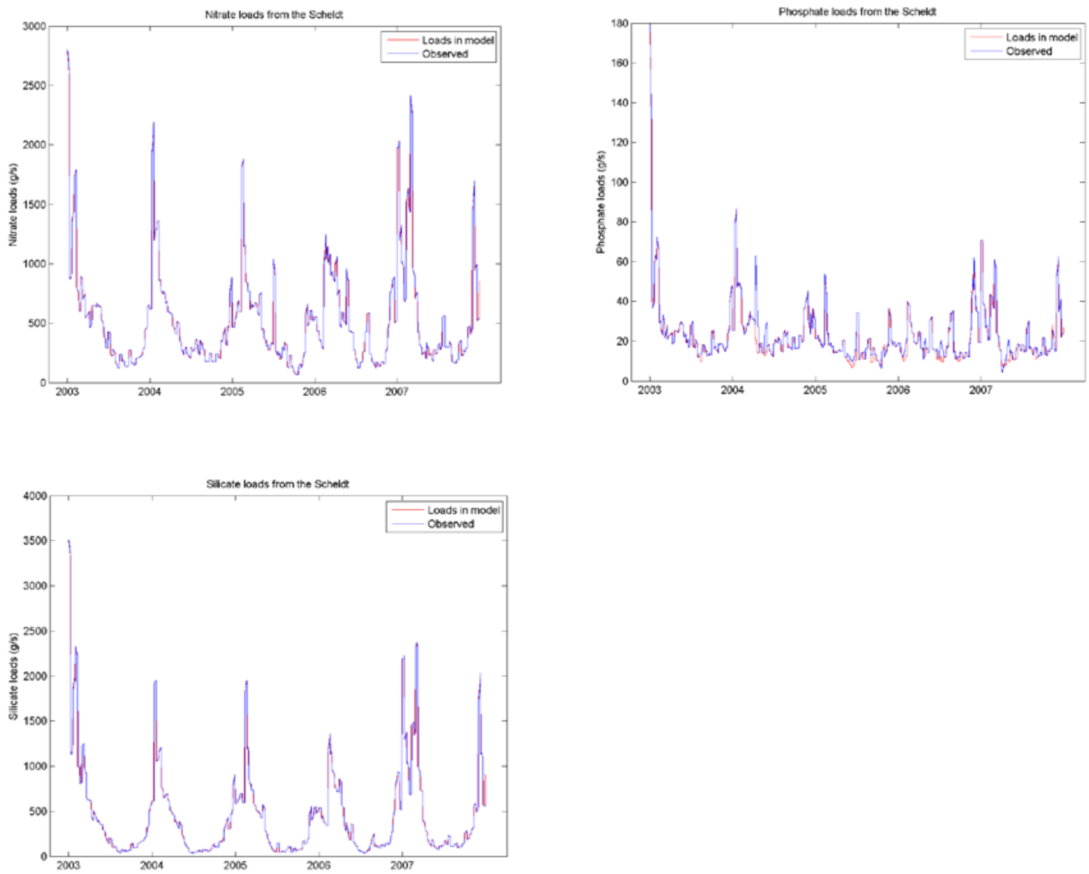
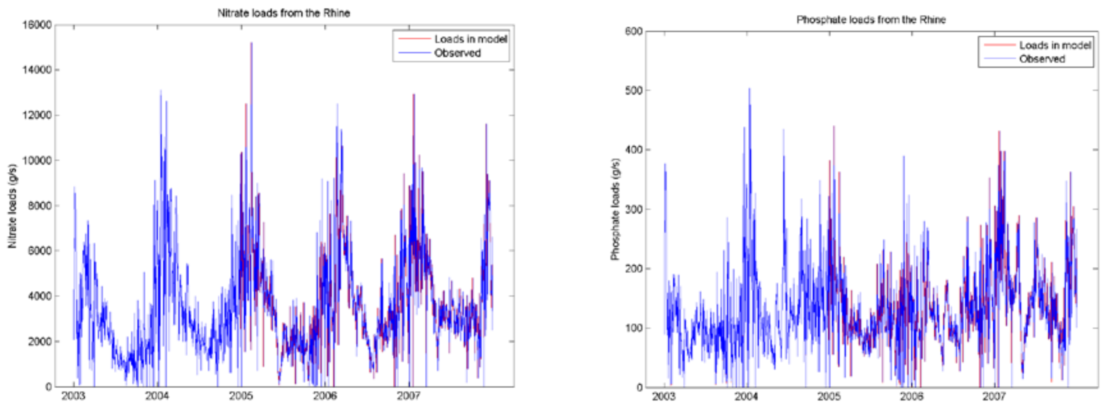


Figure 35. Modelled (red) and observed (blue) nitrate, phosphate and silicate loads from the Scheldt to the North Sea.

5.1.2 River loads from the Rhine



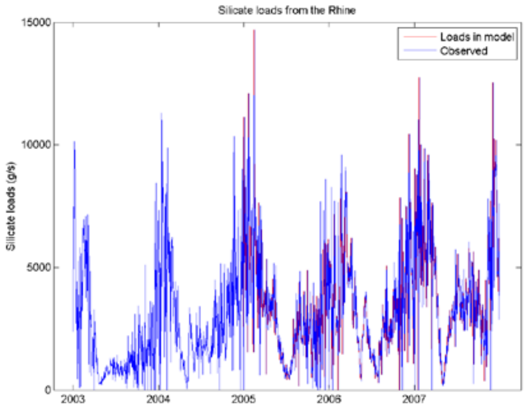
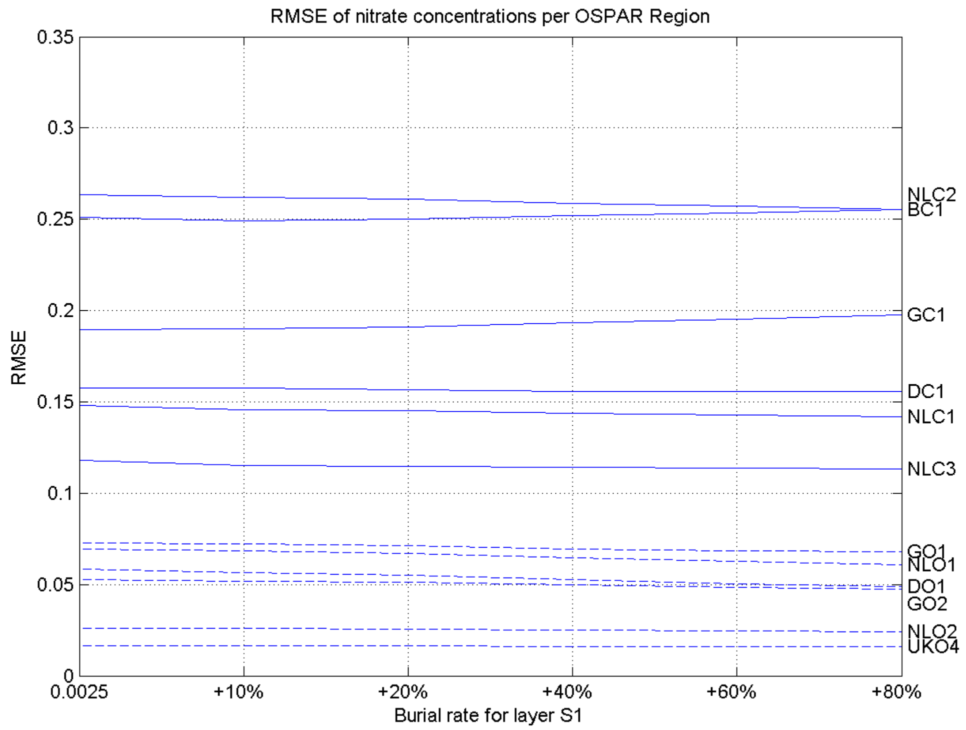
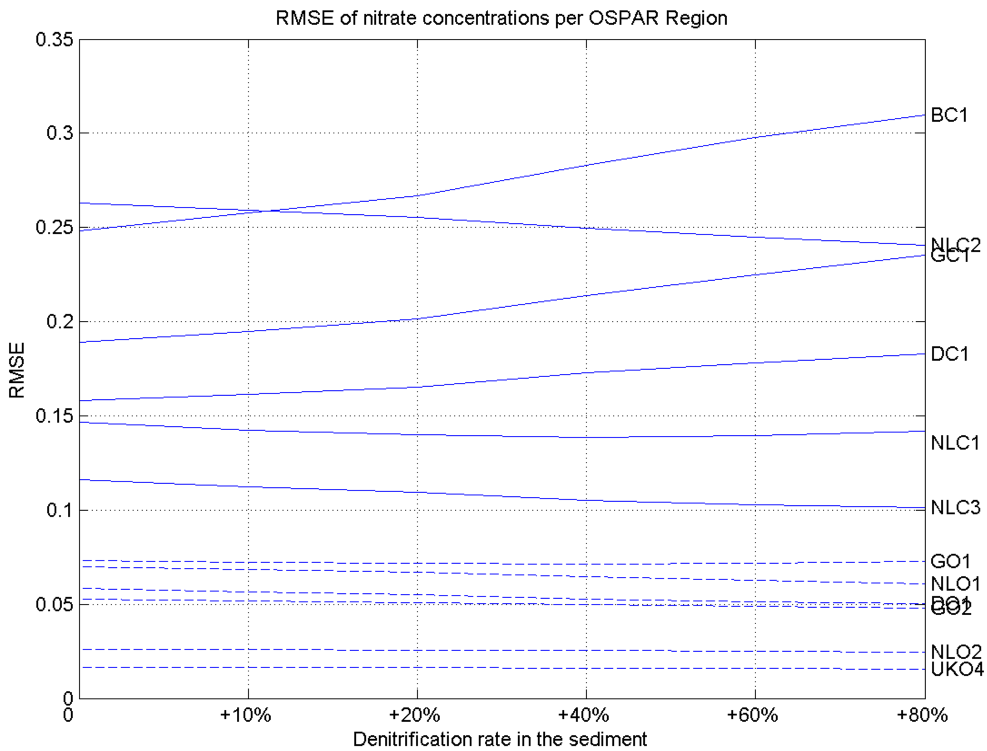


Figure 36. Modelled (red) and observed (blue) nitrate, phosphate and silicate loads from the Rhine to the North Sea.

5.2 Appendix 2 RMSE plots

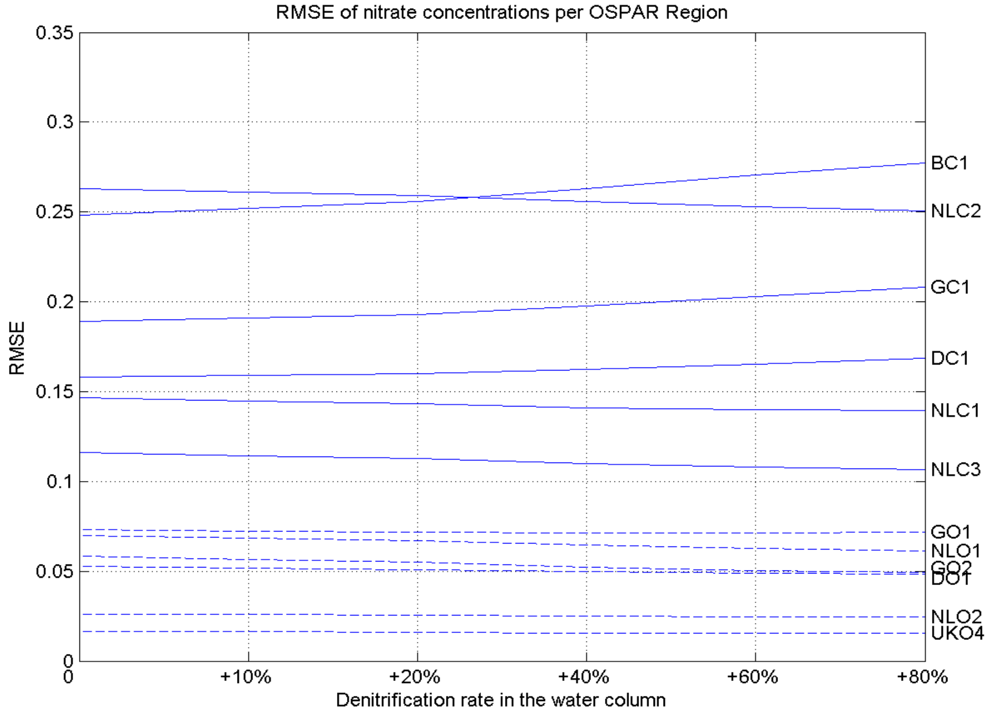


1.

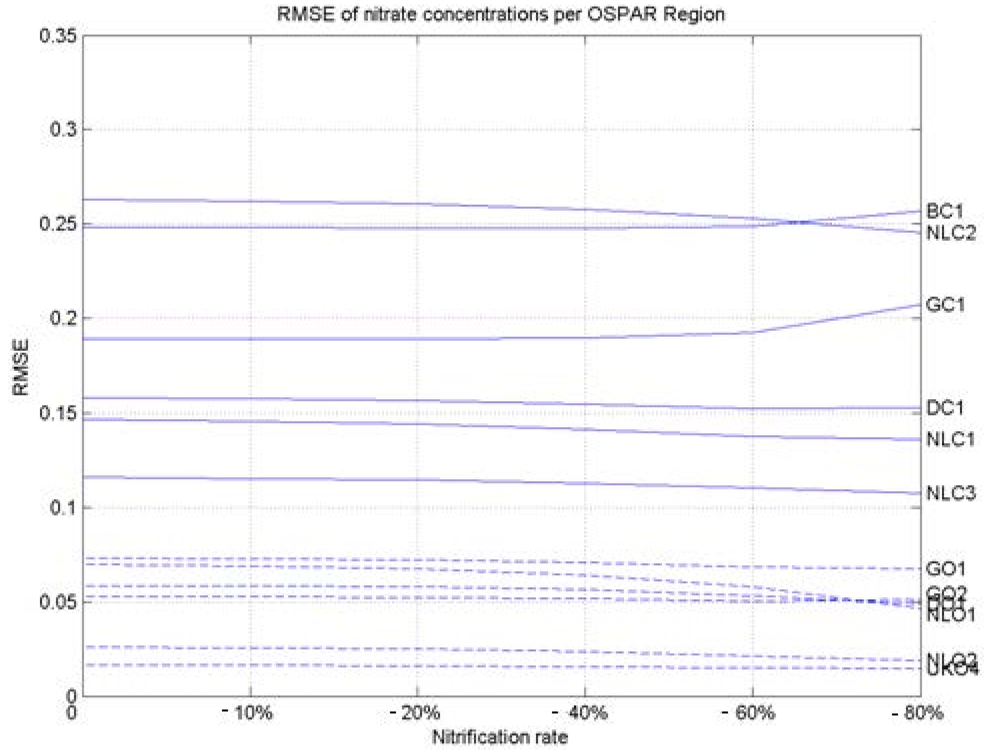


2.

Figure 37. RMSE of modelled nitrate concentrations with respect to in situ measurements for different OSPAR regions for the default parameter setting of burial rate in layer S1 (1) and the denitrification rate in the sediment (2), respectively, and an increase of 10%, 20%, 40%, 60% and 80%. Solid lines picture coastal regions, whereas dashed lines picture offshore regions.

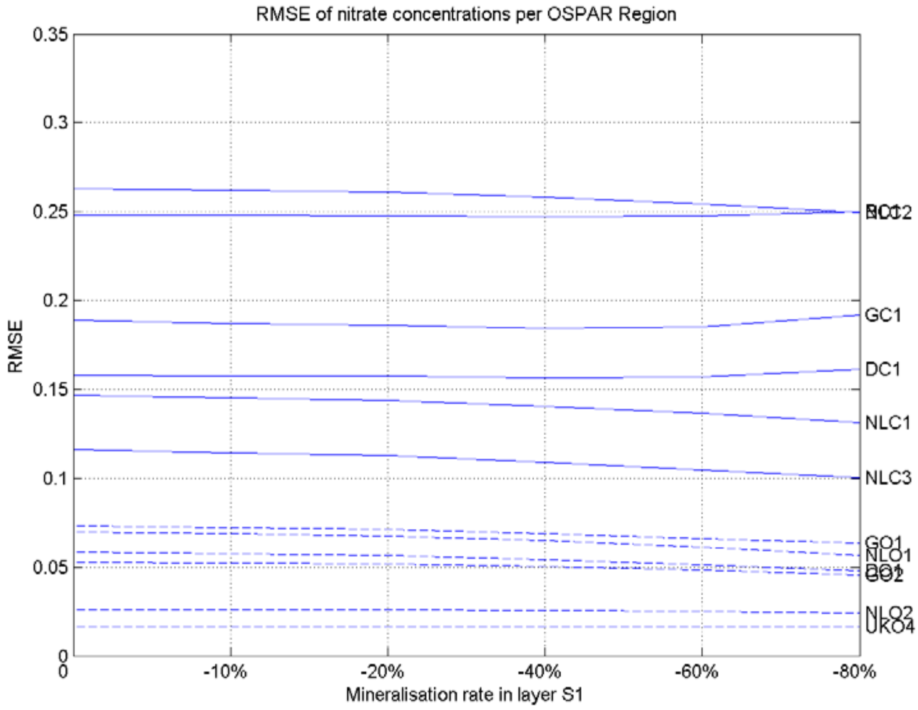


1.

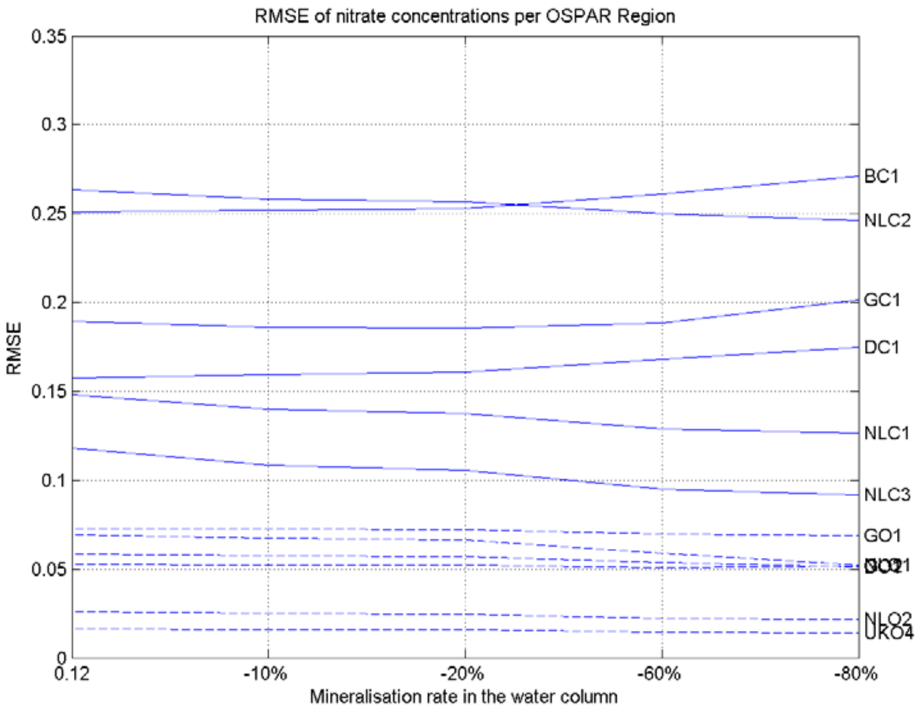


2.

Figure 38. RMSE of modelled nitrate concentrations with respect to in situ measurements for different OSPAR regions for the default parameter setting of the denitrification rate in the water column (1) and the nitrification rate (2) respectively, and an increase versus reduction of 10%, 20%, 40%, 60% and 80%. Solid lines picture coastal regions, whereas dashed lines picture offshore regions.

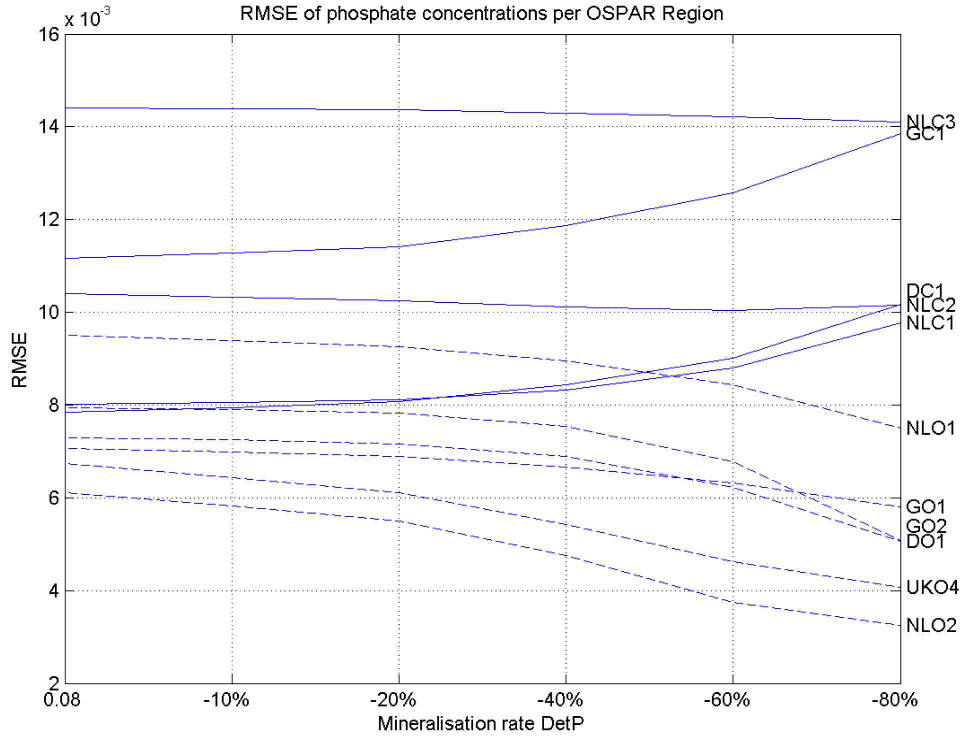


1.

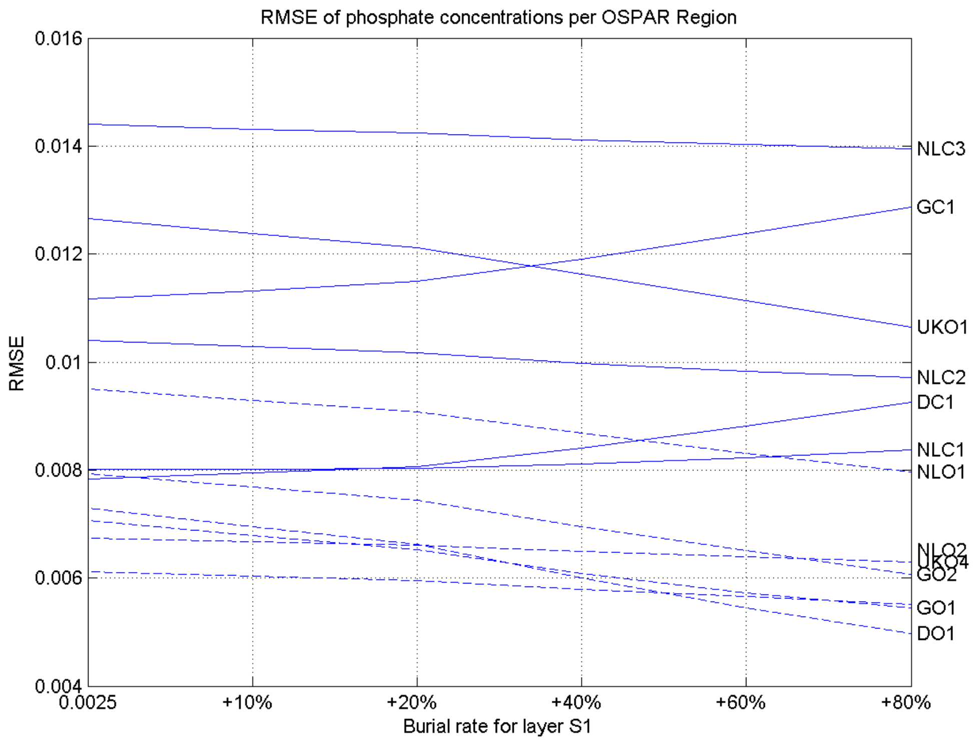


2.

Figure 39. RMSE of modelled nitrate concentrations with respect to in situ measurements for different OSPAR regions for the default parameter setting of the mineralisation rate in the sediment (1) and in the water column (2) respectively, and an increase versus reduction of 10%, 20%, 40%, 60% and 80%. Solid lines picture coastal regions, whereas dashed lines picture offshore regions.



1.



2.

Figure 40. RMSE of modelled phosphate concentrations with respect to in situ measurements for different OSPAR regions for the default parameter setting of the mineralisation rate DetP (1) and the burial rate in layer S1 (2), respectively, and a reduction of 10%, 20%, 40%, 60% and 80%.

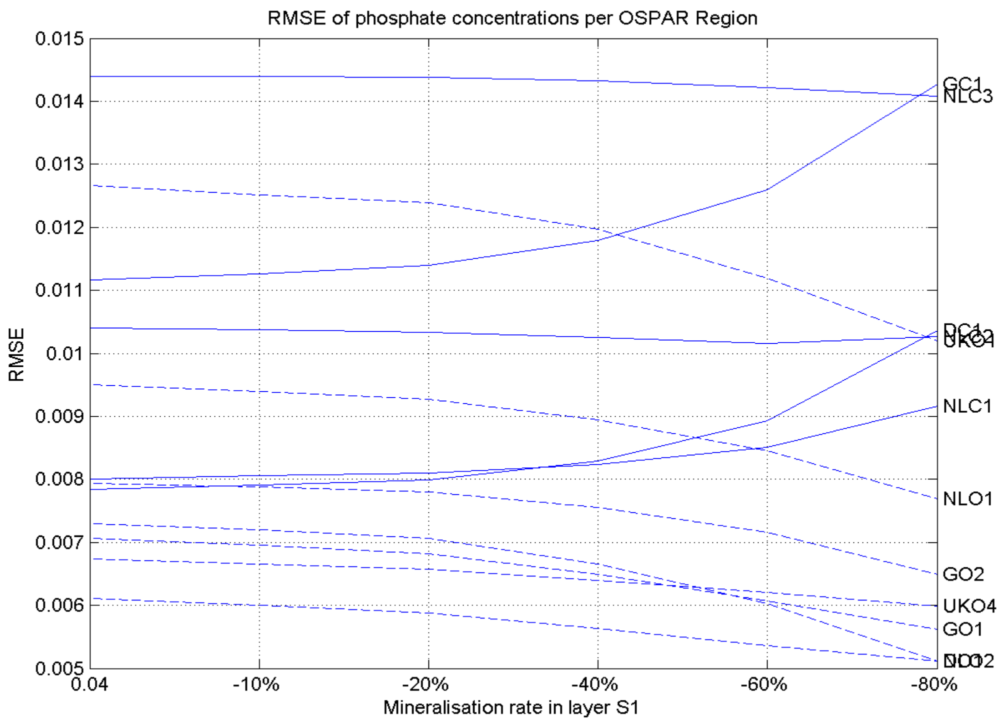


Figure 41. RMSE of modelled phosphate concentrations with respect to in situ measurements for different OSPAR regions for the default parameter setting of the mineralisation rate in layer S1, and a reduction of 10%, 20%, 40%, 60% and 80%.

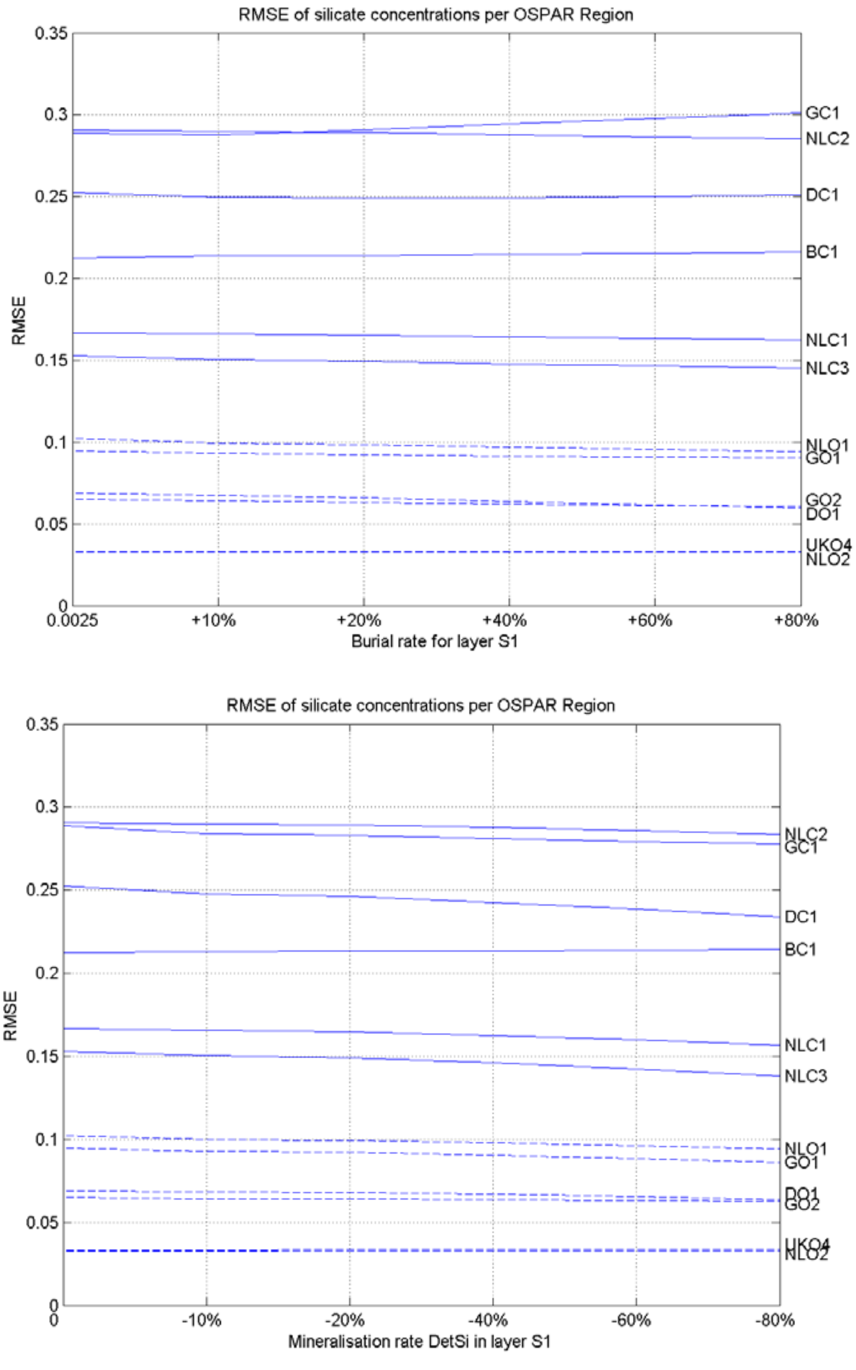


Figure 42. RMSE of modelled silicate concentrations with respect to in situ measurements for different OSPAR regions, for the default parameter setting of the mineralisation rate DetSi in layer S1 (a) and the burial rate for layer S1 (b) and a reduction of 10%, 20%, 40%, 60% and 80%, respectively.

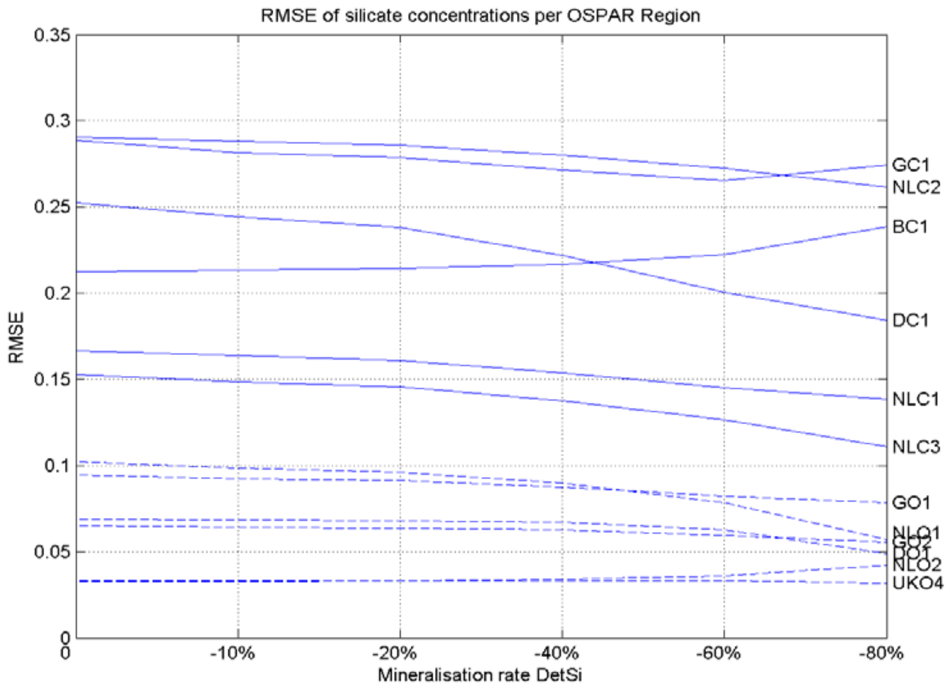


Figure 43. RMSE of modelled silicate concentrations with respect to in situ measurements for different OSPAR regions, for the default parameter setting of the mineralisation rate DetSi in layer S1 (a) and the mineralisation rate DetSi (b) and a reduction of 10%, 20%, 40%, 60% and 80%, respectively.

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