Scoping report on the potential impact of on-board desulphurisation on the water quality in SOx Emission Control Areas

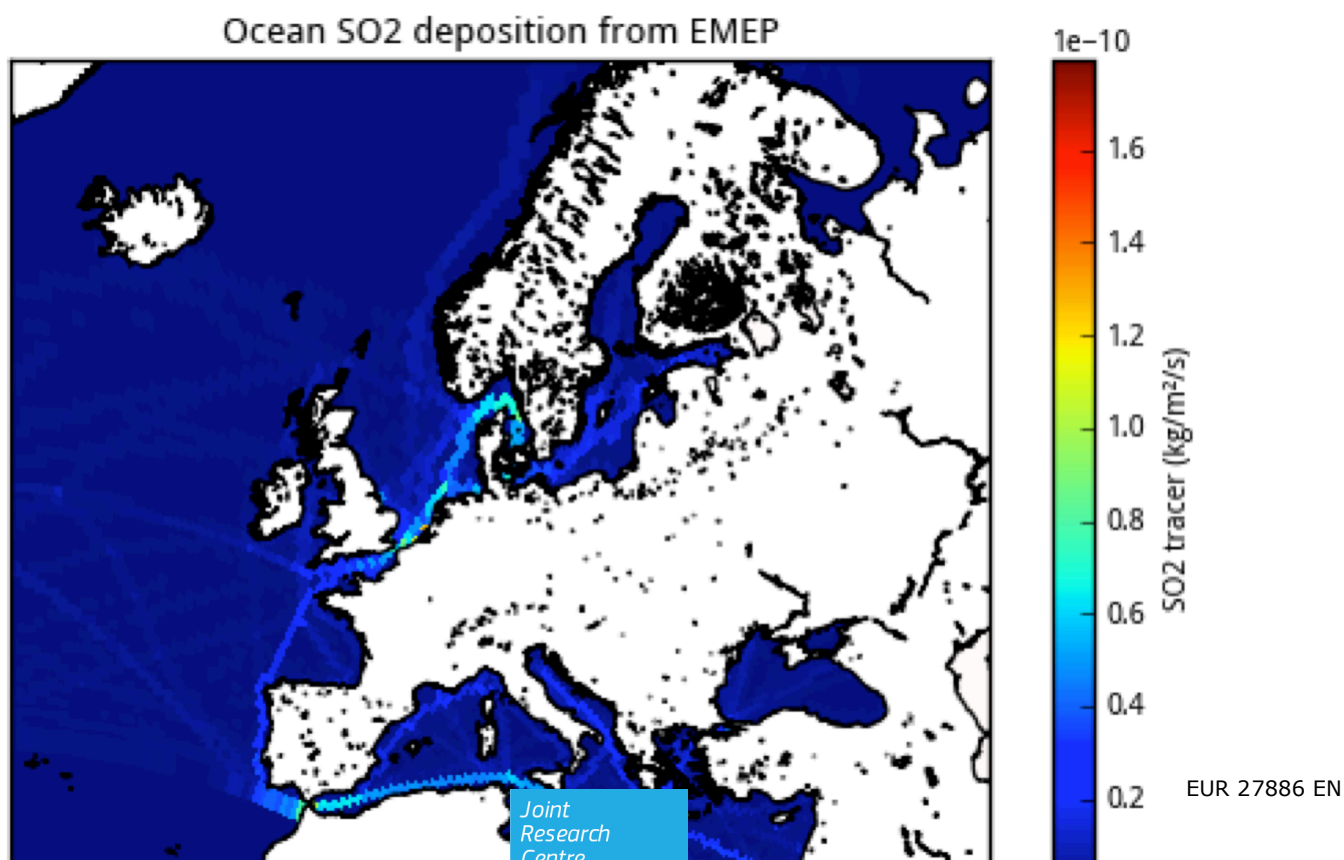Adolf Stips, Karsten Bolding, Diego Macias, Jorn Bruggeman, Clare Coughlan

2016

Ocean SO2 deposition from EMEP

Scoping report on the potential impact of on-board desulphurisation on the water quality in SOx Emission Control Areas

Contact information
Name: Adolf Stips
Address: European Commission, Joint Research Centre, Via Enrico Fermi 2749, I - 21027 Ispra (VA), Italy
E-mail: Adolf.Stips@jrc.ec.europa.eu
Tel.: +390332789876

Table of contents

2

Acknowledgements

Abstract

The input of acid substances (like SO_2) into the sea has been recognized as an environmental issue that needs to be considered in terms of ocean acidification; acid inputs and techniques to deal with them have implications for member states' obligations under the Water Framework Directive and Marine Strategy Framework Directive. This study provides an initial assessment on the potential impact of on-board desulphurisation equipment (open loop scrubbers) on the seawater quality with focus on SOx Emission Control Areas (SECAs). The study focuses on the potential impact of ship-borne SO_2 on acidification (pH) of seawater in comparison to the impact from climate change. The report comprises a literature study and a dedicated modelling exercise covering the North Sea region.

Most available studies and the peer reviewed literature found only a small additional impact from SO_2 emissions on acidification in the various investigated parts of the world ocean. However these studies generally assessed spatially averaged effects and regional and coastal oriented studies are mostly lacking from the literature, which means that potential effects to vulnerable ecosystems in such areas have not previously been considered.

A coupled hydrodynamic-chemistry model was employed to assess the impact of adding SO_2 and CO_2 on the complex carbonate system in sea water.

The impact on the pH decrease in the open North Sea region from discharging the acid wash water into the seawater was found to be small, but not insignificant, and regionally varying. The calculated annual mean decrease of pH due to SO_2 injection for the North Sea total water column is 0.00011; when considering only the change in the surface layer (0-20m), the annual decrease is 0.00024. The total annual impact from increasing atmospheric CO_2 concentrations on the acidification of the North Sea surface area is about 8 times stronger (0.001) than the impact from wash water injection. However because of the pronounced spatial variations the mean impact does not reflect the overall situation well. Consequently we find critical regions with high ship traffic intensity, for example along the shipping lanes and in the larger Rotterdam port area. Here, the contribution from SO_2 injection can be double the impact from increasing CO_2 concentrations and 20 times larger than the North Sea mean value.

These critical regions indicate potential problems related to the surface water quality in ports, estuaries and coastal waters that are subject to regulation under the Water Framework Directive (WFD). In addition, the problem of decreasing pH caused by SO_2 input from ship exhaust gases in regional seas (North Sea) is relevant to the obligation of the Member States to assess the environmental state of their marine areas and to establish a Good Environmental Status (GES) under the Marine Strategy Framework Directive (MFSD), as pH value is one of the GES criteria.

1. Introduction

The presence of sulphur in marine fuel is recognized as an important source of SO_2 (used throughout the report for SO_2 and SO_3) emissions to the air, impacting air quality and contributing to acid rain on land. As a result there have been efforts, including legislative action, to limit the emissions of sulphur oxides by ocean-going ships. As from 1 January 2015, the EU Sulphur Directive requirements impose that ships sailing in the SECAs (Sulphur Emission Control Areas - the Channel, the North Sea and the Baltic Sea) use bunker fuels with a maximum sulphur content of 0.1%, or that this same maximum level of emissions is reached by the use of alternative fuels or compliant abatement technologies. As an alternative to the use of low sulphur fuel, Regulation 14 of MARPOL Annex VI allows for the use of exhaust gas cleaning systems or any other appropriate technological method to limit SO_2 emissions to give a similar effect to using low sulphur fuel.

The Sulphur Directive refers to the 2009 Guidelines for Exhaust Gas Cleaning System (IMO EGCS Guidelines) as applicable standards for the approval of scrubbers. The purpose of the IMO EGCS Guidelines is to specify the requirements for the testing, survey certification and verification of exhaust gas cleaning systems to ensure that they provide effective equivalence in sulphur emissions.

Depending on the type of scrubber applied, the exhaust gas washing liquid is either collected on board or discarded in the open sea. So-called closed-loop scrubbers are based on fresh water and use a reducing agent, such as caustic soda (NaOH) to neutralize the acid. They keep the resulting liquid (sludge) on board[1] and require discharge in port. The alternative technology of open-loop scrubbers (SWS) uses sea water and then discards the used wash water back in the sea, relying on the volume of sea water to dilute the effluent, and on the natural alkalinity of sea water to neutralize the acid. As seawater contains a certain amount of sulphur it is assumed that the additional input of sulphur from scrubbers will not make a big difference.

This was confirmed by a study from the Danish EPA (COWI2012) that investigated the injection of the assumed annual discharge of sulphur acid into the Kattegat and found irrelevant changes of sulphur and alkalinity, even in water bodies of small size (Aarhus Bay). Even though this could be considered as a kind of worst case scenario it is not a very realistic setup of the problem.

Shipping travel mostly follows rather well defined and heavily trafficked shipping lanes that would produce a quasi continuous injection of wash water along them, leading to cumulative effects. The expected maximum levels of sulphur concentrations and minimum pH values under such circumstances are currently unknown. Understanding the effects of these scrubbers on local pH levels is crucial for Member States, that are obliged to assess the environmental state of their marine areas and to establish Good Environmental Status (GES) under the Marine Strategy Framework Directive (MFSD), as pH value is one of the GES criteria. Additionally, the spatially non-uniform acidification contribution from international shipping could be important for understanding global pH changes in the ocean.

Potentially even more problematic are issues related to the surface water quality in ports, estuaries and coastal waters in the scope of the Water Framework Directive (WFD). WFD specifies a list of priority substances and priority hazardous substances for which progressive reduction should be achieved. For marine waters falling under the MSFD regulations the descriptor "Hazardous Substances" D8 would be relevant for GES achievement. Descriptor D8 of the MSFD describes protection against the pollution of

---

[1] Although a certain amount of bleed-off occurs due to water accumulation in the scrubbing circuit

marine waters by chemical contaminants. However, the composition and substances contained in wash water discharge (open-loop scrubber systems), and bleed-off water (closed-loop scrubber systems) are not well known and they depend very much on the type of fuel used. The use of open-loop scrubbers in ports and coastal areas could, because of the small water volumes, also aggravate the above mentioned problem of wash water neutralization and pH decrease.

According to available study reports on the problem of additional acidification from sulphuric acid wash water, a low likelihood of a significant impact is expected. Therefore the focus of this study is to assess the additional impact on pH under rather unfavourable circumstances in terms of SO_2 deposition compared to the acidification caused by increasing atmospheric CO_2. In this context the consideration of scales becomes important; localized SO_2 injections might have a small impact on GES for the overall North Sea, but could impair achieving GES at the local scale.

The modelling study presented here includes the carbonate system, but the model does not have a full representation of the pelagic carbon cycle (omitting the impact of primary productivity during the productive season). The study does not investigate the river contribution in detail. Instead, the focus is on the potential impact of ship-borne SO_2 deposition in comparison to the acidification impact from increasing atmospheric CO_2 concentrations.

2. Objective of the work programme

This work has been carried out under the administrative arrangement between DGENV and JRC (NoENV.C.2/2015/070201/705766), representing deliverable D2.5: Desulphurisation of wash water.

Deliverable 2.5: Desulphurisation wash water: initial scoping report on the potential impact of on-board desulphurisation equipment on the water quality in SOx Emission Control Areas. The report should identify whether, and where, problems could occur in achieving GES. If it finds potential problems (e.g. in certain hot spots) it should identify the necessary modelling work in order to fully determine those problems.

The work programme for assessing the relevance of scrubber wash water discharges in achieving GES especially in relation to pH will be based on a literature review and further include the simulation of simplified scenarios:

This project addresses the following:

- Assess the international peer reviewed literature (top ranked journals) on the thematic of ocean acidification from sulphur emissions.
- Assess available studies, but especially environmental impact studies on the impact from discharge of sulphuric acid to coastal and open sea areas.
- Identify one or more marine areas, which might experience a significant rise in the sulphur input from scrubber technology, and where this may be seen as a potential problem in working to achieve Good Environmental Status (focus is clearly on SECA regions, as the North Sea, Baltic Sea or estuaries in there).
- Establish plausible and worst case assumptions on the maximal possible sulphur emission characteristics of scrubbers from ship traffic in these areas.
- In the chosen marine areas define a limited number of scenarios based on the density of shipping traffic and environmental factors.
- Perform simplified scenario simulations in the selected area(s) and determine, for each of the areas chosen and each of the scenarios defined, the resulting changes in the marine environment in terms of the distribution of sulphur and the change in pH values and its relevance.
- If any significant changes are found, refine the assessment by taking into account the geographical differences of the physical and chemical characteristics of sea water, like total alkalinity.
- Draw conclusions and formulate recommendations based on the achieved results.

What however cannot be done within such a limited project is the assessment of the actual fuel consumption using for example the Automatic Identification System (AIS) for ships, the implementation of a full ecosystem model nor the consideration of all Total Alkalinity sources (as sediment and rivers). Neither do we consider any near field effects, such as the dilution of the scrubber wash water in the vicinity of the vessel and the effects this might have on the effectiveness of the scrubbers in subsequent vessels travelling along a shipping lane.

3. Background information

3.1 Brief chemistry background

Four analytically determinable variables describe the carbonate system (Dickson et al., 2007): dissolved inorganic carbon (DIC), partial pressure of CO2 (pCO2), pH and total alkalinity (TA). Knowledge of any two of these along with basic physical properties is sufficient to derive the other two and the carbonate saturation state.

pH is defined as the decimal logarithm of the reciprocal of the hydrogen ion activity in a solution, which is roughly equivalent to the decimal logarithm of the reciprocal concentration of hydrogen ions (H+) in the solution.

Seawater pH is typically limited to a range between 7.5 and 8.4 (Table 1).

	North Sea	Baltic Sea	Estuaries
Temperature (C)	5-20	0-20	0 -20
Salinity (PSU)	27-35	3-15	0.5 - 17
pH	8.1	7.9-8.4	7.5-8.5
Alkalinity (µmol/kg)	2.200 – 2.600	700 – 2.000	0.1 - 5000

Table 1: Approximate properties of seawater

Changes in sea water pH are buffered by the carbonate system. Hydrogen ions (H+) react rapidly with inorganic carbon species (bicarbonate and carbonate ions) through the following set of reversible reactions:

Equation 1: Carbonate equilibrium reactions

$$H_2O + CO_2 <-> H_2CO_3 <-> HCO_3^- + H^+ <-> CO_3^{2-} + 2H^+$$
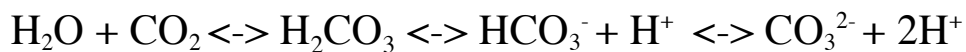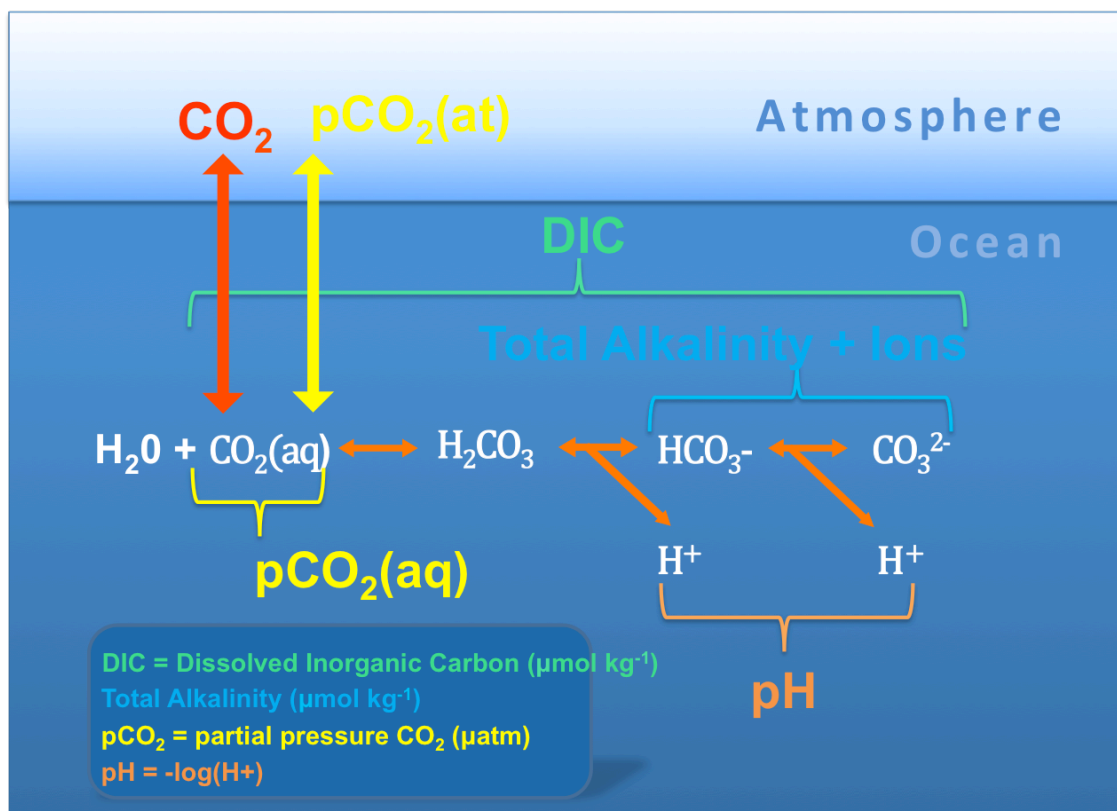
Figure 1: Simplified carbonate system variables and interactions

This set of reactions equilibrates on a time scale of seconds. As a result, addition of a quantity of H+ to the system will not lead to an equivalent increase in the concentration of H+: equilibration of the carbonate system will cause part of the added H+ to be consumed by conversion of carbonate (CO_3^{2-}) to bicarbonate (HCO_3^-), and conversion of bicarbonate to carbonic acid (H_2CO_3); overall, reactions proceed towards the left when H+ is added to the system. Conversely, removal of H+ will be buffered by the reverse reactions (reactions proceed towards the right). The same effect (as adding H+) is obtained by adding CO_2, which thus ultimately increases the H+ concentration in the ocean, and decreases ocean pH.

On time scales longer than a few seconds, the carbonate system can be assumed to be in equilibrium. In that case, the concentration of substrates and products of each reaction are related to each other through known equilibrium constants, and the state of the carbonate system is completely specified by just two variables. Different choices of variables can be used for this purpose, but it proves convenient to use total dissolved inorganic carbon (DIC) and total alkalinity (TA), as both these quantities are conserved in the presence of transport and mixing; pH can be calculated from these two. Total DIC is the sum of all H_2CO_3, HCO_3^- and CO_3^{2-}. Total alkalinity (TA) is commonly defined as "the excess base" in seawater, or the sum of excess proton acceptors, and its component ions. Therefore alkalinity roughly refers to the amount of bases in a solution that can be converted to uncharged species by a strong acid. In practice, it is the weighted sum of a large number of ions, among which HCO_3^- (weight: 1), CO_3^{2-} (weight: 2) and H^+ (weight: -1). The total alkalinity of seawater is ~2.345 (mmol/kg)

Given that pH is specified by the combination of total DIC and TA, addition or removal of dissolved compounds can affect pH only by changing either DIC or TA. For instance, dissolution of 1 mole CO_2 acts to increase DIC by 1 mole; alkalinity is unaffected (each reaction in the carbonate system has no impact on pH; recall alkalinity contributions of HCO_3^-, CO_3^{2-} and H^+ are weighted 1, 2 and -1, respectively). Conversely, addition of 1 mole of H+ decreases alkalinity by 1 mole, but has no impact on DIC. But the resulting

shift from carbonate to bicarbonate decreases the calcium carbonate saturation state (Ω) and causes problems for calcifying organisms (corals, foraminifera, mussels etc.), potentially affecting the whole food chain.

Therefore dissolving CO_2 in seawater increases the hydrogen ion (H+) concentration in the ocean, and thus decreases ocean pH. Ocean acidification thereby decreases carbonate ion levels because some of the additional hydrogen ions combine with carbonate ions (CO_3^{2-}) to form bicarbonate (HCO_3^-).

For all the wet scrubbers, the basic chemistry is similar and can be described along similar principles. SO_2 absorption in seawater is based on the following simplified reactions being in equilibrium:

Equation 2: Sulphur equilibrium reactions

$$2H_2O + SO_2 <\!\!-\!\!> H_3O^+ + HSO_3^- \ \&\ \ H_2O + HSO_3^- <\!\!-\!\!> H_3O^+ + SO_3^{2-}$$

In seawater, which contains oxygen, sulphite (SO_3^{2-}) will quickly oxidise to sulphate. As a result, sulphite concentrations remain low, and the above reactions proceed towards the right. Dissolving SO_2 in seawater thus creates sulphurous/sulphuric acid, which dissociates to increase the hydrogen ion (H+) concentration in the ocean, and thus eventually decrease the ocean pH. However, in contrast to CO_2 adsorption (causing no net change in TA) the adsorption of SOx and NOx reduces the TA and is thereby weakening the ocean's capacity to resist pH changes.

Finally we must consider that both reactions are not independent from each other, but do affect each other, resulting in a double buffering of the SO2 impact on sea water pH, as shown below (Figure 2). Therefore the pH decrease from these two processes cannot be just simply added (actually the adding of SO_2 might cause outgassing of CO_2 back to the atmosphere, depending on saturation and the partial pressure difference between ocean and atmosphere).

Double buffering of the impact of SO2 injection on sea water pH (Figure 2**).**

 (1) Injection of SO2 produces H+.
 (2) H+ is partially consumed in carbonate system reactions, specifically, in conversion of carbonate to bicarbonate (2a) and bicarbonate to dissolved carbon dioxide (or carbonic acid).
 (3) The increase in sea water CO_2 leads to a net decrease of the air$\rightarrow$ sea CO_2 flux. Depending on the original sign of that flux and the size of the perturbation, it may reduce the role of the sea as a CO_2 sink, change it from a sink into a source, or increase its role as a source. In the last two cases, injection of SO2 ultimately causes the sea to vent CO_2 into the atmosphere.

All carbonate system reactions are reversible, as indicated by the two-way arrows; the overall direction in response to SO_2 injection is indicated by the larger arrow heads (Figure 2).
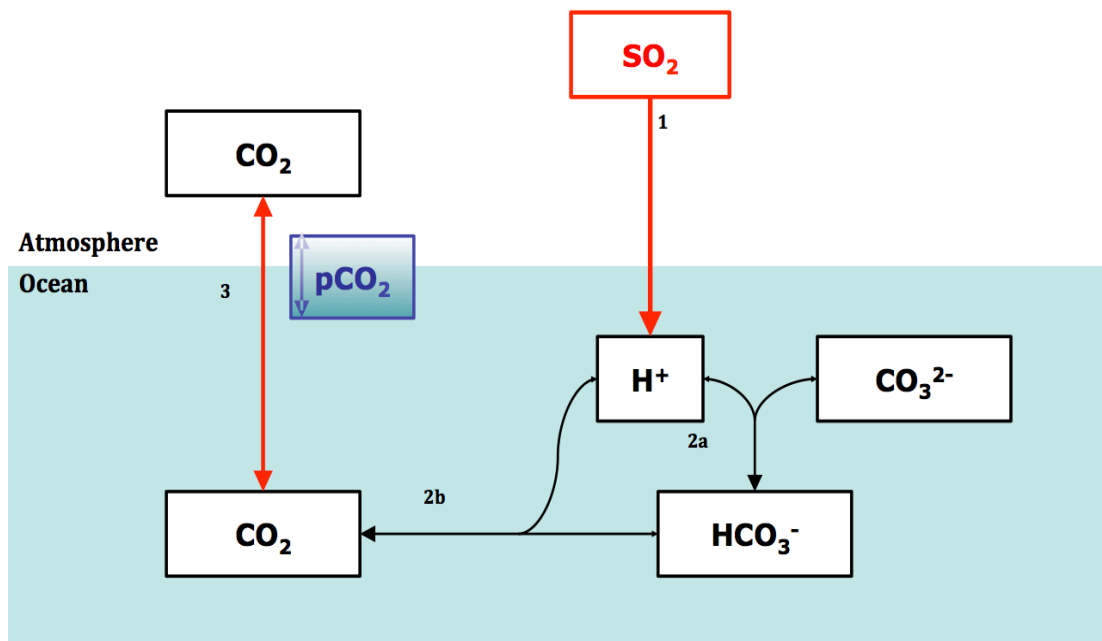
Figure 2: Simplified double buffering SO₂ impact.

3.2 Natural variability

There is natural spatial and temporal variability in carbonate chemistry across the oceans. Surface oceans have an average pH globally of about 8.2, but carbonate parameters will vary regionally (Steinacher et al., 2009), seasonally (McNeil and Matear, 2008), with latitude (Orr et al., 2005), with depth (Caldeira and Wickett, 2003) and with habitat (Striegl et al., 2007), although the primary influencing factors are temperature and upwelling (Royal Society, 2005). These effects impose regional differences in carbonate chemistry (Steinacher et al., 2009); for example the shallowing of carbonate saturation horizons towards the poles (Orr et al., 2005) or the upwelling of CO_2 rich and under saturated water onto western boundary shelf systems (Feely et al., 2008).

Thermal effects play a considerable role in driving the seasonal variation in surface pCO2, particularly in the subtropics (Takahashi et al., 2002). Temperature change affects both the rates of biological calcification as well as primary production and the chemical state of the carbonate system in water. Warming a surface water parcel by 1 ℃, without any other changes in salinity, DIC, or alkalinity levels, results in an increase in pCO2 of ~4 % for water in equilibrium with a present-day atmosphere of about 370 µatm (Takahashi et al., 1993). Coastal upwelling systems consistently experience natural ranges in surface seawater CO_2 concentrations and pH that are among the most extreme in the ocean (Capone and Hutchins, 2013). Upwelling, older, deeper water carries high levels of CO_2, the biogeochemical imprint of accumulated microbial respiration of organic matter, to the surface. As a result, CO_2 levels in surface sea water in upwelling zones can exceed 1000 parts per million (ppm) and pH can drop as low as 7.6–7.7 (Feely et al., 2008).

There may be high spatial and temporal variability shelf seas and reef systems (Blackford and Gilbert, 2007; Santos et al., 2011; Thomas et al., 2004) as a result of several concurrent processes. Primary productivity is often high in these areas leading to a large drawdown of DIC and consequent rise of pH (Thomas et al., 2005). In shallow regions, benthic processes can also significantly affect the pelagic carbon cycle and

alkalinity (Thomas et al., 2009). Terrestrial inputs, in particular from rivers, can also inject significant loads of DIC and total alkalinity (TA) into coastal systems strongly driving the carbonate system (Borges and Gypens, 2010; Gypens et al., 2011), with highly productive shelf and coastal environments producing variations of as much as 1 pH unit (pH 7.5 – 8.5), according to Hinga (2002). Hypoxia in shallow regions leads to even lower pH levels due to the production of CO_2 by heterotrophic degradation of organic matter (Melzner et al., 2012).

3.3 Measured pH variability in the North Sea

Available pH measurements show strong seasonal and regional variations. This is because many different processes influence the carbonate system including the ecosystem primary productivity, alkalinity sources from rivers and from sediments, atmospheric changes of CO_2 partial pressure and human activities.

Surface pH (0 – 20m) has been irregularly measured over the last 50 years or so in the North Sea region. The most comprehensive data compilation is provided by Beare et al. 2013. The data show a rather large scatter (Figure 3) and have a small decreasing trend of -0.00632±0.0036 just significant at the 5% level. The large annual cycle is clearly the strongest signal in the data, additional regional differences result in a large scatter and prevent a solid conclusion regarding the underlying trend. Before 1990 (from 1970 to 1990) the data show a small increasing trend of 0.006 (not significant because of data scarcity), despite the dumping of enormous amounts of sulphuric acid waste from titanium oxide production. However in the published literature, pH measurements made before 1990 are considered methodologically problematic and have a high uncertainty. Beare et al. 2013 conclude therefore, that pH records have not fallen systematically in the central North Sea since the 1950s, although there has been a recent downward trend since the mid 1990s.

From measured pH data shown by Wesslander et al. (2010) we arrive at a similar conclusion for the Baltic Sea (no clear trend), where the pH data also show a strong annual signal and large regional differences.
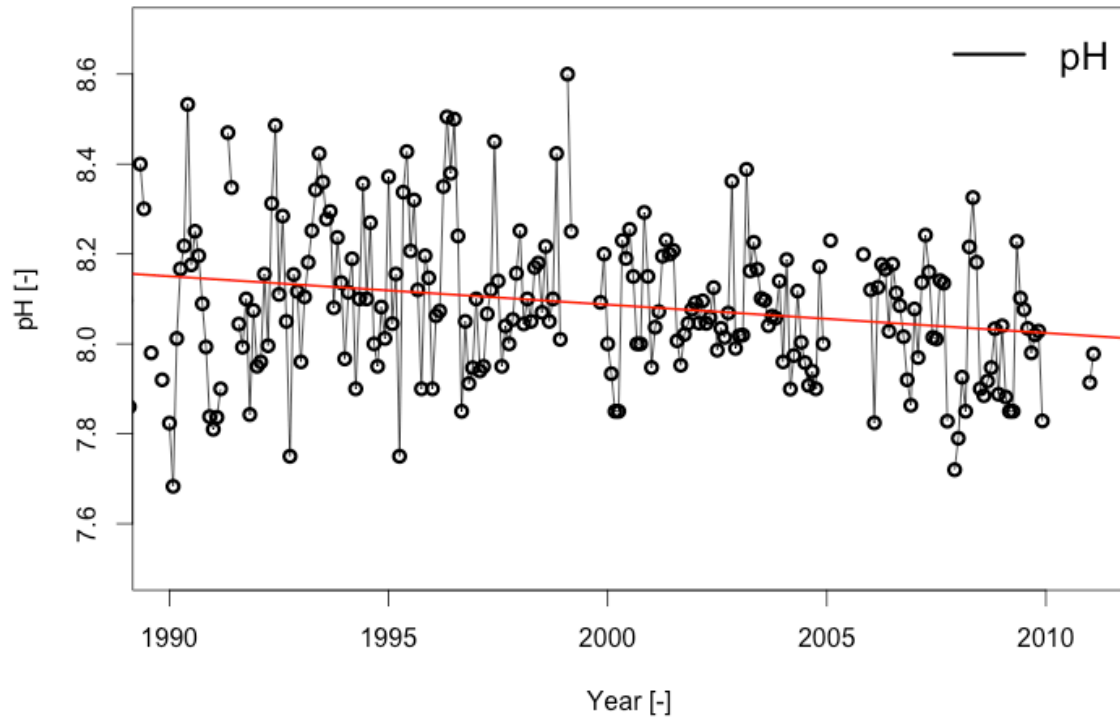
Figure 3: Measured surface ph in the North Sea (data from Beare et al. 2013)

4. State of art – literature review

Due to the more assured scientific validity and independence of peer reviewed literature in contrast to study reports and environmental impact assessments, we consider these two literature categories separately. So far, no specific studies on wash water discharge have been published in the international peer reviewed literature; this literature refers practically to the atmospheric deposition of gases from different origins.

4.1 International peer reviewed literature

D2007: Doney et al. (2007), in a global modelling study, calculated a maximum annual acidification from atmospheric deposition of ca. 0.0004 pH and said that this is ~ 1% of that from CO_2. They included sulphur, nitrogen and ammonia emissions to the atmosphere as well as the buffering capacity of sea water. They concluded that the overall effects are not relevant, but did not exclude that regional effects in coastal waters could be larger.

H2011: Hunter et al. (2011), using three regional models, calculated annual acidification rates of 0.0014, 0.00046, and 0.0008 for the North Sea, Baltic Sea and South China Sea, respectively. They considered the impact of sulphur and nitrogen gases on alkalinity and eventual outgassing of CO_2 as a consequence of sulphur emissions. The pH decrease due to sulphur and nitrogen gases input to the seawater is partially compensated by the pH increase due to loss of CO_2. This regional modelling study (Hunter et al., 2011) concluded that input of sulphur and nitrogen gases would lead to reduced uptake of CO_2 and that the combined effect on pH would be small. This study pointed to the North Sea as the most vulnerable region with regard to acidification.

H2013: Hassellöv et al. (2013) is the only peer reviewed paper found that concludes that significant coastal acidification effects from depositions of sulphur and nitrogen oxides over ocean surface waters can be expected. Hassellöv et al. (2013), using a global 1x1 degree model grid, concluded that a significant increase in coastal acidification in the range 0.0015–0.002pH (this is comparable to the decrease caused by the global CO_2 increase) per year could be observed. Their global value of 0.00037pH decrease is however similar to the result from Doney et al. (2007). Hassellöv et al. (2013) did not allow re-equilibration of pCO2 with the atmosphere in their model (using a closed system), which typically must result in too much acidification. Nevertheless their maximal values are in good agreement with the values from the regional modelling studies for the North Sea by Hunter et al. (2011) and by Hagens et al. (2014), it is simply their interpretation of the significance of a ~0.001pH annual decrease that is different.

H2014: Hagens et al. (2014), in a regional modelling study focused on European regional Seas, investigated the additional pH change due to atmospheric depositions under the IPCC RCP8.5 warming scenario. This scenario is the IPCC worst-case scenario with quasi unrestricted increase in CO_2 emissions and resulting global warming of up to 6 degrees. The calculated contribution of acid deposition is smallest in the NW Mediterranean Sea (7e-6 additional annual pH decrease), probably due to its deep mixed layer and high buffering capacity.

For the Baltic Sea they calculated around 0.0001pH annual decrease, which could be up to about 2% of the total change. The largest absolute additive ΔpH due to atmospheric acid deposition was found in the southern North Sea (0.0005 annual pH decrease). In this case the contribution from acid deposition could be as high as about 10% of total pH change.

B2014: Brynolf et al. (2014), performed a life cycle analysis comparing three alternatives to achieve the goal of reducing sulphur and NOx, instead of using low sulphur marine fuels that fulfil IMO regulations (IMO, 2013a). They considered the use of Heavy Fuel Oil (HFO) combined with SWS, the use of Marine Gas Oil (MGO) and the use of Liquefied Natural Gas (LNG). They concluded that none of the considered three alternatives will significantly reduce the life cycle impact on climate change compared to heavy fuel oil (HFO). However, all alternatives will reduce the impact on particulate matter, photochemical ozone formation, acidification and terrestrial eutrophication potential

O2015: In a recent modelling study Omstedt et al. (2015) examined the effects of historical atmospheric depositions of sulphate and nitrate from land and shipping on the acid-base balance in the Baltic Sea. They concluded that the effect of strong atmospheric acids on Baltic Sea water depends on region and studied period. For the time period from 2001-2010 over the full Baltic they estimated a pH decrease due to shipping of 0.001±0.0006 and a considerably larger decrease (0.007±0.004) when considering all emissions (including land).

Therefore the acidifying effects of sulphur emissions (typically also including nitrogen and ammonia) on the marine environment are generally considered negligible due to the inherent buffering capacity of seawater [Doney et al., 2007; Hunter et al., 2011; Hagens et al., 2014], except for one study that, despite providing similar absolute values, concluded "may lead to significant coastal acidification" [Hassellöv et al. 2013]. Most of the papers reviewed (except that of Brynolf) do not consider international shipping as a significant source of sulphur emissions. In summary, we might preliminarily conclude that acidification impacts attributable to international shipping have not yet been considered explicitly with adequate spatial and temporal resolution, especially in coastal areas. It should be stressed that there is no specific study on the direct effect of sulphur from shipping in a spatially-explicit context.

4.2 Results from environmental impact studies and study reports

By directly discharging sulphuric acid into the North Sea (near to Helgoland), Germany performed a kind of environmental acidification (dilution) experiment for over 20 years covering the period from 1969 to 1989. At that time 750 000 t of sulphuric acid (12% strong (=2.634 mol H+ /L)) were annually dumped into the sea. The pH of the water in the disposal area changed only slightly, due to the buffering capacity of the receiving seawater [Dethlefsen, 1990] and at the time the environmental impact was considered to be small. However, the total amount of sulphuric acid dumped into the North Sea was even much higher. In 1988, titanium dioxide factories in Great Britain, France, and West Germany dumped approximately 4 million tons of titanium waste into the North Sea [Lane, 1991]. This is equivalent to about 2.5 million tons of SO_2 annually. Even at this level of input, according to Taylor [2015] there was no detrimental significant environmental impact.

Both laboratory experiments and field evidence reported by Behrends et al. [2003] indicate that acidic waste streams from SWS introduced in full strength seawater leads to observable effects on ambient pH only for extremely short periods of time. Preliminary laboratory experiments with seawater indicate that at a 1:10 dilution the observable pH change did not exceed 0.1 pH units. For brackish waters a time lag of about one hour was observed. These values comply with EPA requirements. Nitrate open sea discharge from SWS is, due to the high dilution rate, not likely to cause any eutrophying effects. In ports, however, the high concentrations in the discharge stream together with restricted water exchange may lead to nitrate values high enough to cause unwanted effects such as exceptional phytoplankton blooms.

Summarizing the results from Hufnagl et al. (2005) doing measurements in the direct vicinity of the SWS discharge and the nearby sea/port water they stated that in the effluent the pH was decreased by a maximum of two pH units, the sulphate content was slightly increased and the nitrate concentration was doubled. Close to the seawater outlet in the ambient sea waters no decrease in pH, no higher nitrate or sulphate values, and no increased Polycyclic Aromatic Hydrocarbon (PAH) or metal contents were determined. Also no toxicity towards bacteria, zooplankton or mussels was determined for the outlet samples. They are however contradicting themselves when stating that for the North Sea measurements, the PAHs are increased in the outlet water.

A JRC report (JRC 2010) on the assessment of ship emissions briefly considers the use of scrubbers in the annex, and concludes that generally, the amount of sulphur discharged seems to be insignificant compared to the quantity of sulphate that seawater naturally contains. As a precautionary note it is stated "It still remains to be demonstrated whether scrubbing is environmentally suitable for all parts of the environment (shallow water, brackish waters and enclosed port areas)".

An EMSA 2010 report also mentions the problem of scrubber wash water briefly in relation to the recommendation from the Joint Group of Experts for Scientific Aspects of the Marine Environmental Protection (GESAMP). The group recommended, among other things, to strengthen the monitoring programme by imposing continuous monitoring. GESAMP also underlined the need for IMO to consider the potential contribution to ocean acidification of the large scale application of SO_2 capture from ships and the discharge of sulphurous/sulphuric acid containing effluents. It was also agreed that the wash water discharge criteria should be revised in the future as more data becomes available on the contents of discharge and its effects.

A study carried out by the Danish EPA in 2012 (COWI2012) concluded that compared to current environmental acceptability levels the releases from scrubbers can be expected to be considerably below the levels of ecological concern. However, a risk assessment for any specific area must also take existing contamination levels and releases from other sources into account. In the main impact scenario all ships > 2,000 tons DWT are equipped with scrubbers in 2015 and use high sulphur fuel (3.5 %). The results of the modelling for this scenario show that the impact of the discharges of acidic scrubber water (sulphuric acid) on the buffering capacity of sea water in the Kattegat and in Aarhus Bight, respectively, will be negligible. This conclusion applies even to areas with significantly lower buffer capacity than the Kattegat (e.g. the Bay of Bothnia) and for a traffic intensity twice as high as the present. Specific hazardous substances such as heavy metals and metalloids, polycyclic aromatic hydrocarbons (PAH), PCB and oil hydrocarbons will also be released with scrubber water. However, the resulting concentrations in the sea will be orders of magnitude below the levels of concern as expressed e.g. by EU's environmental quality standards (EQS) for the marine

environment. Thus, the concentration of the most critical substances in relation to this criterion, the metals nickel and copper, will still be more than two orders of magnitude below the EQS. No explicit pH decrease was given in the original study, but the total amount of 12.700 tons Sulphur (40.000 tons sulphuric acid) annual input to the Kattegat area was assumed. In an amendment (COWI2013) a maximal pH decrease of 0.01 was estimated for the Sound area (based on a simple box model).

A literature study based on the above mentioned studies by the German environment ministry (UBA, 2014) comes to the conclusion that the available measurements and data on measured pollutants in scrubber wash water do not violate environmental norms and are in agreement with WFD regulation. However, because of the already compromised water quality in German coastal areas (some areas are in bad quality state) they recommend to prohibit the use of SWS in the inner German waters or more general in German coastal waters in order not to compromise the water quality even more.

A literature review provided by Delft (2015) on request by NABU (Naturschutzbund Deutschland) concluded that all measured wash water concentrations are well below the thresholds from the IMO wash water guideline that needs to be met on pH, nitrates, and hazardous hydrocarbons, but the available measurements show variation in pollutant concentrations. They however continue that the currently available research does not irrefutably exclude the deterioration of the environmental status of the vulnerable (near shore) ecosystems, it is not clear if objectives set by the Marine Strategy Framework for achieving 'good environmental status' can be met by the year 2020 and onwards, taking into account a growth in the number of scrubbers installed.

As it appears in the available study reports, the impact of international shipping on pH is not conclusive. In summary we might again preliminarily conclude that acidification impacts attributable to international shipping have not yet been considered explicitly with adequate spatial and temporal resolution, especially in coastal areas. The cumulative effect of long term inputs has not yet been considered and given estimates are based on many simplifying assumptions. As already discovered in the review of the peer reviewed literature, the direct effect of sulphur from shipping has not yet been studied in a spatially-explicit context.

4.3 Summary and conclusions from literature review

In the available peer reviewed literature and institutional study reports we have not found any clear evidence pointing to significant environmental degradation (pH decrease, increase of eutrophication, pollutants) due to the discharge of SWS scrubber wash water to the marine environment. It has however to be considered that all peer reviewed literature as well as the study reports use several simplistic assumptions, such as assuming closed systems (no air-sea exchange), cumulative effects are not considered and in particular previous work does not focus on localized impacts along shipping lanes and in ports or estuaries.

The findings from the literature are summarised in Table 2. This demonstrates that the annual pH decrease resulting from SO_2 emissions in marginal seas (North Sea, Baltic Sea) is comparable to that caused by increasing atmospheric CO_2 concentrations. Therefore currently available research does not irrefutably exclude the deterioration of the environmental status of the vulnerable (near shore) ecosystems (especially since the research to date neglects cumulative and long term effects); it is not clear if objectives

set by the Marine Strategy Framework for achieving 'good environmental status' can be met by the year 2020 and onwards, taking into account an expected growth in the number of scrubbers installed.

Wash water discharging in coastal waters is more problematic and still under consideration within the EU. Few countries have set their own policies. National governments and ports can set limits lower than the WFD limits for concentrations of hazardous substances, or can prohibit the discharge of scrubber wash water. Several countries have restricted the discharge of scrubber wash water:

- Germany prohibited the discharge of wash waters in inland waters rivers (certain ports, including the Kiel Canal);
- Belgium prohibited discharging within 3 km off coast.

The long term impacts of the use of open loop scrubbers should be further investigated systematically by measuring and modelling in order to prevent negative cumulative environmental impacts of scrubber waste water discharge. It should be evaluated whether scrubbers can be used in accordance with the Marine Strategy Framework Directive and the European Water Framework Directive that set maximum concentrations for certain hazardous pollutants, especially in the vicinity of dense shipping routes and vulnerable estuaries.

Study	Area	-ΔpH(SO2)	-ΔpH(CO2)	ΔSO2/ΔCO2 [%]
D2007, H2011, H2013	Global	~0.0004	0.001 – 0.0018	20 - 40
H2011, H2013, H2014	North Sea	0.0005 - 0.0024	0.0001 – 0.0016	100 - 500
H2011, H2013, O2015	Baltic Sea	0.0001 - 0.0005	0.0001 – 0.0018	30 - 100
COWI2013	Sound	0.01		(1000)

Table 2: Annual pH decrease resulting from SO2 and CO2 flux (literature studies)

5. Modelling study on effects from SO$_2$ input on pH changes in the North Sea

5.1 Introduction and SO$_2$ emission data

Through an expert contract (Bolding, 2015) work was carried out to implement and test a coupled physical/chemical model system that can be used to test different SO2 emission scenarios. The main purpose of the contract was to establish a re-usable model configuration that can be used in further – more complex – studies of the problem. The North Sea was selected as a test region. This decision is based on the conclusion from (Hunter et al., 2011) that identified the North Sea as an especially sensitive region to acidification, even more than the Baltic Sea.

The model configuration consists of two independent models that are coupled at runtime. The first model is the hydrodynamical GETM, (General Estuarine Transport Model, (Burchard and Bolding, 2002)). The second is ERSEM (The European Regional Seas Ecosystem Model, (Baretta, 1995) and (Butenschön, et al., 2015)). Specifically, the carbonate component of ERSEM (Blackford & Gilbert, 2007) is used in this study. ERSEM is coupled to the hydro-dynamical model via FABM, (Framework for Aquatic Bio-geochemical Models, (Bruggeman and Bolding, 2014)). There is a clear task division between the two models. GETM is a 3D physical numerical model solving equations for physical variables. GETM is setup for a specified area and for the area integrates the equations for a specified time period. FABM is responsible only for the bio-geochemical processes and relies on the physical model to provide all necessary environmental variables. In addition FABM relies on the physical model to do the temporal integration and advection/diffusion of the bio-geochemical variables. For full information on the task division between the physical model and the bio-geochemical model see (Bruggeman and Bolding, 2014). FABM has been designed to allow for independently developed bio-geochemical models to be combined at run time. One of the major deliveries resulting from this work is a FABM configuration that will allow SO$_2$ scenario testing – not only for the North Sea and Baltic Sea – but in principle for all areas where the necessary forcing data are available. The FABM configuration developed is independent of the model area.

The European Monitoring and Evaluation Programme (EMEP, www.emep.int) provides fields of airborne pollution on standard geographical grids. One of these products contains ship-borne SO2 as annual values. The fields cover an area from 30W to 50E and 30N to 70N with a resolution of 0.1 degrees and covering the time-period from 1990 to 2012. An example field is provided on the front page of this report. A time-series plot of SO2 emissions for a point on the Dutch coast (52N, 4.2E) is given below Figure 4. Note the change in 2005 where an increasing trend changes to a decreasing trend as a result of regulations to control air quality. As it is possible that some part of this missing SO$_2$ has already been charged directly to the sea, we are focusing the work on the maximum emission scenario in 2006. The estimated total ship SO$_2$ emissions for the year 2006 in the North Sea area are about 490000 tons.
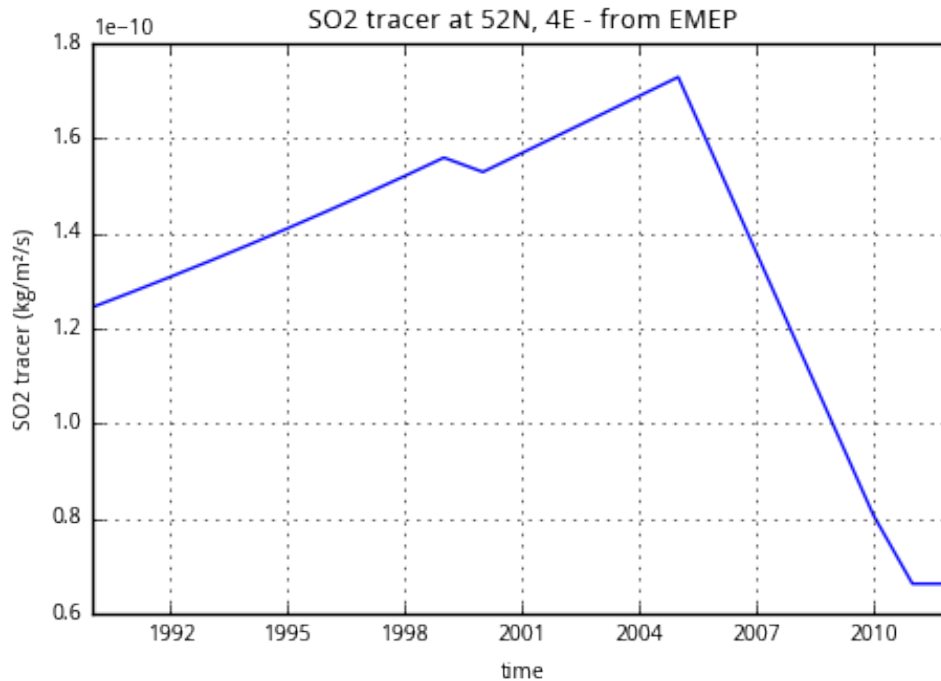
Figure 4: Annual atmospheric SO2 deposition to the North Sea based on EMEP data

5.2 Numerical Model Set-up

For all simulations the hydrodynamic numerical model GETM (General Estuarine Transport Model – http://www.getm.eu) has been used. GETM has been coupled to FABM (Framework for Aquatic Biogeochemical Models – http://www.fabm.net) for the inclusion of the carbonate, SO_2 system. A short description of the model setup is given below.

Here only a brief description of the most relevant requirements for the physical modelling is given. A full description of the GETM model setup including the boundary and atmospheric forcing is given in (Bolding, 2015).

Furthermore, additional scientific publications using GETM as a core element can be found here http://getm.eu.

5.2.1 Hydrodynamic model area

The model area is the North Sea including the English Channel and the Skagerrak and Kattegat. The model area and bathymetry is shown in Figure 5. The model configuration is on a spherical grid. The model grid-size is 112x125 (lon x lat) with a resolution of about 6nm (~10 km) in the horizontal and 30 vertical sigma coordinates.
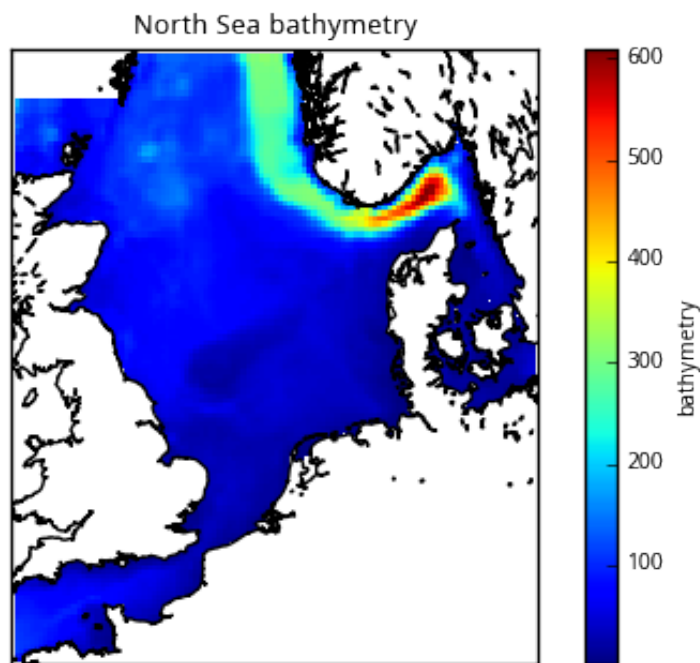
Figure 5: Model bathymetry for the North Sea model setup

5.2.2 Carbonate and SO₂ configuration

As stated in the introduction the final model consists of a physical model and a bio-geochemical model, from which only the chemistry part was exploited. The physical model is a pre-requisite for being able to make bio-geochemical simulations. The carbonate system of the ocean is highly complex but has acquired a large amount of attention over recent years in relation to consequences of climate change. Two main issues are of interest – the ocean as a sink for CO_2 and the consequences on living organisms in the ocean from acidification associated with decreasing pH. Neither of these climate related issues are of direct interest in this report but as a consequence of these issues an elaborate carbonate system model has been implemented in ERSEM (European Regional Seas Ecosystem Model http://www.shelfseasmodelling.org/About/The-European-Regional-Seas-Ecosystem-Model-en) see (Artioli, Blackford og Butenschön) (and references herein).

The entire ERSEM model has been implemented in the FABM (Framework for Aquatic Bio-geochemical Models – http://www.fabm.net, (Bruggeman & Bolding, 2014)) in a modular way and it is possible via FABM configuration to implement only specific components. In the context of this work only the **ersem/carbonate** model component is used. The configuration applied in this study is described further down.

To prepare the original EMEP generated fields for simulations with the GETM/FABM system a few further steps need to be taken. The EMEP data must be interpolated on the model grid and the units of the EMEP based surface forcing must be the same as those used by the carbonate model in FABM. Total alkalinity input from rivers was not considered here.

External FABM forcing needs to be on the model grid of the hydro-dynamical model. The CDO (Climate Data Operators - https://code.zmaw.de/projects/cdo) software from MPI in Germany has been used to re-grid these data. The re-gridded SO_2 field is shown in

Figure 6: Re-gridded SO2 flux [kg/m2/s] from the original EMEP grid to the GETM North Sea set-up., from which the most heavily trafficked regions can easily be identified.

The carbonate model within ERSEM – **ersem/carbonate** – describes the state of the carbonate system by two prognostic variables: total dissolved inorganic carbon (DIC) and total alkalinity (TA). These two variables suffice to compute a range of carbonate system diagnostics, most prominently sea water pH. As described in the section outlining the relevant chemistry, all impacts on pH are accounted for by changes in either total DIC or TA. Addition of 1 unit SO_2 produces 2 units of H+, which decreases alkalinity by 2 units (it does not affect DIC). Conversely, addition of each unit CO_2 does not affect TA but increases DIC by 1 unit.

Accordingly, SO_2 dissolution is modelled as a surface flux of alkalinity, with each unit of SO_2 entering the ocean decreasing TA by two units. In addition, the carbonate system module describes air-sea exchange of CO_2, which is governed by the difference in partial pressure of CO_2 between atmosphere and ocean (the latter set by total DIC and TA), wind speed, and temperature. This functionality is used to simulated the impact of an increase in atmospheric CO_2, but also acts as "pressure valve" when SO_2 is added: the resulting addition of H+ (decrease in alkalinity) will increase the partial pressure of CO_2 in the sea water, causing a decrease in the net air-sea flux of CO_2 (and potential outgassing of CO_2). In turn, that further buffers the pH change due to SO_2. In previous studies this has usually not been taken fully into account.
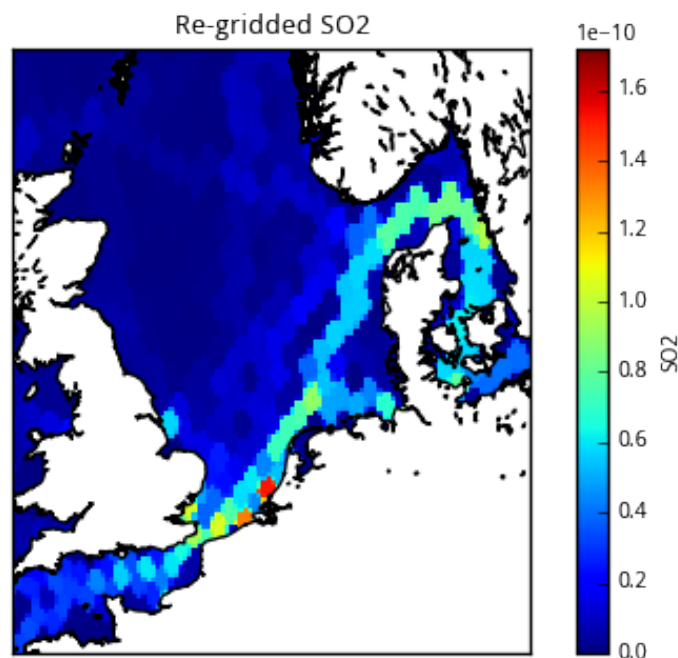

Figure 6: Re-gridded SO2 flux [kg/m2/s] from the original EMEP grid to the GETM North Sea set-up.

5.3 Model simulations

With the model setup described above, 8 basic scenario simulations have been carried out (Table 3). The simulations cover one year (2006) and all apply the same physical environment i.e. no changes have been made to the settings of GETM. Meteorological forcing, boundary conditions and river discharge are kept the same and correspond always to 2006. The only imposed changes (to SO_2 and CO_2 inputs) are done in FABM via changes in fabm.yaml.

Description	Name	SO2	CO2
Reference	R_no_so2_co2_383	None	2006 level (383)
Climate change (CO2)	R_no_so2_co2_400	None	2015 level (400)
SO2	R_so2_co2_383	2006 input	2006 level (383)
SO2	R_so2_co2_400	2006 input	2015 level (400)
Extreme SO2	R_so2x5_co2_383	2006 input times 5	2006 level (383)
Extreme SO2	R_so2x5_co2_400	2006 input times 5	2015 level (400)
Low SO2	R_so2x0.2_co2_383	2006 input times 0.2	2006 level (383)
Low SO2	R_so2x0.2_co2_400	2006 input times 0.2	2015 level (400)

Table 3: Different FABM configurations.

The first simulation serves as a reference simulation using CO_2 inputs for the year 2006, with no SO_2 flux imposed. The second simulation applies CO_2 concentrations from 2015 and also no SO_2 input, so the focus is on the effect of climate change. As this reflects the total change over about 10 years, the resulting pH changes must be divided by 10 to represent average annual changes. CO_2 is a well mixed gas, therefore we apply a spatially constant value over the model area. The third simulation uses SO_2 values from 2006 and CO_2 concentrations from 2006. The fourth simulation uses SO_2 from 2006 and CO_2 concentration corresponding to present day values. The fifth simulation applies 5 times the SO_2 concentrations from 2006 and CO_2 from 2006. The sixth simulation applies 5 times the SO_2 concentrations from 2006 and CO_2 from 2015. Even though the 5 times increased SO_2 input might seem extreme, it should be remembered that the total annual amount of about 2.5 millions tons corresponds roughly to the annual dumping of 2.7 million tons of SO2 equivalent waste during the 1980s. Finally, in order to assess the impact that could be expected when using fuel with low sulphur content, 2 low input scenarios applying 20% of the 2006 SO_2 input were added to the simulations. In order to eliminate possible model bias (due to the discussed limitations, absolute values for pH, DIC and total alkalinity might be not very accurate simulated) we are mainly examining the differences between the reference run and the other runs. As the inherent model bias is about the same for each simulation, we can in this way effectively remove this bias.
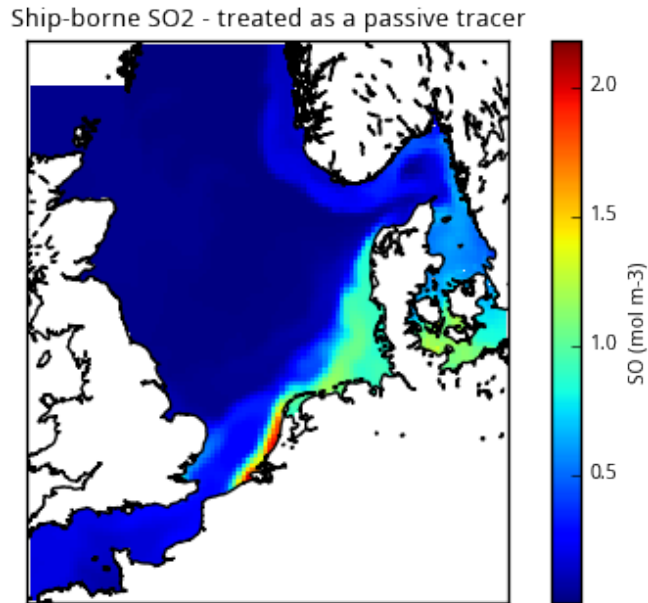
Figure 7: Ship borne SO2 concentrations when treated as passive tracer.

5.4 Simulating spatial variations of SO2 emissions

5.4.1 Simulating the impact of SO2 emissions

In this simulation the effect of the ship-borne SO2 is included in the model simulation. The levels for SO_2 and CO_2 both correspond to 2006. SO_2 emissions are clearly the largest in the Rotterdam port area, as can be seen in Figure 7, which shows the SO_2 distribution when treated as passive tracer (no chemistry). The differences between total water column pH of the run with 2006 SO_2 and 2006 CO_2 (R_so2_co2_383) and the reference run (R_no_so2_co2_383) are very small (usually below 0.001) as can be seen in Figure 8. Slightly larger differences are found when considering the surface values (0-20m), Figure 9. In general the higher values are very similar to the calculations by Hunter 2011, who found an annual decrease in pH of 0.0014 for the North Sea. The spatial distribution of simulated pH decrease largely corresponds to the external SO_2 input; largest decreases are found along the Belgium and Dutch coast, the German Bight and the Danish Straits, all regions with intense ship traffic. Over large parts of the open North Sea there is hardly any pH decrease. It should be therefore evident, that a calculated North Sea mean value is not representative of the actual situation in these critical regions.
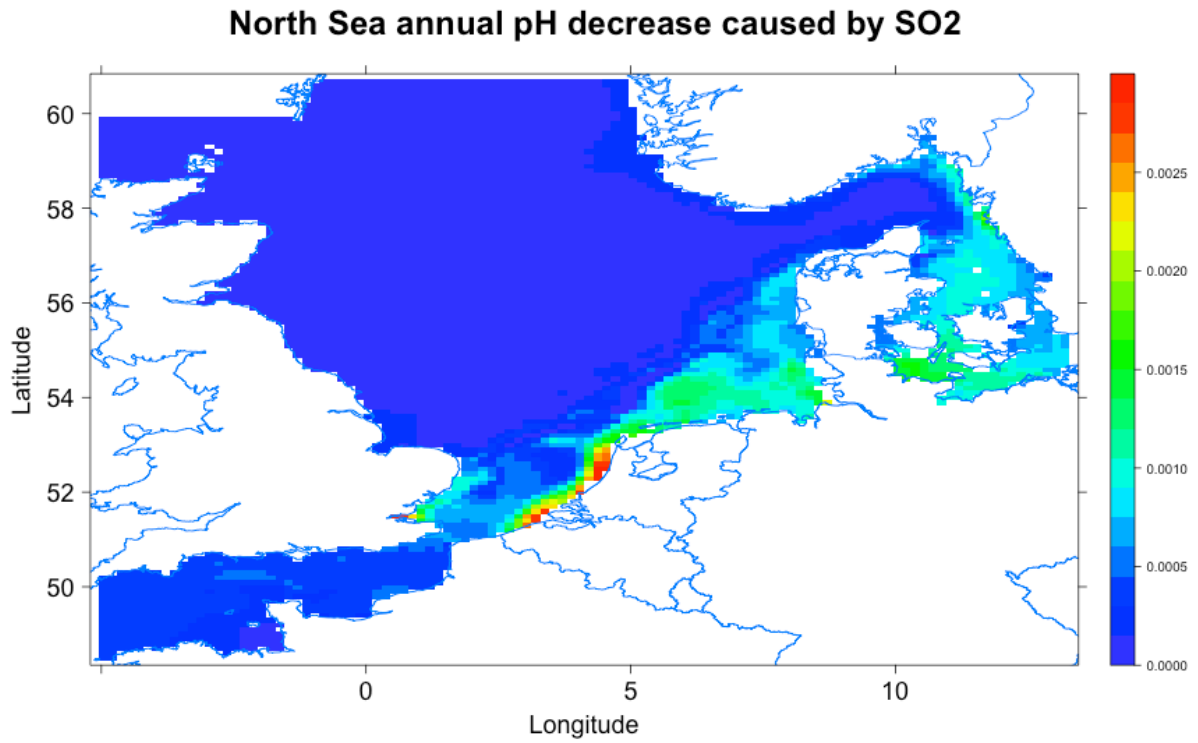
Figure 8: Decrease in full water column pH between reference run and run with 2006 SO2 (R_so2_co2_383)

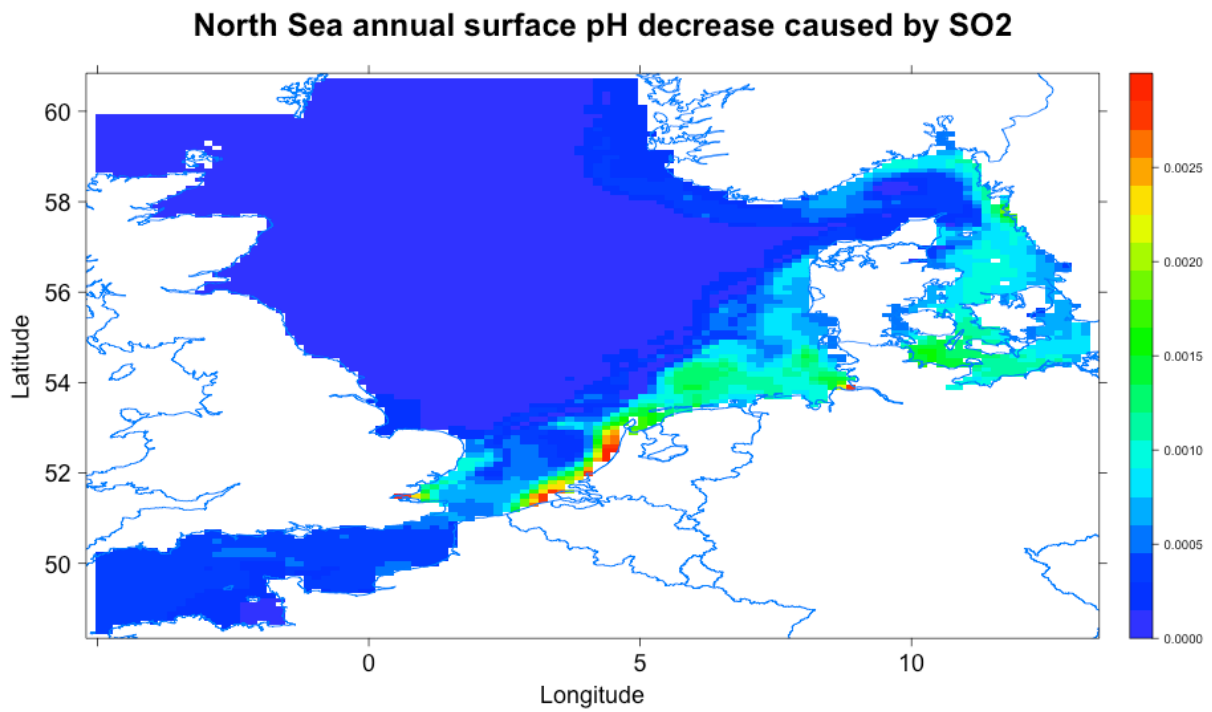*Figure 9: Decrease in surface pH between reference run and run with 2006 SO2 (R_so2_co2_383)*

5.4.2 Simulating the impact of increasing atmospheric CO$_2$

As described above, the increasing atmospheric concentration of CO$_2$ influences the seawater carbonate system and contributes to ocean acidification. We consider this as the background change against which to evaluate the effect from SO$_2$. To evaluate this change separately to the SO$_2$ impact a simulation using 2015 levels for CO$_2$ instead of 2006 levels was performed (R_no_so2_co2_400), applying a spatially constant value over the model area. The difference between this run and the reference (R_no_so2_co2_383) is presented in Figure 10. From this figure in comparison to Figure 9 it is clear that the change resulting from increasing CO$_2$ levels has a largely uniform impact on pH in contrast to the more localised impact from ship-borne SO$_2$ input. The typical annual pH decrease due to CO$_2$ is about 0.001 and values can reach up to 0.003 in certain regions. Therefore, over the whole North Sea CO$_2$ might have a bigger effect on acidification, but on a local scale effects of SO$_2$ inputs are significant.
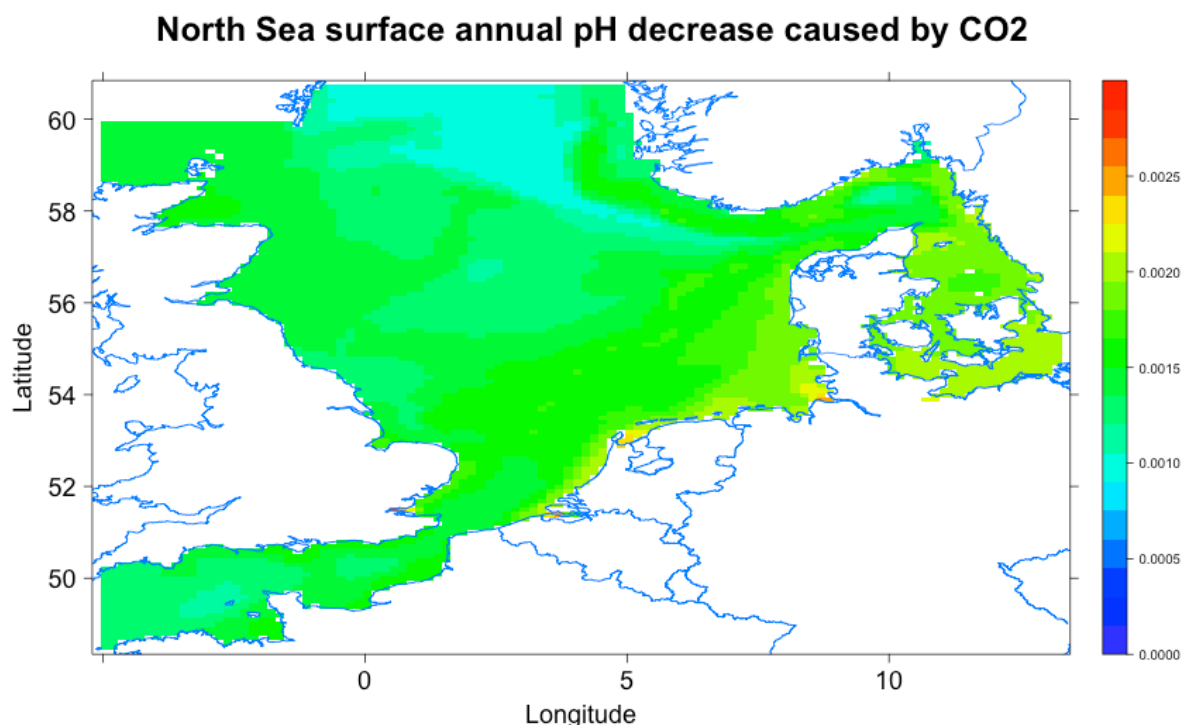

Figure 10: Difference (0.1) in surface pH between reference simulation and simulation with 2015 CO2*

5.4.3 Simulating the impact of SO$_2$ emissions

Two simulations apply a SO$_2$ concentration 5 times the level of 2006 and the CO$_2$ of 2006 and 2015. These simulations are included to test a kind of *worst case scenario* and to detect possible non-linearities. In this simulation we observe a stronger decrease in pH, see Figure 11. As it turns out the effect on the pH of the North Sea caused by this 5 times increasing SO$_2$ emissions is now larger than the effect from increasing CO$_2$, see also Figure 13. It is clearly seen that the area with changes >0.0025 is much larger in this comparison than in the climate change scenario. Furthermore, it is obvious that coastal regions are going to be severely affected in this 'worst case' scenario. Despite the fact that such large SO$_2$ input from ship borne emissions might not be seem likely, it

should be remembered that the total annual amount of SO_2 dumped into the North Sea in the 1980s corresponds roughly with this scenario.
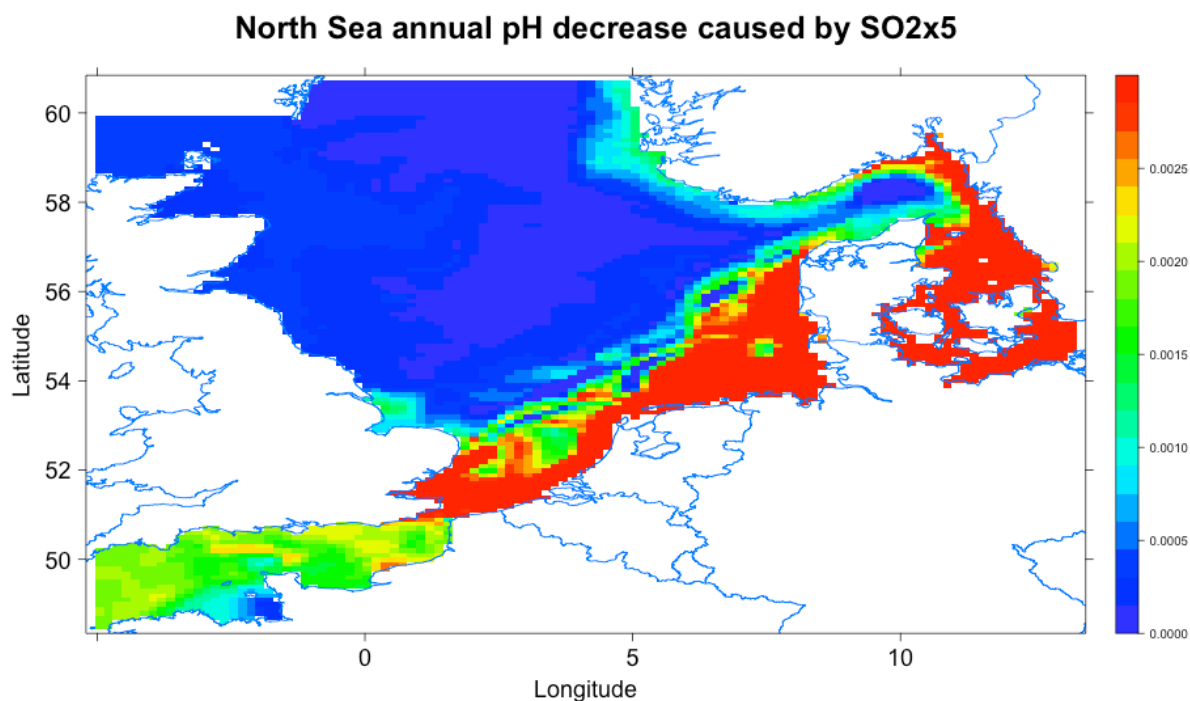
North Sea annual pH decrease caused by SO2x5

Figure 11: Difference in surface pH between simulation with 5 times 2006 SO2 levels and 2006 CO2 levels and the reference run.

5.4.4 Simulating the impact of very low SO2 emissions

The 2 final simulations apply a SO_2 concentration 0.2 times the level of 2006 and the CO_2 of 2006 and 2015. These simulations are included to test the effect of reduced SO_2 emissions, as could be expected when most ships are using fuel with low sulphur content (0.1 %), instead of open loop scrubber. In this simulation we observe a very small decrease in pH, so small that it is not necessary to provide a plot of the results. The effect is nevertheless documented in the respective tables.

5.5 Full North Sea mean values

In order to get an idea about the dilution effect of the overall North Sea water body on the pH changes in comparison to the surface changes, we present here the full water column means (Table 4– annual mean, Table 5– values after 1 year simulation). The total pH decrease calculated for the North Sea full water body annual mean in response to increasing CO_2 concentrations is 0.0008, only slightly smaller as the surface decrease. The mean annual decrease due to SO_2 input is 0.00011 (or 0.00055 for the extreme scenario), so about a factor of 8 smaller than the decrease due to increasing CO_2 concentrations. The difference caused by SO_2 input at the end of the 1 year simulation is 0.00014 (Table 5), a value slightly larger than the annual mean. Over the time span of 1 year both pH and TA are decreasing, as can be seen in Figure 12 and Figure 13. The

adsorption of CO_2 has however no net impact on the TA, the annual mean TA values for the runs with low and high CO_2 are equal (Table 4). There is a seasonal cycle in change in pH (Figure 12) and after a minimum pH is reached in autumn, pH starts increasing slightly again.
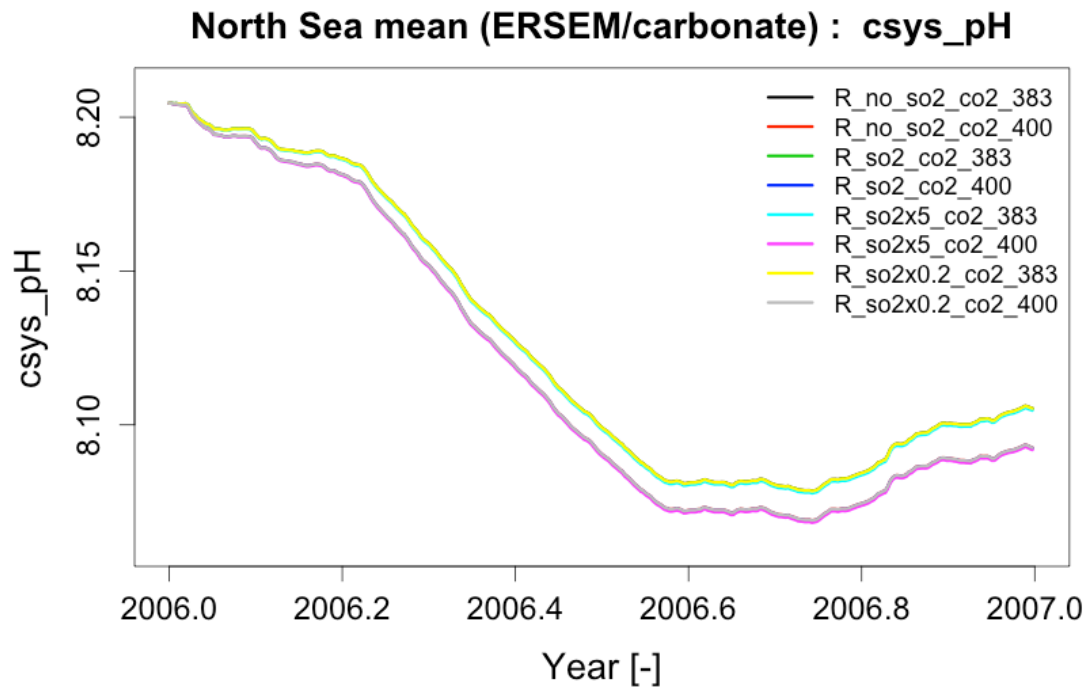

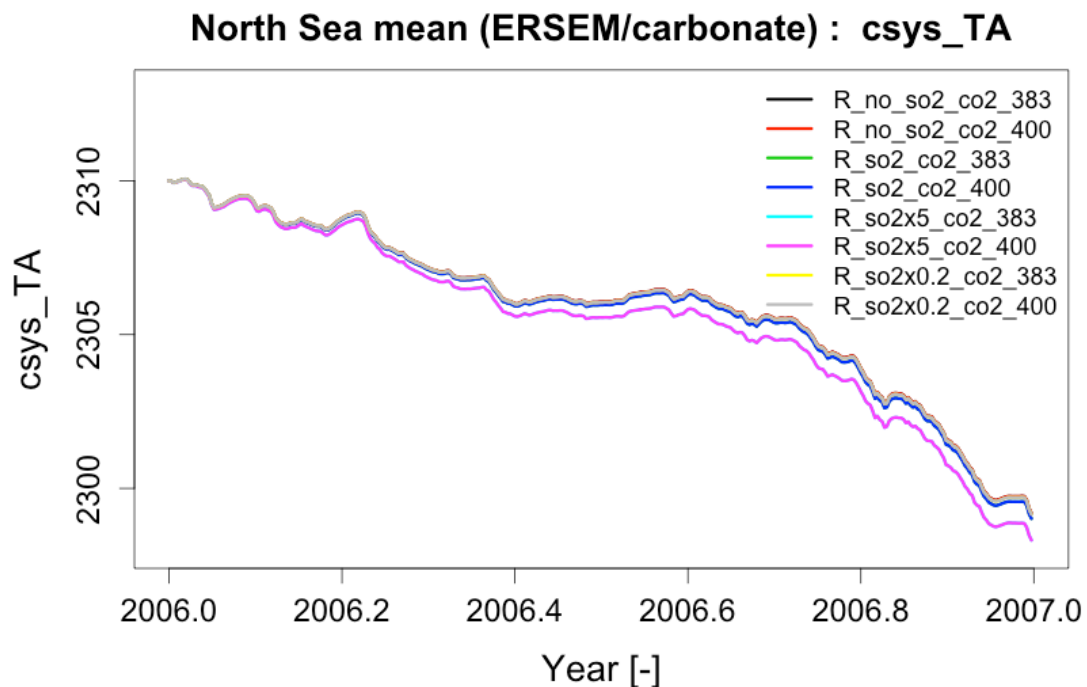*Figure 12: Annual evolution of North Sea mean pH.*

Figure 13: Annual evolution of North Sea mean TA.

Simulation	SO2 [mol/m^3]	TA [μmol/kg]	pH
R_no_so2_co2_383	0	2305.939	8.126809
R_no_so2_co2_400	0	2305.939	8.119067
R_so2_co2_383	0.0484998	2305.841	8.126699
R_so2_co2_400	0.0484998	2305.841	8.118958
R_so2x5_co2_383	0.2424993	2305.450	8.126236
R_so2x5_co2_400	0.2424993	2305.450	8.118523
R_so2x0.2_co2_383	0.0096999	2305.919	8.126787
R_so2x0.2_co2_400	0.0096999	2305.919	8.119045

Table 4: North Sea simulation annual mean of full water body

Simulation	SO2 [mol/m^3]	TA [μmol/kg]	pH
R_no_so2_co2_383	0	2299.191	8.10637
R_no_so2_co2_400	0	2299.191	8.09361
R_so2_co2_383	0.0863215	2299.018	8.10623
R_so2_co2_400	0.0863215	2299.018	8.09347
R_so2x5_co2_383	0.4316079	2298.317	8.10568
R_so2x5_co2_400	0.4316079	2298.317	8.09292
R_so2x0.2_co2_383	0.0172643	2299.157	8.10634
R_so2x0.2_co2_400	0.0172643	2299.157	8.09358

Table 5: North Sea simulation after 1 year of simulation of full water body

Reference	Simulation 2	Annual mean	End of year
R_no_so2_co2_383	R_so2x0.2_co2_383	2.2e-5	2.9e-5
R_no_so2_co2_383	R_so2_co2_383	0.00011	0.00014
R_no_so2_co2_383	R_no_so2_co2_400	0.00776	0.01279
R_no_so2_co2_383	R_so2x5_co2_383	0.00055	0.00069
R_no_so2_co2_383	R_so2x5_co2_400	0.00830	0.01348

Table 6: Decrease in total North Sea mean pH between simulations

5.6 Simulating the surface temporal development

The annual cycle of the evolution of surface (0-20m) pH is clearly distinguishable only for the two different atmospheric CO_2 inputs; it is not possible to identify easily the impact from annual SO_2 emissions, as can be seen in Figure 14. The calculated annual mean values for the North Sea surface waters (upper 20m) are shown in Table 7 and the values reached after 1 year of simulations are shown in Table 8. The units used for SO_2 concentration in water (mol/m^3) and total alkalinity (μmol/kg) remain the same for all following tables. The mean pH difference due to climate change over 1 year is 0.00099 whereas the mean change in response to SO_2 input in one year is 0.00025. On an annual basis the climate change contribution averaged over the full North Sea is about 4 times larger than the impact from SO_2 injection.

This factor of 4 is independent from the background CO_2 concentrations (low atmospheric CO_2 or high CO_2). Using the assumed worst case scenario (SO_2 inputs increased by a factor 5) the mean pH change would increase to 0.00121, which is slightly larger than the decrease caused by the CO_2 scenario. The impact of SO_2 deposition on the carbonate system is indicated by the decreasing trend of surface total alkalinity in Figure 15. The extreme SO_2 emission scenario results in a stronger overall decrease of TA. The simulations with low and high CO_2 cannot be separated from each other in Figure 15. The pH dynamics is however quite different, resulting in higher values at the end of the simulation compared to the annual mean value. This is likely a result of the strong vertical mixing of deeper waters having a higher pH with surface waters in autumn caused by the onset of convection and destratification. Therefore the pH difference between different runs at the end of the simulation can be smaller than the annual mean, see Table 9.

Simulation	SO2 [mol/m^3]	TA [µmol/kg]	pH [-]
R_no_so2_co2_383	0	2291.851	8.09529
R_no_so2_co2_400	0	2291.851	8.08535
R_so2_co2_383	0.11150	2291.624	8.09504
R_so2_co2_400	0.11150	2291.624	8.08518
R_so2x5_co2_383	0.55749	2290.714	8.09408
R_so2x5_co2_400	0.55749	2290.714	8.08415
R_so2x0.2_co2_383	0.02230	2291.805	8.09524
R_so2x0.2_co2_400	0.02230	2291.805	8.08530

Table 7: North Sea surface (0-20m) mean annual values

Simulation	SO2 [mol/m^3]	TA [μmol/kg]	pH [-]
R_no_so2_co2_383	0	2278.018	8.10665
R_no_so2_co2_400	0	2278.018	8.09233
R_so2_co2_383	0.17648	2277.663	8.10640
R_so2_co2_400	0.17648	2277.663	8.09208
R_so2x5_co2_383	0.88240	2276.230	8.10536
R_so2x5_co2_400	0.88240	2276.230	8.09106
R_so2x0.2_co2_383	0.03530	2277.947	8.10660
R_so2x0.2_co2_400	0.03530	2277.947	8.09228

Table 8: North Sea surface (0-20m) values after 1 year of simulation

Reference	Simulation 2	Annual mean	End of year
R_no_so2_co2_383	**R_so2x0.2_co2_383**	4.8e-5	5.1e-5
R_no_so2_co2_383	**R_so2_co2_383**	0.00024	0.00026
R_no_so2_co2_383	**R_no_so2_co2_400**	0.01018	0.01431
R_no_so2_co2_383	**R_so2x5_co2_383**	0.00121	0.00129
R_no_so2_co2_383	**R_so2x5_co2_400**	0.01114	0.01559

Table 9: Decrease in North Sea surface mean pH between simulations
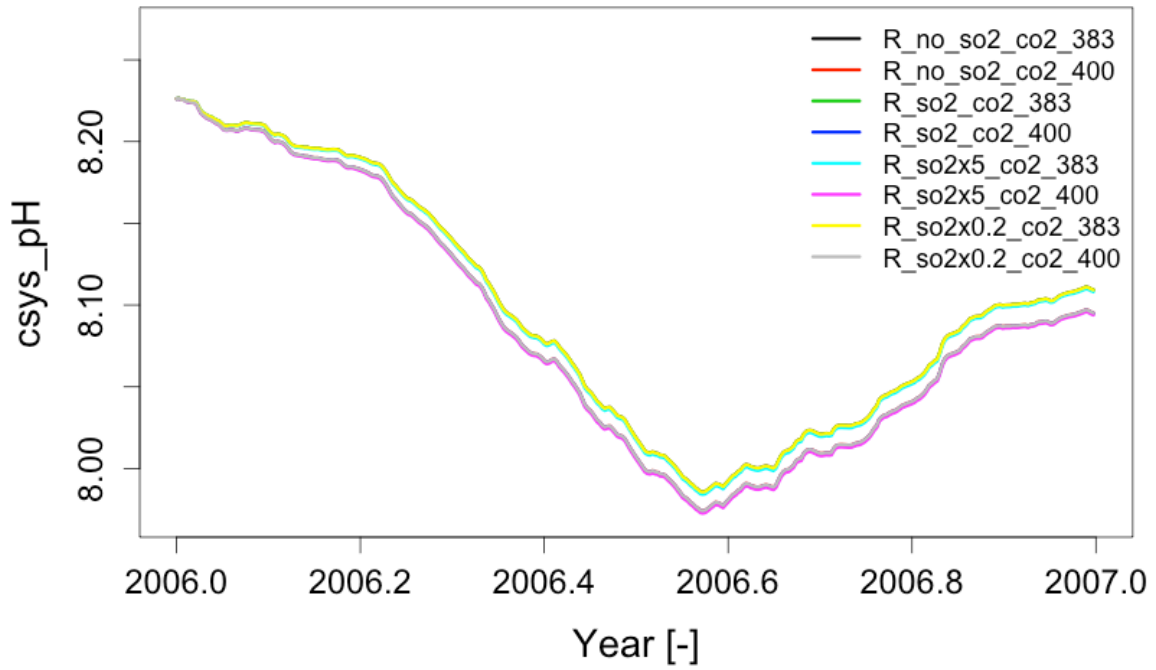
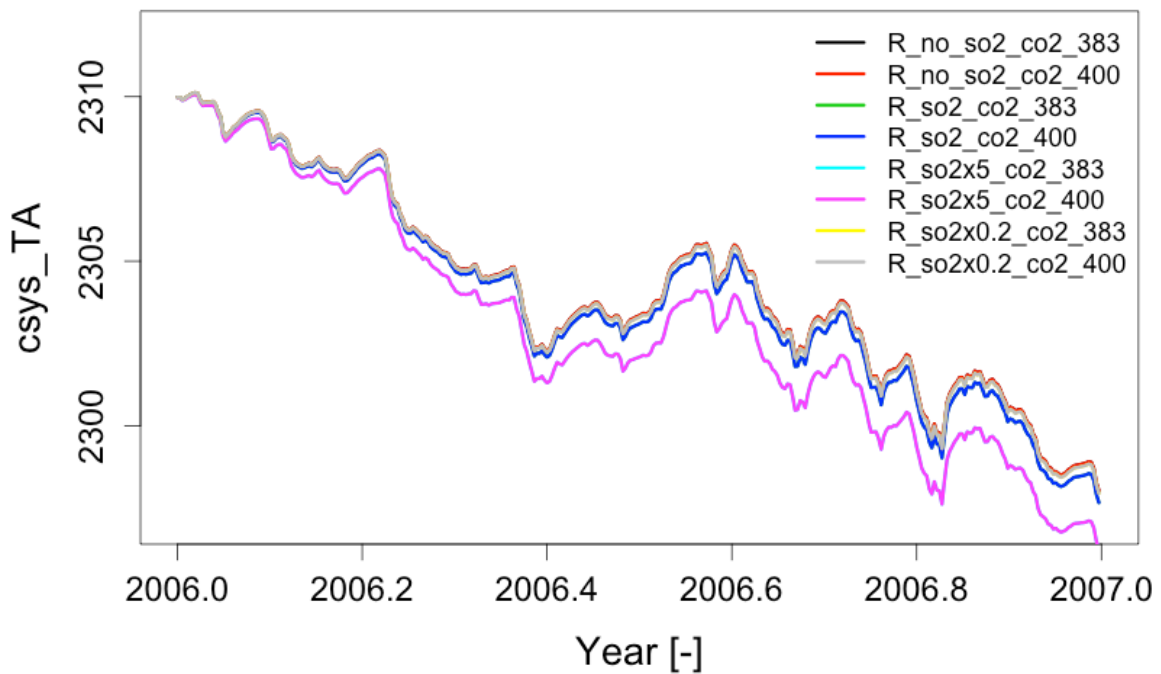*Figure 14: Annual evolution of North Sea pH at the surface (0-20m).*

Figure 15: Annual evolution of surface total alkalinity in the North Sea.

5.7 Hot spot calculation (larger Antwerp/Rotterdam port area)

The Rotterdam port area has by far the highest annual SO2 emissions in Europe, an estimate by ENTEC for 2002 amounts to 3700 tons/year. A rough calculation by (Behrends et al. 2003) using this data suggests that on an annual basis total SO_2 discharge into Rotterdam port waters could contribute about 2×10^{-4} mol H+/L, assuming that all SO_2 is transferred to the aqueous phase. This then would correspond to a decrease of 0.5 – 2 pH units. However this calculation does not take into account the buffer capacity of seawater, the exchange of CO_2 with the atmosphere, nor the tidal exchange with the open sea. Our model results, which consider these neglected factors, show that such a simple calculation is unrealistic, since the calculated pH decrease associated with SO_2 inputs is only in the order of 0.0024. But this is still a 20 times stronger decrease than that calculated for the overall North Sea and is in this region also clearly larger (double) than the change due to increasing atmospheric CO_2 concentrations (~0.001 per year). In the Rotterdam port area the pH change resulting from the SO_2 emissions can be distinguished in Figure 16 from the model runs without SO_2 input, pointing to the likely significant effects in localized hot spots that suffer from high SO_2 depositions.

Reference	Simulation 2	Annual mean	End of year
R_no_so2_co2_383	**R_so2x0.2_co2_383**	0.00038	0.00029
R_no_so2_co2_383	**R_so2_co2_383**	0.00188	0.00149
R_no_so2_co2_383	**R_no_so2_co2_400**	0.01239	0.01640
R_no_so2_co2_383	**R_so2x5_co2_383**	0.00927	0.00761
R_no_so2_co2_383	**R_so2x5_co2_400**	0.02159	0.02397

Table 10: Decrease in Rotterdam region surface pH between simulations.

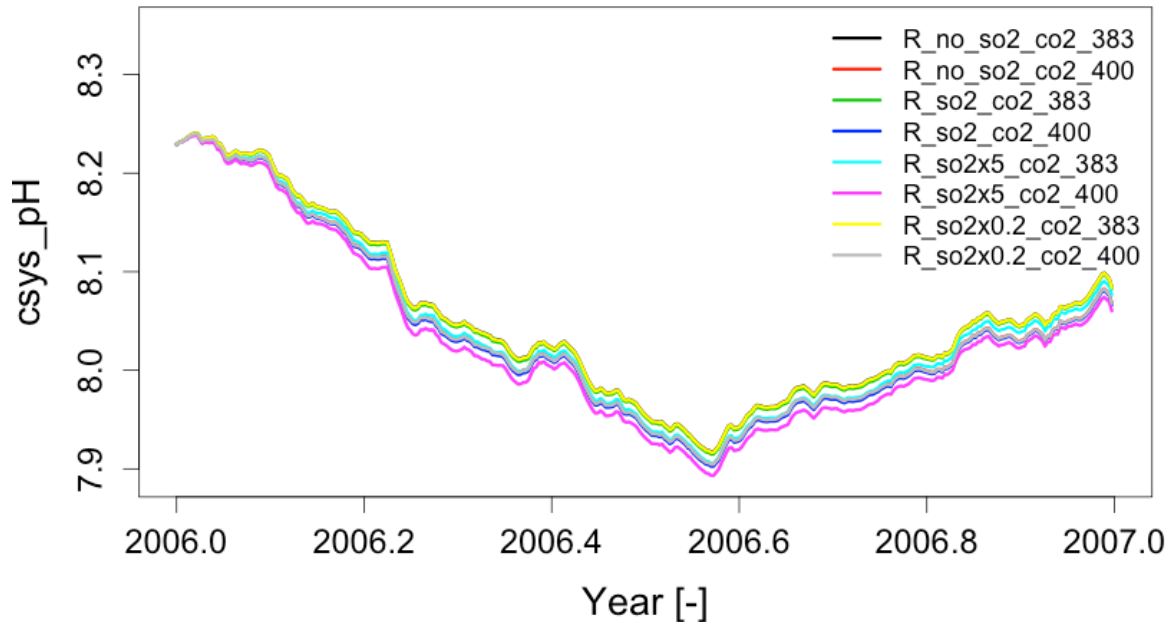## Rotterdam region (ERSEM/carbonate) : csys_pH

Figure 16: Temporally changing pH in the larger Rotterdam port region.

5.8 Simple sensitivity study for importance of river total alkalinity

As the contribution from rivers to the TA of the North Sea is highly variable and not well known, we did not include this contribution in the simulations within the framework of this scoping study. However as a possible large TA input from rivers could principally, due to the related additional buffer capacity, mitigate the pH decrease, especially in the vicinity of the river mouth a simple basic sensitivity test was performed. TA supply in the major rivers was set constant to 2310 µmol/kg, the total amount then depending on the discharge rate. The pH decrease for the North Sea surface waters, for these additional simulations, is given in Table 11. Comparing these values to those from Table 9 (no river TA), we see especially for the overall North Sea region only very small absolute differences between them. In the SO_2 emission case the change is less than 4%. The largest change occurs, as expected, in the vicinity of the river discharge region, which coincides with the highest SO_2 injections. The relative improvement (reduced acidification) in this area is small and limited to a relative change of less than 20% compared to the case without adding TA to the river water. Therefore we might expect a small but not significantly improved sea water buffering capacity, when river TA is fully included in the simulations.

Reference	Simulation 2	Annual mean	End of year
R_no_so2_co2_383	**R_so2x0.2_co2_383**	4.7e-5	5.1e-5
R_no_so2_co2_383	**R_so2_co2_383**	0.00024	0.00025
R_no_so2_co2_383	**R_no_so2_co2_400**	0.00988	0.01416
R_no_so2_co2_383	**R_so2x5_co2_383**	0.00118	0.00126
R_no_so2_co2_383	**R_so2x5_co2_400**	0.01105	0.01541

Table 11: Decrease in North Sea surface mean pH between simulations river TA

Reference	Simulation 2	Annual mean	End of year
R_no_so2_co2_383	**R_so2x0.2_co2_383**	0.00030	0.00023
R_no_so2_co2_383	**R_so2_co2_383**	0.00154	0.00109
R_no_so2_co2_383	**R_no_so2_co2_400**	0.01181	0.01614
R_no_so2_co2_383	**R_so2x5_co2_383**	0.00781	0.00551
R_no_so2_co2_383	**R_so2x5_co2_400**	0.01955	0.02140

Table 12: Decrease in Rotterdam region surface mean pH between simulations river TA

5.9 Impact from SO2 input on Carbon dioxide uptake

While much of the uptake of CO_2 takes place in the open ocean (Takahashi et al., 2002), continental shelves play a significant role through the mechanism of the shelf sea carbon pump. This so called "continental shelf pump" describes the mechanisms that transfer carbon from the atmosphere via the continental shelf to the deep ocean, a process that has also been observed in the North Sea (Thomas et al., 2004; Bozec et al., 2005). Globally extrapolated, the net uptake of CO_2 by coastal and marginal seas is about 20% of the world ocean's uptake of anthropogenic CO_2 (Thomas et al., 2004).

We calculated the total annual net CO_2 uptake of the North Sea to be about 58.4 million tons in 2006 and 68.1 million tons in 2015. However, these numbers are calculated without considering the CO_2 uptake by primary production (ecosystem) and are therefore lower limit estimations. The increase in CO_2 uptake, caused by increasing CO_2 levels, is about 970000 tons annually. The function of the continental shelf pump will however be impaired by the addition of SO_2. The additional input of SO_2 into CO_2 supersaturated water will result in outgassing (or reduced net uptake) of CO_2. Using the real SO_2 input for 2006 we find that the CO_2 uptake for 2006 is reduced by about 240000 tons compared to the fictional uptake in the case of no SO_2 input. The results for the different scenarios are given in Table 13 and range from a minimum of 50000 tons (low SO2 scenario) to a maximum of 1.2 million tons (high SO2 scenario) of CO_2 not

absorbed by the North Sea. As primary production contributes to the uptake of CO_2 these numbers should be considered as upper limit estimates.

Reference	SO2 input	Difference [mmol C/m^2/d]	CO2 [Tons/year]
R_no_so2_co2_383	R_so2x0.2_co2_383	-0.0052	-47601
R_no_so2_co2_383	R_so2_co2_383	-0.026	-238009
R_no_so2_co2_383	R_so2x5_co2_383	-0.13024	-1192243

Table 13: Difference of annual CO2 Air-Sea flux (North Sea)

5.10 Conclusions from the North Sea model study

A complex modelling system consisting of a coupled numerical hydro-dynamical model and a bio-geochemical model able to include the influence of ship-borne SO2 fluxes has been established. The system has been set-up for the North Sea region and 8 basic simulations have been carried out. The physical simulations are realistic in terms of hydrodynamics and applied external forcings – i.e. meteorology, lateral boundary conditions, tides and freshwater fluxes via rivers are all considered. The bio-geochemical simulations are realistic in the sense that they describe the carbonate system at high complexity using the ERSEM/carbonate model. However, a full representation of the carbonate system including an advanced model for the pelagic biological system and proper Total Alkalinity sources from e.g. rivers could not be attempted. The model used here has been applied to the North Sea and has previously undergone basic validation (Artioli et al. 2012), but no dedicated calibration/validation study with regard to SO2 injections has been performed. The aim of this work has been to study the sensitivity of the seawater pH to the additional SO_2 fluxes generated by ships in comparison to changes in response to increasing atmospheric CO_2 concentrations. A comprehensive assessment of the ship emissions is outside the scope of this study, hence the EMEP SO2 emissions from ships used here must be considered as approximate values for the real input. This approach has its limitations due to the non-linear behaviour of the system – especially if regional impacts are strong. Due to the need to complete all the model runs within the time constraints of this project, all the simulations were run for the length of 1 year, assuming a rather fast response of the system that may not be realistic.

Considering all these limitations it is evident that the simulations do contain some bias. A careful model validation is however beyond the scope of this study and is, because of the scarcity of reliable measured pH data, more than likely not feasible to perform. To eliminate the possible model bias that could occur in each individual model run, we do not consider the single simulations in a quantitative manner. Assuming that the inherent model bias for each simulation will be similar for all the simulations, we can eliminate some part of this bias by looking mainly at the differences between the simulations. For estimating the annual pH decrease therefore the reference run is subtracted from the run under consideration.

The calculated annual mean decrease of pH due to SO_2 input for the North Sea total water column is 0.00011 a seemingly small value (Table 6). Considering only the change in the surface layer (0-20m) the annual decrease is 0.00024 (Table 9). In agreement with these small numbers Figure 8 and Figure 9 show a relatively small impact on the pH

with SO_2 emissions and CO_2 levels from 2006 compared to the reference run. The biggest changes are in the areas with highest SO_2 fluxes (Figure 6), as expected. Due to advection/diffusion processes the effect is geographical smeared. Figure 10 shows the impact on pH from the annual change in CO_2 concentration and it is clear that climate change has a slightly bigger general impact on the pH change than the annual SO_2 addition.

The spatially explicit simulations presented here, do however clearly show that impacts vary strongly across the North Sea, with the largest values along the shipping lanes and near to the coast (Dutch coast, German Bight, Skagerrak). In regions with high ship traffic density, such as the Rotterdam port area, the contribution to acidification from SO_2 can be double that from increasing CO_2 concentrations and about 20 times larger than the North Sea mean values (Table 10 and Table 14).

Study	Area	-ΔpH(SO2)	-ΔpH(CO2)	ΔSO2/ΔCO2 [%]
This study	North Sea	0.00011	0.0008	~14
This study	North Sea (0-20m)	0.00024	0.001	~24
This study	Rotterdam	0.0025	0.001	250

Table 14: Annual pH decrease resulting from SO2 and CO2 flux (this study)

Recommendations/improvements for a more detailed follow up modelling study:

1. A comprehensive model calibration/validation exercise should be undertaken to ensure that the model simulates the carbonate system of the investigated water body with sufficient accuracy.
2. Instead of using EMEP emission data, information on ship traffic should be gathered from existing sources such as the Automated Information System (AIS) as well as the amount of fuel used and its sulphur content.
3. Other exhaust components impacting the pH, especially NOx emissions/depositions should be included in the simulations.
4. The numerical model setup should be refined – instead of using rather coarse resolution (6nm), a model setup in the order of 1nm resolution should be implemented, allowing even finer resolution in hot spots.
5. Instead of the applied time slice modelling using time periods of 1 year, longer simulations periods (10-20 years) should be used to investigate cumulative effects and mitigate the effect of approximate initial conditions.
6. Variations in river alkalinity are not considered in this study. However the rivers round the North Sea and Baltic Sea have significantly varying Total Alkalinity concentrations and this effect should be investigated.
7. Total Alkalinity variations coming from the pelagic carbonate system associated with biological activity and from the sediment are not included in this study and should be incorporated via a more complete description of the ecosystem.
8. Extend the area to the full SECA region, covering also the Baltic Sea, likely requiring another model or at least a specific calibration/validation.
9. Further to the baseline scenario several more realistic and policy relevant scenarios should be defined.

6. Discussion and Summary

6.1 Acidification caused by SO₂ and CO₂ emissions

The calculated annual mean decrease of pH due to SO_2 input for the North Sea total water column is 0.00011, a seemingly small value (Table 9, Table 6). Considering only the change in the surface layer (0-20m) the annual decrease is 0.00024 (Table 9). These values represent the lower end of the values found in the literature, see a summary in Table 15.

It is clearly not the scope of this study to analyse in detail the problems with much of the published literature, but we provide some considerations, as to why the values are different. For example, the results from Hassellöv et al. (2013) for the North Sea are about a factor of 10 larger than ours. Major differences to our study are that they considered also NOx input and set this equal to the contribution from SOx (at least a factor 2). Furthermore, they considered also gross emissions (not only shipping). They had many additional simplifications in their model, including no horizontal advection and no re-equilibration of CO_2 with atmosphere. They also used a monthly time step. All these simplifications most likely led to an overestimation of the calculated total surface water acidification in CO_2-supersaturated systems.

We estimated the annual pH decrease caused by increasing atmospheric CO_2 concentrations (0.001) in order to have a reference value we could compare to. The trend from global data according to Bates et al. (2014) is -0.0018±0.0006. For the North Sea Beare et al. 2013 conclude that there is no general trend in the measured data (but it could be -0.006±0.004 for the last 20 years). They also state that because of methodological problems pH measurements before 1990 are generally not very reliable. The large seasonal cycle, strong interannual variability and regional variability result in a rather large uncertainty of the estimated trend. Very similar conclusions are drawn from measurements in the Baltic Sea that show no significant pH trend over the last 20 years (Omstedt et al. 2009). The pH dynamics in shelf seas and coastal waters is mainly determined by a strong annual cycle, interannual variability and regional differences that all result in a large scatter of the data. Under these circumstances we consider that our results on CO_2 related acidification in the North Sea are in agreement with the available measured and modelled data.

Therefore the simulated acidification due to SO_2 emissions for the overall North Sea is about 14% of the CO_2 effect, small but not negligible. Considering only the surface changes the SO_2 impact even reaches up to 25% of the CO_2 contribution. However the presented spatial explicit simulations clearly show that impacts vary strongly across the North Sea showing largest values along the shipping lanes and near to the coast (Dutch coast, German Bight, Skagerrak) and therefore the overall mean values do not reflect the potential for problems in certain localised regions. Indeed focusing on the values of the densely trafficked area around Rotterdam port we found annual acidification rates caused by SO_2 deposition that are in the same order as those from CO_2 acidification (0.002) and up to 20 times larger than the North Sea mean values. Because of the spatial heterogeneity of pH changes, global means or even North Sea means do not reflect the severity of the problem. The strong localised effects we have shown here highlight the fact that the impacts from SO_2 input in European Seas must be addressed with higher resolution regional modelling studies that focus on the areas impacted by shipping activities.

It is important to remember that in this study several aspects could not be considered, for example, emissions might be smaller now than in 2006 due to regulations now in place. On the other hand the very localised input from SWS systems could enhance the impact in shipping lanes and port areas. NOx emissions were also ignored in our study

and they could be a factor of 3-4 larger than SOx emissions (Jalkanen, 2012), bringing the total emissions again closer to our worst case scenario. Finally the alkalinity input from rivers may partially mitigate the problem in regions with significant river discharge, since rivers contribute to the total alkalinity budget. Further the impact of the addition of SO_2 has a complicated effect on the equilibrium state of the carbonate cycle in the ocean that depends on many factors. The model estimates that for every ton of SO2 input, the ocean will not absorb about half a ton of CO_2.

Study	Area	ΔpH (SO2)	Area	ΔpH (CO2)
Doney 2007	Global	<0.0004	Global	~0.001
Hunter 2011	North Sea	0.0014	North Sea	0.0016
Hunter 2011	Baltic Sea	0.0005	Baltic Sea	0.0018
Hassellov 2013	North Sea	0.0024		
Hassellov 2013	Global	0.0004		
Beare 2013			North Sea	0.0
COWI 2013	Sound	0.01		
Hagens 2014	North Sea	0.0005		
Hagens 2014	Baltic Sea	0.0001		
Bates 2014			Global	0.0018
Omstedt 2015	Baltic Sea	0.0001		
This study	North Sea (0-20m)	0.00024	North Sea (0-20m)	0.001
This study	North Sea	0.00011	North Sea	0.0008
This study	Rotterdam	0.0025	Rotterdam	0.001

Table 15: Overview of annual pH decrease in response to ship borne SO2 and CO2 emissions

6.2 Total amount of SO₂ input to the North Sea

In this study we estimated the total SO_2 input from ship emissions to the North Sea region in 2006 to be around 500.000 tons, a number that must be put in some context by comparing it to other relevant data.

Using the STEAM model Jalkanen (2012) estimated, based on AIS observations, for the North Sea SO_2 emissions of about 200.000 tons for 2009. This amount agrees roughly with the data presented here from the EMEP emissions data base for 2009. There is

however a discrepancy in the data between 2006 and 2009, as the data from the STEAM2 model presented by Jalkanen (2014) for the Baltic Sea do not show such a strong decrease (these data decrease from 144.000 tons to 124.000 tons). Over the Baltic Sea the estimated NOx emissions from shipping are about 650.000 tons for 2009.

One of the likely largest environmental experiments was performed in the North Sea when Germany, France, Belgium and UK dumped about 2.7 million tons SO_2 (4 million tons of up to 20% sulphuric acid) into the open North Sea (annually and localized, given values are for 1988). Germany alone dumped about 750000 tons annually of 12% sulphuric acid into the North Sea (near Helgoland) for over 20 years. Most environmental studies performed at the time concluded that this direct dumping into the water did not produce proven detrimental environmental effects (Roekens 1983). Lewis (1985) and Lewis and Riddle (1989) concluded from their modelling studies that the dumping of such amounts of sulphuric acid has a small pH effect on the seawater.

Even very recently Taylor (2015) wrote: " initiated by the European Commission the dumping of highly acid waste from methyl methacrylate production into the North Sea .... despite the absence of any environmental impact was forbidden and this disposal route was terminated by European regulations". When comparing the quantity and scale of the dumping to the expected disposal from SWS, then it could be expected that the maximum of about ~6 pH produced during waste discharge from SWS (compared to ~2.6 pH during dumping) will affect neither the pH values nor the sulphate contents of the receiving waters to a noticeable degree.

However, we would like to state that the quality of the environmental impact studies performed at the time might have been insufficient for such conclusions drawn (just consider the problem of unreliable pH measurements before about 1990). To reassess the impact from these large quantities of dumped sulphuric acid using the established modelling system would not only be an interesting academic exercise but would contribute to the model validation and could help to build up confidence in the simulations.

6.3 Relevance of additional acidification from ship borne SO_2

While there are currently no EU rules regulating the use of exhaust gas recirculation (EGR) on-board ships, there are existing EU rules regulating surface water quality (Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy (Water Framework Directive) and Directive 2008/56/EC of the European Parliament and of The Council establishing a framework for community action in the field of marine environmental policy (Marine Strategy Framework Directive)) as well as the emissions of priority substances and other pollutants including excess nutrients to water (Water Framework Directive and Directive 2008/105/EC of the European Parliament and of the Council on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending Directive 2000/60/EC of the European Parliament and of the Council).

The impact on the pH decrease in the open North Sea region from discharging the acid wash water into the seawater was found to be small but not insignificant and it is regionally varying. The calculated annual mean decrease of pH because of SO_2 injection for the North Sea total water column is 0.00011. The total annual impact from increasing atmospheric CO_2 concentrations on the acidification of the North Sea surface area is about 8 times stronger (0.001) than the impact from wash water injection. Because of the pronounced spatial variations the mean impact does not reflect the overall situation

well. There are several critical regions with high ship traffic intensity, such as along shipping lanes and in port areas. In these areas the decrease of pH from SO2 injection can be as twice as large as the impact from increasing CO_2 concentrations and 20 times as large as the North Sea overall mean decrease.

Therefore this indicates potential problems related to the surface water quality in ports, estuaries and coastal waters that subject to regulation under the Water Framework Directive (WFD). The problem of decreasing pH caused by SO2 injections from ships in the regional seas (North Sea) also has implications for the obligation of the Member States to assess the environmental state of their marine areas and to establish a Good Environmental Status (GES) under the Marine Strategy Framework Directive (MSFD), as pH value is one of the GES criteria.

Lastly it must be considered that the United Nations Convention on the Law of the Sea (UNCLOS) especially Article 194 (Measures to prevent, reduce and control pollution of the marine environment) and Article 195 (Duty not to transfer damage or hazards or transform one type of pollution into another) apply in the case of SOx/NOx emissions. The transfer of acidic emissions (here acidic rain) from the atmosphere to the ocean seems to violate these articles.

7. Conclusion

This initial scoping study on the potential impact of on-board desulphurisation equipment on the water quality in SOx Emission Control Areas comprises a brief literature study and a dedicated modelling study to quantify the additional acidification caused by the deposition of SO2 from ship borne emissions. The available peer reviewed literature and institutional study reports do not provide clear evidence that discharging scrubber wash water to the marine environment causes significant environmental degradation (pH decrease, increase of eutrophication, pollutants). Furthermore most peer reviewed literature as well as the study reports apply simplifications in such a way that they should instead be considered as scenario simulations. The simplified modelling as applied in most peer reviewed studies most likely leads to an overestimation of surface water acidification in CO_2 supersaturated systems. On the other hand the currently available research also does not irrefutably exclude the deterioration of the environmental status of the vulnerable (near shore) ecosystems (especially since they neglect cumulative and long term effects). It is therefore not clear if objectives set by the Marine Strategy Framework for achieving 'good environmental status' can be met by the year 2020 and onwards, taking into account a growth in the number of scrubbers installed.

Therefore, a complex modelling system consisting of a coupled numerical hydro-dynamical model and a bio-geochemical model able to include the influence of ship-borne SO_2 deposition has been implemented. The system has been set-up for the North Sea region but could be applied to other regions as well. The performed physical simulations are realistic in terms of full hydrodynamics and applied realistic external forcings – i.e. meteorology, lateral boundary conditions, tides and freshwater fluxes via rivers are all considered. The bio-geochemical simulations are realistic in the sense that they describe the carbonate system at high complexity using the ersem/carbonate model, and include especially also the bi-directional air-water exchange. There are however several limitations, which we reiterate below. In order to minimise the effect of the inherent bias we only consider the differences between simulations as relevant for this study, rather than absolute values for each simulation.

From this modelling study the calculated annual mean decrease of pH due to SO_2 input to the North Sea total water column is 0.00011, a seemingly rather small value, but equal to about 12% of the greenhouse gas-induced acidification. However because of the pronounced spatial variations the mean impact does not reflect the overall situation well. Consequently we find critical regions with high ship traffic intensity, for example along shipping lanes and in the Rotterdam port area. Here the contribution from SO_2 injection can be as much as 20 times larger than the North Sea mean (annual decrease of 0.0025) and would therefore be about double the impact from increasing CO_2 concentrations. This could be seen from the presented spatially explicit figures and is highlighted by showing the relative decrease of pH from SO_2 input compared to that from increasing CO_2 in Figure 17. Therefore this indicates potential problems related to the surface water quality in ports, estuaries and coastal waters that fall under the regulation from the Water Framework Directive (WFD). The problem of decreasing pH caused by SO_2 input from ships in the regional seas (North Sea) is also a concern for Member States who are obliged to assess the environmental state of their marine areas and to establish a Good Environmental Status (GES) under the Marine Strategy Framework Directive (MSFD), as pH value is one of the GES criteria. Considering that many different anthropogenic impacts are contributing to the acidification of the oceans (rising CO_2-concentration in the atmosphere, climate warming, acid rain, ballast water input, NOx-emissions, etc.), we shall be very careful adding a new source of acid input (precautionary principle of WFD and MSFD).

Further we would like to highlight a common misunderstanding, which we find in a number of studies regarding the environmental impact of scrubber wash water discharge. In these studies, the limits in the discharge guidelines are compared with water quality standards, such as the EU water quality standards (EQS) for the marine environment. Such a comparison may be seen to provide extra safety if the substance in question is reliably diluted further once it has been discharged, but the comparison may be misleading in case of accumulation in the environment. Thus, there is a difference between discharge guidelines and EQS. Discharge guidelines set limits for pollutants in wastewater from a point source, whereas EQS set maximum limits for pollutants in a water body to protect the marine environment. The wash water from EGCS is discharged into such a water body and contains acid substances (SO_2, NOx) as well as persistent organic pollutants like PAH and non-degradable heavy metals, which accumulate in the water and sediments and might exceed the EQS, despite formally fulfilling the discharge regulations.

Finally, based on our model we estimated that the acidification caused by the input of about 500000 tons of SO_2 to the North Sea during 2006 might have prevented the uptake of about 240000 tons of CO_2 during that year. Thus, roughly speaking for every ton of SO_2 input, the ocean will not absorb about half a ton of CO_2. A full assessment of the climate significance of this finding would require a life-cycle assessment of the entire fuel chain since the alternative, desulphurising the fuel in the refinery, also leads to greenhouse gas emissions.
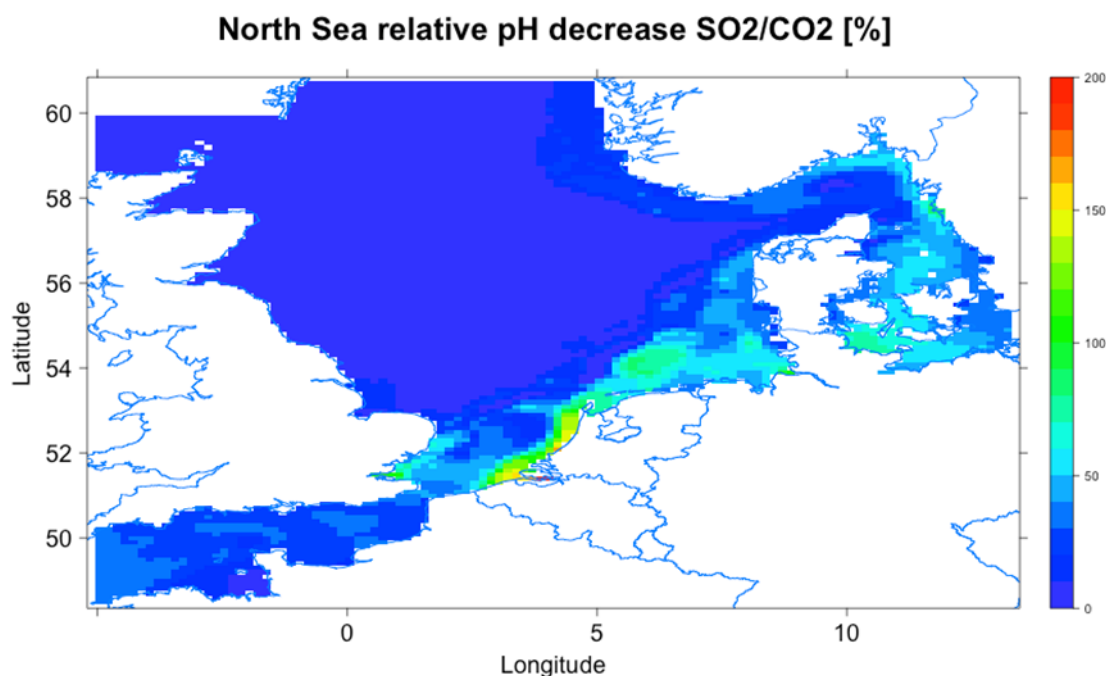

Figure 17: Relative annual pH decrease (in per cent) because of SO2 emissions compared to that resulting from increasing CO2.

Considering the complexity of the issue under investigation this scoping report is by no means fully conclusive and only touches on some of the relevant issues. A more comprehensive assessment is recommended and would require the following tasks to be approached (priority needs to be defined with respect to the study focus):

▪ Carbonate model calibration/validation for the investigated region/water body

- Extension of the modelling region to cover also the Baltic Sea
- High resolution model setup (1nm resolution or better) or nesting
- Multi-annual simulations to assess long term trends
- Using detailed SOx and NOx input from ships (scrubber and atmosphere)
- Considering alkalinity variations from rivers
- Considering alkalinity variations by primary production/sediments in the ecosystem (usage of a full ecosystem model)
- Considering the amount and impact from hazardous substances in the wash water (likely requiring additional lab/field measurements)
- Simulating the impact on pH from the long term SO2 titanoxid waste dumping (validation/framing study).

For example it is known from e.g. (Artioli, et al., 2012) that the rivers around the North Sea and Baltic Sea have highly varying Total Alkalinity concentrations and that this source has considerable uncertainty. Also attempts by other groups at running ocean acidification models (Blackford and Gilbert, 2007; Artioli et al., 2012; Kuznetsov and Neumann, 2013) have highlighted the need to improve the treatment of coastal processes such as river loads, optical properties and parameterisation of total alkalinity; many parts of the carbonate chemistry are just not well understood or even known. There is still significant development needed in order for regional sea models to be able to examine the effects of ocean acidification on ecosystem function and thereby identify the economic and social impacts. There is a lack of observations of basic carbonate parameters across the shelf seas, and high-frequency sampling at time series stations is needed.

Considering the great complexity of the topic at hand and its importance for the environment, the authors propose the following scenarios for possible future work on the environmental impact from SO2 deposition in sea water:

Minimal scenario:

   The work should be focused on a better assessment of impacts from SOx and NOx emissions on acidification, following some of the above proposals for improvement (comprising SO2 quantification, higher resolution, full ecosystem model, inclusion of TA sources) with focus on coastal processes. We estimate that this would require the work of about 3 persons for about 2-3 years ~ 100 mm (~500.000 Euro).

Optimal scenario:

   Setting up a dedicated consortium of 5-10 experienced institutions and doing a comprehensive study, including hazardous substances, covering the full SECA area, regional hot spot investigations, improved modelling, covering basically all the points mentioned in the above improvement list, including some necessary basic research, where needed. The costs for such full study would likely be in the order of ~ 3- 5 Million Euro.

References

1. Artioli, Y., et al. (2012). The carbonate system in the North Sea: Sensitivity and model validation. Journal of Marine Systems, 102-104, 1–13.

2. Baretta, J. W. (1995). The European regional seas ecosystem model, a complex marine ecosystem model. Neth. J. Sea Res , 33, pp. 233-246.

3. Bates, N.R., et al. (2014) A time-series view of changing ocean chemistry due to ocean uptake of anthropogenic CO2 and ocean acidification. Oceanography 27(1):126–141, http://dx.doi.org/10.5670/oceanog.2014.16.

4. Beare D., et al. (2013) Long-Term Trends in Calcifying Plankton and pH in the North Sea. PLoS ONE 8(5): e61175. doi:10.1371/journal.pone.0061175

5. Behrends, B. & Liebezeit, G. (2003). Reducing SOX and NOX Emissions from Ships by a Seawater Scrubber. Report, Research Centre Terramare, Wilhelmshaven, Germany. BP Marine Report.

6. Blackford, J. and Gilbert, F. (2007). pH variability and CO2 induced acidification in the North Sea. Journal of Marine Systems, 64, 229–241.

7. Bolding, K. (2015) Modelling of scrubber wash water dilution in the Baltic Sea. Report for contract C392003BOLD.

8. Borges, A. and Gypens, N. (2010). Carbonate chemistry in the coastal zone responds more strongly to eutrophication than to ocean acidification. Limnol. Oceanogr., 55, 346–353.

9. Bozec, Y., Thomas, H., Elkalay, K., and Baar, H. (2005). The continental shelf pump for CO2 in the North Sea–evidence from summer observation. Marine Chemistry, pages 131–147.

10. Burchard, H., & Bolding, K. (2002). GETM - a general estuarine transport model. Scientific Documentation. European Commission. JRC Technical Report EUR20253.

11. Butenschön, M., Clark, J., Aldridge, J. N., Allen, J. I., Artioli, Y., Blackford, J., et al. (2015). ERSEM 15.06: a generic model for marine biogeochemistry and the ecosystem dynamics of the lower trophic levels. Geosci. Model Dev. Discuss.

12. Blackford, J., & Gilbert, F. (2007). pH variability and CO2 induced acidification in the North Sea. Journal of Marine Systems.

13. Bruggeman, J., & Bolding, K. (2014). A general framework for aquatic biogeochemical models. Environmental Modelling & Software.

14. Brynolf, S., M. Magnusson, E. Fridell, K. Andersson, (2014) Compliance possibilities for the future ECA regulations through the use of abatement technologies or change of fuels. Transportation Research Part D 28 (2014) 6–18

15. Buhaug, J., et al.: Second IMO GHG study 2009; International Maritime Organization (IMO) London, UK, March, 2009.

16. Caldeira, K. and Wickett, M. (2003). Anthropogenic carbon and ocean pH. Nature, 425, 365.

17. Capone, D. and Hutchins, D. (2013). Microbial biogeochemistry of coastal upwelling regimes in a changing ocean. Nature Geoscience.

18. Coughlan, C., N. Hoepffner, A. Stips (2013) Modelling the carbonate system to adequately quantify ocean acidification. JRC Technical Report. EUR26450.

19. COWI2012: Kjølholt, J., S. Aakre, C. Jürgensen, J. Lauridsen Assessment of possible impacts of scrubber water discharges on the marine environment, (COWI, 2012) Danish Environmental Protection Agency

20. COWI2013: Assessment of possible impacts of scrubber water discharges on the marine environment - supplementary note. (COWI, 2013) Danish Environmental Protection Agency

21. Dee, D. P., Uppala, S. M., Simmons, A. J., Berrisford, P., Poli, P., Kobayashi, S., et al. (2011). The ERA-Interim reanalysis: configuration and performance of the data assimilation system. Quarterly Journal of the Royal Meteorological Society.

22. Dethlefsen, V., 1990. Ende der Verklappung von Abfällen aus der Titandioxidproduktion in der Nordsee. SDN

23. Dickson, A. G. (1981). An exact definition of total alkalinity and a procedure for the estimation of alkalinity and total inorganic carbon from titration data. Deep Sea Research Part A. Oceanographic Research Papers.

24. Dickson, A., Sabine, C., and Christian, J., editors (2007). Guide to best practices for ocean CO2 measurements. PICES special publication 3.

25. Doney, S. C., et al. (2009), Ocean acidification: The other CO2 problem, Annu. Rev. Mar. Sci., 1, 169–192, doi:10.1146/annurev.marine.010908.163834.

26. Doney, S. C., et al. (2007), Impact of anthropogenic atmospheric nitrogen and sulfur deposition on ocean acidification and the inorganic carbon system, Proc. Natl. Acad. Sci. U. S. A., 104(37), 14580–14585, doi:10.1073/pnas.0702218104.

27. EC, 2008. Directive 2008/56/EC of the European Parliament and of the Council of June 2008 establishing a framework for community action in the field of marine environmental policy (Marine Strategy Framework). Official Journal of the European Union, Issue L164, pp. 19-40.

28. Eelco den Boer, Maarten 't Hoen (Delft, 2015) Scrubbers - An economic and ecological assessment Delft, CE Delft, March 2015 (on request NABU)

29. Endresen, O., et al. (2003), Emission from international sea transportation and environmental impact, J. Geophys. Res. D: Atmos., 108(D17), 4560, doi:10.1029/2002JD002898.

30. Entec, 2010. Study To Review Assessments Undertaken Of The Revised Marpol Annex VI Regulations, Final report, London: Entec UK Limited

31. European Maritime Shipping Agency (EMSA, 2010) The 0.1% sulphur in fuel requirement as from 1 January 2015 in SECAs - An assessment of available impact studies and alternative means of compliance. Technical report EMSA 2010

32. Eyring, V., I. S. A. Isaksen, T. Berntsen, W. J. Collins, J. J. Corbett, O. Endresen, R. G. Grainger, J. Moldanova, H. Schlager, and D. S. Stevenson, Transport impacts on atmosphere and climate: Shipping, Atm. Env., doi:10.1016/j.atmosenv.2009.04.059, 2009.

33. GESAMP, 2009. Advice by GESAMP on the interim criteria for discharge of washwater from Exhaust Gas Cleaning Systems for removal of sulphur-oxides, London: GESAMP.

34. Gypens, N., Lacroix, G., Lancelot, C., and Borges, A. V. (2011). Seasonal and inter-annual variability of air-sea CO2 fluxes and seawater carbonate chemistry in the Southern North Sea. Progress in Oceanography, 88(1), 59–77.

35. Hagens, M., K. A. Hunter, P. S. Liss, and J. J. Middelburg (2014), Biogeochemical context impacts seawater pH changes resulting from atmospheric sulfur and nitrogen deposition, Geophys. Res. Lett., 41, 935–941, doi: HYPERLINK "http://dx.doi.org/10.1002/2013GL058796" \t "_blank" \o "Link to external resource: 10.1002/2013GL058796" 10.1002/2013GL058796

36. Hassellöv, I.M., D. R. Turner, A. Lauer, J. J. Corbett 2013 Shipping contributes to ocean acidification. Geophys. Res. Letters, 40, 2731–2736, doi:10.1002/grl.50521, 2013

37. Hinga, K. (2002). Effects of pH on coastal marine phytoplankton. Marine Ecology Progress Series, 238, 281–300.

38. Hufnagl, M., G. Liebezeit, B. Behrends, (BP 2005) Effects of Sea Water Scrubbing
BP Marine Report.

39. Hunter, K. A., et al. (2011), Impacts of anthropogenic SO(x), NO(x) and NH (3) on acidification of coastal waters and shipping lanes, Geophys. Res. Lett., 38, L13602, doi:10.1029/2011gl047720.

40. IMO, 2009. 2009 Guidelines for Exhaust Gas Cleaning Systems (IMO Annex 9, Resolution MEPC.184(59), adopted July 17, 2009),, London: IMO.

41. Jalkanen, J.-P., A. Brink, J. Kalli, H. Pettersson, J. Kukkonen and T. Stipa, A modelling system for the exhaust emissions of marine traffic and its application in the Baltic Sea area, Atmos. Chem. Phys., 9 (2009) 9209-9223.

42. Jalkanen, J.-P., J. Kalli and T. Stipa, 2009 The price of sulphur reductions in the Baltic Sea and North Sea shipping BSR Innoship report.

43. Jalkanen,J-P.., L. Johansson, J. Kukkonen A Comprehensive Inventory of the Ship Traffic Exhaust Emissions in the Baltic Sea from 2006 to 2009. AMBIO 2014, 43:311–324, DOI 10.1007/s13280-013-0389-3

44. Kuznetsov, I., T. Neumann, (2013). Simulation of carbon dynamics in the Baltic Sea with a 3D model. Journal of Marine Systems, 111-112, 167–174.

45. Lewis, R.E., Riddle, A.M.; (1989), Sea Disposal: Modelling studies of waste field Marine Pollution Bulletin ,20, 124-129

46. McNeil, B. and Matear, R. (2008). Southern ocean acidification: a tipping point at 450-ppm atmospheric CO2. Proceedings of the National Academy of Sciences of the United States of America, 105(48), 18860–18864.

47. Melzner, F., Thomsen, J., Koeve,W., Oschlies, A., Gutowska,M. A., Bange, H.W., Hansen, H. P., and Körtzinger, A. (2012). Future ocean acidification will be amplified by hypoxia in coastal habitats. Marine Biology.

48. Miola, A., B. Ciuffo, E. Giovine, M. Marra (2010) Regulating Air Emissions from Ships, JRC report EUR 24602

49. Omstedt, A., E. Gustafsson, K. Wesslander, (2009) Modelling the uptake and release of carbon dioxide in the Baltic Sea surface water, Continental Shelf Research, Volume 29, Pages 870-885, ISSN 0278-4343, http://dx.doi.org/10.1016/j.csr.2009.01.006.

50. Omstedt, A., M. Edman, B. Claremar, A. Rutgersson, (2015) Modelling the contributions to marine acidification from deposited SOx, NOx, and NHx in the Baltic Sea: Past and present situations, Continental Shelf Research, Volume 111, Pages 234-249, ISSN 0278-4343, http://dx.doi.org/10.1016/j.csr.2015.08.024.

51. Orr, J., et al. (2005). Anthropogenic ocean acidificaiton over the twenty-first centry and its impact on calcifying organisms. Nature, 437.

52. Royal Society (2005). Ocean Acidification Due to Increasing Atmospheric Carbon Dioxide. Policy document 12/05. Royal Society.

53. Santos, I. R., Glud, R. N.,Maher, D., Erler, D., and Eyre, B. D. (2011). Diel coral reef acidification driven by porewater advection in permeable carbonate sands, heron island, great barrier reef. Geophysical Research Letters, 38(3).

54. Schneider, B. (2011). The CO2 system of the Baltic Sea : biogeochemical control and impact of anthropogenic CO2. In: Global change and Baltic coastal zones. Ed. by G. Schernewski, J. Hofstede and T. Neumann. Dordrecht: Springer Science+Business Media (Coastal research library): 33-49

55. SCOR2009 – Report of the Ocean Acidification and Oxygen Working Group, International Council for Science's Scientific Committee on Ocean Research (SCOR) Biological Observatories Workshop 2009.

56. Steinacher, M., Joos, F., Frölicher, T. L., Plattner, G.-K., and Doney, S. C. (2009). Imminent ocean acidification in the Arctic projected with the NCAR global coupled carbon cycle-climate model. Biogeosciences, 6(4), 515–533.

57. Striegl, R. G., Dornblaser, M. M., Aiken, G. R., Wickland, K. P., and Raymond, P. A. (2007). Carbon export and cycling by the Yukon, Tanana, and Porcupine rivers, Alaska, 2001–2005. Water Resources Research, 43(2).

58. Takahashi, T., Olafsson, J., Goddard, J. G., Chipman, D. W., and Sutherland, S. C. (1993). Seasonal variation of CO_2 and nutrients in the high-latitude surface oceans: A comparative study. Global Biogeochemical Cycles, 7.

59. Takahashi, T., et al. (2002). Global sea-air CO_2 flux based on climatological surface ocean pCO_2, and seasonal biological and temperature effects. Deep-Sea Research II, 49, 1601–1622.

60. Taylor, D., (2015), From "Dilute and Disperse" to "Recycle & Reuse" – Changes in Attitude and Practice of Effluent Management. Still Only One Earth: Progress in the 40 Years Since the First UN Conference on the Environment, 2015, 253-280 DOI:10.1039/9781782622178-00253

61. Thomas, H., Bozec, Y., Elkalay, K., and Baar, H. (2004). Enhanced open ocean storage of CO_2 from shelf sea pumping. Science, 304.

62. Thomas, H., et al. (2005). The carbon budget of the North Sea. Biogeosciences, 2, 87–96.

63. Thomas, H., et al. (2009) Enhanced ocean carbon storage from anaerobic alkalinity generation in coastal sediments, Biogeosciences, 6, 267-274, doi:10.5194/bg-6-267-2009, 2009.

64. UBA2014. Auswirkungen von Abgasnachbehandlungsanlagen (Scrubbern) auf die Umweltsituation in Häfen und Küstengewässern, TEXTE 83/2014, Bremen: Umweltbundesamt (UBA).

65. Ülpre, H., & I. Eames, 2014 Environmental policy constraints for acidic exhaust gas scrubber discharges from ships. Marine Pollution Bulletin 88 (2014) 292–301

66. Wesslander K., A. Omstedt, B. Schneider, (2010) Inter-annual and seasonal variations in the air–sea CO_2 balance in the central Baltic Sea and the Kattegat, Continental Shelf Research, Volume 30, Pages 1511-1521, ISSN 0278-4343, http://dx.doi.org/10.1016/j.csr.2010.05.014.

67. Wood, I.R., R.G. Bell, D.L. Wilkinson, 1993 Ocean disposal of waste water. World Scientific Publishing, Singapore.

52

List of abbreviations and definitions

atm: Atmosphere (unit of pressure)

CDO: Climate Data Operators

CO2:   Carbon dioxide

DWT: Deadweight tonnage

DIC: Dissolved Inorganic Carbon

EGCS: Exhaust Gas Cleaning Systems

EEA: European Environment Agency

EGR: Exhaust Gas Recirculation

EMSA: European Maritime Safety Agency

EMEP: European Monitoring and Evaluation Programme

ENTEC: Entec, UK Limited

EPA: Environmental Protection Agency

EQS: Environmental Quality Standards

ERSEM: European Regional Seas Ecosystem Model

ESSF: European Sustainable Shipping Forum

FABM: Framework for Aquatic Biogeochemical Models

GESAMP: Joint Group of Experts for Scientific Aspects of the Marine Environmental Protection

GETM: General Estuarine Ocean Model

GOTM: General Ocean Turbulence Model

HFO: Heavy Fuel Oil

IMO: International Maritime Organisation

JRC: Joint Research Centre

LNG: Liquefied Natural Gas

MARPOL: International Convention for the Prevention of Pollution from Ships

MGO: Marine Gas Oil

MSFD: Marine Strategy Framework Directive

NABU: Naturschutzbund Deutschland

NCO: netCDF Operators

NO2:   Nitrogen dioxide (Nitrite)

NO3:   Nitrate

NOx: Comprising N2O, NO2 and NO3

Ω: Saturation state (for a mineral)

PAH: Polycyclic Aromatic Hydrocarbon

PCB: Polychlorinated Biphenyl

pCO2:   CO2 partial pressure

R:	Programming language and software environment for statistical computing
SECA:	SOx Emission Control Area
SO2:	Sulphur dioxide (Sulphite)
SO3:	Sulphate
SOx:	Comprising SO2 and SO3
SWS:	Sea Water Scrubber
TA:	Total Alkalinity
UNCLOS:	United Nations Convention on the Law of the Sea
WFD:	Water Framework Directive

List of tables

List of figures

How to obtain EU publications

Our publications are available from EU Bookshop (http://bookshop.europa.eu),
where you can place an order with the sales agent of your choice.

The Publications Office has a worldwide network of sales agents.
You can obtain their contact details by sending a fax to (352) 29 29-42758.

JRC Mission

As the Commission's
in-house science service,
the Joint Research Centre's
mission is to provide EU
policies with independent,
evidence-based scientific
and technical support
throughout the whole
policy cycle.

Working in close
cooperation with policy
Directorates-General,
the JRC addresses key
societal challenges while
stimulating innovation
through developing
new methods, tools
and standards, and sharing
its know-how with
the Member States,
the scientific community
and international partners.

Serving society
Stimulating innovation
Supporting legislation

Publications Office