Potential impact of wash water effluents from scrubbers on water acidification in the southern North Sea

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Definitions and acronyms

CAMS: Copernicus Atmosphere Monitoring Service
CEIP: Centre on Emission Inventories and Projections
COHERENS: COupled Hydrodynamical Ecological model for REgioNal Shelf seas; Luyten (2011)
DIC: Dissolved Inorganic Carbon
GT: Gross Tonnage
EDGAR: Emissions Database for Global Atmospheric Research
EMEP: European Monitoring and Evaluation Programme
FMI: Finish Meteorological Institute
HFO: Heavy Fuel Oil
IMO: International Maritime Organisation
LNG: Liquefied Natural Gas
LSFO: Low Sulphur Fuel Oil taken here as a fuel with a maximum sulphur content of 0.1% m/m (mass by mass)
NOx: Nitrogen oxides
Open-mode scrubbers: include open-loop scrubbers and hybrid scrubbers set in open-loop mode
SECA: Sulphur Emission Control Area
SOx: Sulphur Oxides, including SO, SO_2, SO_3, S_2O, S_60_2, S_2O_2
TA: Total Alkalinity

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Note from the authors during the COVID-19 outbreak

After this study was completed, the COVID-19 started to re-shape the year 2020 in an unforeseen way. The ship traffic density estimation for the year 2020 on which our scenarios were based to estimate the quantity of SOx emitted to the atmosphere and discharged into the water via exhaust gas cleaning system will likely be different than expected. **Nevertheless, this study still brings some very useful information on how the use of open-loop and hybrid (set in open-mode) scrubbers can contribute to the acidification of the southern North Sea, in a business as usual situation.**

1 Summary

Sulphur Oxides (SOx) in atmospheric ship emissions resulting from the burning of fuel with high sulphur content are known to be harmful to human and ecosystem health. Since January 1st 2020, the International Maritime Organisation (IMO) lowered the previous limit for sulphur content in ship fuel from 3.5% m/m (mass by mass) to 0.50%. In the emission control areas (SECAs), the limit for the sulphur content had been set to 1.0% in 2010 and is kept below 0.1% since 2015.

To comply with these limits, ship operators and owners can switch to fuel oil with lower sulphur content (LSFO). Alternatively, they can continue to burn fuel with high sulphur content by using technical means such as exhaust gas cleaning systems (or *scrubbers*) that reduce the atmospheric SOx emissions to a level equivalent to the required fuel oil sulphur limit. Scrubbers use sea water as cleaning media to remove SOx from the air emissions. There are three main categories of scrubbers: (1) the *open-loop* scrubbers that continuously discharge their wash water effluent, (2) the *closed-loop* scrubbers that treat the wash water before it is discharged, and (3) the *hybrid* scrubbers that can switch from open to closed modes. Scrubbers transform the air pollution into direct marine discharge. As hybrid scrubbers are more likely to discharge their sulphur waste into sea water rather than using land infrastructures, they are hereafter taken as open-loop ones.

The effect of SOx contribution from ship on sea water pH is assessed for the English Channel and the southern North Sea by means of a marine biogeochemical model that includes a detailed description of the carbonate chemistry. This model allows testing different scenarios of SOx contribution resulting from the maritime traffic. To this end, realistic scenarios with ship traffic density estimated for the years 2019, 2020 and 2030, assuming a year-to-year ship traffic increase of 3.5% and several SOx pollution reduction strategies have been tested. An additional model simulation with null SOx contribution from the shipping sector is used as a reference level to comparatively assess the impact of each scenario on the sea water pH.

Model results show a pH decrease of 0.004 units over the whole domain in case of a 2019-like ship traffic density with 15% of the fleet (in Gross Tonnage) using open-loop and hybrid scrubber systems. For future scenarios, assuming that 35% of the fleet is equipped with open-loop and hybrid scrubbers, the pH is estimated to decrease by 0.008 to 0.010 units in average over the whole domain. The magnitude of pH changes is not evenly distributed through space. According to the model results, the largest pH changes would occur in areas of high traffic density, such as along the Belgian and Dutch coasts and in the vicinity of large harbours such as Rotterdam.

Ocean acidification rate attributed to climate change is estimated at 0.0017-0.0027 pH units per year. In comparison, the total pH decrease owing to the use of open-loop scrubbers would be equivalent to 2 to 4 years of climate change acidification on average over the whole domain, and to 10 to 50 years, in more local areas. The cumulative impact of ocean acidification due to climate change and to maritime traffic should therefore be considered in ecosystem assessment studies.

2 Introduction

Sulphur oxides (SOx) emissions in the atmosphere from burning fossil fuel are known to have negative impact on both the environment and human health (*e.g.* Barregard et al., 2019). They cause respiratory symptoms and lung disease leading to premature deaths. They increase among other things the risk for stroke, asthma, cardiovascular disease, and lung cancer. They also lead to more acid rain which can harm the agriculture fields and forests, and contributes to the acidification of the oceans. Over the last decades, efforts have been made to lower the SOx atmospheric emissions resulting from burning of gas oils, heavy fuel oil in land-based applications as well as marine fuels.

Since January 1st 2020, the International Maritime Organization (IMO) has banned the use of high-sulphur heavy fuel oil (HFO) at a global scale by lowering the sulphur content limit of the fuel used on board of ship from 3.5% m/m (mass by mass) to 0.5% m/m. In the sulphur emission control areas (SECAs), the sulphur content limit of fuel has been set from 1.0% m/m in 2010 to 0.1% m/m in 2015. It now remains at 0.1% m/m. As an alternative to the use of compliant low sulphur fuel, the MARPOL Annex VI allows for the use of alternative fuel (*e.g.* LNG, methanol), onshore power supply, or other appropriate technological method that limits SOx atmospheric emissions to SOx that would be emitted using a sulphur-compliant fuel. This method includes the installation of exhaust gas cleaning systems, also known as *scrubbers*. So far, scrubbers have been economically more cost-effective than reducing the sulphur content in the fossil fuel, mainly due to the price difference between heavy and low sulphur fuel oils (Yaramenka et al., 2018). Depending on the type of scrubber, the wash water from the exhaust gas cleaning system is either collected on board (*closed-loop* scrubber) or discharded in the open sea (*open-loop* scrubber). *Hybrid* scrubbers can switch from open to closed modes. Open-loop scrubbers are more common than closed-loop ones because of the lower benefit-to-cost ratio due to higher operation and management cost of the latter (Yaramenka et al., 2018).

Despite the positive effect of the use of scrubbers to reduce the atmospheric pollution, questions have been raised on their potential impacts on the marine environment. Open-loop scrubber exhaust gas cleaning systems discharge wash waters directly at sea. These wash waters contain, among others, PAHs, nitrogen, heavy metals (*e.g.* nickel, lead and vanadium) and SOx. The use of scrubbers also allows ship operators to switch back from lighter to heavier fuels as long as the atmospheric content limitation does not exceed the limit allowed, potentially resulting in large amounts of SOx discharged at sea. The number of installed scrubbers highly depends on the oil market and could increase significantly in the coming decades (Kjølholt et al., 2012) along with an increase in maritime traffic and compliance with emissions regulations.

When the wash water from open-loop scrubbers is thrown back into the sea, the discharged SOx are neutralized by the sea water alkalinity. This contributes to the acidification of the ocean and affects the marine carbonate cycle. This process adds up to the ongoing ocean acidification resulting from the increase in atmospheric CO_2 injections to the sea related to the increase in CO_2 concentration in the atmosphere. Negative effects of ocean acidification on coral reefs and limestone-requiring organisms have already been observed and are well known. Scientific studies have already highlighted the negative effects of ocean acidification on some species of clams (Van Colen et al., 2018), oysters (Lemasson et al., 2018), prawns (Dupont et al., 2014) and even fish (Velez et al., 2019).

Several modelling studies have investigated the effect of sulphur discharges into the sea. They showed no significant impact on acidification but, generally, they assessed spatially averaged regional impacts and did not specifically consider the potential impact on smaller coastal areas and/or in areas where shipping lanes are concentrated (*e.g.* Kjølholt et al., 2012 and other references in Stips et al., 2016). In a recent modelling study at the North Sea scale, Stips et al. (2016) found critical regions with high ship traffic intensity (*e.g.* in the vicinity of Rotterdam) where the contribution of SOx to sea water acidification is about 20 times larger than the North Sea mean value. These critical regions indicate potential problems related to the water quality in ports, estuaries and coastal waters that are addressed, among others, by the EU Water Framework Directive (WFD).

Yaramenka et al. (2018) estimated the marine environmental cost in a scenario where scrubbers were installed on board of two operating vessels four times higher than in a scenario where these two vessels were running on light sulphur content oil. Yaramenka et al. (2018) recommended using a modelling approach to study a large area such as the North Sea. Stips et al. (2016) used a marine model with 10 km x 10 km spatial resolution and recommended to further investigate the pH changes with a higher resolution model, using a well calibrated and validated carbonate model over the investigated region and to include the impact of primary productivity on the carbonate cycle.

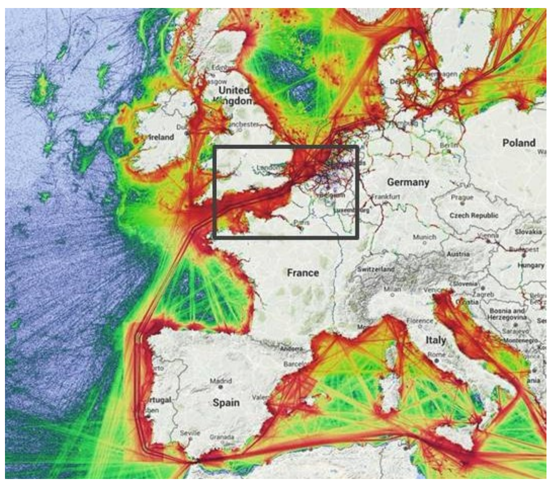

Figure 1: Density map of marine traffic showing the main traffic routes. The black frame represents the marine model domain. The figure is adapted from an image available at marinetraffic.com.

In this study, a marine biogeochemical model was used to simulate (1) the 3D water mass transport, (2) the marine biogeochemical processes involving nutrients, phytoplankton, bacteria and micro zooplankton, and (3) the marine pH changes. The studied domain covers the English Channel and the southern North Sea (*cfr.* Figure 1). Scenarios with SOx contributions from shipping have been designed based on the CEIP (Centre on Emission Inventories and Projections) emission dataset (Crippa et al., 2018) with an expected traffic density for 3 different periods (2019, 2020 and 2030) and emission reduction strategies involving SOx discharge from scrubbers into the sea. A *Reference* scenario where the SOx contribution from maritime traffic is artificially set zero is used for comparison.

3 Project flow

The aim of this investigation is to assess the potential impact of the wash waters released from open-loop scrubber ship installations on the acidification of the southern North Sea. The project flow is summarised in **Error! Not a valid bookmark self-reference.** and the project tasks are described hereafter.

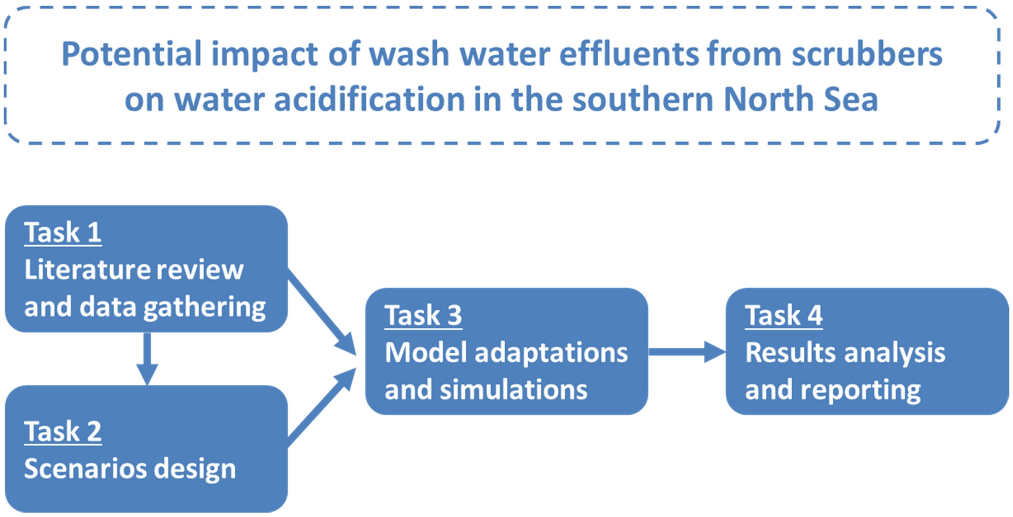

Figure 2: Overview of the workflow followed in this study.

Literature review and data gathering (Task 1)

A literature review on existing studies addressing the potential impact of sulphur ship emissions on ocean acidification is done. Several available data sets including atmospheric, riverine and oceanic information (*e.g.* SOx and nitrogen oxides depositions, shipping traffic road maps and densities, composition of scrubbers wash waters, locations of scrubber wash water release, river input of dissolved inorganic carbon and total alkalinity) are gathered to force the model and/or to build the sulphur pollution scenarios. Datasets that are selected for use in this study are described in Section 0.

Scenarios design (Task 2)

Several scenarios are defined based on available data and information gathered in Task 1 to address the effect of sulphur pollution from ship scrubbers on ocean acidification. First, a reference scenario with no sulphur pollution from ships is defined. Then scenarios including the sulphur atmospheric emissions and marine discharges from ships are designed based on (1) the CEIP emission datasets for the shipping sector, (2) estimated ship traffic density and (3) sulphur reduction strategies. Scenarios are described in Section 4.3.

Model adaptations and simulations (Task 3)

The 3D marine biogeochemical MIRO&CO model (Dulière et al., 2019) is adapted to include the validated carbonate chemistry system based on Gypens et al. (2011). Model boundary conditions (oceanic, riverine and atmospheric) relevant to acidification processes are implemented in the model. The model output is adapted to provide estimations of pH, dissolved inorganic carbon and total alkalinity information. The model is tested carefully and simulations for different SOx pollution scenarios are carried out.

Results analysis and reporting (Task 4)

The results from the model simulations of Task 3 are analysed and used to answer the research question. An estimation of the pH change in the marine environment as a result of the use of scrubber installations to reduce the sulphur atmospheric ship emissions is provided.

4 Methodology

4.1 General description

In this study, the sea water acidity is addressed through its pH. The pH scale is a logarithmic scale. It inversely indicates the concentration of hydrogen ions in the sea water. As the concentration of hydrogen ions increases, the ocean becomes more acid and its pH decreases. The pH scale is the most common scale to assess the acidity of a solution and to assess the impact of the sea water acidity on marine organisms.

A 3D marine modelling approach has been used to estimate the pH in sea water for different sulphur atmospheric emission reduction strategies. This approach is complementary to in-situ measurements and laboratory approaches because it is able to provide an estimation of the pH change over a large domain (*cfr.* Figure 1). The model spatial resolution (~5km) is higher than the spatial resolution of the model set up used in Stips et al. (2016; ~10 km). The 3D modelling tool used here is able to simulate the characteristics and transport of the water masses and has been adapted to include the carbonate chemistry model. It is coupled to a marine biogeochemical model (*e.g.* nutrients, phytoplankton, micro-zooplankton and bacteria) and simulates the effect of biology on the sea water pH, via the total alkalinity and the dissolved inorganic carbon concentration.

Several scenarios of marine SOx contribution from the shipping sector have been designed based on different SOx emission reduction strategies. They include a scenario with no SOx contribution from ships, and scenarios with SOx contributions resulting from different combinations of maritime traffic SOx reduction strategies. Model simulations are carried out for each scenario to estimate the sea water pH over a period of one year. The comparison between the model results for the SOx scenarios with the model results for the *Reference* one (*i.e.* with no SOx pollution from maritime traffic) allows estimating the corresponding changes in sea water pH according to the different scenarios and therefore, to the different SOx reduction strategies.

4.2 Marine biogeochemical model

The 3D marine biogeochemical model MIRO&CO as described in Dulière et al. (2019) is used in this study. MIRO&CO includes the 3D ocean circulation model COHERENS (Luyten, 2011) and the biogeochemical model MIRO (Lancelot et al., 2005). For the purpose of this study, the carbonate chemistry module as in Gypens et al. (2011) has been implemented in MIRO&CO.

4.2.1 Hydrodynamic model

A hydrodynamic model describes the water circulation over a defined area and is based on the conservation of mass momentum and energy. Written down it results in a set of 5 differential equations that are able to describe the flow in any closed system. In this study, the hydrodynamic model COHERENS (COupled Hydrodynamical Ecological model for REgioNal Shelf seas; Luyten, 2011) is used. COHERENS is designed for aquatic biogeochemical and environmental applications. It is able to provide 3D estimations of the marine state variables such as sea temperature, salinity or current. The development of COHERENS is a joint collaboration of scientists at national and international levels, led by researchers at Royal Belgian Institute of Natural Sciences (RBINS). COHERENS is available to the scientific community as a free and well-documented open source code (http://odnature.naturalsciences.be/coherens/).

4.2.2 Biogeochemical model

The biogeochemical model (MIRO) has been specifically developed for *Phaeocystis*-dominated ecosystems such as the southern North Sea (Lancelot et al., 2005). For clarity purpose, a simplified schematic representation of the model is provided in Figure 3. A more detailed schematic representation can be found in Lancelot et al. (2005). Five modules are included to describe the dynamics of: (1) the phytoplankton (*i.e.* diatoms, autotrophic nanoflagellates and *Phaeocystis* colonies), (2) the zooplankton (*i.e.* microzooplankton and copepods), (3) the bacteria, (4) dissolved and particulate organic matter degradation, and (5) the nutrients (*i.e.* nitrate, ammonium, phosphate and dissolved silica) regeneration in the water column and the sediment. A 2D benthic layer allows exchanges between the bottom water and the sediment layer through sedimentation, remineralization and denitrification processes.

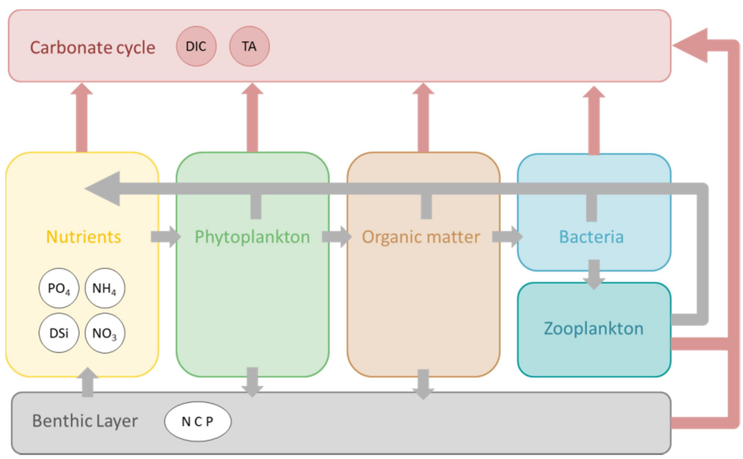

Figure 3: Simplified illustration of the biogeochemical model structure including the carbonate chemistry module. DIC stands for Dissolved Inorganic Carbon; TA for Total Alkalinity; N for Nitrogen; C for Carbone; P for Phosphorus and DSi for Dissolved Silica. The grey arrows represent the biogeochemical processes that link the modules. The red arrows represent the one-way coupling between the carbonate cycle module and the rest of the biogeochemical model.

More particularly, each module describes the processes that drive the dynamics of specific items. The gray arrows in Figure 3 indicate the flow of biogeochemical processes between the modules. To give a hint on how the model works, let's zoom on the phytoplankton module. It includes three phytoplankton groups and simulates processes such as growth, photosynthesis, respiration or excretion for each phytoplankton group. To perform, the phytoplankton module requires information on nutrients availability that is estimated by the nutrient module. In turn, as the phytoplankton assimilates nutrients, the nutrients are taken from the nutrients module and their availability changes. When the phytoplankton produces organic matter, it is passed on to the organic matter module where its dynamics will be addressed by the model considering, among others, the degradation process of different classes of biodegradability for dissolved and particulate organic matter. The biogeochemical processes included in the model have mainly been described and parametrized based on in-situ measurements and lab experiments. For clarity purpose, only a simplified description of the model is here provided.

4.2.3 Carbonate chemistry module

For the purpose of this study, the sea water carbonate chemistry module described in Gypens et al. (2011) has been adapted and implemented into the marine biogeochemical model. This module describes the carbonate system in the water column and the CO_2 exchanges at the air-sea interface.

It includes two additional model state variables: the Total Alkalinity (TA) and the Dissolved Inorganic Carbon (DIC).

The coupling between the carbonate chemistry and the biogeochemical modules is a one-way coupling (*cfr.* red arrows in Figure 3). This means that calculations and model state variables in the biogeochemical model affect the calculations and state variables in the carbonate chemistry module. No feedback from the carbonate chemistry module to the biogeochemical one has been implemented so far.

Total alkalinity

The TA can be defined as the number of moles of hydrogen (H) equivalent to the excess of proton acceptors over proton donors in a sample of 1 kg (Zeebe and Dieter, 2001). It represents the water capacity to resist changes to become more acid. Changes in oceanic TA are related to nitrogen assimilation by plants through their growth process. The NO_3^- uptake by plants is balanced by OH^- production so that alkalinity increases while the NH_4^+ uptake is balanced by the production of H^+ which results in an alkalinity decrease. The TA also changes with the release of dissolved inorganic nitrogen (NO_3^- and NH_4^+) from organic compounds via the remineralization process mostly from the excretion of microzooplankton, copepods and bacteria. The TA does not change according to CO_2 changes (*e.g*. due to CO_2 transfer at the air-sea interface or due to CO_2 plant uptake). The seabed benthic layer contributes to changes in sea water TA through nutrient recycling.

Dissolved Inorganic Carbon

The DIC decreases with the carbon uptake by the phytoplankton through the photosynthesis and increases with the carbon release through the phytoplankton respiration. Excretion of bacteria, microzooplankton and copepods further contribute to increase the DIC. The degradation of organic matter in the seabed benthic layer also indirectly contributes to changes in the sea water DIC.

pH

The sea water pH is calculated from the speciation of the carbonate system from DIC and TA, using carbonic acid dissociation constant given by Dickson and Millero (1987), the boric acid dissociation constant from Dickson (1990) and the CO_2 solubility coefficient as in Weiss (1974). Sea surface salinity and temperature are provided by the marine model. The air-sea CO_2 flux is calculated from the gradient of the partial CO_2 pressure across the air-sea interface and the gas transfer velocity parametrization is a function of the wind speed (Nightingale et al., 2000). The partial CO_2 pressure in the atmosphere is taken equal to 410 ppm for all model simulations. This is representative of the averaged partial CO_2 pressure in 2019 (https://www.co2.earth).

4.2.4 Model set up

The model has been set up for the region between 48.5°N-4°W and 52.5°N-5°E to cover the English Channel and the Southern Bight of the North Sea (Figure 1). The model grid has a horizontal resolution of about 5 km by 5 km and 5 vertical sigma coordinate layers.

A limitation of the hydrodynamic modeling approach is that it is only valid for a closed system. The domain of study here is not fully closed so information is needed at the different boundaries. This information typically consists of a bathymetry, river flow information, wind data and information at the open sea boundaries of the domain. Boundary conditions may vary from one year to another. To allow identifying the pH change in relation to the SOx contribution scenarios rather than in relation to the atmospheric, hydrodynamic or riverine conditions, the latter are kept identical for all scenarios. For consistency, information at the boundaries was all taken for year 2010. The choice of the year was limited by the availability of the river information at the time of the study.

At the river mouths, (bi)-monthly dissolved (NO_3, NH_4 , PO_4 , DSi) and particulate (Norg, Porg) nutrient discharges from observations gathered from national databases (Vlaamse Milieumaatschappij (VMM)-Flanders, Environment Agency (EA)-UK, Rijkswaterstaat-NL, Cellule anti-pollution DDE-FR, Agence de l'Eau Artois-Picardie-FR) have been imposed. DIC and TA at the river boundaries were estimated from averaged available concentrations for the Thames, Seine and Scheldt rivers (Gypens et al., 2011). PH, DIC and TA of the river water are taken as constant for all SOx contribution scenarios. Contributions from SOx reduction strategies from inland navigation are therefore not included in this study.

6-hourly atmospheric boundary conditions including fields of wind, atmospheric pressure, precipitation rate, cloud cover, specific humidity and air temperature were provided by the UK Met Office. Monthly atmospheric depositions of nitrogen from the "European Monitoring and Evaluation Program" (EMEP) were used. A 2D implementation of COHERENS was used to provide water currents and sea surface elevation at the western and northern open sea boundaries.

Initial conditions for physical and biological variables have been generated from a 10-year model simulation (1999-2010; for constituency with the available boundary information). For each scenario, and after a spin up of 2 years, the model simulations were carried out over a whole year. For more information on the model implementation and boundary conditions, please refer to Dulière et al. (2019).

4.3 SOx scenarios

As mentioned in the introduction, several atmospheric emission reduction strategies are possible to comply with the new sulphur regulations:

- Burning LSFO with 0.1% sulphur content limit.
- Using open-loop scrubber system (when burning high sulphur HFO), resulting in SOx reduced atmospheric emissions and direct wash water discharges.
- Using hybrid scrubber systems, resulting in reduced SOx atmospheric emissions and likely also in wash water discharges. For convenience, ships equipped with hybrid scrubbers are here considered as part of the fleet equipped with open-loop scrubbers since they are likely to discharge the wash water effluents at sea rather than in land dedicated structures.
- Using closed-loop scrubber systems. As they remain a minor portion of the fleet, they are not considered in this study.
- Burning fuels with low or zero sulphur (*i.e.* liquefied natural gas or biofuels; not included in this study).

In 2014, the sulphur content limit of 1.0% was still in force and very few ships were equipped with open-loop scrubbers. Therefore, 2014 was chosen as a baseline to build the SOx scenarios, assuming that 100% of the fleet was burning fuel with the 1.0% sulphur content limit. The 2014 geographical location and amount of SOx emissions from the shipping are provided by the Centre on Emission Inventories and Projections (CEIP) on a 0.1°x0.1° lat-lon resolution grid (Figure 4; https://www.ceip.at/new_emep-grid/01_grid_data). CEIP provides an gridded estimation of the emissions from international shipping based on the Copernicus Atmosphere Monitoring Service (CAMS) global shipping emission dataset (CAMS-GLOB-SHIP; Granier et al., 2019) produced by the Finish Meteorological Institute (FMI). CAMS Emissions from ships are based on (1) the Ship Traffic Emission Assessment Model (STEAM; Jalkanen et al., 2016; Johansson et al., 2017), (2) global and regional datasets based on realistic vessel traffic, and (3) technical description of the global fleet. CEIP provides several datasets with annual world air emissions of SOx by sectors including the shipping sector (Cippra et al., 2018). Since the focus of this study is on the impact of SOx emissions by shipping, SOx air emissions from the other sectors are not included in this study.

For each scenario, the contribution from the different SOx emission reduction strategies is estimated based on the following assumptions:

- Ships running on LSFO reduced their SOx atmospheric emissions by a factor of 10 after switching from fuel with a 1.0% sulphur content limit in 2014 to 0.1% after 2015, in the SECA including the North Sea and the English Channel.
- Ships newly equipped with open-mode (open-loop or hybrid in open-loop mode) scrubbers are able to switch back from 1.0% sulphur content fuel to 3.5% sulphur content fuel. They contribute to the SOx marine pollution via their atmospheric emissions and direct wash water discharges. Their total SOx contribution to the sea can be taken as equivalent to the SOx contribution from a similar ship with no scrubber installation (so only atmospheric emissions) and that would burn 3.5% sulphur content limit oil. In comparison to 2014, it is here assumed that ships equipped with open-loop scrubbers have increased the total amount of SOx released to the sea (by air and water discharge) by a factor of 3.5. According to Kjølholt et al. (2012), the maximum sulphur SOx removal in fuel for different scrubber types is between 3 and 5%.
- Both SOx atmospheric emissions and SOx wash water discharges enter the water in the vicinity of the ship track. Note that the model domain has a 5 km x 5 km horizontal resolution. This assumption is later discussed in the report.

SOx contributions from ships are then calculated for each scenario based on (1) the CEIP shipping emission dataset for 2014, (2) an estimation of the ship traffic density increase, (3) an estimation of the ratio of ships equipped with open-mode scrubbers, and (4) the above mentioned assumptions on the SOx reduction strategies. The estimation of the total SOx discharges from shipping can then be summarized as follows:

$$SOx = SOx_{\_2014} \times \Delta traffic \times [n_{LSFO} \times red_{LSFO} + n_{OPEN} \times a_{OPEN}]$$

Where $SOx_{\_2014}$ are the shipping SOx emissions estimated for the baseline year (2014). *Δtraffic* is the maritime traffic density increase between 2014 and the year of the scenario. *Δtraffic* is computed assuming a year-to-year maritime traffic increase of 3.5% in the Greater North Sea (Cotteleer, 2014). n_{LSFO} is the ratio of the fleet that burns LSFO. n_{OPEN} is the ratio of the fleet that is equipped with open-mode (including open-loop and hybrid) scrubbers. The sum of these 2 parameters is equal to 1. red_{LSFO} is the relative decrease in the sulphur atmospheric emission between 2014 and the scenario year for the ship using sulfphur-compliant fuel. red_{LSFO} is set according to the regulations in the maximum allowed sulphur content from 1.0% in 2014 to 0.1% after 2015 over the study area. a_{OPEN}

is the relative increase of sulphur content in the fuel burned on board of ship using open-loop scrubbers compared to fuel with a sulphur content limit of 0.1% as in 2014. It is set to 3.5.

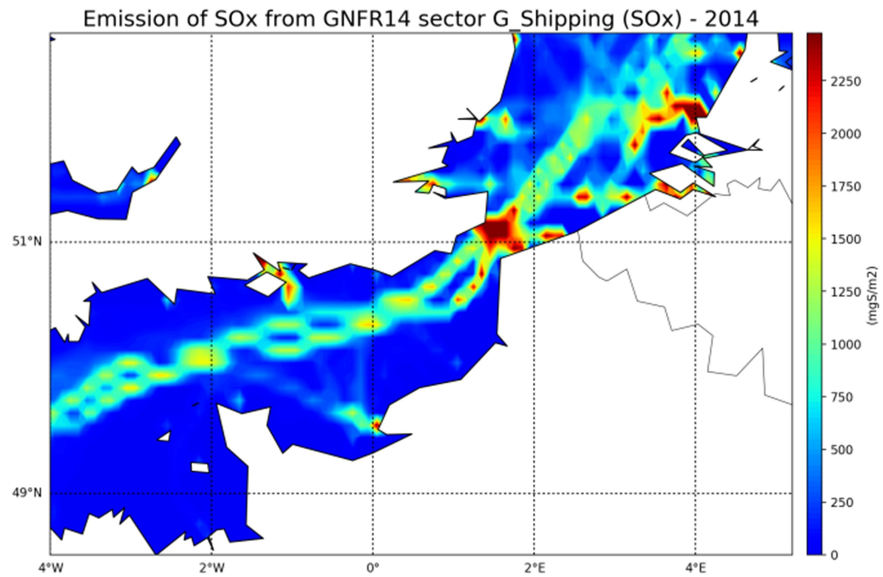

Figure 4: SOx emissions from shipping available from the CEIP gridded dataset for the year 2014. Units are mg SO2 equivalent per m2 and the grid resolution is of 0.1°x0.1°.

In November 2019, about 15% of the global fleet (in Gross Tonnage, GT) was recorded as equipped with scrubbers, mostly open-loop and hybrid ones. This number could reach 35% of the global fleet by 2020. The six following scenarios have been defined:

1. A **Reference** scenario where SOx contribution from maritime traffic is artificially set to zero.
2. A ***2019_15%*** scenario that represents the maritime traffic situation in 2019 with 15% of the fleet (in GT) equipped with open-mode (including open-loop and hybrid) scrubbers, the other 85% of the fleet using LSFO with 0.1% sulphur content limit.
3. A ***2020_35%*** scenario based on an estimation of the expected marine traffic density for 2020 with 35% of the fleet (in GT) using open-loop scrubbers (information from the Clarksons Worldfleet Register of November 2019) and the other 65% of the fleet running on LSFO.
4. A ***2020-0%*** scenario that represents an estimation of the expected marine traffic density for 2020 with the whole fleet burning LSFO.
5. A ***2030_35%*** scenario that represents an estimation of the ship traffic density for 2030, assuming a 3.5% year-to-year traffic increase, and 35% of the fleet (in GT) equipped with open-mode (including open-loop and hybrid) scrubbers.
6. A ***2030-0%*** scenario that represents a 2030-like marine traffic density, assuming a 3.5% year-to-year traffic increase, and a ban on open-loop scrubbers. Ships are all running on LSFO.

Estimated SOx atmospheric emissions and water discharges are all included in the model at the sea water surface. When the SOx reach the sea water, it is directly neutralized by the sea water alkalinity (Winnes et al., 2018). When SO_2 dissolved in sea water, it creates sulphurous/sulphuric acid. This acid dissociates and the concentration of H^+ is increased which in turn, can decrease the sea water pH. Therefore, the SOx discharge from ship emissions is introduced in the model via the alkalinity model state variable as follows: 1 unit of SO_2 equivalent produces 2 units of H^+ which reduces the total alkalinity by 2 units as in Stips et al. (2016). Note that the NOx emissions are kept the same for all scenarios.

$SO_2(gas) \leftrightarrow SO_2(aq)$
$SO_2 + H_2O \leftrightarrow HSO_3^- + H^+$ (sulfurous acid)
$HSO_3^- + 1/2\ O_2 \rightarrow HSO_4^-$ (sulfuric acid)
$HSO_4^- \rightarrow SO_4^{2-} + H^+$ (sulfate)

Overall reaction
$SO_2 + H_2O + 1/2\ O_2 \rightarrow SO_4^{2-} + 2H^+$

Finally, atmospheric currents bringing land-based emissions and riverine discharges of nitrogen and sulphur can further contribute to the ocean acidification. In this study, the land-based emissions and the riverine input are kept constant for all scenarios to clearly assess the impact of shipping only. Note that land-based emissions of SOx were taken as null due to the lack of information on the deposition locations and the short timeframe of the study.

5 Results

5.1 SOx scenarios

Following the methodology described in Section 4.3, the SOx contribution from shipping activities to the sea water estimated for each scenario in comparison to the 2014 *reference* scenario is shown in Figure 5. For the scenario 2019_15% (with a 2019-traffic like density and 15% of the total fleet equipped with open-mode scrubbers), SOx contribution from shipping is equivalent to 72% of the 2014 one. For the other scenarios including 2020_35%, 2020_0%, 2030_35% and 2030_0%, SOx contribution from shipping is equivalent to 156%, 12%, 201% and 16% of the 2014 one, respectively. As shown in Figure 5, the SOx contribution is dominated by the ratio of open-mode scrubbers and to a lesser extent, by the increase in maritime traffic.

	Reference	~2019	~2020	~2020	~2030	~2030
% of open-mode scrubbers	No ship	15%	35%	0%	35%	0%
% of LSFO	No ship	85%	65%	100%	65%	100%
Traffic compared to 2014	No ship	118%	121%	121%	156%	156%
SOx contribution from traffic compared to 2014	-	72%	156%	12%	201%	16%

Figure 5: Summary of the scenarios with the estimated ratio of ships equipped with open-mode (open-loop and hybrid) scrubbers, ratio of ships burning sulphur-compliant LSFO, scenario traffic density in comparison to traffic density of 2014 and estimated shipping SOx contribution ratios between the year 2014 and the SOx scenarios (%). Contributions from ships equipped with open-mode (including open-loop and hybrid) scrubbers are shown in orange; contributions from ships burning sulphur-compliant LSFO are shown in grey. For visual reference, the rectangles with the dotted lines represent the SOx contribution from maritime traffic estimated from the CEIP dataset for the year 2014.

5.2 Model results

PH values for the southern part of the North Sea and the English Channel are estimated by the marine biogeochemical model for the different SOx scenarios described here above. Maps with the yearly averaged pH values are presented in Figure 6. The pH geographical patterns are similar for the *Reference* (where SOx contribution from maritime traffic is set to zero), *2020_0%* and *2030_0%* scenarios. On yearly average, pH values are mainly between 8.055 and 8.060 free scale units across the whole domain and above 8.060 up to more than 8.090 close to the Seine and Thames estuaries and along the Dutch and Belgian coasts.

The *2019_15%* scenario, and to a larger extend also the *2020_35%* and *2030_35%* scenarios, all show a clear reduction in the yearly pH across the whole domain. For the *2019_15%* scenario, the model estimates an averaged pH between 8.050 and 8.055 across the majority of the domain while for the *2020_35%* and *2030_35%* scenarios, the average pH drops to values between 8.040 and 8.055.

The detailed geographical distribution and magnitude of pH changes as a result of the SOx contribution from shipping are presented in Figure 7. Each panel of the Figure 7 presents the differences between the pH as estimated by the model for one specific SOx scenario in comparison to the pH estimated by the model for the *Reference* one. All pH differences are negative, pointing to the fact that on average, the SOx contribution by the maritime traffic leads to marine acidification. The geographical pattern of the main sources of SOx emission (*i.e.* the main shipping routes and major harbours) is clearly visible in the geographical distributions of pH changes for all the scenarios.

2019_15% scenario

For the *2019_15%* scenario that accounts for the 2019-like marine traffic density and 15% of the fleet (in GT) equipped with open-mode scrubber, the marine model estimates an averaged pH decrease by 0.001 to 0.005 in the English Channel and a decrease of 0.003 to 0.008 in the southern part of the North Sea. Along the Belgian and Dutch coasts, the pH decrease is larger and reaches values of 0.005 to 0.031.

2020_35% scenario

For the *2020_35%* scenario which is based on traffic density estimation for 2020, assuming that 35% of the fleet (in GT) is equipped with open-loop scrubbers, the pH decrease is estimated between 0.003 to 0.015 in the English Channel, with a larger decrease close to Southampton. PH decrease in the southern part of the North Sea is estimated from 0.008 to 0.015 in the more offshore waters. It reaches 0.020 close to Felixstowe, and 0.013 to 0.050 along the Belgian and Dutch coasts, respectively.

2020-0% scenario

For the same maritime traffic density as in the above-mentioned scenario but assuming that the fleet does not allow SOx water discharges from shipping, the pH decrease is much less significant, with estimated values between 0.001 and 0.003 over most of the domain, and up to 0.005 close to Rotterdam.

2030_35% scenario

For the *2030_35%* scenario, the marine ecological model estimates a pH reduction between 0.003 and 0.018 in the English Channel, and a larger reduction close to Southampton. In the southern part of the North Sea, the pH reduction is estimated between 0.010 and 0.020 in more offshore waters and down to 0.050 close to Felixstowe. PH decreases reach the value of 0.088 close to Rotterdam.

2030_0% scenario

The model estimation of the pH changes for scenario *2030-0%* is similar to the estimations for scenario *2020_0%* with slightly larger values due to the traffic density increase. The pH decrease is estimated to values between 0.001 and 0.005 over most of the domain and decrease values up to 0.008 close to Rotterdam.

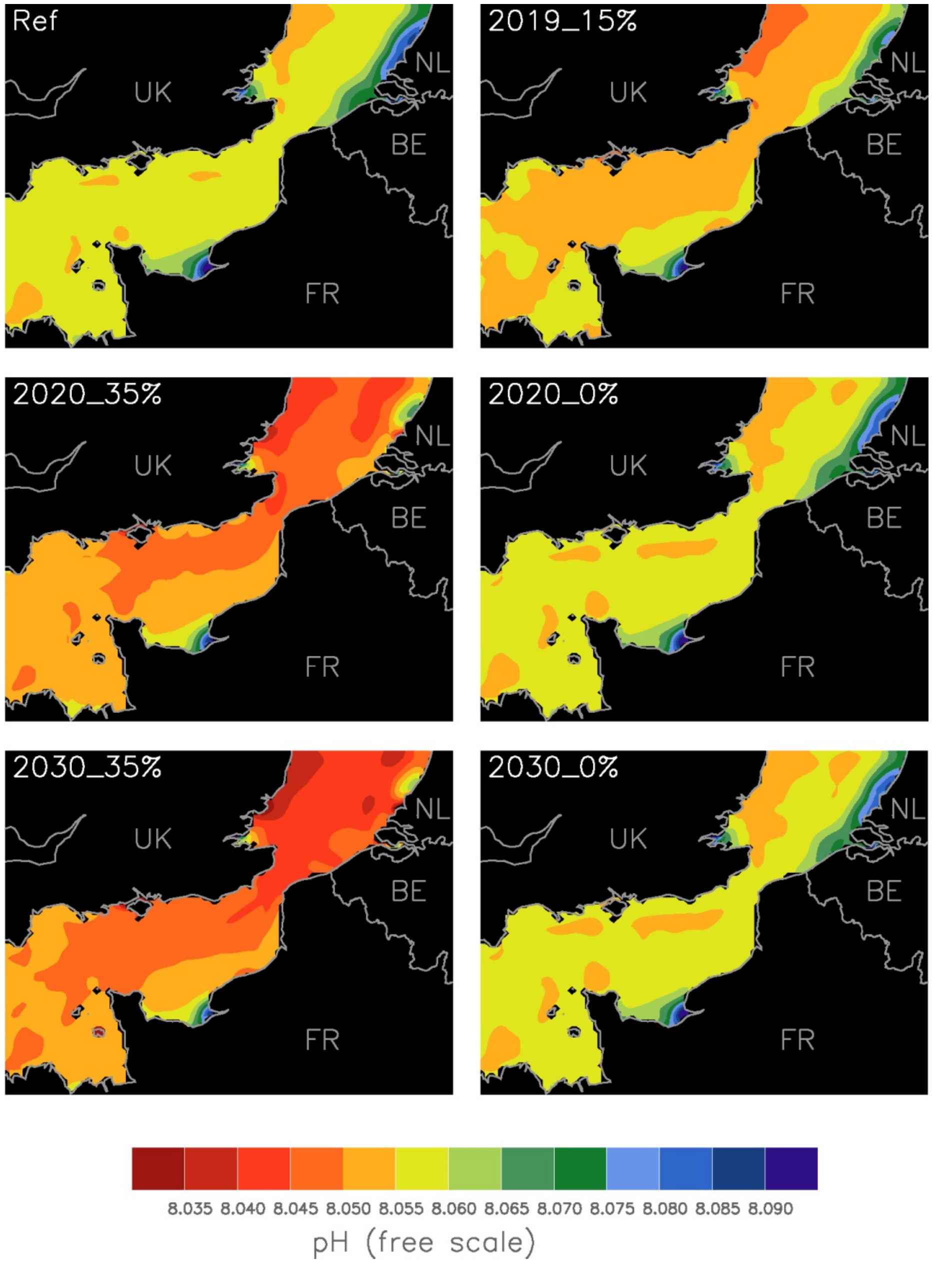

Figure 6: Maps of yearly averaged pH values as estimated by the marine ecological model (MIRO&CO) for different scenarios of SOx contribution from marine traffic: the *Reference* scenario with SOx contribution from maritime traffic artificially set to null (top left panel); the *2019_15%* scenario assuming a 2019-like maritime traffic density and 15% of the fleet (in GT) equipped with open-loop mode scrubbers (top right panel); *2020_35%* and *2020_0%* scenarios, assuming a maritime traffic density as expected for 2020, and 35% and 0% of the fleet equipped with open-loop mode scrubbers, respectively (middle row); *2030_35%* and *2030_0%* scenarios, assuming a maritime traffic density as foreseen for 2030 and, 35% and 0% of the fleet equipped with open-loop mode scrubbers (bottom row). Units are given in free scale.

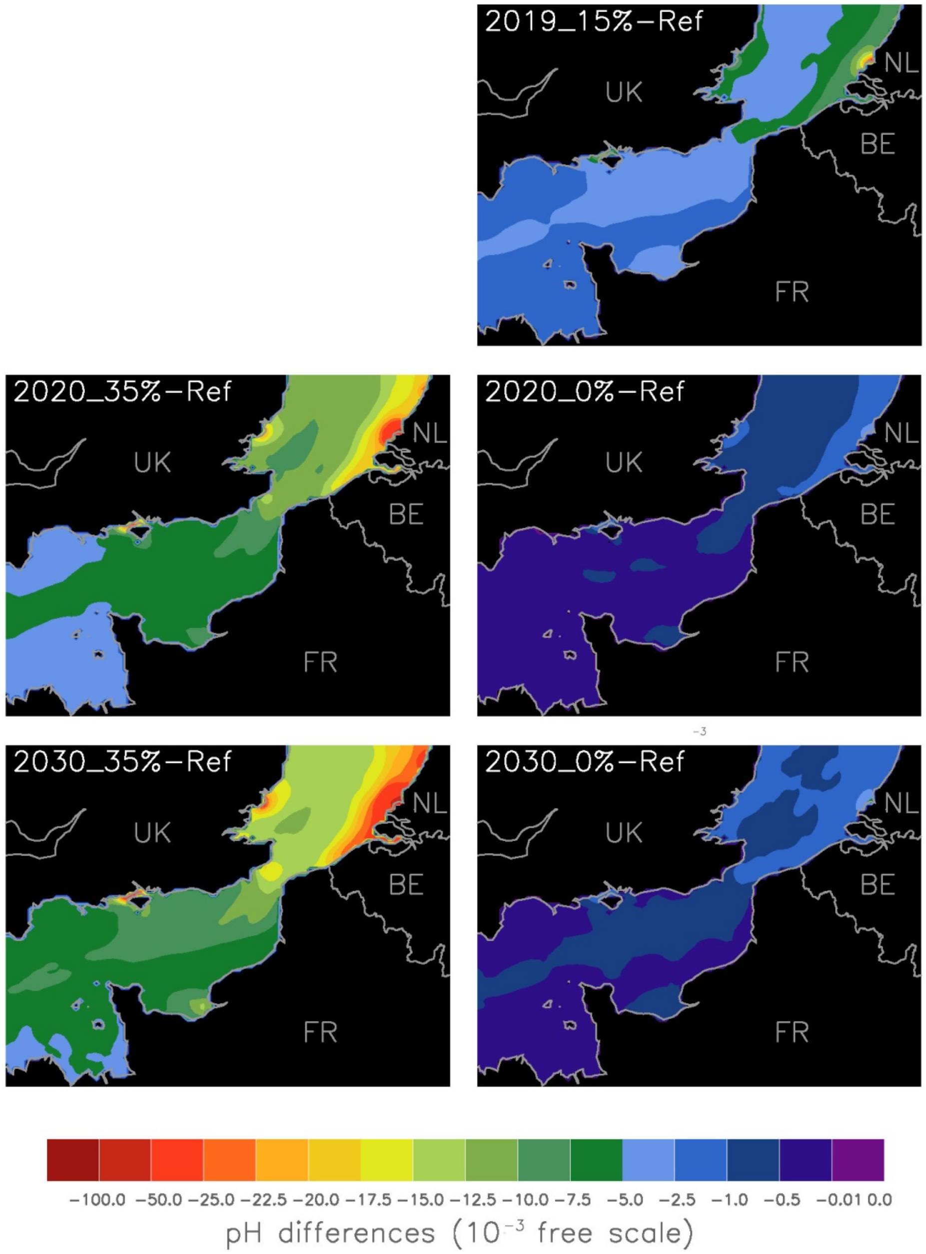

Figure 7: Maps of yearly averaged pH differences between pre-defined SOx marine traffic contribution scenarios and the *Reference* one for which the SOx contribution from maritime traffic is artificially set to null. PH values are provided by the marine ecological model (MIRO&CO) simulations. The top panel represents the pH changes for the *2019_15%* scenario, assuming 2019-like maritime traffic density and 15% of the fleet (in GT) equipped with open-loop mode scrubbers. The middle row represents the pH changes for the *2020* scenarios, assuming a maritime traffic density as expected for 2020 and 35% (left) and 0% (right) of the fleet equipped with open-loop mode scrubbers. The bottom row represents the pH changes for the 2030 scenarios, assuming a marine traffic density as foreseen for 2030, and 35% (left) and 0% (right) of the fleet equipped with open-loop mode scrubbers. Units are given in free scale.

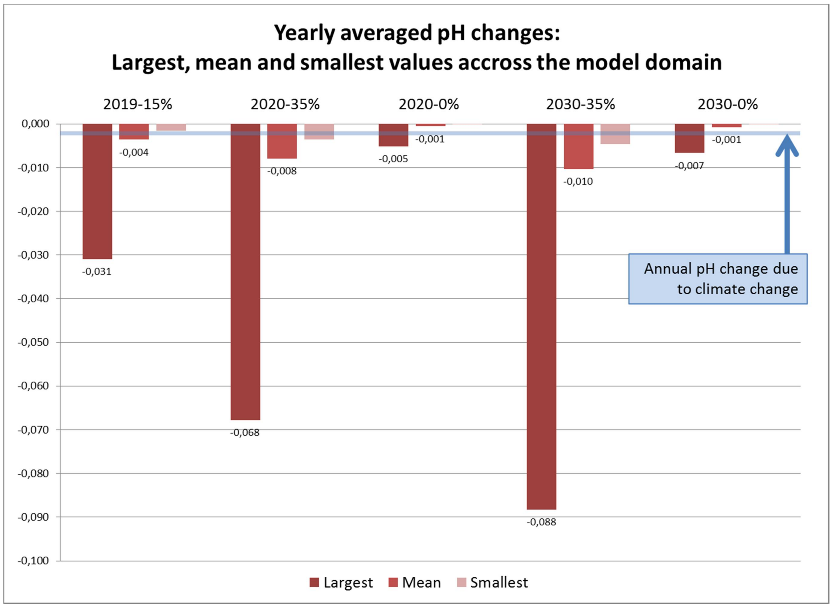

Figure 8: Largest, mean and smallest values computed from the yearly pH differences presented in Figure 7 for the different scenarios of SOx contribution from shipping. Yearly pH differences are computed based on model results by subtracting the yearly averaged pH values estimated for the *Reference* simulation, from the pH values estimated for each of the SOx scenario and averaged over the whole year (*i.e.* 2019, 2020 or 2030). For visual reference only, the annual rate of pH change attributed to climate change is given in light blue.

Largest, mean and smallest values from the geographical annual pH differences that are presented in Figure 7 are given in Figure 8. In comparison to the *Reference* scenario, the scenarios where the use of open-loop mode scrubbers are banned show a pH change of -0.001 on average over the whole domain with maximum changes of -0.005 and -0.007 in yearly average for the *2020_0%* and *2030_0%* scenarios, respectively. For the *2019_15%*, *2020_35%* and *2030_35%* scenarios that permit the use of open-loop mode scrubbers, the model estimates pH changes of -0.004, -0.008 and -0.010 on average over the year and over the whole model domain, with maximum changes in annual mean pH values of -0.031, -0.068 and -0.088, respectively.

6 Discussion

6.1 SOx scenarios uncertainties

The design of the SOx discharge scenarios relies on several hypotheses. The year 2014 was taken as a "background" year when all ships were assumed to burn 1.0% sulphur content compliant fuel. It is also assumed that the geographical pattern of the ship traffic density remained constant over the year and will remain constant in the future. Finally, it was assumed that SOx atmospheric emissions by shipping deposit at the sea surface in the vicinity of its source. Finally, a year-to-year ship traffic density increase rate of 3.5% has been used to estimate the maritime traffic density in 2020 and 2030. These assumptions could be later refined, for instance, as new emission datasets are available.

It was assumed that the ship sulphur reduction strategies are equally distributed among the ships. However, certain traffic lines can be more or less frequently used by ships equipped with open-loop mode scrubbers than others. This might further enhance the acidification in areas where a larger than average ratio of the fleet is equipped with open-loop mode scrubbers. Inversely, the acidification estimation might be lower where a smaller than average ratio of the fleet is equipped with open-loop scrubbers or where hybrid scrubbers are set in closed-loop mode.

The ratios of ships equipped with scrubbers (taken as 15% and 35% for 2019 and future scenarios, respectively), are based on global average estimations and could actually be even larger for the North Sea area. These numbers could later be refined as they strongly impact the quantity of SOx that is discharged at sea.

Model results strongly depend on the CAMS-GLOB-SHIP SOx emission dataset. This dataset is a state-of-the-art, comprehensive and reliable dataset that provides a full geographical gridded distribution of shipping emissions (Granier et al., 2019; Jalkanen et al., 2016). It has been generated using the Ship Traffic Emission Assessment Model (STEAM) that estimates the SOx emission from calculation of ship fuel consumption and Automatic Identification System (AIS) data positions. The ship fuel consumption is calculated based on available ship information including, among others, ship type, fuel type, engines and propellers. It takes into account different parameters such as the ship speed and location (extracted from the AIS data), hull form, propeller efficiency, operation mode or engine load. One limitation of this realistic approach is the availability of the AIS data and the lack of ship information. According to Jalkanen et al. (2016), it can be assumed that the missing AIS data and ship information come mostly from small vessels and that their impact on the emission estimations is negligible. Another limitation of the CAMS-GLOB-SHIP dataset is that it only includes the SOx emissions from international shipping. SOx emissions from inland navigation and port activities are not included.

The SOx discharges from ships equipped with open-loop scrubbers were estimated by assuming that these ships released ~3.5 times more sulphur (via atmosphere exhaust gas and direct water discharge from the scrubber system) than they did in 2014 when the 1.0% sulphur content limit was in force and when they ran on 1.0% sulphur content limit compliant fuel. It is possible that ships equipped with open-loop scrubbers use fuel with sulphur content close to 2.8% which is, so far, the sulphur content of the typical HFO on the market (Winnes et al., 2018). This could reduce the acidification estimation by about 20% but the main trend would remain. In the future however, with the higher demand on LSFO, there is a serious possibility that ships equipped with open-loop scrubbers will run on fuel with higher sulphur content, possibly close to 3.5%.

6.2 Model uncertainties

The model pH estimation depends on the model ability to simulate the physical and biochemical processes of the marine environment. The marine biogeochemical model has been validated in Dulière et al. (2019) and in Lacroix et al. (2007) and the carbonate chemistry module has been carefully validated in Gypens et al. (2011).

The spatial horizontal resolution of the model grid cells is of ~5 km x 5 km. Since the SOx water discharges are assumed to be equally distributed within each of the model cell, a dilution effect is to be foreseen and even further acidification than what is shown in this study can be expected at finer scales.

6.3 Comparison to past studies

Compared to past studies also assessing the sea water acidification in the North Sea due to the use of scrubbers (*e.g.* Stips et al., 2016; Hunter et al., 2011), our model predicts a larger acidification effect. This can partly be explained by the area of study that here includes the part of the North Sea that accounts for the higher maritime traffic density. Also, the model spatial resolution used here is finer, leading to less artificial dilution and relatively more acute pollution effects.

The present study also highlights the largest effects of scrubber operation on acidification of the North Sea in the near-coastal areas, most particularly in the vicinity of major ports, where traffic is denser. This is in agreement with studies such as in Hassellöv et al. (2013) or Stips et al. (2016) that has estimated that the contribution from SOx injection in the Rotterdam port area could be as much as 20 times larger than the whole North Sea mean. These results are compatibles with the present results. Note however that the present study does not include the SOx emissions related to activities into the ports, but only the SOx contributions related to maritime traffic at sea, which is higher in the vicinity of the ports.

6.4 In the context of climate change

The shipping sector is not the only contributor to ocean acidification. At a global scale, in response to the increasing concentration in greenhouse gases in the atmosphere, the ocean surface water pH is decreasing by about 0.0017-0.0027 pH units per year since the late 1980s (Bindoff et al., in press). Provost et al. (2010) analysed in-situ measurements of pH in the North Sea and found a decrease of 0.02 to 0.03 pH unit per year between 1998 and 2006. They also showed that the observed rates of pH change in the Dutch coastal zone could not be explained from the enhanced CO_2 uptake only (estimated at that time of 0.0013–0.0020 unit per year). They suggested that other processes could also play a dominant role in ocean acidification. In this context, and in the light of these results, it is possible that SOx emissions from shipping but also from land-based activities could have significantly contributed to the observed pH changes by Provoost et al. (2010).

In comparison to the change of 0.0017-0.0027 pH units per year in response to climate change, the pH decrease attributed to the shipping sector estimated by the model becomes significant and must clearly be taken into account. Because of the "flushing effect" in the English Channel and in the southern North Sea, we do not expect a significant yearly accumulation of SOx pollution from shipping over that area. Nevertheless, the pH change magnitude in response to SOx pollution due to shipping when open-loop scrubbers are used is equivalent to 2 to 4 years of climate change acidification on average over the whole domain, and to 10 to 50 years, in more local areas. The cumulative impact of ocean acidification due to climate change and to maritime traffic, together with the temperature increase, should therefore be considered in ecosystem assessment studies.

6.5 Potential impacts of ocean acidification

Assessing the impact of such pH changes on the environment, economy or even society is beyond the scope of this study. Some examples of scientific work are mentioned here for informative purpose. First, studies on the biological, ecological and biogeochemical effects of ocean acidification have been carried on calcifying organisms because of their known direct need for carbonate ions during the calcification process. Sea water with low pH is under-saturated in calcium carbonate which makes it more corrosive to limestone. It compromises the creation of shells and skeletons and can lead to the dissolution of existing structures (*e.g.* Bindoff et al., in press).

Most studies have assessed the impacts of a pH change from 8.1 to 7.5-7.8 pH values. This corresponds to the range of pH foreseen for 2100 as a result of climate change (Bindoff et al., in press). In Van Colen et al. (2018), they showed that the early life history of *Limecola balthica* (a clam) was significantly affected by such changes in pH. Among other effects, the mortality rate increased and the shell size decreased. Preliminary results of a Belgian study show that the ocean acidification decreases the surviving rate of *Mytilus edulis* (the blue mussel), reduces its growth and causes stress to the organisms (Jan Vanaverbeke, personal communication). The recent study of the effects of ocean acidification on fish show disturbances in different sensory systems such as olfaction (*e.g.* Velez et al., 2019), hearing (*e.g.* Simpson et al., 2011), and vision (*e.g.* Chung et al., 2014). PH decrease has also been linked to disturbance in general cognitive function of fish (Velez et al., 2019). In turn, this could affect population and ecosystem dynamics, leading to environmental and economic impacts. The northern prawn (*Pandalus borealis*) loses quality in terms of taste, texture and appearance as pH decreases (Dupont et al., 2014). Certain oyster species can also lose their nutritious properties (Lemasson et al., 2018).

7 Conclusions

By means of a marine biogeochemical model and realistic shipping SOx contribution scenarios, this study shows the potential impact of the SOx marine pollution from shipping activities on the acidification of the English Channel and the southern part of the North Sea. More particularly, the model provided estimations of the sea water pH changes in cases of different combinations of maritime strategies to comply with the 0.1% sulphur content limit in fuel. All scenarios show a pH decrease in both offshore and coastal areas.

More than the ship traffic, the sulphur emission reduction strategy, and more particularly the fleet ratio equipped with open-loop and hybrid scrubbers that discharge SOx at sea, has the most impact on the ocean acidification. The use of those scrubbers allows ships to run on heavy fuel and is potentially responsible for a general decrease in pH of at least 0.004 over the whole area of study, including the English Channel and the southern part of the North Sea and to a decrease of 0.031 and more in coastal areas with intense shipping traffic. The model shows that this impact will continue to increase in the future if the maritime traffic further develops and if more ships are equipped with open-mode scrubbers (Turner et al., 2018).

The marine environment is already under a lot of anthropogenic pressures and the results of the present study show that the effect of the open-loop and hybrid scrubbers wash water effluent on the sea water pH is important. Note that this study does not assess the potential impacts of the other contaminants such as NOx, CO_2, PAHs or heavy metals that are also directly or indirectly discharged into the water by scrubber systems. It could be of value to further evaluate the aggregated ecotoxicity of the SOx together with all other contaminants. In addition, ocean acidification does not come alone and is to be added to the climate change pressure to the ecosystems (*e.g.* temperature increase).

Given these conclusions, in addition to further studies, a precautionary approach is recommended. Some countries and regions around the world (*i.e.* Belgium, Finland, Norway, California, China) have already taken steps that limit the use of open loop scrubbers in local ports, inland waters, coastal areas and/or territorial seas in agreement with UNCLOS (United Nations Convention on the Law of the Sea).

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