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Modeling pH changes in coastal seas: why are there regional differences?

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Introduction

Ocean acidification, the lowering in pH driven by the absorption of anthropogenic atmospheric CO_2, is a major problem for present-day oceans. Measurements for the open ocean reveal a decrease in pH of 0.0013-0.0020 unit/yr; however, the few available long-term data sets of coastal regions [1-3] show variable trends, which in some cases exceed the open ocean decrease in pH by one order of magnitude. The differences with the open-ocean rate and among data sets suggest that processes other than enhanced CO_2 uptake alone can lead to coastal acidification.

Research questions

- What is the relative importance of physical and biogeochemical processes responsible for acidification in coastal seas?
- How can we explain variability between the southern North Sea, Baltic Sea, northwestern Mediterranean Sea and South China Sea?

Methods

A box model (Fig. 1) was developed within the modeling software R (v 2.15.1) using the package *AquaEnv* [4] for acid-base computations. Parameter values were mainly taken from [5,6]. Nitrification was included as a fraction of atmospheric NH_3 input according to [7].

CO_2 exchange atmosphere - sea

atmospheric deposition SO_x, NO_x, NH_3

primary production: $CO_2 + H_2O \longrightarrow CH_2O + O_2$

aerobic respiration: $CH_2O + O_2 \longrightarrow CO_2 + H_2O$

nitrification: $NH_3 + 2\,O_2 \longrightarrow NO_3^- + H_2O + H^+$

Figure 1: Schematic overview of coastal sea box model

Regional variability

At present, atmospheric deposition contributes most significantly to total acidification in the North Sea (13-29%) and least in the NW Mediterranean Sea (1.7-3.4%) (Fig. 2). Assuming no changes in input, this contribution will increase during the 21st century (17-41% in the North Sea in 2100) due to a decrease in the seas' buffering capacities.

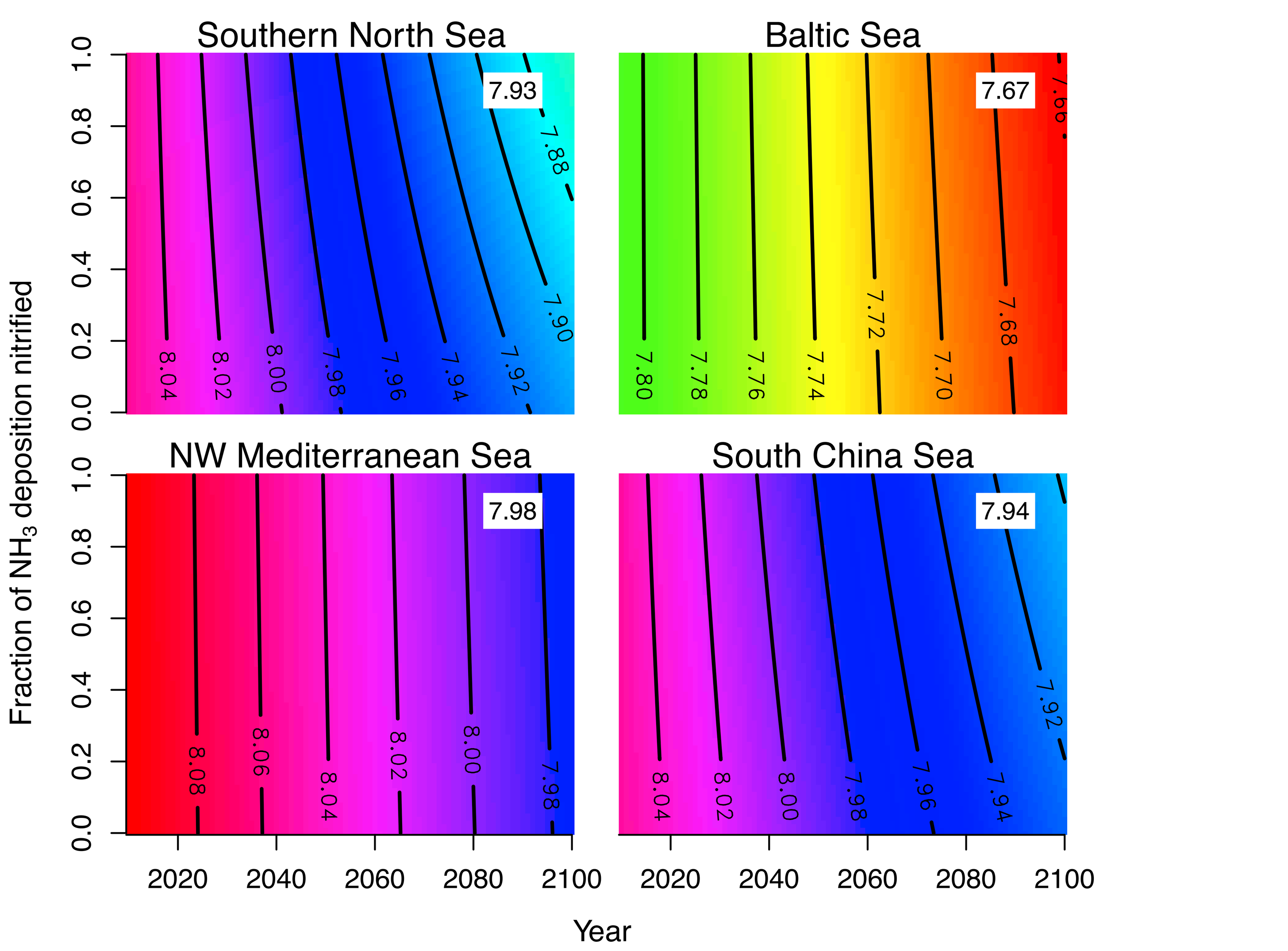

Figure 2: Effect of nitrification on change in pH (total scale) with a constant atmospheric deposition flux and a pCO_2 increase of 1.7 ppmv/yr. White box shows pH in 2100 without atmospheric deposition.

Effect of different processes on pH

By modeling pH explicitly we can show that production and respiration dominate proton cycling (Fig. 3). The increase in cycling intensity with time is due to a 60% decrease in buffering capacity during the 21st century.

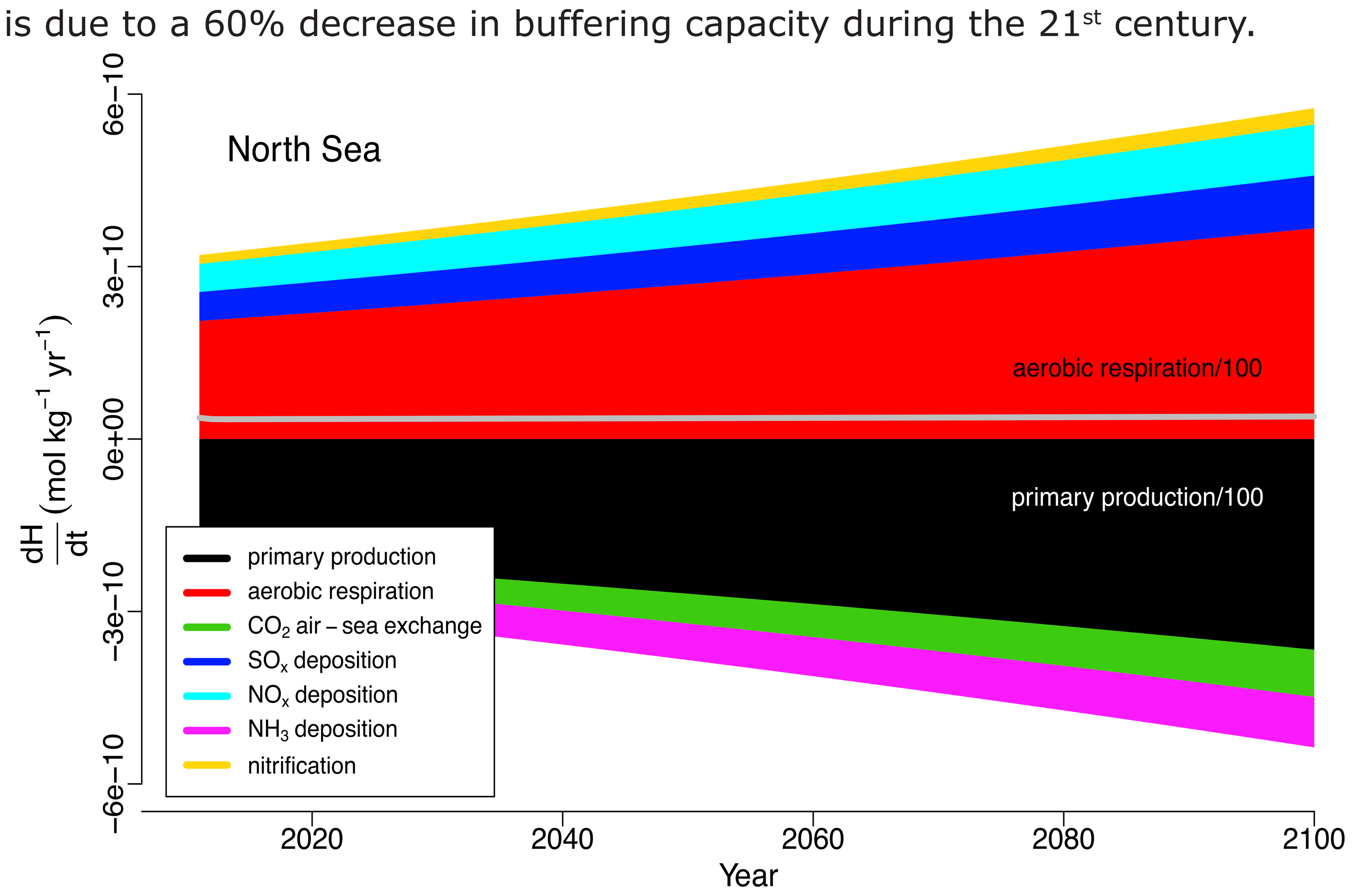

Figure 3: Change in proton concentration for each of the modeled processes using the current inputs (see Fig. 4). Gray line shows the net change. Note the different scale for primary production and aerobic respiration.

Sensitivity analysis

We assessed the response of the model to several disturbances (Fig. 4). The North Sea is more sensitive to changes in the production-respiration balance and atmospheric pCO_2 compared to changes in atmospheric deposition. The Revelle factor shows that the minimum buffering capacity of the North Sea will be reached within or shortly after the 21st century.

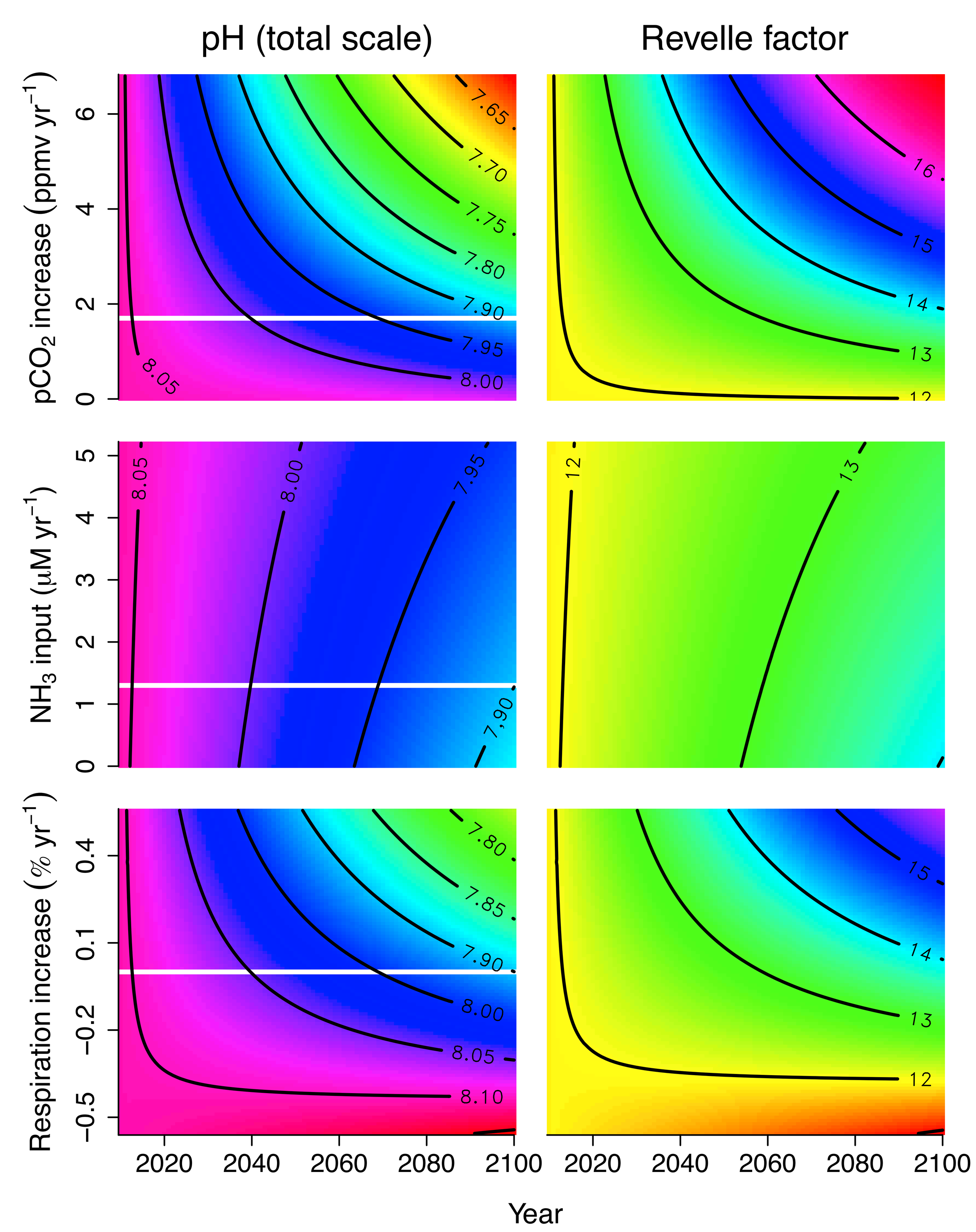

Figure 4: Effects of different pCO_2 growth rate, changes in NH_3 deposition and production-respiration imbalance on North Sea pH (total scale) and Revelle factor. White horizontal lines show current inputs. 16% of the NH_3 deposition is nitrified [7]

Main conclusions

- Atmospheric deposition of sulfur and nitrogen enhances acidification of coastal seas by further decreasing their buffering capacities, especially in the southern North Sea
- Regional differences are a result of both differing atmospheric deposition and production rates and varying buffering capacities
- Production and respiration account for the majority of proton cycling. Hence, disturbing their balance has the most profound effect on pH

References

[1] Provoost *et al.* (2010) *Biogeosciences* **7**, 3869-3878 | [2] Wootton *et al.* (2008) *P Natl Acad Sci USA* **105(48)**, 18848–18853 | [3] Ishii *et al.* (2011) *J Geophys Res*, **116**, C06022, doi:10.1029/2010JC006831 | [4] Hofmann *et al.* (2010) *Aquat Geochem* **16**, 507-546 | [5] Gazeau *et al.* (2004) *Estuar Coast Shelf S* **60**, 673-694 | [6] Hunter *et al.* (2011) *Geophys Res Lett* **38**, L13602, doi:10.1029/2011GL047720 | [7] Yool *et al.* (2007) *Nature* **447**, 999-1002