

Biogeochemical processes and buffering capacity concurrently affect acidification in a seasonally hypoxic coastal marine basin

M. Hagens C. P. Slomp F. J. R. Meysman D. Seitaj J. Harlay A. V. Borges J. J. Middelburg

1. Introduction

Coastal areas experience more pronounced short-term fluctuations in pH than the open ocean due to higher rates of biogeochemical processes such as primary production, respiration and nitrification. These processes can mask or amplify the ocean acidification signal induced by increasing atmospheric carbon dioxide (CO_2) [1]. Coastal acidification can be enhanced when eutrophication-induced hypoxia develops [2]. This is because the CO_2 produced during respiration leads to a decrease in the buffering capacity of the hypoxic bottom water.

4. Process rates

Rates of primary production were determined monthly by light-dark O_2 bottle incubations. Gross primary production displayed two peaks: a small peak in March, which was most clearly visible in an elevated Chl *a* concentration (Fig. 2d), and a major peak in summer. The dominant algae during this latter event were identified as dinoflagellates ('red tide'). Respiration was highest in May, due to an inflow of the spring-blooming haptophyte *Phaeocystis globosa* from the North Sea. During most of the year, the Den Osse basin was a sink for atmospheric CO_2 . Only in autumn, upon termination of water-column stratification (Fig. 1d) and transport of CO_2 -rich bottom waters to the surface (Fig. 2b), CO_2 was emitted to the atmosphere.

2. Lake Grevelingen

Eutrophication-induced seasonal hypoxia is common in coastal waters. Marine Lake Grevelingen, which has limited water exchange with the North Sea, experiences such hypoxia annually in its deeper basins, including the Den Osse basin.





Figure 3: a) Depth-integrated rates of gross primary production and respiration; b) calculated CO_2 air-sea exchange in the Den Osse basin in 2012.

5. Effect of biogeochemical processes on pH

The net change in pH in the Den Osse basin was much smaller than the inand decreases resulting from the separate processes [4]. These processes were so active that the residence time of a proton (H⁺) in the basin was only 15 to 42 days. Gross primary production led to an increase in surface-water pH year-round, but its contribution varied over the year. CO_2 air-sea exchange mostly impacted the pH budget in autumn. At depth, sediment fluxes and nitrification played a major role, in particular in spring and autumn. Respiration was an important process year-round and at all depths. In August, the absolute changes in pH were much larger than in the other months. This was mainly due to high primary production in the surface water, whereas at depth the low buffer factor (Fig. 2c) was the primary cause.

Longitude (°E)

Figure 1: a) Location and b) bathymetry of Lake Grevelingen; c) oxygen concentration (O_2) and d) stratification parameter (φ) at the Den Osse basin in 2012.

Research questions

How do pH and CO₂ in the Den Osse basin vary with depth and time?
What are the driving mechanisms behind its seasonal pH variability?

3. CO₂ and pH in 2012

The Den Osse basin displayed large differences in pH and CO_2 with both space and time. During stratification and hypoxia in August, pH differed by 0.75 units between the oxic surface water and the hypoxic bottom water. The buffer factor [3] correlated positively with pH and varied by a factor 2 with season and up to a factor 5 with depth. This indicates that changes in pH were less buffered when the pH of the water was low. The variability in the buffer factor was mainly driven by the uptake of CO_2 in the surface water in spring and early summer and subsequent release at depth in August. This also explains the strongly negative correlation between CO_2 and pH.







Figure 2: a) pH; b) CO_2 ; c) buffer factor; d) chlorophyll-a (Chl a) at the Den Osse basin in 2012.

 \square CO₂ air-sea exchange

- Vertical transport
- Sediment fluxes
- Gross primary production
- Respiration
- Nitrification
- Temperature change
- □ Closure term (lateral transport)
- Net change in pH

Figure 4: Den Osse pH budgets at 1 and 25 m depth for March, May, August and November 2012.

Conclusions

- CO₂ and pH in the Den Osse basin are strongly negatively correlated and highly variable in both space and time
- Seasonal pH dynamics in the basin are driven by temporal variability in several processes rates and modulated by the buffering capacity

References

[1] Provoost *et al.* (2010) *Biogeosciences* **7**, 3869-3878 [2] Cai *et al.* (2011) *Nature Geosci.* **4**, 766–770 [3] Hofmann *et al.* (2010) *Mar. Chem.* **121**, 246-255 [4] Hagens *et al.* (2015) *Biogeosciences* **12**, 1561-1583.