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Seasonal and long-term changes in pH in the Dutch coastal zone

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Abstract. Recent observations and modelling studies suggest that biogeochemical changes can mask atmospheric CO_2-induced pH decreases. Data collected by the Dutch monitoring authorities in different coastal systems (North Sea, Wadden Sea, Ems-Dollard, Eastern Scheldt and Scheldt estuary) since 1975 provide an excellent opportunity to test whether this is the case in the Dutch coastal zone. The time-series were analysed using Multi-Resolution Analysis (MRA) which resulted in the identification of system-dependent patterns on both seasonal and intra-annual time scales. The observed rates of pH change greatly exceed those expected from enhanced CO_2 uptake, thus suggesting that other biogeochemical processes, possibly related to changes in nutrient loading, can play a dominant role in ocean acidification.

1   Introduction

One of the most pressing concerns facing policy makers and society as a whole is the rapid increase of atmospheric CO_2 levels. Over the past 200 years, the anthropogenic input of CO_2 to the atmosphere has accelerated, as a result of fossil fuel combustion, cement production and land use change. These anthropogenic CO_2 emissions have had two global scale consequences. The first one is climate change. About half of the anthropogenic CO_2 has remained airborne, increasing the CO_2 concentration in the atmosphere from a pre-industrial level of 280 ppm to about 380 ppm today. Being a greenhouse gas, this change in CO_2 concentration is now considered to be the major driver of the observed global warming (IPCC, 2007). The second issue concerns the uptake of anthropogenic CO_2 by the world oceans, causing a shift in the chemistry of seawater. This "other CO_2 problem" is the topic of this paper. Most notably, the invasion of CO_2 into the ocean causes an acidification of the surface ocean, estimated to be a circa 0.1 unit decrease in pH over the past 200 years. Projected increases in atmospheric CO_2 will induce further acidification of oceanic surface waters with 0.4 pH units from circa pH 8.1 now to 7.7 in 2100 (Caldeira and Wickett, 2003).

Ocean acidification is a topic of concern because a decrease in the pH of surface waters has multiple effects on the functioning, productivity, growth and survival of marine organisms. Much attention has been devoted to the potential consequences for calcifying organisms, in particular coral reefs, coccoliths, foraminifera and bivalves (Orr et al., 2005; Gazeau et al., 2007). Ocean acidification decreases carbonate concentrations and thus lowers the seawater calcium carbonate saturation state. Many of these organisms calcify less or even dissolve with only small changes in pH or calcium carbonate saturation states, which can have important economic consequences such as for shell fish yield (Gazeau et al., 2007). The effect of acidification on calcifying organisms is not clear-cut however, as recent experimental evidence suggests some organisms may benefit from the increased dissolved inorganic carbon concentrations associated with ocean acidification (Iglesias-Rodriguez et al., 2008). Acidification of marine waters has also consequences for non-calcifying organisms, such as diatoms, nitrifiers, and heterotrophic bacteria (Doney et al., 2009) and for the penetration of sound in seawater (Hester et al., 2008) affecting the bio-acoustics of marine mammals. Overall, there is a

growing recognition that ocean acidification has relevant and important effects on the performance and survival of marine communities. This has initiated much research on the effect of ocean acidification at all levels of biological organization: cellular, organisms, populations, community and ecosystems.

However, all these ongoing and soon to start research efforts that investigate the effect of ocean acidification on organisms and communities share an important (implicit) assumption. They assume that future pH decreases will occur as estimated by model predictions based on projected increases in atmospheric CO_2, which come down to a decrease of 0.0013 to 0.002 pH units per year (depending on local conditions such as temperature and salinity) (Orr et al., 2005). By its very nature, this CO_2-based estimate constitutes a global average, and because of the rapid mixing of CO_2 in the atmosphere, one would not expect substantial spatial variability in this acidification effect. So the question is whether all ocean areas follow this global average trend? Although there are remarkably few published data on the temporal dynamics of pH based on direct measurements, the open ocean appears to follow the predicted rate of pH decrease. Santana-Casiano et al. (2007) reported a pH decline of 0.0017 units per year in the Atlantic Ocean near the Canary Islands over the period 1995–2004, Dore et al. (2009) documented a long-term decreasing trend of 0.0019 units per year at station ALOHA in the central North Pacific, and Byrne et al. (2010) found pH changes of 0.0017 units per year between 1991 and 2006, also in surface mixed layer of the central North Pacific ocean. All these measurements are consistent with the CO_2-based prediction. However, it is truly questionable whether coastal and shelf areas also obey this globally averaged trend. Recently, Wootton et al. (2008) reported an extensive pH dataset for the coastal water on the Washington Shelf showing substantial variation in pH values across multiple time scales. The pH varied $\sim$0.25 unit over 24 h, up to $\sim$1.0 unit over the seasons, and $\sim$1.5 unit over the entire dataset spanning 8 years. Moreover, over the 8 years period a significant trend was found, with a mean pH decrease of 0.045 (0.039 to 0.054) unit per year, while the rate of pH decline appeared to be accelerating (Wootton et al., 2008). This is an order of magnitude higher than the projected CO_2-based global average rate of change (Orr et al., 2005) and observed open ocean pH decrease (Santana-Casiano et al., 2007; Dore et al., 2009). If the Wootton et al. (2008) pH trend is typical for coastal systems, we have to revise our conceptual view of "uniform" ocean acidification and re-evaluate our experimental design for effect studies.

Recently, Gypens et al. (2009) and Borges and Gypens (2010) presented model analyses of carbonate chemistry and pH changes in the Belgian coastal zone over the period 1951–1998 and showed that changes in carbon cycling related to nutrient supply can counteract or add to the effect of CO_2-induced acidification on the carbonate chemistry and pH of coastal waters. Since 1975, Dutch monitoring authorities
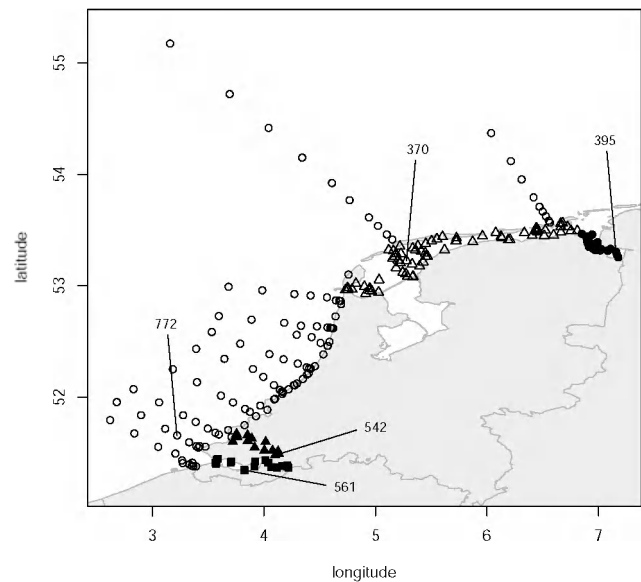

Fig. 1. Map showing all sampling locations of the MWTL dataset. Five geographical areas are distinguished: North Sea (o), Wadden Sea ($\triangle$), Eastern Scheldt ($\blacktriangle$), Western Scheldt ($\blacksquare$) and Ems-Dollard ($\bullet$). Numbers indicate the stations which have been selected for presentation in full detail.

have systematically measured pH in the North Sea and adjacent estuarine and coastal waters (Wadden Sea, Ems-Dollard, Eastern Scheldt and Scheldt estuary). This publicly available database (http://www.waterbase.nl) offers an excellent opportunity to investigate whether ocean acidification is occurring in these systems at the rate expected based on CO_2-induced acidification or whether other processes govern pH dynamics in coastal waters. In this study we will examine the observed long-term trends, and discuss these in terms of biogeochemical processes governing pH in coastal waters.

2   Materials and methods

The data used in this study were collected by the long-term monitoring program (MWTL) of the Dutch water management agency Rijkswaterstaat (RWS). This publicly available database (http://www.waterbase.nl) provides little metadata, but we have contacted the responsible laboratories to obtain methodology and changes therein. We have selected five coastal systems for detailed examination (Fig. 1): the Dutch section of the North Sea, the Western and Eastern Scheldt estuaries, the Wadden Sea and the Ems-Dollard Estuary. These systems differ in nutrients, light penetration and primary production levels (Heip et al., 1995). The Dutch section of the North Sea is situated along the southern bight of the North Sea, and borders a very densely populated area. It receives nutrients mainly from riverine sources (Rhine and Meuse)

and through the English Channel. Most stations are within 50 km of the coast and in the region of river influence, but some are more off-shore. The Eastern Scheldt is an old branch of the river Scheldt, which was cut off from the main river in the 19th century with the result that it became a tidal inlet system. In 1986, a storm surge barrier was constructed which can close off the entire estuary in case there is a risk of flooding. The Eastern Scheldt is rather low in nutrients and light penetration is relative high. The Western Scheldt (also known as the Scheldt estuary) is a nutrient-rich, turbid, tidal estuary (Soetaert et al., 2006). The Wadden Sea is a shallow system comprising intertidal flats, subtidal areas and tidal channels connecting to the sea between the barrier islands. The Dutch part of the Wadden Sea receives nutrients by tidal exchange with the North Sea, and by freshwater discharge from the Rhine via Lake IJssel (Philippart et al., 2007). The Ems-Dollard estuary, finally, is located in the north of the Netherlands, on the Dutch-German border and is like the Scheldt estuary, a turbid, tidal system with low primary production (Middelburg and Herman, 2007).

An important issue when measuring and reporting pH is the pH scale used. Because hydrogen ion activities cannot be determined directly, various operational definitions of pH have been proposed. The pH scale of the US National Bureau of Standards (NBS) is most often used in national monitoring programs and is defined by a series of low ionic strength buffer solutions, which are assigned pH values reflecting the hydrogen ion activity as good as possible. The NBS scale is not the most appropriate scale for measurements in seawater because of the large difference in ionic strength between the buffer solution and the measurement solution. Transferring an electrode from the low ionic strength ($\sim$0.1) buffer solution to the high ionic strength ($\sim$0.7) measurement solution will cause a change in its liquid junction potential, thereby affecting the electrode output voltage. This liquid junction potential will depend on the specific electrode used. In order to overcome this problem, a set of buffers based on artificial seawater have been introduced that take into account protonation of sulfate and fluoride, i.e. the free, total and seawater scales (Zeebe and Wolf-Gladrow, 2001). Although marine chemists commonly use TRIS and AMP buffers and report pH values on the total hydrogen scale, most freshwater and estuarine scientists and monitoring authorities use NBS buffers. The pH data from the MWTL program are also reported on this pH scale. This dataset contains a total of 48330 pH values measured between 1975 and 2006 at 249 stations. At most sampling locations, pH was measured with electrodes and calibrated against standard NBS buffer solutions. A total of 4600 pH values were measured in the laboratory during alkalinity titrations. Methods, equipment and reporting procedures commonly change during long-term monitoring programs and the Dutch program is no exception. We will therefore report and explicitly show such methodological changes as they may induce apparent or mask real trends.

The long-term time series were analyzed by multi-resolution analysis (MRA). This wavelet analysis allows decomposing the observed signal into inter- and intra-annual signals. The dataset was prepared for analysis by calculating monthly averages, and generating values where data was missing using linear interpolation. The time series were decomposed into 8 levels by maximal overlap discrete wavelet transform (MODWT), using the R package waveslim (Whitcher, 2007). The filter applied was the Daubechies least asymmetric wavelet filter of length 8 (LA8). This decomposition results in a set of wavelet vectors D1–D8 and a scaling vector S8. The first component (D1) captures periodicities between 2 and 4 months, the second periodicities between 4 and 8 months, then between 8 and 16 months, and so forth. Long-term and medium-term signals were calculated by adding D6 + D7 + D8 + S8 and D3 + D4 + D5, respectively. The latter captures the seasonal signal. Seasonal patterns were calculated by subtracting the long-term signal from the original time-series and visualized by creating box plots per month. Values obtained from interpolated data points were not included. Finally, seasonal amplitudes were calculated by subtracting average pH values measured in January from those measured in May. This was done using the raw data and only for time series where at least 10 seasonal differences could be calculated. All calculations were done using R (R Development Core Team, 2005).

3 Results

The extensive dataset comprises 249 stations and covers a 31-year period (1975–2006), we therefore show the full dataset for a selection of five stations, that are representative for their respective coastal system (Fig. 2).

3.1 North Sea

The dataset contains pH values from 114 stations in the Dutch part of the North Sea, although most of the time series are fragmentary. The North Sea data depicted in Fig. 2a are from station 772, which is located 20 km offshore from Walcheren (Fig. 1). The North Sea time-series can be subdivided in four sections based on the equipment used and procedures followed. In the first section, between 1975 and 1985, the dataset is rather complete, and pH is reported with only one decimal. In the two following sections, from 1986 to 1990 and from 1991 to 1998, pH is reported with one decimal as well. The data in these sections are fragmentary, and especially the first section where pH was measured during alkalinity titrations in the laboratory is characterized by odd values with pH being as high as 8.6 in winter and as low as 7.7 in summer. The last section (1998–2006) is more or less complete, and pH values have three decimals. Figure 4a shows the results of the multi-resolution wavelet analysis (MRA). For the North Sea station, the long-term signal shows a steady increase in pH between 1975 and 1987, and a
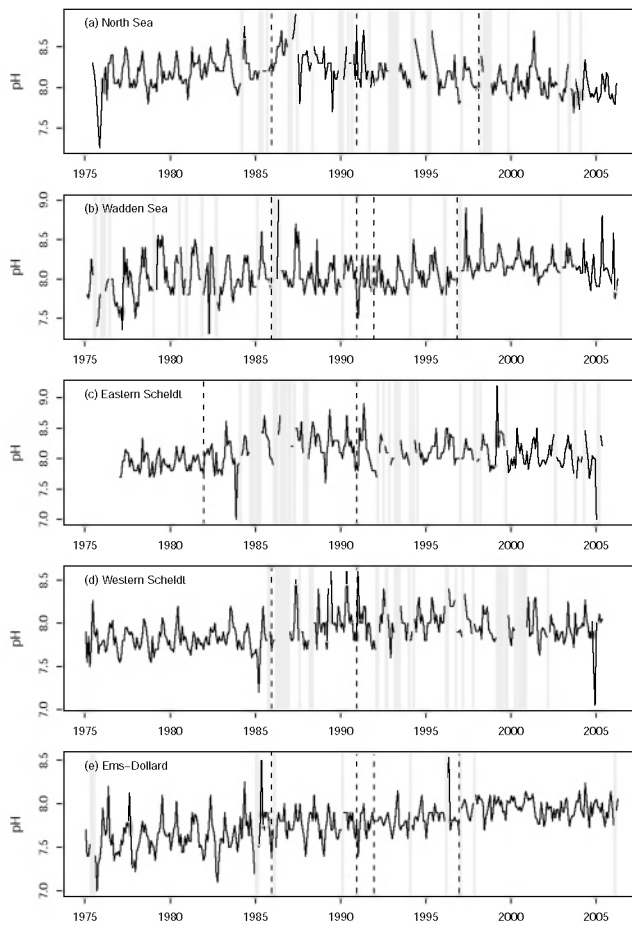
Fig. 2. Raw data from the selected stations. Dotted lines indicate a change of equipment, gray areas show where monthly data is missing. See Fig. 1 for station locations.

decreasing trend afterwards. This trend is present in all North Sea stations with more or less continuous data (Fig. 3). Although data quality in the two middle sections (from 1986 to 1998) is lower, the increasing and decreasing long-term trends identified by MRA using the full time series (Fig. 4a) are fully consistent with linear regression analysis of raw data in the first and last sections (Fig. 5). Regressions of raw pH data with time for individual North Sea stations show increases of 0.01 to 0.025 pH yr^{-1} between 1975 and 1985, and decreases of 0.02 to 0.03 pH yr^{-1} between 1998 and 2006. The medium-term signal constructed from MRA components D3 + D4 + D5 shows a clear seasonal pattern where the dataset is complete (Fig. 4a). Figure 6a show the seasonal pattern observed in the North Sea. pH increases rapidly between March and May, then gradually decreases until stable winter values are reached in September. The seasonal amplitude is related to the distance from the shore (Fig. 7), with deviations from winter values of more than 0.5 pH units at nearshore stations, to less than 0.1 pH unit at the offshore stations located at 100 km or more from the coast.
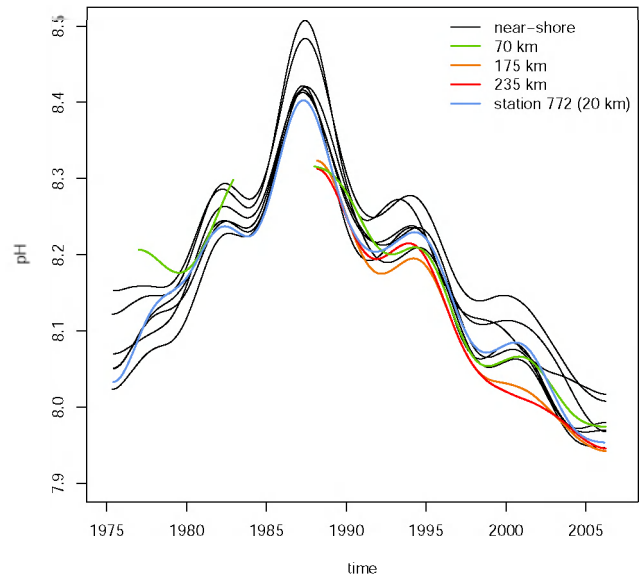

Fig. 3. Long-term (MODWT D6 + D7 + D8 + S8) signals from all North Sea stations with more or less continuous data. Colors depict the distance from shore, the signal from the selected station 772 is shown in blue.

3.2 Wadden Sea

The data for the Wadden Sea station Blauwe Slenk Oost (station 370) are presented in Fig. 2b. Methodology and reporting procedures changed four times over the studied period, in 1986, 1991, 1992 and 1997. From 1999 onwards values are usually reported with two decimals, before that with only one. Winter values of pH appear to be rather constant throughout the first four sections of the time series, with the exception of anomalous low values between 1975 and 1977, and in 1983. In 1997 however, there is a sudden increase of about 7.8 to 8.0 which seems to be related with a change of equipment. The long-term signal extracted with MRA is not a simple as in the North Sea, but the pH decreases similarly during the last few years. Multi-resolution analysis (Fig. 4b) also revealed a seasonal signal, with rather high amplitudes before 1988. The seasonal patterns are comparable to those of the North Sea stations (Fig. 6a), with slightly higher mean seasonal amplitude (Fig. 8).

3.3 Eastern Scheldt

At the Eastern Scheldt station Yerseke (station 542), pH was monitored between 1977 and 2006 (Fig. 2c). During that period, two methodological changes have occurred, one in 1982 and one in 1991. pH values were reported with two decimals between 1982 and 1985 and from 1997 onwards, otherwise with only one. Multi-resolution analysis revealed that pH appears to be stable up to 1983 with winter values around 7.8, after 1983 however there is a sudden increase with winter values of about 8.1. It is unclear whether this
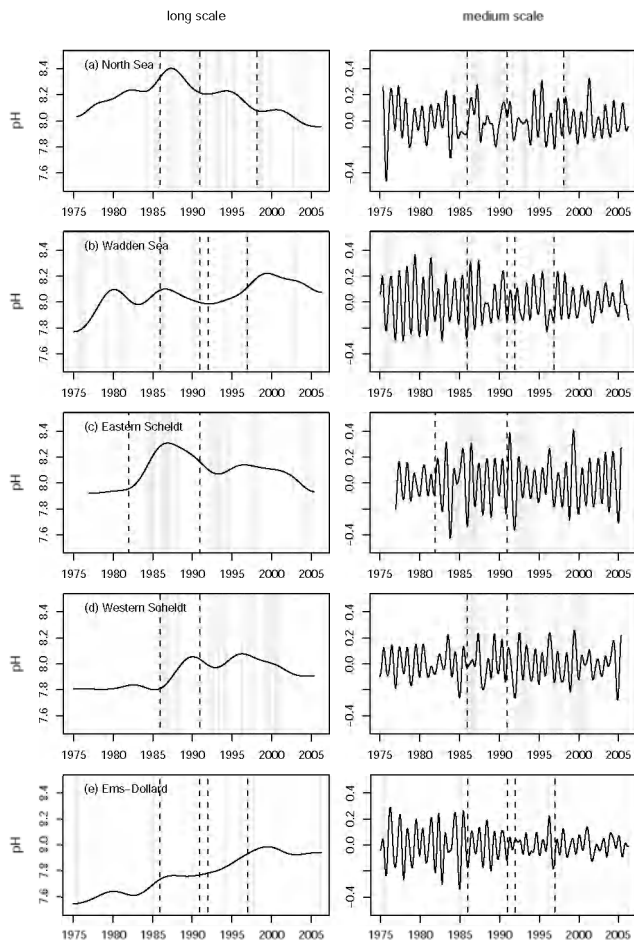
Fig. 4. Medium- (MODWT D3 + D4 + D5, right) and long-term (MODWT D6 + D7 + D8 + S8, left) signals from the selected stations.

increase is real or related to a change of equipment. From the early 1990s onwards pH gradually decreased again (Fig. 4c). The amplitude of the Eastern Scheldt seasonal signal is, at over 0.45 pH units, the highest of all studied systems (Figs. 4, 6, 8).

3.4 Western Scheldt

The Western Scheldt station Terneuzen Boei 20 (station 561) is presented in Fig. 2d. Equipment changes occurred in 1986 and 1991. pH values were initially reported with one decimal but with two decimals from 1997 onwards. Throughout the time series, winter pH has increased from 7.7 to 7.9. Multi-resolution wavelet analysis revealed stable pH from 1975 to 1986, then an increase in pH during the 1990s, but it remains unclear whether this is related to changes in methodology (Fig. 4d). From the mid 1990s onwards pH values appear to decline. The mean seasonal amplitude is lowest of all studied systems, but the variability amongst stations within this estuary is very high (Figs. 6d, 8).
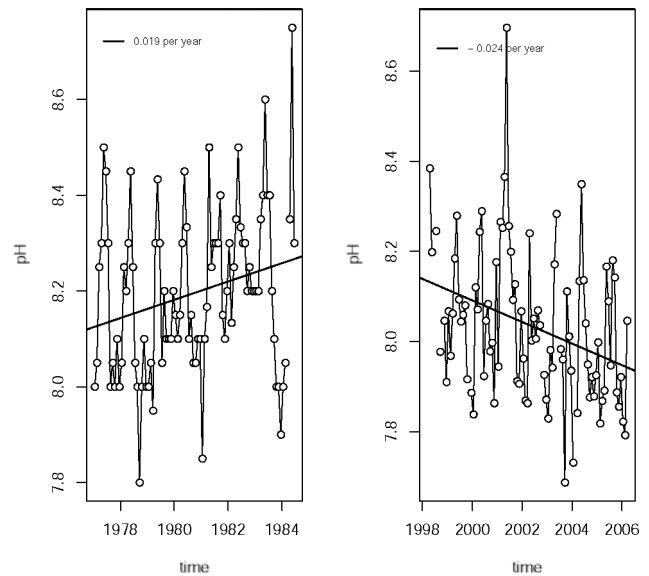

Fig. 5. Within-section linear regressions on raw data from North Sea station 772.

3.5 Ems-Dollard Estuary

The time series from Ems-Dollard station Groote Gat Noord (station 395) is almost complete, but methodological changes occurred in 1986, 1991, 1992 and 1997. Values are reported with two decimals from 1992 onwards. The pH appears to increase continuously throughout the studied period from 7.6 in the seventies to almost 8 in the last few years (Figs. 2e, 4e). Mean seasonal amplitude is low (Fig. 8) and MRA revealed that seasonality was high before 1986 and low after 1996, as observed in the Wadden Sea (Fig. 4b, 4e). This may again be related to shift in methodology.

4 Discussion

Long-term datasets are invaluable for testing our knowledge, but their analysis can be equally challenging. Our study is based on publicly available data for Dutch coastal water from the national monitoring program. These data are of relative low quality, because sensors were not calibrated according to present-day oceanographic standards and details of equipment and methodological changes have not been well documented. Ideally, when equipment or methodology changes, new and old methods should be properly documented, carefully compared and if possible used simultaneously. Unfortunately, this was not the case for the pH measurements of the MWTL program. However, the fact that we observed distinct, coastal system-dependent patterns (Figs. 4, 6), and that extracted trends were present across methodological changes (Fig. 4) and were also observed during periods with consistent methodology (Figs. 4, 5), adds to their credibility.
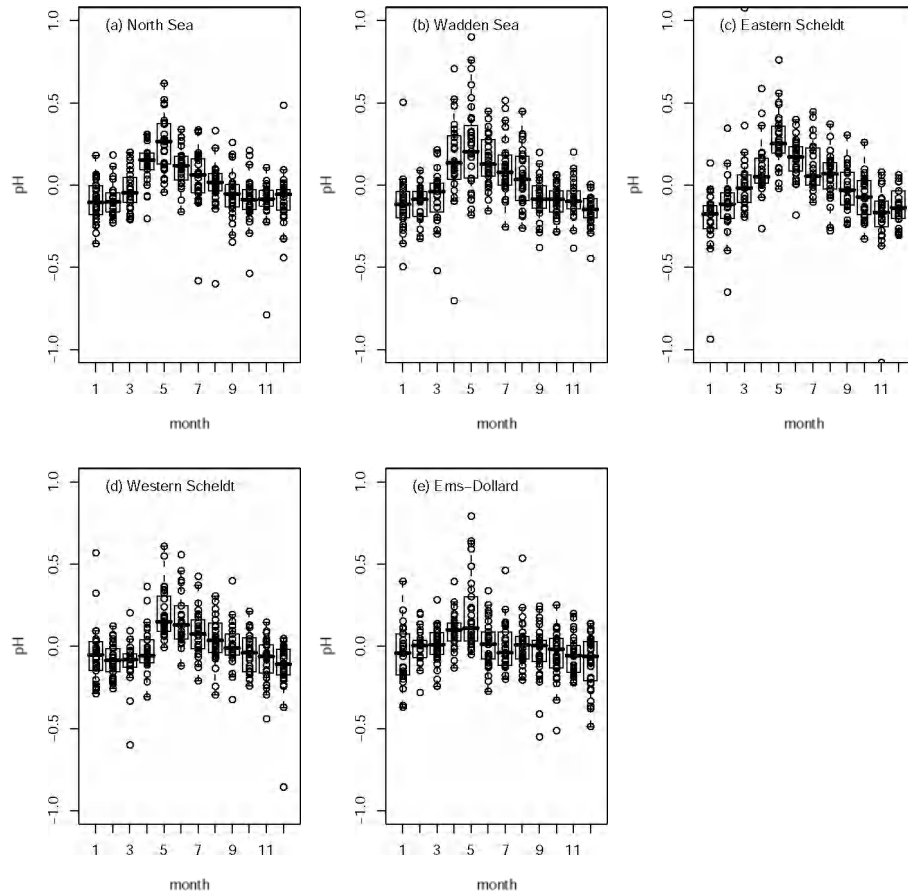
Fig. 6. Seasonal patterns observed at the selected stations. These values were calculated by substracting the long term signal (MODWT D6 + D7 + D8 + S8) from the raw data.

The length and monthly resolution of the MWTL dataset allowed use of multi-resolution wavelet analysis to extract long-term trends and short-term variability. Both long-term and seasonal patterns identified in the MWTL data differ among different parts of the Dutch coastal zone. The amplitude of the seasonal signal varies between 0 and 0.6 pH units, and clearly correlates with system productivity (Fig. 8). An overview of productivity measurements is given in Table 1. The highest mean seasonal amplitude (0.48 pH unit) was found in the Eastern Scheldt, where annual primary production varies between 200 and 550 gC m^{-2} yr^{-1} (Wetsteyn and Kromkamp, 1994). A slightly lower mean amplitude of 0.41 pH units was found for the Wadden Sea, where primary production has varied between 150 and 250 gC m^{-2} yr^{-1} during the last few decades (Philippart et al., 2007). Similar seasonal differences in pH occurred at the near-shore North Sea stations. As the distance from the shore increases, however, the seasonal amplitude diminished (Fig. 7). At the few stations which are located further than 100 km off-shore, mean seasonal differences did not surpass 0.1 pH units. This is in agreement with primary production measurements of

about 170 gC m^{-2} yr^{-1} at off-shore stations and over 300 gC m^{-2} yr^{-1} at near-shore stations (de Vries et al., 1998). In a companion paper by Van Engeland et al. (2010) a similar pattern, with high seasonal variability close to the coast and little or no seasonality at the off-shore stations, was observed for dissolved organic nitrogen concentrations. Average seasonal differences in pH were less pronounced in the Ems-Dollard and Western Scheldt estuaries (Fig. 8). Primary production in de Western Scheldt increases from about 100 gC m^{-2} yr^{-1} at the Belgian-Dutch border to 300 gC m^{-2} at the mouth (van Spaendonk et al., 1993; Kromkamp and Peene, 1995), hence the broad range of observed seasonal differences. The range and magnitude of primary productivity in the Ems-Dollard is comparable to that of the Scheldt estuary (Colijn et al., 1987). Accordingly, seasonal pH differences can be primarily attributed to the shifting balance of production and respiration processes over the season, with pH increases during spring when production increases faster than respiration and vice versa pH decreases during summer and fall when respiration processes are more important than primary production (Fig. 6).
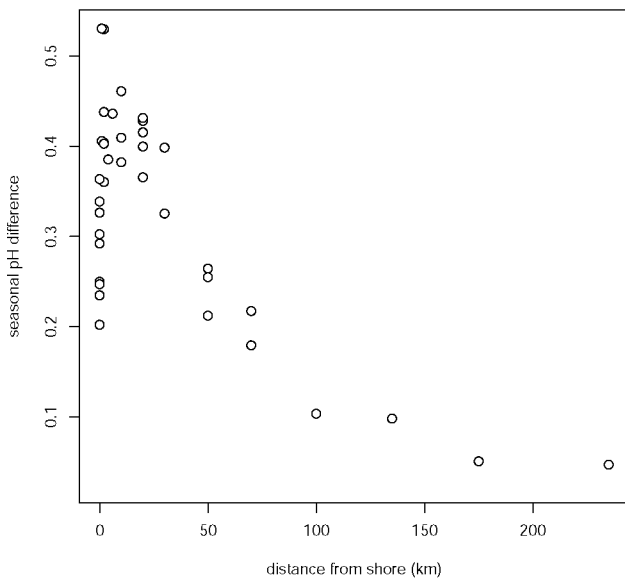
Fig. 7. Mean seasonal amplitudes at the North Sea stations as a function of distance from shore. Seasonal amplitudes were calculated by subtracting values measured in January from those measured in May, after detrending.
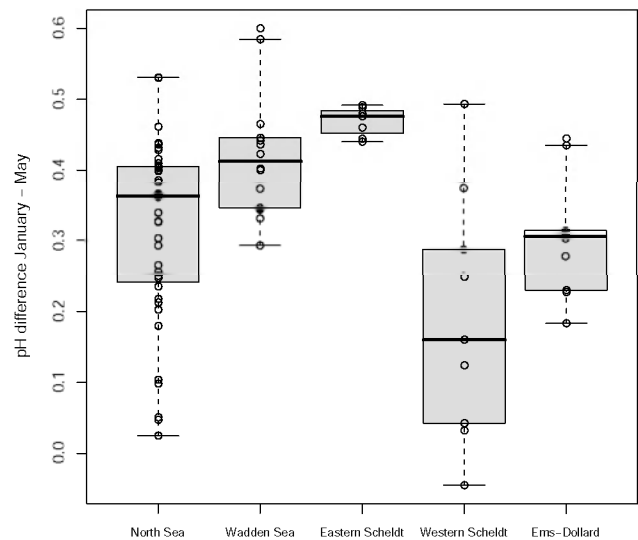

Fig. 8. Per station mean seasonal amplitudes for the different geographical areas. Seasonal amplitudes were calculated by subtracting values measured in January from those measured in May, after detrending.

Long-term trends are system-dependent as well (Fig. 4), and observed rates of change differ in sign and magnitude from those calculated from atmospheric CO_2 projections (declines of 0.0013–0.0020 unit per year). This clearly indicates that additional processes are at play and that these may be more important than enhanced CO_2 dissolution, at least in coastal systems. Recently, the theoretical effects of biogeochemical processes on the pH have been summarized (Soetaert et al., 2007; Hofmann et al., 2008). Primary production, for example, will increase the pH by about 1.3×10^{-3} per µM carbon at pH ~ 8 (Soetaert et al., 2007). Nitrification, however, decreases the pH by about 2.5×10^{-3} per µM carbon under the same conditions. Aerobic respiration tends to lower the pH, while denitrification and sulfate reduction in the sediment increase pH. Outgassing of CO_2 in estuaries and river mouths results in an increase in pH (1.5×10^{-3} per µM carbon). Calcification and carbonate dissolution lead to a lowering and an increase in pH, respectively. The investigated coastal systems have experienced major changes in their biogeochemical functioning and this seems to be reflected in their long-term pH evolution.

In the Western Scheldt and Ems-Dollard estuaries pH values were initially low and increased with time (Figs. 4d, 4e). Both these systems received high ammonium loadings in the past, which resulted in high nitrification rates with associated acid production (e.g. de Bie et al., 2002; Soetaert et al., 2006; Hofmann et al., 2009). Moreover, these systems are turbid and highly heterotrophic with a dominance of organic matter respiration over primary production and high pCO_2

values (Frankignoulle et al., 1998; Middelburg and Herman, 2007). Since the 1980s nutrient, and in particular ammonium, loads have decreased in these systems (Soetaert et al., 2006), and although interference from methodology changes cannot be excluded, this appears to be reflected in the overall increase of pH during the 1980s and 1990s. The modelling study of Hofmann et al. (2009) identified reduced nitrification as one of the causes of the increased pH observed in the Western Scheldt between 2001 and 2004, together with changes in freshwater flow. Primary production on the other hand, which is also potentially affected by changes in nutrients, did not contribute significantly to the pH trend in this turbid estuary. Particulate suspended matter concentrations in the Ems-Dollard estuary have increased due to dredging activities, which may have contributed to the attenuation of its seasonal pH signal (Fig. 4e) by intensifying light limitation of primary production.

All coastal systems, but the Ems-Dollard estuary, show pH decreases during the most recent years (Figs. 3, 4). This decline in pH is small and recent for the Western Scheldt and the Wadden Sea, but in the Eastern Scheldt and coastal North Sea waters pH has decreased significantly since 1987. In the Eastern Scheldt this decline happened after a major increase in the mid-1980s. This corresponds to the construction of the storm-surge barrier and two dams in 1986, whereby the residence time was increased and the freshwater load decreased (Wetsteyn and Kromkamp, 1994).

The time series from the North Sea exhibit a continuous decline of pH since the mid-1980s (Fig. 4a). Although methodology has changed twice during that period, this

Table 1. North Sea primary production measurements.

area	location	time	reference	PP ($gC\,m^{-2}\,yr^{-1}$)
North Sea	coastal	1986	Moll (1998)	>300*
North Sea	off-shore	1986	Moll (1998)	150*
North Sea	coastal	1988–1990	Peeters et al. (1991)	>350
North Sea	off-shore	1988–1990	Peeters et al. (1991)	>150
Wadden Sea	west	1975	Philippart et al. (2007)	100
Wadden Sea	west	1985–2005	Philippart et al. (2007)	100–300
Eastern Scheldt	west	1980–1984	Wetsteyn and Kromkamp (1994)	300–550
Eastern Scheldt	west	1987–1990	Wetsteyn and Kromkamp (1994)	250
Eastern Scheldt	central	1980–1984	Wetsteyn and Kromkamp (1994)	250–400
Eastern Scheldt	central	1987–1990	Wetsteyn and Kromkamp (1994)	250–300
Eastern Scheldt	east	1980–1984	Wetsteyn and Kromkamp (1994)	200–400
Eastern Scheldt	east	1987–1990	Wetsteyn and Kromkamp (1994)	250
Western Scheldt	east	1991	Kromkamp and Peene (1995)	100
Western Scheldt	west	1991	Kromkamp and Peene (1995)	300
Ems-Dollard	west	1976–1980	Colijn et al. (1987)	300
Ems-Dollard	central	1976–1980	Colijn et al. (1987)	100
Ems-Dollard	east	1976–1980	Colijn et al. (1987)	100

*simulation

decreasing trend is confirmed by regressions over a period with consistent methodology (Fig. 5). This means that acidification is happening at rates exceeding 0.02 pH units per year, which is on order of magnitude higher than what is to be expected from atmospheric CO_2 increasing at almost 2 ppm per year (0.0013–0.002 per year). The strong decline of pH in the North Sea implies that CO_2-induced acidification is obscured by changes induced by other biogeochemical processes. One such process contributing to pH decline could be atmospheric nitrogen and sulphur addition (Doney et al., 2007), but atmospheric deposition rates have declined rather than increased during the last two decades (Brion et al., 2004). Keeping in mind the influence of biogeochemical processes on pH as described above, it appears that the observed long-term trend is likely linked to the modified balance between primary production and respiration. A decrease in pH implies a decrease in primary production or increase of respiration during the last few decades. A decrease in primary production is likely given that both nitrogen and phosphorus have been decreasing since the early 1980s (McQuatters-Gollop et al., 2007; Van Engeland et al., 2010).

Recently, Borges and Gypens (2010) presented model simulations of the pH evolution in the Belgian coastal zone. They obtained increasing pH values for the period 1951 to 1990 and declining pH values since then. The decline in pH since 1990 was attributed to a shift in ecosystem metabolic balance from net autotrophy to net heterotrophy because of declining nutrient input and increased N:P ratio of incoming Scheldt estuary water (Soetaert et al., 2006). Nutrient loadings of the river Rhine and its tributary river IJssel have also declined and this has resulted in lower primary production rates in the Wadden Sea and coastal North Sea (Philippart

et al., 2007). Since 1974, the Royal Netherlands Institute of Sea Research (NIOZ) has monitored algal biomass and primary production of coastal North Sea water entering the Wadden Sea. Annual phytoplankton primary production initially increased from about 150 to $350\,gC\,m^{-2}yr^{-1}$, and decreased again to $200\,gC\,m^{-2}\,yr^{-1}$ between 1990 and 2000 (Cadée and Hegeman, 2002). A modelling study of the Belgian coastal zone shows a very similar trend, with a drop from over $300\,gC\,m^{-2}\,yr^{-1}$ to less than $200\,gC\,m^{-2}\,yr^{-1}$ between 1990 and 2000 (Lancelot et al., 2007). This decrease in primary production is consistent with the lower pH values that have been measured the last decade (Fig. 4). The model predictions of Borges and Gypens (2010) support our hypothesis that changes in biogeochemical processes due to changes in nutrient loadings override atmospheric CO_2-induced acidification effects. A preliminary analysis of other variables available through the Waterbase public-domain dataset, such as salinity and chlorophyll-a, did not reveal any long-term patterns that could be related to the decline in pH. However, Van Engeland et al. (2010) performed a detailed analysis of dissolved nitrogen cycling and extracted a long-term trend for ammonium that was very similar to that of pH, but it is not clear how these two are mechanistically related.

5 Conclusions

In summary, our data show that ocean acidification is not exclusively linked to changes in atmospheric CO_2, and could therefore be of a much greater magnitude and less predictable than previously thought, at least in coastal systems. This has recently been confirmed by Wootton et al. (2008), who

observed a similar decline in pH and consequent effects on benthic organisms at a temperate coastal site in the Pacific. Changes in nutrient availability and the related biogeochemical processes were identified in this study as possible drivers of pH in Dutch coastal waters, consistent with model simulations of Borges and Gypens (2010). The availability of an extensive and long-term dataset on pH was essential for identifying seasonal and long-term trends, but the analysis was challenging because of several methodological changes and lack of proper calibration procedures. With this study we have identified a need for high-quality extensive monitoring of pH in different systems, not only for evaluating ocean acidification, but also because it gives valuable information on ecosystem functioning. Furthermore, the possibility of short-term changes of pH at rates considerably larger than those expected from oceanic carbon dioxide uptake should be taken into account for experimental design and assessments.

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