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Ocean Acidification in the Gulf of Mexico: Eutrophication-induced Hypoxia and Maritime Shipping

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Abstract

Ocean acidification is a growing problem throughout the world. Initial focus on the cause of the declining pH largely ignored the problem of eutrophication, a coastal phenomenon caused by large influxes of nutrients, which rapidly degrade the quality of interior waters. The hypoxia associated with eutrophication promotes a reduction in pH. Additionally, gaseous products from the burning of shipping fuels may also be acting to alter the biochemistry of the water in coastal regions. However, the extent to which both eutrophication-induced hypoxia and shipping have on acidification remains unknown. There appears to be much controversy over the feedbacks associated with these processes, most noticeably on the production of the nitrous oxide in hypoxic zones. An examination of literature indicates shipping has only a slight effect on ocean pH with eutrophication being the main contributor. If significant effort is made to reduce anthropogenic nutrient inputs, the impacts on the ecosystem caused by eutrophication could be reversed, but some changes, such as reduced pH, may be harder to combat due to a reduced buffering ability in the Gulf.

Keywords

Eutrophication, Hypoxia, Ocean Acidification, Shipping, Gulf of Mexico, Nitrous Oxide

Introduction

In the last 250 years, atmospheric carbon dioxide (CO_2) levels have risen by 40% (Doney et al, 2009) primarily due to anthropogenic emissions. Deforestation, burning of fossil fuels, and industrialisation have had widespread ramifications for the atmosphere and ocean. Rapid uptake by the oceans from increased atmospheric concentrations has altered the ocean's ability to buffer the effect of the added CO_2, reducing the capacity of the ocean to absorb the gas and in the process, promoting changes to multiple biogeochemical cycles. Upon uptake, CO_2 is involved in a series of reactions, culminating in the production of Hydrogen ions (H^+) which act to reduce the pH of surrounding waters (Doney et al 2009). This is termed ocean acidification (OA). The increase in atmospheric CO_2 since the industrial revolution is perhaps the most defining cause of this pH change where, since the start of industrial revolution, 50% of the world's atmospheric CO_2 has been absorbed by the oceans (Royal Society, 2005). However, it is not just increased CO_2 causing pH to decline; another anthropogenic problem, eutrophication, has been found to alter the chemistry of the water and result in a change in pH. Eutrophication, is caused by an influx of nutrients from agricultural runoff, waste, and atmospheric inputs (Sunda and Cai 2012), most commonly into estuaries and coastal waters. When this occurs, rapid primary production produces algal blooms in the surface waters, promoting respiration and creating hypoxic zones at depth. This, in turn, causes CO_2 production from organic matter (OM) degradation, which increases acidity. Below the pycnocline, where hypoxia develops, additional acidification occurs (Cai et al 2011) due to consumption of O_2 from OM exported from the riverine discharge (Figure 1).

[Figure 1 near here]

Having only been acknowledged as a serious environmental problem since the 1980s, few long term experiments have been carried out (Goody et al 2009), making it difficult to fully understand changes to marine environments as a result of human activities. One comprehensive study on eutrophication-induced hypoxia and acidification is the work by Cai et al (2011) in the northern Gulf of Mexico (nGOM). As an area influenced by large volumes of fresh water and nutrients from nearby rivers, the nGOM is very susceptible to eutrophication. Additionally, the nGoM has a high volume of shipping activity which can result in pollution from ocean-going vessels that also alters the carbonate system. The aim of this literature review is to examine the nGoM and to better understand the processes causing OA.

Northern Gulf of Mexico

Eutrophication Induced Hypoxia and Ocean Acidification

The nGoM, a large semi-enclosed basin (Figure 2), contains one of the largest anthropogenic hypoxic zones in the world (Díaz and Rosenberg 2008) reaching 20000 km^2 and lasting up to 10 months a year (Rabalais et al, 2009). The main factors driving low oxygen concentration below the pycnocline are stratification, river discharge and nutrient loading (Liu et al, 2010). In the nGoM, the Mississippi-Atchafalaya River Basin is the main source of freshwater and nutrients. The Mississippi River is among the top ten rivers in the world for volume of discharge (Rabalais et al, 2009), discharging 380 km^3yr^{-1} of freshwater (Bianchi et al, 2010). The continuous freshwater supply from the rivers supports stratification year round, preventing mixing of hypoxic waters with high O_2 waters above (Liu et al, 2010). Additionally, surface warming in the summer acts to strengthen stratification, worsening the problem (Rabalais et al, 2009).

[Figure 2 near here]

The large riverine flux inputs freshwater, nutrients, and organic and inorganic carbon into the nGoM with the changes in water chemistry negatively impacting the carbonate system. Over the last 50 years, the stoichiometric balance of riverine inputs into the nGoM has changed, increasing the nitrate flux into the system by ~300% (Greene et al, 2009) to over 500kg N km^{-1} yr^{-1} (Howarth et al, 2011), promoting eutrophication (Rabalais et al, 2009). Exchange of deep waters onto the shelf is more limited in the nGoM than most other continental shelves. This can transport enriched nitrate waters further afield, expanding the region susceptible to the effects of nitrate enrichment, increasing the spatial extent of the nGoM hypoxic zone (Howarth et al, 2011) and areas of low pH.

The hypoxia within the nGoM has severely stressed the natural ecosystem of the shelf, with pelagic species experiencing habitat compression due to a shoaling of low oxygen waters, and demersal species and benthic communities displaying aberrant behaviour, migrating to regions of higher O_2 and vastly depleting densities in the hypoxic zone (Breitburg et al, 2002). The nGoM is also home to deep-water coral reefs which will likely suffer dissolution due to OA. Despite the biological impacts being fairly well constrained, the coupling of hypoxia with an increase in CO_2 has been sparsely acknowledged (Melzner et al 2013).

In their study, Cai et al (2011) observed a seasonal trend of surface water eutrophication in the spring and summer accompanied by hypoxia in subpycnocline waters which became more extensive as the summer went on. This hypoxia coincided with small areas of low pH in the spring, followed by prevalent areas of low pH by the end of the summer. Cai et al (2011) believe this irregular change in pH to have acute consequences on the interaction of OA with biochemical processes, such as those where respiration of OM adds CO_2 into the dissolved inorganic carbon pool. Further study by Cai et al (2011) discovered a strong, positive correlation between the subsurface pH and O_2, thereby linking the low pH with O_2 depletion as a result of OM mineralisation. This outcome was termed 'enhanced ocean acidification' (Cai et al 2011) and is predicted to drastically lower carbonate saturation state.

Shipping

The nGoM is a major shipping channel (Figure 2). Many of the ocean-going vessels (OGVs) in the nGoM use fuels that produce nitrogen and sulphur oxides, or SO_x and NO_x, which are deposited into the ocean. With short residence times in the atmosphere, the effects are particularly noticeable in coastal regions and areas of intensive shipping (Hagens et al, 2014). The oxides are deposited as the acids sulfuric acid (H_2SO_4) and nitric acid (HNO_3) which cause a decrease in total alkalinity (TA) of the water (Hunter et al, 2011). TA is the excess of weak bases in seawater (Dickson, 1981). When the addition of CO_2 stimulates dissolution of calcium carbonate, TA changes and causes an increase in acidity (Hunter et al, 2011). However, the pH changes after re-equilibration have been found to be negligible (Hunter et al, 2011). This appears somewhat disputed as Hassellov et al (2013) suggest regional pH reductions are of the same order of magnitude as the CO_2-driven acidification in heavily trafficked waters due to the acids being stronger than carbonic acids formed from CO_2 dissolution. The largest effects of SO_x and NO_x occur in regions where stratification focuses the anthropogenic inputs into a relatively shallow surface mixed layer and in smaller, heavily trafficked basins. As an intensively shipped region susceptible to stratification, the nGoM likely sees large impacts on pH from NO_x and SO_x. The nGoM is already seeing major consequences to the buffering system as a result of eutrophication, so any additional decline in pH will have significantly negative impacts on the biochemistry. It is believed the oxides effectively shut down much of the ocean uptake of anthropogenic CO_2 effectively reducing pH change; however, it should be noted this is at the expense of the important contribution of surface waters as a sink for anthropogenic CO_2 (Hunter et al, 2011).

Nitrous Oxide

Nitrous oxide (N_2O) is a greenhouse gas produced in anoxic conditions in the ocean. With a radiative forcing 200-300 times more powerful than CO_2 (Manne and Richels, 2001), N_2O is one of the most ozone depleting gases on the planet (Khalil and Rasmussen, 1992) and as such its production should be monitored closely. N_2O is produced at depth by nitrifying and denitrifying bacteria under oxic and anoxic conditions, respectively. N_2O and O_2 have an inverse relationship, resulting in large amounts of production in hypoxic zones. This is of concern due to the expansion of oxygen minimum zones (OMZs) across the world over the last 50 years (Stramma et al 2008). As these OMZs increase in size and intensity, production of N_2O will likely increase, resulting in greater emissions into the atmosphere. N_2O is formed as a by-product in nitrification and as an intermediate product in denitrification (Figure 3) and although produced at depth beneath the pycnocline, ventilation pathways due to upwelling can release the gas into the atmosphere (Nevison et al, 2004).

[Figure 3 near here]

As atmospheric CO_2 concentrations have increased, there has been a decrease in ammonia oxidation rates of up to 44%, reducing N_2O production by up to 0.8 Tg N yr^{-1} (Beman et al, 2011) (Figure 3). Additionally, as nitrification rates decline, so too will denitrification rates, further reducing N_2O production; however, there is much controversy in the scientific community regarding N_2O production and pH change so further examination is required.

Discussion and Conclusion

The effects of rises in atmospheric CO_2 alone are extremely detrimental to the oceans. Since pre-industrial times, oceans have seen H^+ concentration increase by ~31%, culminating in a pH decline of up to 0.12 units (Sunda and Cai, 2012). Projections predict pH will decrease a further 0.2-0.3 units by the end of the century (Sunda and Cai, 2012). When additional acidification is considered on top of this, it is likely some regions will exhibit changes much greater than 0.3 units by 2100. In some of the nGoM, seasonal change alone is thought to be as much as 0.35 units (Cai et al, 2011). As this continues to worsen, the capacity of the water to buffer the change will decline further, leaving the nGoM unable to return to typical values observed in the winter.

The nGoM is not the only coastal region found to be particularly susceptible to acidification from eutrophication-induced hypoxia; the East China Sea (Cai et al, 2011) and the Baltic Sea (Sunda and Cai, 2012) both show a decline in water quality because of eutrophication. The work by Cai et al (2011) provided compelling evidence that eutrophication-induced hypoxia is causing decline in pH in both the East China Sea and the nGoM, and should be considered as a serious problem in marine environments. Howarth et al (2011) were in agreement with the findings of Cai et al (2011); however, they posit tropical estuaries and coastal regions are more susceptible to pH change from eutrophication due to larger riverine fluxes of nutrients. Nevertheless, the effect of eutrophication on the carbonate system has been contested; Borges and Gypens (2010) suggest the more nutrients from rives in the surface waters of an estuary, the larger the counter effect on acidification.

If careful effort is made, the nutrient input into the Gulf could be significantly reduced. This should help to reduce seasonal change in pH observed within the OMZ; however, there is always a tipping point in the ecosystem where the ability to reverse the change can become impossible. If the nGoM has reached this tipping point, it is likely the situation will only worsen. It is important other OMZs are not left to become as bad as the nGoM. From the literature available, it is likely shipping has only a slight impact on the pH when compared to the effects of eutrophication but this effect should not be ignored. Further investigation in the nGoM should be carried out not only on the implications of eutrophication-induced hypoxia but also on the impacts of shipping.

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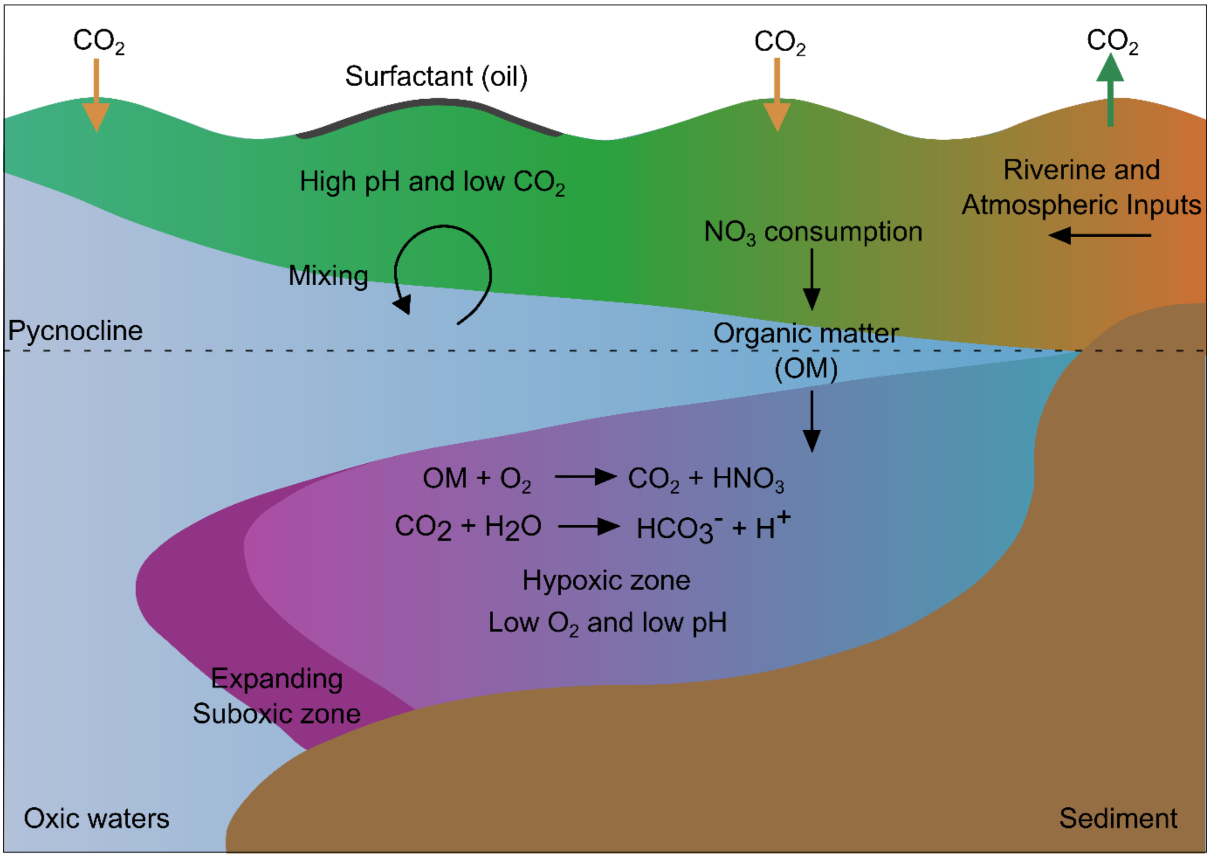

Figure 1 - Simple schematic of eutrophication-induced hypoxia. Nutrients are deposited in the surface waters and are utilised by phytoplankton. Organic matter degradation at depth can result in consumption of oxygen, producing CO_2 as well as other products. The CO_2 then reacts with the water to produce hydrogen ions culminating in reductions in pH. There is no mixing between the water above and below the pycnocline so the deep waters are rarely ventilated and can lead to expanding of the low oxygen regions (dark purple). The surfactant on the surface prevents air-sea flux. Adapted from Cai et al (2011).

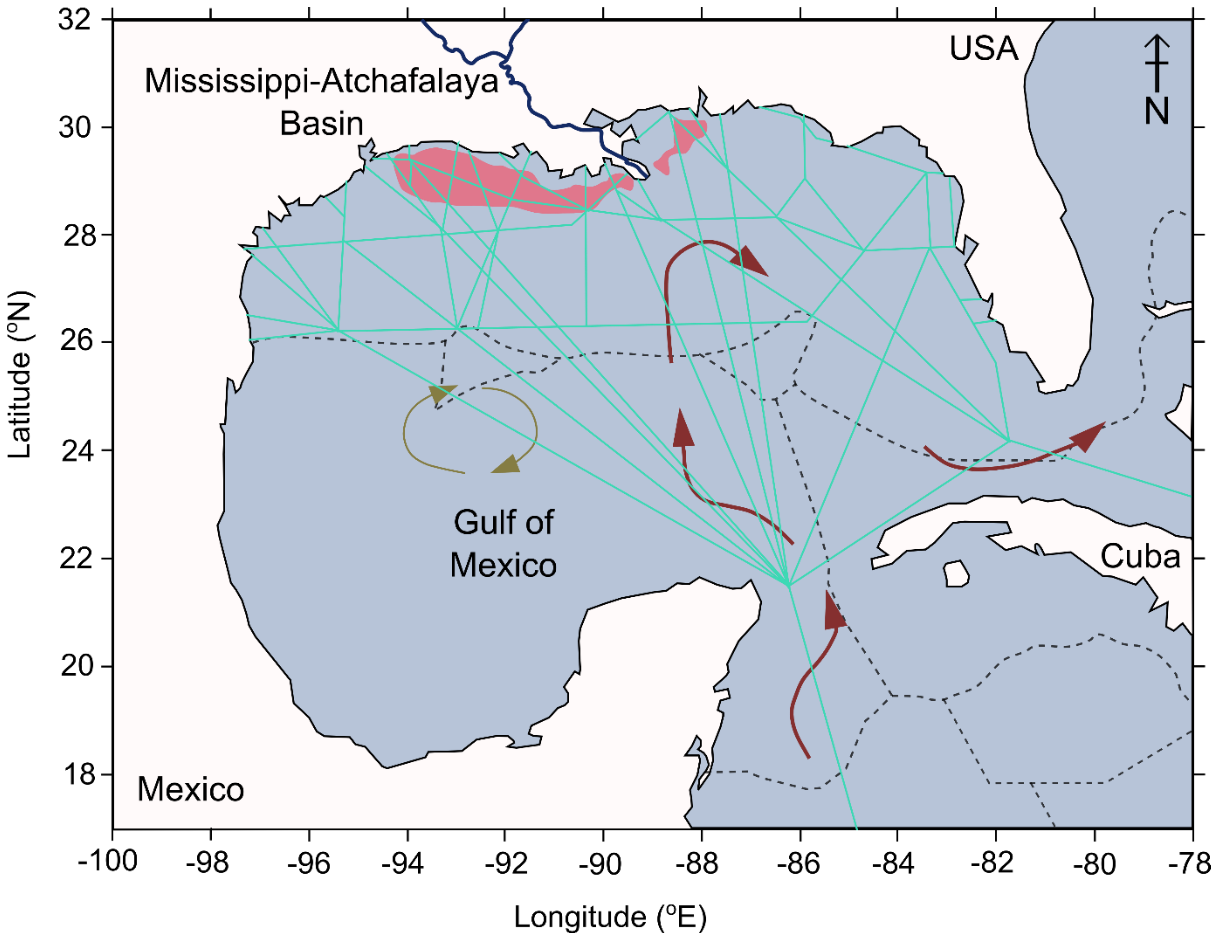

Figure 2 – Simple map of the Gulf of Mexico. The map highlights the region of low oxygen (pink regions), or dead zone, in the north of the Gulf. On top (light blue lines) are the major shipping routes, many of which pass over the dead zone. The Mississipi-Atchafalaya rivers are also included (dark blue line). The mouth of the rivers coincides with the dead zone. The dark red arrows show the route of the Loop Current and the yellow arrows represent the large eddy within the centre of the Gulf. The dashed lines indicate economic exclusion zones. Adpated from various figures in Love et al (2013).

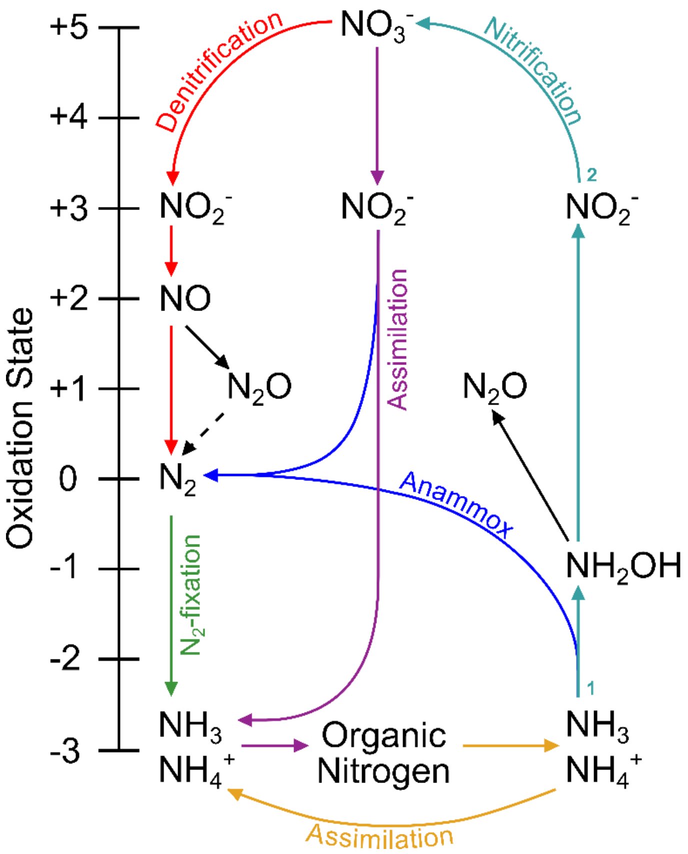

Figure 3 - Simplified diagram of the marine nitrogen cycle. Occurring in several stages, the cycle produces N_2O during nitrification (pale blue) and denitrification (red) as a by-product and intermediate, respectively. Within nitrification, there are two processes: ammonia oxidation (1) and nitrite oxidation (2). N_2-fixation (green), where N_2 is transformed into fixed nitrogen, and assimilation (purple and yellow) both produce ammonia and ammonium. Assimilation from nitrate (purple) to ammonium is known as dissimilatory nitrate reduction to ammonium. Anammox (dark blue) involves both nitrite and ammonia to produce dinitrogen. Adapted from Codispoti et al (2001).

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