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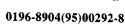
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EFFECTS OF CO$_2$ ON THE OCEAN ENVIRONMENT

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Abstract – The most immediate environmental effect of solving CO$_2$ in the ocean is a reduction of the pH. The present rate of change of pH in the surface mixed layer due to invasion of anthropogenic CO$_2$ from the atmosphere is close to 0.015 pH units per decade. A cumulative reduction of 0.1 units has already taken place during the past 200 years, and a further reduction of 0.2 to 0.3 pH units may occur in the next century. This perturbation may be compared to the existing range of pH in the world ocean of 0.5 pH units, a seasonal amplitude of up to 0.1 pH units locally, and to glacial to interglacial variations of 0.2-0.3 pH units in 10 000 years (0.0003 pH units per decade). Emissions to the atmosphere expose species in almost all ocean surface waters, including high productivity zones, to permanent and uniform reduction of pH. Disposal of CO$_2$ at fixed locations in the ocean can give strong maximum pH reduction at depth where natural variability in pH is smaller and tolerance limits for biota probably narrower.

1. INTRODUCTION

It is well established that emissions of CO$_2$ to the atmosphere may contribute to climate change [1]. This has been the motivation to investigate mitigation options including ocean dissolution of CO$_2$. When CO$_2$ is added to seawater, the pH-value of the water decreases, i.e. it becomes acidified, with potential detrimental effects on marine life [2]. In this paper we briefly review the natural variability of pH in the ocean, and then assess and compare the effects of CO$_2$ on ocean pH in two different cases.

The first case is the business-as-usual scenario, i.e. continued emissions of CO$_2$ to the atmosphere followed by uptake across the air-sea interface. There has already been a noticeable change in ocean carbon chemistry during the past 200 years due to invasion of anthropogenic carbon from the atmosphere [3] [4] [5]. The anticipated future increase in inorganic carbon content in the oceans may lead to significant reductions in pH as noted by Cole *et al.* [6]. In the present paper we elaborate on the rate of reduction of pH, assuming that there exists some upper limit to the rate of environmental change that marine biota will be able to tolerate and adapt to.

The second case is that of direct disposal of CO$_2$. Attention is restricted to dissolution in the water column, i.e. away from the ocean floor. Disposal at depth from a pipe towed by a moving ship [7] has the potential to ensure rapid dilution and thus little or no harm to the marine environment. However, a fixed installation with CO$_2$ supplied via subsea pipeline may be the preferred option since it is probably cheaper, particularly if large diameter pipes are used [8].

Release of liquid CO$_2$ from a fixed point nominally at 1000 m depth would reduce the local pH by 2-3 units within a dissolution zone of a few hundred meter vertical extent and a few tens of meters horizontal extent [9]. Stegen *et al.* [10] used a global ocean circulation model to estimate long term pH perturbations due to disposal of the order 0.01-0.05 pH units in grid cells with several hundred kilometer horizontal extent. We briefly review oceanographic processes that would affect mixing and dilution on temporal and spatial scales between the plume scale and the global scale.

2. NATURAL AND ANTHROPOGENIC pH VARIATIONS

Natural variations

Values of pH ($= -\log[\mathrm{H^+}]$) in the ocean typically range from 7.7. to 8.2 [11]. The highest pH values are found at the surface in high latitudes in summer, and the lowest pH values prevail at depth in 'old' water. There is some ambiguity in the definition of scales and equilibrium constants, which makes it difficult to combine or compare field measurements obtained by different techniques [11]. However, in theory only two of the four parameters: total dissolved inorganic carbon, total alkalinity, partial pressure of CO_2 (pCO_2) and pH that characterize the carbonic acid system in seawater are needed (in addition to temperature and salinity) in order to calculate the other two.

We have used a modified version of the routine described in [12] to calculate pH. Observations from the North Atlantic [13] show seasonal reductions of total inorganic carbon content by 60 to 130 μmol kg^{-1}, accompanied by a 60 to 130 μatm reduction in pCO_2. The reduction in pCO_2 is explained by the transformation of inorganic carbon to organic matter during the spring bloom in combination with the opposing effect of seasonal warming. The associated pH reduction is mainly controlled by the reduction in inorganic carbon and amounts to approx. 0.1 pH units. There is no similar spring bloom in the North Pacific as in the North Atlantic, but winter upwelling of deep waters rich in CO_2 creates a similar amplitude of the seasonal inorganic surface carbon variations [13], and thus also of the pH. Towards the equator, the seasonal amplitude drops significantly in all oceans, although occasional reduction in near surface pH due to upwelling of carbon rich water cannot be ruled out. Below the euphotic zone, i.e. the upper 100-200 m, there is everywhere a very small seasonal variation of pH.

The evolution of ocean pH in the past has been reconstructed based on the pH-dependence of the fractionation of boron isotopes between sea water and precipitated carbonate minerals [14]. 21 million years ago the surface ocean pH was only 7.4 ± 0.2 [14], which is consistent with independent estimates of high atmospheric CO_2 content at that time. During the last glaciation, the surface water pH of the tropical Atlantic and Pacific oceans was 0.2 ± 0.1 higher than in the Holocene, and the pH of deep water was 0.3 ± 0.1 higher than in the Holocene [15]. The time from the last glaciation to the Holocene is of order 10 000 years, giving a rate of change of pH associated with the transition from glacial to interglacial conditions of the order 0.0003 pH units per decade.

Effects of CO_2 emissions

CO_2 emitted to the atmosphere is equilibrated with surface water on a time scale of a few years. Also water in upwelling regions is affected by anthropogenic CO_2, partly because the upwelling water is normally young enough to have been ventilated towards an anthropogenically modified atmosphere, but also because the natural outgassing in such regions is reduced due to the increased atmospheric CO_2 pressure. Perturbation in mean dissolved inorganic carbon and pH over almost the entire ocean surface can therefore easily be calculated from a given atmospheric pCO_2 and background oceanographic data [12].

The cumulative decrease in ocean surface pH due to the increase of atmospheric CO_2 from the preindustrial level of 280 ppm to the present 360 ppm is found in this way to be almost 0.1 pH units in cold waters and slightly less than 0.09 pH units in the warmest surface waters. The rate of change of atmospheric CO_2 was 15 ppm per decade in the 1980s [1], which is found to correspond to a rate of reduction of 0.015 pH units per decade.

In the next century, there is a wide range of possible emission scenarios [1]. Most of these lead to an increase in the rate of change of concentration as time evolves. In view of the many uncertainties of future scenarios, we calculate the pH evolution for three different rates of change of the atmospheric CO_2 content: one low of 15 ppm per decade, one intermediate of 30 ppm per decade and one high of 45 ppm per decade. The results are summarized in Tab. 1. The highest of these scenarios assumes total emissions in the next century of about 2000 GtC, which is still considerably less than that corresponding to the entire fossil fuel reserve.

It is seen from Tab. 1 that a further reduction in pH of 0.2-0.3 units may occur in the next century in addition to the 0.1 reduction that has already taken place. This effect occurs almost uniformly over the entire ocean surface, so there is no way for marine life in the euphotic zone to avoid the reduced pH.

Table 1: Rate of change of pH and cumulative reduction in pH for given increase of pCO_2, and for two different water temperatures corresponding to high and low latitudes. Alkalinity is kept at 2300 μeq kg^{-1}, and initial pCO_2 is the present value of 360 ppm. The 15 ppm per decade case is close to the present situation, but 300-450 ppm increase may well be more realistic than 150 ppm on a time scale of 100 years from now.

Scenario		Rate of change of pH (pH units per decade)	Cumulative reduction (pH units after 100 years)
15 ppm per decade	5 °C	0.016	0.086
	25 °C	0.014	0.079
30 ppm per decade	5 °C	0.031	0.238
	25 °C	0.028	0.219
45 ppm per decade	5 °C	0.045	0.321
	25 °C	0.041	0.296

Effects of ocean dissolution of CO₂

For release from a moving ship [7], the wake behind the towed pipe contributes to dilution, similar to the dispersion of other discharges directly from a moving ship [16]. If small droplets can be sprinkled through the towed pipe, and if hydrate shells do not significantly impair dissolution, a rapid dissolution and small local pH reduction will be obtained. Release from a moving ship is probably the most environment-friendly way to perform ocean disposal.

Release of liquid CO_2 from a fixed point nominally at 1000m depth is expected to create a rising droplet plume above the release depth [9]. Inside the tall (100m or more) and narrow (approx. 10m radius for CO_2 from a 1-2 GW power plant [9]) plume, conditions with pH of 5-6 are unacceptable to most forms of marine life. This would also be the case within downward flowing plumes driven by release of pre-dissolved CO_2, e.g. created by gas lift in an inverted U-tube [17].

Stegen et al. [10] used a global ocean circulation model to estimate long term pH perturbations of order 0.01-0.05 pH units in the grid cells closest to the sites of disposal from a 1 GW coal-fired power plant. On the resolution of such models (275km × 275km at the equator) there is no distinction between disposal from ship or from a fixed point. The largest pH perturbations occur in locations with weak large scale currents, i.e. where the dilution in the model is mainly effected by sub grid scale processes parameterized as diffusion.

If the large scale mean pH perturbations are deemed to be acceptable, there is a need to investigate dispersion and mixing on scales intermediate between the dissolution or plume scale of approx. 100m and the large scales above 100 km. Coarse global models appropriately use explicit sub grid scale diffusivities of order 100-200 m^2 s^{-1} or larger [18] [19], which is large enough to dominate over numerical diffusion [19] [20]. Models with finer resolution should generally use smaller diffusivities since they would explicitly resolve smaller scale currents. While effective diffusivities in shelf areas have been estimated in several experiments [21] and a wide range of values are used in advection-dispersion models [22] depending on the physical conditions in the modelled area, there is less data for intermediate to deep ocean conditions.

A few tracer release experiments, while primarily directed at estimating vertical mixing, have also provided relevant estimates of horizontal diffusivities. An experiment with release at almost 800 m depth about 50 km off the coast near Los Angeles indicated relevant horizontal diffusivities of order 20 m^2 s^{-1} and time scales of 2 to 5 months for reduction of the high streak concentrations obtained by the injection technique down to almost homogenization in the Santa Monica Basin [23]. A similar experiment in the middle of the North Atlantic with release at just over 300m depth indicated horizontal diffusivities of about 3 m^2 s^{-1} [24]. It is quite possible that appropriate diffusivities for the relatively quiescent conditions in the deep ocean below the thermocline are even lower. If so, and if disposal is performed in locations with weak large scale circulation, local mean pH reductions on scales of a few km may be considerably more severe than the large scale mean of 0.01 to 0.05 pH units cited above.

An issue for research is the transition from plume dilution to ambient turbulent mixing [25]. If streaks and filaments of strongly reduced pH water emanating from the dissolution zone can

persist in the environment for days and weeks, the environmental impact of the maximum pH perturbation could be more severe than that of the flux-averaged mean perturbation [26].

3. CONCLUSIONS

If emissions continue, the consequent reduction of near surface pH in large parts of the world ocean will approach the limits of natural variability and may go beyond pH acceptance limits for marine biota. Subsequent effects on organisms and ecosystem structure are not well known. There is no reason to expect dramatic changes, but the possible effects of increasing atmospheric CO_2 on marine life may be a concern regardless of the severity of the greenhouse effect of CO_2.

One of the alternative scenarios, large scale dissolution in the ocean, could have negative effects deeper in the water column, but would, like any CO_2 mitigation or reduction option, reduce the impact in near surface waters. The natural variability of pH at the disposal depths is smaller than in the euphotic zone, so ecosystem tolerance limits are expected to be narrower. On the other hand, most of the biological production including that part which is important for commercial fisheries occurs in the upper layers.

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