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REVIEW

Effects of pH on coastal marine phytoplankton

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ABSTRACT: Twenty-one studies on the effects of pH on marine phytoplankton were found and are herein reviewed. Under laboratory conditions, the optimum pH for growth is between pH 6.3 and 10. Some species can grow well at a wide range of pH, while others have growth rates that vary greatly over a 0.5 to 1 pH unit change. Different clones of the same species were found to have slightly to strikingly different relationships between pH and growth rate. The pH in typical coastal environments may vary by 1 or more pH units, with over 10% of observations being more than 0.5 units above or below equilibrium pH. This range is great enough, relative to the observed pH effect on growth rate for many species, for seawater pH to affect the growth rate, and hence the timing and abundance of coastal marine phytoplankton species. Effects of pH are not limited to extreme pH conditions. The growth rates of some species are influenced significantly by changes in pH near the equilibrium pH of coastal seawater. Care must be taken in growth experiments with phytoplankton to avoid effects due to pH of the culture media. Eutrophication of coastal waters may amplify the range of pH found in coastal environments.

KEY WORDS: pH · Phytoplankton · Eutrophication

INTRODUCTION

The pH of seawater in the open ocean falls within a fairly narrow range, typically 0.3 pH units (Skirrow 1975). In contrast, the pH of coastal waters varies by a much greater range. However, little attention has been paid to the effects of pH on the growth rate and ecology of marine phytoplankton, including those in coastal waters, perhaps because of an open-ocean view of 'a constant pH of seawater'. Authoritative volumes that review the ecology of marine phytoplankton usually do not consider pH as one of the possible factors that influences the growth rate or ecology of marine phytoplankton species. It is rare even to find pH listed as an index entry in such works.

This is in sharp contrast to the literature on freshwater phytoplankton. The sensitivity of lake phytoplankton to pH is of great interest, especially as a result of anthropogenic acidification of lakes. Studies have shown that the species composition of phytoplankton communities in lakes is highly correlated with lake pH (e.g. ter Braak & van Dam 1989, Dixit et al. 1992). It appears possible to discern pH differences in lakes as small as 0.1 pH unit by observing the phytoplankton community structure.

The objective of this paper is to review the pH range in coastal marine environments and assess its influence on the growth rate and ecology of marine phytoplankton. Examples of pH variability in coastal waters are given. Processes leading to pH variability are discussed briefly. The modest volume of literature that has addressed the effects of pH on marine phytoplankton is then reviewed. The information is primarily on growth rate, substrate uptake rate or final population size studies on individual species in culture. Some information is also available on mixed populations in marine enclosures and field populations.

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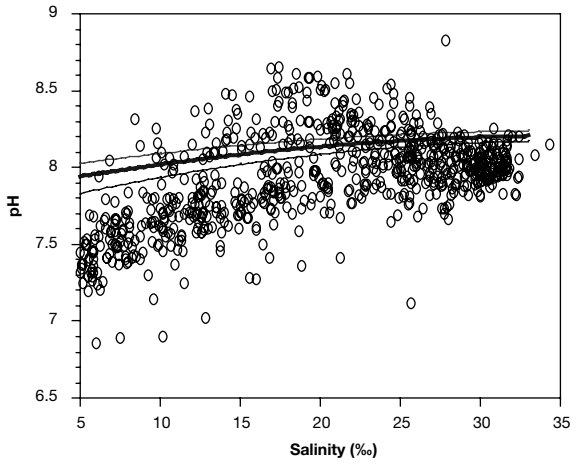

Fig. 1. Observed pH values (○) from a series of surveys in Delaware Bay (Sharp et al. 1980, Culberson et al. 1982, 1987a,b,c, 1988, Lebo et al. 1990). The equilibrium pH values (bold solid line) were calculated from the alkalinity-salinity relationship for the bay at 15°C. The envelope around the equilibrium pH represents the uncertainty in the equilibrium pH resulting from the variability in the alkalinity-salinity relationship and the temperature range for Delaware Bay

The origin of variability in coastal seawater pH

The pH of seawater responds to changes in: (1) the concentration of total dissolved CO_2; (2) alkalinity; (3) temperature; and for deep waters, (4) pressure (Skirrow 1975). In each case, the magnitude of change varies with salinity because the concentration of salt influences the various equilibrium constants and because several components of sea salt are involved in the acid-base reactions of seawater.

The equilibrium pH of surface seawater, for a given temperature and salinity, is the pH of seawater in equilibrium with CO_2 in the atmosphere. At equilibrium pH, the partial pressure of CO_2 in the seawater is the same as that in the atmosphere. In estuarine settings, there is usually a gradient in alkalinity between freshwater alkalinity and seawater alkalinity such that there is a resultant gradient in the equilibrium pH. An example of an estuarine gradient in equilibrium pH is shown in Fig. 1 for Delaware Bay. The upper and lower curves indicate the upper and lower boundary of the pH range resulting from variability in the temperature and the variability in the observed alkalinity-salinity relationship for these observations. The alkalinity of rivers averages about 1000 µeq l^{-1}, but may range from 100 to 5000 µeq l^{-1} (Stumm & Morgan 1996), so the equilibrium pH versus salinity relationship would be different in other estuaries. As the alkalinity of the oceanic end member of estuarine mixing gradients varies little, the equilibrium pH for the higher salinity portions of estuaries will most often be in the 8.0 to 8.2 range. Temperature effects on pH are relatively small. An increase of 20°C in seawater will decrease pH only by about 0.07 (at constant $ppCO_2$ and 30‰).

The gradient in equilibrium pH along a salinity gradient may be one factor that controls the appearance of different phytoplankton species along the salinity gradient. However, the focus of this review is the effect of variability in pH at a particular salinity or at a locale with a relatively narrow range in salinity. In Delaware Bay (Fig. 1), the observed pH values are up to 1.0 units below and 0.6 units above the equilibrium pH envelope.

Fig. 2 shows the observed pH and the equilibrium pH over time for a station in lower Narragansett Bay where the salinity ranges from about 29 to 31‰. Here, the observed pH is 0.5 units above or below the equilibrium pH at different times of the year. Where the pH deviates from equilibrium pH, the partial pressure of CO_2 in the water is correspondingly out of equilibrium with atmospheric CO_2.

Changes in alkalinity and temperature are reflected in the calculated equilibrium pH in Figs. 1 & 2. Hence, the deviations from the equilibrium pH are primarily caused by the metabolic processes of photosynthesis and respiration removing or injecting CO_2, respectively, from or to the water. CO_2 is taken up during plant growth, causing the pH to rise, and is released to water during respiration, causing the pH to fall. Fig. 3 shows the relationship between pH and total CO_2 concentrations for one set of conditions.

The alkalinity of seawater, and hence pH, is also affected by the metabolic uptake and release of nutri-

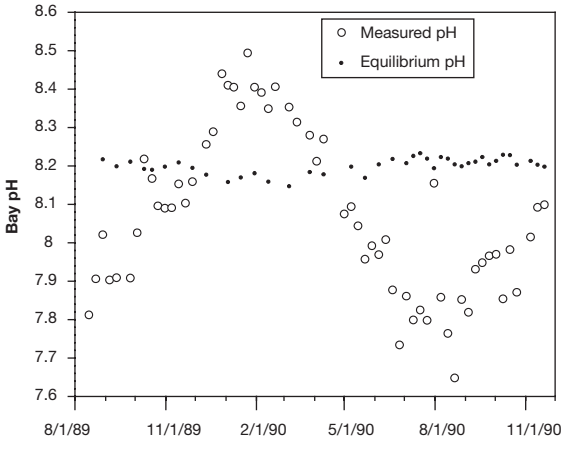

Fig. 2. Observed pH of seawater (○) in Narragansett Bay at the Graduate School of Oceanography pier in lower Narragansett Bay (Hinga 1992). Salinity at this location is 28 to 31‰. The equilibrium pH (•) was calculated for each sample from the measured alkalinity and temperature, and a CO_2 partial pressure of 352 µatm and salinity of 30‰. Dates are mo/d/yr

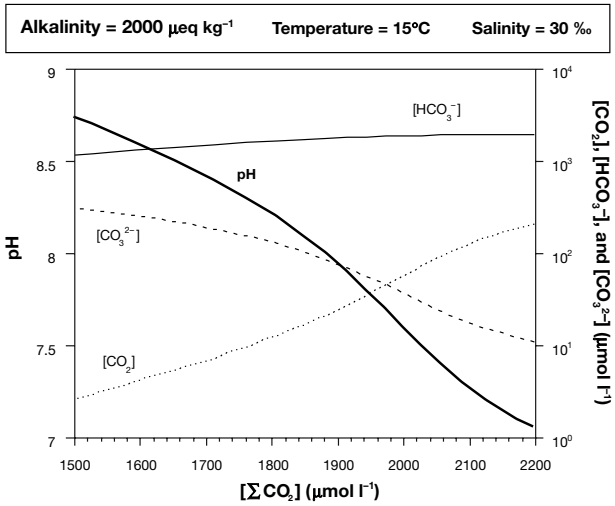

Fig. 3. Total CO_2 versus pH and concentration of CO_2 species. Concentrations and pH were calculated using the equations and constants from Skirrow (1975), Weiss (1974) and Plath et al. (1980)

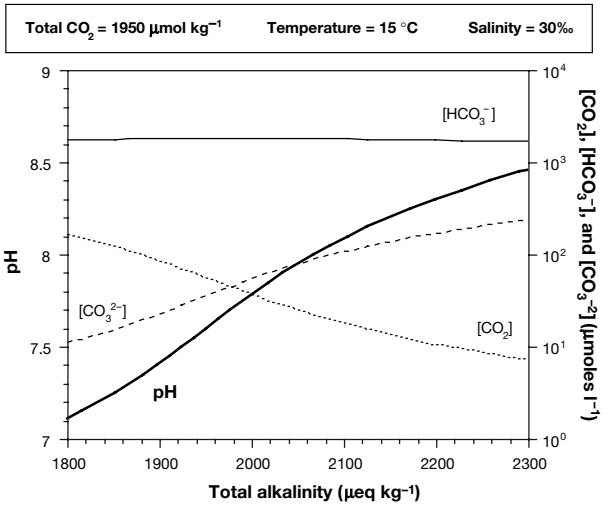

Fig. 4. Alkalinity vs pH and CO_2 species. See Fig. 3 legend

ents, especially the N nutrients (Stumm & Morgan 1996). Uptake of NH_4^+ decreases the alkalinity and lowers the pH. Uptake of NO_3^- increases alkalinity and raises pH. Fig. 4 shows the effect of alkalinity changes on pH and CO_2 concentrations.

Assuming a Redfield ratio for C and nutrients during respiration and plant growth, the changes in pH resulting from changes in total CO_2 can be considerably greater than the pH changes resulting from the proportional changes in alkalinity. This excludes anoxic conditions and conditions where precipitation of calcium carbonate ($CaCO_3$) takes place. Table 1 shows the case of a bloom resulting in the removal of 200 µmol CO_2, 29 µmol N as either NO_3^- or NH_4^+ and 1.9 µmol PO_4^{3-} from 1 l water. The results are provided for 2 conditions: (1) allowing no CO_2 exchange with the atmosphere; and (2) after re-equilibration of CO_2 with the atmosphere.

With an initial pH of 8.17, and with no exchange with the atmosphere, the decrease in CO_2 concentration drives the pH up by 0.40 pH units to 8.57 (Fig. 3). In comparison, the uptake of NO_3^- and PO_4^{3-} in the Redfield ratio to C uptake increases the alkalinity 35 µeq which causes a pH increase of only 0.077 (Fig. 4). Similar calculations can be found in Pruder & Bolton (1979), Stumm & Morgan (1996), and Goldman (1999). An example of nutrient decrease and pH rise over time in a marine enclosure may be seen in McAllister et al. (1961). If the bloom was supported by NH_4^+ instead of NO_3^-, the alkalinity would have decreased by 23 µeq (i.e. the net result of 29 µeq from NH_4^+ and ~6 µeq from PO_4^{3-}) and the pH decreased by 0.056. Any bloom supported by a combination of NO_3^- and NH_4^+ will have even smaller alkalinity driven effects on pH. After equilibration with the atmosphere, the pH change would only be that resulting from the alkalinity changes. It should be recognized that in a coastal environment, the highest concentration of plant C observed does not necessarily comprise all the inorganic C that has been recently removed from the seawater. Grazers and settling may remove significant portions of phytoplankton C that may not be immediately remineralized and transported from the waters containing the bloom (e.g. Rudnick & Oviatt 1986).

The magnitude of the pH change actually achieved in the seawater due to removal or injection of CO_2 by organism metabolism depends upon the rates of

Table 1. Changes in pH from phytoplankton growth with nutrients and CO_2 in the Redfield ratio. For a bloom which consumes: 1.9 µmol kg^{-1} PO_4^{3-}, 29 µmol kg^{-1} NO_3^- or NH_4^+, and 200 µmol kg^{-1} total CO_2, the following changes in seawater pH will occur before and after equilibration with the atmosphere. The initial conditions are pH = 8.17, alkalinity = 2000 µeq kg^{-1}, salinity = 30‰ and temperature = 15°C

Alkalinity change (µeq kg^{-1})	Total CO_2 change (µmol kg^{-1})	pH change initial	pH change after equilibration
+35 (NO_3^-)	0	+0.077	+0.007
−23 (NH_4^+)	0	−0.056	−0.004
0	−200	+0.40	0
+35	−200	+0.44	+0.007
−23	−200	+0.36	−0.004

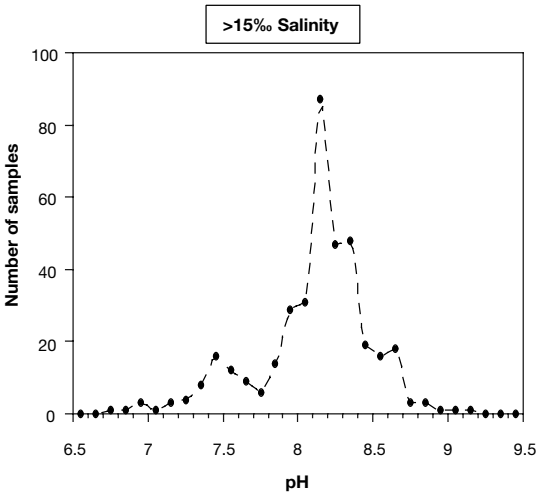

Fig. 5. Number of pH measurements in each 0.1 interval for the lower Chesapeake Bay between 1957 and 1963. Data is from Hires et al. (1963) and data reports cited therein

metabolic input or removal of CO_2 relative to the rate the body of water equilibrates with the atmosphere. The magnitude of metabolically driven changes in CO_2 concentration, and therefore variations in pH, depends on whether a body of water is quiescent or rapidly stirred by wind and waves so as to allow air-sea exchange to proceed quickly. For the Delaware Bay and Narragansett Bay examples shown in Figs. 1 & 2, it is clear that the metabolic processes are fast enough relative to equilibration with the atmosphere to achieve considerable disequilibrium.

Seawater pH in coastal environments

It is useful to examine the variability of pH in a few additional coastal environments to establish the range in pH that is found, and the frequency of different magnitude deviations from equilibrium pH. A series of surveys reported by Hires et al. (1963) provides a description of the pH variability in the Chesapeake Bay. Contours of pH indicated a patchy distribution of pH in the bay. During each of the 24 complete surveys (each taken over 3 d), there was a minimum difference of 1 pH unit between high and low patches of water (i.e. the difference in contour, not the difference between the absolute minimum and maximum measurements). The maximum difference during a single survey was 2 pH units between the highest and lowest contours. The estuarine gradient in equilibrium pH and seasonal temperature variability can only account for about 0.3 units of this variability.

Fig. 5 provides another view of the pH variability for surface waters of lower Chesapeake Bay. The most frequent measurements are near pH 8.0 to 8.2, as would be expected for seawater in equilibrium with the atmosphere. However, there are many measurements having pH well above and below the median pH. Table 2 provides a single statistic to quantify the pH variability in some coastal waters. The statistic is the fraction of samples that are ≥0.5 units either above or below the median pH for that system. In all but 1 case, more than 10% of the samples were ≥0.5 units from the median pH. In small isolated bodies of water, pH extremes can be still greater (Skirrow 1975). Examples of rather large deviations from equilibrium pH have also been reported for less-confined coastal waters. Pegler &

Table 2. The distribution of surface water pH in estuarine environments. For Chesapeake Bay, the data was sorted by salinity so that only the pH of samples between the stated salinity values were included. The STORET data was selected by specifying an area. Areas were chosen to correspond to the average salinity conditions listed

System	Percent of samples ≥0.5 pH from median pH	Median pH	No. of samples	Salinity (‰)	Years covered and source
Lower Chesapeake Bay	18.0	8.2	383	15 to 30	1957–1963 Hires et al. (1963) and data reports cited therein
Tampa Bay (3 regions)					
Central	12.7	8.0	10 890	>25	EPA STORET System[a] 1980 to 1990
Hillsborough Bay	23.8	7.9	3 832	5 to 25	
Old Tampa Bay	14.7	7.9	3 918	5 to 25	
Delaware Bay	32.8	7.8	813	5 to 25	EPA STORET System[a] 1980 to 1990
	14.1	7.8	498	5 to 25	U. of Delaware Data Reports (see Fig. 1)
	1.0	8.0	293	>25	U. of Delaware Data Reports (see Fig. 1)
Tybee Creek (Savannah River)	18.8	7.5	85	>25	1973–1974 Winker et al. (1985)
Puget Sound	11.3	7.9	5 541	>25	EPA STORET System[a] 1980 to 1990

[a]http://www.epa.gov/storet

Kempe (1988) reported a survey in May/June 1986 finding a band of water with pH ≥8.5 extending approximately 300 km along the North Sea coast from the Danish-German border to the western extent of the Waddenzee in the Netherlands. In 1993, Brussaard et al. (1996) observed the pH of water entering the Marsdiep tidal inlet from the North Sea rise from pH 7.9 in late March to pH 8.7 by late April.

The pH of coastal environments has probably been altered through nutrient enrichment. Human activities have lead to a global doubling of N and P concentrations in river waters and increases of 10 to 50 times over natural levels in rivers in industrialized areas (Meybeck 1982). The increased delivery of nutrients to the coastal zone has led to easily observable increases (i.e. doublings) of nutrient concentrations and phytoplankton abundance within coastal waters. A few examples include Chesapeake Bay (Harding 1994, Price et al. 1985), the Mississippi plume (Eadie et al. 1994), the Baltic (Nehring et al. 1984, Rosenberg et al. 1990), the German Bight area of the North Sea (Gerlach 1990), and Tolo Harbor, Hong Kong (Hodgkiss & Chan 1987).

When more nutrients are available, larger blooms may be supported which drive pH to progressively higher levels. Nutrient-enriched environments may lead to more sustained removal of inorganic C from seawater and sequestration of C in sediments, which is later remineralized; thus, driving any seasonal pH cycle, or simply temporal pH variability, to a greater amplitude.

An example of such an effect is shown in Fig. 6 for a 28 mo eutrophication experiment. This study was carried out in 13 m^3 outdoor marine enclosures of the Marine Ecosystems Research Laboratory (MERL; Nixon et al. 1984, Kelly et al. 1985, Oviatt et al. 1986a,b, 1989, Keller 1988a,b, 1989, Keller & Rice 1989, Hinga 1990). Enclosures treated daily with moderate amounts of N and P had an amplified seasonal pH range. Control enclosures without nutrient additions had a seasonal pH cycle similar to that for lower Narragansett Bay, shown in Fig. 2. There are limits as how high the pH cycle can be amplified by nutrient enrichment. In enclosures treated with very high loadings of nutrients, the regular annual cycles of production and pH found in the control enclosures were no longer evident.

An amplification of pH range upon eutrophication was also found in experiments in brackish experimental coastal ponds (salinity approximately 18‰) reported by Laughinghouse & Kuenzler (1971). Control ponds had a short-term (over a few weeks) pH variability of about 0.5 pH unit and only exceeded the range of 7.5 to 8.5 once over 10 mo. The ponds given nutrient additions had a short-term pH variability of about 1.0 pH unit and varied from 7.5 to 10.5 over the 10 mo experiment.

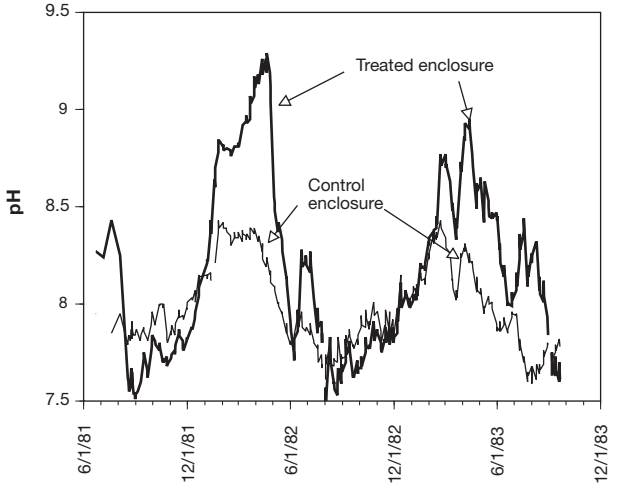

Fig. 6. pH in a control and a nutrient-treated marine enclosure at the Marine Ecosystems Research Laboratory of the University of Rhode Island. Both enclosures had water exchange with Narragansett Bay (low nutrient water) at a nominal rate of 4 % d^{-1}. The treated tank (the 4× treatment) had daily additions of 2.3, 0.18 and 0.17 µmol l^{-1} d^{-1} of NH_4^+, PO_4^{3-} and silicate, respectively. The control enclosure had total inorganic N concentrations in the range 1 to 10 µmol l^{-1}. The treated tank had total inorganic N concentrations typically between 40 and 80 µmol l^{-1}. The data is from Frithsen et al. (1985). Dates are mo/d/yr

It is difficult to generalize a pH response to eutrophication for all coastal ecosystems. Additions of metabolizable organic matter often accompany additions of nutrients. Remineralization of the organic matter may tend to push the pH lower through the generation of CO_2. The net result of additions of organic matter and nutrients on pH in different environments will depend on the ratios of nutrients to organic C, the form of the C, the hydrodynamics of the local environment, the background suspended load of sediments and the response of organisms, including the phytoplankton.

There is an additional small effect on seawater pH that results from anthropogenic modification of the atmosphere. Since pre-industrial times to the present, the atmospheric concentration of CO_2 has risen from approximately 290 to 360 µatm. This change has lowered the equilibrium pH of seawater about 0.1 units (Pilson 1998).

Experimental manipulation of pH

It is not possible to manipulate pH without also affecting some of the other components of seawater (e.g. Figs. 3 & 4). A variety of techniques can be used to establish the range of pH. It is important to understand the ramifications of the type of pH control approach used in different studies. All the studies listed in this

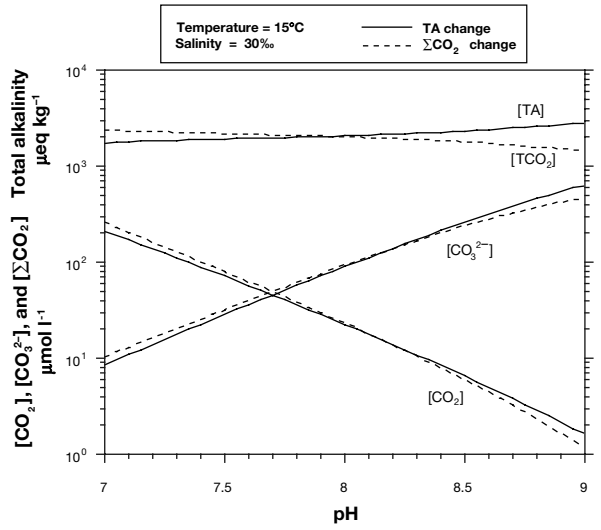

Fig. 7. Comparison of the pH and free CO_2 and carbonate relationships for alkalinity and total CO_2 driven changes in pH. In the case of constant CO_2, the total CO_2 was 1950 µmol l^{-1} In the case of constant total alkalinity, the total alkalinity was 2148 µeq l^{-1} A parcel of seawater starting from these conditions (and at 30‰ and 15°C) that is changed to pH 9 by CO_2 removals will have 1.18 µmol kg^{-1} free CO_2. The same parcel of seawater if changed from pH 8 to 9 by addition of a strong base will have 1.60 µmol kg^{-1} free CO_2. Changing the initial parcel of water to pH 7 by CO_2 injections will result in a free CO_2 concentration of 260 µmol kg^{-1} at pH 9 while making the same pH change with the addition of strong acid will result in a free CO_2 concentration of 212 µmol kg^{-1}. The additions of acid or base (e.g. HCl or NaOH) to achieve this range of pH will change the concentrations of the major ions (e.g. Na^+ or Cl^-) in 30‰ seawater in the order of 0.1%

review demonstrate some pH effect on phytoplankton. The approach used to control pH may: (1) simulate field conditions; (2) not simulate field conditions but may provide insight into the mechanism of a pH effect; (3) approximate field conditions; or (4) solely demonstrate a pH effect (under conditions that do not replicate or simulate field conditions nor provide insight into mechanisms of the effect).

The concentrations of some of the dissolved components in seawater, including those of free CO_2, carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-), co-vary with pH. The pH drift experiments of Goldman (1999) and one experiment by Pruder & Bolton (1979) closely simulate the way pH change occurs in coastal environments, through injections and removals of CO_2. The behavior of species in these experiments should closely simulate the results expected in the field.

In a second type of experimental conditions, both the alkalinity and one other component of the seawater pH-carbonate system were manipulated. Here, the concentration of one component of the carbonate system, free CO_2 was held constant across a range of pH. This was achieved by bubbling a gas mixture through the culture with a set fraction of CO_2, so as to maintain a constant concentration of free CO_2 in the water of each culture. In these experiments, the normal relationship between pH and free CO_2 is not found. While these experiments do not simulate field conditions, they do help determine if observed pH effects (at high pH) are caused by limiting concentrations of free CO_2.

A third type of experiment used an alkalinity adjustment (usually additions of strong acid or base) to achieve the desired pH. This approach gives conditions that approximate the relationship between pH and the dissolved CO_2 species that results from additions or removals of CO_2. For both CO_2 and alkalinity driven pH adjustment, at high pH there is low free CO_2 and at low pH there is high free CO_2 (see Fig. 7). However, the specific concentrations of the dissolved CO_2 species differ slightly between alkalinity adjustment and total CO_2 adjustment (20 to 25% at pH 7 or 9). If a pH effect is the result of growth limitation by the availability of free CO_2, the magnitude of the effect (at a specific pH) determined by alkalinity adjustment may differ slightly from the growth rate at a given pH caused by total CO_2 change.

Where the adjustment of pH was attempted by simply adding acid or base, the change in alkalinity shifts the partial pressure of CO_2 out of equilibrium with the atmosphere. While the initial pH may have been at a desired level, cultures exposed to the atmosphere tended to drift back to the initial pH as the CO_2 in the

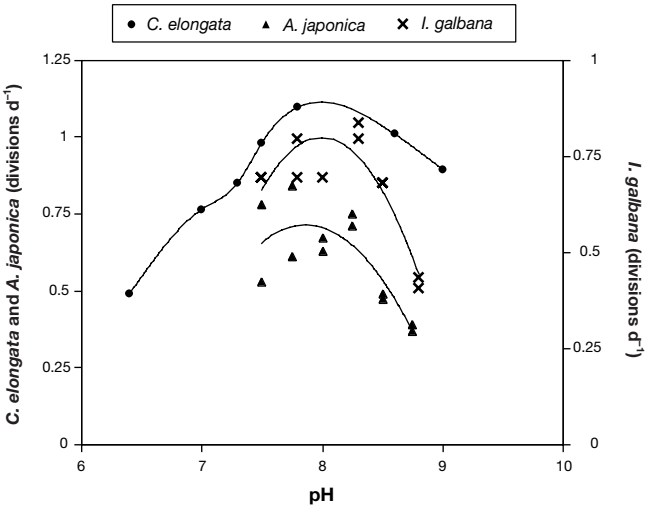

Fig. 8. *Cricosphaera elongata* (Swift & Taylor 1966), *Asterionella japonica* (Kain & Fogg 1958a) and *Isochrysis galbana* (Kain & Fogg 1958b). Growth rates in laboratory cultures. *C. elongata:* average values of 2 to 16 replicate cultures. *C. elongata* at pH 6.4, 7.0 and 7.5 were cultured with air enriched to 5% CO_2 and at the remaining pH with air at 0.03% CO_2. Curve fits are interpolation for *C. elongata* and 2nd degree polynomial for *A. japonica* and *I. galbana*

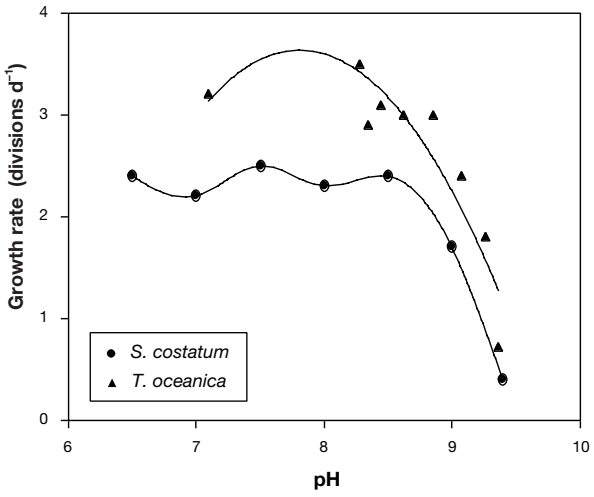

Fig. 9. *Thalassiosira oceanica* (Chen 1986, Chen & Durbin 1994) and *Skeletonema costatum* (Taraldsvik & Myklestad 2000). Growth rates in laboratory cultures. Curve fits are 2nd degree polynomial for *T. oceanica* and interpolation for *S. costatum*. Values for *S. costatum* are the average of 3 cultures

cultures re-equilibrated with the atmosphere. This non-constant pH occurred especially in some of the earlier studies.

As an example, the addition of 0.35 meq l^{-1} of strong acid will drive the pH of seawater from pH 8.1 to pH 7. This also results in a large excess partial pressure of CO_2 relative to the atmosphere. The cultures would lose CO_2 to the atmosphere (and likely to uptake by phytoplankton). Upon complete CO_2 re-equilibration with the atmosphere, the culture would re-stabilize at pH 8.04. In such experiments, the pH was constantly changing. In some studies, the pH was held relatively constant against pH drift by repetitive additions of acid or base. In experiments where short-term measurements were made, there was usually insufficient time for pH to drift appreciably.

In a fourth general approach, a buffer was added to the seawater (Kain & Fogg 1958a,b, Griffis & Chapman 1990) and the alkalinity adjusted. The buffer adds an additional component that participates in the acid-base reactions in the relevant pH range. Hence, the normal relationship between pH and other seawater components (such as free CO_2) may not be found. If the mechanism of the pH effect found for the species in these experiments is related to the concentrations of the normal pH-sensitive components of seawater (other than the hydrogen ion concentration itself), then the pH effect may not be the same as would be found in a CO_2 driven pH change. Experiments under conditions that more closely simulate normal seawater conditions will be needed to see if the observed effect from this type of experiment is relevant to field conditions.

A note of caution should be added. Many of the laboratory studies have few data points with 1.0 pH unit or more difference between treatments. In these cases, neither the pH for maximum growth nor the response to variable pH is well constrained within the range of pH usually expected in coastal ecosystems. The interpretation of many of the experiments could change considerably with the omission or movement of individual points. The few data points, and the scatter evident in some studies may suggest a pH for maximum growth or a response to pH change that is an imprecise reflection of the species or clone behavior. Without further experiments, it is impossible to identify results that are misleading. For the present, there is no option but to work with the data as reported and recognize that future work is necessary to clarify matters.

Effects of seawater pH on phytoplankton

Table 3 lists 21 individual or closely related studies containing information on the effects of pH on marine phytoplankton. Most of the studies were laboratory experiments that determined the effects of pH on growth rate, substrate uptake or the final population levels of populations after an incubation period. Two studies (Yoo 1991, Hinga 1992) found correlations between pH and abundance of dinoflagellates in mixed phytoplankton populations.

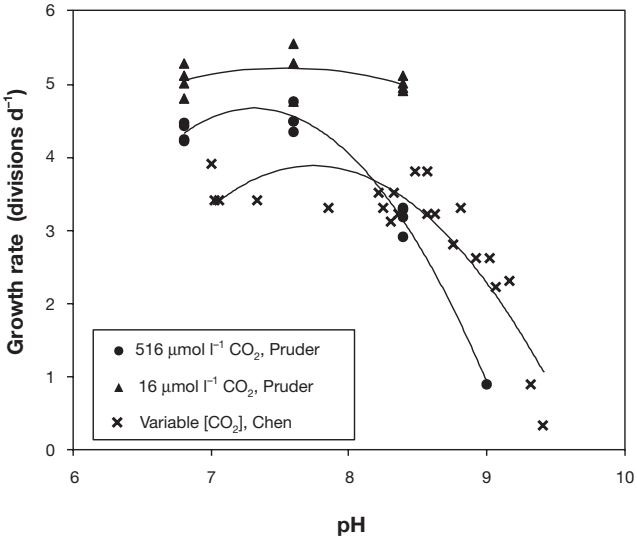

Fig. 10. *Thalassiosira pseudonana.* Growth rates in laboratory cultures. Pruder (1979): 2 free CO_2 concentrations for 2 high light intensity treatments. The cultures at pH 9 did not grow well and this point is an estimate of the average of an unspecified number of replicates. Curve fits are 2nd degree polynomials. Curve fit for the Chen (Chen 1986, Chen & Durbin 1994) study is a 2nd degree polynomial

Table 3. List of studies with information on effects of pH on marine phytoplankton growth

Species	Parameters measured	Method of pH control	Method notes	Source
Mixed *Navicula* spp. and *Nitzschia* spp.	Final cell concentrations	Initial alkalinity adjustment. Non-constant pH	Initial pH set by additions of acid or base; culture pH drifted toward pH ~8 during 5 d cultures	Bachrach & Lucciardi (1932)
Peridinium sp. *Prorocentrum micans* (*Prorocentrum gracile*)	Growth rates	Probably initial alkalinity adjustment. Non-constant pH	Procedure not clearly specified. Presumably the pH was established by additions of acid or base. During the 10 d cultures the pH drifted toward pH ~8	Barker (1935)
Asterionella japonica *Isochrysis galbana*	Growth rates	Repeated alkalinity adjustment. Buffer added	Media buffered with tris, pH adjusted with acid or base. Daily adjustments were made to keep pH within 0.1 to 0.3 of the desired pH	Kain & Fogg (1958a,b)
Emiliania huxleyi (Clone F402, calcifying)	Relative growth rates	Alkalinity adjustment. Buffer added at some pH levels. High $\sum CO_2$ concentrations	Cultures established at high (5 mM $\sum CO_2$) concentrations.	Paasche (1964)
Cricosphaera elongata	Growth rates	Alkalinity adjustment. Two constant free CO_2 concentrations	pH achieved by adjusting alkalinity and bubbling cultures with air at normal, 300 µatm, or enriched, 0.05 atm, CO_2, concentrations	Swift & Taylor (1966)
Phaeodactylum tricornutum (3 clones)	Final cell concentrations	Alkalinity adjustment Constant free CO_2 concentrations	pH achieved by adjusting alkalinity and bubbling with normal air	Hayward (1968)
Monochrysis lutheri *Phaeodactylum tricornutum*	Photosynthesis and respiration Final cell concentrations	CO_2 adjustment	Cultures bubbled with air with 0.5% or 20% CO_2 at variable rates such that 'by the end of the 48 h growth period the pH increased or decreased.' Phytosynthesis and respiration measurements made at end of growth period. pH and CO_2 drifted during final cell concentration measurements	Humphrey (1975)
Amphidinium carterae *Biddulphia aurita* *Chaetoceros didymum* *Chroomonas* sp. *Cylindrotheca closterium* *Dunaliella tertiolecta* *Gymnodidium splendens* *Monochrysis lutheri* *Nitzschia* sp. *Nitzschia closterium* *Phaeodactylum tricornutum*	Ranges and optima for growth, photosynthesis and respiration	See above	See above	Humphrey (1975)
Thalassiosira pseudonana	Growth rates	Alkalinity adjustment. Constant free CO_2 concentrations	pH achieved by adjusting alkalinity and bubbling cultures with O_2-N_2-CO_2 mixtures. Experiments were run primarily at aqueous CO_2 concentrations of 16 or 159 µmol l^{-1}	Pruder (1979) Pruder & Bolton (1979)

Table 3 (continued)

Species	Parameter measured	Method of pH control	Method notes	Source
Phaeodactylum tricornutum *Dunaliella tertiolecta*	Steady state C concentrations	CO_2 adjustment (in chemostat)	Plankton species grown in continuous cultures. pH maintained by a pH-stat system which bubbled air enriched with 1% CO_2 on demand to keep pH constant	Goldman et al. (1982a,b)
Skeletonema costatum	NO_3^- uptake rate	CO_2 adjustment	pH achieved for 1 h measurements by bubbling 100% CO_2 at rate just sufficient to balance CO_2 uptake by culture and maintain desired pH within ± 0.15	Thoresen et al. (1984)
Thalassiosira pseudonana *Thalassiosira oceanica*	Growth rates	CO_2 and alkalinity adjustment for some cultures	The methods of alkalinity adjustment and bubbling with fixed CO_2 concentrations were used for different experiments	Chen (1986 Chen & Durbin (1994)
Mixed phytoplankton populations	C uptake rates	Alkalinity adjustment		Chen (1986 Chen & Durbin (1994)
Pyrodinium bahamense	Final cell concentrations (Growth rates)	Techniques not given		Blackburn & Oshima 1(989)
Gonyaulax polyedra *Thoracosphaera hemii* *Coccolithus pelagicus* *Ditylum brightwellii*	Growth rates	CO_2 adjustment. Buffer added in treatment (pH 7.6 to 7.8)	Bubbling with normal air 320 ppm CO_2 for pH 8.2 or addition of buffer and bubbling with air at 510 ppm CO_2 for pH 7.6 to 7.8	Griffis & Chapman (1990)
Mixed dinoflagellates	Stepwise multiple correlation analysis			Yoo (1991)
Mixed dinoflagellates	Correlations in mesocosm studies			Hinga (1992)
Phaeodactylum tricornutum *Emiliania huxleyi* (2 clones)	Growth rates	Alkalinity adjustment. Constant free CO_2 concentrations	Bubbled with air and pH control through additions of bis-Tris phosphate	Johnston (1996)
Amphora coffeaeformis *Cocconeis scutellum* *Navicula corymbosa* *Navicula mollis*	Growth rates	Repeated alkalinity adjustment	Daily additions of acid or base	Wang et al. (1998)
Stephanopyxis palmeriana *Coscinodiscus* sp. *Ditylum brightwellii*	Growth rates	pH drift experiments	Cell growth drew down $\sum CO_2$ raising pH	Goldman (1999)
Alexandrium minutum	Growth rates	Alkalinity adjustment	Not stated if there were repeated alkalinity adjustments to correct for pH drift	Hwang & Lu (2000)
Skeletonema costatum	Growth rates Cellular constituents	Repeated alkalinity adjustment	Mechanical system to monitor pH and add acid or base as needed	Taraldsvik & Myklestad (2000)

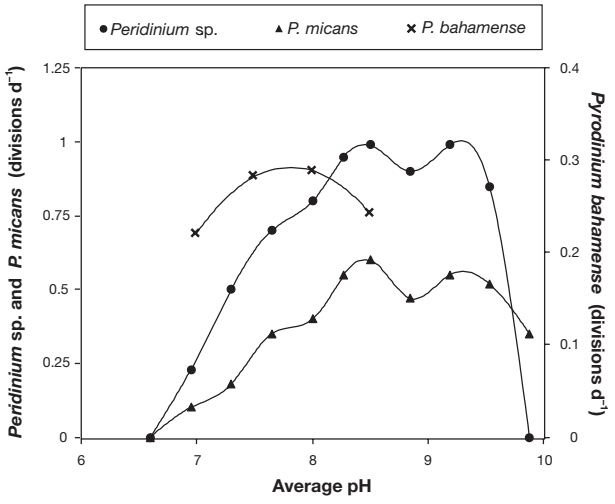

Fig. 11. *Peridinium* sp. and *Prorocentrum micans.* Growth rates from Barker (1935). The pH of the cultures drifted considerably during the experiments. Growth rates were plotted against the pH estimated to be halfway between the initial and final pH. *Pyrodinium bahamense.* Growth rates (Blackburn & Oshima 1989) calculated from initial and final population levels assuming exponential growth and no lag period. This provides a minimum growth rate estimate as any lag period after inoculation would require that the growth rate during log growth actually be greater than the minimum rate calculated. Curve fits are interpolations

The data suitable for graphical representation are replotted in Figs. 8 to 20 with a uniform pH scale. With 3 exceptions, each point shown in these figures represents the results from an individual culture or a single measurement. For *Cricosphaera elongata* in Fig. 8. (Swift & Taylor 1966), for *Skeletonema costatum* in Fig. 9 (Taraldsvik & Myklestad 2000) and one point for *Thalassiosira pseudonana* in Fig. 10 (Pruder 1979) each point represents the average value of replicate cultures.

Curve fits were made to each data set plotted in Figs. 8 to 20 to show the general trends of the data and to help distinguish the data for different species plotted in the same graph. The fits are not intended to represent functional relationships. The lines drawn from the curve fits were restricted to the range of the data. Curve-fit lines that extend to the edges of the graph indicate that there were data points above pH 10 or below pH 6. Data from studies that were not appropriate for graphing are listed in Tables 4 & 5.

pH for maximum growth

Fig. 8 shows, for *Cricosphaera elongata*, *Asterionella japonica* and *Isochrysis galbana*, responses to pH that might be expected from the distribution of pH found in coastal seawater. Each of these species has maximum growth rate near equilibrium pH. Their growth rates fall off progressively with higher or lower pH. These 3 species should grow fastest at the most commonly occurring pH. Johnston (1996) found 2 clones of *Emiliania huxleyi* (Fig. 12) to have fastest growth near pH 8. The C uptake measurements in 5 different mixed phytoplankton populations (Chen 1986, Chen & Durbin 1994) found maxima in C uptake rates at pH ranging from about 7.8 to 8.1 (Fig. 20).

Results for *Skeletonema costatum* in a study by Taraldsvik & Myklestad (2000) indicate a broad region around equilibrium pH where the growth rate was nearly constant (Fig. 9). Above pH 8.5, the growth rate dropped off sharply. It should be noted that the concentration of cellular constituents did not have a similar broad plateau encompassing equilibrium pH. The per cell content of β-1,3-glucan had a maximum at pH 8.0 and decreased markedly at higher and lower pH. Also, the per cell concentration of total free amino acids was highest at pH 6.5 to 7.0 and decreased with increasing pH up to pH 9.4.

Thalassiosira oceanica (Fig. 9) and *T. pseudonana* (Fig. 10) from studies by Chen (1986) and Chen & Durbin (1994) appear to exhibit a broad plateau of constant growth rate. Unfortunately, data are missing in the crucial range for *T. oceanica*. For *T. pseudonana*, the data indicate a plateau from approximately pH 7 to 8.5 where the growth rate does not change with pH. Results for *T. pseudonana* (Fig. 10) from Pruder (1979) at CO_2 concentrations more representative of present

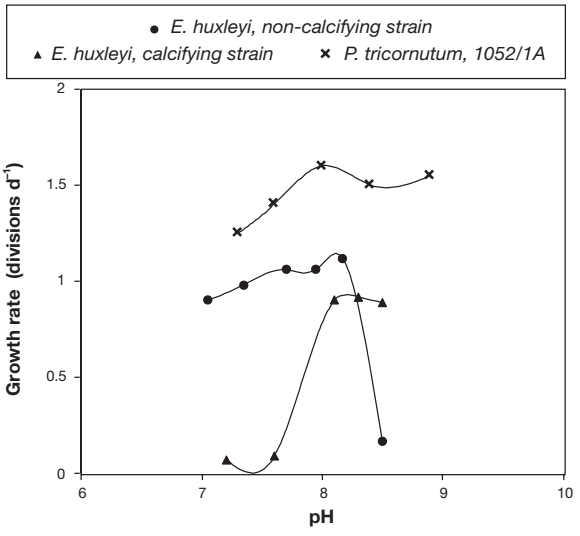

Fig. 12. *Emiliania huxleyi* (2 clones) and *Phaeodactylum tricornutum.* Growth rates from Johnston (1996). Curve fits are interpolations

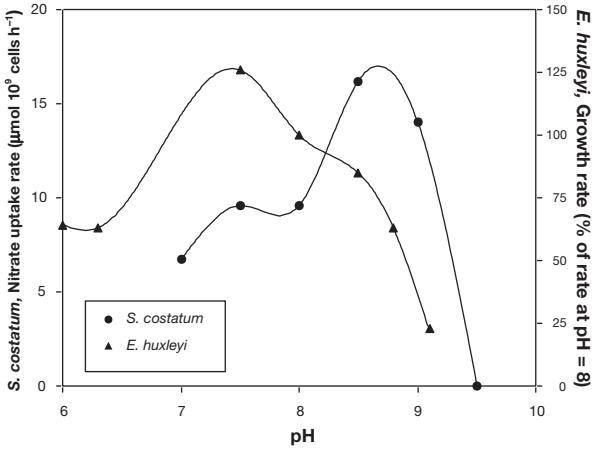

Fig. 13. *Skeletonema costatum.* Nitrate uptake rate (Thoresen et al. 1984). *Emiliania huxleyi.* Growth rate relative to growth rate at pH 8 (Paasche 1964). Curve fits are interpolations

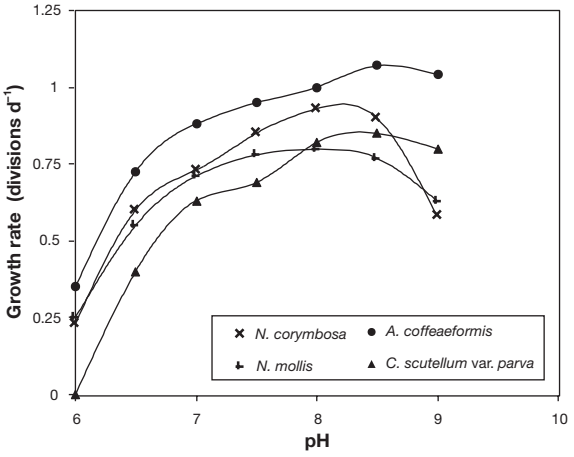

Fig. 14. *Navicula corymbosa*, *Amphora coffeaeformis*, *N. mollis*, and *Cocconeis scutellum* var. *parva*. Growth rates (Wang et al. 1998). Curve fits are interpolations

day seawater (16 µmol l^{-1}) also indicate little change in growth rate over a range of pH 6.8 to 8.4. In an experiment where the pH was allowed to drift to higher values as the culture drew down the CO_2, Pruder & Bolton (1979) found that *T. pseudonana* grew at a constant rate until pH 8.8 to 8.9 was reached, then stopped. Growth resumed in the culture upon the addition of acid and the lowering of the pH. In similar pH drift experiments, Goldman (1999) found *Stephanopyxis palmeriana*, *Coscinodiscus* sp. and *Ditylum brightwellii* to have a constant growth rate from pH 8.1 up to pH 8.45, 8.51 and 8.31, respectively. Above these values, the growth rates decreased. These experiments defined the point at high pH where growth rate slowed, but due to the nature of the drift experiments, the low pH limit of constant growth was not determined. Other examples of maximum growth rate being near equilibrium pH are the benthic diatoms *Navicula corymbosa* and *Navicula mollis* (Fig. 14) and *Dunaliella tertiolecta* (Fig. 15).

A number of species that appear to have fastest growth rates at low pH were reported by Humphrey (1975) and are listed in Table 4. Among those species is *Monochrysis lutheri*, which appears to have a maximum photosynthesis to respiration ratio and growth rate at pH about 7.5 (Figs. 16 & 17). Paasche (1964) found a clone of *Emiliania huxleyi* (Fig. 13) to grow best at a pH of about 7.5.

Table 4. Results reported by Humphrey (1975). Ranges for growth (defined as more than 1 division in 48 h) and maxima are from Humphry's Fig. 3. Range tested and the pH at which the single highest values found are from Humphry's Table 1. A criteria for 'range in maxima' in cell concentration, photosynthesis, or P/R ratio is not given in the original paper. The original paper provided graphs of the data for *Monochrysis lutheri* and *Phaeodactylum tricornutum* (Figs. 16 & 17 of this paper), but it is not clear how the range in maxima were defined. Results are based upon 5 cultures for each species

Species	pH ranges for growth (Range tested)	Maxima in cell concentration (pH at maximum value)	Maxima in photosynthesis (pH at maximum value)	Maxima in P/R ratio (pH at maximum value)
Amphidinium carterae	7.0–10.1 (5.9–10.1)	7.0–10.0 (7.0)	7.3–8.3 (8.2)	7.6–8.6 (7.6)
Biddulphia aurita	6.1–8.7 (6.1–8.7)	7.4–8.6 (7.5)	7.3–7.8 (7.4)	7.3–7.8 (7.8)
Chaetoceros didymum	7.0–9.0 (5.7–9.0)	7.3–9.0 (7.5)	7.3–8.8 (7.5)	7.3–7.9 (7.2)
Chroomonas sp.	7.0–9.0 (6.1–9.5)	7.5–9.3 (8.1)	7.4–7.7 (7.5)	7.4–7.7 (7.5)
Cylindrortheia closterium	5.9–8.5 (5.9–9.9)	6.4–8.3 (7.3)	6.0–7.7 (7.4)	6.9–7.9 (7.6)
Dunaliella tertiolecta	6.0–9.3 (6.0–9.3)	6.4–8.3 (8.3)	7.1–8.1 (7.1)	7.5–8.1 (8.1)
Gymnodinium splendens	7.0–8.9 (6.1–8.9)	7.3–8.0 (7.3)	7.4–7.7 (7.6)	7.3–7.8 (7.5)
Monochrysis lutheri	5.9–9.0 (5.9–9.8)	7.4–8.5 (7.5)	7.3–7.6 (7.3)	7.3–7.7 (7.3)
Nitzschia closterium	5.3–9.8 (5.3–9.8)	6.4–7.8 (6.3)	5.9–6.4 (6.3)	6.3–7.8 (7.6)
Nitzschia sp.	6.7–9.5 (6.0–9.5)	7.5–9.6 (7.6)	7.3–9.1 (7.3)	7.3–9.1 (7.6)
Phaeodactylum tricornutum	6.1–10.0 (6.1–10.0)	7.3–9.5 (7.8)	6.4–7.0 & 9.4–10.0	6.5–9.5 (7.1)

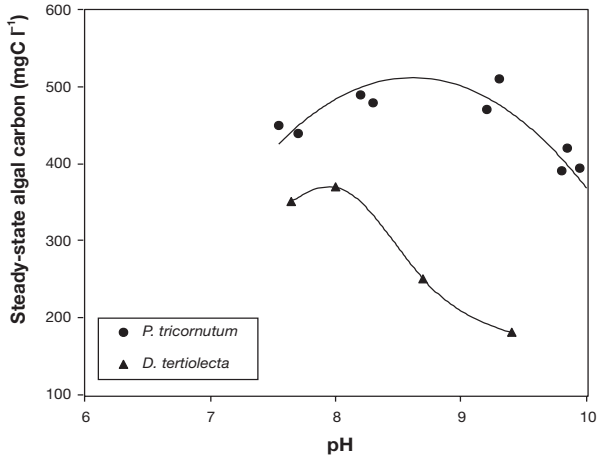

Fig. 15. *Phaeodactylum tricornutum* and *Dunaliella tertiolecta* grown in continuous cultures (Goldman et al. 1982a). Steady state algal C. Curve fit for *P. tricornutum* is a 2nd order polynomial. Curve fit for *D. tertiolecta* is interpolation

Other species, clones or groups have pH optimum for growth rate (or substrate uptake) well above equilibrium pH. Growing fastest at pH 8.5 or higher are *Peridinium* sp. and *Prorocentrum micans* (Fig. 11), the *Skeletonema costatum* clone used by Thoresen et al. (1984; Fig. 13), *Amphora coffeaeformis* and *Cocconeis scutellum* var. *parva* (Fig. 14) and a mixture of *Navicula* spp. and *Nitzschia* spp. (Fig. 19). *Phaeodactylum tricornutum* has little change in growth rate from pH 7.5 (or below) to pH 9.5 (Figs. 12 & 15 to 18, Table 4). *P. tricornutum* can tolerate high pH and grow reasonably well above pH 10, a trait not common among the phytoplankton. The pH for maximum growth rate is not well constrained in a species with such little change in growth rate, but in most studies, *P. tricornutum* appears to grow fastest at pH higher than equilibrium.

Table 5. Growth of phytoplankton at pH 7.6 to 7.8 and 8.2 from Griffis & Chapman (1990). Growth rates are K_{10} values

Species	pH 7.6 to 7.8	pH 8.2
Gonyaulax polyedra	Mortality	0.061
Thoracosphaera hemii	Irregular growth	0.037
Coccolithus pelagicus	0.010	0.056
Ditylum brightwellii	0.167	0.074

There are 2 studies that correlated the appearance of phytoplankton species with pH in marine ecosystems. Yoo (1991), using a stepwise multiple correlation between dinoflagellate species abundance in Masan Bay (Korea) and environmental parameters, found that pH was the leading factor correlating with abundance. Diatoms did not have a similar correlation with pH. Dinoflagellate abundance was higher with high pH. A correlation between high pH and dinoflagellate abundance in marine enclosure experiments was reported by Hinga (1992). Weekly phytoplankton counts were analyzed from 17 enclosure years of a nutrient addition experiment and from 6 enclosure years of a CO_2 C isotope experiment. A total of 1200 observations were available with pH and phytoplankton counts. Among those counts were 57 occurrences when dinoflagellate populations exceeded 100 cells ml^{-1}. The distribution of occurrences of dinoflagellate abundance exceeding

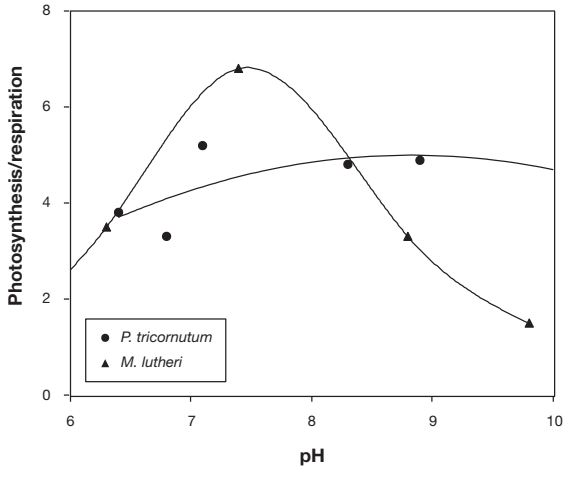

Fig. 16. *Phaeodactylum tricornutum* and *Monochrysis lutheri*. Photosynthesis/respiration ratio (Humphrey 1975). Curve fit for *P. tricornutum* is a 2nd order polynomial. Curve fit for *M. lutheri* is interpolation. Data from these experiments also appear in Table 4

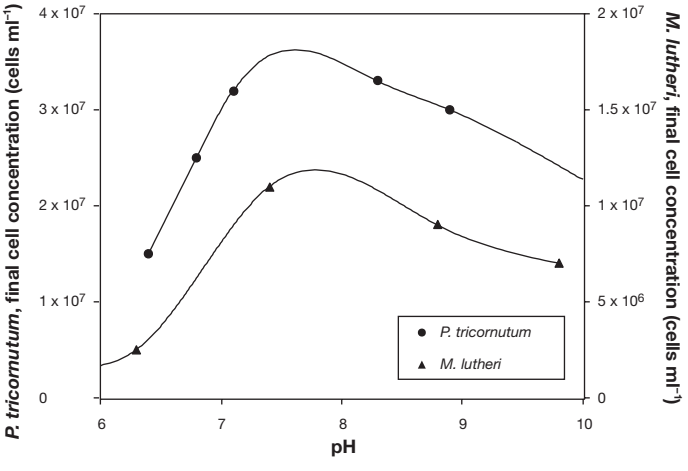

Fig. 17. *Phaeodactylum tricornutum* and *Monochrysis lutheri*. Final cell concentrations (Humphrey 1975). Data from these experiments also appear in Table 4. Curve fits are interpolations

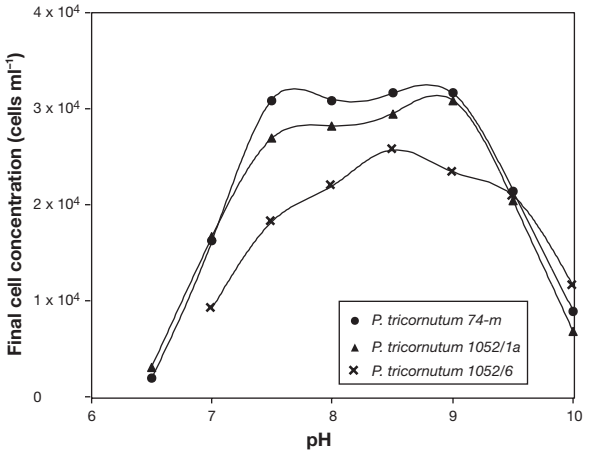

Fig. 18. *Phaeodactylum tricornutum.* Final cell concentrations for 3 clones (Hayward 1968). Curve fits are interpolations

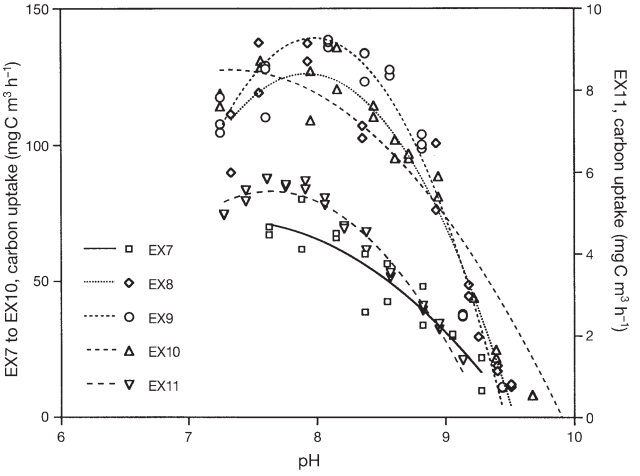

Fig. 20. C fixation measured by ^{14}C uptake in mixed populations of phytoplankton (Chen 1986, Chen & Durbin 1994). The pH of the water from each enclosure before the pH was adjusted was EX7 = 9.05, EX8 = 8.93, EX9 = 8.82, EX10 = 8.94 and EX11 = 8.21. Curve fits are 2nd order polynomials

100 cells ml^{-1} are shown in Fig. 21. The high dinoflagellate populations occurred almost exclusively during the relatively infrequent periods of high pH. There were 6 dinoflagellate blooms with populations above 500 cells ml^{-1}. All 6 blooms occurred at pH 8.4 or greater. These dinoflagellate blooms developed after the pH was raised by a diatom bloom or an experimental procedure. Species found at high pH in these enclosure experiments were *Peridinium* spp. (by far the most common), *Heterocapsa triquetra*, *Exuviella* sp., *Amphidinium* sp., *Gymnodinium* sp., *Scrippsiella* sp. and *Dissodinium lenticulum*. Not all dinoflagellate species had an association with high pH. Blooms (over 100 cells ml^{-1}) of *Prorocentrum redfieldi* and *Prorocentrum gracile* were found at pH 8.0 to 8.1. *Dinophysis acuminata* was found in high abundance in a single month long bloom that occurred at pH <7.5.

The pH for maximum growth (maxima in final cell concentration, growth rate, or substrate uptake rate) for each study are shown in Figs. 8 to 19 and from Table 4 are compiled in Fig. 22. Where there was a range of pH that could represent a broad maximum,

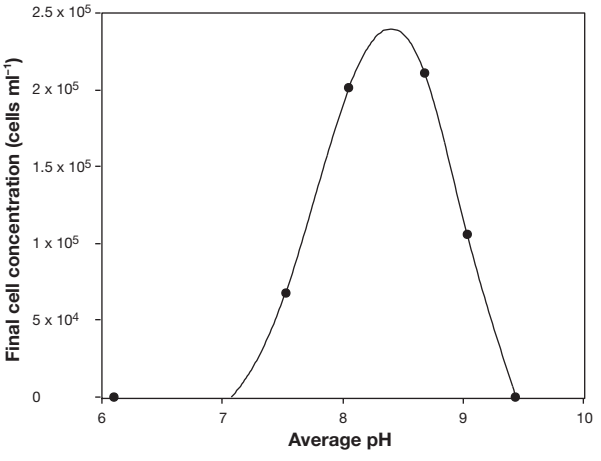

Fig. 19. Cultures dominated by *Navicula* spp. and *Nitzschia* spp. Final cell concentrations (Bachrach & Lucciardi 1932). Only the results of their plugged experiment (cultures covered with paraffin oil) are shown here. In the plugged experiment, the pH of the cultures was relatively stable. Final cell concentrations are plotted against the average of initial and final pH for the cultures. Curve fit is interpolation

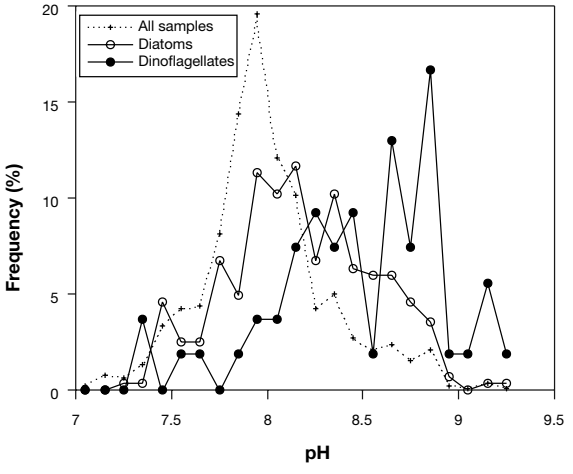

Fig. 21. Frequency of dinoflagellate and diatom abundances of over 100 cells ml^{-1} and frequency of all pH measurements where phytoplankton cells were counted in 2 marine enclosure experiments (Hinga 1992). Intervals of 0.1 pH

bars connect the high and low pH of that region. Maxima are found at pH as low as 6.3 and as high as 10. The species in Fig. 22 are grouped by taxonomic class. Clear preference for low or high pH does not appear to be a characteristic of any class. The 3 classes with several species each have species with maxima above and below equilibrium pH. Chlorophyceae and Cryptophyceae are represented by only 1 species each.

Among the diatoms, pH at maximum rate ranges from 6.3 (*Nitzschia closterium*) to about 10. The preference for high pH is represented by most of the results for *Phaeodactylum tricornutum* and by *Navicula* spp. and *Nitzschia* spp. Five species have maxima at pH of 7.5 to 8 and 2 have maxima at about 8.5. Although there are only 2 data points per species (Table 5), Griffis & Chapman (1990) found the diatom *Ditylum brightwellii* grew faster at pH 7.6 to 7.8 than at pH 8.2.

The 5 dinoflagellates have maxima at pH as low as 7.0 (*Amphidinium carterae*) and as high as 9.5 (*Peridinium* sp.). *Gymnodidium splendens* had a maxima at pH 7.3 to 7.6, *Prorocentrum micans* at pH 8.5 and *Pyrodinium bahamense* at pH 8.0. *Gonyaulax polyedra* and *Thoracosphaera heimii* were unable to grow, or grew poorly at pH 7.6 to 7.8 (Table 5); therefore, these 2 species may possibly be grouped with dinoflagellates that grow better at high pH (unless they have a very narrow range of pH for growth). Hwang & Lu (2000) reported that *Alexandrium minutum* grew faster at pH 7.5 than at 8.5.

Three of the prymnesiophytes had maxima at pH below 8. The remaining species had a maximum at 8.2. *Coccolithus pelagicus* grew faster at pH 8.2 than at lower pH (Table 5).

Sensitivity to pH range

Only a subset of the studies can be used to examine the sensitivity to a range in pH. Sensitivity is used here

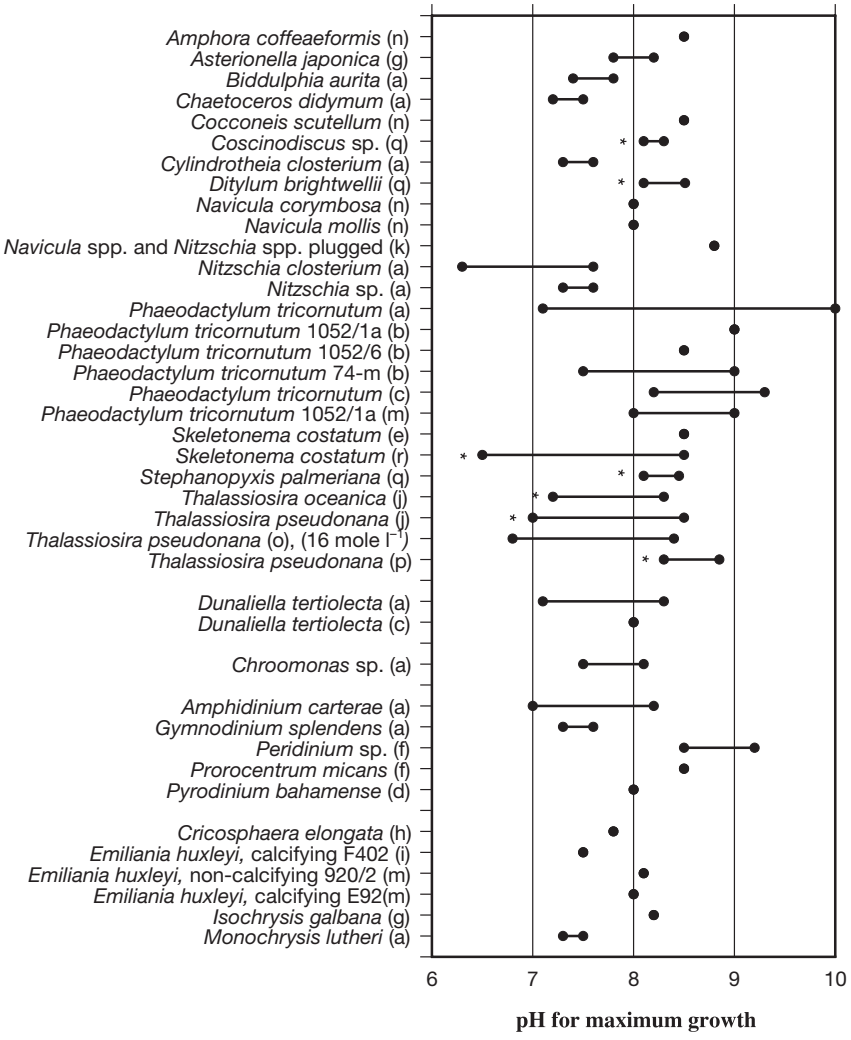

Fig. 22. Maxima in growth, growth rate, substrate uptake, production or photosynthesis/respiration ratio (P/R). Where there was no clear maximum resulting from high values at 2 widely different pH values, the high and low pH values of the broad maximum were plotted and connected. Bars marked with * indicate where the data did not extend to lower values so the range for constant growth may extend to lower values. For the studies by Humphrey (1975), the range bars represent the range of different estimates of maxima from the 3 types of measures he reported (Table 4). Sources are indicated in parentheses: (a) Humphrey (1975); (b) Hayward (1968); (c) Goldman et al. (1982a); (d) is Blackburn & Oshima (1989); (e) Thoresen (1984); (f) Barker (1935); (g) Kahn & Fogg (1958a,b); (h) Swift & Taylor (1966); (i) Paasche (1966); (j) Chen & Durbin (1994); (k) Bacharach & Lucciardi (1932); (m) Johnston (1996): (n) Wang et al. (1998); (o) Pruder (1979); (p) Pruder & Bolton (1979); (q) Goldman (1999); (r) Taraldsvik & Myklestad (2000)

to describe the magnitude of change in growth rate at pH higher and lower than the pH for maximum growth rate. The sensitivity to changes in pH cannot be determined from studies where only final cell density was reported. The percentage difference in final population levels for different pH levels, assuming exponential growth, depends upon the length of the incubation. Longer incubation periods would give a higher apparent sensitivity to pH variability than shorter incubation periods.

The changes in growth rate (or substrate uptake) for a given change in pH vary considerably. Some species are rather insensitive to changes in pH. Most notable of these is *Phaeodactylum tricornutum*, which has been examined more times than any other species. *P. tricornutum* grows readily from pH 6.1 to over 10. The ability to tolerate and grow in extremely high pH is why *P. tricornutum* often dominates large scale outdoor cultures where pH is not regulated and may rise above 10 (Goldman et al. 1982b).

As noted above, there are a number of examples of species which have a broad plateau of nearly constant growth. These include *Skeletema costatum* (Taraldsvik & Myklestad 2000; Fig. 9), *Thalassiosira oceanica* (Fig. 9) and *T. pseudonana* (Fig. 10) However, unlike the case for *Phaeodactylum tricornutum*, the growth rates drop off sharply at pH above the broad plateau of no change in growth rate. By pH 9 *S. costatum*, *T. oceanica* and *T. pseudonana* grew at about half their maximum rate and by pH 9.5 grew at less than 20% of their maximum rate. Other examples of a plateau include the region of constant growth in the pH drift experiments (Goldman 1999) for *Stephanopyxis palmeriana*, *Coscinodiscus* sp. and *Ditylum brightwellii*.

The 4 species of benthic diatoms (Fig. 14) are rather insensitive to changes in pH. At 0.5 pH units above or below their maximum growth rate, these species grew only 4 to 7% slower than at their maximum. At 1 pH unit above or below their maximum, their growth rate was only reduced by 12 to 37%.

However, there are species relatively sensitive to changes in pH. The most striking example is that of the 2 clones of *Emiliania huxleyi* (Johnston 1996). These 2 clones had strikingly and conversely different changes in growth rates from each other at high and low pH (Fig. 12). For example, the growth rate of the calcifying clone decreased to only 10% of its maximum growth rate with an decrease in pH from 8.1 to 7.6. The non-calcifying clone dropped to 14% of its maximum growth rate with an increase of pH from 8.17 to 8.5.

The NO_3^- uptake rate of *Skeletonema costatum* in the experiments of Thoresen et al. (1984; Fig. 13) drops off sharply at the high pH. The uptake rate is reduced by only 15% at pH 9 from the maximum rate found at pH 8.5. However, the species failed to grow at pH 9.5. Similarly, a *Peridinium* sp. (Fig. 11) grew at 85% of its maximum rate at pH 9.5, but failed to grow at all at pH 9.8.

Fig. 23 provides a graphical summary of the growth rate sensitivities derived from Figs. 8 to 16. Most species, or clones, grow at over 80% of their maximum growth rate within 0.5 pH unit of their optimum pH. There are a few examples of species or clones that grow much more slowly even with this small a change in pH. At 1.0 pH unit above or below the pH optimum, most species or clones have growth rates that are 50 to 80% of their maximum growth rate.

DISCUSSION

Seawater pH may exert an influence on phytoplankton growth via a number of possible mechanisms. At high pH, C limitation may occur especially in species that cannot utilize bicarbonate (Raven 1970, Burns & Beardall 1987, Nimer & Merrett 1992). Seawater pH may change the chemical speciation of elements in seawater, for example Cu, that might have an inhibitory effect on phytoplankton (Kester 1986). Changes in pH of natural waters may have an indirect effect

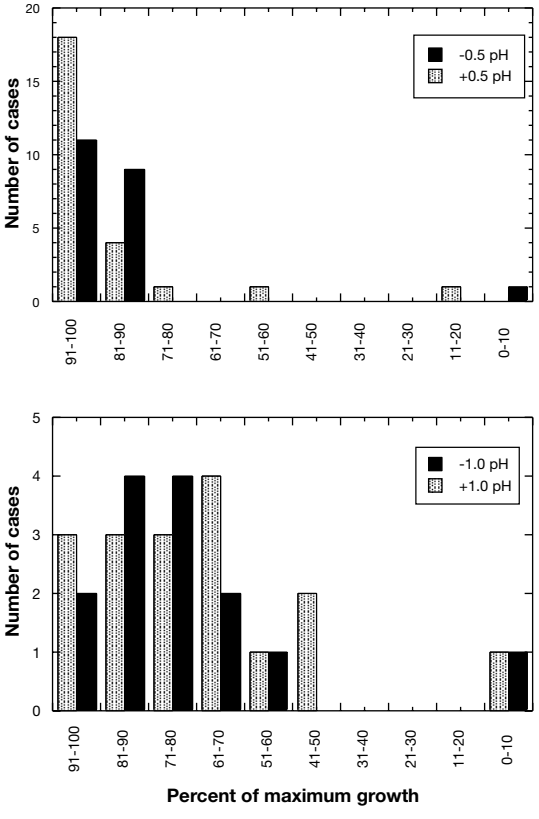

Fig. 23. Reductions in growth rate or substrate uptake rate, at ± 0.5 pH (upper panel) and ± 1.0 pH (lower panel)

on phytoplankton by altering equilibria between sorbed and dissolved phases of metals, hence altering dissolved metal concentrations (Granéli & Haraldsson 1993).

There may be an ion balance effect. At high or low pH, cells may have to spend energy maintaining an internal pH necessary for cell function (Raven 1980, Raven & Lucas 1985). Finally, the reaction rate of enzymes is pH dependent. Deviation from optimum pH for intracellular or surface membrane bound enzymes may impair cellular function. It seems likely that seawater pH may affect phytoplankton cells by multiple mechanisms simultaneously. Further, there is no reason to expect all species to have the same physiological mechanism for their exhibited pH effects. For example, different species have different capabilities for production of extracellular carbonic anhydrase to speed up the equilibrium between bicarbonate and free CO_2 (Nimer et al. 1997), a strategy to allow growth where free CO_2 may be limiting by metabolic drawdown of free CO_2 concentrations near the cell.

The studies reviewed here provide only slight insight into the mechanisms of the pH effect. C limitation due to low concentrations of free CO_2 may well be the mechanism for reduced growth rate at high pH for some of the species. However, this mechanism seems very unlikely to account for the reduction in growth rate where observed at low pH. For the studies where cultures were grown at a fixed free CO_2 concentration across a pH range, the observed pH effects are not due to a limitation of free CO_2 concentrations. Those experiments include results for the species *Cricosphaera elongata* (Fig. 8), *Thalassiosira pseudonana* (Fig. 10, Pruder 1979), *Emiliania huxleyi* (Fig. 12) and *Phaeodactylum tricornutum* (Figs. 12 & 18).

Goldman (1999) drew a similar conclusion in laboratory experiments with *Stephanopyxis palmeriana*, *Coscinodiscus* sp. and *Ditylum brightwellii*. Cultures of these diatoms were allowed to grow and draw down the CO_2 and raise the pH. Once the pH of cultures rose above pH 8.45 for *S. palmeriana*, 8.51 for *D. brightwelli* and 8.31 for *Coscinodiscus* sp., the growth rate for each species decreased from the constant growth rate at lower pH. As the growth rate of these species was not affected by turbulent mixing, Goldman (1999) concluded that free CO_2 limitation was not the cause for the decreased growth rate.

Even though the physiological mechanisms of pH effects on phytoplankton growth may not be well understood, it is still possible to infer the possible ecological consequences of the observed pH effects. Humphrey (1975) in his study of pH effects determined the pH range that will support growth for individual species (Table 4). Some of these species have limits for growth that fall within the range of pH found occasionally in coastal environments. For example, *Biddulphia aurita* did not grow above pH 8.7 and *Cylindrotheca closterium* did not grow above pH 8.5. *Amphidinium carterae*, *Chaetoceros didymum*, *Chroomonas* sp. and *Gymnodinium splendens* did not grow below pH 7.0. A pH near the extreme values found in coastal environments, pH over 9 or below 7, will exclude certain species from growing and hence occurring in the community except as a residual from earlier growth.

The ability of extreme pH-tolerant species to dominate in high pH conditions was observed in direct competition experiments. Goldman (1982b) conducted competition experiments in continuous culture between *Phaeodactylum tricornutum* and *Dunaliella tertiolecta*. As would have been predicted from the relationship between pH and algal biomass for each individual species (Fig. 15), the relative dominance in 2 species continuous cultures was influenced by pH. At higher pH, *P. tricornutum*, which is known to grow well at high pH, dominated over *D. tertiolecta*, which has maximum growth near pH 8.0.

There are 4 species for which there are more than 1 study. In 2 cases, the studies give a similar picture of the pH response of the species. All the studies of *Phaeodactylum tricornutum* indicate a very wide pH range for growth and a tolerance of very high pH (Figs. 12 & 15 to 18, Table 4). The 2 studies of *Thalassiosira pseudonana* show a similar response in each case (Fig. 10) with a broad region of pH from about 7 to 8.2 or 8.5 with little change in growth rate. At higher pH the growth rate in both studies drops off sharply. The 3 clones of *Emiliania huxleyi* show strikingly different behavior (Figs. 12 & 13). As 2 of the clones were grown under identical experimental conditions, the differences between them at least are not an experimental artifact. If it is found that species commonly have strains with very different response to pH change, a pH effect on the timing and abundance of a species may not be exhibited at the species level. Different strains could grow under different pH conditions. Nevertheless, a pH effect would still be important in determining the timing and abundance of different clones of the same species.

In the 2 studies with *Skeletonema costatum* (Figs. 9 & 13) the growth rate study indicates a broad plateau in growth rate (Fig. 9), while NO_3^- uptake rate study indicates a preference for high pH (Fig. 13). Given that the amino acid composition of *S. costatum* cells was pH dependent (Taraldsvik & Myklestad 2000), it seems possible that the NO_3^- uptake rate at variable pH is not directly correlated to growth rate. Hence, the different patterns exhibited by the 2 *S. costatum* studies may indicate real differences between clones, or may simply be a result of the use of non-equivalent measures of growth rate.

The results of the C uptake experiment by Chen (1986) and Chen & Durbin (1994) indicate that pH affects rates of primary production (Fig. 20). Carbon fixation rate for each of the 5 mixed phytoplankton communities was highest near pH 8 and decreased with increasing pH. At pH 9 the carbon fixation rates were about 50% of the maximum rates. The pH values used in these experiments do not extend to very low pH, but for 3 of the 5 communities there are also indications of a decrease in primary production rate toward low pH. At the time of sampling the communities for the carbon uptake experiments, the pH of the water in the enclosures used for Expts 7, 8, 9 and 10 was between 8.8 and 9.1. The composition of the community had not developed with species that were better able to fix carbon at high pH. Hence, blooms may be self limiting when sufficient CO_2 is taken up to drive the system to high pH. The effects of pH are not limited to the more extreme levels of pH. As already discussed, many species have maximum growth at pH above or below equilibrium pH. Accordingly, their growth rates change significantly with pH changes near equilibrium pH (e.g. Figs. 11 & 13).

The effects of changes in growth rate near equilibrium pH can be illustrated by modeling a simple growth experiment. Fig. 24 shows how the final population abundance is affected by pH for a 2 species calculation where 1 species has maximum growth at low pH and the other at high pH. The growth rates for *Asterionella japonica* (Fig. 8) were used to represent a species with maximum growth rate at low pH (7.8). The growth rates for the *Peridinium* sp. (Fig. 11) were used to represent a species with maximum growth at high pH. Final populations after 7 d exponential growth from equal initial abundance for each species were calculated. At low pH, 7.6 to 7.8, the *Peridinium* sp. would only make up 7 to 12% of the final total abundance. At pH 8, *Peridinium* sp. constitutes 22% of the final total abundance. At pH of 8.3, *Peridinium* sp. makes up 50% of the total abundance and at pH 8.5 constitutes 78% of the total abundance. The example is not expected to predict real situations as the growth rates of phytoplankton are influenced by many factors in addition to pH. However, it does illustrate that changes in pH, which are not far from equilibrium pH, may influence the relative abundance of species in mixed populations.

There is, at present, no direct evidence to link pH and the occurrence of nuisance phytoplankton species. Indeed, one nuisance species, *Pyrodinium bahamense* has nothing in its response to pH (Fig. 11) to suggest that extreme pH conditions would lead to blooms. Nevertheless, it is tempting to hypothesize that pH contributes to the apparent worldwide increase in outbreaks of nuisance blooms (e.g. Hallegraeff 1993).

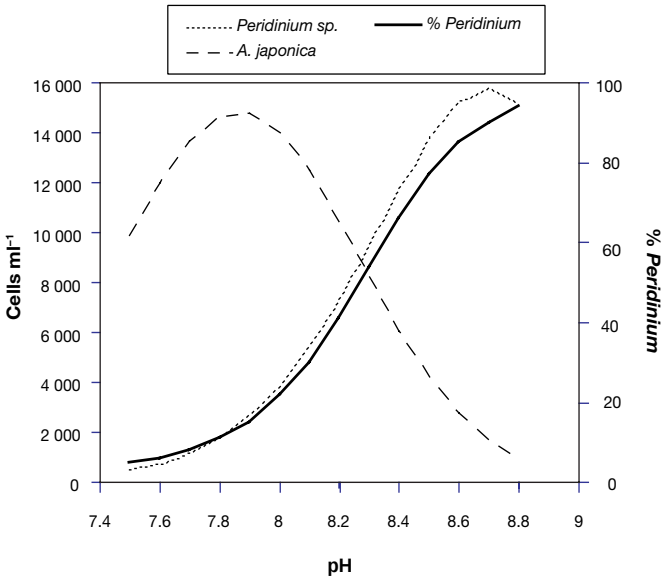

Fig. 24. *Peridinium* sp. and *Asterionella japonica*. Final population levels after 7 d exponential growth from initial population levels of 10 cells ml^{-1}. Growth rates at each pH were calculated from 2nd order polynomial curve fits to the data in Figs. 7 & 11. The percent *Peridinium* is the percent of the combined populations of the 2 species

Extreme pH values (i.e. 7 or 9) occur infrequently, as do many nuisance blooms. With the eutrophication of coastal ecosystems, the pH of coastal environments may be driven to more frequent or greater extremes (e.g. Fig. 6), giving greater opportunity for species with tolerance to extreme pH to bloom. The pH variability in an environment subject to both nutrient enrichment and organic C enrichment depends upon many hydrographic and ecological factors, as discussed above. Hence, each estuary will have a unique response. There may be no general pattern of pH variability shared among estuaries, other than an increased frequency of extreme values with timing that is difficult to predict. This, in turn, may lead to increased frequency of previously rare occurrences of certain species.

SUMMARY AND CONCLUSIONS

The pH of seawater in many coastal environments routinely varies by 1 pH unit from about pH 7.5 to 8.5. There are occasional occurrences of pH greater than 9 or less than 7. pH values outside the range of 7.0 to 8.5 can preclude the growth of some species. At extreme pH, only species with a tolerance for high or low pH would grow and dominate the community. Some species have maximum growth near equilibrium pH and others have a range of pH, encompassing equilibrium pH, where growth rate is not affected by changes in

pH. The growth rate of these species will be largely unaffected by small changes near equilibrium pH. Other species have maximum growth at pH above or below equilibrium pH (Fig. 22). The growth rate of these species changes at pH near equilibrium pH. Hence, for these species, their growth rate and abundance in a mixed community could be influenced by pH variability even near equilibrium.

If a coastal ecosystem has a regular pH cycle, pH may play a role in a seasonal succession of phytoplankton species. Seawater pH may limit the rate of primary production, growth, and total abundance of phytoplankton in blooms. Phytoplankton communities were able to fix C only half as fast at about pH 9 compared to pH 8. This reduction may allow sinking and grazing to reduce the size of the population from that which would have been obtained without a pH effect on C fixation.

pH effects should be considered when culturing phytoplankton or conducting laboratory studies of phytoplankton growth rates as a function of nutrients, trace elements or light etc. Laboratory cultures are often grown at relatively high cell densities; hence, there is greater likelihood that the cultures may take up enough CO_2 to significantly alter the pH of the system. If conditions in the experiments are not controlled for pH, effects attributed to other factors may in reality be a pH effect.

Finally, the existing data suggest that it is inappropriate to *a priori* exclude pH as a factor in coastal marine phytoplankton ecology. It seems probable that upon further study, pH will prove to be a non-trivial factor in phytoplankton dynamics in coastal environments.

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