Global declines in oceanic nitrification rates as a consequence of ocean acidification

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Ocean acidification produced by dissolution of anthropogenic carbon dioxide (CO_2) emissions in seawater has profound consequences for marine ecology and biogeochemistry. The oceans have absorbed one-third of CO_2 emissions over the past two centuries, altering ocean chemistry, reducing seawater pH, and affecting marine animals and phytoplankton in multiple ways. Microbially mediated ocean biogeochemical processes will be pivotal in determining how the earth system responds to global environmental change; however, how they may be altered by ocean acidification is largely unknown. We show here that microbial nitrification rates decreased in every instance when pH was experimentally reduced (by 0.05–0.14) at multiple locations in the Atlantic and Pacific Oceans. Nitrification is a central process in the nitrogen cycle that produces both the greenhouse gas nitrous oxide and oxidized forms of nitrogen used by phytoplankton and other microorganisms in the sea; at the Bermuda Atlantic Time Series and Hawaii Ocean Time-series sites, experimental acidification decreased ammonia oxidation rates by 38% and 36%. Ammonia oxidation rates were also strongly and inversely correlated with pH along a gradient produced in the oligotrophic Sargasso Sea ($r^2 = 0.87$, $P < 0.05$). Across all experiments, rates declined by 8–38% in low pH treatments, and the greatest absolute decrease occurred where rates were highest off the California coast. Collectively our results suggest that ocean acidification could reduce nitrification rates by 3–44% within the next few decades, affecting oceanic nitrous oxide production, reducing supplies of oxidized nitrogen in the upper layers of the ocean, and fundamentally altering nitrogen cycling in the sea.

Atmospheric carbon dioxide (CO_2) concentrations are projected to double over the next century as human societies continue to burn fossil fuels and biomass (1), yet a large proportion of emitted anthropogenic CO_2 will dissolve in the ocean rather than accumulate in the atmosphere (1–4). Dissolution of CO_2 in seawater produces a weak acid that has decreased surface ocean pH by ~0.1 below preindustrial levels, and an additional 0.3–0.4 decline is expected by the year 2100 (2, 4). This more than twofold increase in surface ocean hydrogen ion concentrations [H^+] will be accompanied by increasing CO_2 partial pressures (pCO_2), increasing bicarbonate ion concentrations [HCO_3^-], decreasing carbonate ion concentrations [CO_3^{2-}], and multiple shifts in trace metal and nutrient chemistry (2–4). Predicting the responses of marine organisms, ecosystems, and biogeochemical processes to these fundamental changes in ocean chemistry is consequently a major scientific challenge (5–9). Although marine bacteria and archaea constitute the majority of biomass in the sea, sustain a large percentage of global primary production, and govern biogeochemical cycling of carbon and nitrogen (10), we lack a clear understanding of how they will react to ocean acidification (9, 11).

In an acidifying ocean, microbial community responses to reduced seawater pH and elevated pCO_2 may act as positive or negative feedbacks to perturbation of the carbon and nitrogen cycles, and guilds that carry out critical biogeochemical processes may be affected in unanticipated ways. For instance, microbial nitrification changes the oxidation state of nitrogen available to other organisms from reduced ammonium (NH_4^+) to oxidized nitrate (NO_3^-); nitrification subsequently supplies oxidized electron acceptors to anaerobic nitrogen loss processes such as denitrification and, perhaps more importantly, ultimately feeds all NO_3^--supported "new" production in the ocean (12). Oceanic nitrification also has a direct climate feedback because it is a substantial natural source of the greenhouse gas nitrous oxide (N_2O) to the atmosphere (13). We present here several lines of evidence indicating that nitrifiers may be sensitive to future changes in seawater pCO_2 or pH levels.

Because the two steps of nitrification (ammonia oxidation to nitrite and nitrite oxidation to nitrate) are mediated by groups of ammonia and nitrite oxidizers that are chemoautotrophic and actively convert inorganic carbon into biomass (14, 15), nitrifiers could exhibit a "CO_2-fertilization" effect due to undersaturation of ribulose bisphosphate carboxylase oxidase (RuBisCO) at present-day CO_2(aq) concentrations. For example, recent evidence suggests that some marine N_2-fixing cyanobacteria grow more rapidly and fix atmospheric nitrogen at higher rates under elevated pCO_2 (reviewed by ref. 11). However, cultivated strains of ammonia-oxidizing bacteria (AOB) contain putative carbon concentrating mechanisms (CCMs) that could reduce their sensitivity to changes in pCO_2 (16), and ammonia-oxidizing archaea (AOA) use a fundamentally different carbon fixation pathway (17–19). This archaeal 3-hydroxypropionate/4-hydroxybutyrate pathway appears to be more energetically favorable than the Calvin–Benson–Bassham cycle (18, 19) and utilizes HCO_3^- as an inorganic carbon source rather than CO_2 (18). The presence of putative CCMs in AOB and lack of RuBisCO in AOA suggest that increased CO_2 concentrations may not strongly "fertilize" oceanic ammonia oxidation, but this has not been thoroughly tested.

In contrast, laboratory- and field-based studies indicate that reduced pH has a nearly universal detrimental effect on nitrification, with lower ammonia oxidation rates and slower AOB growth rates occurring under reduced pH in freshwater (20), soils (21, 22), activated sludge (23–25), and bacterial cultures (26–32). Reduced pH can inhibit AOB and AOA because uncharged ammonia (NH_3)—rather than NH_4^+ ion—is the substrate used (28, 29). The NH_3/NH_4^+ equilibrium is pH sensitive (i.e., $NH_3 + H^+ \rightleftarrows NH_4^+$; $pK_a = 9.3$) (33) (Fig. S1), and use of NH_3 rather than NH_4^+ by AOB is evident from changes in affinity observed with changing pH (28). Cultures of the widespread marine AOB *Nitrosococcus oceani*, for instance, display maximal oxidation rates at pH 8, but these rates decline 20–36%

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as pH is decreased or increased by 0.4–0.5 units (29). Decade-long experimental acidification of freshwater lakes also terminated nitrification activity, and NH_4^+ subsequently accumulated over the course of several years (20). Despite this clear sensitivity to pH, only a single study examined the effects of pH change on ammonia oxidation rates in the ocean, finding decreased rates following large pH changes (>0.5) in coastal waters (8). How predicted levels of atmospheric CO_2-driven ocean acidification will affect ammonia oxidation rates throughout the ocean is not known.

In light of these limited observations, and the pace and global extent of ocean acidification, we examined the response of ammonia oxidation rates to reduced seawater pH and elevated pCO_2 in a series of experiments conducted in the oligotrophic Sargasso Sea (two experiments), at the Bermuda Atlantic Time Series (BATS), at the San Pedro Ocean Time-series (SPOT) site off the coast of Los Angeles, California, and at station ALOHA of the Hawaii Ocean Time-series (HOT) program in the oligotrophic North Pacific subtropical gyre (two experiments) (Fig. 1 and Table 1). Because nitrification is typically most active near the base of the euphotic zone, the depth at which water was collected for experiments (240 m in the Sargasso Sea, 175 m at HOT, 150 m at BATS, and 45 m at SPOT) was selected on the basis of in situ temperature and chlorophyll fluorescence profiles (Fig. S2). Rates of ammonia oxidation were determined by adding ^{15}N-labeled NH_4^+ ($^{15}NH_4^+$) at low levels (20–50 nM) to seawater (34), and pH/pCO_2 levels were manipulated in several ways (Table 1).

Results and Discussion

In all six experiments, $^{15}NH_4^+$ oxidation rates decreased in response to decreasing pH_{total} values from 7.99–8.09 to 7.85–7.99. Modest pH changes produced modest decreases in $^{15}NH_4^+$ oxidation rates, and doubling of seawater pCO_2 reduced rates by 8–38%. $^{15}NH_4^+$ oxidation rates were significantly lower in reduced pH treatments when compared with controls in experiments in the Sargasso Sea, at BATS, at SPOT, and at HOT 210 (one-way ANOVA $F = 9.78–32.2$, df = 1, $P = 0.003–0.035$; Fig. 2). For the HOT 209 experiment, rates were 8% lower in the $pH_{total} \sim 7.85$ treatment compared with the control ($pH_{total} \sim 7.99$) but this decrease was not statistically significant (ANOVA $F = 1.30$, df = 1, $P = 0.31$; Fig. 2).

In both Sargasso Sea experiments, a spectrum of pCO_2 concentrations (348–460 μatm) and pH_{total} values (7.99–8.09) elicited consistent $^{15}NH_4^+$ oxidation rate responses. Seawater pH treatments of 8.09 (±0.01 SD), 8.08 (±0.02), and 8.02 (±0.02) in one of the Sargasso Sea experiments yielded corresponding mean oxidation rates of 1.58 (±0.16), 1.37 (±0.35), and 1.29 (±0.45) $nmol \cdot L^{-1} \cdot d^{-1}$ (Fig. 3). Seawater pH barely differed between treatments in the other Sargasso Sea experiment (averaging 8.00 ± 0.01 and 7.99 ± 0.01) and $^{15}NH_4^+$ oxidation rates were nearly identical, averaging 1.01 (±0.48) and 1.02 (±0.1) $nmol \cdot L^{-1} \cdot d^{-1}$. Across these two experiments—both conducted in oligotrophic waters from 240 m depth—rates were linearly correlated with both pCO_2 ($r^2 = 0.89$, $P < 0.05$) and pH_{total} ($r^2 = 0.87$, $P < 0.05$) (Fig. 3). These samples were treated identically with gentle bubbling of different air:CO_2 mixtures as the only variable, and all were manipulated with gas for 4 h. Ammonia oxidation rates therefore appear to be highly sensitive to changes in pH and pCO_2 given their reaction to moderate changes in pH_{total} (<0.10) in the oligotrophic Sargasso Sea.

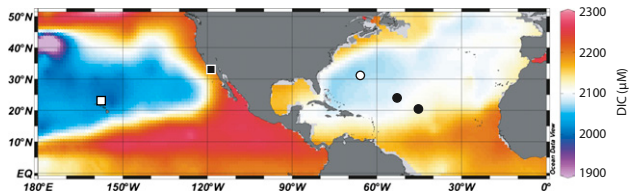

Fig. 1. Experiment locations overlaid on dissolved inorganic carbon (DIC) concentrations at 200 m depth from Goyet et al. (52). The location of the HOT experiments is denoted by the white square, the SPOT experiment is denoted by a black square, BATS is denoted by a white circle, and the locations of the two Sargasso Sea experiments are denoted by black circles.

Changes in biogeochemical activity occurred rapidly, as differences in oxidation rates were evident within 3 h of exposure to reduced seawater pH and elevated pCO_2 at SPOT, but remained significantly different after 40 h of incubation (Fig. S3*A*). Experimental ocean acidification suppressed $^{15}NH_4^+$ oxidation rates by 40% at 3 h (ANOVA $F = 9.09$, df = 1, $P < 0.04$), by 18% at 20 h ($F = 3.37$, df = 1, $P = 0.14$), and by 26% at 40 h ($F = 9.89$, df = 1, $P < 0.04$) (Fig. S3*A*). Rates exhibited a decline over time in all treatments but did not show evidence of convergence: $^{15}NH_4^+$ oxidation rates at 40 h differed more between treatments than those measured at 20 h. Our findings indicate that regions of low ambient pH such as upwelling zones are not immune to future acidification-driven declines in ammonia oxidation rates: SPOT is located in a region of naturally low ambient pH (35), but rate reductions at SPOT were comparable to those in other regions of the ocean and represent the largest absolute decrease. In other words, our results indicate no evidence for nitrifier acclimation to reduced pH in a region where acclimation might be expected.

Reducing seawater pH also suppressed $^{15}NH_4^+$ oxidation rates at BATS and Station ALOHA, where decades-long declines in seawater pH due to ocean acidification are well documented (36, 37). Microbes experience natural daily, seasonal, and interannual variability in pH throughout the sea, but the experimental pH change that we introduced mimics average conditions expected later this century; accordingly, this change was greater than what typically occurs naturally at either time series site (Fig. S4). In our experiments, pH_{total} reached lower levels than those documented at 150 m depth at BATS or 175 m depth at Station ALOHA. Extrapolating from observed trends, average pH_{total} values equivalent to those induced in our experiments would occur in 2138 at BATS and in 2070 at HOT, but these thresholds would be crossed intermittently before these dates due to seasonal and interannual variability in pH. Because variability in pH is more pronounced at HOT (37), experimentally induced pH changes were more similar to values that microbial communities have been previously exposed to—e.g., pH_{total} was reduced to 7.85 vs. a measured low of 7.88 at HOT. However, comparing controls and treatments, pH_{total} changed by similar amounts (8.06–7.93 and 7.99–7.85) and rates decreased by similar percentages (36 and 38%) at BATS and HOT 210, respectively (Fig. 3).

Temporal variability in pH and spatial variability with depth or across different regions—e.g., between upwelling regions and midocean gyres—could in principle be used to examine pH effects on nitrification without direct manipulation of pH (9). However, few measurements of ammonia oxidation rates have been made, and they typically display irregular patterns in space and time (12, 38–40). At station ALOHA, for instance, measured nitrification rates range over two orders of magnitude (38, 39) and $^{15}NH_4^+$ oxidation rates measured in this study differed between two consecutive cruises (Fig. S5 and *SI Results and Discussion*). During HOT 209, pH_{total} at 175 m (averaged from values at 150 and 200 m) was 7.94, and we measured pH_{total} of 7.99 during HOT 210, yet nitrification rates were threefold greater during HOT 209. This variability stems from the multiple environmental factors that affect ammonia oxidation rates, including substrate availability, light, and dissolved oxygen concentrations, in addition to pH (15).

Table 1. Overview of experiments, including date, duration, pH treatments and means of manipulation, carbonate system parameters measured, depth of seawater collection, volume of each incubation replicate, temperature, and the concentration of $^{15}NH_4^+$ added

Location	Date	Time, h	pH treatments [means of manipulation]	Carbonate system parameters	Depth, m	Volume, L	Temperature, °C	$^{15}NH_4^+$, nM
Sargasso 1	5/17/08	11	8.00, 7.99 [4 h CO_2; all manipulated]	TA, DIC	240	2	17.7	50
Sargasso 2	5/19/08	18	8.09, 8.08, 8.02 [4 h CO_2; all manipulated]	TA, DIC	240	2	18.4	50
BATS	5/24/08	10	8.06 (control), 7.99, 7.93 [4 h CO_2; control not manipulated]	TA, DIC	150	2	18.4	50
SPOT	6/18/08–6/23/08	120	8.00–8.01 (control), 8.05–8.07, 7.91–7.96 [120 h CO_2; control not manipulated]	pH, DIC	45	20	11.5	20
HOT 209	2/18/09–2/19/09	25	~8 (control), ~7.8, ~7.6, ~7.5 [25 h acid; control not manipulated]	pH*, DIC	175	1	18.9	50
HOT 210	4/28/09–4/29/09	25	7.99 (control), 7.85, 7.63, 7.42 [25 h acid; control not manipulated]	pH, DIC	175	1	19.8	50

pH likely plays an indirect role in controlling ammonia oxidation rates because it changes the chemical speciation of NH_3/NH_4^+ and covaries with other factors with depth and across ocean basins. In our dataset, for example, $^{15}NH_4^+$ oxidation rates were greatest at SPOT where pH is naturally low—but SPOT is exposed to seasonal upwelling that may reduce pH (35) and would also increase nutrient supply and production and presumably respiration, remineralization, and nitrification. Given that experimental locations differed in initial NH_4^+ concentrations (53 nM at SPOT and undetectable elsewhere), relative depth in the water column (Fig. S2), and overall N supply through nitrogen fixation, deposition, runoff, and upwelling, it is not surprising that rates in control incubations were uncorrelated with pH (Table S1). Our experimental results are instead consistent with the idea that as acidification progresses over the next century, pH could become an increasingly significant limiting factor by affecting the equilibrium between NH_3 and NH_4^+. NH_3 concentrations were therefore calculated on the basis of in situ pH, the pK_a, and $[NH_4^+]$ (*SI Results and Discussion*) and were correlated with ammonia oxidation rates across the HOT, SPOT, and BATS experiments ($r^2 = 0.789$, $P < 0.05$) and within the Sargasso experiments ($r^2 = 0.868$, $P < 0.05$) (Table S1). $[NH_3]$ was also significantly related to $^{15}NH_4^+$ oxidation rates across the full dataset ($r^2 = 0.337$, $P < 0.05$). We also found that the percentage change in $[NH_3]$, $[H^+]$, and pH was correlated with the percentage change in $^{15}NH_4^+$ oxidation rates ($r^2 = 0.810$–0.846, all $P < 0.05$) (Table S1). These observations suggest that declining $[NH_3]$ with ocean acidification is the driving factor behind reduced $^{15}NH_4^+$ oxidation rates measured in this study.

Competition for NH_4^+ with other organisms that are more successful under low pH/high pCO_2 could also affect nitrification rates, but there was little evidence of this in our experiments. For example, Horz et al. (41) attributed reduced AOB abundances in California grassland exposed to elevated CO_2 to unsuccessful competition with heterotrophic bacteria for NH_4^+, but in the SPOT experiment the data suggested no systematic stimulation of heterotrophic growth: After 5 d of incubation, there was no significant difference in [^{3}H]leucine bacterial production among treatments ($P > 0.05$ for all time points; Fig. S3*B*). [^{3}H]thymidine incorporation was higher in the reduced pH treatment compared with an elevated pH treatment, but neither one was significantly different from the control, and [^{3}H]thymidine incorporation was variable over the course of the incubation (Fig. S3*C*). Nor was

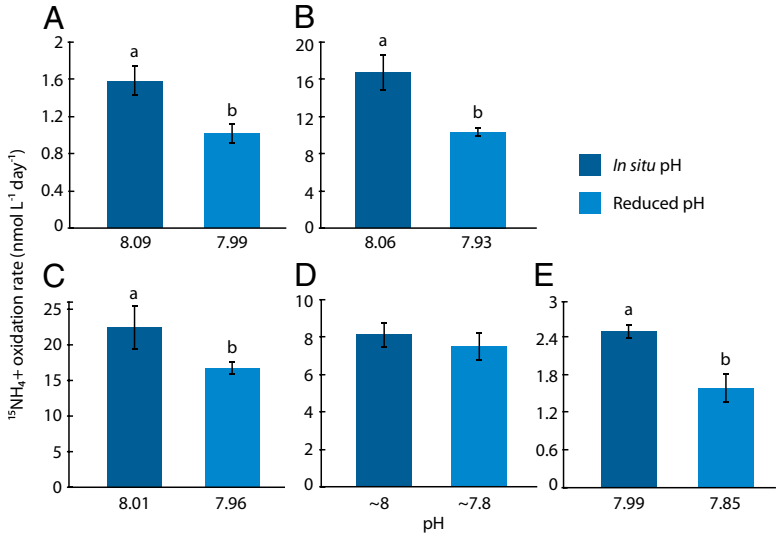

Fig. 2. Reductions in ammonia oxidation rates in ocean acidification experiments in (*A*) the Sargasso Sea, at (*B*) BATS, at (*C*) SPOT, at (*D*) HOT 209, and at (*E*) HOT 210. pH_{total} values are noted along the horizontal axis (calculated pH_{total} values are shown for the HOT 209 experiment). Statistically significant differences among means ($P < 0.05$) were determined via one-way ANOVA, and error bars denote 1 SD of triplicate treatments. Ammonia oxidation rates at SPOT were calculated from the linear accumulation of ^{15}N label in the oxidized pool over the course of the experiment; all other values represent end-point measurements.

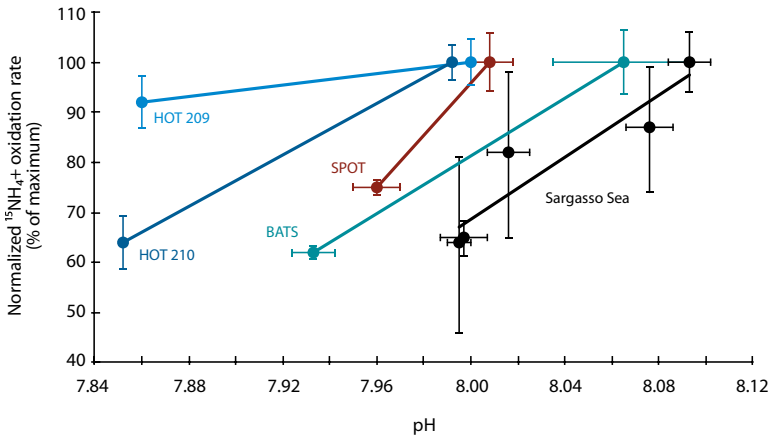

Fig. 3. Correspondence between ammonia oxidation rates and pH_{total} for all experiments. Ammonia oxidation rates were renormalized to the maximum rate measured in the experiment. For the Sargasso Sea regression line, $y = 310x - 2{,}410$, $r^2 = 0.87$, and $P < 0.05$. Calculated pH_{total} values are shown for HOT 209, and error bars denote 1 SD among triplicate treatments, except in the case of rate measurements in the Sargasso Sea, where error bars denote the SE of triplicate measurements.

there any evidence that physical disruption affected bacterial production through release of organic carbon, as these two treatments exposed to gentle bubbling used to equilibrate seawater were significantly different from one another, but were not significantly different from the unbubbled control. Finally, it is unlikely that phytoplankton successfully competed for NH_4^+ as all incubations were conducted in the dark, and water was collected from below the euphotic zone (Fig. S2).

We instead observed a rapid and sustained decline in rates at SPOT (Fig. S3*A*), and ammonia oxidation decreased irrespective of how pH was manipulated. In the Sargasso Sea, all treatments, including controls, were manipulated by bubbling with gas mixtures; at BATS and SPOT, an unbubbled control was compared with gas treatments; and at HOT, target treatments were achieved by treating seawater with trace metal-clean acid. Regardless of the method chosen to manipulate the seawater buffer system, all experimental approaches produced similar results (Table 1 and Figs. 2 and 3). This outcome strongly suggests that measured decreases in ammonia oxidation rates are not driven by experimental techniques or shifts in carbonate alkalinity (42), but are a direct function of changing pH. This finding is furthermore consistent with what little is known about pH effects on marine nitrification and nitrifying bacteria. An experiment examining the possible effects of deliberate waste CO_2 disposal on oceanic nitrification at two depths in the Juan de Fuca Strait, for example, showed decreases in ammonia oxidation rates as pH was sequentially reduced from 8 to 6 in 0.5 increments (8); decreasing pH also monotonically decreased rates during HOT 209. Declines in cell-normalized ammonia oxidation rates for *N. oceani* cultures at pH >8 and <8 (29) are consistent with our findings as well: Rates decreased in the SPOT experiment both when pH_{total} was increased to 8.07 and decreased to 7.91 relative to the control (8.00; Table S2).

Our results demonstrate that oceanic ammonia oxidation rates decrease due to pH changes (of 0.05–0.14) that mimic anticipated near-future levels of CO_2-driven ocean acidification. Although sensitivity to pH change is a long-recognized characteristic of nitrification (20–32), little information is available for marine organisms and ecosystems, and these few studies have manipulated pH by >0.4 (8, 29). The six experiments reported here were also performed at NH_4^+ concentrations (50–73 nM) that more closely reflect conditions found throughout most of the ocean (34, 39, 43). In contrast, the experimental approach of Huesemann et al. (8) involved addition of 1,000-fold greater concentrations of NH_4^+ (50 μM of unlabeled NH_4^+ vs. 20–50 nM of ^{15}N-labeled NH_4^+), and pH effects on nitrification in activated sludge and pure cultures have been measured at concentrations of at least 20 μM and up to 20 mM NH_4^+ (23–32). A fundamental advantage of using an isotopic tracer is the ability to measure oxidation rates at low nutrient concentrations; this is a critically important issue when dealing with microorganisms that are adapted to oligotrophic conditions and are extremely responsive to changes in substrate availability. The cultivated marine AOA *Nitrosopumilus maritimus* exhibits remarkable affinity for NH_3, for instance, and accelerates oxidation rates 50-fold within minutes of NH_3 addition (44). Experimentally reducing pH at unrealistic concentrations of 20,000–20,000,000 nM [NH_4^+] shifts the chemical equilibrium away from NH_3 toward NH_4^+, but the absolute NH_3 concentration still remains orders of magnitude greater than those found in the sea.

At pH 8.0 in the ocean, NH_3 constitutes just 5% of total NH_3 + NH_4^+, and by 2100, ocean acidification could reduce available NH_3 by 50% (33) (Fig. S1). Chemical reequilibration between NH_3 and NH_4^+ occurs rapidly, but ocean acidification further depresses low NH_3 concentrations and may exacerbate an already stressed existence. In the water column, adaptive responses to reduced pH involve transport of NH_4^+ into the cell and maintenance of a basic internal pH or use of urea (CH_4N_2O) as an ammonia source (refs. 22 and 30 and references therein). However, both of these strategies require ammonia oxidizers to expend energy to transport nitrogen into the cell and ultimately deliver

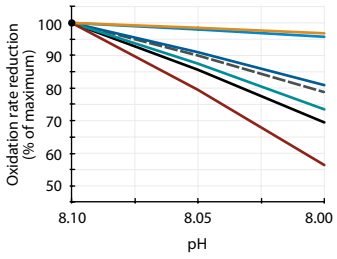

Fig. 4. Renormalized acidification-driven decreases in ammonia oxidation rates. Rate reductions are expressed as a percentage decrease in rates in acidified seawater compared with controls and are normalized to a 0.1 unit decrease in pH from 8.1 to 8. Previously reported data for >0.5 pH changes in Huesemann et al. (8) are included for comparison and denoted by the orange line; other colors are for experiments that are identical to those in Fig. 3. The mean reduction is denoted by the dashed gray line.

NH_3 to ammonia monooxygenase, and pH may also affect enzyme activity directly (30).

In fact, nitrification was severely inhibited in experimentally acidified freshwater lakes, where micromolar concentrations of combined NH_3 + NH_4^+ were left unused at low pH, and nitrate was not produced (20). Rudd et al. found that even over the course of 7–10 y, aquatic ammonia oxidizers did not acclimate to experimentally reduced pH (20). Although it is important to carefully qualify extrapolations from short-term manipulative experiments such as ours (days) to long-term microbial responses to ocean acidification (decades), the acidified lake study demonstrates that our experimental results are consistent with those from longer-term manipulations in other aquatic ecosystems. Unfortunately, analogous long-term experiments that examine the response of marine nitrification rates to large-scale, sustained alteration of ocean pH will be difficult to carry out: Nitrification rates are greatest at depths of tens to hundreds of meters in the ocean (13, 15, 34, 38, 39, 43), and nitrification is strongly tied to other biogeochemical processes in the sea (10, 14).

Ocean pH will invariably decline, on average, as atmospheric CO_2 concentrations rise. The oceans' response to acidification will not be uniform: Different regions (35, 45) and different depths (37) already exhibit different trends, and the activities of microbes and other organisms may accelerate or modulate these trends (9, 37, 45). Keeping spatial and temporal variability and the limited duration of our experiments in mind, it is nevertheless instructive to use our results to estimate the potential overall impact of acidification on marine nitrification and associated nitrogen cycle processes. All published data indicate that ammonia oxidation slows as pH decreases (8, 20–32), and our results are no different: Across multiple experiments conducted in high and low productivity regions of two oceans (Fig. 1), ammonia oxidation rates declined by 8–38% (Figs. 2 and 3). Renormalized to pH change of 8.1–8.0 (*SI Results and Discussion*), and including data from a previous experiment in the North Pacific Ocean (8), ammonia oxidation rates decrease from 3 to 44%, with a mean decrease of 21% and a median decrease of 23% (Fig. 4). Should these findings apply broadly, ammonia oxidation rates would decline by 3–44% in response to the 0.1 decrease in ocean pH expected over the next 20–30 y.

Such a change would have major implications for the global marine nitrogen cycle. Oceanic ammonia oxidation produces the potent greenhouse gas N_2O (13), representing at least half the total oceanic source (46) or ~17% of all natural N_2O emissions (47). A 3–44% decrease in oceanic nitrification N_2O production would reduce emissions by ~0.06–0.83 Tg $N{\cdot}y^{-1}$ globally, which is comparable to all current N_2O production from fossil fuel combustion and industrial processes (0.7 Tg $N{\cdot}y^{-1}$) (47). Future changes in upper ocean temperature (1) and oxygen concentrations (48) could also strongly influence the oceanic source of N_2O, generating climate feedbacks (46) that should be further explored through observation, experimentation, and modeling.

At the base of the euphotic zone, suppression of ammonia oxidation will skew the distribution of dissolved nitrogen species where competition for nutrients is intense. According to recent estimates, nitrification within the euphotic zone supplies NO_3^- that supports ~32% of global oceanic primary production, with another ~26% of oceanic primary production supported by upwelled, previously nitrified NO_3^- (12). As NO_3^- is assimilated by phytoplankton and eventually remineralized to NH_4^+, ocean acidification would substantially reduce the proportion converted back to NO_3^- by nitrification, ultimately depleting upper water column NO_3^- over time. With a 3–44% reduction in ammonia oxidation rates, at least 1% and up to 25% of global marine primary production would be supported by regenerated NH_4^+ rather than NO_3^-. Coupled with higher NH_4^+ supplies derived from CO_2-fertilized increases in nitrogen fixation rates (11), this substantial shift in the chemical form of nitrogen supplied to phytoplankton communities would favor smaller organisms that are more competitive for NH_4^+. NO_3^--supported production specialists, such as large diatoms, would be at a disadvantage—with potentially important implications for oceanic food webs, fisheries, and carbon export to the deep sea (12). Our findings indicate that, as anthropogenic CO_2 invades the ocean, pH-driven reductions in ammonia oxidation rates could fundamentally change how nitrogen is cycled and used by organisms in the sea.

Materials and Methods

Sample Collection and Experimental Manipulation. Water samples were collected from Niskin-type bottles mounted on a rosette directly into incubation bottles to minimize disturbance (*SI Materials and Methods*). Bottles were quickly sealed and were unsealed only for attachment of gas lines for air:CO_2 mixtures, for milliliter additions of $^{15}NH_4^+$ or trace metal-clean hydrochloric acid (HCl), or for sample collection during the SPOT experiment. The effect of reduced pH and elevated pCO_2 was examined using two approaches (49): either by addition of dilute, trace metal-clean hydrochloric acid (HOT experiments) or by bubbling with air:CO_2 gas mixtures (all other experiments). For BATS, HOT, and SPOT, controls consisted of $^{15}NH_4^+$-amended but otherwise untreated seawater, whereas all treatments were manipulated (gently bubbled) with air:CO_2 mixtures in the Sargasso Sea (see *SI Materials and Methods* for additional detail). All treatments in all experiments were performed in triplicate.

Carbonate System and Ammonia Oxidation Measurements and Calculations. Seawater CO_2 parameters were verified by measurement of two carbonate system parameters: total alkalinity (TA) and dissolved inorganic carbon (DIC) in the Sargasso Sea and at BATS and pH and DIC at SPOT and HOT. Details of these measurements are available in *SI Materials and Methods*. HOT 209 pH samples were not properly collected, but values are likely similar to HOT 210 given the correspondence between HOT 210 and archival data and that identical experimental procedures were followed for both HOT 209 and 210. $^{15}NH_4^+$ oxidation rates were measured by addition of 20–50 nM of stable isotope tracer and accumulation of ^{15}N label in the oxidized NO_2^- + NO_3^- pool following incubation. In-depth discussion of measurements and calculations is available in *SI Materials and Methods*.

Bacterial Production and Statistical Analyses. [^{3}H]Thymidine incorporation (50) and [^{3}H]leucine (51) were measured using previously published methods. Statistical analyses were conducted in MATLAB 7.6.0 (R2008a).

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