The Effects of CO_2 Disposal on Marine Nitrification Processes

Michael H. Huesemann (michael.huesemann@pnl.gov, 360-681-3618)
Pacific Northwest National Laboratory – Marine Sciences Laboratory
1529 West Sequim Bay Road
Sequim, WA 98382

Ann D. Skillman (ann.skillman@pnl.gov, 360-681-3649)
Pacific Northwest National Laboratory – Marine Sciences Laboratory
1529 West Sequim Bay Road
Sequim, WA 98382

Eric A. Crecelius (eric.crecelius@pnl.gov, 360-681-3604)
Pacific Northwest National Laboratory – Marine Sciences Laboratory
1529 West Sequim Bay Road
Sequim, WA 98382

Abstract

In an attempt to reduce the threat of global warming, it has been proposed that the rise of atmospheric carbon dioxide concentrations be reduced by the ocean disposal of CO_2 from the flue gases of fossil fuel-fired power plants. The release of large amounts of CO_2 into mid or deep ocean waters will result in large plumes of acidified seawater with pH values ranging from 6 to 8. In an effort to determine whether these CO_2-induced pH changes have any effect on marine nitrification processes, surficial (euphotic zone) and deep (aphotic zone) seawater samples were sparged with CO_2 for varying time durations to achieve a specified pH reduction, and the rate of microbial ammonia oxidation was measured spectrophotometrically as a function of pH using an inhibitor technique. For both seawater samples taken from either the euphotic or aphotic zone, the nitrification rates dropped drastically with decreasing pH. Relative to nitrification rates in the original seawater at pH 8, nitrification rates are reduced by ca. 50% at pH 7 and more than 90% at pH 6.5. Nitrification is essentially completely inhibited at pH 6.

Consequently, the disposal of CO_2 into mid or deep oceans will most likely result in a drastic reduction of ammonia oxidation rates within the pH plume and the concomitant accumulation of ammonia instead of nitrate. It is unlikely that ammonia will reach the high concentration levels at which marine aquatic organisms are known to be negatively affected. However, if the ammonia-rich seawater from inside the pH plume is upwelled into the euphotic zone, it is likely that changes in phytoplankton abundance and community structure will occur. Finally, the large-scale inhibition of nitrification and the subsequent reduction of nitrite and nitrate concentrations could also result in a decrease of denitrification rates which, in turn, could lead to the buildup of nitrogen and unpredictable eutrophication phenomena. Clearly, more research on the environmental effects of ocean disposal of CO_2 is needed to determine whether the potential costs

related to marine eco-system disturbance and disruption can be justified in terms of the perceived benefits that may be achieved by temporarily delaying global warming.

Introduction

The combustion of fossil fuels during the last two centuries has significantly increased the concentration of carbon dioxide in the atmosphere. This, in turn, is likely to result in global warming and a wide range of concomitant negative environmental and social impacts such as sea-level rise, species extinction, loss of agricultural production, and mass migrations of affected human populations [1,2].

In an effort to reduce the future potential impacts of global warming, three different technological mitigation strategies have been proposed for reducing atmospheric carbon dioxide levels. First, the amount of CO_2 per unit power generation and end use could be significantly reduced by increasing the energy efficiency of power plants, buildings, appliances, automobiles, etc. Second, a shift from fossil to solar energy sources such as wind, biomass, or photovoltaics would completely eliminate any carbon dioxide emissions that are currently associated with power generation. Third, carbon dioxide could potentially be removed from either the atmosphere or from the flue gases of power plants by sequestering it in terrestrial ecosystems, geological formations, or oceans [3].

A number of different ocean disposal strategies have been proposed. These include the release of dry ice cubes from a stationary ship, the introduction of liquid CO_2 onto a seafloor depression forming a “deep lake”, the release of CO_2 enriched seawater at 500-1000 m depth, and the injection of liquid CO_2 at 1000-1500 m depth from a stationary outlet or from a pipe towed by a moving ship [3-5]. The release of CO_2-enriched seawater or liquid CO_2 will result in large pH plumes near the injection points. For example, based on modeling results of a specific CO_2 disposal scenario by Herzog et al. [5], the pH near the injection point is less than 5.8 and the steady-state plume of seawater with a pH less than 6.6 is at least 25 km long and 1000 m wide. Another three-dimensional ocean model simulation of a 20-year continuous CO_2 injection at 1720 m off the coast of North Carolina indicated that the pH plume could be more than 1000 miles long and would reach equatorial waters [3]. Finally, based on the modeling of various CO_2 disposal scenarios, Caulfield et at. [6] found that the volume of seawater with a pH under 7 could be hundreds of cubic kilometers.

Very little is currently known about the potential environmental effects of CO_2 disposal in oceans [4-13]. A team of scientists at the Massachusetts Institute of Technology used existing literature data on the toxicity effects of reduced pH to marine zooplankton and benthos and combined them into a model expressing mortality as a function of pH and exposure time for various CO_2 disposal scenarios [4-8]. As expected, mortality increases with the length of exposure to acidic seawater and with decreasing pH. A group of Japanese scientists studied the effects of CO_2 induced seawater acidification on the survival of three different species of nematodes and on the growth rate of eleven different marine bacteria [9]. They found that both nematodes and bacteria were so

resistant to the high concentrations of CO_2 that drastic impacts in terms of survival or growth were observed only under conditions where the pH was below 5.5-6.0. Considering that most of the acidified seawater plume would have a pH greater than 6 [5], these data suggest that the impacts of CO_2 disposal on marine microorganisms should be minimal or negligible.

It should be noted, however, that the Japanese study focused only on the effects of CO_2 on bacterial growth rates but not specific transformations that are mediated by marine microorganisms. For example, it is not known how the marine nitrogen cycle is affected by the disposal of large amounts of CO_2 into the mid or deep ocean. Figure 1 shows a conceptual model of the oceanic nitrogen cycle including estimates of the various nitrogen transport rates (in 10^{12} g or Tg N/y) [14]. Most of the nitrogen from phytoplankton growing in the euphotic zone is continuously and rapidly recycled by bacteria and zooplankton. On an annual basis, approximately 6900 Tg N are assimilated by phytoplankton and ca. 6300 Tg N are regenerated and recycled. The remaining 600 Tg N escape the euphotic zone and sink as particulate organic material into the aphotic zone[1].

While slowly sinking through intermediate and deep waters towards the ocean floor, aerobic bacteria first convert the particulate organic nitrogen into dissolved organic nitrogen and subsequently cause the release of free ammonium into the seawater (i.e., remineralization and ammonification, respectively). In the presence of oxygen, ammonium is readily oxidized to nitrite and then to nitrate by marine bacteria *Nitrosonomas* and *Nitrobacter*, respectively, in a stepwise process called nitrification. The resulting nitrate accumulates in the deep ocean but is eventually upwelled back into the euphotic zone where it serves as "new nitrogen" for the growth of phytoplankton. In comparison to the relatively small inputs of nitrogen to the euphotic zone via rivers (35 Tg/y), precipitation (59 Tg/y), and fixation (15 Tg/y), the import of "new nitrogen" from the aphotic zone is very substantial (600 – 2400 Tg/y) and serves as an important nutrient source for oceanic primary productivity as well as world fisheries [14-17].

While there is limited evidence that marine nitrification rates are reduced as seawater becomes more acidic [18-21], there are no studies on the effects of CO_2-induced pH changes on ammonia-oxidation rates. It is therefore the objective of this study to address this important knowledge gap and to explore various potential ecological impacts that may result from the disruption of the marine nitrogen cycle by the disposal of CO_2 into the oceans.

Materials and Methods

Seawater was collected in a 20 L polyethylene bottle from 0.5 meter below the surface of Sequim Bay, Washington (48° 07.920'N 123° 04.530'W) or from a depth of 160 meters in the Strait of Juan de Fuca, Washington (48° 16.532'N 123° 03.093'W) using a Niskin bottle. The temperature, pH, dissolved oxygen (DO) concentration and salinity

[1] More recent estimates indicate that planktonic production demand for nitrogen is ca. 8000 Tg/y, a third of which (ca. 2400 Tg/y) may be "exported" to the aphotic zone [15,16].

(S) of the samples were measured and the seawater was transferred to the laboratory. Upon collection, the surface water sample had a temperature of 11°C, pH 8.13, DO 8.2 ppm and salinity of 32 $^{0}/_{00}$. The deep water sample had a temperature of 10°C, pH 7.73, DO 5.4 ppm and salinity of 33 $^{0}/_{00}$.

Nitrification rates were measured using inhibitors of chemoautotrophic nitrifying bacteria during short-term 24 hour incubation experiments following the procedures by Bianchi et al. [22]. Allylthiourea (ATU) was used to block the NH_4^+ to NH_2OH step of ammonia oxidation which is catalyzed by a mono-oxygenase enzyme [23]. The oxidation of NO_2^- to NO_3^- was inhibited by adding $NaClO_3$ [24,25] and the resulting buildup in NO_2^- concentrations was measured with or without inhibitors as described below.

A 3.5 L aliquot of either the surface or deep seawater was placed in a flask and the substrate NH_4Cl was added to a final concentration of 50 uM. The pH of the sample was adjusted to the required value by either adding NaOH or by sparging with CO_2 gas. A 650 mL aliquot was placed in a glass bottle with minimum headspace in order to prevent gas exchange with the air in the bottle; this was the sample without inhibitors. An additional 650 mL was placed in another bottle and ATU was added to a final concentration of 10 mg/L. Chlorate ($NaClO_3$) was added to the remaining pH 8.0 seawater plus substrate to a final concentration of 10 mM and the pH was adjusted to 8.0, if necessary, before 650 mL was aliquoted to three replicate glass bottles with minimal headspace. Additional 3.5 L aliquots of seawater were adjusted to either pH 7.5, 7.0, 6.5 or 6.0 by sparging with CO_2 gas, and inhibitors were added as described for the seawater sample at pH 8.0.

The samples were incubated in the dark at 15 °C, and 30 mL samples for measurement of nitrite were collected at 0, 6, 12 and 24 hrs and were held at –20 °C prior to analysis. The DO and pH of the samples were measured at 0 and 24 h and were found to be stable over the experimental period. Nanomolar concentrations of nitrite were determined by colorimetric analysis [26] using a 10 cm pathlength at 543 nm. Calibration curves were generated for nitrite concentrations ranging from 2 to 1000 nM, and the correlation coefficient (r^2) between optical density measurements and nitrite concentrations was 0.999. The production rates of nitrite (i.e., the ammonia oxidation rates) were measured in the bottles containing substrate plus chlorate inhibitor by calculating the difference in nitrite concentrations between 6 hrs and 12 hrs of incubation. The nitrite concentration did not increase in the samples with ATU inhibitor showing that nitrite production in the other bottles was due to bacterial nitrification [23].

Results and Discussion

Figure 2 shows nitrification rates as the function of pH for seawater samples taken from both the euphotic and aphotic zone. In both cases, the nitrification rates drop drastically with decreasing pH. Relative to nitrification rates in the original seawater at pH 8, nitrification rates are reduced by ca. 50% at pH 7 and more than 90% at pH 6.5. Nitrification is essentially completely inhibited at pH 6. Although the seawater samples

were taken at different depths, the effects of pH on nitrification rates appear to be similar.

The finding that nitrification is inhibited at low pH values is generally supported by earlier results reported in the literature. Srna and Baggaley [18] observed a ca. 50% reduction in marine ammonium oxidation rates as the pH dropped from 7.8 to 7.3. In a study on marine biological filters, Wickins [19] also found a continuous decrease in ammonium oxidation rates as the pH was lowered from 8.0 to 6.3. Similarly, Ward [20] showed that ammonium oxidation rates by *Nitrosococcus oceanus* were optimal at pH 8 and were reduced by more than 50% at pH 6. By contrast, Furukawa et al. [21] reported only a slight reduction in the nitrification rate as the pH decreased from 8.0 to 7.0 in an acclimated marine nitrifying sludge. A number of studies on non-marine nitrification systems also confirm the inhibition of ammonia oxidation at low pH values [27-30]. For example, in an early study by Engel and Alexander [27], respiration rates by *Nitrosonomas europaea* at pH 6 were 65% reduced compared to the respective rates at pH 8. Similarly, Wild et al. [28] observed a maximum nitrification rate in a wastewater treatment plant at pH 8.4 while it was reduced to ca. 15% at pH 6.

It has been suggested by several investigators [25,31] that ammonia (NH_3) rather than ammonium (NH_4^+) serves as the actual substrate for the ammonia mono-oxygenase enzyme. Since the ratio of ammonia (NH_3) to ammonium (NH_4^+) is drastically reduced with decreasing pH, it follows that at lower pH values less substrate (i.e., NH_3) is available to the enzyme responsible for ammonia oxidation. Consequently, it is not surprising to observe a reduction in ammonia oxidation rates with decreasing pH values (Figure 2).

The deep-sea environment is generally considered to be very stable, and temporal or spatial changes in physicochemical factors are extremely small. Based on this assumption, it has been suggested that deep-sea organisms must be exceptionally sensitive to environmental disturbances because any species with the ability to adapt to changes have long been eliminated in the process of evolutionary selection in this stable eco-system [10]. It is therefore not surprising that a major change in proton concentrations (by a factor 100 or 2 pH units) would result in the inhibition of ammonia oxidation. Since nitrifying bacteria are chemolithoautotrophs that obtain all of their energy requirements from the oxidation of ammonium or nitrite, it can be concluded that a pH-induced inhibition of ammonia oxidation will also lead to a drastic reduction in the growth rate of nitrifying bacteria such as *Nitrosonomas* and *Nitrobacter* [14,17]. By contrast, the earlier Japanese study [9] found that the growth rate of marine bacteria was not affected unless the pH was lower than 6.0. However, none of the eleven species of screened marine microorganisms included *Nitrosonomas* or *Nitrobacter.* Thus, while some marine bacteria appear to be tolerant to pH changes, others such as the nitrifiers are considerably more sensitive.

As shown in Figure 1, the ammonia oxidation rate in undisturbed seawater at pH 8 was approximately 20 nM/d for both surfical and deep water samples. The magnitude of observed nitrification rates in this study are comparable to those reported in the

literature. A recent review on the marine nitrogen cycle indicated that the rates of nitrification in the open ocean are in the range of a few to a few hundred nanomolar per day [17]. Measurements of nitrification rates off the Southern California coast indicated maximum ammonium oxidation rates of ca. 40 nM/d [29,30]. Considering that the samples taken in this study contained seawater that is circulated into the Strait of Juan de Fuca from the Pacific Ocean, our measured maximum nitrification rates (at pH 8) compare favorably to those reported by other investigators in the Pacific off the Southern California coast.

In the absence of detailed information on the location of the CO_2 injection point, the size of the resulting pH plume, and relevant ocean circulation patterns, it is difficult to predict the specific environmental impacts that might result from the inhibition of nitrification within the pH plume. Assuming that remineralization and ammonification are not inhibited by CO_2-induced pH changes, the low pH within the plume will most likely result in the reduction of ammonia oxidation rates and the concomitant accumulation of ammonia (instead of nitrate). Considering that nitrate concentrations in the deep ocean reach around 30 uM [14,17], a long-term inhibition of nitrification could increase ammonium concentrations to the same level (i.e., ca. 30 uM or 540 ug/L) within the pH plume.

According to EPA ambient water quality criteria for ammonia in saltwater [31], marine aquatic organisms should not be affected unacceptably (in terms of lethality) if the four-day average concentration of un-ionized ammonia (i.e., NH_3) does not exceed 35 ug/L and the one-hour average concentration does not exceed 233 ug/L once every three years on average. Assuming that approximately 540 ug/L ammonium would accumulate within a deep-ocean pH plume, the fraction of ammonium that is not ionized at pH 6 would be only ca. 0.017% (@ T=10°C and S =18-22 $^0/_{00}$) [33,35]. Thus, the concentration of un-ionized ammonia inside a plume of pH •6 would be only 0.1 ug/L and would most likely not cause unacceptable toxicity effects to aquatic organism according to EPA guidelines.

If the ammonium-rich water within the pH plume is upwelled and mixes with overlying seawater, the pH will rise and the fraction of un-ionized ammonia will increase. For example, at pH 8 approximately 1.63% of ammonium is not ionized (same temperature and salinity as above) and this would result in higher ammonia concentrations (i.e., 0.00163•540 ug/L = 8.8 ug/L). However, since significant dilution is necessary to increase the pH, the effective ammonia concentration in up-welled, mixed water should be much smaller than the theoretical maximum of 8.8 ug/L. Consequently, it is unlikely that any ammonia toxicity effects will occur in up-welled, ammonium-rich waters from CO_2-induced pH plumes.

The fate of upwelled ammonium in overlying seawater with a higher pH is twofold. First, in the absence of light, nitrification will resume and nitrate will be formed. Second, in the presence of light, phytoplankton will readily assimilate ammonium as a source of nitrogen for growth. However, ammonium (NH_4^+) concentrations as low as 1 uM have been found to partially or fully inhibit the uptake of nitrate [36]. Since diatoms generally

show a preference for growth on nitrate while phytoplankton such as dinoflagellates take up ammonium preferentially [36], it is likely that the upwelling ammonium will enhance the growth of dinoflagellates relative to diatoms. This shift in the phytoplankton community composition will inevitably lead to changes in the ocean food web structure and dynamics with, in turn, could have negative impacts on fisheries [3]. In addition, it is also possible that the increased upwelling of ammonium could result in harmful algal blooms which in turn might be threatening to human health [37].

Since nitrite and nitrate both serve as substrates for denitrifying bacteria, it is possible that the inhibition of nitrification and the subsequent reduction of nitrite and nitrate concentrations could result in a decrease of denitrification rates [14,15,17]. As shown in Figure 1, global loss of nitrogen from the oceans via denitrification is around 100 Tg/year. More recent estimates indicate that water column denitrification processes could account for losses of nitrogen ranging from 64 to 290 Tg/y [15]. Denitrification in the open ocean occurs in so-called oxygen minimum zones such as off the coast of Peru, in the Arabian Sea, and the Eastern Tropical North Pacific [14,17]. If the up-welling water in these oxygen minimum zones is low in nitrite and nitrate concentrations due to a CO_2-induced inhibition of nitrification at depth, denitrification processes could be substantially reduced resulting in the buildup of nitrogen and concomitant eutrophication phenomena. The potential ecological impacts of this eutrophication (e.g., oxygen depletion with associated toxicity to aquatic organisms) are difficult to predict without specific information about the location and size of the pH plume.

In conclusion, the disposal of CO_2 into mid or deep oceans is expected to cause significant inhibition of microbial nitrification processes within the pH plume which, in turn, is likely to result in various marine ecosystem disturbances such as changes in phytoplankton community structures and potential eutrophication phenomena. In the absence of specific information about the location and size of the pH plume and regional ocean circulation patterns, it is difficult to predict the exact magnitude and severity of potential ecological impacts. Clearly, more research on the environmental effects of ocean disposal of CO_2 is needed to determine whether the potential costs related to marine eco-system disturbance and disruption can be justified in terms of the perceived benefits that may be achieved by temporarily delaying global warming [12].

Acknowledgements

This research was conducted as a laboratory directed research and development (LDRD) project for the U.S. Department of Energy by Pacific Northwest National Laboratory under contract DE-AC06-RLO1830. We would also like to thank Mr. Paul Farley for piloting the research vessel and assisting with the seawater sampling effort.

References

1. Houghton, J., *Global Warming: The Complete Briefing*, Cambridge University Press, 2nd edition, 1997.

2. Rayner, S., and E.L. Malone, editors, *Human Choice and Climate Change*, Volumes 1-4, Battelle Press, Columbus, Ohio, 1998.

3. *Carbon Sequestration Research and Development*, Report by U.S. Department of Energy, Office of Science and Office of Fossil Energy, DOE/SC/FE/1, December 1999.

4. Caulfield, J.A., D.I. Auerbach, E.E. Adams, and H.J. Herzog, "Near Field Impacts of Reduced pH from Ocean CO_2 Disposal", *Energy Convers. Mgmt. (Suppl.)*, **38:**S343-S348, 1997.

5. Herzog, H.J., E.E. Adams, D. Auerbach, and J. Caulfield, "Environmental Impacts of Ocean Disposal of CO_2", *Energy Convers. Mgmt.*, **37(6-8):**999-1005, 1996.

6. Caulfield, J.A., E.E. Adams, D.I. Auerbach, and H.J. Herzog, "Impacts of Ocean CO_2 Disposal on Marine Life: II. Probabilistic Plume Exposure Model Used with a Time-Varying Dose-Response Analysis", *Environmental Modeling and Assessment*, **2:**345-353, 1997.

7. Adams, E.E., J.A. Caulfield, H.J. Herzog, and D.I. Auerbach, "Impacts of Reduced pH from Ocean CO_2 Disposal: Sensitivity of Zooplankton Mortality to Model Parameters", *Waste Management*, **17(5/6):**375-380, 1997.

8. Auerbach, D.I., J.A. Caulfield, E.E. Adams, and H.J. Herzog, "Impacts of Ocean CO_2 Disposal on Marine Life: I. A Toxicological Assessment Integrating Constant-Concentration Laboratory Assay Data with Variable-Concentration Field Exposure", *Environmental Modeling and Assessment*, **2:**333-343, 1997.

9. Takeuchi, K., Y. Fujioka, Y. Kawasaki, and Y.Shirayama, " Impacts of High Concentrations of CO_2 on Marine Organisms: A Modification of CO_2 Ocean Sequestration", *Energy Convers. Mgmt. (Suppl.)*, **38:**S337-S341, 1997.

10. Shirayama, Y., "Biodiversity and Biological Impact of Ocean Disposal of Carbon Dioxide", *Waste Management*, **17(5/6):**381-384, 1997.

11. Haugan, P.M., "Impacts on the Marine Environment From Direct and Indirect Ocean Storage of CO_2", *Waste Management*, **17(6/5):** 323-327, 1997.

12. Dewey, R.K., G.R. Stegen, and R. Bacastow, "Far-Field Impacts Associated with Ocean Disposal of CO_2", *Energy Convers. Mgmt. (Suppl.)*, **38:**S349-S354, 1997.

13. Golomb, D., "Transport Systems for Ocean Disposal of CO_2 and Their Environmental Effects", *Energy Convers. Mgmt. (Suppl.),* **38:** S279-S286, 1997.

14. Libes, S. M., *An Introduction to Marine Biogeochemistry*, John Wiley and Sons, Inc., New York, 1992.

15. Capone, D.B., "The Marine Microbical Nitrogen Cycle", In: Microbial Ecology of the Oceans, D.L. Kirchman, editor, Wiley-Liss, New York, 2000, pp. 455-493.

16. Falkowski, P.G., R.T. Barber, and V. Smetacek, "Biogeochemical Controls and Feedbacks on Ocean Primary Production", *Science*, **281:**200-206, 1998.

17. Ward, B.B., "Nitrification and the Marine Nitrogen Cycle", In: Microbial Ecology of the Oceans, D.L. Kirchman, editor, Wiley-Liss, New York, 2000, pp. 427-453.

18. Srna, R.F., and A. Baggaley, "Kinetic Response of Perturbed Marine Nitrification Systems", *J. Wat. Pollut. Control Fed.*, **47(3):**472-486, 1975.

19. Wickins, JF., "Studies on Marine Biological Filters", *Water Res.*, **17(12):**1769-1780, 1983.

20. Ward, B.B., "Kinetic Studies on Ammonia and Methane Oxidation by *Nitrosococcus oceanus*", *Archives of Microbiology*, **147:**126-133, 1987.

21. Furukawa, K., A. Ike, and M. Fujita, "Preparation of Marine Nitrifying Sludge", *Journal of Fermentation and Bioengineering*, **72(2):**134-139, 1993.

22. Bianchi M., P. Morin, and P. Le Corre, "Nitrification Rates, Nitrite and Nitrate Distribution in the Almeria-Oran Frontal Systems (Eastern Alboran Sea)", *Journal of Marine Systems*, **5:**327-342, 1994.

23. Hall G.H., "Measurement of Nitrification Rates in Lake Sediment: Comparison of the Nitrification Inhibitors Nitrapyrin and Allylthiourea", *Microbial Ecolology*, **10:**25-36, 1984.

24. Belser L.W. and E.L. Mays, "Specific Inhibition of Nitrite Oxidation by Chlorate and its Use in Assessing Nitrification in Soils and Sediments", *Applied Environmental Microbiololgy*, **39:**505-510, 1980.

25. Hynes R.K. and R. Knowles, "Inhibition of Chemoautotrophic Nitrification by Sodium Chlorate and Sodium Chlorite: A Reexamination", *Applied Environmental Microbiology*, **45:**1178-1182, 1983.

26. Bendschneider K., and R.J. Robinson, "A New Spectrophotometric Method for the Determination of Nitrite in Sea Water", *Journal of Marine Research*, **11:**87-96, 1952.

27. Engel, M.S., and M. Alexander, "Growth and Autotrophic Metabolism of *Nitrosonomas Europaea*", *Journal of Bacteriology*, **76:**217-222, 1958.

28. Wild, H.E., C.N. Sawyer, and T.C. McMahon, “Factors Affecting Nitrification Kinetics”, *Journal WPCF*, **43(9):**1845-1854, 1971.

29. Myerof, O., *Arch. F. die ges. Physiologie*, **166:**416, 1916.

30. McHarness, D., and P. McCarty, “Field Study of Nitrification with the Submerged Filter”, Office of Research and Monitoring, U.S. EPA, Washington, D.C., 1973.

31. Suzuki, I., U. Dular, and S.C. Kwok, “Ammonia or Ammonium Ion as Substrate for Oxidation by *Nitrosonomas europaea* Cells and Extract”, *Journal of Bacteriology*, **120(1):**556-558, 1974.

32. Ward, B.B., R.J. Olson, and M.J. Perry, “Microbial Nitrification Rates in the Primary Nitrite Maximum off Southern California”, *Deep Sea Research*, **29:**247-255, 1982.

33. Ward, B.B., “Nitrogen Transformations in the Southern California Bight”, *Deep Sea Research*, **34:**785-805, 1987.

34. U.S. Environmental Protection Agency (EPA), *Ambient Water Quality Criteria for Ammonia (Saltwater)*, EPA 440/5-88-004, April 1989.

35. Bower, C.E., and J.P. Bidwell, “Ionization of Ammonia in Seawater: Effects of Temperature, pH, and Salinity”, *J. Fish. Res. Board Can.*, **35:**1012-1016,1978.

36. Dortch, Q., “The Interaction Between Ammonium and Nitrate Uptake in Phytoplankton”, *Marine Ecology Progress Series*, **61:**183-201, 1990.

37. DeYoe, H.R., and C.A. Suttle, “The Inability of the Texas “Brown Tide” Alga to Use Nitrate and the Role of Nitrogen in the Initiation of a Persistent Bloom of this Organism”, *Journal of Phycology*, **30:**800-806, 1994.

Figure Captions

Figure 1 The marine nitrogen cycle including estimates of nitrogen transport rates in 10^{12} g N/y. (adopted with permission from Figure 24.13 in reference 14)

Figure 2 Nitrification rates as a function of pH in seawater samples taken from the euphotic (@ 0.5 m) and aphotic (@ 160 m) zone. The plotted data represent the average of three replicate measurements and the length of the error bar equals one standard deviation.

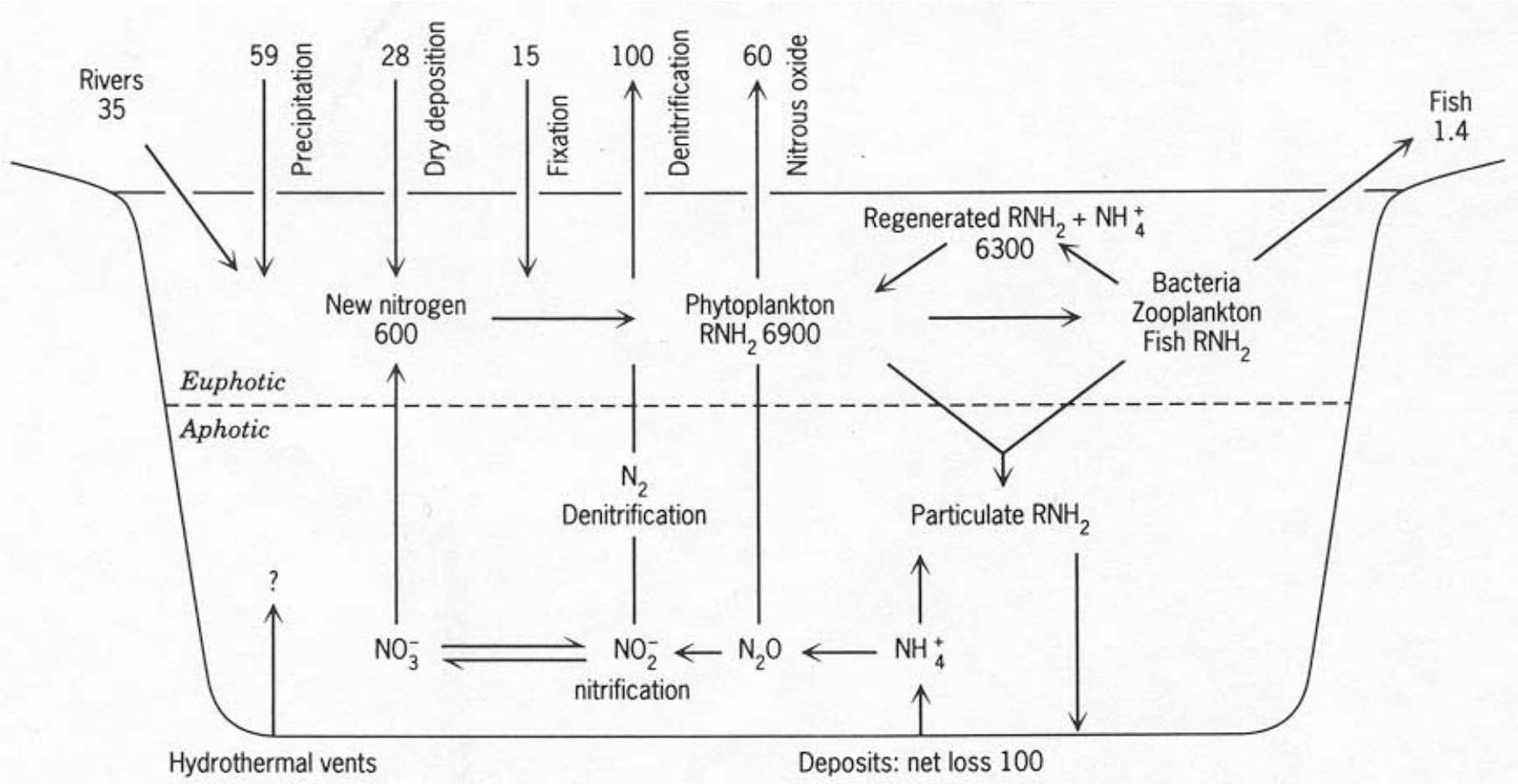
Rivers
35
59
Precipitation
28
Dry deposition
15
Fixation
100
Denitrification
60
Nitrous oxide
Fish
1.4
Regenerated RNH2 + NH4+
6300
New nitrogen
600
Phytoplankton
RNH2 6900
Bacteria
Zooplankton
Fish RNH2
Euphotic
Aphotic
N2
Denitrification
Particulate RNH2
?
NO3−
NO2−
N2O
NH4+
nitrification
Hydrothermal vents
Deposits: net loss 100

Figure 1

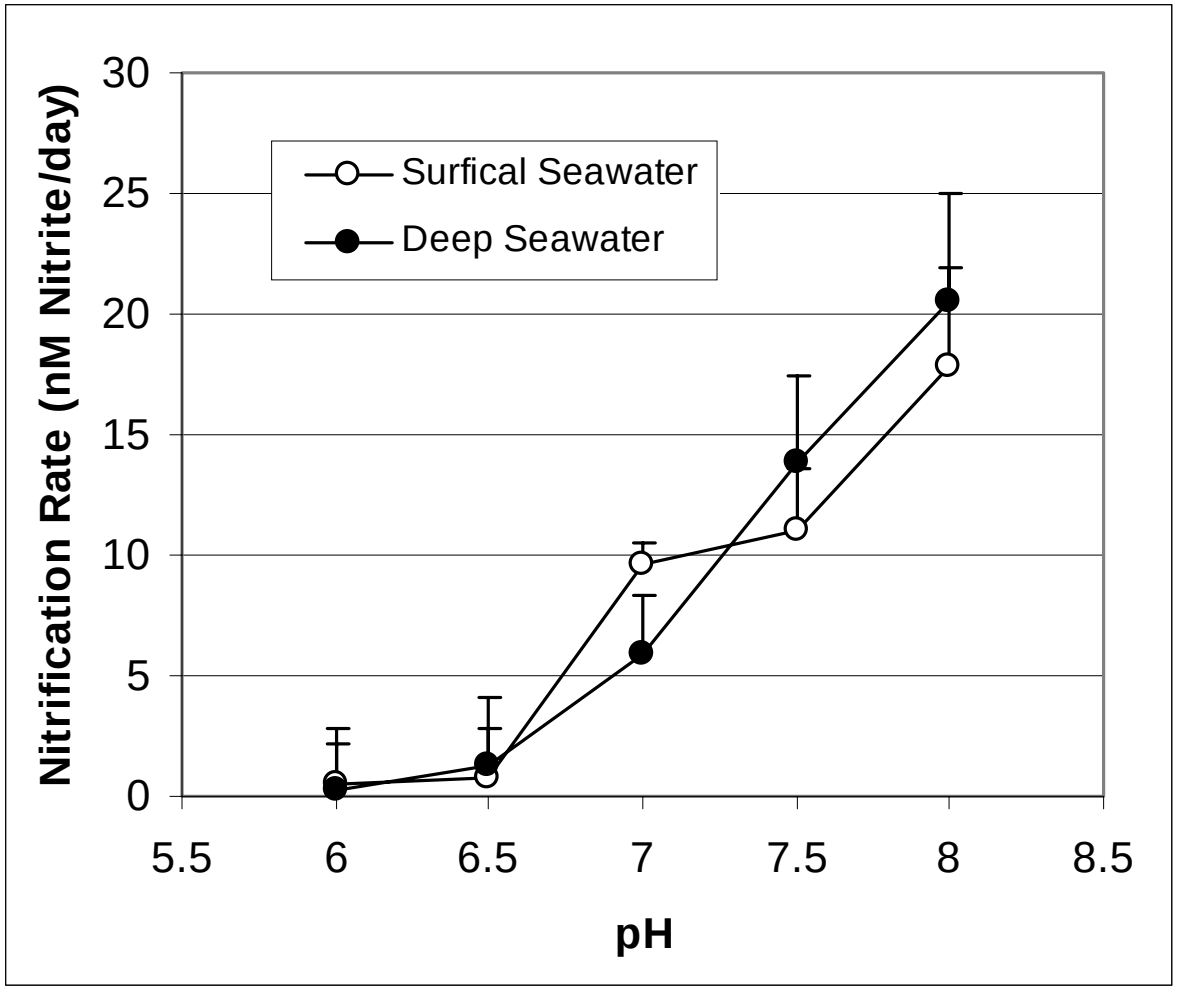
Nitrification Rate (nM Nitrite/day)
30
25
20
15
10
5
0
Surfical Seawater
Deep Seawater
5.5
6
6.5
7
7.5
8
8.5
pH

Figure 2