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Eddy resolving nutrient ecodynamics in the global Parallel Ocean Program and connections with trace gases in the sulfur, halogen and NMHC cycles

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ABSTRACT

Ecodynamics and the sea-air transfer of climate relevant trace gases are intimately coupled in the oceanic mixed layer. Ventilation of species such as dimethyl sulfide and methyl bromide constitutes a key linkage within the earth system. We are creating a research tool for the study of marine trace gas distributions by implementing coupled ecology-gas chemistry in the high resolution Parallel Ocean Program (POP). The fundamental circulation model is eddy resolving, with cell sizes averaging 0.15 degree (lat/long). Here we describe ecochemistry integration. Density dependent mortality and iron geochemistry have enhanced agreement with chlorophyll measurements. Indications are that dimethyl sulfide production rates must be adjusted for latitude dependence to match recent compilations. This may reflect the need for phytoplankton to conserve nitrogen by favoring sulfurous osmolytes. Global simulations are also available for carbonyl sulfide, the methyl halides and for nonmethane hydrocarbons. We discuss future applications including interaction with atmospheric chemistry models, high resolution biogeochemical snapshots and the study of open ocean fertilization.

Keywords: marine ecodynamics, gas chemistry, sulfur cycle, organohalogen cycle, global simulation, high resolution

1. INTRODUCTION

The global climate community is currently engaged in an effort to construct biogeochemically complete earth system models¹. An understudied link between the chemistry of ocean and atmosphere is comprised by transfer of trace gases such as dimethyl sulfide and methyl bromide². To support upcoming research in this area, we are augmenting a detailed ocean circulation model with ecodynamical processing for dissolved gases of climate import. An ultimate goal is to participate in earth system simulations. More immediately we hope to contribute to the interpretation of large scale concentration distributions³⁻⁶. The Los Alamos National Laboratory Parallel Ocean Program (POP) is adopted as our framework, in part because it will serve as a component of upcoming climate system models. It can be run at resolutions ranging upward from 0.1 degree, over ocean basin and global scales^{7,8}. Several groups are incorporating macro- and micronutrient driven ecology into POP. We are adding a simulator for transformations of dissolved trace gases as well. Iron and nitrogen cycles operating within the OGCM are appended by representations of chemistry for volatile sulfur, carbon and organohalogen species^{9,10}.

We describe here the development of the overall model, and some early results. Specifications are listed for the Parallel Ocean Program. Low dimensionality tests of our ecology and chemistry routines are sketched. Extension into the global code is outlined along with results of validation exercises. Future research is touched upon in a concluding discussion. Some will involve the interaction of POP ecochemistry with regional or global atmospheric chemistry/transport codes^{11,12}. Because it seems unlikely that decadal to century scale biogeochemistry will soon be run at subdegree resolution, we discuss the possibility that long term, coarse computations could be punctuated by several year, biogeochemical snapshot experiments. We further suggest that the need for high resolution trace gas calculations could be explored by analyzing transects through ocean-only runs. Informal comparisons could be conducted with fine structure seen in both aircraft and ship data²³⁻¹⁶. Coupled biogeochemistry codes will be used at some point to study feedback loops from continental nutrient mobilization through ocean fertilization and alterations to marine tropospheric chemistry²⁷⁻¹⁹.

2. BACKGROUD AND MODELS

Biogeochemistry routines will be a hallmark of the coming generation of earth system models, and trace gas transfer constitutes a prime link between ocean and atmosphere. The best understood agent of transfer is dimethyl sulfide²⁰. Its precursor dimethyl sulfoniopropionate is produced by phytoplankton as an osmolyte²⁵. As marine plants senesce, die and are

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grazed upon by zooplankton both DMS and DMSP enter the water column. Bacterial processing, photolysis, enzyme chemistry and ventilation all affect their distributions. DMS crosses the ocean interface, and in the remote atmosphere determines the abundance of cloud condensation nuclei^{2,21}. Analogous marine and tropospheric geocycling occurs for a variety of other climatically relevant trace gases, with more or less emphasis on some of the component pathways. A short list of species which cross the sea surface and possess rich atmospheric chemistries would include the methyl halides^{4,22}, nonmethane hydrocarbons^{23,24}, carbonyl and hydrogen sulfide^{3,25,26} and nitrous oxide²⁷.

Several climate simulation groups now aim to construct earth system models². An emphasis on biogeochemistry will be inevitable. Coupling of atmospheric and ocean general circulation is already underway. The Los Alamos National Laboratory Parallel Ocean Program is often considered as a component, because it has attained ultrahigh resolution^{8,28,29}. Multiple biogeochemistry groups are engaged in the insertion of marine nutrient cycling routines into POP. Classical ecodynamicists focus upon details of the nitrogen and iron cycles^{30,31}. In our team at Los Alamos, we are constructing streamlined nutrient routines tailored to the testing of dissolved gas chemistry mechanisms^{9,10,32}.

The Parallel Ocean Program is an evolved, ultrahigh resolution form of the Bryan Cox Semtner Chervin family of general circulation models^{7,33,34}. Depth coordinates are geometric, with 25 meter resolution near the surface. Horizontal grid sizes of 0.1 degree have been achieved over the entire North Atlantic basin⁸. POP has been run at an average of 0.15 degree globally⁷; a one tenth degree version is in the planning stages. The tight meshes are sufficient in many cases to resolve oceanic mesoscale eddies. POP was in fact developed as a tool for the study of fine scale transport of heat and momentum through the surface ocean. The code was constructed by a team of oceanographers and fluid dynamicists working together with the Los Alamos Advanced Computing Laboratory (ACL). Their efforts were facilitated by access to the world's most powerful supercomputers, which are resident on site. In the present project we utilize the same machines.

The effort to incorporate nitrogen/iron cycling is centered at the U.S. National Center for Atmospheric Research^{29,30,31,35}. We rely to some extent on the algorithms generated there, but our ecodynamics are somewhat simplified. Resources are concentrated upon connection of dissolved trace gas mechanisms to the ecology. For example, the sulfur cycle of Gabric et al.^{36,37} is adapted and provides distributions of DMS and DMSP in planktonic and dissolved phases. With regard to other subsurface volatiles we have designed our own mechanisms^{9,10}. These often contain chemical rate constants we were personally involved in measuring^{25,38,39}, for chlorination and hydrolytic removal processes. Biological interactions are usually empirically determined^{40,41}.

Our most recent tracer list includes components of the nitrogen cycle (phytoplankton, zooplankton, bacteria, nitrate, ammonium, dissolved organic nitrogen, nonliving particulate organic nitrogen), a coupled iron cycle (atmospheric and dissolved bioavailable forms) and the gases DMS, OCS, NH₃, the methyl halides, and several pure hydrocarbons. Less volatile precursors/products such as DMSP, inorganic sulfide and methanol are incorporated into the water column mechanisms as well. Chemistry of the alkyl nitrates is beginning to be elucidated for the euphotic zone (personal communication with Elliot Atlas). It appears that atmosphere-like photo-oxidation chemistry degrades light alkanes, generating aqueous peroxy radicals. These react with nitrogen in the various higher oxidation states along the element's geocycle. RONO₂ are thus produced in proportion to dissolved organics and also to inorganic nitrogen species. All of the latter are tracked in the Los Alamos biogeochemical POP. We plan to introduce the hydrocarbon/nitrate chemistry soon.

3. SIMULATIONS AND RESULTS

All ecodynamics and gas chemistry routines are refined and tested initially in a two dimensional test program. A series of vertical column models is extended along the international date line, through the central Pacific. Eddy diffusion coefficients are taken from standard parameterizations and are sometimes Richardson number based^{9,30,42}. Although advection is not simulated, vertical motion is defined to a large extent in the central ocean by transfer across the shallow or seasonal thermocline, and by deep convection. Both processes can be represented effectively in a single column. Several types of nitrogen cycle have been assessed in the two dimensional context. Some are traditional phytoplankton-zooplankton representations with implied or actual bacterial loops (NPZ models)^{30,43,44}. We have also introduced sophisticated density dependent mortality terms. Iron cycling is patterned after the geochemistry described in Fung et al.²⁹ and Moore et al.³¹.

For chlorophyll NPZ models of vintage middle 1990's tend to overestimate peaks and underestimate minima, as judged in our tests against satellite data^{6,45}. The density dependent terms bring about better agreement in nitrogen limited portions of the open ocean². Coupling of the iron cycle further improves the comparisons in high nutrient low chlorophyll zones²⁰. The Gabric et al.^{36,37} sulfur cycle sets output rates for DMS and DMSP via direct exudation and during planktonic

grazing/senescence. It was designed originally to reproduce the results of tank experiments, and has been most often applied to bloom situations in the open sea. We found in our two dimensional experiments that the Gabric mechanism for DMS is akin to the NPZ models, in that it over and undershoots highs and lows respectively⁵. A potential explanation is offered by Andreae²⁵ and has been followed up by others. Marine plants may produce the DMS precursors primarily as osmolytes. Since nitrogen containing compounds can serve the same purpose, the sulfur cycle becomes more important under nitrogen stressed conditions. We plan very soon to break our single, global phytoplankton species down into a fraction representing the diatoms and a second bin encompassing the dinoflagellates, coccolithophorids and other small autotrophs. In doing so we will follow the algorithm of Moore et al.³¹. The smaller species are more productive under nutrient stressed conditions, and are known to contain high concentrations of dimethyl sulfoniopropionate. By keying the vigor of the sulfur cycle to taxonomically resolved intracellular DMSP we are hoping to raise DMS concentrations in the central gyres.

The other climate relevant trace gases are sparsely measured relative to dimethyl sulfide. Methyl bromide is perhaps the second most widely studied compound^{4,46}. We have compared our two dimensional, middle Pacific results against oceanographic cruise data where appropriate. Results are encouraging. The same can be said with respect to carbonyl sulfide, the methyl halides, and some of the nonmethane hydrocarbons, but with decreasing confidence. In most of the global high resolution runs, all the above gases are carried as chemically and ecodynamically active tracers. Production rates are transferred directly from the low dimensionality studies.

Our biogeochemical POP simulations to date have been spun up over a sequence of ancestral, coarse resolution Bryan-type GCM runs⁷. The cornerstone has been a multiyear computation at global 1/6 degree, extending from 1985 to 1998. The fine mesh calculation was driven with ECMWF winds and Barnier type heat and fresh water fluxes⁴⁷. POP and its biogeochemical support can thus be initialized at any point in the 1990's. Biology of the surface ocean can be brought into steady state in as little as 3 years beginning even from crude initial conditions^{9,43,44}. Time constants in the dissolved trace gas system are limited in part by ventilation, which occurs in less than 100 days almost anywhere in the ocean⁴⁸.

Most of our global trace gas simulations begin in 1995, and extend through 1997. We are thus able to pick up the onset of the large 1997-1998 El Nino⁶. Comparisons with satellite chlorophyll climatologies⁴⁵ and with data for specific time periods⁶ appear promising and are now being formalized. Against the accumulated dimethyl sulfide measurement data base⁵, our POP results show the same problems mentioned above for two dimensional test runs (overshoot and undershoot). The solutions are likely also similar and involve increasing the taxonomic resolution for phytoplankton. Horizontal distributions for all the trace gases show complex mesoscale (10-100 km) structure. This is attributable to differential production/decay along the eddies and filaments which constitute ocean weather.

4. DISCUSSION

We ultimately envision the incorporation of our dissolved trace gas chemistry into the coming generation of high resolution earth system models. In the near term, however, we must be content with more direct applications and with demonstrations of capability. For example, with an ecodynamical and trace gas supporting POP version running at high resolution (global 1/6 degree), it should be possible to elucidate the potential of eddy resolving simulations. We intend to run synthetic transects through our calculated global data sets, and display the fine structure therein. The results will be compared with analogous detail embodied in aircraft and oceanographic measurements^{4,13-15}. It will be clear that peaks observed with order 10-100 km width at half maximum are related in part to mesoscale (oceanic) ecochemistry transport.

Increasing computational power will soon enable remarkable new approaches to earth system simulation. Some will involve the biogeochemical connections between ocean and atmosphere. We currently compute sea-air fluxes by fixing gas phase concentrations at regional average values. Separation of the effects of atmospheric production/loss will require full coupling across the interface. We hope to attach our ecochemical POP to the NCAR MOZART tropospheric chemistry model^{21,12}. The result will constitute a major step in the direction of system level simulation of the global environment.

Climate change is intimately tied to evolution of the human energy economy over the next few centuries, with several inherent time constants on the order of decades or longer². Detailed earth system simulations must eventually reach the century scale. In the foreseeable future, however, long term calculations must be coarse in their gridding. There will thus be a market for high resolution snapshot runs, branching from the coarse baseline every few decades and covering several years in greater detail. At global 1/6 degree or even better, coupled trace gas chemistry could serve as a prototype. Dimethyl sulfide,

ozone precursors/controllers and the links they form between ocean and atmosphere biogeochemistry will be treated briefly but explicitly.

Earth system influences on the ocean will in part be physical², new modes of atmospheric circulation will alter the vertical mixing structure of the water column, while a global temperature rise will tend to induce stratification. But there will also exist biogeochemical loops from the atmosphere to the sea and back again. The codes we produce will be well suited to investigation of such issues. Economic growth in developing countries and in particular in Asia will fertilize the open ocean through nitrogen mobilization^{28,49}. Much of the surface sea (about 20%) is in fact iron limited^{29,20}. Modernization of agriculture and mineral suspension by an enlarging vehicle fleet will take place hand in hand with coal burning in the China of the next century. Increased dust loading will be operated on by acid hydrometeors, enhancing iron bioavailability²⁷. Nonlinear changes in iron deposition will affect the North Pacific and the tropics. Nutrient injections will in general alter trace gas distributions in the mixed layer and so also patterns of sea-air transfer. It is also possible that iron deposition will stimulate nitrogen fixation, by cyanobacteria such as trichodesmium⁵⁰.

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REFERENCES

1. American Meteorological Society CSM Issue, *Journal of Climate*, **11**, 1998.
2. IPCC, *Climate Change 1995: the Science of Climate Change*, Cambridge University Press, 1996.
3. P.S. Weiss, J.E. Johnson, R.H. Gammon, and T.S. Bates, "Reevaluation of the open ocean source of carbonyl sulfide to the atmosphere", *J. Geophys. Res.*, **100**, 23083-23092, 1995.
4. J.M. Lobert, J.H. Butler, S.A. Montzka, L.S. Geller, R.C. Myers, and J.W. Elkins, "The ocean as a net sink for atmospheric methyl bromide", *Science* **267** 1002-1005, 1995.
5. A.J. Kettle et al., "A global database of sea surface dimethylsulfide (DMS) measurements and a procedure to predict sea surface DMS as a function of latitude, longitude and month", *Global Biogeochem. Cycles* **13**, 18715-18721, 1999.
6. F.P. Chavez, P.G. Strutton, G.E. Friederich, R.A. Feely, G.C. Feldman, D.G. Foley, and M.J. McPhaden, "Biological and chemical response of the equatorial Pacific Ocean to the 1997-1998 El Nino", *Science* **286**, 2126-2131, 1999.
7. M.E. Maltrud, R. Smith, A.J. Semtner, and R.C. Malone, "Global eddy resolving ocean simulations driven by 1985-1995 atmospheric winds", *J. Geophys. Res.* **103**, 30825-30853, 1998.
8. R. Smith, M.E. Maltrud, F.O. Bryan, and M.W. Hecht, "Numerical Simulation of circulation in the North Atlantic Ocean at 1/10 degree", submitted to *J. Phys. Oceanogr.*, 1999.
9. S. Chu, L.A. McNair, S. Elliott, C.A. Lai, O.A. Hurricane, R.P. Turco, and R.C. Dugdale, "Ecodynamics and dissolved gas chemistry routines for ocean circulation models", *Computers and Chemistry* **23**, 447-467, 1999a.
10. S. Chu, L.A. McNair, and S. Elliott, "Ecodynamics and dissolved gas chemistry models for the North Pacific Ocean", in *Air Quality and Atmospheric Science*, edited by C. Fu, Z. Yutian, Z. Yun and K. Dae-Seon, 662-678, China Ocean Press, Beijing, 1999b.
11. G.P. Brasseur, D.S. Hauglustaine, S. Walters, P.J. Rasch, J.F. Muller, C. Granier, and X.X. Tie, "MOZART: A global chemical transport model for ozone and related chemical tracers, Part 1. Model description", *J. Geophys. Res.* **103**, 28291-28335, 1998.
12. D.A. Hauglustaine, G.P. Brasseur, S. Walters, P.J. Rasch, J.F. Muller, L.K. Emmons, and M.A. Carroll, "MOZART: A global chemical transport model for ozone and related chemical tracers, Part 2. Model evaluation", *J. Geophys. Res.* **103**, 28291-28335, 1998.
13. D.R. Blake, T. Chen, T.W. Smith Jr., C.J.L. Wang, O.W. Wingenter, N.J. Blake, and F.S. Rowland, "Three-dimensional distribution of nonmethane hydrocarbons and halocarbons over the northwestern Pacific during the 1991 Pacific Exploratory Mission (PEM-West A)", *J. Geophys. Res.* **101**, 1763-1778, 1996.
14. N.J. Blake, D.R. Blake, T.Y. Chen, J.E. Collins, G.W. Sachse, B.E. Anderson, and F.S. Rowland, "Distribution and seasonality of selected hydrocarbons over the western Pacific basin during PEM West A and B", *J. Geophys. Res.* **102**, 28315-28331, 1997.
15. M.O. Andreae, "The ocean as a source of atmospheric sulfur compounds", in *The Role of Air-Sea Exchange in Geochemical Cycling*, edited by P. Buat-Ménard, D. Reidel, Dordrecht, 331-347, 1986.
16. T.S. Bates, J.D. Cline, R.H. Gammon, and S.R. Kelly-Hansen, "Regional and seasonal variations in the flux of oceanic dimethylsulfide to the atmosphere", *J. Geophys. Res.* **92**, 2930-2938, 1987.

17. Zhuang, G., Z. Yi, R.A. Duce & P.R. Brown (1992) Chemistry of iron in marine aerosols, *Global Biogeochem. Cycles* 6, 161-173.
18. S. Elliott, D.R. Blake, R.A. Duce, C.A. Lai, E.I. McCreary, L.A. McNair, F.S. Rowland, A.G. Russell, G.E. Streit, and R.P. Turco, "Motorization of China implies changes in Pacific air chemistry and primary production", *Geophys. Res. Lett.* 24, 2671-2674, 1997.
19. I.Y. Fung, S.K. Meyu, I. Tegen, S.C. Doney, J.G. John, and J.K.B. Bishop, "Iron supply and demand in the upper ocean", *Global Biogeochem. Cycles* 14, 281-295, 2000.
20. A.J. Watson, and P.S. Liss, "Marine biological controls on climate via the carbon and sulphur geochemical cycles", *Phil. Trans. R. Soc. Lond. B* 353, 41-51, 1998.
21. R.J. Charlson, J.E. Lovelock, M.O. Andreae, and S.G. Warren, "Oceanic phytoplankton, atmospheric sulfur, cloud albedo and climate", *Nature* 326, 655-661, 1987.
22. H.B. Singh, L.J. Salas, and R.E. Stiles, "Methyl halides in and over the eastern Pacific", *J. Geophys. Res.* 88, 3684-3690, 1983.
23. M. Ratte, C. Plass-Dulmer, R. Koppmann, J. Rudolph, and J. Denga, "Production mechanisms of C2-C4 hydrocarbons in seawater: Field measurements and experiments", *Global Biogeochem. Cycles* 7, 369-378, 1993.
24. E. Atlas, W. Pollock, J. Greenberg, L. Heidt, and A.M. Thompson, "Alkyl nitrates, nonmethane hydrocarbons and halocarbons over the equatorial Pacific Ocean during SAGA-3", *J. Geophys. Res.* 98, 16933-16947, 1993.
25. S. Elliott, E. Lu, and F.S. Rowland, "Rates and mechanisms for hydrolysis of carbonyl sulfide in several types of natural water", *Environ. Sci. Technol.* 23, 458-461, 1989.
26. J. Radford-Knoery, and G.A. Cutter, "Biogeochemistry of dissolved hydrogen sulfide species and carbonyl sulfide in the western North Atlantic", *Geochim. Cosmochim. Acta* 58, 5421-5431, 1994.
27. J.A. Fuhrman, and D.G. Capone, "Possible biogeochemical consequences of ocean fertilization", *Limnol. Oceanogr.* 36, 1951-1959, 1991.
28. R. Smith, J.K. Dukowicz, and R.C. Malone, "Parallel ocean general circulation modeling", *Physica D* 60, 38-61, 1992.
29. J.K. Dukowicz, R. Smith, and R.C. Malone, "A reformulation and implementation of the Bryan Cox Semtner ocean model on the Connection Machine", *Atmos. Ocean. Tech.* 10, 195-208, 1993.
30. S.C. Doney, D.M. Glover, and R.G. Najjar, "A new coupled, one-dimensional biological-physical model for the upper ocean: applications to the JGOFS Bermuda Atlantic Time Series (BATS) site", *Deep-Sea Res. II* 43, 591-624, 1996.
31. J.K. Moore, S.C. Doney, J.A. Kleypas, D.M. Glover, and I.Y. Fung, "An intermediate complexity marine ecosystem model for the global domain", submitted to *Deep Sea Research II*, 2000.
32. L.A. McNair, S. Chu, S. Elliott, M. Maltrud, O. Wild, and R.P. Turco, "A suite of ecodynamics models for north Pacific ocean biogeochemistry", in *Environmental Sciences and Environmental Computing*, edited by P. Zannetti and Y.Q. Zhang, Vol. I, FiatLux Publications & EnviroComp Institute, 1998.
33. A.J. Semtner, "History and methodology of modeling the circulation of the world ocean", in *Advanced Physical Oceanographic Numerical Modeling*, edited by J. J. O'Brien, D. Reidel, Dordrecht, 23-32, 1986.
34. A.J. Semtner, and R.M. Chervin, "Ocean general circulation from a global eddy-resolving model", *J. Geophys. Res.* 97, 5493-5550, 1992.
35. S.C. Doney, "Major challenges confronting marine biogeochemical modeling", *Global Biogeochem. Cycles* 13, 705-714, 1999.
36. A. Gabric, N. Murray, L. Stone, and M. Kohl, "Modeling the production of dimethyl sulfide during a phytoplankton bloom", *J. Geophys. Res.* 98, 22805-22816, 1993.
37. A. Gabric, G.P. Ayers, and G.C. Sander, "Independent marine and atmospheric model estimates of the sea-air flux of dimethyl sulfide in the Southern Ocean", *Geophys. Res. Lett.* 22, 3521-3524, 1995.
38. S. Elliott, and F.S. Rowland, "Nucleophilic substitution rates and solubilities for the methyl halides in seawater", *Geophys. Res. Lett.* 20, 1043-1046, 1993.
39. S. Elliott, and F.S. Rowland, "Methyl halide hydrolysis rates in natural waters", *J. Atmos. Chem.* 20, 229-236, 1995.
40. R.P. Kiene, and T.S. Bates, "Biological removal of dimethyl sulphide from sea water", *Nature* 345, 702-705, 1990.
41. D.B. King, and E.S. Saltzman, "Removal of methyl bromide in coastal seawater: Chemical and biological rates", *J. Geophys. Res.* 102, 18715-18721, 1997.
42. W.G. Large, J.C. McWilliams, and S.C. Doney, "Oceanic vertical mixing: A review and a model with a nonlocal boundary layer parameterization", *Rev. Geophys.* 32, 363-403, 1994.
43. M.J. Fasham, J.L. Sarmiento, R.D. Slater, H.W. Ducklow, and R. Williams, "Ecosystem behavior at Bermuda station S and ocean weather station India: A general circulation model and observational analysis", *Global Biogeochem. Cycles* 7, 379-416, 1993.

44. J.L. Sarmiento, R.D. Slater, M.J. Fasham, H.W. Ducklow, J.R. Toggweiler, and G.T. Evans, "A seasonal three dimensional ecosystem model of nitrogen cycling in the North Atlantic euphotic zone", *Global Biogeochem. Cycles*, **7**, 417-450, 1993.
45. R.J. Gurney, J.L. Foster, and C.L. Parkinson, *Atlas of Satellite Observations Related to Global Change*, Cambridge University Press, 1993.
46. J.M. Lee-Taylor, S.C. Doney, G.P. Brasseur, and J.F. Muller, "A global 3D coupled atmosphere ocean model of methyl bromide", *J. Geophys. Res.* **103**, 16039-16057, 1998.
47. B. Barnier, L. Siefridt, and P. Marchesiello, "Thermal forcing for a global ocean circulation model using a three year climatology of ECMWF analyses", *J. Mar. Syst.* **6**, 363-380, 1995.
48. W.S. Broecker, and T.H. Peng, *Tracers in the Sea*, Eldigio, 1982.
49. K.A. Fanning, "Influence of atmospheric pollution on nutrient limitation in the ocean", *Nature* **339**, 460-463, 1989.
50. D.M. Karl, "A sea of change: Biogeochemical variability in the North Pacific subtropical gyre", *Ecosystems* **2**, 181-214, 1999.