Time-series records of pCO_2 and NO_3 during the OMP Field Program:
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Background: Coastal margins are some of the most biologically productive areas of the ocean and may significantly contribute to CO_2 cycling on a regional and global scale. The complex physical oceanography and large seasonal variability in freshwater input has typically made these areas difficult to study. Processes such as air-sea exchange, rates of transformation between organic and inorganic carbon pools, and exchange of materials between the coastal and open ocean are not well understood. The DOE Ocean Margins Program (OMP) has focused on coastal waters off Cape Hatteras, North Carolina where shelf water leaves the continental margin, transporting carbon, in various forms, to the open ocean. Both mooring and ship-based field programs were undertaken to characterize carbon fluxes in this area. Our role in this multidisciplinary collaborative effort has been to determine CO_2 and NO_3 variability within the mooring control volume using *in situ* CO_2 and NO_3 sensors.

The specific goals of this research are to 1) determine daily and seasonal variability of seawater pCO_2 (partial pressure of CO_2 and NO_3 in Middle Atlantic Bight (MAB) waters 2) estimate seasonal CO_2 fluxes between the MAB shelf and the atmosphere, and 3) determine the primary controls of surface seawater pCO_2 in this coastal system. During the first phase of the DOE-OMP (1992-1995) we developed the Submersible Autonomous Moored Instrument for CO_2 (SAMI- CO_2) which is designed to measure seawater CO_2 on ocean moorings for extended periods.

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In preparation for the 1996 field program we built six SAMI-CO₂s (DeGrandpre) and 4 nitrate osmoanalyzers (H. Jannasch, Monterey Bay Aquarium Research Institute). The instruments were tested and calibrated during Fall 1995 just prior to the winter deployment. SAMI-CO₂s, nitrate osmoanalyzers, and O₂ sensors (C. Wirick, BNL) were fixed on a single cage designed to hold the 3 instrument types. This is the first time that pCO₂, NO₃ and O₂ have been determined simultaneously on a mooring and represents a landmark in the way we study ocean biogeochemical processes. The instrument arrays were successfully deployed within the OMP biogeochemical box off Cape Hatteras during two field efforts in 1996. During these two periods we obtained over 11,000 measurements of pCO₂ and over 8000 measurements of NO₃.

Data processing and interpretation: The CO₂ and NO₃ data collected during the OMP experiment have been reduced and subjected to quality assurance procedures. Quality assurance was based on shipboard measurements provided by Brookhaven National Lab (BNL) researchers (C. Wirick, C. Flagg). Time-series of pCO₂ have been converted to total CO₂ using BNL's alkalinity relationship which has been derived from shipboard measurements of temperature and salinity. The air-sea CO₂ flux has been calculated using the Liss and Merlivat and Wanninkhof gas transfer models which require ΔpCO_2 , the air-sea CO₂ difference, and winds (measured on nearby NOAA buoys). Community metabolism has been estimated from total CO₂ time series and O₂ time series provided by BNL.

The quality assured data has been interpreted and presented at national meetings (see below). A portion of the results from the field work have been published (see below). Additional manuscripts are currently being prepared for submission to peer-reviewed journals.

Publications and Presentations Resulting from the Grant

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- DeGrandpre, M.D., McGillis, W.R., Frew, N.M. and Bock, E.J., Laboratory measurements of seawater CO₂ gas fluxes, in *Proceedings of the Third International Symposium on Air-Water Gas Transfer*, B. Jahne and E.C. Monahan eds., pp. 375-383, AEON publ., 1995.
- DeGrandpre, M.D., Hammar, T.R., Wallace, D.W.R., and C.D. Wirick. (1997). Simultaneous mooring-based measurements of seawater CO₂ and O₂ off Cape Hatteras, North Carolina, *Limnol. and Oceanog.*, **42**, 21-28.
- DeGrandpre, M.D., Baehr, M.M. and T.R. Hammar. Development of an optical chemical sensor for oceanographic applications: The Submersible Autonomous Moored Instrument for Seawater CO₂, in *Chemical Sensors in Oceanography*, M. Varney ed., Gordon and Breach publ., in press.
- DeGrandpre, M.D., Hammar, T.R., and C.D. Wirick. (1998). Studies of coastal CO₂ and O₂ dynamics using moored autonomous sensors, in *Proceedings Ocean Community Conference*, November 1998, Baltimore, MD, 797-801.
- DeGrandpre, M. D., Baehr, M., Jannasch, H. W., Hammar, T. R. Time-series records of pCO₂ and NO₃ during the OMP field program, poster session at the DOE-Ocean Margins Program Data Workshop, January 1997, Savannah, GA.
- DeGrandpre, M.D., Hammar, T., Wallace, D., Wirick, C. Simultaneous mooring-based measurements of seawater pCO₂ and O₂ off Cape Hatteras, NC, presented at the American Society of Limnology and Oceanography National Meeting, February 1997, Sante Fe, NM.
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- Baehr, M.M., DeGrandpre, M.D., and T.R. Hammar. *Towards calibration-free optical chemical sensors*, American Chemical Society (ACS) National Meeting, August 1998, Boston, MA.
- DeGrandpre, M.D., Hammar, T.R., and C.D. Wirick. *Studies of coastal CO₂ and O₂ dynamics using moored autonomous sensors*, Marine Technology Society National Meeting, November 1998, Baltimore, MD.
- DeGrandpre, M.D., Olbu, G., and C.D. Wirick. *Net community production in coastal waters: estimates from mooring-based measurements of pCO₂ and O₂*, American Society of Limnology and Oceanography National Meeting, February 1999, Sante Fe, NM.