OS12E-182 1330h POSTER

Interannual to interdecadal changes of water temperature, sea-level displacement, and sea-ice concentrations in the Bering Sea and associated atmospheric circulation changes

Shoshiro Minobe[1,2] (+81-11-706-2644; minobe@ep.sci.hokudai.ac.jp)

[1]Division of Earth and Planetary Sciences, Graduate School of Science, Hokkaido University, N10 W8, Sapporo 060-0810, Japan

[2]Frontier Research System for Global Change, Kanazawa-ku, Shouwa-machi, Yokohama 3173-25, Japan

The Bering Sea Sea-Surface Temperatures (SSTs), subsurface temperatures, sea-level displacements (SLDs), sea-ice concentration and associated atmospheric circulations are analyzed to identify dominant interannual to interdecadal variations. Seasonally combined EOF analysis of the SSTs in the Bering Sea provides seasonally dependent EOF1, which exhibits smallest amplitudes in winter and largest ones in summer. The corresponding yearly-sampled PC1 is characterized by the warming trend through the record (1925-2001) with the warmest year in 1997, which is followed by rapid cooling until 1999. The warming from1995-1997 and cooling from 1997-1999 are commonly found in heat storage, and also accompanied by SLD raise and fall, respectively. The cooling and SLD fall in the late 1990s might be related with a possible *major* regime shift in 1998/1999, which were suggested by several papers (Minobe 2000, Hare and Mantua 2000, Schwing and Moore 2000). The sea-ice variability corresponding to the SST PC1 is prominent in spring in the eastern Bering Sea with correlations as high as 0.7. The correlations between the SST PC1 and sea-level pressures suggests that the spring atmospheric circulation anomalies play an important role in the variations of ocean and ice in the Bering Sea.

OS12F HC: Hall III Monday 1330h

Algal Blooms, Red Tides, Brown Tides, and Pfiesteria II

OS12F-183 1330h POSTER

Utility of the Algal Photo-pigment Gyroxanthin-diester in Studies Pertaining to the Red Tide Dinoflagellate Karenia brevis (Davis) G. Hansen & Moestrup

Barbara A Berg[1] (941-388-4441; barbib@mote.org)

Bradley A Pederson[1] (941-388-4441; pederson@mote.org)

Gary J Kirkpatrick[1] (941-388-4441; gkirkpat@mote.org)

Chris J Higham[1] (941-388-4441; chigham@mote.org)

David F Millie[2] (941-388-4441; dmillie@mote.org)

[1]Mote Marine Laboratory, 1600 Ken Thompson Pkwy, Sarasota, FL 34236, United States

[2]U.S. Departrment of Agriculture, Agricultural Research Service, New Orleans, LA 70124, United States

Discrimination of the algal photo-pigment gyroxanthin-diester (through High Performance Liquid Chromatography) can be applied to studies of Karenia brevis (Davis) G. Hansen & Moestrup as a biomarker and an indicator of both phytoplankton taxonomy and photophysiology. Few other species of phytoplankton in the eastern Gulf of Mexico contain gyroxanthin-diester therefore this pigment can be used as a biomarker for K. brevis in these waters. Four years of HPLC data, collected in nine independent field studies of the ECOHAB Florida project, were used to demonstrate the utility of gyroxanthin-diester in studies involving K. brevis. A weak linear relationship existed between the abundance of K. brevis and the concentration of gyroxanthin-diester however the presence and relative abundance of K. brevis was obtained from HPLC data. When gyroxanthin-diester was present its ratio to chlorophyll a was found to be constant. A comparison of the ratios of gyroxanthin-diester/chlorophyll a and gyroxanthin-diester/diadinoxanthin also provided information concerning photo-physiological state. Taxonomic composition, including the contribution of K brevis to total community composition, was determined using gyroxanthin-diester and ChemTax.

OS12F-184 1330h POSTER

Seasonal Variations in Ciliate Ingestion Rate and its Relationship to *Synechococcus* Abundance in a Coastal Marine Environment

Jeng Chang[1] (886-2-24622192 ext.5308; jengchang@mail.ntou.edu.tw)

Kung-Ming Chen[1]

[1]Institute of Marine Biology, Taiwan Ocean University, Keelung 202-24, Taiwan

At a sampling location on the northern coast of Taiwan (25° 08.5' N, 121° 47.7' E), the abundance of both *Synechococcus* and aloricate oligotrichous ciliates showed substantial seasonal variations with high values occurred in summer. Using the method of fluorescently labeled prey, *Synechococcus*-sized particles appeared to be the preferred food for ciliates, but particles of other sizes were also ingested. The ingestion rates measured at constant temperature varied seasonally. The highest ingestion rate, 86 *Synechococcus* cells ciliate^{-1} hr^{-1}, was observed in summer when *Synechococcus* abundance reached 5.8×10^4 cells ml^{-1}, and a good correlation could be established between *Synechococcus* abundance and ciliate ingestion rates. When *Synechococcus* abundance was kept constant, a separate set of experiments indicated that the effect of temperature on ingestion rate was small in the range between 20 and 30°C. Our results suggested that the seasonal variation in ciliate ingestion rate was mainly controlled by *Synechococcus* abundance in the water column.

OS12F-185 1330h POSTER

The feeding by the larvae of the mussel Mytilus galloprovincialis on red tide dinoflagellates

Seong Taek Kim[1] (82-63-469-4608; kimst@kunsan.ac.kr)

Hae Jin Jeong (hjjeong@kunsan.ac.kr)

Chang Hoon Lee

Jae Yoon Song

Won Ho Yih

[1]Dept. of Oceanography, Kunsan National University, Myrong Dong san 68, Kunsan 573-701, Korea, Republic of

We investigated grazing rates of the larvae of Mytilus galloprovincialis as a function of the larval age and prey concentration when feeding on the red-tide dinoflagellates Prorocentrum minimum, Cochlodinium polykrikoides, Alexandrium affine, Scrippsiella trochoidea, Prorocentrum micans, and Lingulodinium polyedrum. M. galloprovincialis larvae ingested all prey species used in this study. Ingestion rates of the larvae on unialgal diets of C. polykrikoides, S. trochoidea, and P. micans increased rapidly with increasing larval age up to 17-21 d, but were saturated at older ages, while those for the other prey species continuously increased. Ingestion rates of 25-d old larvae on unialgal diets of the red tide dinoflagellates increased rapidly with increasing prey concentration up to 1,000-3,000 cells ml^{-1} , but were saturated or showed only a slight increase at the higher prey concentrations. Maximum ingestion and clearance rates of 25-d old larvae on these dinoflagellates were 14-69 ng C predator^{-1}d^{-1} and 1.5-11.4 l predator^{-1} h^{-1}, respectively. M. galloprovincialis larvae exhibited higher maximum ingestion and clearance rates than previously reported for the mixotrophic dinoflagellate Fragilidium cf. mexicanum, the heterotrophic dinoflagellates Protoperidinium cf. divergens, P. crassipes, Polykrikos kofoidii, or the small ciliate Tiarina fusus, but lower rates than the large ciliates Strombidinopsis sp. and Favella sp. when grown on the same prey species. Grazing coefficients calculated by combining field data on abundances of Mytilus larvae and co-occurring red tide dinoflagellates with laboratory data on ingestion rates obtained in the present study suggest that M. galloprovincialis larvae usually has a small grazing impact on the populations of red tide dinoflagellates due to the predators low density.

OS12F-186 1330h POSTER

Changes in Seasonal Growth Break Occurrence in Hard Clams, *Mercenaria mercenaria*, Under Brown Tide Conditions Using Stable Oxygen Isotope Analysis

Douglas C Potts[1] (1-631-632-3038; potts@msrc.sunysb.edu)

Robert M Cerrato[1] (Robert.Cerrato@sunysb.edu)

[1]Marine Sciences Reseach Center, Stony Brook University, Stony Brook, NY 11794-5000, United States

Hard clams are a significant economic resource of Great South Bay, New York, but their abundance has dramatically declined in the past two decades. One possible contributing factor to this decline is the appearance of brown tides, monospecific phytoplankton blooms of *Aureococcus anophagefferens*, which have been shown to hinder bivalve feeding under high densities. Since the appearance of brown tides in 1985, shells appear to have more seasonal growth breaks at harvestable size suggesting a greater age and therefore slower growth. The ratio of $\delta\ ^{18}O$ to $\delta\ ^{16}O$ in calcium carbonate is indicative of the temperature and salinity of the surrounding water at the time of deposition. Therefore oxygen isotope analysis of the shell around a growth break can indicate its season of formation. Shells of clams that have either never been exposed to brown tide or experienced blooms of varying duration and density were analyzed using stable isotope mass spectrometry combined with historical water temperature and salinity information to determine the season of creation for multiple growth breaks. Analysis indicated that growth breaks occurred more frequently in clams exposed to brown tides of long duration and high concentration, making the clams appear older at the time of harvest then they actually were. Accurate aging of clams has important implications for population studies and stock management decisions.

OS12F-187 1330h POSTER

Hard Clams (Mercenaria mercenaria) May Play Key Role in Preventing Outbreaks of Brown Tides (Aureococcus anophagefferens) in Long Island Estuaries

David A Caron[1] ((213) 740-0203; dcaron@usc.edu)

Darcy J Lonsdale[2]

Robert M Cerrato[2]

Rebecca A Schaffner[1]

Julie M Rose[1]

[1]Department of Biological Sciences, University of Southern California, 3616 Trousdale Parkway, AHF 301, Los Angeles, CA 90089-0371, United States

[2]Marine Sciences Research Center, State University of New York at Stony Brook, Stony Brook, NY 11794-5000, United States

Harmful algal blooms called brown tides, caused by the pelagophyte Aureococcus anophagefferens, have occurred sporadically in coastal waters of Long Island, New York and elsewhere since 1985. Blooms of this minute (=2-3 m) alga have resulted in significant environmental damage and considerable economic loss. We have been experimentally examining the factors leading to the initiation of these blooms, and factors that might prevent their occurrence. We have conducted experiments in 300 liter mesocosms with natural seawater and under ambient conditions of light and temperature. Experimental setups with and without hard clams (Mercenaria mercenaria) demonstrated dramatic differences in the accumulation of A. anophagefferens biomass. Moderately high abundances of hard clams (densities sufficient to produce filtration rates resulting in the turnover of =25% of the water in the mesocosm per day) prevented any significant buildup in the absolute abundance of A. anophagefferens during 7-10 day experiments. Differences in the absolute abundance of A. anophagefferens in mesocosms with and without hard clams differed by as much as three orders of magnitude after one week. In addition, hard clams prevented a shift in the composition of the phytoplankton assemblage to dominance by the brown tide alga. Our evidence strongly indicates that differences between historical and present abundances of hard clams in L.I. estuaries may be an important factor in explaining the occurrence of brown tides during the past 16 years.

OS12F-188 1330h POSTER

Relationships Between Oceanographic Satellite Data and the Toxic Dinoflagellate, *Alexandrium*, in the Gulf of Maine

Remy Luerssen[1] (207 581 4333; remy.luerssen@maine.edu)

Andrew Thomas[1] (207 581 4335; thomas@maine.edu)

[1]University of Maine, School of Marine Sciences Libby Hall, Orono, ME 04469-5741, United States

Qualitative and quantitative relationships between satellite derived sea-surface temperature (SST), chlorophyll patterns and the distribution of *Alexandrium*, the

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toxic dinoflagellate species responsible for harmful algal blooms (HABs) in the Gulf of Maine (GOM) are examined. Daily images coincident with five ECOHAB survey cruises in 1998 and 2000 are composited over each cruise period to create mean patterns for each sample period. Contours of surface *Alexandrium* concentrations superimposed on images of SST and SST frontal zones show that high concentrations of *Alexandrium* are located primarily in the eastern Maine coastal current (EMCC) and that frontal zones in this region generally act as boundaries to their surface distributions. The most consistent results of a series of linear regressions are a linear relationship between satellite SST and *Alexandrium* that was used in a simple model to extrapolate/interpolate the distribution of *Alexandrium* based on satellite data. The regression results also suggest a seasonally shifting optimal temperature range for maximum *Alexandrium* concentrations. No qualitative or quantitative relationships between the SeaWiFS chlorophyll data and GOM *Alexandrium* distributions were found. Relationships between satellite-measured SST patterns and toxicity events in the western GOM were examined during a paralytic shellfish poisoning (PSP) closure in May 2000 to test the hypothesis that toxicity events in the western GOM require a transport mechanism linking *Alexandrium* cells in the EMCC to shellfish beds in western GOM. Thermal patterns evident in the satellite SST data at the time of the May 2000 closure were consistent with enhanced connectivity and advection between the two regions. Ten years (1990-1999) of retrospective toxicity data from five sites along the coast of Maine and coincident AVHRR SST data are used to test the temporal stability of this relationship. Results show that the occurrence of strong thermal gradients between eastern and western GOM, indicative of reduced alongshore connectivity, play a role in the occurrence and timing of toxicity event in the western GOM.

OS12F-189 1330h POSTER

Growth and Grazing Rates of the Prostomatid Ciliate Tiarina fusus on Red Tide and Toxic Algae

Hae Jin Jeong (82-63-469-4608; hjjeong@kunsan.ac.kr)

Joo Yih Yoon

Jae Seong Kim

Yeong Du Yoo

Kyeong A Seong

We investigated growth and grazing rates of the prostomatid ciliate Tiarina fusus when feeding on several species of red-tide and/or toxic algae (RTA). T. fusus ingested the dinoflagellates Lingulodinium polyedrum, Scrippsiella trochoidea, Heterocapsa triquetra, Prorocentrum minimum, Amphidinium carterae, and the raphidophyte Heterosigma akashiwo, but rarely consumed the dinoflagellate Ceratium fusus, and did feed on the dinoflagellate Prorocentrum micans. T. fusus exhibited positive growth on L. polyedrum, S. trochoidea, and H. akashiwo. Specific growth rates of T. fusus increased rapidly with increasing density of L. polyedrum, S. trochoidea, and H. akashiwo before saturating between 500-1,000 ng C ml^{-1} . Maximum specific growth rate of T. fusus feeding on L. polyedrum (0.47 d^{-1}) was much higher than when feeding on S. trochoidea (0.13 d^{-1}) or H. akashiwo (0.10 d^{-1}). Threshold prey concentrations (where net growth = 0) for L. polyedrum, S. trochoidea, and H. akashiwo. were 34-160 ng C ml^{-1}. Maximum ingestion rates of T. fusus on L. polyedrum, S. trochoidea, and H. akashiwo were 23.4, 10.2, and 6.5 ng C $predator^{-1}$ d^{-1}, respectively, while maximum clearance rates were 4.5, 0.2, and 0.6 l $predator^{-1}$ h^{-1}, respectively. T. fusus exhibited comparable or higher maximum growth, ingestion, and clearance rates than previously reported for the mixotrophic dinoflagellate Fragilidium cf. mexicanum or the heterotrophic dinoflagellates Protoperidinium cf. divergens and P. crassipes, when grown on the same prey species. Grazing coefficients calculated by combining field data on abundances of T. fusus and co-occurring RTA with laboratory data on ingestion rates obtained in the present study suggest that T. fusus sometimes has a considerable grazing impact on the populations of H. akashiwo.

OS12G HC: 319 B Monday 1330h

Novel Techniques for Chemical Characterization in Marine Systems I

Presiding: **H E Hartnett,** Rutgers University**; L Minor,** Old Dominion University

OS12G-01 1330h INVITED

Comprehensive Two-Dimensional Gas Chromatography: A New Tool for Geochemical Research

Christopher Reddy[1] (creddy@whoi.edu)

Li Xu[1] (lxu@whoi.edu)

Timothy Eglinton[1] (teglinton@whoi.edu)

Richard Gaines[2] (rgaines@cga.uscg.mil)

Glenn Frysinger[2] (gfrysinger@cga.uscg.mil)

[1]Woods Hole Oceanographic Institution, 360 Woods Hole Rd, Woods Hole, MA 02543, United States

[2]United States Coast Guard Academy, 24 Mohegan Ave, New London, CT 06320, United States

Recent analytical and conceptual advances in chromatography have led to the development of comprehensive two-dimensional gas chromatography (GCxGC), which has a tremendous capability to separate, identify, and quantify trace organic compounds in complex geochemical samples. GCxGC uses two different chromatography columns coupled serially by a thermal modulator to produce a volatility by polarity separation and distribute compound peaks across a two-dimensional retention time plane. This is in contrast to "heart-cutting" two-dimensional GC, which only allows select components in the first column to be rechromatographed on a second column. The GCxGC two-dimensional separation produces an order of magnitude more resolved peaks than traditional GC methods, and the grouping or ordering of the peaks in the GCxGC chromatogram facilitates the identification of unknown compounds. Furthermore, spatial band compression during modulation has the additional advantage of more than an order of magnitude increase in signal-to-noise ratio, thus improving the detection and quantification of minor components. For example, we have used GCxGC to investigate the composition and distribution of alkenones (35 to 39 carbons) in Black Sea sediments. These compounds differ in chain length, degree of unsaturation, and position of the ketone group (either methyl or ethyl). In this case, GCxGC analysis resolved and helped tentatively identify more of these compounds than was previously thought to exist. New alkenones include C35:2Me, C37:4Et, C37:1Me, C38:4Me, C38:1Et, and C39:4Et. (Alkenone nomenclature is as follows: Cx:y Me or Et, where x is the total number of carbons in the compound, y is the number of double bonds, and Me or Et designates methyl or ethyl ketones, respectively). It is especially worth noting that the placement of the ketone group by one carbon unit (methyl or ethyl) allowed for discrete bands of these compounds to be resolved. We have also found that GCxGC may be equally adept in determining the alkenone unsaturation index in total sediment extracts and hence avoiding time-consuming "clean-up" steps when using these compounds for paleothermometry. Another application of GCxGC that we are exploring is resolving the unresolved complex mixture (UCM) of petroleum hydrocarbons. These compounds are the most abundant, ubiquitous, and understudied class of organic contaminants in estuarine and coastal sediments. The term UCM is derived from traditional GC and refers to a hump of unresolved and, hence, unidentified hydrocarbons in gas chromatograms. Initial efforts have been able to separate and identify discrete bands of normal, branched, one-ring, and two-ring alkanes and one-, two-, and three-ring aromatics. Additional applications focused on natural and anthropogenic organic compounds as well as future efforts will be discussed.

OS12G-02 1345h INVITED

A Molecular Multi-Isotopic Approach for the Study of Organic Matter Cycling in the Oceans

Timothy I Eglinton[1] (508-289-2627; teglinton@whoi.edu); Nao Ohkouchi[1] (508-289-2641; nohkouchi@whoi.edu); John M Hayes[2] (508-289-3345; jhayes@whoi.edu); Alex Sessions[2] (508-289-3546; asessions@whoi.edu); Ann Pearson[3] (617-384-8392; pearson@eps.harvard.edu); Ann P McNichol[2] (508-289-3394; amcnichol@whoi.edu); Daniel Montlucon[1] (508-289-2821; dmontlucon@whoi.edu)

[1]Woods Hole Oceanographic Inst., Marine Chemistry and Geochemistry Dept., Woods Hole, MA 02543

[2]Woods Hole Oceanographic Inst., Marine Geology and Geophysics Dept., Woods Hole, MA 02543

[3]Harvard Univ., Earth and Planetary Sciences Dept., Cambridge, MA 02138

Over the past several years it has become feasible to measure the isotopic characteristics of individual organic compounds in complex natural matrices such as marine sediments. In addition to the stable isotopes of carbon, techniques have been developed for examining natural abundance variations in other stable isotopes (D/H, δ^{15}N and δ^{18}O), as well as for radiocarbon at the molecular-level. Here, we illustrate how multi-isotopic measurements on individual compounds can improve our understanding of organic carbon cycling in the ocean.

Coupled measurements of δ^{13}C and Δ^{14}C better define organic carbon inputs, both in terms of quantity and mode of transport: δ^{13}C measurements on molecular markers (biomarkers) of marine primary productivity (e.g., algal sterols, fatty acids, alkenones) may help to define environmental conditions and the physiological status of by the precursor organisms; Δ^{14}C measurements on these same compounds provide a temporal context for the processes that act upon phytoplanktonic organic matter, from its synthesis in the surface ocean to its burial in marine sediments. We have observed, for example, that sediment redistribution processes such as resuspension and lateral advection can significantly "pre-age" organic matter that is preserved in some sedimentary regimes. When paired with similar measurements on vascular land plant biomarkers (e.g., epicuticular waxes, lignin phenols), constraints can be placed on the terrestrial residence time of the latter and on the importance of terrigenous organic carbon in marine sediments. Recently, we have expanded this multi-isotopic approach to include compound-specific D/H measurements, and found this can provide complementary information to that available from carbon isotopes.

In addition to describing this multi-isotopic approach, this paper will describe methods and existing challenges associated with molecular-level radiocarbon measurements, and discuss future analytical developments.

OS12G-03 1400h

A Compound-Specific Isotopic Tracer for Organic Nitrogen Source: Amino Acid 13C Fractionation Patterns

Matthew McCarthy[1] (831 459-4718; mdmccar@cats.ucsc.edu)

Ciny Lee[2]

John Hedges[3]

Ron Benner[4]

Marilyn Fogel[5]

[1], Ocean Sciences Dept., University of California at Santa Cruz, 1156 High St, Santa Cruz, CA 95064, United States

[2]Marine Sciences Research Center, SUNY at Stony Brook

[3]School of Oceanography, University of Washington, Seattle, WA

[4]Department of Biological Sciences, University of South Carolina, Columbia, SC

[5]Carnegie Geophysical Laboratory, 5441 Broad Branch Rd., Washington, DC

Most of the organic nitrogen which can be identified at the molecular level in organisms, sinking particles, and dissolved matter is present as amino acids. Unfortunately, in the geochemical realm, molecular-level amino acid analysis has had limited ability to provide source information because overall amino acid compositions from different sources are too similar. On the isotopic level, however, distinct biochemical pathways associated with differing metabolic processes result in characteristic stable isotopic fractionation patterns. In