

OS41H-12 1135h

A Proton Buffering Role for Silica in DiatomsAllen J. Milligan¹ ((609) 258-4674; allenm@princeton.edu)Francois M.M. Morel¹¹Princeton University, Guyot Hall Geosciences Department Princeton University, Princeton, NJ 08544, United States

Diatoms concentrate carbon in order to overcome the carbon oxidation reaction of RubisCO encourage the carboxylase reaction. Diatoms possess a carbon concentrating mechanism which utilizes an extracellular carbonic anhydrase (CA) and catalyses the equilibrium reaction between bicarbonate and CO₂. Forms of CA which have high catalytic rates require a pH buffer to either provide or receive a proton in the dehydration / hydration reaction. The proton transfer reaction between the pH buffer and the active site has been shown to be the rate limiting step in catalysis. We have found evidence that the siliceous cell wall of diatoms is an effective pH buffer and that it enables the enzymatic conversion of bicarbonate to CO₂, an important step in the acquisition of inorganic carbon by these organisms. We find that diatom silica has the appropriate buffering capacity and pKa to provide pH buffering to CA. Using membrane inlet mass spectrometry we demonstrate that both bovine and diatom CA's can be catalytically active in a system buffered with cleaned diatom silica. In situ experiments show that live cells of *T. weissflogii* do not require a pH buffer to exhibit catalytically active CA but that the green algae *Chlamydomonas* requires pH buffering. We hypothesize that diatoms possess the capacity to utilize the pH buffering ability of the silica cell wall to aid in uptake of bicarbonate, the major inorganic carbon source in seawater.

OS41I HC: 317 A Thursday 0830h**Biogeochemical Processes in Anoxic and Suboxic Environments II****Presiding:** M Scranton, State

University of New York; J Murray, University of Washington

OS41I-01 0835h

Ventilation of the Black Sea: New Hydrographic and Nutrient Data From the 2001 R/V Knorr CruiseJames W. Murray¹ ((206) 543-4730; jmurray@u.washington.edu)Sergey K. Kononov² (sergey@alpha.mhi.iuf.net)Temel Oguz³ (oguz@ims.metu.edu.tr)Sukru Besiktepe³ (sukru@ims.metu.edu.tr)Suley Tugrul³ (tugrul@ims.metu.edu.tr)¹University of Washington, School of Oceanography Box 355351, Seattle, WA 98195-5351²Marine Hydrophysical Institute, Kapitanskaya St., 2a, Sevastopol 99000, Ukraine³Middle East Technical University, Institute of Marine Sciences P.O. Box 28, Erdemli-Icel 33731, Turkey

The sampling plan of the 2001 Knorr research cruise was designed to examine variability associated with the Bosphorus inflow along the SW coast near Turkey and the NW shelf area near Ukraine. The cruise was divided into two legs of approximately 10 days each. There were 48 scientists from five countries participating. A web site describing the cruise is available at www.ocean.washington.edu/cruises/Knorr2001.

The only source of salinity to the Black Sea is the Bosphorus inflow. The only source of cold water is the surface. Thus, distributions of hydrographic data can be used to evaluate variability in the Black Sea due to variable inputs from the Bosphorus and variable intrusions from the surface. Variability in oxygen from both sources influences the depth and intensity of the suboxic layer. The cold intermediate layer in 2001 had lower oxygen than in previous years suggesting lower rates of ventilation than in the past. The density of the first appearance of sulfide was the same, however.

Oxygen input with the Bosphorus inflow is an important sink for the upward flux of sulfide and the stations in the SW corner of the Black Sea were well sorted to observe these intrusions.

OS41I-02 0850h

The Lateral Flux of Oxygen From the Bosphorus Into the Black Sea: Controls on the Distributions of Oxygen, Sulfide and Redox ChemistrySergey K. Kononov¹ (sergey@alpha.mhi.iuf.net);James W. Murray² ((206)543-4730;jmurray@u.washington.edu); George W. Luther³ ((302) 645-4208; luther@udel.edu); Ken O.Buesseler⁴ ((508) 289-2309; kbuesseler@whoi.edu);Gernot Friederich⁵ ((831)775-1713;frge@mbari.org); Brad Tebo⁶ ((619) 534-5470;btebo@ucsd.edu); Leonid I. Ivanov¹(leonid@alpha.mhi.iuf.net); Anatoly Samodurov¹ (ass@alpha.mhi.iuf.net)¹Marine Hydrophysical Institute National Academy of Sciences of Ukraine, Kapitanskaya St. 2a, Sevastopol 99000, Ukraine²University of Washington, School of Oceanography Box 355351, Seattle, WA 98195-5351³University of Delaware, College of Marine Studies, Lewes, DE 19958⁴WHOI, Dept. of Marine Chemistry and Geochemistry, Woods Hole, MA 02543⁵MBARI, 7700 Sandholdt Road, Moss Landing, CA 95039⁶Scripps Institution of Oceanography, 9500 Gilman Drive, La Jolla, CA 92093-0202

The lateral flux of oxygen input from the Bosphorus plays an important control on the vertical oxic/anoxic structure and redox budget of the Black Sea. We use the results of numerical modeling calibrated and verified against historical data from 1960 to 1995 and the most recent data from the 2001 Knorr cruise to support the following points: 1. Injection of Mediterranean water into the Black Sea results in intrusions of oxygen in the suboxic and anoxic layers. 2. The volume of these intrusions and the lateral flux of oxygen decreases exponentially towards the deeper layers of the main pycnocline. 3. The lateral influx of oxygen results in oxidation of sulfide inside the anoxic zone. As much as 70% of the total vertical flux of sulfide is oxidized by this oxygen, mainly through redox Mn(II) - Mn(III,IV) cycling of manganese. This appears to be the main reason for the stable density of the onset of sulfide in the main pycnocline, even though the depth of both the onset of sulfide and pycnocline vary by more than 20 meters on the time scale of decades. 4. The lateral flux of oxygen appears to be the main reason for the presence of the suboxic layer, as the downward flux of oxygen is exhausted at the depth of the upper boundary of the suboxic layer and the position of the lower boundary is mainly controlled by the lateral flux of oxygen. The suboxic zone can exist when the flux of organic matter is enough to deplete the downward flux of oxygen and the lateral flux of oxygen is sufficient to compensate the upward flux of sulfide and other reduced substances. 5. Both climate- and human-induced changes in the flux of nutrients and oxygen are essential for the temporal evolution of the suboxic zone and the entire biogeochemical structure of the Black Sea water column.

OS41I-03 0905h INVITED

Mediterranean Inflow Through the Bosphorus Injects Massive Amounts of O₂ into the Suboxic Zone of the Southwest Black SeaGeorge W. Luther¹ (302-645-4208; luther@udel.edu);Donald B. Nuzzio² (908-788-7022); Brian Glazer¹;Sergey K. Kononov³ (sergey@alpha.mhi.iuf.net);Gernot Friederich⁴ (frge@mbari.org); Robert E.Trouwborst¹; Alexander Romanov³; Brad M.Tebo⁵¹Univ. of Delaware, College of Marine Studies, Lewes, DE 19958, United States²Analytical Instrument Systems, Inc. Road, 1059C Old York, Ringoes, NJ 08851, United States³Marine Hydrophysical Institute, 2 Kapitanskaya St., Sevastopol 99011, Ukraine⁴MBARI, 7700 Sandholdt Rd., Moss Landing 95039, United States⁵Scripps Institution of Oceanography, University of California San Diego, 9500 Gilman Drive, La Jolla, CA 92093-0202, United States

An in situ voltammetry analyzer from Analytical Instrument Systems, Inc. coupled to the MBARI CTD-pump profiler system was deployed to determine the redox chemistry of the upper 200 m (from the oxic to suboxic to anoxic zones) of the western Black Sea. Solid-state gold-amalgam electrodes were used to measure

O₂, H₂S and polysulfides (S_n²⁻) at < 1 meter resolution. In the Southwest, massive intrusion of O₂ (from 10 to 100 micromolar concentrations) into the suboxic zone was measured over intervals of 4 to 5 meters and correlated with increases of temperature of only 0.2 to 0.3 °C. Up to 3 submaxima of O₂ could be detected in the suboxic zone and 2 subminima of H₂S in the H₂S zone could be detected. O₂ and H₂S were not observed to co-exist at any depth. This "fingering" of O₂ was not observed in the West or Northwest section of the Black Sea and leads to significant consequences on the oxidation of manganese and sulfide in the southwestern section of the Black Sea. We present data from the in situ work as well as from a voltammetric flow cell and from discrete samples. High resolution data are essential to determine the chemical characteristics of the water column.

OS41I-04 0920h

Spatial and Temporal Variations in the Hydro-chemical Properties of the Black Sea Upper Layer Water ColumnIlkay Salihoglu¹ (+90 324 521 2150; ilkay@metu.edu.tr)Suleyman Tugrul¹ (+90 324 521 2406; tugrul@ims.metu.edu.tr)¹Ilkay SALIHOGLU, METU Institute of Marine Sciences, P.O.BOX 28, Erdemli/ICEL 33731, Turkey

In this report we utilized Knorr-2001 Black Sea cruise nutrient data to evaluate spatial variability in the hydro-chemical properties (dissolved oxygen (DO), nitrate, phosphate, silicate, dissolved iron and manganese) of the upper layer water column of the Black Sea, including the upper depths of the anoxic layer. Nutrient profiles reveal that the photic zone waters contained very low concentrations of nitrate-nitrite (0.05-0.1 μM) and phosphate (0.02-0.04 μM) ions. The cold intermediate layer (CIL) in the coastal waters became poor in nitrate as compared to the late 1980-1995 period data, during which the open sea contained higher nitrate values at the depth of the nitrate maximum. Interestingly, in May-June 2001, the oxycline of the deep basin commenced at a shallower density surfaces as compared to the onset of nitrate. This finding indicates that denitrification processes became effective within the steep oxycline and caused nitrate lost from the water column. Comparison of long-term nitrate profiles in the studied sites confirms our idea. Combined profiles of the nitrate and DO data also indicate that the upper nitricline sharpened and deepened whilst the oxycline was modified by sinking particulate organic matter (POM). In the open sea the suboxic boundary (DO < 10 μM) has moved upward slightly and the DO deficiency (<5.0 μM below the 15.5 density surface) appeared to have increased in the suboxic zone, supporting the increasing nitrate loss from the transition zone. In the deep basin, the dissolved manganese concentrations become detectable consistently at about 15.85-15.90 σ density surfaces where the both DO and nitrate dropped to very low levels. Though the slopes of nitricline and oxycline were modified the sulphide bearing anoxic waters have remained almost at the same density surface in recent years, suggesting the existence of the other oxidizing agents (e.g. manganese) within the interface. In coastal margin off the Bosphorus Strait, the intrusion of the Mediterranean inflow to the Black Sea intermediate depths could be traced by its high nitrate values. In the shelf break; the excess oxygen in the Mediterranean inflow oxidize all sulfides in the receiving water masses whilst the nitrate and ammonia co-existed at elevated concentrations, indicating lower oxidation rate of ammonia. Such similar features were also observed in the coastal waters off Sakarya, in the southern Black Sea. In the suboxic interface between 16.1-16.35 σ density surfaces of this site, the concentrations of nitrite, intermediate product of redox reactions of dissolved inorganic nitrogen compounds, increased to levels of 0.2-0.35 μM in a water column of about 30 m thick, where the DO and nitrate both ranged between 30-45 μM and between 2-2.8 mM, respectively. This suboxic water also contained measurable concentrations of both dissolved manganese ions and ammonia (determined by colorimetric method) at 1.0-3.0 μM levels.

OS41I-05 0935h INVITED

High Resolution Measurements of Carbon Dioxide Distributions in the Black Sea: Indication of Horizontal Mixing Processes in the Suboxic Zone and Unexpected Surface Layer Carbon DeficitGernot E Friederich¹ (831-775-1713; frge@mbari.org)William T Hiscock² (wthiscoc@rsmas.miami.edu)George W Luther³ (luther@udel.edu)

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During the May to June 2001 Black Sea expedition aboard the R/V Knorr, detailed inorganic carbon data was collected. Utilizing a profiling pump and rapid equilibration techniques, the partial pressure of carbon dioxide (pCO₂) was measured with a depth resolution of about 1 meter from the sea surface into the upper portion of the anoxic zone (200 m). Total carbon dioxide (TCO₂) analyses were made on-line from the pumped stream providing depth resolution of about 5 meters. During the first leg of this cruise alkalinity, pH and TCO₂ data was also collected and analyzed aboard from bottle samples. Sea surface pCO₂ and TCO₂ data were collected on transects between the Turkish and Ukrainian coasts during the second leg of the cruise.

Between the seasonal thermocline and the depth where oxygen is depleted, TCO₂ and pCO₂ increase in the manner that would be expected from the aerobic oxidation of organic carbon, reaching a maximum of about 1600 ppm. In the suboxic zone, however, there is a marked decrease of pCO₂ to about 1300 ppm before slowly increasing again in the sulfide layer. The CO₂ changes in the sulfide layer appear to occur in accordance with anaerobic oxidation of organic matter coupled with a slight increase of total alkalinity. Conditions in the suboxic zone make pCO₂ an extremely sensitive indicator; a 10 micro molar change of TCO₂ translates to a 100 ppm change of pCO₂ in this layer. While it has previously been hypothesized that the apparent CO₂ deficit in the suboxic zone could be explained by in-situ carbon fixation, data presented here is consistent with the lateral injection of a mixture of shelf and Bosphorus inflow waters into the suboxic zone. Profiles in the southwestern Black Sea give clear evidence of recent inflow events. Thin layers with negative pCO₂ anomalies as great as 500 ppm were found in this region associated with small positive temperature and salinity anomalies. This direct infusion of relatively oxygenated waters into the suboxic zone may have significant influence on the chemical transformations in this region.

Sea surface pCO₂ was below atmospheric values at all stations and during all transects. In some regions, sea surface pCO₂ was up to 160 ppm below atmospheric values. Given the low nitrate concentrations observed in the Black Sea, it is difficult to reconcile this result with the assumption that the sea surface was near atmospheric equilibrium with respect to CO₂ at the termination of wintertime mixing.

OS411-06 0950h

Particulate Manganese Concentration and Oxidation State in the Suboxic Zone of the Black Sea.

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The Black Sea is a classic site for describing redox cycling of manganese between its oxidized and reduced forms across the oxic/anoxic interface. During the 2001 Knorr Cruise samples were collected to determine the concentration and oxidation state of particulate manganese (i.e., MnOx). Total manganese and oxidized equivalents of manganese were determined using atomic absorption spectrophotometry and the iodometric method, respectively. Dissolved manganese was determined using the formaldoxime method.

Particulate manganese was low in the surface waters and cold intermediate layer and increased to high values in the suboxic zone. Maximum values were higher near the SW margin (~100 micromoles/l) than in the central western gyre (~30 micromoles/l), as seen in previous results. The SW margin station was characterized by a double maximum at density values of 15.90 and 16.20. The deeper maximum probably reflects oxidation of manganese by oxygen in the intrusion of the Bosphorus plume.

The oxidation state of Manganese (MnOx) ranged from x = ~1.5 for the shallow samples in the central

gyre to values consistently about 1.8 to 1.9 in the sub-oxic zone. Total particulate Mn and oxidized equivalents correlated significantly with r₂ = 0.99 and a slope equivalent to MnO_{1.83}. These results will be discussed considering alternative pathways of oxidation of Mn(II).

OS411-07 1005h INVITED

Manganese Cycling in the Suboxic Zone of the Black Sea

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The maintenance of a stable suboxic zone in the water column of the Black Sea has been explained by either lateral input of oxidized species (O₂ or Mn oxides) or unusual reactions, perhaps microbially-mediated, between reduced Mn, N and S species and oxidized N and Mn species. Shipboard measurements of dissolved and particulate Mn concentrations were made in water samples collected from the northwest shelf, western gyre, Bosphorus shelf and southwest coastal regions of the Black Sea during a cruise in May-June 2001. Similar to previous cruises, we found that Mn was enriched only at $\sigma_T > 14.5$ and that distribution of total Mn (relative to density) was similar at all stations deeper than 200m. Just north of the Bosphorus, mixing between high-salinity Mediterranean water and Mn-enriched, medium-salinity Black Sea water was observed. The low density (σ_T 14.5) Black Sea water near the Bosphorus and the northwest shelf water (σ_T 14.4) contained $< 1 \mu\text{M}$ total Mn and both particulate and dissolved Mn varied little with depth. The deeper western gyre and coastal stations showed typical suboxic zone distributions; particulate Mn maxima occurred in the suboxic zone and dissolved Mn maxima occurred just below the appearance of HS⁻. Total Mn distributions (relative to density) were similar at all western gyre and coastal stations, but coastal stations had larger particulate Mn maxima (1-3 μM) than observed in the western gyre (particulate [Mn] ≤ 600 nM). These observations support the lateral advection hypothesis put forth by investigators on the 1988 cruise wherein Mn oxides are formed in coastal mixing regions of the Black Sea and advected along isopycnals into the central gyres. This model requires an injection of suitable oxidants (e.g. O₂, NO₃⁻, NO₂⁻) at depth for the formation of Mn oxides. Interestingly, we observed significant variability in Mn data from our three casts at one of the coastal stations (BS1-10). Light transmission, dissolved and particulate Mn, O₂, and HS⁻ data from several casts indicated interleaving of water masses with characteristic chemical signatures and penetration of oxidants across isopycnals of greater density where large quantities of reduced Mn occur. Such mixing processes likely produce the large particulate Mn maxima observed along the coast during both the 2001 and 1988 cruises. Culture studies indicated that Mn oxide-reducing and S⁰-disproportionating bacteria were prevalent throughout the suboxic zone. These results support the suggestion that the Mn cycle is key to the maintenance of the suboxic zone in the Black Sea.

OS411-08 1040h

Nitrogen species and stable isotopes in the Black Sea

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Fixed nitrogen (NO₃ + NH₄) is completely depleted throughout the Black Sea basin within the suboxic zone at a density of 15.95. The vertical distributions suggest that reactions are occurring in the suboxic zone which both reduce nitrate and oxidize ammonia anaerobically. This may occur as the hypothesized anammox reaction, written as $3\text{NO}_3^- + 5\text{NH}_4^+ + 4\text{N}_2 + 9\text{H}_2\text{O} + 2\text{H}^+$. Previous measurements of N₂/Ar gas ratios showed a maximum in N₂ concentration at $\sigma_t = 15.95$ and suggested that the diffusive flux of fixed nitrogen (NO₃ + NH₄) into the suboxic zone was balanced by the outward flux of N₂.

New data were collected during the 2001 R/V Knorr Black Sea Cruise to examine these processes in more detail. Samples were collected at stations in the center of the western gyre and near the SW coast for the concentration and $\delta^{15}\text{N}$ of NO₃, NH₄, PON, and N₂. The nitrogen isotope measurements should help distinguish the mechanism and location of these reactions. At both stations N₂ increases to a maximum at a density of about $\sigma_t = 15.95$. The $\delta^{15}\text{N}$ -N₂ profile shows a minimum at $\sigma_t = 15.95$, corresponding to an apparent fractionation effect (calculated by a closed system Rayleigh approach) of ~ -30 per mil. $\delta^{15}\text{N}$ -NO₃ is about 8 per mil at the density of the nitrate maximum ($\sigma_t = 15.60$), then increases to a maximum of 18 per mil at $\sigma_t = 15.90$. The closed system Rayleigh apparent fractionation effect for NO₃ is about -9 per mil, suggesting that either the nitrate isotopes or nitrogen gas isotopes are partially determined by processes other than nitrate reduction.

OS411-09 1055h INVITED

Concentration and Isotopic Compositions of Nitrous Oxide in the Black Sea.

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A major goal of the May-June 2001 Black Sea expedition was to understand the dynamics of the nitrogen cycle under a range of redox conditions including oxygenated surface waters, the suboxic zone and anoxic, sulfide-rich deep waters. To contribute to this goal, nitrous oxide samples were collected from the Bosphorus inflow, the center of the western gyre, the Danube sediment fan and northern and southern shelf break stations. Samples were analyzed for concentration and ¹⁵N/¹⁴N and ¹⁸O/¹⁶O ratios of nitrous oxide. Select samples were also analyzed to determine the intramolecular distribution of ¹⁵N within the linear NNO molecule. ¹⁵N tracer addition experiments were conducted at several depths in the western gyre station to establish mechanisms and rates of nitrous oxide production.

Microbial production yields nitrous oxide that is depleted in heavy isotopes relative to its sources, whereas consumption yields isotopically enriched nitrous oxide. Initial results from the western gyre station show that the concentration of nitrous oxide in the surface oxygenated layer is close to or slightly below saturation with respect to the atmosphere. Nitrous oxide concentration declines rapidly within the suboxic zone, defined as those depths at which oxygen concentration is below 10 μmol and sulfide remains undetectable. This decline in concentration is accompanied by an enrichment in ¹⁸O but a depletion in ¹⁵N. This depletion is most pronounced in the end position nitrogen. Further samples will be analyzed to confirm this unusual isotopic signal and to better understand its cause.

OS411-10 1110h

Aerobic and Anaerobic Anoxygenic Photosynthetic Bacteria in the Black Sea

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The distribution and photosynthetic properties of aerobic and anaerobic anoxygenic photosynthetic bacteria in the Black Sea have been characterized using Infrared Fast Repetition Rate (IRFRF) fluorometry. The aerobic photosynthetic bacteria were recently found to be ubiquitously present in the upper open ocean, and their characteristic pigment, Bacteriochlorophyll a, (BChl_a) represents between 0.5% to 10% of total photosynthetic pigments. These organisms are close relatives of the anaerobic purple bacteria. We hypothesized that the presence of the shallow anoxic layer in the Black Sea may create a unique environment where both aerobic and anaerobic photosynthetic bacteria are present in the water column. During a June 2001 expedition to the Black Sea, we detected the presence of BChl_a in the upper portion of the water column, and BChl_e at the top of the anoxic anoxic layer. The distribution of BChl_a appears to correlate with that of Chl_a, while BChl_e is only present at a very thin interface between the suboxic and anoxic zones. Such a characteristic distribution of BChl_e can be explained by the "sulfochlorine" phenomenon, where both light and H₂S determine the vertical distribution of green sulfur bacteria. Additionally, the distribution of BChl_e may be controlled by the presence of minute concentrations of oxygen atop of the H₂S layer. We describe the IRFRF signature of the aerobic and the green sulfur bacteria, quantify their concentrations in the water column, and discuss their photosynthetic competence.

OS41I-11 1125h INVITED

Unusual Radium Isotope Distributions in the Black Sea

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In Spring 2001 we conducted measurements of the radium quartet (Ra-223, Ra-224, Ra-226 and Ra-228) in the western Black Sea to be used as tracers of cross shelf transport. Samples were collected along three main transects: two over the southwest shelf to the interior basin, and one over the northwest shelf. Several surprising features in the distribution of the short-lived isotopes appeared. Radium-223 (11.4 day half life) was low throughout the sampling lines, suggesting (1) extremely slow offshore water mass transport rates or (2) minimal groundwater input along the coastlines. Unsupported Radium-224 (3.7 day half life) was lowest over the shelves, and increased with distance from shore; activities beyond the shelfbreak and into the interior basins were uniformly high. This pattern, the reverse of the normal horizontal distribution where Radium-224 is highest on the shelf and near zero beyond the slope, suggests minimal input from the coastlines and a water column source in the interior basins. Possible sources for the excess Ra-224 will be discussed, as well as implications for using these isotopes as horizontal mixing tracers in the Black Sea.

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Denitrification Produced ¹⁵N Enrichment in the Arabian Sea: A Quantitative Assessment

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The Arabian Sea is one of the principal regions in the world's oceans for water column denitrification, accounting for approximately a third of the total. A combination of high organic matter flux and poor intermediate water mass ventilation creates the extensive OMZ necessary for denitrification to take place. We have analyzed nine hydrographic profiles collected during the JGOFS Arabian Sea program for the $\delta^{15}\text{N}$ of NO_3^- to

both estimate the isotopic fractionation factor for denitrification and to examine the influence of circulation patterns on the distribution of $\text{NO}_3^- \delta^{15}\text{N}$. Amongst other findings, maximal $\delta^{15}\text{N}$ values at depth range between 11 and 17 ‰, but source waters for upwelling are more typically near 8 ‰ consistent with flux-weighted averages for sediment traps.

While the isotopic fractionation factor (ϵ) varies only narrowly between stations, the actual magnitude depends on the method chosen for calculation of NO_3^- anomaly. If the N* method is used, ϵ is near 20 ‰. Nevertheless, the tight relationship between NO_3^- anomaly and $\text{NO}_3^- \delta^{15}\text{N}$ allows for a more detailed $\delta^{15}\text{N}$ map to be generated based on the extensive JGOFS hydrographic data set. Taking into account associations with water masses and literature estimates for their fluxes into and out of the Arabian Sea, the influence of Arabian Sea denitrification on global marine $\delta^{15}\text{N}$ will be estimated.

OS41I-13 1155h

Isotopomer compositions of nitrous oxide in the eastern tropical North Pacific

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Nitrous oxide is an important greenhouse gas and an agent in stratospheric ozone depletion. The oceans are a major natural source of nitrous oxide; however, the reactions producing nitrous oxide in the oceans are poorly understood. We present here stable isotope and isotopomer (intramolecular distribution of ¹⁵N within the linear NNO molecule) results for nitrous oxide in the eastern tropical North Pacific. Isotopomer compositions of nitrous oxide have wide variations in natural environment. Therefore, the isotopomer ratios will be very useful tool to reveal the origin and to solve the global cycle of nitrous oxide. Here we named the intramolecular sites of N₂O as N^βN^αO, the middle position as alpha site and the end position as beta site. We call the mean of isotopic compositions of the two nitrogens, conventional $\delta^{15}\text{N}$, as $\delta^{15}\text{N}^{\text{bulk}}$, and " $\delta^{15}\text{N}^{\alpha}$ - $\delta^{15}\text{N}^{\beta}$ " as "Site preference". The eastern tropical North Pacific (ETNP) is the significant source of nitrous oxide to the atmosphere and one of the major regions of the world ocean where denitrification occurs. The concentration of nitrous oxide reaches a maximum above the oxygen minimum zone (OMZ) and declines rapidly as oxygen becomes depleted. Therefore we expect that its source is nitrification. Below the nitrous oxide maximum we find evidence of nitrous oxide reduction, presumably by denitrification, resulting in areas where nitrous oxide is undersaturated with respect to the atmosphere. In this research, we can see relationship between the isotopomer compositions of nitrous oxide and each mechanism, nitrification and denitrification. These results can be used to analyze the other oceans data, and help to solve the mechanisms of production and decomposition of nitrous oxide. Samples were collected in The Eastern Pacific Redox Experiment (EPREX) in May-June 2000. Stations are located from the oligotrophic, oxygen-rich waters of the central North Pacific gyre near Hawaii (22.75°N, 158°W), Station ALOHA (St.1), to the highly productive, oxygen-poor waters of the Eastern Tropical North Pacific near Mexico (15°N, 98°W), Station 6. Isotopomer ratios of nitrous oxide were measured at Station 3 (16°N, 136°W) and Station 5 (16°N, 107°W). This is the first data of the isotopomer ratio of nitrous oxide in the ETNP. In this research, below the OMZ, nitrous oxide is consumed by denitrification. In this area, alpha site of nitrogen and oxygen is strongly enriched by reduction of nitrous oxide, but beta site of nitrogen is constant or slightly enriched. On the other hand, from subsurface nitrous oxide maximum to the deeper area where the concentration of nitrous oxide lower gradually, alpha site of nitrogen and oxygen is strongly enriched but beta site of nitrogen is depleted. This means that

the mechanisms declining the concentration of nitrous oxide are different between two areas. This difference can be detected only by the isotopomers, but can't be detected by bulk isotope ratios.

OS41J HC: 323 A Thursday 0830h

New Insights Into the Ecology of Pelagic Animals From Applications of Electronic Tags

Presiding: J Polovina, NMFS,
Honolulu Laboratory; G Boehlert,
NOAA, NMFS, PFEL,

OS41J-01 0830h

Environmental Influences on Movements and Depth Distributions of Tunas and Billfishes

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Numerous studies have attempted to explain the movements and distribution of tunas and billfishes by correlating catch statistics with environmental conditions averaged over time and space. Such correlations do not necessarily elucidate the requisite relationships because the data are often not gathered simultaneously, and because error terms are too broad to demonstrate meaningful relationships. Moreover, using catch statistics to determine the effects of environmental conditions on catch statistics can never prove causation and result in tautology, unless independent measures of fish abundance are available. Other studies have correlated catch statistics with satellite-derived sea surface temperature data, but tunas and billfish do not live exclusively at the surface. More importantly, they regularly experience thermal gradients (1 C per m depth) during their rapid and repetitive vertical movements which are orders of magnitude steeper than sea surface temperature gradients (1 C per km). We suggest that sea surface temperature gradients are undetectable and are, therefore, unlikely to determine horizontal movements or aggregation. Direct observations of tunas and billfishes behaviors (collected via acoustic telemetry or electronic data-recording tags) can, however, be readily combined with information on their physiologically-based environmental tolerances, forage abundance, and appropriate satellite derived oceanographic data to provide the needed information.

We are currently combining several types of spatio-temporal scales of observational data with modeling efforts to provide key information on movements of Atlantic bluefin tuna (*Thunnus thynnus*). These include fine-scale foraging, searching, and travel patterns of individuals, school organization, association with environmental features in the Gulf of Maine, and large-scale movements in the North Atlantic. Our analyses utilize a Lagrangian (individual-based), spatially-explicit model of the region's bluefin tuna schooling population, and spatial analyses correlating bluefin distribution and environmental variables using simple and partial Mantel tests. This approach also provides a means of utilizing observational data to simulate time-series of regional abundance.

OS41J-02 0845h INVITED

Movements of blue whales in the eastern north pacific

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The estimated 2,134 blue whales feeding in summer off California constitute the largest remnant population of this species in the world and perhaps 25 percent of the worldwide population, yet little is known of individual foraging ranges or the stocks seasonal distribution throughout the rest of the year. Since 1993, Oregon State University has tagged 100 blue whales off central/southern California with Argos (satellite-monitored) radio tags to examine summer feeding, fall