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The non-linear responses of marine optical signals have made coastal ocean areas of Case 2-type waters a challenging environment for remote sensing. Hyperspectral remote sensing with its continuous, high-resolution spectral information has long promised to help in unraveling some of the difficulties by bringing to bear the mathematical tools of imaging spectroscopy onto the non-linear problem. However, these tools require a high confidence in the absolute radiometric calibration of the hyperspectral sensor. During the 2001 Hyperspectral Coastal Ocean Dynamics Experiment (HyCODE) at the Long-term Ecological Observatory-15 m (LEO-15) site off the coast of New Jersey, we collected multiple days of high altitude imagery in support of the ONR objectives to develop in-situ optical hyperspectral algorithms and nowcast-forecast techniques. An explanation of the calibration techniques and data produced by the Portable Hyperspectral Imager for Low Light Spectroscopy II (PHILLS II) will be presented, as well as comparisons between the hyperspectral imagery and in-situ data.

OS21A-14 0830h POSTER

Application of Remote Sensing Multitemporal/Multisensor Data Analysis and GIS Database for Coastline Change Monitoring and Nearshore Morphology Detection in Rio Grande do Norte State, Northeast Brazil

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The objective of this study was to define an operational methodology using remote sensing and geographic information system techniques for monitoring and predicting shoreline change and nearshore composition/structure identification in northeast Brazilian EW-oriented coastline. This area is inserted on the PETROBRAS oil exploration research. The multitemporal approach used remote sensing technology either on a large scale with the most aerial photos and medium scale with SPOT-HRV/HRVIR and Landsat TM/ETM+ satellite data integrated through a GIS database with ancillary maps (eg. topography, bathymetry, geology), physical parameters (eg. currents and wind velocity/direction, tidal observation, beach profile) and sediment analysis (eg. in situ van-veen collected samples).

The temporal images comparison method (visual/digital) was applied for qualitative and semi-quantitative (images spatial resolution dependent) data analysis of sediment budget to this coastal system. The results showed that most accretion areas are due to sediment capture on E-W oriented sand spits while erosion areas are linked to large scale bottom morphology. The changes are mainly due to longshore drift contributions and negative sediment budget.

Knowing that detecting features on remotely sensed imagery is dependent upon the type of targets on surface, size, association and tone distribution, many digital image processing procedures were tested to provide enhanced images to a properly interpretation. Using RGB and IHS color composites allowed to distinguish between carbonate, terrigenous and mixed sands deposits in nearshore until around 25 meters depth. Seawater in this coastal region was very clear at the time of

satellite scanning path. Highly turbid water was concentrated in a zone a few hundred meters large beside beach line through which huge quantities of sand and clay are transported to the west by currents parallel the shoreline. The sediment character distribution were confirmed by analysis of vanveen collected samples. High-pass filtering applied to single visible or infrared bands highlighted some important offshore morphologic features that can represent successive beachrocks lines, sandbars strongly oriented probably sustained by structurally controlled blocks edges, as well as sand waves highly dependent upon the deep currents. Regional lineaments maps of coastal zone obtained by directional filtered images combined with actual land forms features and drainage system showed a indisputable evidence of continuity offshore of these morphostructural lineaments.

The study confirmed that remote sensing and GIS integration techniques are essential tools for shoreline morphodynamic controls, nearshore composition detection, offshore features identification, monitoring and predicting onshore-offshore sediment budget balance on cyclic movement.

OS21B HC: Hall III Tuesday 0830h

Novel Techniques for Chemical Characterization in Marine Systems II

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

OS21B-15 0830h POSTER

Mass spectrometric characterization of 13C-tracers: applications for biogeochemical study

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Stable isotope tracers have been widely used to study biogeochemical cycles of carbon and nutrients. A new mass spectrometric approach was developed in my lab to characterize 13C-lipids in tracer microcosm experiments. The principal of this approach was based on the quantitative shifts in m/z of 13C-lipids characteristic fragments. The shifts vary with carbon number and labeling content in these fragments. In biogeochemical tracer experiments, the 13C-labeled (uniformly or specifically) lipids can be readily distinguished from natural counterparts by calibrating with a series of mixtures of 13C-labeled and unlabeled standards. New 13C-labeled lipid compounds produced from organic matter degradation can be monitored by examining 13C fragments in their mass spectra. An advantage of this approach is the capability of examining intramolecular relationship between organic substrates and metabolism products by analyzing details of mass spectra. For example, analysis for labeling content of newly produced compounds (partially- or uniformly-labeled) indicated two different metabolism pathways: resynthesis and inter-transform from substrates. This approach has been successfully applied to study (1) effects of redox conditions on organic matter degradation, (2) role of benthic macrofauna in sediment diagenesis of algal material, and (3) influences of biological and physical mixing processes on organic carbon cycling.

OS21B-16 0830h POSTER

Nanomolar Detection for Phosphate and Nitrate Using Liquid Waveguide Technology.

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The ability to detect ambient concentrations of nitrate and phosphate is of vital importance in understanding the cycling of these nutrients, particularly in the oligotrophic regions of the world's oceans. Various methods and novel technologies have been employed over recent years to address the problems of analysing these nutrients at the ambient nanomolar concentrations found in oligotrophic oceanic regions. With advances in long path-length Liquid Waveguide Capillary Cells there is the ability to use these in conjunction with sensitive segmented flow colorimetric analysis systems to produce analytical methods for the nanomolar detection of nitrate, nitrite and phosphate. Preliminary data are presented here for phosphate concentrations from samples analysed during a cruise to the nutrient depleted Eastern Mediterranean Cyprus Gyre region, with a detection limit for phosphate of less than 2 nanomoles per litre. Also reported are nitrate results

from the surface waters of the oligotrophic Northern Indian Ocean with a detection limit of 1 nanomole per litre.

OS21B-17 0830h POSTER

Iron Isotopic Composition of Marine Samples

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Iron is an essential micronutrient in the ocean and a limiting nutrient in high nitrate, low chlorophyll (HNLC) regions of the ocean. Although the importance of iron in the ocean has been recognized in the past decade, it is difficult to study because of its complex chemistry and behavior, and the difficulty in obtaining measurements without contamination. Fractionation of iron isotopes could be an effective tool to investigate and quantify the marine geochemistry of iron. Initial studies of iron isotopes show measurable fractionation in both abiotic and biological processes (Bullen and McMahon, 1997; Beard and Johnson, 1999; Zhu et al., 2000; Anbar et al., 2000; Belshaw et al., 2000). For example, a 1.4 permil (56/54 Fe) variation in iron isotopes of seawater over the past 7 Ma has been inferred from a paleorecord of iron isotopes reconstructed from a Fe-Mn nodule (Zhu et al., 2000). This study will address questions about the iron cycle using direct measurements of stable Fe isotopes in marine samples. Trace metal clean plankton tows were collected in the tropical eastern Atlantic (10°N, 45.5°W), filtered, and then measured for their iron isotopic composition. Measurements were made using a Micromass IsoProbe Multi-collector ICPMS. This system uses a hexapole collision cell to reduce molecular interferences and improve transmission. Initial results using a microflow PFA nebulizer, argon and hydrogen collision gases, and standard-sample bracketing give an external precision better than 0.2 (2σ) permil in the 56/54 Fe. Iron was mobilized from plankton tow samples by two different digestion methods: nitric acid/hydrogen peroxide digestion and muffle furnace combustion. Then the iron was purified by anion exchange chromatography. Replicates of one plankton tow sample have an iron isotopic value that is 0.42±0.2 (2σ) permil depleted relative to measured igneous rock samples (56/54 Fe ratio). This measurement demonstrates that iron in the upper ocean is fractionated from continental rock sources. It is possible that this iron isotope fractionation is due to marine organisms, although other possibilities must first be ruled out (e.g. fractionation during release from dust). If the iron fractionation is biological, iron export from the euphotic zone should lead to progressive light isotope depletion, similar to the carbon and nitrogen isotope systems. Iron stable isotope measurements may thus yield information about the degree of iron utilization in the upper ocean.

OS21B-18 0830h POSTER

The Use of Staining Techniques and Flow Cytometry to Identify and Isolate POM Subclasses for Organic Mass Spectrometric Analyses

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Flow cytometric sorting is a useful technique for identifying and isolating sub-populations of particles within natural particulate organic matter (POM) samples. It has recently been used to isolate phytoplankton and non-phytoplankton "detrital" particles on the basis of chlorophyll autofluorescence and forward light scatter. Because autofluorescence was used to distinguish "phytoplankton" from "detritus" no preservation or staining techniques were necessary. Therefore, by applying direct temperature-resolved mass spectrometry (DT-MS) to the sorted subclasses, a comparison of the chemical characteristics of "phytoplankton" and "detritus" was made(1,2). While this is a useful initial approach for demonstrating the morphological and chemical heterogeneity of water-column POM, it suffers from distinct limitations. Non-fluorescent cells, such as heterotrophic bacteria and zooplankton (that have not just eaten a phytoplankton cell) are included within the "detrital" pool of POM. In this study we attempt to include these cells within our POM subclasses.

In order to identify bacterial and eukaryotic cells within natural aquatic particle samples, various nucleic acid stains (SYTO 16, DAPI, SYTOX, etc.) are being tested. In addition to optimizing staining times and concentrations, we are examining the effects of the staining procedures on the molecular-level characteristics of the particles. Although the relative sensitivities of the stains to various cell and virus types need

to be further constrained, initial results look promising. Pyrolysis-gas chromatography-mass spectrometry shows that the membrane permeable nucleic acid stain SYTO 16 does not alter the molecular-level characteristics of POM. Therefore it appears possible to use staining and flow cytometry to identify the cells, flow cytometric sorting to isolate them from the rest of the natural aquatic particles, and DT-MS to determine the chemical characteristics of the cell vs. non-cell particle populations.

(1) Minor, E.C., T.I. Eglinton, R. Olson, J.J. Boon (1998). *Organic Geochemistry* 29(5-7): 1561-1582.

(2) Minor, E.C., T.I. Eglinton, J.J. Boon, and R. Olson (1999). *Analytical Chemistry* 71(10): 2003-2013.

OS21B-19 0830h POSTER

A New Rapid Chemical Method for Analyzing Si, Ca, Al, and Other Elements in Marine/Freshwater Particles and Sediments.

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A new chemical method has been developed to determine Si, Ca, Al, and other elements (Fe, Mg, Sr, Mn, Ba, P, V, Ni, Cu, Ti, S) in particles and sediments from marine and freshwater environments. The procedure has been tested on sediment trap materials, sediments and suspended particles that have been collected on polycarbonate and polyethersulphone filters with the use of in-situ filtering equipment. The procedure uses Teflon pressure vessels and microwave oven heating to dissolve the samples in a HNO₃/HF solution. Variable acid and pressure conditions are explored to insure complete sample dissolution and to prevent Ca precipitation and Si volatilization in the presents of HF. The procedure achieves complete dissolution of a 10mg sample in 15 minutes. The solutions are prepared for the ICP-MS with the addition of In as an internal standard and for the ICP-ES with the addition of scandium Sc as the internal standard. A Teflon/sapphire nebulizing unit is used to quantify Si in the presents of HF. The respective precision (cv) and accuracy as recovery rates (percent) of the following elements in reference solutions are presented: (Si, 4.61, 103.1), (Ca, 3.63, 99.8), (Al, 6.39, 101.5), (Ba, 1.64, 95.7), (Fe, 7.37, 104.2), (Mg, 8.40, 100.1), (Sr, 5.74, 99.8).

OS21B-20 0830h POSTER

A Sensitive Determination of Iodide Species in Fresh or Saline Matrices Using High Performance Liquid Chromatography and UV/Visible Detection

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Iodide is determined directly using a new method combining anion exchange chromatography and ultraviolet visibility detection. Iodate and the total of organic iodine species are determined as iodide with minimal sample preparation.

The method has been successfully applied to measure the concentrations of iodide species in rains, fresh surface waters and ground waters, estuarine waters of different salinities, and seawaters. The detection limit is 0.4 ppb with less than 5% relative standard deviation. Analytical accuracy was tested against certified reference material SRM 1549, powdered milk (NIST) and through the method of standard additions. The organic decomposition technique yielded recoveries of greater than 90% for known solution concentrations of L-thyroxine, SRM 1549 milk, and iodinated humic and fulvic materials.

OS21B-21 0830h POSTER

Application of X-ray photoelectron spectroscopy (XPS) and density fractionation to study organic-mineral interactions in marine sediments

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Interactions between organic matter and minerals are important for the preservation of organic materials in marine sediments. Recent evidence suggests that these interactions may not be due to protection of the organic matter via simple sorption to minerals, but rather that the organic matter is acting as a glue between mineral particles resulting in aggregate formation. Density fractionation into multiple density intervals is a powerful approach for investigating the patchy nature of organic matter distribution because isolates with varying organic matter loadings can be obtained. The aggregate surfaces can be examined using X-ray photoelectron spectroscopy (XPS), since this technique is restricted to the top 10 nm of the sample surface. XPS gives quantitative information on all the elements on the surface, except H and He, and in addition, gives some information on the chemical bonding of carbon and nitrogen. We used these techniques, along with more standard geochemical tools, to study sediment samples along two transects: one off the coast of Washington, and one off the western coast of Mexico. These transects span a wide range of oxygen exposure times (OET), from a few days in the oxygen deficient zone off Mexico, to a thousand years in the deepest sites off Washington. We will present our results and describe how XPS can be used to study changes in oxidation state of the organic matter along the transects and how that relates to OET. Furthermore, the potential of XPS to give information on the location of the OM on the mineral surfaces will be discussed.

OS21B-22 0830h POSTER

A high temperature combustion instrument comparison for measurement of dissolved organic nitrogen in seawater

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In a recent comparison of total dissolved nitrogen (TDN) in seawater, relatively good agreement was found among 30 analyses using a variety of UV oxidation, persulfate oxidation and high temperature combustion (HTC) methods; but the resultant dissolved organic nitrogen (DON) agreement was not good enough. Since the tightest agreement and best prospects for easy future analyses lay with HTC, further evaluation of these methods was pursued. We assembled instruments in one location to investigate similarities and differences in combustion systems, plumbing, and nitrogen detection. Upon establishing comparability in recovery of inorganic and organic nitrogen compounds and deciding upon modifications of individual instruments, authors returned their home laboratories. A series of samples from estuarine to deep ocean were collected that varied in TDN from about 5 to 80 µM N, with 20 to 95 percent of the TDN representing DON. This comparison used 4 stand-alone instruments (manufactured by Antek, Dohrmann, Shimadzu, Skalar) and 4 hybrid setups with combustion through Shimadzu TOC analyzers linked to Antek, Seivers, Skalar, and Yanaco NO analyzers. Results will be presented of TDN, DON, and DOC from this comparison.

OS21B-23 0830h POSTER

Development of Compact UV Laser Induced Fluorescence Instrument and Preliminary Measurements of Organics in the Gulf of Mexico

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We have developed a high-PRF, 266 nm laser based Laser Induced Fluorescence (LIF) instrument that is 1000 times more sensitive than existing in situ fluorescence sensors (SAFire) for the detection of colored dissolved organic matter (CDOM) in ocean water. The increased sensitivity is due to the use of a pulsed UV laser instead of a continuous spectral lamp for excitation, and the ability to use high-PRF boxcar integrators and sensitive optical photomultiplier tubes to detect and average the weak CDOM fluorescence signal. Our portable LIF system consisted of a (4x) Nd:YAG microchip laser source (5 mW, 8 kHz) operating at 266 nm, 13 optical filter channels ranging from 239 nm to 685 nm in combination with absorption filters with cut-off at 280 nm and 295 nm, and a PMT detector and a boxcar integrator averager system. A laptop computer was used for data acquisition (via GPIB interface) and controlling the filter wheels. A software program was written in Labview to acquire, store and monitor the optical channels in real-time. The emission channels were switched every few seconds, resulting in a complete scan in about one minute.

The LIF system has recently been tested aboard a cruise in the Gulf of Mexico. The instrument sensitivity was tested in a variety of water masses using the ships underway water supply. The fluorescence signal from CDOM near 450 nm originating from clean seawater 100 miles off-shore in the Gulf of Mexico had a signal-to-noise of greater than 120. To compare the detection limits of the system, quinine sulfate was used as the fluorescence standard. The detection limit of the portable LIF system was measured to be 0.001 ppb of quinine sulfate. It was determined that the sensitivity of the portable LIF system was much greater than our previous systems; the detection limit of SAFire (Wet-labs; portable system) was 1 ppb and FluoroMax (JY SPEX; Lab system) was 0.05 ppb of quinine sulfate.

OS21B-24 0830h POSTER

Preparation of Reference Material for Nutrients in Seawater (RMNS) on the Seawater Base

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Kansai Environmental Engineering Center Co., Ltd. has carried out the oceanographic survey in the western North Pacific Ocean since 1990. We are carrying out the long-term monitoring observation with high quality at research cruises in the open ocean. Nutrient measurements are one of the most important components of the long-term monitoring in ocean. For example, for the nitrate measurement during the WOCE, the required accuracy was better than 1 percent, and the repeatability (precision) was 0.2 percent. In order to improve the quality of nutrient measurements, it is necessary to make reference materials with high quality. Reference materials for nutrients in seawater (RMNS) on the seawater base were developed by using autoclave. The seawater had been sampled in the North Pacific Ocean and was filtered through a 0.45 micrometer membrane filter. The seawater in a stainless steel container of 40 liters was autoclaved in a huge autoclave (W,145cm H,155cm D,290cm) at 120deg., 2 hours, 2 times. Polypropylene bottles of 100 ml capacity and the polypropylene caps were also autoclaved before filling the seawater. The autoclaved seawater of 90 ml was filled in polypropylene bottles, and Ppolypropylene bottle was sealed in a clean bench in a clean room. Since the stainless steel container entered into the huge autoclave from the normal environment side and taken out to the clean environment side after the sterilization, the degree of cleanliness of the autoclaved seawater was ensured. The homogeneity of our RMNS is as follows and the standard deviations of the analytical results were same as the repeatability of the measurements of the same sample. Example of analysis of RMNS (microM at 20deg.)

Bottle No	NO3	NO2	SiO2	PO4
No 1	17.47	0.95	153.8	1.43
No 2	17.56	0.96	154.0	1.42
No 3	17.49	0.95	153.8	1.42
No 4	17.56	0.93	153.9	1.41
No 5	17.55	0.93	154.7	1.43
Ave.	17.53	0.95	154.0	1.42
S.D.	0.04	0.01	0.38	0.01

We are able to prepare 300 bottles per a lot by this method nowadays. However, it is not sufficient in one lot 300 bottles in order to distribute worldwide. Although the number of 300 bottles are not enough to

deliver our RMNS worldwide, we could make a pier to start new ages when nutrients analysis is easily carried out with better traceability and high quality. We are going to start a cooperative measurement in some laboratories on land and multiple research cruises using our RMNS.

OS21B-25 0830h POSTER

Reference Material for Nutrients in Seawater: Results of Long-term Storage Experiments and how to and who Certify it?

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We have been carried out the long-term storage experiments of the reference material for nutrients in seawater (RMNS) for up to 4 years. The importance of reference material for nutrients in seawater is now well recognized. The needs of RMNS are increasing in international hydrographic program to have better traceability as well as a basis for quality control and quality assurance in the measurements of nutrients in seawater. Our approach to preparing RMNS using autoclaving was developed and tested by previous researchers. We believe that to supply our RMNS to the oceanographic community worldwide, the RMNS should be stable more than 2-3 years because of the reasons as follows. 1) The several months leading time before shipping is needed to test the homogeneity of the RMNS. 2) To establish the traceability between batches of RMNS, it will also take some months. 3) During the several years period of international program, it is better to use less number of batches. 4) Although, we can not certify the RMNS yet at the present time, it will take several months to put the concentrations of the RMNS and issue the certificate of the RMNS. The details on the preparation of our RMNS will be presented separately by one of the co-authors of this study in this meeting. The samples for long-term storage experiment are prepared in November 1996 and the latest measurement was done in Feb. 2001. Two independent measurements were done just after preparation to put the initial values for nitrate, nitrite, phosphate and silicate. Kansai Environmental Engineering Center (KANSO) put 23.07 +/- 0.13 umol/l for nitrate, 1.27 +/- 0.01 umol/l for nitrite, 0.42 +/- 0.07 umol/l for phosphate and 57.09 +/- 0.34 umol/l for silicate respectively. Japan meteorological Agency (JMA) put 23.41 +/- 0.04 umol/l for nitrate, 1.28 +/- 0.01 umol/l for nitrite, 0.41 +/- 0.03 umol/l for phosphate and 57.57 +/- 0.99 umol/l for silicate, respectively. Two independent measurements were in good agreement, then we could confirm the homogeneity of our RMNS and good traceability between two laboratories. The results of our long-term experiments showed that homogeneity and stability are maintained for about 4 years. JMA put 22.86 +/- 0.14 umol/l for nitrate, 1.30 +/- 0.01 umol/l for nitrite and 0.39 +/- 0.03 umol/l for phosphate in July 2000, respectively. KANSO put 23.33 +/- 0.42 umol/l for nitrate, 1.27 +/- 0.01 umol/l for nitrite, 0.39 +/- 0.03 umol/l for phosphate and 56.92 +/- 0.73 umol/l for silicate in Feb. 2001, respectively. Our results, then, had demonstrated that the RMNS can be obtained using autoclaving and can be stored for about up to 4 years. We are going to conduct a field application experiment using JMA's 5 research vessels throughout one year to verify the RMNS and clarify the potential problems in the real cruises. To certify the RMNS, the only way now is to conduct laboratory comparison experiments by some laboratories which have higher skill in nutrients measurements and have been keeping the better within lab. traceability for long time.

OS21B-26 0830h POSTER

Determination of the Organic Complexation of Mercury in Galveston Bay Estuarine Water Using Competitive Ligand Equilibration Techniques

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It is well recognized that Hg interacts strongly with organic matter in aquatic systems and that this interaction is important in its aqueous biogeochemical cycling. While Hg-organic ligand interactions have been widely predicted from our knowledge of the environmental chemistry of Hg, very little is known about the nature and strength of the interactions from a thermodynamic perspective. Competitive ligand equilibration (CLE) approaches have been used to estimate the complexation of several metals with natural organic ligands in seawater, but to date, this approach has not been reported for Hg. Here, we report initial results to determine the complexation of Hg by natural organic ligands in estuarine water using CLE approaches. The CLE approach for determining Hg speciation in natural waters is complicated by the fact that Hg-natural organic ligand complex(es) readily extract (> 75%) into non-polar solvents. To apply the CLE approach, a competitive ligand must compete with the natural organic ligand(s) such that a portion of the naturally extractable Hg remains in aqueous solution rather than be extracted into the non-polar solvent. This approach is opposite that of most CLE approaches, where the competitive metal-ligand complex extracts into the solvent and the natural metal-ligand complex remains in aqueous solution. A ligand which appears to meet these criteria is 1, 2-dimercaptopropanol (BAL). We are currently developing a solvent extraction procedure using BAL as the added ligand and extraction with CCl₄ to isolate the natural organic complexes of Hg from the Hg bound to the competitive ligand. Mercury measurements are conducted using cold vapor atomic fluorescence spectrometry. Mercury natural organic ligand complexation capacity and natural ligand concentrations are determined using linearization techniques applied to Hg titrations of the natural water sample combined with equilibrium modeling of the inorganic solution speciation of Hg. Ultra-filtration of natural water samples is being used to investigate the role of Hg-colloid interactions in interfering with the CLE and solvent extraction process. Initial results suggest that a major portion of the Hg present in Galveston Bay estuary is complexed by a very small concentration of natural ligand with a conditional stability constant > 10²⁵.

OS21B-27 0830h POSTER

The offset table of IAPSO Standard Seawater and its application to the observational results.

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The comparison of batches of IAPSO standard seawater (SSW) is important to high quality hydrographic studies. There are a lot of works for batch-to-batch differences of SSW and the results have been summarized up to P129 as a so-called 'offset table'. In this study, we examined some of recent batches of SSW and propose the updated offset table up to P140. We apply this table to the observational data such as WOCE expedition data to show how the corrections lead to much better data not only at the regional scale of the Philippine Sea but also the basin scale of the Pacific Ocean and Atlantic Ocean. We also apply the table to the most recent result of observations made at the North Pacific (P17 revisit) as a part of Sub-Arctic Gyre Experiment granted by Ministry of Education, Culture, Sports, Science and Technology of Japan. To apply the offset table retrospectively means to accept tacitly the hypothesis that the batch to batch difference of SSW was not caused only by the aging effect but also, to a considerable extent, the reflection of the initial offset. We conducted the comparison of the PSS78 standard KCl solutions made from the different high quality chemicals and found the batch and/or company dependency. This may be one of the possible cause of initial offset of SSW.

OS21B-28 0830h POSTER

Two Analytical Intercomparison Exercises for Iron in Seawater

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Over the past decade, there has been a rapid development of analytical methods for measuring iron at picomolar levels in seawater. The lack of rigorous inter-comparison exercises and appropriate reference materials means oceanographers have little ability to distinguish between environmental variability and analytical data quality. There is thus an urgent need for standardisation in order to ensure the highest possible integrity, reliability and comparability of reported data. Clearly, with so many sampling and analytical variants in current use, it is difficult to attribute concentration differences to one particular step in the overall process without first determining differences between analytical methods.

This paper presents the results of two analytical intercomparison exercises conducted to determine whether methods were analytically indistinguishable and to attempt to explain any systematic bias in Fe concentrations by examining their operational nature. The first exercise was held at sea during a north-south transect of the Atlantic Ocean (October 2000). To minimise differences from possible sampling contamination, one standard underway (1-2 m) protocol was used. Over 200 samples (1 per h) were collected for dissolved Fe (DFe, <0.2 μm) over 12 d and analysed immediately. Four different analytical methods were used, based upon three variants of flow injection with luminol chemiluminescence (FI-CL) and cathodic stripping voltammetry (CSV). During the second exercise, which was lab-based, samples from 6 depths at 3 stations in the Southern Ocean were analysed for DFe (<0.4 μm) and total dissolvable iron (unfiltered, TDFe), using FI-CL and FI-spectrophotometry (FI-SP).

During the shipboard intercomparison (DFe range 0.02-1.61 nM), there was some scatter between surface profiles and consistent methodological differences were not always obvious. In general, CSV measured 0.08 nM more than one FI-CL method, which measured 0.13 nM more than the other two. Statistical analyses (paired two-tailed t-test) show that each analytical method gave significantly different DFe concentrations at the 95% confidence interval. Results from the lab-based exercise were more encouraging (Fe range 0.12-0.93 nM). Good agreement was noted for DFe profiles for the stations near the Sub-Antarctic Front and in the Polar Frontal Zone, although there was discrepancy for a station in the Sub-Antarctic Zone. Here, FI-CL recorded 0.07-0.16 nM DFe more than FI-SP at each depth, with greater differences recorded below the mixed layer. TDFe profiles were less consistent, reflecting the added complexity of analysing partially digested particulate material in the samples. FI-SP gave higher TDFe values (~0.12 nM) than FI-CL.

Reasons for the differences between analytical methods will be discussed. These include the role of organic complexes and colloids, variability in system sensitivities, nature and pH of sample pretreatment, and extraction and preconcentration of Fe from the seawater matrix.

OS21B-29 0830h POSTER

The Release of Thiols from Marine Algae in Response to Copper Stress –the Application of a Solid Phase Extraction and HPLC Determination of Fluorescently Derivatized Thiolic Compounds

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A new method was developed for determination of dissolved thiols in surface using solid-phase extraction to preconcentrate the thiol-monobromobimane (mBB) derivatives, followed by HPLC analysis of the fluorescently tagged compounds. Considerable effort was devoted to optimizing the experimental conditions to maximize derivatization efficiency. The amount of the reducing agent, tri-*n*-butylphosphine (TBP), is critical for the successful total thiol determination. The thiol fluorescence signal could be totally suppressed if the mole ratio between TBP and mBB is greater than one. We suspect that the tendency of mBB, with unsaturated-bonds, to attract the electron-enriched TBP could decrease its affinity to thiols. Experiments,

conducted to determine if the presence of copper affected fluorescence signals of thiols, showed no measurable effect. Good recovery of tagged-thiols spiked in a NaCl (0.5M) solution is obtained by using the Waters HLB reserved phase resin, while blank levels of glutathione, gamma-glutamylcysteine, and phycochelatin-2, are extremely low. For 100 ml samples spiked with 10 nM thiol standards, the average recovery on the 60mg resin cartridge is $42.7 \pm 4.2\%$, $108.2 \pm 5.4\%$, $112.7 \pm 6.5\%$, and $101.5 \pm 7.8\%$ for cysteine (Cys), glutathione (GSH), gamma-glutamylcysteine (γ EC), and phycochelatin-2 (PC-2). Using this method, a preliminary study showed a clear dose-response release of GSH from a marine algae species, *Thalassiosira weissflogii*, under different concentration levels of copper additions (from 0 to 500 nM). When inoculated in natural seawater, the release of GSH appears to be inversely related to the concentrations of natural organic matter, reflecting the net effects of both the natural organic matter and ligands released from algae on the bioavailability of copper.

OS21B-30 0830h POSTER

RATS: A Robotic Analyzer for the TCO₂ System in Sea Water from Moorings

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RATS is an instrument designed to make the measurements needed to determine the speciation of the carbonate system in sea water. Determination of the carbonate system is based on the measurement of TCO₂ and pH. It is designed to operate completely independently and to be deployed for prolonged periods, duration being determined by the current limit of ~1000 sample analyses. RATS can operate at full ocean depth, but testing of components has presently been limited to the pressure equivalent of 900 m. TCO₂ is determined by allowing the CO₂ from an acidified sea water sample to pass through a semi-permeable membrane and react with NaOH. Reaction decreases the NaOH conductivity in proportion to the amount of CO₂ in the sample. pH is measured spectrophotometrically after the methods pioneered by Bob Byrne and co-workers. Provision is made for *in situ* standardization of both TCO₂ and pH at any desired frequency.

Presently the instrument is operating in the lab in its integrated form. TCO₂ analyses carried out over a period of ~60 days vary about the mean by slightly less than 0.3%. For shorter time intervals (1-2 days) variation is ~0.2%. The standard deviation of pH measurements carried out over a 70+ day period is <.002 pH units. RATS is scheduled for its first ocean tests in Jan-Feb 2002.

OS21C HC: Hall III Tuesday 0830h

Satellite-Measured Ocean Color Variability in the Ocean III

Presiding: A Thomas, University of Maine; C McClain, NASA GSFC

OS21C-31 0830h POSTER

Seasonal and Interannual Phytoplankton Variability in the Gulf of Maine

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Four years (1997-2001) of ocean color data from the SeaWiFS mission provide the first synoptic quantification of phytoplankton variability on seasonal and inter-annual time scales for the Gulf of Maine. The climatological seasonal cycle shows elevated concentrations (>2.0 mg m⁻³) throughout the year within 30km of the shore and a strong modulation of the amplitude of seasonal cycles over shallow bathymetry in other regions. Deeper basins exhibit a canonical Sverdrup seasonal cycle with a strong spring bloom (> 2.0 mg m⁻³) in March-April, a fall bloom in October-November and concentrations of ~1.0 in summer and ~0.5 in winter (December-February). Strong tidal mixing over shallow bathymetry supports elevated concentrations (>

2.0 mg m⁻³) throughout the year on Georges Bank and sustained elevated concentrations throughout the summer over Browns Bank. EOF decomposition of the 4 year time series of monthly composites quantifies the strong dominance of the seasonal cycle (93% of the variance) and shows it to be anomalously weak in late 1997 and throughout 1998. The second mode (2.6%) shows a broad seasonal maximum in late summer (Sept-Oct) strongest in coastal regions and over shallow banks, clearly out of phase with three regions of known strong advection/mixing (the Eastern Maine Coastal Current, the southern Scotia Shelf and Nantucket Shoals). Inter-annual differences in the timing of the spring and fall blooms over much of the domain are consistent with differences in the strength and timing of wind mixing. A 3d coupled biological-physical model captures the dominant seasonal variability and spatial pattern over the interior Gulf.

OS21C-32 0830h POSTER

Quantitative, space-based measurements of ocean suspended calcium carbonate with MODIS and SeaWiFS

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Suspended calcium carbonate (particulate inorganic carbon; PIC) plays a major role in ocean biogeochemistry and little is known about its oceanic distribution. Recently, algorithms have been implemented with MODIS and SEAWIFS for detection of surface PIC concentrations. In this paper, we describe the accuracy of the satellite PIC algorithm, based on simultaneous satellite and ship measurements. We also show the first monthly global composites of oceanic PIC, integrated over the euphotic zone (based on satellite estimates of K_{par}). Results show relatively high PIC concentrations in specific portions of the North Atlantic and Black Sea, plus in the Antarctic convergence during austral fall. Values of integrated global euphotic PIC concentrations will be presented.

OS21C-33 0830h POSTER

A multi-year record of bio-optical properties in the Gulf of Maine

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Bio-optical data have been compiled from the Gulf of Maine as part of a ship of opportunity program between 1998 and 2001. Data from surface waters were taken aboard the M/S Scotia Prince passenger ferry that crossed between Yarmouth, Nova Scotia, and Portland, Maine, from May through October of each year. Flexibility in sailing days allowed us unprecedented abilities to sample during clear-sky conditions, when ocean color satellite viewing was optimal. This presentation represents a synthesis of the first three years of measurements, over 3600 sea-truth satellite observations within ±6h of a satellite overpass. One clear result is the connection between hydrography and optics; there was a prevalence of Case II surface water throughout the entire transect for most of the cruises, which was well correlated to salinity. Even far offshore, using standard criteria for defining particulate and dissolved Case II conditions, most of the samples were strongly Case II in character. Also of interest was the significant scattering of the colored dissolved organic matter, which was inversely correlated to salinity in the Eastern Maine Coastal Current. We will present a statistical analysis of volume scattering function shapes

relative to coastal volume scattering functions of Petzold. Errors in SeaWiFS normalized water-leaving radiance were highly correlated between wavelengths, with some apparent dependence on the atmospheric models used to derive the radiances. The slopes of the size distribution functions of particulate matter also were compared. There were clear changes in phytoplankton community structure and slope of the particle size distribution, associated with water mass variability.

OS21C-34 0830h POSTER

Physical Forcing of Plumes and Blooms in the Santa Barbara Channel: An Integrated Satellite Approach

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Satellite images of sea surface temperature (SST) and ocean color products are used to assess phytoplankton dynamics and the extent of terrestrial discharge in the Santa Barbara Channel (SBC). Over three and a half years (October 1997 - June 2001) of AVHRR, SeaWiFS, *in situ* measurements, and supporting data are analyzed. Match-up analyses between *in situ* and satellite data show reliable SST retrievals from AVHRR while improvement is needed for retrievals of SeaWiFS products in the region. However, spatial/temporal patterns for all SeaWiFS products are qualitatively consistent on both seasonal and episodic time scales. Monthly climatologies of SST, chlorophyll, and water leaving radiance at 555nm show blooms associated with high water turbidity and runoff in winter, whereas in late spring blooms are associated with upwelling and cool SSTs. Analysis of monthly composites demonstrates that local winds and terrestrial discharge are well correlated with spatial patterns of upwelling and runoff. A set of empirically defined plume and bloom indices is developed based upon field data sets. These show that plumes are found episodically in response to discharge events and affect 20 - 60% of the SBC whereas blooms occur more regularly and cover 50 - 95% of the channel. Further evidence illustrating the spatial effects of upwelling, advection, runoff events, and remote forcing (such as the 1997/1998 El Niño) on blooms and water turbidity will be presented.

OS21C-35 0830h POSTER

Seasonal and inter-annual variability of the particulate backscattering coefficient over the global ocean.

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The global distribution and the annual and inter-annual progression of the particulate backscattering coefficient, b_{bp}, is analyzed from the Sea-viewing Wide Field-of-view Sensor and inverse modeling. The retrieved b_{bp} values are compared with *in situ* measurements made in various oceanic areas. The seasonal and inter-annual variability of b_{bp} between the years 1998 and 2001 are provided for each major oceanic basins. Moreover, the patterns of the remotely sensed b_{bp} are compared to those of the chlorophyll concentration, Chl, in order to determine whether b_{bp} provides additional biogeochemical information. Because b_{bp} is not sensitive to the dissolved material, it can be used as an index of the particulate load that mostly consists of particulate organic carbon, POC, in open ocean (biogenic CaCO₃ particles and terrigenous particles may also contribute episodically to b_{bp}). The interpretation of b_{bp} in terms of POC is discussed.