

OS42R-10 1605h

Influence of Boundary Currents on Cross-shelf Transport in the Mid-Atlantic Bight: Radiochemical and Hydrographic Studies

Linda L Rasmussen¹ (508-289-3466; raz@mit.edu);
Glen Gawarkiewicz² (gleng@whoi.edu); Ken O Buesseler¹ (kbuesseler@whoi.edu); Matthew A Charette¹ (mcharette@whoi.edu); M. Susan Lozier³; W. Brechner Owens²

¹Woods Hole Oceanographic Institution, Department of Chemistry and Geochemistry, MS 25, Woods Hole, MA 02543, United States

²Woods Hole Oceanographic Institution, Department of Physical Oceanography, MS 21, Woods Hole, MA 02543, United States

³Duke University, Earth and Ocean Sciences, Durham, NC, United States

From 1999-2001 several cross-shelf sections spanning the continental shelf and slope were sampled in the Mid-Atlantic Bight. The sections contained strong shelfbreak jets with maximum along-front velocities of up to 70 cm/s. In addition, the majority of the sections contained features related to the proximity of Gulf Stream warm-core rings or streamers. Naturally occurring short-lived radium isotopes with coastal sources were used to trace water masses originating in the inner shelf. These tracers, Ra-223 and Ra-224, indicated very little transport across the shelfbreak within the timescales of the isotopes (20-30 days). However, unusually high levels of Ra-224 (half-life 3.7 days) were detected on several occasions beyond the shelfbreak in water with salinities of 35 to over 36 ppt. The high salinity and absence of Ra-223 point to a source other than the adjacent shelf. Water subsequently collected at the west wall of the Gulf Stream on the Cape Hatteras shelf shows a similar isotope ratio and contains extremely high levels of Ra-224. Using published Gulf Stream drifter and larval transport rates, it is apparent that this region could be the source for high offshore Ra-224 levels as far north as Nantucket Shoals. Thus, it is possible that transport by the Gulf Stream, from remote shelf locations, may be a source of geochemical signals on the MAB slope that is of equal or greater importance than local, direct transport across the shelfbreak front.

OS42R-11 1620h

Constraining the Sources and Fluxes of Organic Carbon to Continental Shelf and Slope Waters Using Natural ¹⁴C and ¹³C

James E. Bauer¹ (804-684-7136; bauer@vims.edu)

Ellen R.M. Druffel² (949-824-2116; edruffel@uci.edu)

¹School of Marine Science, VIMS, College of William and Mary, P.O. Box 1346, Gloucester Point, VA 23062-1346, United States

²Department of Earth System Science, University of California, Irvine, CA 92697, United States

Dissolved and particulate organic carbon (DOC and POC, respectively) in ocean margins may have a variety of both old and young marine and terrestrial sources, and the qualitative and quantitative evaluation of these sources is a considerable challenge to marine geochemists. While natural isotopic signatures of DOC and POC lack the specificity of organic biomarkers for source identification, they may offer more integrated estimates of potential sources, provided the isotopic signatures of the various sources can be adequately constrained. Historically, stable isotopes have been used more frequently for assessing coastal organic matter sources, but recently natural ¹⁴C has also been used effectively, and offers certain advantages over stable isotopes as a result of its much greater dynamic range.

We present here an extensive dataset on the natural $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ composition of DOC and POC in continental shelf and slope waters of the western North Atlantic collected over two years. The ranges in both $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ of DOC and POC are among the greatest ever observed for a marine system. The DOC of shelf and shallow slope waters is deduced to be comprised of 3 main end-members: young terrestrial C, young marine C from contemporary primary production, and old oceanic DOC. The DOC in deeper slope waters is comprised of old C (>~4,000 yrs in age) ranging from -23.7 to -21.3‰ in $\delta^{13}\text{C}$. The POC from shelf and surface slope waters is deduced to be comprised of a mixture of modern aged marine and terrestrial C. However, POC from slope waters shows a striking positive correlation between $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$, and indicates that the oldest (to ~5,000 yrs in age) material has the most terrestrial (i.e., ¹³C-depleted, to ~-31‰) character. The DOC and POC of slope waters is universally older and more depleted in ¹³C than open

ocean DOC of the N. Atlantic. We also show results of a dual isotopic multiple source model that constrains the contributions to shelf and slope DOC and POC of old and young marine (including sedimentary) and terrestrial/riverine material to these pools.

OS42R-12 1635h

Inferring Physical Processes Using Phytoplankton Structure and Bulk Optical Properties in Coastal Waters.

Mark A Moline¹ (mmoline@calpoly.edu)

W. Paul Bissett³

Robert Chant²

Scott Glenn²

Oscar M. Schofield²

¹California Polytechnic State University, Biological Sciences Department 1 Grand Ave., San Luis Obispo, CA 93401, United States

²Rutgers University, Institute of Marine and Coastal Sciences 71 Dudley Rd., New Brunswick, NJ 08901, United States

³Florida Environmental Research Institute, 4807 Bayshore Blvd. Suite 101, Tampa, FL 33611, United States

The nearshore waters off the central New Jersey coast are characterized by a two-layered system separated by a strong offshore pycnocline. The onshore expression of this density gradient fluctuates in response to the episodic upwelling and downwelling events, with a spreading of the isopycnals in intermediate conditions. Phytoplankton responses to this physical structure are varied, with the chlorophyll maximum located either on or within the pycnocline layer, suggesting differential mixing. During the summer of 2001, multiple transects of physical, optical and biological data were collected at the Long-term Ecological Observatory (LEO-15) to examine the biological response to pycnocline dynamics. While biological material is distributed cross-shore along the pycnocline, generally increasing inshore (>15µg/L), it is not known whether the origin of the material offshore is the same as that along the coast. A time series of satellite ocean color data suggests that the origin of biological material along the pycnocline may be dependent on the episodic events. Bulk optical properties along with discrete measurements of phytoplankton taxonomic structure will be used as tracers to examine and differentiate the physical processes in the study area.

OS42S HC: 319 A Thursday 1330h

Chemical Oceanography: Metals

Presiding: J Resing, Pacific AMRine

Environmental Lab; R T Powell,

Louisiana Universities Marine

Consortium

OS42S-01 1330h

Distribution of Dissolved Aluminium in Surface Coastal Waters of the Northeast Pacific

Claire Merrin¹ (clairemerrin@hotmail.com)

Kristin Orians¹ (orians@eos.ubc.ca)

¹University of British Columbia, Departments of Chemistry and Earth & Ocean Sciences, Oceanography, Vancouver, BC V6T 1Z4, Canada

Dissolved Al concentrations were determined across a series of horizontal surface transects along the Northeast Pacific, off the coast of Big Sur, California to Vancouver Island, British Columbia. This region of coastline allows the relative importance of different modes of input of Al to be assessed. The work reported here forms part of larger study of the California Current system carried out in June/July 1997. Dissolved Mn and Ga distributions from the study were compared with the Al data.

Average concentrations of Al ranged from 0.4-0.7nM. These values are consistent with observations of Al, ranging from 0.3-1nmol/kg in California Current waters off Santa Cruz. Higher concentrations of Al (1.1nM) were observed in the lowest salinity waters (21) sampled at WCST09. These waters initially form a shallow lens overlying the California Current and are then transported and mixed both vertically and horizontally. The lens extends offshore, moves south and west and retains its low salinity, high silicate signal as far south as WCST07, more than 200km south of the head of the river. In contrast to both Ga and Mn

which remain elevated above background as far south as WCST07; Al signals decrease rapidly to background values beyond WCST09. Trace metal versus salinity plots indicate the rate of removal for Mn and Ga to be considerably slower than that observed for Al. This agrees well with previous estimates of surface ocean residence times for these elements.

Summer upwelling off the coasts of Oregon, Washington and California did not appear to provide dissolved Al to overlying surface waters. This is in direct contrast to dissolved Mn and Ga, which both show elevation in upwelled waters, and we suggest that the lack of an elevated signal for Al reflects its rapid removal from the water column.

OS42S-02 1345h

The Distribution of Particulate, Colloidal and Dissolved Mercury and Monomethyl Mercury in the San Francisco Bay Estuary

Key-Young Choe¹ (409-740-4768; kchoe@tamug.tamu.edu)

Gary A Gill¹ (gillg@tamug.tamu.edu)

Ron Lehman¹ (lehmanr@tamug.tamu.edu)

Seunghee Han¹ (shan@tamug.tamu.edu)

¹Texas A&M University Department of Oceanography, 5007 Avenue U, Galveston, TX 77551, United States

Surface water samples were collected from the San Francisco Bay estuary in September October 2000 and March 2001, and total mercury (THg) and monomethyl mercury (MeHg) concentrations were measured in unfiltered, filtered (< 0.45 µm), colloidal (1 kDa - 0.45 µm), and dissolved (< 1 kDa) fractions. The particulate (> 0.45 µm) THg concentration ranged between 5.3 and 163 pM. Suspended particulate matter (SPM) and particulate organic carbon (POC) played important roles in the particulate THg distribution in the northern reach and South Bay, respectively. The filter-passing THg constituted only 12 ± 7 % (n = 29) of the unfiltered THg concentration. Colloidal THg accounted for 38 ± 18 % (n = 9) of the filter-passing THg in fall and 57 ± 10 % (n = 12) in spring. Distribution coefficient assessment revealed that THg had a greater affinity for particulate material in September October, but similar affinity for both colloidal and particulate material in March. A steady-state, non-conservative, estuarine mixing model suggests internal sources of particulate, colloidal and dissolved THg within the estuary in September October, but net sinks of colloidal and dissolved THg in March. The particulate MeHg concentration ranged between 0.09 and 0.40 pM during the low flow condition and between 0.10 and 0.95 pM during the high flow condition. The correlation between particulate MeHg concentrations and SPM or POC was stronger during the spring than in the fall, indicating that interaction between particulate MeHg and SPM varied with season. The filter-passing MeHg consisted of 57 ± 17 % of the unfiltered pool in the fall and 37 ± 12 % in the spring. However, the percent colloidal MeHg in the filter-passing fraction was higher in the spring (56 ± 13 %) than in the fall (32 ± 9 %). Higher partitioning coefficients between colloidal and dissolved MeHg (log Kc = 5.6 ± 0.3) than those between particulate and dissolved MeHg (log Kp = 4.9 ± 0.5) suggest that MeHg is preferentially associated with colloidal material that is mostly composed of organic matter. In general, MeHg concentrations were very well correlated with organic carbon content in filter-passing, colloidal and dissolved fractions, confirming the importance of organic matter in MeHg transport. A non-conservative estuarine mixing model suggests that significant amounts of particulate, colloidal and dissolved MeHg are removed in the estuary in both seasons.

OS42S-03 1400h

Iron Speciation in the Gulf of Mexico

Rodney T. Powell¹ (985-851-2825; rpowell@lumcon.edu)

Amy Wilson-Finelli¹ (afinelli@lumcon.edu)

William M. Landing² (850-644-6037; landing@ocean.fsu.edu)

¹Louisiana Universities Marine Consortium, 8124 Highway 56, Chauvin, LA 70344

²Department of Oceanography, Florida State University, Tallahassee, FL 32306-4320, United States

In an attempt to more fully understand the chemical processes that control Fe concentrations in surface waters, the Surface Water Iron Speciation Study (SWISS) began in 2000. We are attempting to characterize as many aspects of the Fe cycle as possible in an area that has predictable periods of high and low atmospheric deposition. Collaborators are measuring aspects such as aerosol solubility, particulate Fe, total

dissolved Fe, reduced Fe, colloidal Fe, hydrogen peroxide, light attenuation and even thorium. We hope to fully characterize the processes that lead from Fe solubilization to stabilization in the water column and eventually to uptake by phytoplankton. To date, two cruises have occurred during low dust (spring) and high dust (late summer) periods. This talk will focus on the role of organic Fe complexing ligands in controlling the chemistry of Fe during these two contrasting periods. We will present results of aerosol leaches in order to demonstrate the importance of ligands in the initial solubility of Fe as well as their importance in stabilizing Fe in surface waters. We will present data from a variety of oceanographic regimes (oligotrophic, shelf and coastal waters) in attempt to quantify differences in ligand concentrations and stability constants. Size fractionation studies of organic Fe complexing ligands were conducted using cross-flow ultrafiltration in an attempt to understand differences in ligands between the various oceanic regimes.

OS42S-04 1415h

Colloidal Iron and Iron Redox Speciation in the Gulf of Mexico: Results from the SWISS Project

William M. Landing¹ (850-644-6037; landing@ocean.fsu.edu)

Rodney T. Powell² (985-851-2825; rpowell@lumcon.edu)

¹Department of Oceanography, Florida State University, Tallahassee, FL 32306-4320, United States

²Louisiana Universities Marine Consortium, 8124 Highway 56, Chauvin, LA 70344, United States

As part of the NSF-funded Surface Water Iron Speciation Study (SWISS), we studied the effects of atmospheric input of soluble Fe on the concentrations and speciation of Fe in the southern and eastern Gulf of Mexico in April and August 2001. In addition, we conducted photochemical incubation experiments to study Fe photoreduction and re-oxidation. Colloidal Fe and DOC were isolated using a Filtron CFP system (1,000 dalton). Samples for on-board Fe(II) and total dissolved Fe measurements were collected from the RV Pelican using a towed hydrodynamic "batwing" fitted with Teflon tubing to deliver water to the clean lab area in the wet lab. Filtered samples were collected using 0.2 μ m cartridge filters. The flowing stream of seawater was split to allow on-line measurements of Fe(II) and hydrogen peroxide using flow-injection chemiluminescence techniques. A detailed vertical profile of unfiltered and 0.4 μ m filtered samples was collected in the southern Gulf using Teflon-lined 30 L Go-Flo bottles on Kevlar line.

The concentrations of Fe(II) were generally low (<0.5 nM), while the total dissolved Fe ranged as high as 3-5 nM in the surface waters of the eastern Gulf of Mexico. Total dissolved Fe concentrations were generally higher in the late summer, after a prolonged period of Saharan dust transport and deposition.

The samples, including the vertical profile and colloidal Fe and DOC samples, have been returned to the FSU clean lab for analysis. We will discuss the horizontal and vertical distribution of dissolved and colloidal Fe in the Gulf of Mexico and how they are influenced by soluble Fe input from aerosol deposition.

OS42S-05 1430h

The Speciation and Solubility of Aerosol Iron in the Gulf of Mexico: Results from the SWISS Project

Clifton S. Buck¹ (850-644-6753; cbuck@ocean.fsu.edu)

William M. Landing¹ (850-644-6037; landing@ocean.fsu.edu)

Joseph Resing² (206-526-6184; resing@pmel.noaa.gov)

Geoffrey T. LeBon² (306-526-6184; lebon@pmel.noaa.gov)

¹Department of Oceanography, Florida State University, Tallahassee, FL 32306-4320, United States

²Joint Institute for Study of the Atmosphere and Ocean, NOAA/PMEL 7600 Sandpoint Way NE, Seattle, WA 98115, United States

As part of the NSF-funded Surface Water Iron Speciation Study (SWISS), we collected 12-hour integrated (day/night) aerosol samples aboard the RV Pelican (LUMCON) from April 16-27, 2001 and August 11-25, 2001 in the southern and eastern Gulf of Mexico. The goal of the research was to measure the solubility and redox speciation of aerosol Fe in continental US aerosols (Spring) and Saharan dust (late Summer). Four replicate samples were collected using an automatic sector-controlled aerosol sampling system that collected only when the wind was $\pm 75^\circ$ off the bow of the ship and exceeded 0.2 m/sec. Aerosols were collected on 47 mm PCTE and polypropylene filters at a

face velocity of 40-50 cm/sec for roughly 12-hour periods, filtering up to 35 m³ of air onto each filter. The filters were quickly leached with 50-100 mL of freshly-collected 0.4 μ m filtered surface seawater at natural pH (8-8.4). This solution was then immediately measured for Fe(II) and total soluble Fe using a FeLume chemiluminescent system. A replicate PCTE filter was analyzed for total Fe (and other elements) using energy-dispersive X-ray fluorescence at the NOAA/PMEL laboratory. A replicate polypropylene filter was returned to FSU where it was leached with 50 mL of un-acidified ultrapure water to measure the concentrations of soluble cations and anions using flame AAS and ion chromatography.

The concentrations of total aerosol Fe ranged from 5-30 nmol/m³ and correlated strongly with Al. The total soluble Fe ranged from 1-5% (mean 3 \pm 1%) of the total aerosol Fe. On the April 2001 cruise, the soluble Fe(II) ranged from 3-52% (27 \pm 13%) of the total soluble Fe, while in August 2001, the soluble Fe(II) ranged from 50-96% (71 \pm 13%) of the total soluble Fe. Higher chloride levels were strongly correlated with lower soluble Fe(II) concentrations. Using an aerosol dry deposition velocity of 1 cm/sec, the flux of total aerosol Fe ranged from 4-23 (10 \pm 6) μ mol/m²/day. The total soluble Fe flux ranged from 0.11-0.69 (0.29 \pm 0.16) μ mol/m²/day in April 2001 and 0.03-0.16 (0.10 \pm 0.03) μ mol/m²/day in August 2001. The flux of soluble Fe(II) ranged from 0.02-0.20 (0.07 \pm 0.05) μ mol/m²/day in April 2001 and 0.03-0.14 (0.07 \pm 0.02) μ mol/m²/day in August 2001. These dry deposition fluxes of soluble Fe will be compared to upwelling fluxes, and the fate of the soluble aerosol Fe in the surface waters will be discussed.

OS42S-06 1445h

Bulk deposition collected at Ragged Point, Barbados: an estimate of the atmospheric deposition of iron in African dust to the equatorial North Atlantic Ocean

Jerome J Perry¹ (850 644 6753; jperry@mailier.fsu.edu)

William M Landing¹ (850 644 6037; Landing@ocean.fsu.edu)

Joseph M Prospero² (305 361 4159; jprospero@rsmas.miami.edu)

¹Florida State University, Department of Oceanography, Tallahassee, FL 32306-4320, United States

²Rosenstiel School of Marine and Atmospheric Science, University of Miami 4600 Rickenbacker Causeway, Miami, FL 33149, United States

It has long been understood that long-range atmospheric transport of aerosols is important to trace element budgets in the surface waters of the open oceans. For at least the past 20 years there has been an interest to estimate the deposition of North African mineral aerosols (i.e., Al, Fe, Mn, PO₄) along the equatorial North Atlantic Ocean. Previous estimates of deposition have been based on a limited number of rainfall and/or aerosol samples collected either on open ocean vessels (representative of a limited number of rainfall and dust events) or by aerosol collection at remote locations (with deposition calculated from a deposition velocity). We collected bulk deposition samples at a remote island location in order to estimate the total atmospheric deposition (wet + dry) of trace metals to the surface waters of the equatorial North Atlantic Ocean.

A continuous record of bulk deposition samples was collected for roughly 2 years on the AEROCE tower located at Ragged Point, Barbados. There was a strong seasonality observed in the trace metal flux, and we estimate that an average of 14.4 μ mol Fe/m²/day was deposited on the surface waters via atmospheric deposition during the wet season (May to October) and an average of 2.52 μ mol Fe/m²/day during the dry season (November to April). The results of an event rainfall filtration study in Florida showed that 2.5 to 12% of the Fe in mineral aerosols was soluble in rainfall. Preliminary results of a study performed in the Gulf of Mexico showed that 2 to 4% of the Fe in aerosols was immediately solubilized in seawater. Assuming that wet deposition is about equal to dry deposition for North African mineral dust along the equatorial North Atlantic Ocean, the average solubility of bulk deposition would be 5-6 percent. Therefore, atmospheric deposition of dissolved Fe (925 \pm 775 nmol/m²/day) was equal to, or greater than, the amount of dissolved Fe upwelled (216 \pm 134 nmol/m²/day) to the surface waters during the wet season, and the combined dissolved Fe flux (atmospheric + upwelling) yields a residence time of 49 \pm 43 days. Note that the average atmospheric deposition (925 nmol/m²/day) over the course of a day would generate an average dissolved Fe concentration of 0.34 nM each day, using a vertical mixing rate of 5 m/day. Powell and Donat (2001) have reported 0.33 nM excess natural Fe binding ligands in the surface waters of the equatorial North Atlantic Ocean, providing a process to retain a significant fraction of the atmospherically derived dissolved Fe for phytoplankton growth.

The other elements that were measured for this study were Na, Mg, Al, P, Cl, K, Ca, B, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Hg, Pb and the rare earth elements (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu).

OS42S-07 1520h

Using Natural Tracers (Rn-222 and Th-234) to Describe Marine Physical and Chemical Processes in the Gulf of Mexico

Matthew C Allen¹ ((252)-413-6132; mca0623@mail.ecu.edu)

D. Reide Corbett¹ ((252)-328-1367; corbettd@mail.ecu.edu)

¹East Carolina University, Department of Geology, Greenville, NC 27858, United States

During April and August of 2001, a combination of natural tracers were used to examine particle scavenging and removal and surface water mixing rates. Stations were occupied in the Loop Current and the southern and northeastern Gulf of Mexico (GOM) representative of oligotrophic, and coastal water masses respectively. At each station, in situ measurements were made (temperature, salinity, fluorescence) and water samples were collected at varying depths in the water column, focusing on surface waters and the pycnocline. Water samples were analyzed for dissolved and particulate Th-234 activities and Rn-222 activities. These two natural tracers have been used extensively in the past to provide insight into particle residence times and surface water mixing rates. Th-234 (t_{1/2} = 24.1 days) residence times in the water column provide insight as to the efficiency and rate of removal processes. While Rn-222 (t_{1/2} = 3.85 days) residence times provide insight into the time scale of mixing processes in the water column. The deficiency of radon in near surface waters resulting from loss to the atmosphere can be used to define both the rate of vertical mixing and the rate of gas exchange between the ocean and the atmosphere. Estimates of these surface water processes, as well as spatial and temporal relationships between the two cruises will be discussed.

OS42S-08 1535h

Evidence of Enrichment in Dissolved Iron in the Mediterranean Surface Water After High Saharan Dust Inputs during the oligotrophic season

Cecile Guieu¹ (guieu@obs-vlfr.fr)

Stephane Blain² (Stephane.Blain@univ-brest.fr)

Yann Bozec³ (bozec@nioz.nl)

Celine Ridame¹ (ridame@obs-vlfr.fr)

Geraldine Sarthou² (Geraldine.Sarthou@univ-brest.fr)

¹LOV - UMR CNRS 7093, BP 8 Quai de la Darse, Villefranche-sur-Mer 06238, France

²LEMAR - UMR CNRS 6539, Place Nicolas Copernic, Plouzan 29280, France

³NIOZ, Department of Marine Chemistry and Geology, P.O. Box 59, Texel, NLD NL-1790

The input of elements from the atmosphere to the water column is particularly important regarding geochemistry in a semi-enclosed sea like the Mediterranean Sea. In particular, the Mediterranean Sea receives considerable amounts of dust originating from North-Africa which is rich in elements of biogeochemical importance such as iron and phosphorus. During the oligotrophic period (generally from June to October), the surface waters are isolated from the intermediate and deep waters, so the upward transport of nutrients from deeper waters to the surface layer is weak. During this period, the atmosphere becomes the main pathway for iron input to the surface waters. From June to September 1999, the Saharan dust was collected at two coastal sites of the North-western Mediterranean Sea: a total dust flux of 2.4 t.km⁻² and 5.9 t.km⁻² was recorded respectively at Villefranche-sur-Mer and in Corsica; in September 1999, after that these high Saharan dust inputs occurred, water samples were collected during the PROSEPO oceanographic campaign (PRODUCTIVITY of PELagic Oceanic Systems) from western to eastern Mediterranean Sea. According to the hydrological parameters measured during the campaign, the surface mixed layer was 15 meters thick at the DYFAMED station in the Ligurian Sea. The dissolved iron concentrations measured in this layer were 1.3 nM. Below the surface mixed layer, the concentration dropped down to ~0.5 nM, meaning that there was an increase in the surface waters of ~0.8 nM (ie 800 nM.m⁻³) iron when compared to the underlying waters. We have then considered that in the surface mixed layer a total amount of dissolved iron of 800 nm.m⁻³ x 15 m³ = 12 000 nmol

was introduced from June to the end of September. In an attempt to correlate the observed enrichment with the inputs of Saharan dust that may have fallen in the central Ligurian Sea (from extrapolation of the fluxes measured at two coastal sites of the Ligurian Sea), the amount of dissolved iron that can be dissolved from this dust was calculated. Taking into account the approximations done for this calculation, we can consider that the calculated amount of dissolved iron (9 700-24 000 nmoles) resulting from the Saharan inputs was of the same order of magnitude of what was found in the field (12 000 nmoles). This study confirms that the atmospheric input of Saharan origin is the main source of dissolved iron in the Western-Mediterranean and that this input may be significant regarding the biological functioning of the Mediterranean, in particular during the oligotrophic season.

OS425-09 1550h

Solubility of Aerosol Iron Along an Intense Dust Deposition Gradient in the East Atlantic

Alex R Baker¹ (+44 1603 593394; alex.baker@uea.ac.uk)

Tim D Jickells¹ (+44 1603 593117; t.jickells@uea.ac.uk)

¹School of Environmental Sciences University of East Anglia, Earlham Road, Norwich NR4 7TJ, United Kingdom

Deposition of dust from the atmosphere can be a significant source of iron to surface seawater, especially in remote ocean regions. This is significant because iron is now recognised to be a potentially limiting nutrient for phytoplankton growth and the overall solubility of iron in seawater is extremely low. One of the major uncertainties in our understanding of the influence of atmospheric iron inputs on phytoplankton growth is the extent to which aerosol iron is soluble in seawater, since iron which is not released from aerosol particles is likely to remain unavailable to phytoplankton.

We have collected size-fractionated aerosol samples along a transect from 20°N to 20°S during cruise ANT18-1 of RV *Polarstern* (Bremerhaven - Cape Town) in October 2000. Samples from the northern end of this transect showed high loadings of Saharan dust, while samples from further south contained aerosol from the remote South Atlantic and in some cases also aerosol originating in southern Africa. Iron, aluminium, manganese and supporting major ion concentration and deposition flux data for the transect will be presented. Aerosol iron solubility and the relative rates of air-to-sea nutrient deposition along the transect will be discussed.

OS425-10 1605h

Sea-Surface Dissolved Iron Distribution and Atmospheric Iron Inputs in the East Atlantic

Geraldine Sarthou¹ (33-2-98498673;

Geraldine.Sarthou@univ-brest.fr); Alex Baker² (Alex.Baker@uea.ac.uk); Stephane Blain¹ (Stephane.Blain@univ-brest.fr); Eric P. Achterberg³ (E.Achterberg@plymouth.ac.uk); Dorothee Bakker² (D.Bakker@uea.ac.uk); Marie Boye⁴ (boye@obs-vlfr.fr); Andrew R. Bowie³ (Andrew.Bowie@utas.edu.au); Adele Chuck² (a.chuck@uea.ac.uk); Peter L. Croot⁴ (Croot@nioz.nl); Patrick Laan⁴ (patrick@nioz.nl); Hein J.W. de Baar⁴ (debaar@nioz.nl); Timothy D. Jickells² (T.Jickells@uea.ac.uk)

¹LEMAR/UMR6539/IUEM, Technopole Brest-Iroise, Plouzané 29280, France

²School of Environmental Sciences, University of East Anglia, Norwich NR47TJ, United Kingdom

³Department of Environmental Research Centre, University of Plymouth, Plymouth PL48AA, United Kingdom

⁴NIOZ, Postbus 59, Den Burg 1790 AB, Netherlands

During cruise ANT18-1 (October 2000, R/V *Polarstern*), underway sea-surface dissolved iron (DFe) distribution and atmospheric iron deposition were investigated, along a north-south transect in the Eastern Atlantic Ocean (27°N/16°W-19°S/5°E). Underway water samples were collected using a fish towed from a winch extended ca. 5 m from the hull of the vessel and deployed at 2-3 m below the surface. Dissolved Fe surface water concentrations (DFe) were measured by flow injection analysis with chemiluminescence detection (Obata et al., 1993). Size-segregated aerosol samplers were collected using Graseby-Anderson high volume samplers and Fe was extracted into ammonium acetate buffer (pH 4.7) to give a measure of soluble Fe. Fe deposition fluxes were at least two orders of

magnitude higher in the Saharan dust plume than at the equator or at the extreme south of the transect. DFe concentrations ranged from 20 pM to 1.1 nM and has a similar distribution as atmospheric Fe deposition. The highest DFe concentrations in the north Atlantic were observed in regions influenced by the Saharan plume and in the Intertropical Convergence Zone, where higher dry and wet deposition occurs. The lowest concentrations were found in the south Atlantic, characterised by much lower atmospheric deposition. This is the first time that such low DFe values have been reported for the Atlantic Ocean. Distribution of Fe concentrations in surface waters can be explained by a combination of inputs (atmospheric deposition, lateral and vertical transport) and removal (active biological uptake and scavenging). This study confirms the significant role of atmospheric input on the iron cycle in the Eastern Tropical Atlantic Ocean.

OS425-11 1620h

Copper Speciation and Bioavailability in Three Impacted Marine Estuaries

Martin M Shafer¹ (608-262-0140;

mmshafer@facstaff.wisc.edu); Steve R Hoffmann¹ (608-265-5085; hoffmann@cae.wisc.edu); Dawn A Karner² (608-224-6230; dkarner@mail.slh.wisc.edu); Jocelyn Hemming² (608-224-6230; hemminjc@mail.slh.wisc.edu); Joel T Overdier¹ (608-265-6493; overdier@facstaff.wisc.edu); David E Armstrong¹ (608-262-0768; armstron@engr.wisc.edu)

¹University of Wisconsin-Madison, Environmental Chemistry and Technology, 660 North Park Street, Madison, WI 53706, United States

²University of Wisconsin-Madison, State Lab of Hygiene - Biomonitoring, 2601 Agriculture Drive, Madison, WI 53707, United States

This paper will present an overview and preliminary findings of an ongoing study designed to develop a robust model of Cu bioavailability in marine estuaries. Our principal focus is the identification and parameterization of relevant metal-ligand interactions which influence Cu uptake and effect in target algal species.

We are applying and coupling a set of complementary chemical speciation tools to bioavailability as quantified in three species of marine algae (*Thalassiosira weissflogii*, *Tetraselmis maculata*, *Emiliania huxleyi*). Multiple endpoints including: (1) cellular budgets of trace metals, (2) molecular biomarkers (thiol species including phytochelatin), and (3) growth characteristics, are measured. Our chemical speciation tools include voltammetry (adsorptive cathodic stripping voltammetry (CSV) and anodic stripping voltammetry (ASV)), and kinetic separations on chelating-resins. Ultrafiltration at both 1 kD and 10 kD is also being applied to physically fractionate ligand pools. For our study systems, we have chosen three impacted marine estuaries with major contrasts in ligand source, type, and abundance, as well as significant gradients in trace element levels. These are: (a) San Diego Bay, California, (b) Norfolk Harbor-Hampton Roads-Elizabeth River, Virginia, and (c) Cape Fear River system, North Carolina.

Field studies conducted in Cape Fear (October 2000), Norfolk (October 2000, July 2001), and San Diego (February 2001, May 2001, September 2001), confirm the existence of large gradients in metal speciation and metal-binding ligand levels and strength, both between and within systems. In San Diego Bay, levels of strong ligand [L1] increase markedly from North to South Bay. In areas with low [L1], total dissolved Cu levels may exceed [L1]. Since the strong ligand is saturated, levels of weaker ligands [L2] play an important role in regulating Cu availability. The increase in strong ligand levels in South Bay more than compensates for the rise in Cu levels, and predictions that Cu bioavailability would be less and now primarily under [L1] control are borne out by the bioassays. The Cape Fear system is completely dominated by strong ligand (e.g. [L1] = 10x [Cu]), and "free" Cu levels are therefore extremely low (pCu = 14-15). A much smaller fraction of total filterable Cu is bioavailable in this system in comparison with San Diego Bay.

Early results indicate that predictable and reproducible relationships exist between the copper bioavailability measures and levels of strong ligand (L1) and weaker ligands (L2). Progress is also being made on identifying the source and nature of the metal-binding ligands. Detailed pigment analyses, e.g., suggest a close coupling with cycles of dominant aquatic organisms in the water columns of the study sites. It is hoped that these efforts will support the development of practical, speciation-based, water quality criteria.

OS425-12 1635h

Mechanisms Controlling Strong Copper-Complexing Ligands in the Cape Fear Estuary, North Carolina

Gerald Christopher Shank^{1,2} (910-962-3458; shankc@uncwil.edu)

Stephen A. Skrabal² (910-962-7160; skrabals@uncwil.edu)

Robert F. Whitehead² (910-962-7798; whiteheadr@uncwil.edu)

Robert J. Kieber² (910-962-3865; kiebert@uncwil.edu)

¹University of North Carolina at Chapel Hill, Marine Sciences Department, Venable Hall, CB 3300, Chapel Hill, NC 27599-3300, United States

²University of North Carolina at Wilmington, Chemistry Department, Dobo Hall, 601 South College Road, Wilmington, NC 28403, United States

Physical, chemical, and biological mechanisms that control the cycling of strong copper-complexing ligands are being investigated in the organic-rich Cape Fear Estuary in southeastern North Carolina. Dissolved copper speciation in this system is controlled by complexation with very strong ligands (log $K' = 13-15$), whose concentrations (10 - >100 nM) greatly exceed total dissolved copper levels (<10 nM). Data collected over a two-year period show a recurring lower estuarine peak in ligand concentrations (50-100 nM) at salinities of 20-30. Ultrafiltration analyses reveal that 84-95% of the ligands are colloidal (>1kDa and <10kDa), with the highest colloid fractions near the observed ligand peak in the lower estuary. We are investigating whether sediment flux is a major source of strong ligands to the Cape Fear system. Biological processes, especially bacterial and phytoplankton production, may be significant sources of strong Cu-complexing ligands to this estuary. Photochemical processes also appear to be important in controlling ligand concentrations. Our data provides evidence that the Cape Fear Estuary may serve as an important source of strong Cu-complexing ligands to the nearshore coastal ocean through tidal exchange and river flow.

OS42T HC: 317 B Thursday 1330h

Ocean Dynamics and Instabilities III

Presiding: J A Whitehead,

Department of Physical Oceanography;
F W Primeau, Dept. of Earth System
Science, UCI

OS42T-01 1330h

Mesoscale Wind Stress Curl Variations Induced by Oceanic Islands, and Their Implication for Wind-Driven Ocean Circulation

Cedric Chavanne¹ (cedric@soest.hawaii.edu)

Pierre Flament¹ (pflament@soest.hawaii.edu)

¹University of Hawaii, Department of Oceanography 1000 Pope Rd., Honolulu, HI 96822, United States

Oceanic islands with high topography can drastically affect the atmospheric flow. Sharp horizontal wind shear lines often form on the edges of the island lee, resulting in rapid variations of the Ekman transport in the ocean, leading to strong upwelling and downwelling, and spinup of mesoscale eddies.

These processes are the strongest when the wind direction is most regular, and where the atmospheric marine layer is capped by an inversion, forcing the wind to skirt round the island instead of flowing over it. Those conditions are met for volcanic archipelagos lying in the trade wind belt, such as Hawaii in the Pacific, reaching 4200 m altitude, and Cape Verde in the Atlantic, reaching 2800 m.

Using the NSCAT scatterometer at 25 km resolution, we have constructed the mean atmospheric flow over 42 weeks of data (from mid-September 1996 to late June 1997), in the lee of these archipelagos. The average wind stress curl (WSC) displays dramatic variations between and in the immediate lee of all major islands of both archipelagos. A dipole is associated with each major island, with positive WSC on the northern side of the lee and negative on the southern side, extending several island diameters downwind, at least 400 km for the island of Hawaii, and 300 km for the smaller islands of Cape Verde. The extrema of WSC reach a magnitude of 2.10-6 Pa/m in both cases, corresponding to Ekman pumping velocities of 3 m/day for Hawaii and 4 m/day for Cape Verde.