3rd GEOTRACES Data-Model Synergy Workshop

14-17 November 2011 Universitat Autònoma de Barcelona, Spain

Abstract Collection





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Suspended Particulate Matter in a Semienclosed Marine Area Receiving Significant Riverine Freshwater Inputs - Northern Thermaikos Gulf, NW Aegean Sea - Greece

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Thermaikos Gulf is situated in the northwest Aegean Sea (Greece), it is a shallow, substantially tideless, semi-enclosed area and receives significant freshwater inputs and suspended particulate matter. Most of the particulate matter discharged from the rivers is deposited within the prodelta area and along the western part of the Gulf.

The aim of this work is to present the spatial distribution and temporal variation as well as the compositional variability of the suspended particulate matter, during a twelve month period (2006-2007).

Water samples were collected every month in a number of stations from three different depths (1 m bellow sea-surface, 10 m depth, 2 m above sea-bottom) and filtered to obtain suspended particulate matter. The geochemical properties of suspended particulate matter were determined by thin-film X-ray Fluorescence spectrometry.

Correlation analysis showed that the elements Al, Si, Fe, Ti, K, Mg, V, have terrigenous origin, i.e. detrital aluminosilicates minerals. Chromium, Ni and Co, are of natural origin; they are derived from the river watersheds as mafic and ultramafic detrital material. Sulphur, Zn and Cu are derived from partly treated domestic and industrial effluents. A part of Ca represents the autocthonous biogenic fraction i.e. biogenic carbonates.

Neodymium exchange between dissolved and particulate phase in the Lena River estuary and Laptev Sea.

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The Nd isotopic composition (eNd) and concentration (CNd) are presented for filtered water (0.22 μ m), leached sediments and suspended particulate matter (SPM) sampled in August 2008 from the Lena River, the delta and along a transect stretching from the river mouth to 77° N in the Laptev Sea. The results will be discussed in terms of exchange of Nd between different phases during transport from continental sources to the ocean.

Filtered water, from 65° N to the Lena river mouth at 73° N, shows large variations in both CNd (500 to 1000 pmol/kg) and ϵ Nd (-12.5 to -16.1) with higher CNd and less radiogenic ϵ Nd at the river mouth. This suggests varying sources along the river with addition of Nd from a less radiogenic source in the north. In the low salinity zone (0-5 PSU) the CNd show almost conservative behaviour but at higher salinities (10-25 PSU) removal of Nd is observed. The ϵ Nd in in the 0 to 20 PSU region is more radiogenic then expected from a mixture between waters from Lena and an Atlantic water component. At higher salinities, below the halocline, the ϵ Nd approaches the Atlantic water composition.

Dominating carrier phases and removal mechanisms for Nd where investigated using a four step sequential leaching procedure of sediments and SPM. The major fraction of Nd (50 to 95%) is associated with high concentration of Fe (50 to 80%). The major carrying phases identified for Nd is iron oxhydroxides and to a lesser extent an organic phase, whereas Mn is not important.

The dissolved Nd in the Laptev Sea shows loss of Nd in the low salinity zone through flocculation of iron colloids. In the river there is an incomplete exchange between the ε Nd in the leachable fractions and the filtered water. However, in brackish and sea water there is a complete isotopic exchange between water, sediments and particles which indicates a rapid exchange processes. These results can be used to understand the widely observed effects of exchange of Nd between sediments and overlying shelf waters, here observed within the estuary of a major river.

Trace metals in suspended and rapidly sinking particles of the Brasil Basin and a 3D- model for their distribution in the water column

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During the German GEOTRACES Cruise A11 (Meteor M81/1) in the subtropical Atlantic Ocean (February/March 2010) particulate trace metals were sampled (by using in-situpumps), primarily to study the vertical distribution of particulate trace elements in the water column in relation to gradients of dust deposition and organic productivity. When compared with earlier cruises to the same stations along a transect through the oligotrophic, low-dust Brasil basin, the vertical distribution of Al, Fe, Mn, Ni, Cd, Cu and Pb in the SPM show a low seasonality and interannual variability. Below the surface mixed layer, the particulate trace metals exhibit extreme differences in the vertical distribution depending on the major form of their particulate transport. A comparison between the trace elements in the SPM with the compositions of rapidly sinking particles obtained from time-series sediment traps revealed element-specific differences which were relatively low suggesting some exchange between these two particle classes. Several observations in the Brasil basin of a close correlation between the vertical fluxes of particulate Al with those of particulate organic carbon suggest that the small dust particles are removed from the mixed layer by forming aggregates with sticky organic particles. These aggregates might become large enough to leave the surface ocean rapidly, sink, disaggregate, re-aggregate, etc., thus producing the observable vertical distribution of e.g. particulate Al and related elements. For this assemblage of processes acting on the distribution of suspended particles (including aggregation between organic and mineral particles, disaggregation, joint sinking) a 3D-model has been developed for the whole subtropical North Atlantic. The simulated concentration profiles of refractory trace metals (in suspended dust particles) show a similar pattern as in the observed vertical concentration profiles. The model suggests a strong relation to the rate of atmospheric dust deposition, while the influence of the export production is unexpectedly low.

Quantitative optical assessment of particle concentrations during GEOTRACES global surveys and process studies

Keynote

James Bishop

Department of Earth and Planetary Science, University of California

Particle pools often are a tiny fraction of total element concentration in water samples, yet it is biotic and abiotic particle formation, vertical transport and remineralization of particles that gives rise to the non-conservative behaviour of half of the elements in the periodic table. CTD's are the heart of all water column sampling for GEOTRACES. Over the past decade a variety of particle concentration sensors have been developed that permit quantitative measures of particulate properties to full water column depth. This presentation reviews the application and methodology of transmission, birefringence, and scattering sensors in the context of their deployment during GEOTRACES global surveys.

Optical proxies of biogeochemical variables in the ocean

Keynote

Emmanuel Boss, University of Maine

In this talk I will review the use of measurements of optical properties to constrain the biogeochemical properties and processes associated with particles and dissolved substances in the ocean. These measurements include in-situ spectral absorption, angular scattering, attenuation, fluorescence and ambient light, as well as water leaving radiance (measured locally or remotely, e.g. from satellites). The utility and limitations of such measurements will be discussed and examples of deployment strategies will be presented. I will end with a note regarding likely future trends. The talk will be accompanied with demonstrations of the basic concepts associated with the interaction of light with matter.

Measuring particle fluxes and sinking rates- how can polyacrylamide gel sediment traps help?

Keynote

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Many particle-reactive and bioactive trace elements and isotopes are carried by sinking particles to depth, thus setting up surface to depth concentration gradients and influencing their residence time and cycling in the oceans. Unfortunately this flux is difficult to determine directly via sediment traps so several alternative methods have been developed. These include radionuclide mass balances, such as ²³⁴Th, or via the determination of particle abundances in the water column and application of a sinking rate model to resolve flux, F, from F = C * w, where C is the concentration of a given class of suspended particles that are sinking at a rate of w (m/d). The particle concentrations can be determined by camera systems or filtration, however accurate determination of w is more problematic. This talk will briefly review flux methods and focus on a new application of polyacrylamide gel sediment traps for the determination of the size spectra of sinking particles collected in traps. When the gel trap data are compared to the same size spectra in the water column, average sinking rates can be quantified (McDonnell and Buesseler, L&O, 2010). An early analysis of such spectra from the W. Antarctic Peninsula and Bermuda (BATS) suggest that the largest particles are not necessarily the fastest sinking, and that the relationship of size vs. w varies with season, depth and location. The application of this method and potential to calibrate w across a wide study area will be discussed.

Particle Dynamics in the Ocean

Keynote

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Particulate material plays an important role in the biogeochemical cycling of elements in the oceans. We need to improve our understanding of the bulk properties and interactions of particles (because this is what is generally measured) as well as particle properties and interactions at an individual level because this is what determines rates and scales of interaction and transformation. Sinking particles transport material vertically, providing nutrition for organisms in the deep ocean. Chemical and biological transformations of this material determine in part the vertical profiles of elements and compounds and, on a global scale the fate of this material plays a role in determining the sequestration of atmospheric carbon by the oceans. Understanding the dynamics of particulate material is crucial in determining its role in these processes. In particular, we need to understand the processes affecting how fast particles form, how fast they sink, how fast they are utilized and broken apart. Many of these dynamical processes are interdependent and depend on both the interactions of particles with each other and the interactions between particles and their environment. However, on the scale of individual particles, this is something that we know little about. Our understanding of particle-zooplankton interactions has improved dramatically, but has yet to be fully incorporated into dynamical models. In addition, the properties of particles themselves (their composition, settling speed etc) determine their interactions with organisms, their environment and each other. We need to better connect our understanding of the bulk behavior of particles with our understanding of individual particles. This connection is also important to modeling efforts because we cannot directly incorporate detailed interaction models into large-scale biogeochemical models. We therefore need simpler models (or paramterizations) that capture enough of the detailed mechanisms to be useful in predicting spatial and temporal variability in these processes, but which remain computationally practical.

Isotopic model of oceanic silicon cycling: the Kerguelen Plateau case study

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A box model is presented describing the time evolution for the three Si isotopes (or total concentration and natural isotopic composition), both in the dissolved and biogenic pools. Temporal variations are controlled by uptake, dissolution (both with isotopic fractionation), settling/export and mixing/advection (without isotopic fractionation). The basic building blocks are combined to form a setup for the Kerguelen Plateau where distinct "plateau" and "out-plateau" areas exist. In addition, the model distinguished between surface (0-100m) and subsurface (100-400m) water. This resulted in a model composed of 8 compartments, each containing three variables (the three Si isotopes) whose time evolution can be modelled. The model does not assume steady state, and can therefore be used to simulate transient event like blooms.

We applied the model to simulate the 2004-2005 growth season during which measurements are available at the end of the growth season (KEOPS cruise: KErguelen Ocean and Plateau compared Study). The model parameterisations were kept as simple as possible. Notwithstanding its relative simplicity, the model is able to reproduce the KEOPS measurements satisfactorily, except for a slight underestimation of the bSiO₂ enrichment in box 1 (surface plateau). Production and dissolution rate estimates, as well as the total Si fluxes related to export and mixing/advection are compared to previous literature values, when available, and match well.

An important advantage of the model is that a simultaneous estimation of all fluxes is possible, over the whole growing period. The model is made of generic process building blocks and can be easily adapted to different study domains, having their own specific spatial structure and Si dynamics, including non-oceanic environments such as freshwater or sea ice. Different time scales can also be considered.

ASSESSING THE IMPORTANCE OF ATMOSPHERIC DEPOSITION ON THE EASTERN MEDITERRANEAN SEA BIOGEOCHEMISTRY

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The impact of atmospheric deposition, suggested as the main external source of nutrients to the East Mediterranean Sea, on the marine ecosystem is here investigated. For the first time, atmospheric deposition measurements of Dissolved Inorganic Phosphorous and Nitrogen over Crete are used synergistically with marine ecosystem observations of nutrient availability and chlorophyll by mean of a 1-dimensional ocean biogeochemical model. The 1-dimensional ecosystem model taking into account the atmospheric inorganic N and P inputs and the physical and biological mechanisms that may transport excess N from the ocean surface to the thermocline, is appropriately modified to simulate the sea water observations at the Cretan sea. The impact of the atmospheric inputs of these nutrients on the marine ecosystem and the underlying biogeochemical and physical processes are investigated. The model successfully reproduces observations of production rates and biomasses of phytoplankton and bacteria in the region. The atmospheric deposition of N and P to the East Mediterranean is shown to increase the primary production by 1-35% depending on season with the maximum impact calculated for summer and fall. Biomasses subsequently increase by 2-26% for phytoplankton and up to 7% for bacteria. Simulations indicate that continuous atmospheric inputs of nutrients over several decades can maintain the anomalously high N-to-P ratio observed in the East Mediterranean seawater.

Particle dynamics and biogeochemical cycling over the NW Atlantic margin

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Continental margins play a crucial role in global biogeochemical cycles of many bioactive elements, and underlying sediments can yield some of the most exquisite archives of past ocean and climate variability, yet they are characterized by highly complex and dynamic physical and biogeochemical processes. Geochemical tracers may be particularly valuable for deconvoluting particle sources, transport mechanisms and sedimentation processes in such spatially and temporally heterogeneous systems.

The Northwest Atlantic margin is influenced by large-scale currents, notably the Deep Western Boundary Current (DWBC) and the Gulf Stream, that can entrain sediments from different source regions and disperse particulate materials both along- and across-margin into the ocean interior via intermediate and bottom nepheloid layers. We are exploiting strong natural geochemical gradients in the study area through the use of an array of organic and inorganic tracer properties (notably radiocarbon, biomarker abundances and isotopes, neodymium isotopes, and U-series isotopes) of surface sediments, sinking particles (intercepted by time-series sediment traps), suspended particles (collected via in situ filtration) and dissolved species, in concert with an on-going physical oceanographic observation program, in order to constrain the particle provenance and transport pathways. Radiocarbon measurements on sinking and suspended particles reveal the presence of aged carbon at depth, and a strong inverse relationship between radiocarbon and aluminum abundance. These observations imply significant mobilization and transport of resuspended sediments over the margin. Marked variations have also been observed in detrital Nd isotopic compositions, with *eNd* in sedimentary and sinking particles reflecting the influence of alongmargin particle transport via the DWBC intertwined with local resuspension processes. Measurements of a diverse suite of U-series isotopes varying in half-life and particle reactivity are being used to further constrain the source, magnitude and time-scales of lateral particle supply. In particular, ²³⁰Th and ²³¹Pa measurements in sediment traps confirm extensive lateral transport, while mid-water excesses in short lived Ra isotopes suggest advection from the shelf to the slope, perhaps via intermediate nepheloid layers.

Collectively, these observations will enable us to develop an understanding of the interplay between particle dynamics, biogeochemical processes and sedimentary records on this, and potentially on other, continental margins.

Distribution of neodymium and silicon isotopes in Eastern Equatorial Pacific seawater

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The Rare Earth Element (REE) neodymium (Nd) is introduced into seawater through continental weathering and exchange with the continental shelves. Due to its intermediate oceanic residence time it is a powerful chemical water mass proxy and can also be applied for the reconstruction of past ocean circulation. The stable isotopes of silicon (Si) are a powerful tool in marine sciences to investigate biological processes, such as present and past nutrient utilization. Over the last years, a large number of Nd and Si isotope data have been produced for Atlantic seawater but only very few data are available for the Pacific Ocean. We have produced and want to discuss the first dissolved Nd and Si isotope data (including concentrations) for the Eastern Equatorial Pacific (EEP), where one of the globally largest Oxygen Minimum Zones (OMZ) is located. Samples were recovered along several zonal and meridional sections during "FS Meteor" cruises M77/3 and M77/4 in 2009 in the frame of the German coordinated research programme SFB 754. All data were produced according to established GEOTRACES protocols.

The data demonstrate that both isotope systems are to a large extent controlled by hydrography, which is particularly true for the deep waters. Surface waters in the study area show a wide isotopic range (ε_{Nd} = -8 to ε_{Nd} = +3), due to contributions from land, which are partly transferred to deeper waters through scavenging and remineralisation. Subsurface water masses originating from the western and central Pacific, such as the Equatorial Undercurrent has an ε_{Nd} = -1.8, whereas other (sub)surface currents are less radiogenic (ε_{Nd} = -4). Deep and bottom waters at the southernmost stations (14°S) of the study area (ε_{Nd} = -7) are clearly influenced by less radiogenic water masses originating from the Southern Ocean.

For Si isotopes, in areas and during phases of intense upwelling the fractionation of Si isotopes was observed to be weaker (δ^{30} Si=1.8‰) due to upwelling driven supply of less fractionated Si from water depths of 50 to 150m, whereas under weak upwelling conditions the surface waters are heavier (δ^{30} Si=2.8‰) due to more complete utilization of the available dissolved silicic acid.

Sensitivity of biogeochemical models to the treatment of particle dynamics. Keynote

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The past decade has seen the rapid development of marine biogeochemical models of increasing complexity. These models are often part of coupled Earth System models and used for the evaluation of future changes in biogeochemical cycles in response the climate change. While the description of upper ocean ecosystems has steadily increased in complexity, we have to admit that the biological pump is often represented in a simplistic way. This is in part due to the fact that processes controlling the transport and fate of particles across the water column remain poorly understood. In addition, data sets suitable for model validation (e.g. sediment trap data, particle concentration, size distribution ...) are still sparse. Adding TEI cycles to these models holds the promise of an additional and independent constraint on model parameterisations. In the first part of my presentation, I take advantage of sensitivity studies carried out with the NEMO/PISCES model to discuss minimum model complexity and key processes in the context of carbon cycle research.

Next, I will present examples of TEI studies carried out with NEMO/PISCES and present knowledge gained from expanding the model to these tracers. I shall conclude by highlighting critical knowledge gaps and needs for additional, respectively new observations from the point of view of large scale biogeochemical modeling.

Transparent exopolymer particles, DOM-POM transformations, and (ir)reversible svavenging: Merging the lessons from different research approaches

Keynote

Walter Geibert, University of Edinburgh

The study of particle dynamics in the ocean is the research subject of different disciplines, which currently co-exist rather that merge. From a biological perspective, recent studies have focused on the role of transparent exopolymer particles (TEP), formed by excretions of microorganisms, in the aggregation of particles, controlling settling velocities and the incorporation of ballast minerals. Marine organic geochemistry has yielded new insights into the chemical composition of dissolved organic matter (DOM) and its relation to the particulate pool. In marine inorganic chemistry, studies of element speciation and ligands have contributed to the description of particle-solution equilibria, especially in surface waters, and GEOTRACES will be a unique opportunity to understand how this process continues in deeper waters in order to explain the reversible particle scavenging pattern there. However, the terminologies and concepts in the research fields differ, though they have large overlaps. This talk will explore where the terms for marine particle dynamics overlap, where they differ, and what we can learn about the continuous transition from the dissolved to the particulate pool (and back) by merging the research fields.

After outlining how the different disciplines define their subject, the similarities and differences between the approaches will be investigated. Finally, a synthesis will be attempted, summarizing the state of knowledge, and identifying the main gaps. Particular attention will be paid to recent progress in analysing the molecular structure of dissolved organic matter by ultra high resolution mass spectrometry (FT-ICR-MS), which point to the possibility of fully reversible transitions from aggregated to disaggregated substances in the deep sea. This continuum from the dissolved to the particulate pool- and back- may explain the apparent reversibility of absorption, a fact that may be used to better understand and simulate the mechanisms that underlie particle formation.

Particles in hydrothermal plumes – biotic or abiotic, regulators of hydrothermal fluxes or active sinks for global ocean TEI budgets?

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Hydrothermal plumes are systems that contribute significant gross fluxes of TEIs to the oceans yet these fluxes are modified significantly in buoyant and non-buoyant hydrothermal plumes due to quenching effects that lead to rapid precipitation of polymetallic sulfides as soon as fluids exit the seabed and Fe- and Mn-rich oxyhydroxides that precipitate more slowly within the dispersing hydrothermal plume. While three classes of TEIs distributions have been recognized for 20 years or more (chalcophile, oxyanion and scavenged) with respect to Fe distributions in hydrothermal plume particles, it is only in the past 5 years that significant new breakthroughs have become available to investigate what processes might be responsible for these TEI behaviors including studies of both dissolved and particulate TEI speciation, the role of organic carbon complexes in particle biogeochemistry and the potential importance of microbially mediated Fe and Mn oxidation. With the advent of the US GEOTRACES section from Peru to Tahiti in 2013, including interception of the southern East Pacific Rise hydrothermal plume, it is timely to pool the state of the art in hydrothermal studies with the expertise of other ocean biogeochemistry TEI researchers specializing in dissolved-particulate interactions and that is why I am most keen to participate in this particular workshop.

Mesozooplankton diel migration balances twilight zone carbon budgets

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Downward fluxes of particulate organic carbon (POC) through the 'twilight zone' (upper 100-1000 m) are attenuated by abiotic and biotic processes. The latter includes activities such as the repackaging and remineralization of POC by bacteria, zooplankton and other heterotrophic organisms. Mesozooplankton in the twilight zone are hypothesised to satisfy their metabolic demands by feeding directly or indirectly (via feeding on microzooplankton and faecal pellets) on sinking POC. We compared mesozooplankton carbon demands during night and day with POC flux attenuation at two sites at the Porcupine Abyssal Plain (PAP), in the Northeast Atlantic, in summer 2009. Vertical profiles of mesozooplankton biomass were converted into carbon demand using well-established allometric equations. POC flux attenuation between 50-600 m was measured using five neutrally buoyant sediment traps at different depths. Integrated mesozooplankton carbon demand between 200-1000 m was higher than the reduction in POC flux in that depth range. However, the reverse pattern was apparent between 50-200 m suggesting that mesozooplankton in the 200-1000 m depth range satisfy their carbon demands by grazing in the surface ocean during the night and then migrating deeper into the ocean during daytime. We address this hypothesis by showing that there is sufficient POC present in the upper ocean for the major classes of migratory zooplankton, larger copepods and euphausiids, to satisfy their daily metabolic demands by feeding in the upper 100 m. Mesozooplankton permanently residing and feeding at depths \geq 200 m were responsible for only half of the POC flux attenuation, with the remaining attenuation being likely due to microzooplankton and bacteria. Our study demonstrates that a more detailed understanding of the trophic ecology of the twilight zone is necessary in order to accurately quantify elemental cycling in this environment.

Iron recycling by mesozooplankton supports phytoplankton growth in the Irminger Basin

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Estimates of export production for the subarctic North Atlantic range from 36 to 100 g C m⁻² yr⁻¹, indicating that this region plays an important role in the global carbon cycle. The highnutrient, low-chlorophyll (HNLC) conditions prevalent in this region suggest that growth of the resident phytoplankton communities, and hence atmospheric carbon drawdown, are ironlimited. Heterotrophic bacteria, microzooplankton and viruses are well known to recycle iron. Few studies have examined the importance of mesozooplankton for iron regeneration.

Five hour starvation experiments were used to quantify the release of dissolved iron and ammonia by natural mesozooplankton communities from the Irminger Basin in July and August 2010. Average ammonia excretion rates were 50 ng N ind⁻¹ h⁻¹ during the first 2 h and 35 ng N ind⁻¹ h⁻¹ thereafter. Iron concentrations increased rapidly during the first 30 minutes and plateaued after 2 h. Iron release during the first hour ranged from 2 - 13 pmol dFe ind⁻¹ h⁻¹, potentially supplying up to 67% of the iron required for primary production in the Irminger Basin. Mesozooplankton may thus be an important recycler of iron, and need to be taken into account when assessing what governs the biological carbon pump and productivity in HNLC regions.

Carbon export spatial variability: What scale to consider?

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Particles are the major vector of carbon transfer from the surface layer to the deep in the open ocean. Sediment traps have been used extensively for more than 3 decades to measure the amount of material transiting through the mesopelagic (100-1000 m) zone. However these traditional tools, used alone, do not provide insight on small spatial and temporal variability in carbon export. Over the past decade, the development of robust optical sensors has gone a long way toward overcoming the challenge of sampling biological parameters at scales that are similar to those captured by physical and chemical sensors. Recently the Global Biogeochemical Flux program for the Ocean Observatories Initiative (GBF-OOI) suggested that optical tools such as the Underwater Vision Profiler (UVP) would be valuable components of the GBF-OOI for the observation of biological and biogeochemical processes in the ocean. In this context, merging optical measurements of particle sizes to sediment trap fluxes estimations appear to be a promising approach to estimate carbon export variability from basin to regional scales. Using the OPEREX cruise as an example, I will show that particle size distribution used with sediment traps flux measurement allowed to identify processes affecting carbon export at scale that sediment trap alone could not resolved in the past. Observations and modeling analyses of the particle size distributions from two transects across a pair of eddies indicated that horizontal turbulent stirring partly controlled the spatial distribution of the nitrogen fixing cyanobacterium Trichodesmium spp., potentially enhancing new primary production and particle export in the vicinity of Station ALOHA. Furthermore, In addition to gravitational sinking, stretching by the mesoscale eddy field produces submesoscale features that mediate carbon export via frontogenetically-generated downwelling currents. These results highlight that studies seeking to resolve the magnitude and variability associated with POC export, may need to account for small-scale spatial variability in physical dynamics as controls on carbon export. Sampling strategies that better resolve small-scale variability using a combination of towed and autonomous platforms (e.g., gliders) coupled with high-resolution modeling and remote sensing should be pursued.

Monitoring the impact of ocean acidification through ²³⁰Th – where and when?

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Particle reactive radionuclides provide a potential tool for detecting and monitoring largescale impacts of progressing ocean acidification which is a consequence of marine uptake of anthropogenic CO₂ from the atmosphere. Among such impacts are a change in biocalcification and related changes in marine particle fluxes. Due to its strong particle reactivity ²³⁰Th is a good candidate for reflecting such changes through time series of vertical profiles. We employ a biogeochemical ocean general circulation model for establishing when and where one could potentially successfully detect such impacts from ²³⁰Th measurements. It turns out that significant changes in marine water column ²³⁰Th activity due to changes in biological CaCO₃ formation at the sea surface result with about the same temporal detection threshold as for alkalinity itself. Nevertheless, selected ²³⁰Th measurements can provide useful additional constraints for the potential findings from alkalinity time series and thus narrow down uncertainties. We provide a recommendation on measurement intervals and most suitable measurement sites for ²³⁰Th based on our model results.

Why coagulation theory is important for oceanic biogeochemistry.

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Vertical flux is about settling particles; coagulation theory describes how physical processes change particle sizes, abundances, and vertical flux. Coagulation theory has been successful in predicting maximum particle concentrations, vertical fluxes, and isotopic distributions on particles. It provides predictions to test. It also suggests that different modes of feeding on particles have very different implications for nutrient cycling in the euphotic zone and on export to the mesopelagic. With the development of new instrumentation to measure particle distributions, the time is right to tie coagulation theory into geochemical models. We have been using a profiling particle counter to examine particle distributions within the upper 100m at hourly intervals. The observations are generally consistent with coagulation theory. They do suggest a zone of intense particle grazing at the base of the euphotic zone that controls particle export to the mesopelagic.

Theoritical and experimental tracks that could improve the understanding of particle/dissolve exchange processes

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The annual global river discharge of suspended particulates likely exceeds 19×10^{15} g/y (*Peucker-Ehrenbrink, 2009*), about 50 times the global dust input to the ocean $(0.425 \times 10^{12}$ g/y; *Jickells et al., 2005*), implying that release to seawater of even a small fraction of the material deposited along the margins could have a significant impact on the biogeochemical cycles. This estimate of suspended particulate matter transported by rivers to the ocean most likely represents the lower limit as it probably underestimates contributions from small rivers as well as coastal or glacial erosion. Constraining the importance of this source of lithogenic elements to seawater could therefore considerably modify our understanding of the modern ocean and its response to global changes in the past and future. *Jeandel et al (2011)* suggested that sediments of continental origin deposited along ocean margins are capable of releasing a significant proportion of their constituting elements to seawater. These authors underline that this release could significantly contribute to the geochemical and isotopic budgets of various species in the oceans, including Si. However, the release processes are not yet understood, and there is an urgent need to progress in this issue yielding an important component of the land-to-ocean flux.

Theoretically carbonate, organic, or Fe-Si complexation on the particle surface can modify the solubility of mineral species. Direct or indirect impact from bacterial activity and/or the differential dissolution of minerals within the particle pool can also occur and yield this release. This talk will propose how different surface particle speciation can enhance element releases. It will also propose several experimental tracks and how the use of cutting edge analytical tools allowing the direct exploration of the particle surface speciation could help our oceanographic community to progress in the understanding of these processes, an essential prerequisite for the Earth System modelling.

Modeling metal micronutrient concentrations and isotopes

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Analysis of trace-element isotope ratios (e.g. d⁵⁶Fe, d⁶⁶Zn, and e¹¹⁴Cd) in seawater is an emerging technique to study marine biogeochemical cycles. Simple 1-dimensional models provide a powerful tool to explore how paired measurements of metal concentrations and stable isotope ratios can provide sorts of information that cannot be learned from either dataset alone. Metal concentrations and isotope ratios are often correlated in the water column. For example, high [Fe] in suboxic basins is correlated with low d⁵⁶Fe, and low [Cd] and [Zn] in surface waters is correlated with high $e^{114}Cd$ and $d^{66}Zn$. However, because these superficial correlations can mask subtle differences between isotopic and concentration data, understanding subtle differences is key to applying new isotopic tracers in the ocean. For example, the flux of isotopically light Fe from reducing sediments in the San Pedro Basin leads to low d⁵⁶Fe and high dissolved [Fe]. Modeling [Fe] and d⁵⁶Fe together allows us to quantify the effects of important processes such as the sedimentary flux of Fe, the d⁵⁶Fe of this flux, the precipitation rate of dissolved Fe in the water column, and the isotope effect of precipitation. These values are crucial for using d⁵⁶Fe to trace different sources of iron to the oceans. The inverse correlation between [Cd] and e^{114} Cd in the surface ocean is caused by biological Cd uptake. However, the expression of this signal throughout the thermocline can be interpreted either as due to mixing or as due to remineralization of sinking particles. When these two end-member cases are examined in a simple 1-d model, they produce strikingly different e¹¹⁴Cd profiles, suggesting that paired [Cd] and e¹¹⁴Cd might be used to differentiate between mixing and remineralization processes. Particulate cycling of trace-metal isotopes is also incorporated into models of d⁶⁶Zn. Specifically, characteristically 'kinky' Zn isotope profiles can be interpreted either as signatures of temporal variability (deviation from steadystate) or signatures of Zn scavenging onto particles. In our simple models, either process can produce profiles similar to observed dissolved [Zn] and dissolved d⁶⁶Zn profiles. However, the particulate d⁶⁶Zn profile predicted by these two models is very different.

Use of laser diffraction methods to obtain in-situ particle size distribution. Examples from the Mediterranean Sea and the Black Sea

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The observation of particles and their behaviour in the ocean has attracted the interest of oceanographers since the early 1970s. The measurement of particle size distribution (PSD) is important for a better understanding of various processes interplaying in aquatic systems. In 1995, a new instrument was commercially available from Sequoia Scientific Inc., named LISST (Laser In-Situ Scattering and Transmissometry). LISST operation is based on laser diffraction or laser light scattering, which is the most common technique for measuring detailed particle size. The use of LISST provides the opportunity to study *in situ* PSDs, in high vertical resolution, and in 32 pre-defined size classes. HCMR owns one of the few LISST-Deep (operating depth 3000 m) instruments, which measures particles in the range 1.5-250 μ m.

In the framework of SESAME Integrated Project funded by the EU, LISST-Deep was tested for the first time in the Black Sea (October 2007), in the Danube delta area, and in the Eastern Mediterranean (spring and summer of 2008). In the Black Sea, median particle diameter (D50) varied from 5 to 225 μ m, but high values were biased by the influence of schlieren, i.e. intense light scattering occurring in sharp pycnoclines. Excluding the biased values, average D50 is within the range 40-60 μ m.

In the oligotrophic Eastern Mediterranean, LISST operated near the detection limits, as particle volume concentrations were generally less than 5 μ l/l. During March-April 2008, D50 range was 32-186 μ m (mean 86 μ m), whereas during August-September 2008 D50 range was 38-230 μ m (mean 83 μ m). Although highest values were recorded in both cruises in the upper 100 m, where phytoplankton populations predominate, similar PSDs were observed throughout the water column, up to 3000 m-depth.

According to our observations, both in the shallow NW Black Sea and the deep Eastern Mediterranean, particles in suspension appear in the form of aggregates (microflocs and/or macroflocs). We suggest that flocculation process is the controlling mechanism that binds inorganic particles and organic matter composing aggregates an order of magnitude larger than their initial components. In conclusion, LISST is a reliable instrument capable for *in situ* measurements of high resolution and could support potential GEOTRACES experiments related to particle biogeochemistry and associated processes.

Modeling the distribution of rare earth elements in the ocean: sensitivity to scavenging processes and particle fluxes

Samar Khatiwala, Xinyuan Zheng, Tinna Jokulsdottir, and Gideon Henderson

We apply a fast offline global ocean circulation model based on the transport matrix method (TMM) to simulate the distribution of rare earth elements (REEs) in the ocean. We use the TMM framework, which allows us to rapidly compute equilibrium tracer distributions, to systematically explore the sensitivity of REE tracer fields to various sources and sinks, including river and aeolian deposition, internal recycling, and exchange with margins. In particular, we have implemented parameterizations for a number of scavenging processes, including reversible and irreversible scavenging, and boundary exchange. Scavenging coefficients and other parameters are varied and the simulated REE fields compared with observations. We also investigate the impact of prescribed particle fields on REE distributions. Specifically, we apply particle fields computed using a novel biologicallycoupled, Lagrangian, particle model driven by global gridded fields of SST, satellite-derived primary production, and other environmental parameters (see the abstract by Jokulsdottir et al.). In addition to describing the main scientific results we will also present a quick overview of the TMM framework and the (freely available) code we have developed for simulating REEs in the ocean.

Sensitivity of biogeochemical models to particle export and recycling

<mark>Keynote</mark>

Iris Kriest, Leibniz Institute of Marine Science (IFM-GEOMAR), Kiel, Germany

In global biogeochemical models various formulations for particulate organic matter export, sinking, and remineralization are used. These are implemented either via explicit detritus compartment(s) and properties, or via functions that describe the combined effects of organic matter flux to the ocean interior and remineralization.

In any case, the parameters that govern these processes are not well constrained, and may vary in reality due to particle aggregation and composition, food web structure, etc.. In addition to the uncertainty associated with particle flux description, empirical data sets of particle flux are sparse, and associated with methodological problems. It is thus difficult to constrain global models from the local observations directly.

As an alternative approach, here the consequences of different particle flux/remineralization descriptions for the simulated distribution of more easily observable quantities, such as nutrients or oxygen, are examined. Sensitivity studies have been carried out via long term simulations of global biogeochemical models. The sensitivity of the models to changes in remineralization length scale over the observed range is compared to the impact of of other biogeochemical parameters such as growth rate or nutrient sensitivity of phytoplankton, to transport derived from different circulation models, numerical scheme for particle sinking, and lower model boundary conditions.

A global compilation of large-volume filtration data for the upper 1000 m

Keynote

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As many GEOTRACES programs are incorporating in-situ pumping into their cruise plans, the analysis of particulate compositions in the sinking (>51um) and suspended (<51um) size fractions provides some insight into the division between the vertical flux and standing stock of particle-associated elements, particularly in the absence of sediment traps. The use of insitu pumps further allows the simultaneous analysis of a multitude of parameters from the same sample in each size fraction, providing the major particulate composition context to the trace element and isotopic measurements that are at the heart of GEOTRACES.

Marine particles in the open ocean are dominated by biogenic constituents (particulate organic carbon, $CaCO_3$, opal). The magnitude and relative proportion of these major biogenic phases may affect the partition coefficients of trace elements onto particles, as well as influence the strength and efficiency of vertical particle flux through direct or indirect ballasting effects. This has implications for the cycling of trace elements as well as the biological carbon pump.

I will present the results of a recent compilation of a global data set of 62 open ocean profiles of size fractionated particulate organic carbon (POC), CaCO₃, and opal concentrations collected using large volume in-situ filtration (LVFS and MULVFS systems) in the upper 1000m over the last 30 years (Lam et al. 2011, Global Biogeochemical Cycles, Vol. 25, GB3009, doi:10.1029/2010GB003868). In this work, we analyzed POC concentration profiles from the sinking (>53um) size fraction as a complement to POC flux profiles for understanding the global variability in the strength and efficiency of the ocean biological carbon pump, and examined the potential role of biogenic ballast minerals (CaCO₃ and opal). I will present a summary of this work, and extend it to include a survey of the global variability in the suspended (<53um) size fraction.

Toward a better understanding of Nd isotopes in the North Pacific: observations and modeling of boundary exchange

Jordan Landers, Samar Khatiwala, Bob Anderson, Steve Goldstein

While epsilon Nd maps elegantly with salinity and other tracers to articulate watermasses in the North Atlantic, its distribution in the Pacific is less clearly described by a simple two end member mixing model. Instead, a combination of mechanisms, primarily boundary exchange processes such as terrestrial dust fluxes, ground and river water are called on to explain the differences observed between the two ocean basins. By comparing epsilon Nd measurements made on authigenic Fe-Mn oxides on surface sediments from a range of depths and distances from the continental margin, to model results we are able to shed some light on the influence of these additional variables on the otherwise ocean circulation-dominated distribution.

Fertilizing the Photic Zone: where do the bioactive trace elements come from?

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Phytoplankton productivity in the oceans is partly controlled by the input of biologicallyrequired trace elements to the photic zone. Iron limitation is thought to limit phytoplankton productivity in perhaps 40% of the global ocean. In some areas, atmospheric deposition can be the dominant input pathway, and can be estimated from aerosol and rainfall sampling. The distribution of dissolved Al can also be used to infer atmospheric deposition rates of mineral dust. For other bioactive TEIs, vertical mixing from below the photic zone can be the most important source. This can be estimated from advection/diffusion modeling of the vertical profiles (or entire sections) of these elements. This approach also allows one to identify areas where input due to horizontal mixing must dominate.

We take advantage of the calculation functions within Ocean Data View to combine measured ocean sections of bioactive TEIs from the CLIVAR/Repeat Hydrography project with model estimates of vertical velocity and vertical turbulent mixing to calculate the vertical input/removal rates of TEIs from the photic zone. These estimates are then compared to the biological requirement for each TEI based on "Redfield" stoichiometry and estimates for "new" production, acquired from satellite ocean color data. We also compare these estimates of TEI biogeochemical cycling rates with measurements of soluble aerosol input, obtained from aerosol sampling along each section. Horizontal mixing input is indicated in areas where vertical mixing input and atmospheric deposition are not sufficient to balance the biological requirements.

WHAT CAN PAIRED MEASUREMENTS OF TH ISOTOPE ACTIVITY AND PARTICLE CONCENTRATION TELL US ABOUT PARTICLE CYCLING IN THE OCEAN?

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The ability of paired measurements of thorium isotope activity and particle concentration to inform about the kinetics of solution-solid exchange and particle transformation in ocean waters is examined. Our approach relies on data assimilation experiments with a model of trace metal and particle cycling in the deep sea. First, the model is used to simulate vertical profiles of (i) the activity of ^{228,230,234}Th in the dissolved phase, small suspended particles, and large sinking particles, and (ii) the concentration of small and large particles. The profiles are then subsampled and contaminated with random noise to generate a pseudo data set that mimics data to be gathered at stations of GEOTRACES sections. The data are assimilated into the model with arbitrary values of the rate constants (adsorption, desorption, (dis)aggregation, remineralization, and sinking) in an effort to recover the actual values used to generate the data. Experiments are performed using generalized least-squares with varying assumptions about data noise, data sampling, and model errors. We find that accurate and precise recovery of the rate constants is possible when all the data have a relative error of less than 20% and model errors are negligible. Data sampling appears to be less critical, provided that the activity and concentration gradients are properly resolved. Estimating cycling rates from data with larger errors and/or at locations where model assumptions (e.g., negligible effect of advection) are not tenable would remain challenging. On the other hand, the paired data set would improve significantly the relative precision of rate constants compared to that of previous estimates ($\geq 100\%$), even with current estimates for data uncertainties and with acknowledgement of significant model errors. We conclude that the data set to be gathered at GEOTRACES stations should dramatically enhance our understanding of solution-solid exchange and particle transformation in the ocean, in particular at locations where the model would provide an accurate description of Th and particle cycling.

Fe:C ratios of sinking particulate material in the upper mesopelagic: measurements from drifting sediment traps and in-situ pumps in the Irminger and Iceland Basins.

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Despite the attention paid in recent years to various aspects of the marine biogeochemistry of iron, there have been relatively few direct measurements made of particulate iron (PFe) in material sinking through mesopelagic depths of the ocean. Given the significant degree of attenuation of particulate organic carbon, nitrogen and phosphorus fluxes in the subsurface ocean, the fate of sinking PFe will have important consequences for the ratio of iron to these elements in water convectively mixed or entrained back to the surface.

Here we present PFe, POC and PON data from sinking particles collected using neutrallybuoyant PELAGRA sediment traps deployed at 80 - 400m depth in the Irminger and Iceland basins during July-August 2010. Also shown are measurements made on >53um-sized particles collected on the same cruise, using high-volume *in situ* pumps.

Effects of particulate abundance on reversible exchange of dissolved Al in the Central North Pacific and Western Arctic Oceans

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Dissolved aluminum profiles in the Central North Pacific Ocean demonstrate classic scavenged-type trace element behaviour. In contrast, dissolved Al concentrations in the Arctic Ocean exhibit linear increases with depth. Similar linear increases observed for 234Th are modeled based on reversible exchange upon particulate surfaces in the water column, prompting investigation of reversible exchange processes associated with Al.

Degradation of particulate matter in the water column in concert with reversible exchange is predicted to increase dissolved Al concentrations with depth, hypothesized to be of significance given lower particulate flux in the Western Arctic basin as a result of stratification and ice cover. Therefore, this work investigates effects of SiO2, POC, and CaCO3 particulate abundance within one-dimensional equilibrium and kinetic reversible exchange models applied to dissolved Al profiles in the Western Arctic and Central North Pacific. Model results are fit to observed profiles through optimization of rate and equilibrium constants, in addition to parameters controlling particulate dissolution and remineralisation in the water column. Additionally, an Al source term is investigated given release of incorporated Al upon dissolution of diatomaceous SiO2. Results indicate that lower particulate abundance of SiO2 in the Arctic replicates linear and scavenged Al profiles in the Central North Pacific and Western Arctic, respectively, utilizing kinetic and equilibrium models. This work suggests the importance of particulate abundance and recognition of reversible exchange as a control on dissolved Al distributions. Increased understanding of Al biogeochemical cycling will aid evaluation of particulate flux within Th models for the estimate of carbon flux.

Estimation of sinking particle fluxes from local measurements of particle size distributions, sinking velocities, and densities

Andrew M. P. McDonnell(1,2)* and Ken O. Buesseler(1)

The measurement of the elemental fluxes of carbon, nutrients, and trace metals associated with sinking particles in the oceans is an important component of our understanding of ocean biogeochemical dynamics. Unfortunately, conventional sediment trapping methods used to quantify these fluxes throughout the water column are not capable of fully capturing the spatial and temporal variability in the elemental fluxes that exists the oceans. In this talk, we describe a new method for estimating the fluxes of biogeochemically important elements at high spatial and temporal resolutions from measurements of the particle concentration size distribution taken with an in situ camera system. This is accomplished through local calibrations of the average sinking velocity size distribution and elemental particle densities. This method, as tested in the subtropical North Atlantic Ocean and the Southern Ocean, demonstrates considerable skill in the estimation of particle fluxes and enables a dramatic improvement in the coverage of flux measurements well beyond what is possible with conventional sediment traps. Importantly, this all can be accomplished with only minor additions to busy ship-based sampling plans. The local calibrations of sinking velocity and elemental particle density proved to be critical for the accuracy of the flux estimations, as these properties substantially time. vary in space and

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Tracers of particle and plankton dynamics in the NW Mediterranean Sea

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The open sea observatory DYFAMED in the NW Mediterranean has been a platform for long-term monitoring over the past two decades. Besides regular water column studies and continuous particle flux measurements with sediment traps, several national and international process-oriented projects have focused on the dynamics of particles and plankton and how they relate to the flux and export of carbon and other elements in the sea. Within these studies, naturally-occurring isotopes of ²³⁸U series have been used to estimate particle flux, carbon export and the dynamics of settling material. Various plankton species take up these radionuclides and release them in biogenic particles (viz. fecal pellets) thereby playing an integral role within the processes governing particulate organic carbon flux. A review of key results will be presented, highlighting the relevance of natural-series radionuclides as a tool for understanding some key biogeochemical processes in the oceans.

Is the free cupric ion concentration a master variable controlling the vertical distribution of copper in the water column?

James W Moffett and Jeremy E Jacquot

Depth profiles of Cu show significant depletion in surface waters, indicating biological uptake, but vertical distributions do not look like nutrients. Instead, there is a relatively linear increase with depth similar to Th-230.

This has been attributed to the effects of particle scavenging in deep waters, which is thought to be more important for Cu than for Cd or Zn, which have characteristic nutrient-like concentrations. However, Cu does not behave like typical scavenged elements either (for instance Al), since concentrations increase with depth and are higher in the Pacific. Moreover, there is no in situ deep water source to account for this increase, as exists for the radiogenic Th-230.

Recent measurements of Cu speciation on the GEOTRACES North Atlantic Zonal Transect show that Cu is strongly complexed by organic ligands from the surface to the seafloor. The ligands are thought to be biologically produced, and bind Cu most strongly in the euphotic zone. Suprisingly, Cu is also bound extremely strongly throughout the water column, even within the benthic nepheloid layer. Free Cu concentrations in deep waters range from 10E-14 to 10E-13 M, less than 0.01% of total Cu. We argue that total Cu accumulation in deep waters is controlled by soluble organic ligands with the rate of removal determined by sinking particle flux, and the reversible distribution of Cu between soluble ligands and binding sites on particles that is determined by free cupric ion concentrations.

Speciation of Suspended Particulate Matter in the Western North Pacific Ocean

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Vertical profile seawater samples collected during the 2002 Intergovernmental Oceanographic Commission Contaminant Baseline Survey were analyzed for dissolved and suspended particulate matter (SPM) concentrations of Mn, Co, and Cd, along with SPM concentrations of lithogenic (Al, Ti), biogenic (P) and redox (Ce) tracers. By comparing the SPM trace metal concentrations against average "extended Redfield" and crustal estimates, an approximate speciation of SPM was determined. Elevated surface Co concentrations result from lateral subsurface input superimposed on the upwelling of Co-rich deep waters. This subsurface source is coincident with dissolved and/or particulate Mn inputs, suggesting that lateral margin inputs contribute more than Mn and Fe to the western Subarctic Gyre (WSAG). In contrast, SPM Cd concentrations reside primarily in biogenic particles and may be influenced by margin inputs, even though Cd itself does not seem to be delivered from the margin but may be scavenged by margin material. In summary, material derived from continental margins can directly or indirectly influence the biogeochemistry of some trace metals (e.g., Co and Cd), but physical processes hold significant influence over dissolved trace metal distributions in the western North Pacific. These results demonstrate that SPM speciation is an approximate but useful tool that reveals more information about the exchange between dissolved and particulate phases than dissolved profiles alone.

Particulate iron, aluminum and manganese in the Pacific equatorial undercurrent and low latitude western boundary current sources.

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A major advance in our understanding of the ocean trace metal cycle has been recognition of the significant role of coastal sources. There are many diverse mechanisms of particulate trace metal supply from coastal regions facilitated by advection in strong currents. The equatorial Pacific is one such example where coastal metal sources make a major impact. We collected and analyzed water column samples from 0 to 1000m from the central and western equatorial Pacific and from the northeastern coastal margin of New Guinea and New Ireland for total particulate Fe, Al and Mn. These new data were compared with previously published data for dissolved and total acid soluble Fe, Al and Mn. Leachable and refractory Fe, Al and Mn were calculated. There were large zonal gradients for all three particulate metals near the depth of the Pacific equatorial undercurrent. The subsurface maxima were highest in the west (145°E) and decreased significantly to 140°W. The maxima in all three particulate metals were at the same depth in the equatorial transect. The PFe and Pal concentrations were much higher along the NE coast of Papua New Guinea and New Ireland. There were significant correlations between PFe and Pal in the NGCU and NICU and equatorial stations. The correlations with PMn were variable suggesting that PMn may have some different sources. In all samples the leachable particulate fraction increased from Al < Fe < Mn. There were maxima in PFe_{ref} and PAl_{ref} in the NGCUU and NICU not seen in the PFe and Pal data. The primary source of PFe and PAI appeared to be material of riverine origin from the continental margin of Papua New Guinea and New Ireland. To understand how a particulate iron maximum could be maintained at a constant depth (density) across the equatorial Pacific we applied a simple model where leachable particulate iron (LPFe) was described by the balance between input of PFe due to advection balanced by losses due to remineralization and particle sinking.

Trace element composition of size-fractionated particles in the Mauritanian upwelling zone of the E. North Atlantic U.S. GEOTRACES section

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Sinking (>51 μ m) and suspended (~0.8-51 μ m) particulates were collected via *in situ* filtration during the US GEOTRACES North Atlantic Zonal Transect on the R/V Knorr in October-November, 2010. Total and acetic-acid leachable compositional profiles for key trace elements and isotopes (TEIs—Fe, Al, Zn, Mn, Cd, Cu) and other TEIs of interest (e.g. Co, Ti, Ba, V, Ni, Mo, P) were measured from four stations along the eastern tropical North Atlantic oxygen minimum zone (OMZ) extending from the coast of Mauritania to the Cape Verde Islands. This dataset provides a first look at full ocean-depth (16-point) profiles of sizefractionated particulate trace elements in this productive and biogeochemically complex region. Many elements present similar depth-profile shapes, indicating shared inputs, outputs Total concentrations of Al, Fe, and Ti all showed crustal and particulate dynamics. composition, and profiles indicated particulate inputs from lithogenic dust deposition from the Sahara in addition to resuspended particles from the African margin and bottom nepheloid layers. These lithogenic elements all had low leachable fractions (<8%), and had a significant proportion (60-75% in the surface; \sim 25% below) partitioned to the large size fraction. In contrast, elements more closely tied to the cycling of biogenic particles had higher leachable fractions (35-100%) and a smaller proportion partitioned to the large size fraction (<20% at all depths). The sinking and suspended particulate profiles of Al, P, and Ba are examined in closer detail, offering insights into the behaviors of lithogenic particles, biogenic particles, and size-fraction particle dynamics, respectively.

On the paleoceanographic potential of Nd isotopic composition (ε_{Nd})

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Covariation of Nd isotopic composition (e_{Nd}) with salinity and potential temperature, particularly in the Atlantic ocean, indicates the potential of e_{Nd} as a water mass tracer (e.g., Goldstein and Hemming, 2003). Moreover, e_{Nd} can be extracted from marine sediment cores and shows considerable variations on glacial-interglacial time-scales that are assumed to reflect past changes in ocean circulation (e.g. Rutberg et al., 2000).

We included isotopes of Nd into a cost-effcient, low resolution model of intermediate complexity and are able to reasonably simulate both, e_{Nd} as well as Nd dissolved concentration (Rempfer et al., 2011). However, yet considerable uncertainties are associated with the exact nature and magnitude of Nd-sources and sinks, e.g., it was shown that reversible scavenging of Nd by settling particles is an important component of the Nd-cycle (Siddall et al., 2008; Arsouze et al., 2009; Rempfer et al., 2011). On the other hand, it remains unknown whether Nd is preferentially scavenged by certain particle-types.

Our comprehensive approach, together with the computational efficiency of our model, allows us to evaluate the paleoceanographic potential of e_{Nd} . In this study we apply freshwater fluxes to the North Atlantic, as well as to the Ross and Weddell Seas, thereby modifying the meridional ocean overturning circulation. These experiments allow us to examine how well e_{Nd} reflects changes in the ocean overturning circulation for the first time.

Ecosystem composition as well as productivity (and thus particle export fluxes) have not been constant in the past (e.g.. Gil et al., 2009). Similar to previous modelling studies (e.g. Schmittner, 2005), the marine ecosystem, and thus export fluxes, are affected by reorganisations in the ocean overturning circulation in our model. In additional model simulations we therefore examine to what extent marine sediment records of eNd at different locations might be affected by variations in the magnitude and composition of particle export fluxes.

Particulate Matter in the upper 1000m of the water column from 62°N to 5°S, Eastern Atlantic Ocean from the A16N CLIVAR-Repeat Hydrography Cruise

Pamela Barrett and Joseph Resing (Corresponding Author)

We plan to show particulate data from the A16N transect through the north eastern Atlantic Ocean. Suspended particulate matter from the top 1000m of the water column at 52 stations from $62^{\circ}N$ to $5^{\circ}S$ was collected with a resolution of approximately 1 - 2 degrees during the northern hemisphere summer from June 20 to August 7, 2003. The samples were collected by filtering approximately 8L of seawater though acid-cleaned 0.4 µm polycarbonate filters and analyzed for concentrations of Al, Si, P, K, Ca, Ti, V, Cr, Fe, Ni, Cu, Zn, and Sr by energy-dispersive X-ray fluorescence.

These sections demonstrate that the particulate matter signal in the eastern Atlantic Ocean is dominated by Saharan dust inputs, although European and other anthropogenic sources are significant for some trace elements such as V, Cr, Ni and Cu. The deposition of dust to the surface ocean is controlled by the seasonal transport of Saharan dust across the Atlantic Ocean which follows the seasonal migration of the Intertropical Convergence Zone between 0 -10° N during the northern hemisphere winter and $10 - 20^{\circ}$ N throughout the summer. The relatively short residence time for particulates in the surface ocean results in suspended particulate concentrations and compositions mirroring this seasonal signal. The rapid transport of this particulate matter to the sub-surface results in the entire upper water-column particulate signal being dominated by the deposition of Saharan dust. The large dust load appears to enhance scavenging of dissolved metals from the water column, promoting, in part, shortened residence times for dissolved Al in the surface ocean and the removal of remineralized dissolved Fe at depth, which results in the elevated N:Fe ratios reported by Measures et al. (2008).

Our data also reveal a deficit of particulate calcium (pCa) in the water column at depths below 450m between $5 - 20^{\circ}$ N, coincident with low pH and high DIC found in the oxygen minimum zone of the eastern Atlantic. Relative to crustal abundance, the deficit in pCa appears to be primarily in the biogenic fraction. Calculations indicate lowered saturation states for calcite and aragonite throughout this region below 450m, although waters remain supersaturated with respect to the mineral phases.

Variations in particle size and density: implications for the ballast hypothesis

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Large fast sinking marine snow aggregates, are a major pathway for the transfer of particulate organic carbon from the surface to the deep ocean, regulating atmospheric CO_2 levels on climatically significant timescales. Size and density influence particle sinking speed, which is an important determinant of the remineralisation depth, thus the quantity of carbon sequestered into the abyss. We collected two types of particles, marine snow aggregates (> 90% of total particles) and aggregate protist complexes (< 10 % of total particles) at various depths between 50 and 400 m from the North Atlantic and Arctic. Measurements were made of particle sinking speeds $(12 - 445 \text{ m day}^{-1})$ and diameter $(195 - 1257 \mu\text{m})$. Particle excess densities were calculated to be 0.01 (\pm 0.001) and 0.04 (\pm 0.02) g cm⁻³ for MSA and APC respectively, based on literature values of aggregate organic matter density and particle porosity. Only particle size positively correlated with sinking speed, suggesting size regulates sinking speed rather than density in the top 400 m. This is supported by a simple model suggesting MSA sinking speeds are more sensitive to changes in particle size than density. However, as particles become smaller with depth (> 500 m) the sensitivity of sinking speed to changes in density increases relatively. This compares to the modelled APC sinking speeds which show a greater sensitivity to excess density than size, implying for this subset of particles ballasting occurs. We conclude a critical threshold between sinking speeds controlled by size, and those controlled by density must be determined by the POC: biomineral ratio and that the dominance of density over size (i.e. ballasting) in determining sinking speeds may be restricted to smaller particles in the deep ocean.

Partition coefficients of trace elements: from the ocean to the models

Keynote

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The chemical behavior of particle-reactive metals such as Th, Pa, Nd and other REE is often characterized by a partition coefficient between seawater and marine particles in agreement with the reversible scavenging model developed to explain the distribution of Th isotopes. Precisely constraining these partition coefficients and there dependency to the chemical composition of the marine particles is a serious challenge for fully using Th, Pa, Nd as ocean tracer and paleotracer and for modeling them. Partition coefficients have been studied using many approaches:

- Correlation of trace elements with the main components of marine particles. However, fortuitous correlations between components produce conflicting interpretations (eg: ²³⁰Th). This approach mainly applied to sediment trap must be extended to suspended particles.

- Sorption experiments using natural or artificial seawater and particles.

- for elements derived from continental erosion (Nd, ²³²Th, Hf), the authigenic fraction of particles is determined by leaching, although the selective dissolution of authigenic phases is rarely demonstrated.

- More recently the development of physical phase separation technics have brought new insights by partially isolating/enriching some carriers.

- the development of the analysis of individual particles allows the unambiguous determination of some carriers. Particle observation should be systematically coupled to particulate matter analysis.

Besides these methodological aspects, some fundamental aspects of the tracer's behavior must be addressed:

- kinetics as marine particles are not necessarily at equilibrium with the local seawater as demonstrated by the multi-tracer approach.

- the role of the colloidal phase.

- the possible role of mineralization in changing the bulk composition of particulate matter and hence its bulk partition coefficient.

Practical impacts of these methods and of their pitfalls will be discussed both in terms of experimental procedures and of modeling of Pa, Th and Nd. Several models "successfully" represent the Nd concentration and isotopic composition in the ocean but use in fact significantly different particle dynamics and partition coefficients, calling for more data to constrain the models.

Chemical characteristics of iron-rich nano- and colloid-sized particles in the South Atlantic and Southern Oceans

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A novel synchrotron-based technique was applied to show for the first time the variability in the chemical properties of iron-rich nano- and colloid-size particles in oceans. Although, the role of iron in ocean primary productivity is well known, there is no consensus or understanding of the extent of its bioavailability. Currently, iron in oceans is operationally defined and is based on size with $<0.2 \ \mu m$ fraction considered as dissolved and bioavailable. The use of operational definition is the norm for the lack of an available robust method to chemically characterize iron in small size fractions. The size-based paradigm; however, fails to take into account the chemical speciation that primarily controls the behavior of any element in nature. As such, the current classification system for iron is inadequate and possibly the cause of failure to explain the observed variability in bio-inorganic interaction of iron and hence productivity in different parts of the oceans. In this study we not only show ubiquitous presence of nano- and colloid-size iron particles that may be considered "dissolved" but with our method we are able to show their distinctly variable chemical characteristics. We classify the observed particles into five distinctive categories according to their Fe valence state with each phase expected to behave differently. Furthermore, we show wide variation in the spatial distribution of these phases in the ocean. Of note is the increased significance of ferrous rich species in the higher latitudes. Solubility differences and spatial variability of observed pure and mixed Fe-rich phases is likely to control iron uptake pathway and phytoplankton growth.

Bottom and intermediate nepheloid layers

Keynote

Michiel Rutgers van der Loeff and Sven Kretschmer Alfred Wegener Institute, Germany

In the deep ocean, the depth profile of suspended particles (SPM), mostly measured as beam attenuation, usually shows a minimum at mid-depth. Below this clear water minimum, SPM load gradually increases and often a dramatic increase is observed close to the seafloor, the benthic nepheloid layer (BNL). In the deep water and especially in this BNL, particles can be transported over very large distances. Thus, the BNL is affected by horizontal advection, fresh new particle rain and exchange with the surface sediment by the resuspension-settling cycle. Reversible particle-water exchange (scavenging and release) and grain size sorting will continue to adjust the distribution of trace elements and their isotopic composition over the particulate and dissolved phases. We want to discuss how this interaction between vertical and horizontal transports affects the tracer signals recorded in the surface sediments.

Lessons learned from sediment traps and other strategies about organic C fluxes – challenges and questions for the TEI community

Keynote

Richard Sanders, Jennifer Riley, Fred LeMoigne, Sarah Giering, Chris Marsay, Adrian Martin, Richard Lampitt

all at the National Oceanography Centre, Southampton, U.K.

The biological carbon pump, mediated principally via the sinking of organic matter from the surface ocean, is a significant term in the global carbon cycle. It transfers annually 5-15 GT C yr⁻¹ out of the photic zone, an amount comparable to the annual accumulation of CO₂ in the atmosphere driven by anthropogenic processes, and mediates a storage of CO₂ in the ocean interior without which atmospheric CO_2 would be much larger than it is today. Yet most of the material exported from the photic zone does not penetrate the deep ocean, instead it is mineralised in the twilight zone with fluxes in the thin 100m thick layer under the photic zone being extremely rapidly attenuated. The shape of this attenuation varies in time and space yet appears to be a critical determinand over atmosphere - ocean CO₂ partitioning. Attempts to predict this attenuation using independent measures of heterotrophic activity have often to not yield the observed pattern of attenuation implying substantial uncertainties in one or more of the terms that enter into the comparison. In this talk we will describe direct estimates of particle flux made using drifting neutrally buoyant traps together with associated radiochemical assays, individual assays of sinking material and associated estimates of heterotrophic activity. We show that frequently a subset of the pelagic planktonic pool contributes disproportionately to carbon export, that multiple pools of organic matter delineated by sinking rate occur and finally that, although we can make substantial progress towards closing the mid water C budget we still have a significant excess of carbon consumption over supply. We believe that this is due to erroneous steady state assumptions, a hypothesis we explore via simple numerical models.

Biopolymers as carriers of natural (Th, Pa, Pb, Po, Be) radionuclides in aquatic systems

Keynote

Peter H. Santschi, Chia-Ying Chuang, Kathleen A. Schwehr, Chen Xu and Saijin Zhang (Texas A&M University at Galveston, TX 77553, USA)Abstract

Th(IV), Pa(IV,V), Po(IV, II,-II), Pb(II) and Be(II) radioisotopes are important proxies in oceanographic investigations, e.g., for tracing particle dynamics and particulate organic matter (POC) fluxes out of the euphotic zone, and for studying boundary scavenging, paleoproductivity and ocean circulation. Even though considered routine, these approaches rely on often poorly constrained, empirically determined and variable isotope ratios or ratios to POC. Previously published laboratory and field investigations suggest that a number of biopolymers, potentially produced by both phytoplankton and bacteria, could be carrier molecules for most of these isotopes, rather than purely inorganic surfaces [e.g., 1-8]. We hypothesize that specific binding by bio-macromolecules located on the surface or interior of marine particles and colloids, as well as redox processes mediated by these biomolecules, control marine scavenging of the different radioisotopes [Figure 1]. The most efficient binding of many of these isotopes likely occurs to acid polysaccharide- and proteincontaining biomolecules, i.e., proteoglycans or glycoproteins. Ongoing experiments attempt to separate, identify and characterize radioisotope carriers that are hypothesized to be effective binding ligands for a particular radionuclide. Our interdisciplinary research project requires an array of instrumental approaches (e.g., HPLC, GC-MS, NMR) for characterization studies, in combination with controlled laboratory and field experimentation. Laboratory studies consist of comparative uptake experiments of a suite of naturally occurring radionuclides to a number of substrates, including model organic and inorganic compounds, marine colloidal and particulate organic matter, and biopolymers harvested from cultures. The field program includes collections and characterization of diverse types of suspended and sinking organic matter from different parts of the ocean. 10s of mg of colloidal and particulate organic matter samples were collected in the Pacific Ocean using ships from our collaborating institutions in Taiwan. New and unpublished experiments carried out so far indicate that when organic matter is present in diatom frustules grown in the lab, and cleaned to selectively remove organic matter, the presence of diatom-associated organic matter greatly enhances particle-water partitioning and shows high selectivity to all radionuclides, including those of Th, Pa, Po, Pb and Be. The highly selective adsorption on different particles and colloids of different origins resulted in evident fractionations. This suggests that chemical composition and types of organic functional groups are indeed crucial factors in the fractionation of all selected radionuclides in seawater. These preliminary results have both biogeochemical and paleo-oceanographic implications.



Fig. 1: Schematic of interactions between (radioactive) metal ions and marine particle assemblages.

References

- Quigley, M.S., Santschi, P.H., Hung, C.-C., Guo, L., and Honeyman, B.D. 2002. Limnology and Oceanography, 47, 367-377.
- [2] Guo, L. Hung, C.C. Santschi, P.H. and Walsh, I.D. 2002. Mar. Chem., 78, 103-119 (2002).
- [3] Santschi, P.H., Hung, C.-C., Guo, L., Pinckney, J., Schultz, G., Alvarado-Quiroz, N., and Walsh, I. Geophysical Res. Lett., 30, Art. No. 1044 (2003).
- [4] Roberts, K.A., Santschi, P.H., Hung, C.-C., Xu, C., Conte, M.H. 2009. Earth Planet Sci. Lett., 286, 131-138 (2009).
- [5] Hung, C.-C., Xu, C., Santschi, P.H., Zhang, S., Schwehr, K.A., Quigg, Guo, L., Gong, G.-C., A., Pinckney, J., Long, R., and Wei, C.-L. Mar. Chem, **121**, 132–144 (2010).
- [6] Xu, C., Santschi, P. H., Hung, C.-C., Zhang, S., Schwehr, K,A., Roberts, K.A., Guo, L.D., Gong, G.-C., Quigg, A., Long, R., Pinckney, J., Duan, S.W., Amon, R., Wei, C.-L. Mar. Chem., 123, 111–126 (2011).
- [7] Zhang, S., Xu, C., and Santschi, P.H. 2008. Marine Chemistry, 112, 81-92.
- [8] Xu, C., Zhang, S., Chuang, C.-Y., Miller, E.J., Schwehr, K.A., Santschi, P.H. 2011. Marine Chemistry, in press.

Potential of inverse methods in studies of ocean biogeochemical cycles Keynote

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Abundance, vertical flux as well as adsorption/desorption properties of particles are important factors affecting the oceanic distributions of many TEIs. While most of these controlling parameters can be measured directly (in the field or under laboratory conditions), obtaining reliable, basin-wide or global averages is still very difficult because of large spatial and temporal variability. Results from numerical models complement the direct measurements and can help quantifying the parameters on regional and global scales. In this talk I review existing inverse models aiming at quantifying particle flux, remineralization rates and scavenging properties and highlight their capabilities and limitations. Data requirements and potentials for improvements are also discussed.

Using Isotopes to Reconstruct Glacial Ocean Nitrogen and Carbon Cycles

Andreas Schmittner, Oregon State University

Carbon and nitrogen isotopes are among the most measured data from sea floor sediments. They contain information about nitrogen and carbon cycling in the past. We have implemented nitrogen (δ 15N) and carbon (δ 13C) isotopes in a global ocean circulation biogeochemistry model. Nitrogen isotopes are influenced by nutrient uptake by phytoplankton, denitrification, I will present initial results from simulations of the Late Holocene (LH) and the Last Glacial Maximum (LGM) in comparison to existing compilations of sediment data. Nitrogen isotope data have been compiled by the PAGES working group NICOPP (Nitrogen Cycling in the Ocean, Past and Present). Initial core top data reveal complex patterns such as high values along the eastern boundaries and towards the interior subtropical gyres and in the Arabian Sea and low values along the western boundaries, along the equator at high latitudes and in the Mediterranean. The model reproduces many of these patterns. Possible reasons for discrepancies are discussed. LGM data show lower values in regions affected by denitrification and higher values in regions affected by nitrogen fixation, qualitatively consistent with the model results. Reduced denitrification, both in the water column and in the sediments and reduced nitrogen fixation are most likely the reasons for these changes. The model does not reproduce the elevated nitrogen isotope values found in the LGM sediment data from the Southern Ocean. The model is also unable to reproduce the very negative $\delta 13C$ values measured in glacial sediments of the South Atlantic. Both model deficiencies are presumably caused by the lack of iron limitation of phytoplankton in the model. Increased aeolian dust fluxes during the glacial could have increased nutrient drawdown in the Southern Ocean, increasing the efficiency of the biological pump and reducing atmospheric CO2. Including iron cycling in the model will therefore be important in order to improve LGM simulations in the future.

Sampling particles in the ocean: Go-Flo bottles vs. in situ pumps

Keynote

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During GEOTRACES Intercalibration and Methods Development effort, we worked to optimize and compare techniques for the accurate and precise sampling and determination of suspended particulate trace metals (TMs) from full water column profiles in various oceanic regimes. The goal was to determine the best particle collection and analysis methods for future GEOTRACES ocean basin sections and to carry out laboratory intercalibration to arrive at community consensus on analytical methods and results. Results from the Atlantic and Pacific Intercalibration cruises (IC1 and IC2; 2008-09) will be presented, with a focus on the feasibility of accurate and precise determination all key GEOTRACES and other TMs of interest, from relatively small volume (~5-10L) samples collected from rosette-mounted Go-Flo bottles. I will summarize our findings with respect to filter type, practical performance, blanks and potential artifacts such as dissolved metal adsorption. Details of the filtration methodology will be described, with an emphasis on minimizing element-dependent particle settling artifacts and determining appropriate procedural blanks. Digestion methods for particulate samples will be evaluated and results from an interlaboratory intercalibration exercise will be presented, with a summary of ICP-MS analytical approaches. Results for samples collected using Go-Flo bottles will be compared with parallel samples collected with large-volume in situ pumps. The advantages and limitations of each method will be compared, and indeed the limitations on the design of a definitive methodological comparison experiment will be discussed. Finally, highlights of the distributions of particulate TMs revealed during the Intercalibation cruises will be presented as potential fodder for hypotheses to be tested during future GEOTRACES field studies.

The role of suspended matters on Fe horizontal transport from continental shelf to the ocean interior

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Recent studies have indicated that the oceanic transport processes of Fe from the continental shelf are increasingly recognized as important for Fe supply to the open ocean. In this study, to obtain insights into the role of suspended matters on horizontal transport of Fe from continental shelf to the ocean interior, we measured suspended matter concentrations in the sea water and Al, Mn, Fe and Ba concentrations of it. The suspended matters were collected, by using a large volume in-situ filtration system, in the intermediate layer of the Sea of Okhotsk along the transect from the continental shelf to the open ocean. The sampling depths targeted the layer having a density of 26.7-27.0 sigma-theta which corresponds to the cold and dense water on the continental shelf (dense shelf water: DSW). DSW flows out into the ocean interior with a lot of particles at the shelf. The suspended matter concentration in the sea water decreases with distance offshore, and Al concentration in the suspended matter also decreases. In addition, the ratios of Ba, Mn and Fe to Al increase with distance offshore. Assuming that the suspended matters in the intermediate layer are influenced mainly by horizontal transport from the continental shelf to the ocean interior and Ba can be used as a proxy for organic matter, the results indicate that the proportions of non-lithogenic material like organic matter, and probably labile Mn and Fe in the suspended matter increase in the course of DSW while the suspended matter itself decreases. This might be caused by the loss of dense particles like lithogenic matter, and the increases of probably labile Mn and Fe which might be derived from organic matter and/or redox-mobilized labile sources at the continental shelf.

Role of episodic events on the settling particulate matter composition and element fluxes in Alfonso Basin, La Paz Bay, Gulf of California: 2002-2008 sediment trap series

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The oceanic biogeochemical cycle creation requires settling particulate matter composition and vertical element flux quantification. This approach was conducted in Alfonso Basin, 410 m deep part of La Paz Bay, Gulf of California, with a desertic-arid limate. Settling particulate matter was collected each 7-15 days by an automated sediment trap during 2002-2008. Major and trace elements were determined using instrumental neutron activation analysis. The particles collected so far show that the total mass flux, composition and different particulate element fluxes show a high variability, not exactly coinciding with each other. Some element changeability seems to be influenced by different origin extraordinary events. Tropical cyclone effect was noted for "Ignacio" (24-26 August, 2003), "Marty" (21-23 September, 2003) and "Henriette" (4-5 September, 2007) hurricanes, on scandium composition, and represents the fluvial terrigenous input. Dust storm effect was found for scandium content and fluxes, related to increased aeolian input during strong northwestern winds on fall-winter. Plankton blooms in June and August of 2002 enhanced the calcium and bio-calcium content in settling particles. A reported silicoflagellate bloom during December, 2007 correlated with the highest particulate calcium and bio-calcium flux. Earthquake influence wasn't registered during the time period, even for a maximum 6.3 magnitude event.

Associations and enhanced enrichments of some micronutrients, chalcophilic and redox-sensitive trace elements in time-series sinking particles from Alfonso Basin, SW Gulf of California

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Alfonso Basin is a natural sedimentation environment in the La Paz Bay, southern Baja California Peninsula, located an arid subtropical region characterized by limited land runoff with a productive surface layer overlying a well-developed Oxygen Minimum Zone, very attractive for regional paleooceanographic studies because of excellent lamination of its sediments. A time-series sediment trap program was initiated in 2002 and is still in action to help understand the processes controlling variations in the biogeochemistry of this environment. INAA, ICP-MS and ICP-OES analyses, as well as flame AAS were made for major and trace elements in 105 subsamples of material collected at 350 m depth during 2002-2005. Principal component analysis, including data for organic and inorganic carbon, biogenic silica and the lithogenic fraction, yielded four factors. Factor 1 (25% of the total variance) showed high eigenvalues for the classical terrigenous aluminosilicate elements: Al, Fe, Mn and Sc. High loadings also occurred for the group of light to medium REEs (except for Eu). The latter are frequently associated with acid source rocks, such the granites and rhyolitic volcanics exposed on the margin of the bay. Factor 2 (18%) grouped mainly REEs, with high loading on the heavier members of the series that are more typical of basic rocks (thick sequences of andesitic volcanics occur to the NW), as well as Ni and Rb. Factor 3 (12%) appears to represent carbonate organism production, with high loadings for inorganic carbon, Ca and moderate levels for organic carbon, while % litho is moderately negative, as is biogenic silica. The fourth factor (9%) is characterized by high negative loadings for Cd, Co, Se and moderately negative values for organic carbon. Moderate positive loadings occur only for Sr and, at lower levels, for U, Sb and % lithogenic. This suggests that this grouping is related to particles that have been partially transformed within the Oxygen Minimum Zone. The results will be examined for distinctive periods within the time-series, such as the hurricane-influenced months of August-September 2003, the generally very low fluxes during 2005, and unusual peaks during winter 2002.

The elements listed in as controlled by last factor (mainly micronutrients and chalcophilic elements) are enriched in sinking particles of a time series, especially in some periods. The average enrichment factors (EFs), estimated using Sc as a normalizer, show high values during 2003-2005: Se (117-927), Sb (10-53), Cd (17-41), As (14-19), Pb (3-36), Sr (3-10), U (2-6), Ca (3-5), Zn (3-5), Cu (1.3-5.4), Ba (1.8-4.3), Mo (2-2.8), Co (1.9-3.6). They were generally enriched during anomalous 2002 year especially Se (1448), Sb (470), As(239), U(61), Cd (35), Sr (31), Mo(26), Zn(15), Ca (11), Cs (9), Rb (6.5). Such an increase of EFs of some elements (As, Mo and U) occurred mainly during late spring-summer of 2002, on first stage of moderate El Niño, when the waters from subtropical and tropical Pacific Ocean presumably entered into the La Paz Bay, carrying less oxygen, less terrigenic material and bringing tropical and subtropical plankton species. These specific conditions favoured to decrease of the remineralization rates of sinking biogenic particles, to possible formation of less soluble Cd, Cu and Zn sulphides, as well as to Mo and U particle scavenging in their lower (+4) oxidation state.

Quantifying the role of bacterial extracellular enzymes in particle remineralization processes

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Bacteria are critical for organic matter transformation in the water column. Extracellular enzymes are the key mechanism used by bacteria to consume organic matter which is formed in the surface ocean via primary production. Bacteria can only transport bits of organic molecules into the cell, and have adapted to overcome this constriction by producing extracellular enzymes to cleave bits of organic matter from larger molecules, effectively transferring an essential function to the external environment. In order to assess the nonlinear effects of remineralization, we have developed a model to look at production and activity of bacterial extracellular enzymes in the context of marine ecosystems. Parameters include six state variables: dissolved organic matter, particulate organic matter, free-living bacteria, particle-attached bacteria, extracellular enzyme, and hydrolysate. Some important dynamics incorporated in the model stem from experimental discoveries: extracellular enzymes lifetimes are temperature dependent ranging from 24 to 100 hours or more; hydrolysate and enzymes diffuse from particles to the surrounding seawater. The latter dynamic, in particular, determines the interaction between particles and dissolved phases in the pelagic environment and is therefore likely involved in trace element cycles.

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Observing particles in situ using optical cameras

Keynote

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Ouantifying chemical elements fluxes through trophic webs and from the surface to the deep ocean requires the ability to detect and identify all organisms and particles in situ and in a synoptic manner. An idealized sensor should observe both the very small particles and protozoa and the extremely large particles such as aggregates, and plankton. Such an instrument would reveal an astonishing amount and diversity of living and non-living particles present in parcel of water. However, from the sensors perspective, any detected object is a particle, living or not and the difference may be hard to tell. Living particles can be bacteria, phytoplanktonic and zooplanktonic organisms. Particles range from micrometric detritus to assemblages of complex detritus forming aggregates; the latter can also include living cells of phytoplankton or can be colonized by microbes and even small zooplankton. It is very important to distinguish particles nature (living, non living, organic, minerals) because it has an impact on elements pathways within trophic webs and on vertical fluxes. A convenient way to analyze the size properties of particles is to first sort them according to their nature and their size and then compute a size distribution histogram. Unfortunately past sensors did not achieve this goal easily because of their inability to determine particles nature or to be deployed in a synoptic manner. However, recent technological developments now allow better measuring in situ particles and plankton optical properties and size distributions in a way that synoptic surveys are possible. This presentation deals with particle and plankton size distributions, particle geometry, nature and spatial distribution obtained from these instruments. Finally, we will suggest how these new data sets could be integrated into sizestructured mathematical models of biogeochemical fluxes.

Sensitivity of TEI cycles to metal-organic complexes in biogeochemistry models **Keynote**

Alessandro Tagliabue

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The importance of organic complexation to the oceanic cycling of trace elements is now well established. This aspect has received particular attention with regard to the cycle of iron (Fe) due tothis elements role as a limiting nutrient in regions of the world's Oceans important for carbon cycling and air-sea CO2 exchange. Dissolved Fe (dFe) species, including those in the colloidal size fraction, are known to be almost 100% complexed to one or more types of organic ligands (L), which has impacts on the residence time of dFe in the ocean. Traditionally, ocean models have assumed fixed concentrations of Fe binding ligands and full bioavailability of organically bound Fe (FeL), which is at odds with current measurements that suggests variable concentrations of L that are beginning to illuminate potential production pathways. Moreover, FeL appears accessible to the biota, although less so than uncomplexed dissolved forms. In this talk, I will briefly review how Fe

complexation is considered in current models and then introduce new advances that aim to reproduce the observed variability in the measured oceanic distributions of ligands. To address bioavailability implications, different assumptions are made regarding the specific nature of the bioavailable Fe pool, as well as the affinity different phytoplankton may have for different Fe species. Of particular interest will be how these assumptions govern viable dFe uptake strategies in different ocean regions, both now and in the future. Throughout I will focus on how organic complexation of dFe, and its variability, impacts upon dFe losses via controls on scavenging and biological uptake rates. Finally, I will outline potential new means by which coupled modelexperimental approaches may reduce uncertainties.

A global compilation of over 13,000 dissolved iron measurements: focus on distributions and processes in the Southern Ocean

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Due to its importance as a limiting nutrient for phytoplankton growth in large regions of the world's oceans, ocean water column observations of concentration of the trace- metal iron (Fe) have increased markedly over recent decades. Here we compile >13,000 global measurements of dissolved Fe (dFe) and make this available to the community. We then conduct a synthesis study focussed on the Southern Ocean, where dFe plays a fundamental role in governing the carbon cycle, using four regions, six basins and five depth intervals as a framework. Our analysis reveals the importance of biological activity and dFe inputs in governing the inter-region and inter-basin differences in surface dFe, respectively. In deep waters, the major controls of inter-region and inter-basin dFe variability are ligand distributions and deep dFe inputs or water mass characteristics, respectively. We find that even in regions where many dFe measurements exist, the processes governing the seasonal evolution of dFe remain enigmatic and missing measurements during key seasonal transitions make it difficult to quantify and understand surface water replenishment processes. Statistical differences exist in the measured dFe between measurements taken over the period 1989-2002 and 2003-2008, which may reflect progress in clean sampling and analysis techniques. Finally, we detail the degree of seasonal coverage by region, basin and depth. By synthesising prior measurements we suggest a role for different processes and highlight key gaps, which we hope can help structure future research efforts in the Southern Ocean.

The role of complexation in metal partitioning between solution and particles **Keynote**

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The GEOTRACES protocols do not address the question of the chemical speciation of trace metals, but include a size-based separation between dissolved and particulate metals. This approach has proved a successful base for the development of intercalibration and quality assurance procedures. However, it is the chemical speciation within these fractions that determines the biogeochemical activity and fate of the individual trace metals. This presentation will focus on the dissolved fraction. When considering this fraction it is important to remember that the original justification for a division at 0.45 μ m was to separate sedimenting particles (colloids). This has led to the concept of "truly dissolved", consisting of entities smaller than 1 nm, where chemical speciation can be described in terms of complexation. It is important to note that humic substances and other organic materials, whose interactions with trace metals are often treated as complexation, fall within the colloidal size range.

Within the truly dissolved fraction, complexation of trace metals by inorganic ligands constitutes the base for studies of chemical speciation. Hydroxide and carbonate are the dominant ligands for most trace metals, with the exception of soft or (b)-type metals such as Cd, Ag and Hg, where chloride is the dominant ligand. The inorganic chemical speciation of a trace metal in seawater is readily calculated provided that the relevant thermodynamic data are available. These data may take the form of conditional (concentration-based) stability constants, or thermodynamic (activity-based) stability constants together with the relevant activity coefficients. Whichever form is used, the resulting speciation will be a function of four master variables: salinity, temperature, pressure (depth) and pH. In surface ocean waters, temperature is the master variable providing the largest source of variability. However, when considering the entire water column, changes in pressure and pH are also expected to contribute significantly.

Many trace metals are also complexed by poorly defined organic ligands. Competitive ligand techniques such as CLE-CSV are used to characterise this binding, treating the organic material as simple ligands, and thus ignoring the complexity of the organic material. Techniques based on ligand competition may provide an incomplete picture of metal binding since the binding strengths characterised are restricted to a limited range, the detection window, although this can be overcome by using several competing ligands of different binding strength.

How can information on chemical speciation contribute to GEOTRACES and to an understanding of dissolved-particulate partitioning? GEOTRACES is for the first time

providing quality-controlled distributions of dissolved trace metals in the oceans. Descriptions of the chemical speciation of these metals would lead to corresponding distributions of the biogeochemically active metal species (free metal ions or specific complexes). This information will be essential in developing mechanistic insights into the fluxes and fate of trace metals, including key processes such as dissolved-particulate partitioning. The first step would be to assess the availability of the relevant data. Complexation by organic matter is expected to be a major limitation, most particularly for those metals that are strongly complexed by these ligands.

Role of plankton in the cycling of trace elements & isotopes

Keynote

Ben Twining, Bigelow Laboratory for Ocean Sciences

Planktonic organisms play several important roles in the cycling of trace elements in the open ocean. Phytoplankton accumulate bioactive metals and export these in sinking biomass. Phytoplankton can also alter the speciation of dissolved metals in the euphotic zone through ligand production and cell-surface redox processes. Zooplankton recycle plankton-associated elements back to the dissolved phase, potentially in different forms, and also enhance vertical element fluxes through migration and production of rapidly-sinking fecal pellets. Furthermore, plankton biomass comprises a significant portion of particulate matter in the Plankton thus mediate many transformations of trace elements between open ocean. particulate and dissolved forms in the upper ocean. I will review the state of knowledge regarding these processes in the upper ocean, including results from multi-disciplinary efforts to quantify metal accumulation and cycling within plankton communities and recent measurements of trace metal composition of plankton in different ocean basins. Much of our understanding of metal-plankton interactions has been the result of experiments with cultured phytoplankton, and I will assess the application of these data to natural systems. I will also discuss recent techniques such as sorting flow cytometry and single-cell element analysis that are enabling more targeted studies of trace metal accumulation by plankton, allowing us to move beyond a generalized stoichiometric view of trace element accumulation by plankton.

Aluminium in a general circulation model compared with the West-Atlantic section cruises of Geotraces-Netherlands

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A model for aluminium is implemented in PISCES, the biogeochemical component of the ocean general circulation model NEMO. The model considers two forms of aluminium (dissolved and adsorbed/particulate). By comparing model results with the observations done in the Geotraces project, free parameters in the model are adjusted to fit the spatial distribution of the data. In this way a 3D picture of aluminium is obtained that best fits the data. It is assumed that dust is the most important input for aluminium in the ocean. The output of an atmospheric dust model is used to force the model. Starting from a reference experiment, which more or less reproduces the Atlantic GEOTRACES-NL observations, we set up simulations where we change core parameters like the solubility of dust and the partition coefficient for the amount of dissolved relative to adsorbed aluminium. In this way we test the sensitivity of the model and see whether the current model can capture the observations reasonably well or whether we need other sources like sediment input or other processes besides scavenging, e.g. the biological incorporation of aluminium into diatoms. We show the effects of changing several parameters and sources, among the insignificance of dust dissolution in the deep ocean and in the model the need for biological incorporation of

aluminium into diatoms.

ANALYSIS OF SINKING PARTICLE SPEED THROUGH THE WATER COLUMN USING ²¹⁰Po-²¹⁰Pb CONCENTRATION PROFILES

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A simple one-box model of ²³⁴Th uptake and removal in the water column is widely used to calculate downward ²³⁴Th and POC flux. The elemental pair of ²¹⁰Po-²¹⁰Pb is frequently proposed as an alternative method to estimate carbon fluxes which should offer significant advantages due to its different half-life (138 days) and biogeochemical behaviour. Due to its long half-life, a ²¹⁰Po deficit is maintained below the euphotic zone and penetrates much further into the twilight zone than ²³⁴Th. However to use ²¹⁰Po and ²¹⁰Pb profiles to analyse the twilight zone it is essential to have full knowledge of the mechanisms and processes that affect ²¹⁰Pb and ²¹⁰Po activities at depth in both dissolved and particulate phases. These include sinking particle sizes and velocities, advection effects, integration times, etc.

Using the ²¹⁰Po method still poses several unanswered questions e.g. is it accurate to use a one-box model when such a variety of parameters are involved or to assume steady state conditions and which would be the expected depth for ²¹⁰Pb and ²¹⁰Po to reach secular equilibrium. We address these issues by modelling ²¹⁰Po activity down the water column. The model is compared to profiles from a cruise on RRS Discovery to the PAP site in summer 2009. Modelled ²¹⁰Po activities are in very good agreement with experimental values, although at 1000 m modelled values are usually higher that the experimental ones. A key output from the model is downward sinking velocities. This rises from (45±25) m·d⁻¹ at 50 m, to (70±25) m·d⁻¹ and (80±15) m·d⁻¹ at 150 and 500 m. For 50 m, values show a high (60%) standard deviation, which is reduced to 35% at 150 m and 20% at 500m. Despite the scatter an increase of the velocity is observed from the shallower to the deeper depths. Our conceptual model of particle flux based on these data consists of two pools of material with the faster sinking pool dominating deeper in the water column and a slow sinking pool making a more significant contribution in the upper ocean. This model is consistent with upper ocean data from the same cruise obtained using the marine snow catcher.

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δ^{13} C and δ^{15} N in PM as Tools to Mapping Provenance of Organic Carbon in Eutrophic Coastal System

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Guanabara Bay is circumscribed by the city of Rio de Janeiro (Brazil) and is dominated by seawater influence. This urban estuary for a number of low runoff rivers (total runoff of about $150 \text{ m}^{-3}\text{s}^{-1}$) receives large load of untreated sewage and industrial wastes, serving also as base for activities related to offshore petroleum exploration. In the photic zone limited to 0.5 - 2.5 m depth primary production can reach 2 g C m⁻² day⁻¹ while below that zone, in certain areas, oxygen concentrations are often under the limits requires by aerobic higher life. Despite intense heterotrophic respiration carbon fluxes to sediments increased from 4.2 mol C m⁻² year⁻¹ to 42 mol C m⁻² year⁻¹ within the last 100 years, partly due to high sedimentation rates. Due to the complex nature of this tropical marine system little is still known about the relative importance of different source of organic carbon to the bay and on the relevance of denitrification and nitrification reactions to the nitrogen cycle.

 δ^{13} C _(PDB) and δ^{15} N _(N2) were determined in particulate organic matter (POM) collected in Guanabara Bay (15 stations in winter and 20 stations in summer), in some of the affluent rivers (6 stations), in mangrove sediment cores and leaves. δ^{13} C in *Laguncularia, Avicennia* and *Rhizophora* leaves ranged from - 27.3 to - 30.7‰ while in sediment organic matter values were heavier, in the range of - 24.1 and - 27.6‰, due to degradation processes and mixing with some fraction of aquatic biomass. In winter most POM showed

 δ^{13} C below 19‰ but δ^{15} N varied from about -4 to +11 ‰ demonstrating the influence of different processes as nitrification (values around and below 0‰) or/and the presence of blue green algae. Denitrification may contribute to some of the POM enriched in ¹⁵N since in some areas of the bay bottom waters and sediments are suboxic or anoxic. In the summer only some of the most sewage contaminated rivers POM showed δ^{15} N negative values, which may derive from ammonium assimilation in aquatic algae, and large shift in δ^{13} C compared to winter. Most POM samples from the bay had δ^{15} N in the range expected for phytoplankton and δ^{13} C below -19 ‰ that seems to be the lower limit for δ^{13} C in marine biomass in the area. Although winter is the driest season δ^{13} C more negative than -20‰ in several stations in the bay show that influence of terrestrial organic matter is more prominent in this season possibly because of the higher phytoplankton production in summer.

Cycling of organic Fe-binding ligand in 3D biogeochemical model

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The abundance of organic Fe-binding ligands strongly influences the bioavailability and photochemical cycling of dissolved iron (DFe) as well as the reactive fraction of DFe available for particle adsorption, and thus its residence time. New insights into the sources and fate of these ligands have been gained over the last decade and patterns of spatial variability are beginning to emerge. Most biogeochemical models including DFe, however, fix organic ligands to an observed mean concentration and ignore spatial variability.

In this study, sources and sinks of organic ligands through biological production and consumption, photochemical and microbial degradation, were explicitly described in a threedimensional model. The observed deep ligand profiles (below 1000 m) and their inter-basin variability are well reproduced assuming a microbial degradation time-scale of 100 years, given the ventilation times of the different deep ocean basins. Biological consumption and photochemistry strongly affect the surface concentration of ligand as well as the absolute steady-state concentration in deep water. We discuss how well the available ligand data is able to constrain the rates of these processes.

It is still contentious whether the grouping of Fe-binding ligands into two distinct classes - a strong ligand that is often assumed to be a siderophore, and a weaker ligand - is indeed a general phenomenon in the ocean or at least partially an artefact of electrochemical measurement methods. We introduced two ligand classes into the model: strong ligands are assumed to be more photolabile and produced biologically under Fe-limitation; whereas weak ligands are less photolabile and produced by decomposition of organic matter. Model runs considering only one or two ligand classes were compared to observations in order to obtain a hint if the introduction of a second organic ligand class is necessary to explain DFe and total ligand distribution.

Net effect of dust particles on dissolved iron in seawater during DUNE

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A DUst experiment in a low Nutrient low chlorophyll Ecosystem (DUNE), an artificial seeding experiment in large clean mesocosms, was carried out in summer 2008. One focus of this project is to investigate the role of dust particles at Fe cycling. A rapid decrease of dissolved iron (DFe) inside the mesocosms was observed within the first hours after the dust addition, and this lower concentration remained until the end of the experiment (8 days after the dust addition). Due to low biological productivity at the experiment site, biological consumption of iron can not explain the magnitude of DFe decrease.

To understand processes regulating the observed DFe variation, we simulated the experiment using a one-dimensional model of the Fe biogeochemical cycle, coupled with a simple ecosystem model. Different size classes of particles and particle aggregation are taken into account to describe the particle dynamics. DFe concentration is regulated by dissolution from dust particles and adsorption onto particle surfaces, biological uptake, and photochemical mobilisation of particulate iron.

The observed DFe decrease after dust addition is well reproduced in the model and essentially explained by particle adsorption and particle aggregation that produces a high export within the first 24 hours. The estimated particle adsorption rates range between the measured adsorption rates of soluble iron and those of colloidal iron, indicating both processes controlling the DFe removal during the experiment. A dissolution timescale of 3 days is used in the model, instead of an instantaneous dissolution, underlining the importance of dissolution kinetics on the short-term impact of dust deposition on seawater DFe.

Sensitivity studies reveal that initial DFe concentration before dust addition was crucial for the net impact of dust addition on DFe during DUNE. Based on the balance between abiotic sinks and sources of DFe, a critical DFe concentration has been defined, above which dust deposition acts as a net sink of DFe, rather than a source. Taking into account the role of excess iron binding ligands and biotic processes, the critical DFe concentration might be applied to explain the short-term variability of DFe after natural dust deposition in different ocean regions.