The Southern Ocean Cadmium Isotope Divide

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We report Cd isotope and concentrations data in a transect of surface waters continuously sampled in the Southern Ocean along the Zero Meridian (47$\deg$S-63$\deg$S, ANT24-3 cruise, Cape Town-Punta Arenas, February-March 2008). The objective is to examine 1) the efficacy of Cd isotope fractionation to respond to changes in (i) biological productivity in this High-nutrient-Low-Chlorophyll region and (ii) ocean circulation in the wind-driven upwelling system of the Antarctic Circum-Polar Current (ACC) and 2) how these could relate to the efficiency of the biological carbon pump.

Our results show a strong northward gradient in both Cd concentrations and isotopic compositions interrupted by an abrupt change in the sense of variations at about 56$\deg$S. The remarkable coincidence between the Cd isotope divide and the location of the Southern Boundary of the ACC and, the evidence for advection of the Cd isotope and elemental signal by northward Ekman transport in the surface layer demonstrate that Cd isotopes trace surface ocean circulation regimes. Co-variations between Cd isotopes and concentrations exhibit two negative correlations and separate the waters from the ACC and the Weddell Gyre into distinct Cd biogeochemical provinces. The arrays depict Rayleigh fractionation kinetics and imply a greater isotope effect of Cd biological consumption in the ACC vs. Weddell Gyre. Strengthening of the biological Cd isotope signal along the ACC array reflects progressive Cd depletion resulting from enhanced biological uptake as UCPW flows northward feeding the low latitudes thermohaline circulation.

The increase in magnitude of Cd isotope fractionation from the Weddell Gyre into the ACC can be accounted for by differences in phytoplankton biomass and species distribution along the Zero Meridian and, possibly, variations in the physiological mechanisms of biological Cd uptake. Our results open up new perspectives for paleoceanographic applications of Cd isotopes as a novel proxy for past changes in the “biological carbon pump”.

Development of biomimetic sensors for measuring trace-metal element concentrations

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A large variety of trace-metal elements (TME) occur in natural systems in small concentrations, they are ubiquitous in the earth's crust, and when present in sufficient concentrations, may be toxic to living systems [*Vasyukova*, 2010]. Their natural levels in soil vary widely. Natural distribution patterns of trace elements in soil have been affected by a variety of anthropogenic activities, including mining, agriculture, waste disposal, and transportation.

The goal of this work is to develop fiber optic biosensors to detect TME in surficial waters (low salinity…). Such novel sensors are based on the use of artificial non-biological physicochemical recognition elements called molecularly imprinted polymers (MIPs) [*Andersson*, 2000; *Pichon et al.*, 2008] which are specially developed to bind calixarene molecules. Calixarenes are commonly used as ion-complexing and selective extraction agents of metallic ions such as lanthanides and actinides with high extraction efficiencies [*Grütner et al*, 2002; *McMahon et al.*, 2003]. The resulting low cost and selective calixarene-based mimetic sensors are advantageous to traditional speciation methods such as gas chromatography and/or high performance liquid chromatography coupled to inductively coupled plasma mass spectrometry. The development of these sensors requires the production control of MIPs for calixarenes, the integration of MIPs with the fiber optic instrument, measurement tests and characterization.

Since this biomimetic sensor technology can be adapted readily to other biomolecules such as organic trace elements, successful demonstration of this research work would support continued development of a technology that could radically change the measurement of TMEs at every stage, and could be extended to other studies (high salinity water…).

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Trace elements in the ocean: Getting at the source.

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This is an exciting time for research on trace elements in the ocean. Old paradigms are being challenged while new sampling strategies, such as those designed for GEOTRACES, are revealing information about biogeochemical cycles at unprecedented resolution. This talk will review recent indications that hydrothermal systems represent a more significant source of certain trace elements than previously thought, whereas dust may represent a less significant source of micronutrients to High-Nutrient Low-Chlorophyll regimes. Multi-element studies along ocean sections provide unique insights into the sources and internal cycling of trace elements, but also reveal puzzling features of certain trace element distributions for which the underlying supply mechanisms remain undetermined. The comprehensive survey of the global ocean employed by GEOTRACES, involving key trace elements and isotopes that possess a broad range of biogeochemical characteristics, holds great promise for resolving long-standing questions about sources of trace elements. The presentation will conclude by proposing a strategy that employs multiple thorium isotopes to quantify the supply of certain lithogenic trace elements by aerosol dissolution and/or by mobilization from ocean margin sediments.

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Southward transport of subtropical and alongshore properties by eddies south of Africa

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Two eddies, one anticyclonic and the other cyclonic, intersected south of South Africa during the BONUS-GoodHope 2008 hydrographic transect, illustrate the capacity of such structures to transport subtropical properties into the Subantarctic Zone in that region. The anticyclone is an Agulhas ring with swirl velocities as high as 1 ms-1, although it was 9.5 months old when sampled. Its core is characterized by a 500 m thick vertical homogeneous layer indicative of winter convection and transfer of atmospheric tracers to the ocean. The cyclone, marked by a pronounced low oxygen anomaly revealing an origin at the continental slope, was 4.5 months old and had swirl speeds of 0.3 ms-1. From their kinematics and water mass properties both eddies were found to transport water from their formation region down to 900 m, the water trapped below this depth being either from the northern Subantarctic Zone, or local water. Due to their differing vertical structures, the anticyclone (cyclone) is more prone to transport South Indian ocean Central Water (Intermediate Water) southward. Both structures show pronounced tracer anomalies (CFCs, nutrients,. . .), which either characterize the eddies formation locations, or (for the anticyclone) signal intense air-sea exchanges.

The IMBER project: Connections to Traces and Tracers

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IMBER (Integrated Marine Biogeochemistry and Ecosystem Research) is a core project of the International Geosphere-Biosphere Programme (IGBP) and the Scientific Committee on Oceanic Research (SCOR). IMBER's focus is ocean biogeochemical cycles and ecosystems, which is reflected in the primary project goal of investigating the sensitivity of marine biogeochemical cycles and ecosystems to global change, on time scales ranging from years to decades. IMBER research is structured around four themes that consider 1) the transformation and transport of elements involved in biogeochemical cycle interaction with food web dynamics, 2) how marine biogeochemical cycles and ecosystems respond to global change, 3) the capacity of the ocean to control the climate system via atmospheric composition and ocean heat, and 4) the implication of changes in the open ocean for human society. The IMBER regional and national research programmes have research components that focus on understanding processes that control marine primary production and the implications of changes in this production for biogeochemical cycling and food web productivity. These studies incorporate tracers as tools to investigate carbon and nutrient cycling, trophic pathways, coastal-offshore exchanges and export from the surface ocean to mesopelagic environments. This poster provides an overview of IMBER and highlights science results from IMBER regional and national programmes that contribute to the quantification and understanding of carbon production, carbon export, and subsequent energy transfer through marine food webs.

TRACERS OF ECOSYSTEM CHANGE IN THE BLACK SEA NORTHEASTERN PART

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Gelendzhik Bay, located in the northeastern part of the Black Sea, is interesting to that on its example it is possible to investigate occurring ecosystem variations. The state of the bay waters and the ecosystem as a whole is caused by seasonal and annual variability of natural factors and a degree of an anthropogenous load. Monitoring of hydrological and hydrochemical conditions of waters and the state of the phytoplankton community of Gelendzhik Bay is held annually for 12 years in the winter and summer seasons. As a result of the lead researches the basic parameters-trasers of variations in a bay have been identified. Development of the phytoplankton community in the Bay depends on the temperature mode, concentration of the mineral nitrogen, phosphorus, silica and on the water pollution. Changes of the water temperature have a significant importance in recent years. The water pollution has great influence on the marine ecosystem. Technogenic impurities and organic matter coming with a continental runoff pollute waters of a bay. The higher values of biochemical oxygen consumption are the indicator of high organic matter content. Increasing discharge of organic matter with household drains great part of which are the nitrogen-containing substances, leads to increase of the concentrations of well assimilated by phytoplankton ammonia nitrogen in sea-water. Nitrogen/phosphorus stehiometry ratio changes in conditions of increasing of total nitrogen content. Phosphorus could become an element, which constrains the development of autotrophic organisms on considered part of bay. However last years phosphates concentrations increase even during the summer period in spite of active photosynthesis. The biogenic base does not limit the development of phytoplankton. This leads to the intensive production of organic matter in the marine environment and eutrophication of waters. The increase of average values of water temperature in winter and summer causes the high rates of production-destruction processes not only in the warm season, but also in the winter. Particular attention is given to inter-annual variability in water temperature in winter and summer. Data of last few years, especially in 2009 and 2010 years showed a high dependence of the state of phytoplankton community from the thermal regime. The state of phytoplankton community on biomass and species composition in winter 2010 year is much differed from parameters of winter of the last year. In the abnormally warm winter 2009 year algae Pseudosolenia calcar-avis was dominated (80% of the number), their biomass is on several orders higher than the biomass of all other algae. In winter 2010 year this alga was practically absent, as well as in the cold winter of 2006 and 2008 years. Phytoplankton community during the winter 2010 year was restored, that evidenced by the dominance of the most common in the Black Sea algae genera Sceletonema and Thalassionema. Abnormally hot summer of 2010 year, as well as the hot summer of 2009 year, again assisted intensive progress Pseudosolenia calcar-avis, number of which exceeded 90%. The dominance of algae Pseudosolenia calcar-avis indicates a violation of the phytoplankton community and the ecosystem as a whole. Water exchange of the bay from the open sea is an important factor for restoring its natural conditions. Clarification of waters of a bay from impurity depends on the wind circulation of waters, which supply entrance of the Black Sea water to the bay. Analysis of materials hydrological, hydrochemical and hydrobiological researches of Gelendzhik Bay showed: • a characteristic feature of hydrological and hydrochemical conditions of Gelendzhik Bay – spatial and short-period temporal variability; • supersaturation of water with oxygen (nearly 20%) in summer shows a high intensity of the process of photosynthesis; • throughout the year, even in summer, there are higher concentrations of nutrients as a result of destruction of large quantities of organic matter. Nutrient base does not limit the development of phytoplankton; • at present, the concentration of organic matter, water temperature and biochemical oxygen consumption were the main tracers of production-destruction processes, state of the ecosystem; • in the phytoplankton community in previous years the bulk of the biomass were algae Dinoflagellatae, characterized by the greatest stability to the eutrophication of waters and man-made pollution. In 2009 year and summer of 2010 year diatoms Pseudosolenia calcar-avis dominated; • increase in average water temperature, especially in winter, high values of biochemical oxygen consumption, the introduction of alien species and their rapid development – key indicators of changes of the Black Sea ecosystem.

Using the Transport Matrix Method for ^{231}Pa/^{230}Th and e_{Nd} modeling

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The Transport Matrix Method (TMM) is a computational framework that is used for simulations of biological and geochemical tracers in ocean models. It is several orders of magnitude faster than a traditional general circulation model (GCM), accurate, and convenient. One advantage of using this method rather than a regular GCM is that a large number of sensitivity tests can be performed at little cost. Here, we use the TMM to simulate the distribution of ^{231}Pa/^{230}Th and e_{Nd}. Pa, Th and Nd are trace elements in the ocean, and their isotopes are widely used in modern and paleoceanography as circulation, particle flux or ventilation rate proxies. The TMM has been implemented in two different GCMs (MIT and ECCO). Dissolved-particulate interactions are parameterized via a reversible scavenging model using two sets of particles: a model-derived (PISCES) and a satellite-derived distribution. We performed further sensitivity tests to evaluate the influence of the various model parameters: scavenging coefficients for different types of particles (POC, silicates, carbonates, atmospheric dusts), sinking velocities of the particles, different parameterization of particle distributions, and sources of the element (for e_{Nd}). We find that the distribution of both ^{231}Pa/^{230}Th and e_{Nd} are highly sensitive to different particle distributions and scavenging coefficients. Our simulations therefore highlight the need for an accurate representation of particles fields and dissolved-particulate interactions and emphasize the need for further model (both dynamical and geochemical) intercomparisons using the TMM.

Ground Water Fluxes – An indication of anthropogenic impacts on coastal Mudbank generation

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Along the southern tip of Arabian Sea, investigations in coastal regions off submerged porous lime shell beds had indicated the evidence of subterranean flows to coastal ocean with considerable fluxes of brackish water into coastal ocean and the coastal budgets of nutrients and coastal productivity were strongly impacted by such flows. During the low tides, ground water of the region contaminated by coastal sanitation deficiencies is sucked through the porous lime beds into the surf zone and that acts similar to hydrologic pump. The activated trending faults in the regions of submerged porous lime shell beds are probably coupling the adjacent watershed and the sea. The present investigation showed a fertilization of the coastal waters by the injection of nutrients by hitherto unknown process. The high levels of nitrate-N, ammonia, enriched particulate organic carbon and Chlorophyll *a* at localized coastal regions point to clear near shore nutrient sources. A band of high N/P funneling out during non-mud bank period could be a clear indication of an 'external source' of nitrogenous compounds to the coastal water. These rich sources of nutrients deserve identification as it is traced far away from any river mouth. The existence of subterraneous channels as the artifacts of porous nature of the lime shell base of the region transporting the nitrogenous compounds cannot be ruled out in the region. The human population of the coastal belt with more than 70 % of households without proper sanitation facilities had resulted in widespread use of septic tanks and induces nutrients to the coastal aquifer. The ground water in the region had nitrate (in sediment extract) up to 12 μM, ammonia (in water) 8μM, urea (in water) 14 μM, urea (sediment extract) 15 μM. The ground water flux is controlled by a critical water level difference between the Lake and sea to be sufficient to overcome the frictional resistance of the porous sediment medium. The water level in the lake depends on the monsoon floods, and the variability in monsoon precipitation, sea level and on global warming. Significance of this study is that subterranean flows could redefine the very concept of formation of *mudbanks*, which is presently recognized only as an oceanographic process. The formation of mudbank is not entirely forced by coastal processes; instead a remote forcing from the land involving a climate controlled subterranean flow through the submerged lime shell beds appears to be an initiative mechanism. The increased fresh water input through these passages stratifies the coastal waters by forming a surface lid of low saline waters, thereby diverting the incoming currents and wave energy to the bottom to disturb the bottom sediments. The idea that land-use mosaic among sub-watersheds influence coastal processes such as *mudbanks* forms may apply globally to any coastal regions hugged by wetlands and underlain with porous deposits to develop process similar to *mudbanks.*

Keywords : groundwater fluxes, productivity, mudbanks

Shelf-ocean exchanges in the Canaries-Iberian Marine Ecosystems (CAIBEX)

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CAIBEX aims to study the importance of coastal upwelling and the resultant exchange of water parcels, organic materials and planktonic biota with the open ocean in the Iberian and Canaries Large Marine Ecosystems. Parallel observational programs were carried out in two zones of recurrent upwelling filaments off Cabo Silleiro (42N), Northwestern Iberia and Cabo Ghir (30N), Morocco, with monthly surveys over an annual cycle 2008-9 and intensive experiments in summer 2009. The aim of the interdisciplinary observations and modeling in the two areas is to reveal how the mesoscale interactions between upwelling, current jets, filaments and eddies govern the fate of water parcels and their content as they pass through the coastal transition zone. A combination of spatial SeaSoar and MiniBat surveys, repeated CTD sections, shipborne ADCP, moored current and hydrographic observations and Lagrangian drift studies has been implemented from several vessels. First results confirm the Iberian region's strong short-term variability throughout the year. The Moroccan region shows evidence of upwelling year round. The evolution of a filament was monitored with drifting buoys, equipped with ADCP, CTD or incubation rigs. Its overall structure appears initially to be well modeled in the Caibex ROMS simulation. Linking the two intensive studies was the CAIBOX cruise which observed surface to bottom conditions from the Iberian and NW African coasts to the open ocean to provide the boundary conditions and context for the two studies. The data are analyzed by inverse modeling techniques to control the inputs and outputs to the region.

Biomarkers as tracers of biogenic fluxes in the SW Black Sea

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Gaining insight on the export of biogenic material is one of the tasks of the EU-funded project SESAME. To this purpose, a mooring line was deployed for 1 year (2007-2008) in the SW Black Sea, equipped with two sediment traps set at mid- and deep waters. The settling material was analyzed to obtain bulk parameters (total mass, lithogenic, carbonate, organic carbon and opal fluxes). Lipid biomarkers were also investigated as tracers of the organic carbon sources and of processes controlling carbon export/cycling. We specifically focused on biomarker tracers of terrestrial organic carbon and of specific phytoplankton sources (e.g., coccolithophorids, diatoms...) and zooplankton. The occurrence of biomarker tracers allowed assigning major sources of the export organic carbon. Their temporal variability coupled with bulk biogenic parameters enabled explaining the temporal patterns of export biogenic material (carbon, opal, carbonate) and assessing primary controls.

Cross-shelf exchange in the Beaufort Sea

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The Canadian IPY-GEOTRACES sampling program took place from August 27, 2009 through September 12, 2009 in the Arctic Ocean, on the CCGS Amundsen icebreaker. Starting in the Mackenzie River delta and continuing into the Beaufort Sea, its aim was to investigate the impact of climate change on the nutrient and carbon cycles in the Arctic Ocean using a multi-tracer approach. Here we will present measurements of $_{224}$Ra, $_{228}$Ra and $_{226}$Ra from seawater samples collected on the shelf and slope of the Beaufort Sea as well as in the deep Canada Basin. Large volumes of seawater (140-280 L) were sampled using a rosette and filtered onboard through MnO$_{2}$-coated fiber. Samples were counted for $_{224}$Ra within 2-3 days of sampling on an alpha counter and additional measurements were performed in the laboratory. Measurements of the long-lived isotopes $_{226}$Ra and $_{228}$Ra are currently being performed using gamma spectrometry at the underground laboratory in Ferrières, France. Ra-226 and $_{228}$Ra were also sampled by pumping seawater with large volume in-situ pumps through uncoated polypropylene cartridges filled with MnO$_{2}$ fiber and will be measured shortly, in Ferrières. Using the radium isotopes, our goal is to gain insight into fundamental processes governing the shelf-open ocean exchange in the Arctic Ocean by evaluating cross-shelf carbon fluxes and water mass transport.

The biogeochemical cycle of dissolved cobalt in the Atlantic and the Southern Ocean south off the coast of South Africa.

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Dissolved cobalt (DCo) concentrations were measured by flow-injection analysis and chemiluminescence detection in filtered (0.2 μm), acidified and UV-digested samples at 12 deep stations in order to resolve the several biogeochemical provinces of the Antarctic Circumpolar Current and to assess the vertical and frontal structures in the Atlantic sector of the Southern Ocean. DCo concentrations ranged from 5.73 ± 1.15 pM to 72.9 ± 4.51 pM. The distribution of DCo was nutrient-like in surface waters of the subtropical domain with low concentrations in the euphotic layer due to biological uptake. The biological utilization of dissolved cobalt was proportional to that of phosphate in the subtropical domain with a DCo:Phosphate depletion ratio of 44 μM/M. In deeper waters the distribution indicated remineralization of DCo and inputs from the margins of South Africa with lateral advection of enriched intermediate and deep waters to the southeastern Atlantic Ocean. In contrast the vertical distribution of DCo changed southward, from a nutrient-like distribution in the subtropical domain to scavenged-type behaviour in the domain of the Antarctic Circumpolar Current and conservative distribution in the Weddell Gyre. There the cycle of DCo featured low biological removal by Antarctic diatoms with input to surface waters by snow, removal in oxygenated surface waters, and dissolution and stabilization in the low-oxygenated Upper Circumpolar Deep Waters. DCo distributions and physical hydro-dynamics features also suggest inputs from the Drake Passage and the southwestern Atlantic to the 0° meridian along the eastward flow of the Antarctic Circumpolar Current. Bottom enrichment of DCo in the Antarctic Bottom Waters was also evident, together with increasing water-mass pathway and ageing, possibly due to sediment resuspension and/or mixing with North Atlantic Deep waters in the Cape Basin. Overall atmospheric input of soluble Co by dry aerosols to the surface waters was low but higher in the ACC domain than in the northern part of the section. At the highest latitudes, it is possible that snowfall could be a source of DCo to surface waters. Tentative budgets for DCo in the mixed layer of the subtropical and the ACC domains have been constructed for each biogeochemical region encountered during the cruise. The estimated DCo uptake flux was found to be the dominant cobalt flux

along the section. This flux decreases southward, which is consistent with the observations that DCo shows a southward transition from nutrient-like towards conservative distribution in the mixed layer.

Lead and Lead Isotopes in the Atlantic and Indian Ocean

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Lead and Lead Isotopes in the Atlantic and Indian Ocean We will present data on the evolving anthropogenic lead penetration into the Atlantic and Indian Oceans. In the Atlantic Ocean, there are sites with multidecadal (Bermuda) and decadal data that show lead decreasing in the upper ocean in response to the phaseout of leaded gasoline; the decrease depends as expected on the degree of connection to the ocean surface as shown by anthropogenic transient tracers. The Pb isotope composition evolves as dominant U.S. gasoline Pb (Pb-206/Pb-207 1.20) was overcome by dominant European gasoline Pb in the 1990's, and now is composed of approximately equal amounts of US and European industrial Pb (Pb-206/Pb-207 1.15). We will show a section of 10 stations from the subtropical W.N. Atl. to the tropical W.N. Atlantic (2002,2005) that shows Northern Hemisphere Pb penetrating the southern hemisphere in Labrador Sea Water and GIN Overflow Water, sandwiched between low-Pb waters of Antarctic origin. We will also show a section of 8 stations from Lisbon to the Cape Verde Islands collected on the first US GEOTRACES Transect (2010). In the Indian Ocean, we will show data from 11 stations from the 2009-2010 Japanese GEOTRACES Transect in the North and South Indian Ocean between 18degN and 65degS. It could be argued that there is NO previous valid Pb data from this basin. In response to later industrialization, no northern deep water source, and a two-decade lag of leaded gasoline phaseout, anthropogenic Pb has not penetrated as deeply in the Atlantic (little occurring below about 2000m), but the surface waters of the Indian Ocean are now higher than in the North Atlantic and North Pacific (40-80 pmol/kg).

Controls on and variability in particle export and flux attenuation in the ocean’s twilight zone

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Pelagic foodwebs drive a flux of >10 Gt C yr^{-1} that exits surface waters, mostly via sinking particles through the ocean’s “biological pump”. Most of this particle flux is remineralized in the poorly studied waters of the twilight zone, i.e. the layer underlying the euphotic zone and extending to 1000 m. Changes in the the magnitude of this pump and the length scales of remineralization will impact oceanic CO_2 uptake. It has been difficult to compare the strength and efficiency of the biological pump in the twilight zone between oceanic provinces/regions due to: 1) variability in methods (traps, radionuclides, other budgets/models), 2) a lack of data (fluxes and supporting process information), especially covering seasonal/annual time-scales, and 3) the metrics used to parameterize export efficiency and flux attenuation. This presentation will review our knowledge of flux variability and attenuation in the twilight zone and expand the analyses presented in Buesseler and Boyd (L&O, 2009) to other sites and using other flux methods. What is also important to consider, are the spatial scales of net primary production and export, which likely differ and hence introduce another level of uncertainty in our ability to understand oceanic CO_2 uptake and C export. At present, we have a poorly constrained estimate of carbon sequestration via the biological pump, which, along with our limited understanding of the processes that control its magnitude, hinders our ability to predict the strength of oceanic uptake of CO_2 and how this will be altered by a changing climate.

Metal environmental enrichment (Cr, Ni & Co) in the Northern Galician coast driven by the Cape Ortegal geological complex (SW Europe)

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Geological complex close to the shoreline could be significant contributors of trace metal to the coastal environment. This a key question poorly considered that could be blend with anthropogenic contamination events. Therefore, the aim was to research the influence of chromium (chromite and chromospinel) and nickel (gersdorfite and pentlandite) minerals associated with ultrabasic rocks of Cape Ortegal and pirrotites of Herbeira Massif, on its adjacent coastal area of north Galicia.

To achieve this objective three task were established: (a) the tributary rivers Mera, Landoi and Lourido that flow from Ortegal hillside to the Ortigueira Ria were fortnightly sampled during 2008 and dissolved and particulate Cr and Ni concentrations analysed; (b) the surface sediment of Northern Galician Rias and their adjacent shelf was sampled in July 2008 and total and labile (SM&T extraction) Cr and Ni determined; (c) samples of mussels and fucus were seasonally collected during 2008 inside the Ortigueira Ria and theirs Cr and Ni contents quantified. Dissolved trace metals (DNi) was analysed by ICPMS while particulate samples were mineralized in a microwave following EPA procedures and particulate nickel (PNi) analyzed by GFAAS. Certified reference material and procedural blanks were used.

Levels of Cr in surface sediments (<2 mm) ranged 200-930, 230-1340 and 290-1660 $mg \cdot kg^{-1}$ in inner and outer ria and shelf, respectively. Results confirm a high enrichment of Cr, five to forty times, higher than background concentration of other Galician rias. Labile Cr was also significant: 0.1-1.7 $mg \cdot kg^{-1}$ (up to 0.3% of total Cr). Using Mg as a particle tracer it maybe concluded that Ortegal Cape was the Cr source. Moreover, rivers indicate the same pattern: Landoi and Lourido in Ortegal area had 7-48 and 5-81 nM of dissolved Cr and 0.2-0.8 and 0.2-1.3 $g \cdot kg^{-1}$ of Cr in SPM while out of Ortegal complex Cr in Mera River was <0.2nM and <0.3 $g \cdot kg^{-1}$. In biota, Cr levels (2.0-3.5 $mg \cdot kg^{-1}$ dw) were similar to mussels of other coastal rias whilst in fucus higher levels were found in Ortigueira (7-16 $mg \cdot kg^{-1}$ dw).

The Ortegal Cape was also identified as the main Ni source using Mg as a particle tracer. Levels of Ni in coastal surface sediments (<2 mm) ranged 100-620, 140-470 and 160-1360 $mg \cdot kg^{-1}$ in inner and outer ria and shelf of Ortigueira, respectively; these concentrations decreased to 5-160 and 4-87 $mg \cdot kg^{-1}$ in the neighbouring rias of Barqueiro and Viveiro. Results pointed to a high sedimentary Ni enrichment, four to twenty times respect to usual rias background concentrations, in the coastal environment of the Ortegal Cape. Moreover, that Ni in sediments is 0.3-0.8% bioavailable (up to 24 $mg \cdot kg^{-1}$). Fluvial discharges also indicated the same geological source: Lourido and Landoi transport 190±95 and 80±30 nM of DNi and 24±17 and 95±90 nM of PNi while out of Ortegal complex Mera River had 15±7 nM of DNi and 4±3 nM of PNi. In biota, Ni levels (3.4-6.9 $mg \cdot kg^{-1}$, dw) were similar to mussels of other rias whilst in fucus the highest concentrations were found in Lourido mouth (46 $mg \cdot kg^{-1}$, dw), decreasing to ria mouth (8.5 $mg \cdot kg^{-1}$ dw).

Coastal enrichment in trace metals can also occur due to natural contributions apart from anthropogenic contamination. It is the observed case of Cr and Ni in the fluvial, estuarine and marine environment close to Cape Ortegal as result of the presence of chromium and nickel minerals.

This communication is a contribution to the research project CTM2007-62546-C03-01/MAR (CICYT) and to the Spanish-Portuguese Action ref. 2007PT0021.

Radionuclides as tools to study the role of the Arctic Sea Ice in the interception, transport and redistribution of particulate matter and chemical species

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The Arctic Ocean is characterized by being covered by sea ice with a large degree of seasonal variability between summer and winter. Along the whole life cycle of sea ice, diverse physical and chemical processes determine the concentration of the sea-ice sediments (SIS) and the chemical species entrapped in it and their final fate. Initially, sea ice incorporates particles (SIS) and associated chemical species (metals, nutrients, contaminants, etc.) during its formation mainly in the continental shelves, while dissolved solutes are excluded. As sea ice drifts offshore to the central Arctic Basin, it intercepts chemical species from the atmosphere and, the sediments in the ice may also incorporate some chemical solute compounds from the surface waters by scavenging (although this is likely small). Eventually, transported components, chemical species and SIS, are released to the underlying water column during melting. Thus, sea ice becomes an important transport and distribution agent. However, the efficiency of interception of atmospheric fluxes by sea ice, the origin of the entrapped SIS and transit times of sea ice in the Arctic, as well as the importance of the transport of chemical species and particulate matter (SIS) and its release in the ablation area are all poorly understood. In an attempt to address these questions, a suite of natural (7Be and 210Po-210Pb) and artificial (137Cs, 239,240Pu) radionuclides were analysed in samples from precipitation, sea ice, surface water, water beneath ice and sea-ice sediments collected during the ARK XXII/2 expedition in 2007. The distributions of 7Be and 210Pb showed enrichment in sea ice (129 ± 90 and 5.1 ± 2.9 Bq·m-3, respectively) with respect to surface water (7.1 ± 1.3 and 1.1 ± 0.36 Bq·m-3, respectively). Given that only 4% of the total amount of 210Pb in sea ice comes from seawater and that any 7Be (T1/2 = 53 days) trapped in sea ice during its formation has decayed during drift, the direct atmospheric flux appears as the most important source of both radionuclides in sea ice. From mass balance calculations we estimate that sea ice intercepts about 30% of the 7Be atmospheric flux. This figure may be extrapolated to other chemical species with atmospheric sources, such as metals, nutrients, and contaminants. Given that 7Be and 210Pb are intercepted and accumulated during sea ice transit and also scavenged by SIS, we can use both radionuclides to assess sea ice transit time. Using the 210Pb inventory in ice floes respect to the 210Pb atmospheric flux intercepted by sea ice and the 7Be/210Pbex activity ratio in SIS, we estimated transit times from less than 0.5 to 3 years along the Eurasian Basin. Results are consistent with information reported by satellite maps and back-trajectories analysis of the sampled sea ice floes. Indeed, the SIS presence indicates that the ice floes come from continental shelves, and their origin can be constrained using artificial radionuclides (137Cs and the 239,240Pu) in SIS. Data shows that most of the SIS in the Eurasian Basin originated from the Siberian shelves, in agreement with back-trajectory analyses and main drift patterns. The relevance of sea ice as a significant transport and source of radionuclides in melting areas, such as the Fram Strait, is reflected in the annual fluxes of dissolved 7Be and 210Pb carried by sea ice (67 ± 55 and 13 ± 7 Bq·m-2·y-1, respectively), which are comparable to atmospheric inputs in this region (113-131 and 10-18.3 Bq·m-2·y-1, for 7Be and 210Pb). In addition, the annual mass flux of SIS to the Fram Strait, assessed using a 7Be mass balance and the mean annual ice area efflux through the Fram Strait, is on average 240 (4.5 - 1700) ·106 tons. As a reference, the discharge of sediment load from Arctic rivers is of about 115·106 tons per year.

Dertical diffusivities for passive and active tracers

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In most past studies, the vertical diffusivities of all tracers were taken to be the same irrespectively of whether the tracer was active (e.g., T, S) or passive (e.g., CO2). We have now derived a vertical diffusivity for a truly passive tracer (one that does affect the density and thus the velocity field) and compared it with that of the T and S fields. The results are as follows. Only in the doubly stably stratified case ($T_z>0$, $S_z<0$) is the difference between passive and active tracer insignificant. In SF (salt fingers) case, the passive tracer diffusivity is up to a factor of two smaller than that of salt (which is the largest) while in the case of DC (diffusive convection), the passive tracer diffusivity is up to a factor of two smaller than that of heat (which is the largest). These results indicate a significant difference between active and passive scalar diffusivities.

The algebraic expressions for the heat, salt and passive scalar diffusivities were obtained by solving the RSM (Reynolds Stress Model) which includes both double diffusive processes and shear. The model predictions were tested against NATRE data.

REFERENCE:

V.M.Canuto, Y.Cheng and A.M.Howard, Vertical diffusivities for passive and active tracers, Ocean Modelling, 2010, in press

Mesoscale induced eddy velocities for passive and active tracers

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It has been known for some time that *mesoscales* (M, 10-100km horizontal size) cannot be represented by an horizontal diffusivity alone since the anti-symmetric part of the diffusivity tensor gives rise to an advection to be added to the mean Eulerian one. This eddy induced velocity is often referred to as *bolus velocity* and the sum of the latter with the mean velocity is known as the residual mean velocity. The inclusion of this feature has proven highly beneficial to the performance of OGCMs (ocean global circulation models). Lack of a proper differentiation between passive and active tracers forced modelers to adopt the form of the bolus velocity for the buoyancy field (an active tracer) to describe passive tracer such as CO2 whose dynamics is an integral part of climate studies. In a recent study, we have shown that the assumption is not correct and we have derived the form of the eddy induced velocity for an arbitrary tracer. The final result is analytical and easy to implement in OGCMs. Results will be shown to highlight the difference between the old and the new bolus velocities.

Reference: V.M. Canuto, and M.S.Dubovikov, Comparison of four mixed layer mesoscale parameterizations and the equation for an arbitrary tracer, *Ocean Modelling*, 2010, submitted.

Multidecadal evolution of Black Sea hydrodynamics and biogeochemistry

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In the framework of the EU Southern European Seas: Assessing and Modelling Ecosystem changes (SESAME) integrated project, the long term functioning of the Black Sea hydrodynamics and biogeochemistry has been investigated using a 3D coupled hydrodynamical-biogeochemical model describing the food web from bacteria to gelatinous carnivores and explicitly representing processes in the anoxic layer down to the bottom. The hydrodynamical model is run during 40 years while the biogeochemical model is run during key time slices selected during the last 50 years (e.g. pristine, eutrophication, post-eutrophication, present).

The skills of the coupled model are deeply assessed using a hierarchy of techniques following the type and availability of observations (in situ and satellite). These techniques include the use of statistics dedicated to a point to point direct comparison, EOF decomposition and analysis of the spatio-temporal distribution of model errors.

A particular attention is given to the North-Western shelf and to the fate of the riverine material, for which we quantified sequestration and degradation on the shelf as well as the export in different form towards the deep sea. It has been found that the representation of benthic processes is very critical in order to get an acceptable distribution/budget of nutrients for the shelf and the deep sea over several years.

In a first step, a characteristic functioning of the shelf ecosystem is drawn from different climatological simulations corresponding to the selected time slices. Self-organizing maps are used to assess typical seasonal cycles and to define coherent regions of enhanced variability or stronger sensitivity in relation to water quality indicators.

Then, looking at an inter-annual evolution, several propositions are made to link observed changes of this characteristic functioning with variation in the hydrodynamics caused by atmospheric variations and/or modifications of the riverine materials linked to human activity.

In particular, the synergy between climatic oscillation and human induced pressure will be explored as it is believed that the drastic changes experienced by the Black Sea in the late eighties result from combined pressures of different types.

Trace elements and stable isotopes in Cerastoderma glaucum shells : exploring environmental and contamination tracers in a coastal lagoon.

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Molluscs incorporate in their tissues and shells the trace elements present in their medium, which makes them potential tracers of the chemistry of their environment. However, element concentrations and isotopic ratios in molluscs are also determined by environmental factors such as temperature and complex biological processes. Biological factors induce variability between species but also variability between individuals of the same species, which needs to be assessed. We explore here the biological and environmental influences on the concentration of a wide range of elements and on stable isotope ratios (δ18O, δ13C, δ15N) in tissues and shells of the cockle Cerastoderma glaucum from a coastal lagoon in Southern France. This species has a strong potential as an environmental archive because of its wide distribution area from England to eastern Mediterranean and its large tolerance to salinity and temperature variations. Shell samples were collected in Arnel and Prévost coastal lagoons and cultivated during three months in tanks under constant temperature and salinity conditions. Water chemistry was monitored in the culture tanks as well as in the lagoon, the river input, and the sea. Trace element analyses (LA-ICP-MS) in shells from the same environment show a high degree of variability that may overwhelm the environmental signal in a number of cases. High resolution analyses along the shell growth axis show variations through time related to seasonal temperature and salinity variations, redox conditions, metal bioavailability and shells life history. Decontamination kinetics in molluscs could be constrained for heavy metals contamination.

Surface delta^{13}C-POC, cholesterol and brassicasterol decline from Cape Basin to the northern Weddell Gyre (Southern Ocean): is the signal conserved in the deep ocean?

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Reconstructions of past ocean productivity and inorganic carbon content from proxies, such as C-isotopic composition of organic material contained in sediment profiles, are essential to investigate the linkage between climate and ocean productivity. This necessitates a detailed understanding of the biological carbon pump, a major process controlling carbon transport to the deep ocean and the sediments. While C-isotopic compositions have been studied widely in this context, little is actually known about possible diagenetic effects changing the isotopic composition during transit of the sinking organic material through the water column. Also, the relative importance of different microbial and zooplankton components contributing to the C-export flux and the variation of these contributions with depth will affect the signal finally delivered to the sediments. We investigated these possible effects by studying the occurrence and the spatial variability (with depth and latitude) of specific lipidic compounds (biomarkers) in particulate organic matter recovered from the whole water column. During the Southern Ocean BONUS-GOODHOPE expedition (Feb.-Mar. 2008, R/V *Marion Dufresne*), complete depth profiles particulate organic matter were sampled along the Greenwich Meridian, using large volume in-situ filtration systems, for analysis of POC and sterols concentrations as well as delta^{13}C isotopic composition. Five stations were selected on the basis of their zonal characteristics: S1 (36°S, 13°E) and S2 (42°S, 8°E) in the Subtropical Zone, S3 (47°S, 4°E) in the Subantarctic Zone, S4 (51°S, °E) in the Polar Front Zone and S5 (57°S, 0°E) in the Weddell Gyre (Antarctic Zone).

In surface water, delta^{13}C of POC as well as sterol compounds clearly show the well known correlation with surface $CO_{2\ aq}$ (delta ^{13}C decreases with increasing surface $CO_{2\ aq}$ concentration from north to south), though slopes of the linear regressions differ slightly: -0.6 ± 0.1 permil (delta ^{13}C-POC; $y = -0.6x - 13.7$), -0.9 ± 0.1 permil (delta^{13}C-cholesterol; $y = -0.9x - 17.0$) and -1.1 ± 0.1 permil (delta^{13}C-brassicasterol; $y = -1.1x - 14.1$). In the deeper layers, the covariance between delta^{13}C of the different organic compounds with surface $CO_{2\ aq}$ is well maintained revealing fact that the composition of suspended organic matter at great depth is closely linked to physical and ecological conditions prevailing in local/regional surface waters. However, we do observe that sterol compounds tend to become significantly enriched in ^{13}C (by up to 5 permil) with increasing depth. Thus, while our results highlight the fact that deep ocean particle populations do conserve the latitudinally varying imprint of surface ocean CO_2 on their isotopic composition (despite a potential effect of homogenization due to mixing and advection) biogeochemical processes are enriching the studied sterol compounds in ^{13}C. Such enrichment is likely present also in other lipid compounds and needs to be corrected for to recalculate surface water $CO_{2\ aq}$ from deep ocean organic material. Some possible mechanisms leading to ^{13}C enrichment will be discussed, but more studies are needed to understand the exact processes leading to the observed isotopic enrichment with depth.

Water column processes of particulate matter in the South China Sea and its significance for some paleo-proxies

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The scientific questions in this paper are focused on how water column processes of particulate matter affect geochemical paleo-proxies such Corg, opal and chlorin as paleo-production (PP), UK37 as paleo-SST and d13Corg as source of organic matter. Comparisons between sedimentary organic carbon, chlorine and opal concentrations and accumulate rates and their fluxes and vertical change in water column indicate that organic carbon in sediment is relatively a good paleo-PP in the South China Sea, but chlorine and opal are not because sedimentary biogenic component is strongly affected by carbonate dissolution and lithogenic dilution in this oligotrophic, low PP marginal sea. Exceptions may be found in areas with a relative shallow water depth, stable sedimentation rate and good organic mater preservation, where chlorine and opal could also be used as good paleo-PP proxies. In most cases, sea surface temperature (SST) estimated by UK37 in settling particulate matter differs from the upper layer remote sensing data, and there was also decoupling of particulate matter UK37 signals between upper and deep traps during the same periods, all attributable to the advection of particles. On the other hand, the variation of coccolith bloom season as well as their living depth fluctuation in the euphotic layer could have also accounted for this phenomenon. There was no significant change of UK37 index during particle settling in the water column. Although UK37 temperature derived from settling particles disagrees with remote sensing SST, a good correlation between the sediment UK37 temperature and the annual average temperature from the upper layer (30m) in the SCS confirms the empirical linear curve of UK37 and SST, and suggests that a long term sediment record (decadal to millennial) may smooth the short term fluctuations of environment signals. The increasing of C/N ratio from water column particles to sediment can be attributed to selective decomposition. The distribution of d13Corg in surface sediments, which indicates more organic matter in the shallow area than in the deep sea basin, was affected by terrestrial input, especially in areas near the Pearl River Estuary, north-east corner of the SCS, the Mekong River Delta and Sunda shelf. The abnormally light d13Corg in these areas likely resulted from rapidly increasing pCO2 due to recent human activities.

Observing characteristics of maximum dissipation spectrum over a continental shelf and slope in South China Sea

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Using in-situ measured data at South China Sea (SCS) in May and June, 1998, and the data from the Asian Seas International Acoustics Experiment (ASIAEX) 2001 in South China Sea (SCS), within internal brand, the peak frequencies of the dissipation spectra (PFDS) about baroclinic horizontal or vertical components are indicated along depth and spatial position over continental shelf and slope. For the frequency more than PFDS, we found that that the power spectra of velocity (u, v, w) are universal functions with respect to PFDS at the same depth. That is the spectrum falloff rates with the same value at the same depth for different sites. In addition, the falloff rate of non-dimension velocity power spectra of v is fast than that of u. The characteristics of PFDS are that in continental shelf region, PFDS for horizontal components increase fast till a high value in thermocline, and are lower than that in vertical direction along depth. PFDS in vertical direction increase along depth. Conversely, in the sill of the slope, the PFDS in vertical direction decrease along depth and PFDS in horizontal direction are of largest value. In the slope, regard to horizontal direction, PFDS in thermocline increase fast and till very close to that in vertical direction. Below the thermocline, PFDS are lower than that in vertical direction.

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Physical speciation of iron in the Atlantic sector of the Southern Ocean along a transect from the subtropical domain to the Weddell Sea Gyre

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Distributions of total dissolvable iron (TDFe; unfiltered), dissolved iron (DFe; 0.2 mm filtered), and soluble iron (SFe; 0.02 mm filtered) were investigated during the BONUS-GoodHope cruise in the Atlantic sector of the Southern Ocean (34°S/17°E–57°S/0°, February–March 2008). In the mixed layer, mean values of 0.43 ± 0.28 and 0.22 ± 0.18 nmol $L-1$ were measured for TDFe and DFe, respectively. In deeper waters, TDFe and DFe concentrations were 1.07 ± 0.68 and 0.52 ± 0.30 nmol $L-1$, respectively. DFe concentrations decreased from the north (subtropical waters) to the south (Weddell Sea Gyre). In the subtropical domain, dusts coming from Patagonia and southern Africa and inputs from the African continental margin may explain high DFe and TDFe concentrations in surface and intermediate waters. Results from numerical models gave support to these hypotheses. In the Antarctic Circumpolar Current domain, estimation of the median advective time of water masses suggests that sediment inputs from the Antarctic Peninsula, South America margin, and/or South Georgia Islands could be an important source of Fe. Except in the subtropical domain where 0.4–0.6 nmol $L-1$ of SFe were observed in the upper 1500 m, all stations exhibited values close to 0.1–0.2 nmol $L-1$ in surface and 0.3–0.5 nmol $L-1$ in deeper waters. For all stations, colloidal Fe (CFe) was a minor fraction of DFe in surface waters and increased with depth. Colloidal aggregation, sinking of CFe, and assimilation of SFe, followed by rapid exchange between the two fractions, are suspected to occur.

Settling particulate matter composition and element flux quantification in Alfonso Basin, La Paz Bay, Gulf of California: 2002-2008 sediment trap series

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Modern geochemistry does not only study the element contents in separated compartments of the Earth system, but also focuses on the characterization of biogeochemical cycles of elements. The creation of these cycles in the marine environment requires the quantification of vertical fluxes of settling particulate matter and the particulate elements transported to the bottom. These fluxes depend on the composition and amount of sedimentary particles, formed in the upper layer of the aqueous reservoir, their transformations in the water column, as well as their final deposition at the bottom. The objective of this work is to study the settling particle composition and the particulate element fluxes to the Alfonso Basin (410 m deep), La Paz Bay, and try to find their possible contribution sources. This embayment is located in the southern part of the Baja California Peninsula. An important characteristic of this area is the desertic arid climate with very low precipitation ($<$ 200 mm/yr), occurring mainly during the passage of tropical cyclones, as well as a high probability of dust storms. Settling particulate matter was collected by an automated sediment trap during 2002-2009 with a periodicity of 7-15 days. Major and trace elements were determined using instrumental neutron activation analysis. The present study also partially includes the 2002-2005 database [Rodríguez Castañeda, 2008]. At the actual moment we can conclude that the total mass flux, composition and different particulate element fluxes show a high variability and do not exactly coincide with each other. However, some element behavior seems to be influenced by different extraordinary events. Tropical cyclone effect on settling particulate matter, specially noted for “Ignacio” (22-27 August, 2003), “Marty” (18-14 September, 2003) and “Henriette” (30 August - 6 September, 2007) hurricanes, was found for Sc and Fe, representing the fluvial terrigenous input. Reported planktonic blooms for the study area, especially on June and July of 2002 and December of 2007, were affecting Ca, Ba and U contents, as well as their fluxes, defining the marine biogenic supply. Dust storm effect was found for Sc, Fe and As, being related to aeolian input due to strong northeast winds, acting mostly on fall-winter in the study area. And finally, suboxic conditions of the water column of the La Paz Bay could be creating authigenic particles, due to reduction of some redox-sensitive elements, transferring them from the dissolved to particulate phase, as could be the case for U and As. Some elements did not show a relation to only one phenomena, but to a variety of them. So in consequence these might be controlled by a combination of processes and interactions.

Multi-time Scale Analysis among Ocean Biogeochemical, Tracer, and Proxy Time Series Using the Empirical Mode Decomposition

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Classical techniques for time-series analysis on ocean biogeochemical, tracer, and proxy data rely too strongly on having a constant sampling rate, which poorly adapts to the uneven time recording of biogeochemistry variables; new, more flexible methods issued from Non-Linear Physics are hence required. In this paper, Huang's Empirical Mode Decomposition (EMD) (Huang et al., 1998) was used for the analysis of biogeochemical time series (1996-2006) obtained from the Carbon Retention in A Colored Ocean Project (CARIACO). The main idea of EMD is to estimate a signal as a sum of a trend and superposed oscillations. When this is done for all the oscillations composing a signal, the high frequency time series is called an Intrinsic Mode Function (IMF) and the low frequency part is called the residual. The procedure is then applied again to the residual, considered as a new times series, extracting a new IMF using a spline function, and obtaining a new residual. After the decomposition process is terminated, the EMD method expresses a time series as the sum of a finite number of IMFs and a final residual. To measure the degree of temporal correlation of two variables, a method was used to relate couples of modes from different series by calculating the instantaneous phase differences and correlations among the associated modes. The correlation coefficients among the trends of various variables show the long-term linkages and feedbacks in ocean biogeochemical processes.

Behavior of Silicon Isotopes ($\delta^{30}Si$) of dissolved Si in the Atlantic and Indian Sectors of the Southern Ocean

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Silicon isotopes are a paleoceanographic proxy whose use in the Southern Ocean would be improved by a more detailed understanding of the distribution and behavior of these isotopes in the modern day Atlantic and Indian sectors. We report here the silicon isotopic composition ($\delta^{30}Si$) of dissolved silicon (DSi) from 42 surface water samples, spanning the Drake Passage to the Kerguelen Plateau and the Atlantic Polar Front to the edge of the shelf ice, taken between the beginning of February and the end of March 2007. We also report results from 6 CTD profiles taken during the cruise. The $\delta^{30}Si$ of DSi in surface waters were strongly correlated to DSi concentrations, supporting the use of $\delta^{30}Si$ as a proxy for DSi removal. The "open system" fractionation observed, ϵ = -1.4 per mil, agree well with results from previous work in other areas. The estimate of the initial $\delta^{30}Si$ of DSi of +1.4 per mil matches observations of the $\delta^{30}Si$ of DSi in deep waters in the CTD profiles and in the Pacific sector. Using these values gave reasonable estimates for DSi draw down in the past from the $\delta^{30}Si$ of sediment cores. However, isotopic fractionation during silica dissolution appeared to influence the $\delta^{30}Si$ of some surface water samples, inviting further study of this phenomenon.

Transient redox species as tracers of oceanographic mixing and transport

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A number of redox species have the potential to be used as tracers of ocean mixing over different time scales (minutes to decades) related to the kinetics of their oxidation or reduction. A prime example of this is from the Peruvian Oxygen Minimum Zone, where recent work as part of SFB754 (Climate-Biogeochemistry Interactions in the Tropical Ocean) at the IFM-GEOMAR has shown the role that different mixing environments(upwelling, mixed layer turnover, eddy induced mixing) covering a range of time scales(hours to days) have on Fe(II), H2O2 and Iodide profiles in the water column. On longer time scales (years) results from the Southern Ocean, during a GEOTRACES IPY expedition, suggests iodide has potential as a tracer for recently formed Antarctic deep water. This presentation will examine a suite of easily measureable redox tracers and illustrate their potential applications to different ocean mixing scenarios.

2) Comparison of Ostracod Communities Distribution in Littoral and Sub tidal regions of Bahrakan (Persian Gulf)

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Ostracods are second most dominant group of meiobenthos proceeding nematodes. The animals are considered as food sources for most epibenthic organisms. They also play a vital role in the food chain. The sampling was carried out from autumn 2009 to summer 2010 in Bahrakan region (North of Persian Gulf). To achieve the aims of the project 7 intertidal sites and 7 sub tidal sites were selected. Using van Veen grab and corer (8.5cm2 area), samples were taken and most parameters such salinity, dissolved oxygen and temperature in water and as well as total organic matter, total organic carbon and grain size were analyzed. The ostracods were fixed by formaldehyde, stained using Bangal Rose and separated with floating method on carbon tetrachloride. The biodiversity indices especially those are Brillouin, Hill, Simpson and Margalef were determined using PRIMER 5.0. The results indicate highly significant variation in the diversity and density of ostracods and environmental factors in different seasons at two regions. The number of identified species totalled up to 35 in which the following are the most dominant ones: Venericythere darwinii, Asymmetricythere indoiranica, Asymmetricythere whatleyi, Hemicytheridea paiki. At all occasions the indices showed higher levels than those of sub tidal excluding domination index. The values of indices were higher in winter than other season. Diagram of CCA showed that salinity in intertidal region and dissolved oxygen were the most effect in sub tidal region on density of ostracods.

Dissolved Aluminium and Manganese in the Arctic-Atlantic-Antarctic Oceans

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Samples were collected for dissolved Manganese (Mn) and Aluminium (Al) with an ultraclean all-titanium CTD system (de Baar et al. 2008, MarChem, 111, 4-21) during the IPY-GEOTRACES program of the Arctic ARK XXII/2 (2007) and Antarctic ANT XXIV/3 (2008) expeditions aboard RV Polarstern and the GEOTRACES West Atlantic expeditions (2010) legs 1 and 2 aboard RV Pelagia. This resulted in a comprehensive dataset of dissolved Mn and Al in the surface and deep basins of the Arctic Ocean, northwest Atlantic Ocean and the Antarctic or Southern Ocean. The distributions of these trace metals vary remarkably between the different oceans. In the surface Southern Ocean the concentrations of dissolved Mn were extremely low and showed a nutrient type behaviour. In the Atlantic surface waters the concentrations of Mn were elevated, in line with previous observations, and in the Arctic concentrations were even more elevated due to fluvial input. Deep concentrations of Mn were much more consistent between the ocean basins, except in regions where hydrothermal input is of importance. This hydrothermal influence can be observed on a basinwide scale. Concentrations of dissolved Al were generally higher in the Arctic Ocean and decreased through the Atlantic Ocean and lowest concentrations were observed in the Southern Ocean. Exceptions to this trend are the extremely elevated surface concentrations at mid latitudes in the Atlantic Ocean, most likely due to Saharan dust input. In the Atlantic Ocean the Antarctic Intermediate Water and Antarctic Bottom Water with an Antarctic origin had much lower Al concentrations than the North Atlantic Deep Water of Nordic origin. The general water column distribution of Al showed strong nutrient type behaviour in the Arctic Ocean, somewhat nutrient type behaviour in the Atlantic Ocean and scavenging type behaviour in the Southern Ocean.

Novel Ultraclean PRISTINE® sampler for the GEOTRACES Program

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Novel butterfly-valve type ultraclean samplers have been developed and constructed of ultraclean PVDF plastic manufactured in an ultraclean factory in Austria (www.georg.fischer.at). The samplers are closed when passing through the ocean surface and next open at subsurface. The opening is very large for excellent flow-through during downcast and upcast. Teflon valves for subsampling are placed at lowest position to ensure draining complete sampler including settling particles. Top valve can be connected to gas pressure for pressure filtration at bottom subsampling valve. We will bring one PRISTINE sampler to the Liege Colloquium to be placed with a poster.

The 24 samplers of 27 Litres each are mounted on an all-titanium TITAN® frame deployed with a new Kevlar hydrowire cable with internal signal cables. This allows for the rapid ultraclean sampling of the deep oceans for concentrations of trace metal elements aluminium, manganese, iron, cobalt, copper, nickel, zinc, silver, cadmium, platinum and lead (Fe, Mn, Al, Co, Cu, Ni, Zn, Ag, Cd, Pt, Pb), as well as the stable isotope systematics of several such trace metals, notably iron, copper, zinc, cadmium and lead (Fe, Cu, Zn, Cd, Pb).

During two Netherlands North Atlantic GEOTRACES cruises in April-July 2010 the 49 deployments of the TITAN frame with 24 samplers was flawless with 100% closing of the samplers, i.e. overall 49x24 = 1176 times perfect functioning. Examples of excellent concentration data values of dissolved Fe and other metals along deep ocean sections obtained with the PRISTINE samplers during these cruises will be shown.

Differential retention of dissolved barium and silicon in the Atlantic, Indian and Australian sectors of the Southern Ocean

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Since the GEOSECS cruises in the 1970s it is well known that dissolved barium and silicon in the water column correlate tightly, but also that slight differences exist between ocean basins, reflecting differences in the biogeochemical cycling of these elements. The cycles of these two elements differ because different players are controlling their water column distributions - biogenic Ba-barite being associated with undefined plankton detritus while the silicon distribution is mainly determined by diatoms. In the Southern Ocean the combination of an intermediate and a deep water re-circulation cell (Toggweiler et al., 2006) favors diatom predominance and an efficient retention of Si (Sarmiento et al., 2007). It is not known to what extent these conditions also control the distribution of Ba in the Southern Ocean. Here we investigate the variability of Si and Ba between the major Southern Ocean basins and along water circulation pathways. For this purpose, we compiled dissolved barium and silicon data from 10 Southern Ocean cruises that took place between 1987 and 2008 in the Atlantic, Indian and Australian sectors, the Weddell Gyre, Prydz Bay and Drake Passage. The comparison of spatially weighted average concentrations between major systems revealed characteristic Si and Ba signatures as well as a clear gradient of Si enrichment vs. Ba from the Weddell Gyre eastward along the path of the Antarctic Circumpolar Current (ACC), reflecting a less efficient retention of Ba in the Southern Ocean domain relative to Si. This synoptic picture of Si/Ba behaviour is still incomplete since Ba data for the ACC in the Pacific sector are very scarce. The few Drake Passage data, however, reveal some enrichment again of Ba and Si (but slightly more so for Si) compared to the Australian sector, stressing the need for Ba data in the pacific ACC. The GEOTRACES programme would represent a nice opportunity to fill this gap.

A generic approach to the concept of water renewal: theory, idealised examples and realistic application to Lake Tanganyika and the Scheldt Estuary

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The concept of water renewal refers to the processes by which water initially located in the domain of interest (the “original water”) is progressively replaced by water originating from its environment (the “renewing water”). Determining the rate at which water renewal is achieved is of use in many hydrodynamical, pollution and ecological studies.

Over the last few decades, many methods were suggested for quantifying water renewal rates. Most of them, be they based on *in situ* measurements or numerical results, aimed at estimating relevant timescales. Herein, a generic approach to such timescales is presented that relies on the Constituent-oriented Age and Residence time Theory (CART, www.climate.be/CART). Accordingly, by solving a partial differential problem in a backward mode, the residence time of the original water may be calculated at any time and position, i.e. the time needed for every particle of this water type to reach for the first time an open boundary of the domain. Additional information may be obtained by estimating the age of the renewing water, which is defined at any time and location as the time that has elapsed since entering the domain. To obtain this timescale, one must solve a partial differential problem in a forward mode. Clearly, the age of the renewing water and the residence time of the original water are complementary, diagnostic quantities, whose domain-averaged values are seen to be equal at a steady state.

Upon estimating its residence time, an original water particle is discarded as soon as it hits one of the open boundaries of the domain of interest, thereby ignoring the possibility that this water particle may re-enter the domain at a later time. As this is unlikely to be acceptable in all water renewal studies, an alternative approach is suggested, that consists in estimating the exposure time, i.e. the time spent in the domain of interest. This timescale may be estimated in the domain and its environment — while the residence time of the original water and the age of the renewing water are defined only in the domain of interest. If this alternative strategy is selected, there is no need to split the water into two categories, original water and renewing water.

In the domain of interest, the exposure time is always larger than the residence time, and the relative difference between them is termed the “return coefficient”. The latter measures the propensity for a water parcel to re-enter the domain of interest after leaving it for the first time.

All of the above timescales may be calculated in a Lagrangian framework, by having recourse to relevant random walk algorithms. However, in the present study, most of the developments are performed in a Eulerian mode, making it possible to establish rather easily

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properties that the timescales under consideration satisfy at any time and position. The physical meaning and the usefulness — as diagnostic quantities — of these timescales is illustrated by tackling a couple of idealised, zero- or one-dimensional flow configurations that allow analytical solutions to be obtained.

Using the unstructured-mesh, finite-element Second-generation Louvain-la-Neuve Ice-ocean Model (SLIM, www.climate.be/slim), the flows in the upper layer of Lake Tanganyika and the Scheldt Estuary are simulated along with the abovementioned timescales. By doing so, a picture of the long-term transport properties is obtained that is of use to gain insight into the fate of contaminants or the ecology of the domains of interest.

pCO2 and dissolved inorganic carbon distribution of the mixed layer during the Bonus-Goodhope cruise.

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In the frame of the Bonus-Goodhope cruise we aimed to investigate how air-sea CO_2 fluxes relate to carbon export assessed from geochemical multi-proxy approach in the biologically active mid-latitude zone of the S.O. In order to address this question, we carried out underway pCO_2 and DIC (dissolved inorganic carbon) discrete measurements in order to assess the spatial distribution of the partial pressure of CO_2 (pCO_2) at the surface and the vertical distribution of dissolved inorganic carbon respectively. Using the distribution of DIC and TA, we constructed a carbon budget for the mixed layer in order to determine the seasonal net community production (NCP_{season}) in the different oceanic provinces covered by the Bonus-Goodhope project. We compared NCP_{season} with C export derived from the ^{234}Th approach. We observed that NCP_{season} was highest at the Southern Antarctic Circumpolar Current front (SACCF) and decrease slightly northwards, while the lowest value was observed in the Weddell gyre. A dramatic decrease of C export compare to the NCP $_{season}$ appear at the Sub-Antarctic front, suggesting that high mesopelagic respiration or physical processes prevent C export to the deep water layer in this area.

Deep water mass structure and circulation in the South Atlantic

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The main task of the research is to determine the origin and the pathways of the North Atlantic Deep Water (NADW) components and in the South Atlantic. There are some conceptions about the NADW structure. Classical concept [Wust, 1935] proposed that the NADW consists of 3 components: upper, middle and lower waters. From another point of view, which is based on CFC‘s distribution [Rhein et al., 1995], the NADW should be divided into 4 parts: the shallow upper water (SUNADW), the layer from the Labrador Sea and two lower layers the old and the overflowing (LNADW-old, OLNADW). During this work the structure of NADW including 4 layers was redefined and described more accurately, in a counterbalance to aforesaid conceptions [Rhein et al., 1995].

Role estimation of the global biological filters in trace element geochemical migration in the ocean.

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Over the recent 30 years numerous data on the trace metal content in the marine biota were published, however the geochemical consequences of trace metal bioaccumulation are still poorly documented. An ettempt to quantify the trace element accumulation potential of the biological communities in areas with high abundance of biota, such as estuarine (nearshore) zones, photic layer of the ocean and the deep-sea hydrothermal vent fields, is made in this work. These areas are known to be highly productive ones where biogeochemical processes are very intensive.

From the estimation it follows that in estuarine areas phytoplanktonic community is the most powerful trace metal bioaccumulator corresponding to its highest biomass. The second place belongs to widespread benthic organisms - bivalve mollusks. Trace metal content in *Mytilus spp.* mussels evaluated in µg per g of the whole body (with regard to the weight portion of constituting tissues) let the author to estimate first a contribution of carbonate shells to trace metal bioaccumulation in the biomass of these organisms. More than 60% of Cr, Mn, Fe, Cu, Ni, As, Se, Sb, Pb total content in the *Mytilus* whole body is associated with carbonate biomineralization; while Zn, Ag and Cd prevail in the soft tissues.

In the ocean, due to both direct and indirect influence of the biological production, majority of trace metals exist in the geochemically mobile forms. Comparison of the residence time (τ) of Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb in the ocean and duration of their phytoplanktonic cycles (T_{bio}) showed that the latter is much shorter. The largest acceleration was revealed for such toxic metals as Pb, Zn, Cu, Cd. There is a trend of direct relationship between τ and T_{bio}.

High concentration coefficients ($n \cdot 10^2$-$n \cdot 10^6$) relatively the biotope water were determined for a majority of trace metals, not only in the hydrothermal bottom organisms' soft tissues but in the mussel carbonate shells as well. Likewise the nearshore mollusks shells of deep-sea hydrothermal mussels play an important role in the trace metal accumulation in their whole body [Demina, 2010; Demina et al., 2010].

There are foundation to suppose hydrothermal fauna to be a new biological filter. A new approach for comparison of trace metal bioaccumulation in the biomass of biological communities of the estuarine areas, open ocean photic layer and deep-sea hydrothermal vent fields, is offered. This approach showed that the chemosynthetic based bottom hydrothermal fauna can remove 100-1000 times higher trace metal than the photosynthetic communities inhabiting shallow and deep sea areas.

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Trace elements in the deep-sea hydrothermal ecosystems: tracers of the biogeochemical processes

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The deep-sea hydrothermal vent fields represent geochemically interesting areas where processes of trace metal dispersion and concentration coexist. Water of the faunal biotopes is an example of diluted hydrothermal fluids while biological communities carry out trace metal bioaccumulation. Based on our latest results and relevant publications we summarize properties of trace metal biogeochemistry in deep-sea hydrothermal ecosystems at the Mid-Atlantic Ridge (MAR) and East Pacific Rise (EPR). Unlike the major ions, the trace metal concentrations decreases sharply during fluid dilution with seawater but stay much higher in water above the fauna settlements compared to the reference ocean water [*Sarradin et al.,* 2008; *Demina et al.,* 2010; *Demina*, 2010]. We have revealed that total amounts of Fe and Mn in the water can serve as tracers of mixing zone at the 9°50'N vent field, EPR along with earlier well documented measurements of temperature, pH and H_2S concentration [Sarradin et al., 1999].

The trace metals under consideration (Fe, Mn, Zn, Cu, Co, Ni, Cr, Pb, Cd, Ag, As, Sb, Se, and Hg) are concentrated differently from water and food in the different organs and organisms depending on the faunal pattern distribution around vent source, trace metal concentration in the biotope water, trophic level and specific difference of organisms. Among the animals a particular champion on trace metal content was found to be a polycheta *Alvinella pompejana* inhabiting the hottest places of the vent chimneys at the 9°50'N field, EPR. In separate tissues (tubes covered with filamentous bacterial mats) metal content reached the following values (% dry weight): 16.1 Fe, 3.73 Zn, 1.08 Cu, 0.07 Ni, 0.04 Co, Pb, Mn, As, 0.005 Cr, 0.002 Cd, 0.0007 Sb, 0.00006 Hg. Contrasting geochemical behaviour was revealed for Cu enriched soft tissues of different organisms, and Mn accumulating in the mussel shells mostly. New data on the trace metal behaviour during the biomineralization in case of carbonate shells of mussels and clams from MAR and EPR, as well as the authigenic porous aragonite from the Lost City vent site are discussed. Inter-site comparison of the trace metal partitioning within different tissues of the *Bathymodiolus spp.* mussels showed that a statistically significant difference occurred only between the high-temperature and low-temperature (Menez Gwen, MAR) vent sites.

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Molecular iodine emission rates of different thallus parts of *Laminaria digitata* determined using incoherent-broadband cavity-enhanced absorption spectroscopy

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Elemental iodine escapes the ocean in the form of molecular iodine (I_2), or bound in volatile iodo-carbons (e.g. CH_3I, CH_2I_2, ...) [*Carpenter*, 2003]. Once released into the atmosphere, these species undergo photolysis by solar radiation generating atomic iodine, which is known to be one of the most important catalytic species of a complex chemistry promoting the destruction of ozone and the formation of marine aerosols. Both phenomena can potentially affect the atmospheric radiation balance.

On various Atlantic coasts of northern Europe, I_2 concentrations typically exceed those of volatile iodo-carbons. At times of very low tides, when brown macroalgae of the upper sub-littoral zone are exposed to air, maxima in I_2 number densities have been observed [*Saiz-Lopez and Plane*, 2004]. This cyclic emission of I_2 has been recognized to also correlate strongly with ozone depletion events and aerosol formation [*O'Dowd et al.*, 2002; *McFiggans et al.*, 2004], suggesting that molecular iodine emitted by air-exposed macroalgae represents the dominant source for atomic iodine in coastal atmosphere [*Dixneuf et al.*, 2009]. Only a few studies on I_2 emission from brown macroalgae have been published [*Palmer et al.*, 2005; *Ball et al.*, 2010; *Laturnus et al.*, 2004; *Bale et al.*, 2008]. The data suggest that biogenic I_2 emission rates need to be considered in the context of several parameters such as the species' biotic and abiotic environmental impacts and the physiological status of the alga.

In this work time-resolved flux measurements of I_2 emitted by the brown macroalgae *Laminaria digitata* were achieved using incoherent-broadband cavity-enhanced absorption spectroscopy (IBBCEAS) [*Fiedler et al.*, 2003]. In IBBCEAS, the light from a bright incoherent source (e.g. a short-arc lamp) is transmitted through an optically stable cavity and dispersed with a grating monochromator and detected by a sensitive charged coupled device (CCD) detector. The IBBCEA measurements on fresh algal samples took place at the Finavarra research station, Co. Clare, Ireland, in November 2009. I_2 emission rates of three different (air-exposed) thallus parts of *L. digitata* were investigated in relation to the alga's dry weight and surface area, under low light and dark conditions [*Nitschke et al.*, 2010]. In order to address important aspects of the physiology of iodine in *Laminariales*, I_2 emission rates were measured (for the first time) in conjunction with the physiological stress experienced by the alga upon air-exposure, based on the alga's photosynthetic performance. The study revealed that the emission of I_2 is spatially inhomogeneous over the thallus; initial I_2 emission rates (measured within 30 min of exposure to air) were highest for stipes (median values: 2999 and 5222 pmol g^{-1} dw min^{-1} in low light and dark, respectively) and lower, by one order of magnitude, for meristematic regions and distal blades. I_2 emission rates were not affected by the light regimes tested. Moreover, the results indicate the presence of an iodine pool in the alga, which is easily volatilised and depleted due to air-exposure, even under apparently low stress conditions.

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Artificial Radionuclides : unique tools to investigate the circulation at various scales over the North West European Shelf.

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The nuclear fuel reprocessing plant located at La Hague (Normandy-France) releases under control in the centre of the English Channel various dissolved radionuclides, principally 3H, 106Ru, 137Cs, 90Sr, 125Sb and 99Tc. It is along with the Sellafield plant (UK), one of the main source of artificial radionuclides located on the North West European shelf. This source is precisely known because schedulings and quantities of each release have been recorded for now more than 26 years. Theses tracers have thus been used for a long time to investigate water masses dispersion at various space and time scales (e.g. Salomon et al, 1988, 1991, Bailly du Bois et al, 1993, 1995, Bailly du Bois and Guéguéniat, 1999, Bailly du Bois and Dumas, 2005).

On the one hand, at large scales, conservative tracers, with long half-life, such as Antimony 125 or Technetium 99 (respectively 2.76 and 2.105 years) give a good synoptic picture of the dispersion of the plume and insights of the low frequency circulation (over months) in the eastern English channel and the southern north sea: in particular, dilution rates and transit times have been deduced from mass balance between releases and measured quantities in the two basins. It is noticeable that theses data are well designed to calibrate wide models.

On the other hand, the tritium within the molecule HTO has the same behaviour as H2O and is thus very easy to sample in seawater. This provides a good means of investigations for high frequency circulation (scales of 40 km and period from hours to days). As hydrodynamics in the region of the outfall is very energetic (tidal currents of more than 5 m/s), the mixing induced is very large leading to a well mixed water column that can be relevantly sampled at three meters depth from two kilometers from the outfall on. In this area, sampling of the plume at a frequency of 30 sec allow to make up a view of the plume advection and dispersion, to assess its dilution rate, its horizontal mixing and and further to calibrate and validate numerical models.

Last but not least, this bidimensional horizontal picture has recently been extended to a fully three dimensional view thanks to a pioneering device (DYDESA : DYnamic DEpth SAmpler) which give a view of 2DV sections of the plume.

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Use of passive and active tracers in a biogeochemical-3D model to assess the role of river inputs on the Bay of Biscay, English Channel and southern North Sea.

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In most cases, eutrophication of a coastal zone is a multi-source phenomenon. The questions often raised by authorities about these different sources are: what are their marine area of influence and their respective role in the eutrophication process?

A first approach uses the hydrodynamical model alone with a passive tracer for each river to delineate the statistical marine receiving area of the main watersheds of the domain. The use of different percentiles (respectively 10, 50, 90) of the distribution of tracer values at each node of the grid over several years enables to map the dilution areas of each river plume respectively for low water regime, mean flow rate regime and flood regime.

A second approach uses a complete coupled biogeochemical-hydrodynamical model, along with a tracking technique which allows to follow any evolutive signature (in this case: nitrogen origin) and its age in the trophic network. This approach shows the gradual distortion of signature from the pure passive dilution when we look at higher and higher trophic levels. The study has been applied to the main tributaries of the domain, i.e the Loire and the Seine river (France), the Scheldt river (Netherlands) and the Thames river (UK), in order to estimate their respective contribution to primary and secondary production. Results from the real time application are available at www.previmer.org.

Seasonal Follow-up of the heavy metal contents of an estuarine system Tahaddart: (Moroccan Atlantic coast)

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Estuaries and coastal circles count among the most exposed zones to the various types of pollution, among others metallic. This kind of pollution is due to direct contributions from industrialization or to urbanization, often important in these zones, or to indirect contributions by rivers and by atmospheric way (Bryan 1984). The contamination of these ecosystems by heavy metals constitutes one of the major problems in environmental toxicology. Unlike organic pollutants, heavy metals are not, practically, the object of reaction of biological or chemical degradation; they can of this fact accumulate in food chains. The present work is a contribution of our laboratory to the program WATER DEMAND INTEGRATION, its objective is to characterize the state of the geochemical pollution and its temporal evolution during one year, of an estuarine system, in this particular case that of Tahaddart of the Moroccan Atlantic Coast. The sampling was made according to a new approach based essentially on the analysis of the leashes of floods and the tide freshly deposited. The study of the seasonal follow-up of heavy metal contents in the cream of mud during one year showed that, altogether, the estuary of Oued Tahaddart remains not polluted to little pollute. The state of healthiness of this ecosystem is due to its protection. Indeed, the estuary of Oued Tahaddart is a SIBE (Site of Biological and Ecological Interest) and a site RAMSAR protected by international agreements. The estuary of Oued Tahaddart can be considered as a clean studio site, and could be taken as a reference for the most part of the Moroccan and northwest African estuaries. However, a light impact on the quality of sediments is noticed since the starting of the highway use.

Keywords: Estuary, Tahaddart.

GREEN MERCATOR: Integration of biogeochemistry into Mercator Ocean operational systems

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The integration of marine biogeochemistry to operational systems is a timely development within the context of international initiatives focused on carbon monitoring and accounting, as well as science-based management of marine ecosystems and resources.

The objective of the Green Mercator (Mercator-Vert project) is to implement a marine biogeochemical and ecosystem component at the global scale into MERCATOR operational systems. The global configuration of the state-of-the-art multi-nutrient and multi-plankton biogeochemical model PISCES has been successfully integrated to operational Mercator Ocean systems.

In order to evaluate the impacts of physical data assimilation on modeled biogeochemical tracer distributions, two simulations were carried out: (i) a biogeochemical simulation forced by a physical free run (without physical data assimilation) and (ii) a biogeochemical simulation forced by a physical reanalysis (with physical data assimilation). We present a first evaluation of the capability of GREEN MERCATOR models to reproduce large scale distributions of biogeochemical tracers. To this end model output is compared to climatologies and data from one time series stations. The comparison of simulated biogeochemical fields provides a first assessment of impacts of physical data assimilation on modeled biogeochemical tracer distributions.

Holocene evolution of deep circulation in the northern North Atlantic constrained by sedimentary radiogenic tracers

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In this study we measure the Sm, Nd and Pb isotope signatures of the clayey fraction of deglacial and Holocene sediments from 4 deep North Atlantic cores. Radiogenic isotopes are use to trace the particle provenance. Temporal changes in the relative contribution of the different source-areas bring information on the deep circulation pathways (e.g., Fagel et al., 2004, Paleoceanography and references therein). Our aim is to reconstruct the main deep circulation changes over the Holocene in the northern North Atlantic. We compare the isotopic signatures at the inlet of the Labrador Sea (MD99-2227, 3460 m) with two sediment cores retrieved along the gyres of North Atlantic Deep Water (NADW) components. Cores were collected along fractures zones on the Mid-Atlantic Ridge: MD99-2254 on the Eastern side of the Bight Fracture Zone (2440 m) and HU91-045-080 on the western side of the Charlie Gibbs Fracture Zone (CGFZ, 3024 m). An additional core HU91-045-091 (3870 m) was taken on the Western side of the CGFZ, in the Labrador Sea but out of the Present deep circulation gyre. Core HU91-045-091 is chatacterized by a stable Sm, Nd and Pb composition. Its location is under the influence of proximal supplies from Labrador Sea margins. We conclude that the core HU91-045-091 remains sheltered from the deep circulation gyre over the Holocene. In contrast, significant shifts in the radiogenic composition of the sedimentary fractions are evidenced during the last 6 kyr for the other sites. Cores HU91-045-080 et MD99-2254 from the Eastern Atlantic basins are both characterised by a sharp increase in the chemical Sm/Nd ratio and the Nd composition at ca. 6 kyr BP. Those geochemical changes reflect a different composition of the particles driven by the deep currents through time. They imply a reorganisation of the deep North Atlantic components in the Eastern North Atlantic basins. A similar shift was observed but later (at 3 kyr BP) in core MD99-2227. Those compositional shifts all record a higher contribution of volcanic-derived material relative to crustal supplies, suggesting higher relative contributions from water masses that follows or crosses the Mid-Atlantic Ridge topography, i.e., the North East Atlantic Deep water (NEADW) components, in the deep circulation gyre. Likely Pb isotope signatures of deep sediments significantly evolve during the Holocene. The sedimentary mixings record changes in the relative contribution of the crustal material from the northern North Atlantic margins. The Eastern supplies from Western European margin are progressively diluted by more contribution from northern Greenland or Scandinavian margins. The observed spatial and temporal changes in the Nd and Pb isotopic composition of the northern North Atlantic sediments confirm the variability of the deep circulation over the Holocene, with the inception of the Present deep circulation gyre during the last 3 kyr.

Anthropogenic carbon inventory in the Gulf of Cadiz

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The area covered by the Gulf of Cadiz and the Strait of Gibraltar plays a relevant role in the general circulation of the North Atlantic due to the channelization of the water exchange between the Atlantic Ocean and the Mediterranean Sea. Several studies have confirmed that the North Atlantic is the most important sink for atmospheric CO_2 [*Takahashi et al*, 2009; *Sabine et al*, 2004] but there still remain uncertainties about the total amount of CO_2 stored in this region and the anthropogenic CO_2 (C_{ANT}) exchanged between the Mediterranean and the Atlantic.

During the P_3A_2 oceanographic cruise performed in the Gulf of Cádiz and the nearby Strait of Gibraltar in October 2008, extensive measurements of the carbon system parameters (pH_T,A_T, C_T) and others related (Dissolved Oxygen and nutrients) were carried out to analyse their distribution. In addition, in order to study the spatial variability of the anthropogenic carbon in the region, three of the most recent observational methods to estimate C_{ANT} concentration (φC_T^o, ΔC^* and TrOCA) were applied to the dataset. The attained results are presented here and discussed in relation to the three water masses clearly identified in the area: North Atlantic Central Water (NACW), North Atlantic Deep Water (NADW) and Mediterranean Water (MW), which were shown to contain different C_{ANT} concentration. Overall, NADW exhibited the lowest C_{ANT} concentration whereas NACW was C_{ANT} enriched. Furthermore, data confirmed previous finding indicating a net import of C_{ANT} from the Atlantic Ocean to the Mediterranean Sea through Gibraltar [*Huertas et al*, 2009]. The C_{ANT} inventory was also calculated in the basin by considering the three different methods applied and scaled in relation to that of the North Atlantic.

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Changes in the deep water circulation of the Arctic Ocean during the last 30 years inferred from the distribution of ^{230}Th in the water column

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Dissolved ^{230}Th was first measured in the water column of the Arctic Ocean in 1983 from an ice camp over Alpha Ridge (Bacon et al., 1989). Subsequently, an additional 23 profiles were measured at various locations between 1987 and 2009 in the Eurasian and Canadian Basins (Cochran et al., 1995; Scholten et al., 1995; Edmonds et al., 1998; 2004; Francois et al., unpub.). These profiles can be compared in space and time to infer changes in the deep water circulation of the Arctic Ocean. In particular, it can be shown that, prior to the early 1990's, a water mass remained largely isolated from the general circulation of the Arctic Ocean, under permanent ice cover over Alpha Ridge and in northern Makarov Basin. This relative isolation is based on the very high dissolved ^{230}Th concentrations measured at these two locations in 1983 and 1991, respectively. In the mid-1990's, the pattern of Arctic deep water circulation started to change, resulting in the displacement of some of this previously isolated water mass into the surrounding basins, first in the Norwegian Sea, and most recently in Canada Basin. These data further illustrate the potential of ^{230}Th as a powerful tracer of deep water circulation.

NORTH-EAST ATLANTIC WATER MASS GEOCHEMICAL TRACERS DURING THE PAST 60 YEARS AND BEYOND (NEWTON)

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The North Atlantic surface ocean circulation is composed of two major wind driven gyres (subpolar and subtropical gyre) throughout which the properties of the North Atlantic current and thus the Nordic inflow are set. North Atlantic Oscillation and variable fresh water fluxes impact the properties, mass balances and strength of both gyres influencing deep convection in the Arctic Ocean. At thermocline depth, boundary currents and basin scale re-circulation patterns (eddy driven gyres) are intimately link to the surface circulation patterns, and which feed salinity and heat into the overall mass balance of the Nordic inflow. Those surface and mid-depth circulation patterns are today monitored using hydrographical data, ARGO floats and satellite observations. However, little is known about the circulation patterns on time scales of decades to centuries beyond the instrumental records. Throughout the French national project NEWTON we have tested whether the lack of long term records of the Atlantic Ocean surface and mid-depth circulation patterns can be overcome through the use of geochemical water mass tracers such as radiocarbon and neodymium isotopes recorded in deep-sea corals and mollusk shells. Seawater radiocarbon was reconstructed from historical mollusk shells and U-series dated deep-sea corals dwelling in the northeast Atlantic during the past 60 years and beyond. Nd-isotopes were explored solely on deep-sea corals. Here, the resulting tracer time series (at annual to decadal resolution) will be compared to results of ocean modeling and reconstructions of historical T, S patterns. We demonstrate that both tracers can record the mass balance, state of ventilation and provenance of surface and mid-depth water masses along the European margin and that both are predominantly reflecting west-east and south-north advection patterns. The present day and recent north-east Atlantic circulation patterns are well evident in the tracer time-series and our findings are in agreement with hydrographical observations. Even the link between NAO and surface to mid-depth ocean circulation is clearly revealed. Thus, using geochemical tracers recorded in mollusks and deep-sea corals provides direct measures of north-east Atlantic advection patterns allowing in the future to extend instrumental records backwards. In addition, a new tracer for the reconstruction of ocean temperatures have been found in deep-sea corals.

Silicon pool dynamics and biogenic silica export in the Antarctic Circumpolar Current inferred from Si-isotopes.

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This study presents the first complete summer Antarctic Circumpolar Current (ACC) transect of δ^{30}Si of silicic acid ($Si(OH)_4$) (surface to bottom) including adjacent subsystems (SubTropical Zone and the northern part of the Weddell Gyre), sampled during the BONUS-Goodhope project. The results are discussed in terms of source, pathway, and fate of silicon across the different Southern water masses and the interaction of the latter with the water masses from other oceanic basins. In the Southern Ocean silicon isotopic variations (δ^{30}Si) of $Si(OH)_4$ are large in the upper 1000m and reflect the effect of the silica pump superimposed to the meridional transfer across the ACC. The latter are due to the transport of Antarctic surface waters northward by a net Ekman drift under the influence of the Southern Ocean westerly winds and their convergence and mixing with warmer upper-ocean Si-depleted waters to the north. We determined different ACC mixing interfaces: the Antarctic Surface Water (AASW), the Antarctic Intermediate Water (AAIW), and the thermoclines in the low latitude areas. The residual silicic acid concentrations of the end-members control the δ^{30}Si alteration of the mixing products. Except for the AASW, all mixing interfaces have a highly Si-depleted mixed layer as end-member. These processes deplete the silicic acid AASW concentration across the different interfaces northward without significantly changing the AASW δ^{30}Si. The circulation and hydrology of the ocean is expected to be different between glacial/interglacial periods. A modification of the ocean's circulation would alter the δ^{30}Si of the subsurface water masses and in turn the source δ^{30}Si of the surface waters fuelling $bSiO_2$ production. This effect has to be better constrained for a safely utilization of this proxy in the past oceans. During the circumpolar baroclinic transport of the ACC, there is a slight but significant Si-isotopic lightening of the silicic acid pools from the Indo-Atlantic to the Australian sectors. This results either from the dissolution of biogenic silica in the deeper layers and/or from an isopycnal mixing with deep water masses in the different oceanic basins: North Atlantic Deep Water in the Indo-Atlantic, and Indian Ocean deep water in the Indo-Australian sector. This eastward lightening is further transmitted to the subsurface waters, representing mixing interfaces between the surface and deeper layers. Using the Si-isotopic constraint, we estimate for the Greenwich Meridian a net biogenic silica production at 4.5 ± 1.1 and 1.5 ± 0.4 mol Si m^{-2} for the Antarctic Zone and Polar Front Zone, respectively, in agreement with previous estimations. The summertime Si-supply into the mixed layer via vertical mixing was also assessed at 1.5 ± 0.4 and 0.1 ± 0.5 mol Si m^{-2}, respectively.

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Dissolved and particulate REE patterns and Nd isotopes along the Bonus GoodHope (BGH) section

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Dissolved ($\leq$0.4 μm) and suspended particle concentrations of Rare Earth Elements (REEs) have been measured in seawater along the Bonus GoodHope (GEOTRACES/IPY) section in the Atlantic sector of the Southern Ocean (R/V Marion Dufresne). The dissolved REE concentrations increase with depth, in similar ranges as nearby historical data (e.g. from 11 to 33 pmol$\cdot$kg^{-1} for Nd) [German et al., 1995; Jeandel, 1993]. Dissolved REE patterns -normalized to PASS- evidence a clear enrichment of HREEs relative to LREEs together with a pronounced Ce depletion at all the stations (Ce anomaly ranging from 0.06 to 0.14). A positive dissolved Gd anomaly (Gd/Gd* of 1.2-1.3) also appears as a common feature in all the measured REE patterns, as already pointed out by De-Baar et al. [1985]. The origin of such Gd enrichment in seawater is still under debate: hypotheses propose a differential chemical behavior of this element with respect to the other REEs in terms of weaker binding constants of Gd^{3+} with particle surfaces or its preferential complexation with organic ligands. However, positive anomalies are also observed in the suspended particles (Gd/Gd* from 1.0 to 1.4), suggesting that it rather reflects the composition of the source materials.

Off the African continent, a station located in the Subtropical Region shows flat (crust-like) PASS-normalized patterns of particulate REEs, different from the other open stations, what indicates an important influence of continental inputs [Tachikawa et al., 1999] likely form the African margin sediments. Indeed, neodymium isotopic composition as negative as ϵ_{Nd} = -14 has been observed at 2000 m depth in this area, in agreement with an imprint from the South African margin material that presents ϵ_{Nd} of -12 to -14 [Hegner et al., 2007]. Using Al content in suspended particles as a lithogenic tracer, we show that almost all particulate Ce is of continental origin, as somehow expected due to the proximity of the African margin. Exceptions to this feature are the shallowest and deepest samples (30 m and 5000 m depth, respectively), which contain up to 60

Contrastingly, in the open ocean, PASS-normalized REE patterns in particles are seawater-like pointing to either a predominant authigenic contribution or that the exchange between dissolved and particulate phases occurring in the water column is achieved. The dissolved/particulate exchange processes are being studied and will be explored in more detail when the whole set of ϵ_{Nd} data will be acquired.

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On the use of sub-mesoscale tracer information for the control of ocean circulations

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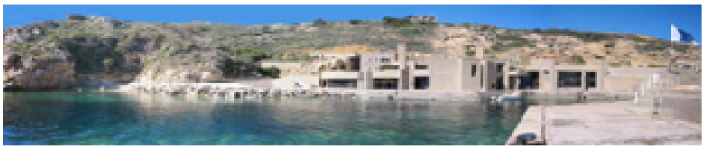
In the ocean, turbulent dynamics encompasses a wide range of scales and is characterized by high energy levels including at smaller scales such as the so-called sub-mesoscales (e. g. Klein et al, 2010). Ocean observations from space include chlorophyll and sea surface temperature (SST) measurements that are of great interest for synoptic ocean studies. These tracer fields reveal also a clear signal at the sub-mesoscales in most regions of the world ocean. There is more and more evidence that the understanding and modelling of the physico-biogeochemical behavior of the ocean requires to know more about those various scales, to understand their role and interactions and to adequately represent or parameterize the mesoscales and the sub-mesoscales in ocean models. In this regard, tracers are of great value as they are the only fine resolution observations that provide insights on those scales and in particular on the sub-mesoscales.

In this work, our objective is to explore the feasibility of using tracer information at the sub-mesoscales to possibly control ocean dynamic fields. In order to do so, we choose an image data assimilation strategy in which a cost-function is built that aims at minimizing the misfits between some image of sub-mesoscale flow structure and tracer images. In the present work we have explored the extent to which the Finite-Size Lyapunov Exponent (FSLE) can be considered as a proxy characterizing the sub-mesoscale flow structure. The FSLEs represent the stretching of the geophysical fluids (Lehahn et al, 2007) and extremal values can be seen as frontal barriers in the studied fluid. The choice of Lyapunov Exponents as a proxy for tracers is motivated by d'Ovidio et al (2004), where similar patterns between tracers and FSLE images are evidenced.

A prerequisite to the study is that the relation between the ocean dynamics and FSLE can be inverted, that is to say that the sub-mesoscale information transmitted through the intermediate FSLE proxy is effective in controlling the ocean system.
This assumption is tested in a 10 by 10 regional piece of ocean in the North East Atlantic. The ocean dynamical variable to be corrected is the mesoscale altimetric velocity field. Therefore, the sensitivity of FSLE horizontal patterns to velocity errors is investigated. To do so, a Gaussian velocity error field is created using up to fifteen years of altimetric data. A cost function is then defined to measure the misfit between the Lyapunov exponents computed using velocities with errors and the Lyapunov exponents derived from a 'true' (error free) velocity. It is found that a global minimum can be identified in this cost function proving that the inversion of FSLE is feasible.

These results show the feasibility of assimilating sub-mesoscale into ocean models for the control of mesoscale dynamics and larger scales. But the calculations must be extended and generalized. Use of SST tracer data from a numerical simulation also proved to be successful. A further step must be the use of actual sub-mesoscale images from chlorophyll or SST. The difficulty remains in identifying properly frontal structures in tracer images so that an equivalent of FSLE image using a real snapshot of a tracer is computed. Other proxies than Lyapunov exponents may also be thought of.



STARESO (STAtion de REcherches Sous-marines et Océanographiques) and STARECAPMED (STAtion of Reference and rEsearch on Change of local and global Anthropogenic Pressures on Mediterranean Ecosystem).

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STARESO (STAtion de REcherches Sous-marines et Océanographiques) is a field marine station, located in the Calvi Bay (West Corsica) that belongs to the University of Liege (Belgium). The station has been founded in 1970 and actually operated by STARESO s.a.s.

STARESO is located inside a very preserved marine site. The Station is open to foreign researchers for samplings or workshops (www.stareso.com; stareso@stareso.com), it provides for scientists and oceanographers a very easy access to Mediterranean coastal and open ocean ecosystems.

STARESO research activities are based on a local scientific staff, the University of Liège Oceanography Department of and numerous international collaborations. Research topics ranged from general marine biology to physics of the ocean.

Actually the University of Liege and STARESO are developing an integrated research project called STARECAPMED: STAtion of Reference and rEsearch on Change of local and global Anthropogenic Pressures on Mediterranean Ecosystem.

The project is based on ten actions on the coastal Mediterranean zone and on near open ocean:

-Physico-chemical framework : CTD, nutrients, weather…

-CO2 : climate changes, pH, metabolic rates…

-Plankton: phytoplancton, zooplancton…

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-Soft substrate: macrofauna, indicators, seascape...

-Rocky substrate and vagile fauna: algae, invasive species, « coralligène », seascape…

-Databank

-Modelisation : currents, ecosystem, nutrient fluxes…

-Ecotoxicology : trace metals, stable isotops

-Scientits-Managers-public Interface: website, dissemination, education…

Coordinator : Pierre Lejeune. President : Gérard Bonifacio

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Seasonal and depth-related variations of δ^{13}Corg and δ^{15}N in settling particles from the open Eastern Mediterranean Sea (NESTOR site)

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The Eastern Mediterranean Sea (EMS) is an oligotrophic basin that presents unusually high N:P molar ratio (up to 28:1) and depleted δ^{15}N values in nitrates and suspended material compared to other oceanic settings (Emeis et al, 2010). In order to investigate the significant biogeochemical features and provide new insights on the temporally and spatially sources of nitrogen and carbon in the region, we have examined long-term records of δ^{13}C and δ^{15}N in sinking particulate matter intercepted in sediment traps. The time-series collection of the sinking material was performed with two mooring lines, deployed from November 2006 to November 2008 at successive ater column depths (700, 1200, 2000, 3200 and 4500 m; NESTOR 4.5), and (5200 m; NESTOR 5.2) in the SE Ionian Sea, where the deepest part of the Mediterranean Sea is located (Calypso Deep; off Peloponnese).

Total organic carbon and total nitrogen contents decrease with depth, except of few cases (e.g. winter of 2006-2007), where sinking matter isolated from the deeper sites exhibit high OC and Ntot contents. Our hypothesis, supported by physical data is that enhanced deep water formation occurring in the southern Adriatic Sea is probably responsible for the delivery of 'fresh' organic matter to the deeper Nestor sites at that time. The δ^{15}N values of sinking particulate nitrogen, ranging between -0.52 and 5.89 ‰, found to be lower compared to the values recorded in other oceanic sites. Low δ^{15}N values, close to the atmospheric ratios in the EMS aerosols are related probably to the hydrological shift in the 1990s, rather than to enhanced N fixation rates (Mara et al., 2010; Emeis et al., 2010). During summer, preferential remineralisation of light nitrogen lead to increasing δ^{15}N values in settling particles with depth. This seasonal and depth-related increase in the δ^{15}N signal is in accord with the findings of a previous study on mesozooplankton assemblages isolated from shallow (700 m) and deep (2700 m) waters, that document increasing length of the food chain with increasing depth.

The δ^{13}Corg of sinking matter ranged from -22.7 to -27.3 ‰, exhibiting lower values at higher depths. Based on the δ^{13}Corg values, we have estimated the relative proportions of marine and terrestrial OM with a two end-member model at various depths. Although the predominant source of settling particle is planktonic in the shallower traps, the lower values at higher depths suggest the delivery of terrestrial OM in the deep Nestor sites, due probably to lateral transport from the Peloponnese shelf .

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Carbonate system buffering in the water masses of the Southwest Atlantic sector of the Southern Ocean during February-March 2008

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Carbonate system variables were measured in the South Atlantic sector of the Southern Ocean along a transect from South Africa to the southern limit of the Antarctic Circumpolar Current (ACC) in February-March 2008. Eddies detach from retroflection of the Agulhas Current located north of the Subantarctic Front (SAF). The eddies increase the gradients observed at the fronts so that minima in fCO2 and maxima in pH in situ on either side of the frontal zone are observed, while within the frontal zone fCO2 reached maximum values and pH in situ was a minimum. Mixing at the frontal zones, in particular where cyclonic rings were located, brought up CO2-rich water (low pH and high nutrient) that spread out the fronts where recent biological production favored by the nutrient input increases the pH in situ and decreases the fCO2 levels. Vertical distributions of water masses were described by their carbonate system properties and their relationship to CFC concentrations. Upper Circumpolar Deep Water (UCDW) and Lower Circumpolar Deep Water (LCDW) had pHT,25 values of 7.56 and 7.61, respectively. UCDW also had higher concentrations of CFC-12 ($>$0.2 pmol kg-1) as compared to deeper waters, revealing the mixing with recently ventilated waters. Calcite and aragonite saturation states (Ω) were also affected by the presence of these two water masses with high carbonate concentration. Ωarag = 1 was observed at 1000 m in the subtropical area and north of the SAF. At the position of the Polar front and under the influence of UCDW and LCDW Ωarag = 1 deepen from 600 m to 1500 m at 50.37ºS, and it reaches to 700 m south of 57.5ºS. High latitudes are the most sensitive areas under future anthropogenic carbon increase. Buffer coefficients related to changes in [CO2], [H+] and Ω with changes in CT and AT showed the minimum values are found in the Antarctic Intermediate Water (AAIW), and UCDW layers. These coefficients suggest that a small increase in CT will sharply decrease the pH and the carbonate saturation states. Here we present data that are used to suggest that south of 55ºS by the year 2045 surface water will be undersaturated in aragonite

Tracer transport modeling on Kuroshio subsurface water intrusion onto the shelf of East China Sea

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Using results of a high resolution ocean model (Guo et al., 2003JPO; 2006JPO), a series of passive tracer numerical experiments were carried out to examine the Kuroshio water intrusion processes onto continental shelf of East China Sea. The passive tracers are given as a boundary condition along 24N, from Taiwan to 125E, representing the Kuroshio surface and subsurface waters. Firstly, the tracer was set to the whole water column. The distribution of tracer on the continental shelf indicates a clear seasonal variation of Kuroshio water intrusion in the surface layer, which is strong in winter and weak in summer. On the other hand, the tracer can be found in the bottom layer of the outer shelf (100-200 m) throughout the year, which starts to intrude onto the inner shelf (50 100 m) in spring, reaches the area close to Chinese coast (0-50 m) in early summer and stays there until later summer. It is found that the development of bottom Ekman layer over the inner shelf associated with the intensification of Taiwan Strait Current from spring to summer is responsible for the onshore transport of tracer in the bottom layer from outer shelf to inner shelf while the coastal upwelling associated with the southwesterly wind is responsible for the appearance of tracer near Chinese coast. To examine the contribution from the Kuroshio water in different depths, the calculations were repeated with the tracer being set to 0-50 m, 50-100 m, 100-200 m, 200-500 m, 500-1000 m, respectively. It is found that the tracers from the shallow layers (50-100, 100-200 m) contribute more to the western shelf of ECS than those from deep layers (200-500, 500-1000 m). On the other hand, the tracers from deep layers contribute more to the eastern shelf than those from shallow layers. Such results provide an interpretation on the observed higher bottom nutrients concentration in the western shelf than in the eastern shelf of ECS.

The impact of Superoxide (O2-) on trace metal redox cycles and the reactivity with dissolved organic matter

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The superoxide (O2-) radical is suspected to be a critically important species involved in the redox cycling of metal ions in natural waters. In sunlit surface waters O2- is a major product of the photooxidation of colored dissolved organic matter (CDOM) and it can also be produced via phytoplankton metabolic processes. Inorganic and organic complexes of Cu(II)/Cu(I) and Fe(II)/Fe(III) can react rapidly with O2- leading to a catalytic cycle for superoxide decay but also reactions with dissolved organic matter are suggested as reaction pathway. Our work conducted during the IPY Geotraces cruise ANTXXIV-3 found Cu to be the major sink of O2- in the Southern Ocean despite being strongly organically complexed. This indicates that the Cu organic complexes react directly with O2-. Contrastingly the reaction with Fe was relatively slow throughout the water column. In the eastern tropical Atlantic (unlike the Southern Ocean) we found a significant reactivity of O2- with CDOM. Maximal reaction rates were adjected to the chlorophyll maximum which suggests production or release of unbleached organic material. This work highlights poorly understood processes which impact on the biogeochemical cycling of relevant trace metals and CDOM in the open ocean.

A reduced estimate of the strength of the ocean's biological carbon pump

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A major term in the global carbon cycle is the ocean's biological carbon pump which is dominated by the sinking of small organic particles from the surface ocean to its interior. Several different approaches to estimating the magnitude of the pump have been used, yielding a large range of estimates. Here, we use a large database of thorium-derived export measurements to estimate globally integrated particle export. Each thorium derived estimate of POC flux was combined with an estimate of productivity made using remote sensing techniques. The resultant set of export ratios correlated strongly with seasurface temperature, allowing a global field of export ratio to be obtained. This was then combined with a global productivity field to estimate integrated export 5 GtC yr-1, at the low end of the range of most current estimates. Potential causes and consequences of this result will then be discussed.

Comparing gas transfer velocities measured with tracer mass balance and CO_2 eddy covariance

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Quantifying air-sea gas exchange is important for understand global biogeochemical cycles. In the last two decades, the $^3He/SF_6$ dual tracer technique and eddy covariance of CO_2 have emerged as the leading methods for quantifying gas transfer velocities (k) in the ocean. However, large-scale field experiments have shown different functional dependences of k on wind speed, even during the same experiment, with the $^3He/SF_6$ dual tracer method favoring a quadratic dependency (e.g., Nightingale et al., 2000; Ho et al., 2006; Ho et al., submitted), and the eddy covariance yielding a higher order cubic dependence (Wanninkhof and McGillis 1999; McGillis et al., 2001; Edson et al., submitted). In this contribution, we explore the causes of this discrepancy by examining: 1) field data collected during these experiments; and 2) the processes that might lead to the observed differences using a 1-D numerical model of the upper ocean. The ultimate goals are to reconciling this apparent difference in techniques, and determine the most appropriate functional form to use for modeling global biogeochemical processes.

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A NEW TRACING TOOL: DIRECT MEASURES OF PARTICLE DISPERSION IN THE OCEAN AND APPLICATION TO NUMERICAL MODEL VALIDATION

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Dispersion estimates were measured through the use of magnetically attractive particles (MAPs) and moored magnetic-collector arrays. Collectors were moored within predicted dispersal domains (nominally 2–$4 \times 10^3\ km^2$) enveloping putative "sink" locations based on empirically-driven, 200 m and 2 km resolution, 3D hydrodynamic models. At a source location within a given array, $\approx 10^9$ MAPs (nominally 300 μm diameter) of a near-surface buoyancy were released and allowed to disperse over time (nominally 5–7 d) after which the collector array was retrieved and the number of MAPs captured by each collector were enumerated. These numbers were then used to estimate dispersion and the relative probability of physically-driven Lagrangian exchange within the dispersal domain. The estimates were then used to validate the hydrodynamic models (real-time conditions) by comparing the time integral of the model-particle concentrations at each of the collector locations (expected) against the MAP abundance estimates at each collector in the field (observed). Deviations between the expected and observed were used to assess model parameters. Our results show that a higher than expected random walk diffusion parameter is necessary for the models to best reproduce the observed MAP dispersion.

Barite crystals facies in the Southern Ocean: towards a better understanding of bio-organo-mineralisation mechanisms

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Among the approaches developed this last decade to resolve the issue of the controls on particle transfer efficiency to, and organic carbon remineralisation in the mesopelagic zone, stands the study of particulate biogenic barium (Baxs)- barite ($BaSO4$) distribution in the water column. This approach relies on the formation of nano- to micro- barite crystals in association with sinking decomposing organic matter, in a world ocean mostly undersaturated for barite, and the release of these crystals after remineralization of the organic matter carrier. The water column distribution of barite in suspended matter reflects production of barite to take place mainly below the surface layer and to be ongoing mainly through the mesopelagic zone. However, the exact mechanism by which barite precipitates is still a matter of debate. Barite crystals in suspended matter collected during the BONUS-GOODHOPE cruise (2008) were examined by scanning electron microscopy and energy dispersive X-ray spectrometry (SEM-EDX). The different facies and compositions of marine barite crystals from surface and mesopelagic depths are compared to investigate whether these carry information on the bio-organo-mineralization mechanisms. These results are compared with Baxs and barite profiles determined by ICP-MS and SEM-EDX analysis, respectively.

Land-to-ocean processes on and along the Kerguelen plateau traced by the REE concentrations and Nd isotopic composition

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One of the KErguelen Ocean and Plateau compared Study objectives (KEOPS, 19 Jan-13 Feb 2005, R/V "Marion-Dufresne") was to determine the natural fertilizing mechanisms responsible for the bloom regularly observed on the Kerguelen plateau in austral summer. Coupled with physical measurements, a multi-proxy investigation was carried out in order to better constrain the sources of micro nutrients, as well as the water mass and particle pathways. Dissolved REE concentrations, dissolved radium isotope activities and recently dissolved δ^{30}Si data strongly suggest that elements are released from the basalts sediment deposited on the shelf of Heard Island *(Zhang et al., 2008; van Beek et al., 2008; Fripiat et al, 2011).* This mechanism is suspected to provide significant amounts of iron into the plateau waters, hypothesis recently confirmed by the measurements of total dissolvable iron (TDFe, *Chever et al, 2010)* and iron isotopes (*Radic, 2011, Lacan et al, this volume*). However surface waters were depleted in dissolved iron at the cruise time (*Blain et al, 2007)*, making us suspect that in addition to the biological consumption, strong scavenging affects these waters. These observations raise questions such as i) differentiating the net input resulting from the dissolved/particle exchange and ii) understanding processes releasing elements from the lithogenic material.

We present dissolved and particulate Nd isotopic compositions, measured on and off the plateau, expressed as ε_{Nd}=[(^{143}Nd/^{144}Nd)$_{sample}$/(^{143}Nd/^{144}Nd)$_{CHUR}$]-1)*10,000 where "CHUR" is a reference. These isotopes bring new insight on the scavenging, mixing and exchange processes at play in this area. At open ocean stations, circumpolar deep waters are characterized by dissolved ε_{Nd} of – 9.9 ± 0.2, value increasing to -8.6 ± 0.3 when the same waters flow along the eastern slope of the Plateau, whereas Nd concentration simultaneously drops by a factor ~2. Suspended particles at the HNLC station (C11, open ocean water column) display isotopic compositions similar to the dissolved ones, suggesting efficient dissolve/particle exchange. Both the input of radiogenic Nd (explaining the ε_{Nd} increase) and its obvious subtraction reveal that strong "Boundary Exchange" is acting along the slope. On the Plateau, most of the dissolved values are above -8, the most radiogenic ones (-4.8) being observed at the station nearby Heard Islands. These radiogenic waters are also characterized by less pronounced Ce anomaly (in the dissolved phase) than the non radiogenic ones, clearly confirming the recent release of basaltic particles. The suspended material display ε_{Nd} values ranging from -1.8 close to Heard to -6.1 in the middle of the plateau (station A3). This gradient suggests dissolve/particulate exchange during the water transit above the plateau.

These different data sets allow the estimate of input and scavenging rates on and off the plateau.

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Ventilation of intermediate and deep waters in the Nordic Seas

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The Nordic Seas is a well known source area for the North Atlantic Deep Water. During the last decades large changes have been reported in the Greenland Sea deep waters (e.g., Karstensen et al., 2005) but the question is how these changes have propagated into the other parts of the Nordic Seas. In order to evaluate this we utilize the comprehensive CARINA dataset (Key et al., 2010) which covers the time period from 1982 to 2006. We evaluate variability and trends in the ventilation of the Nordic Seas basins from observed CFC data. The results are discussed in parallel with observed evolutions in hydrography and hydrochemical data. In the Iceland and the Norwegian Seas clear ventilation are observed at all depths, whereas the Greenland basin only show steady ventilation down to approx. 1500 m, with observed deeper ventilation during the early 2000s. The evolution in the different basins are discussed and compared and we estimate rates of ventilation and exchanges in the Nordic Seas.

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The ^{3}He Flux Gauge

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Quantification of fluxes is an important part of developing a deeper understanding of ocean processes and biogeochemical cycles. Observation and modeling of the distributions of radioactive and transient tracers continues to provide us with valuable insights and constraints on ocean ventilation, mixing, circulation, and carbon fluxes. The character of such information is largely oriented toward the transport of surface-derived characteristics into the ocean interior and abyss. Another important aspect of ocean biogeochemical cycles is the return of material to the surface layer. For example, the supply of nutrients to the euphotic zone from the thermocline and the deep ocean sets a fundamental limit on the new biological production on annual and longer timescales. On even longer time-scales, the influx and uptake of elements associated with volcanically driven hydrothermal systems on the sea floor plays a role in the global geochemistry of the oceans.

The stable, inert isotope ^{3}He is a valuable part of the oceanographer's toolkit for studying many of these processes. When coupled with the bomb-fallout isotope tritium (^{3}H), it can be used as a powerful dating tool for studying water mass subduction and thermocline ventilation ranging from seasonal to multi-decade time-scales. As useful, however, is documenting the fate of the tritiugenic ^{3}He produced in the thermocline: its return to the sea surface by upwelling and mixing produces a measurable excess that can be used to determine a flux using known gas exchange rates. That is, ^{3}He in the thermocline behaves as a pseudo-nutrient whose production (by tritium decay) is absolutely known, and whose transport is unambiguously physical. The ^{3}He flux thus determined can be used gauge the return fluxes biogeochemically important materials to the euphotic zone. In the abyssal ocean, the injection of volcanic ^{3}He from submarine hydrothermal systems provides marine geochemists with yet another flux gauge. On a local to regional scale, ^{3}He provides a useful measure of dilution scales, allowing the use of element/^{3}He ratios to diagnose water column removal or production rates. Because we know the global hydrothermal ^{3}He flux, documentation of element/^{3}He ratios permits the estimation of global fluxes.

I present some examples of the ^{3}He flux gauge methods with a view to demonstrating and discussing their strengths, weaknesses, and limitations. Attention is given first to estimation of nutrient fluxes to the euphotic zone on annual to decade time-scales. The discussion is extended to using the regional and temporal evolution of the ^{3}He-NO_3 relationship to diagnose winter-time biogeochemical processing of these tracers. Second, I discuss the concept of using Fe/^{3}He ratios to estimate global hydrothermal input of iron to the deep ocean.

Nutrients conditions controls on phytoplankton communities in Chukchi Sea during Aug. to Sep., 2008

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Abstract:The Chukchi Sea shelf is one of the highest productive area in the the world due to inflow of nutrient-rich Pacific water. The structure of phytoplankton communities would be affected by different nutrients conditions in Chukchi Sea. Photosynthetic pigments and nutrients (nitrate, phosphate, silicate) were studied during the third China Arctic Research Expedition, from Aug. to Sep., 2008. And the structure of phytoplankton communities were discussed under different nutrients conditions. The results showed nutrients conditions were much different not only affected by different characteristics of Bering Strait inflow currents, but also affected by phytoplankton depletion. pigments and phytoplankton communities in the Chukchi showed spatial and temporal variation during Aug. to Sep. Along 168ºW, from Bering Strait to north in Chukchi sea, diatoms dominated over the shelf where controlling by high nutrients inflow water in the upper layer in early Aug. With the nutrients depletion, the structure of phytoplankton communities changed to smaller ones with dinoflagelates and prasinophytes increasing in Sep. The stations influenced by Alaska coastal current with low salinity and low nutrients, smaller phytoplankton such as prasinophytes, chlorophytes and cryptophytes were dominated. Prymnesiophytes were found at high latitude area (higher than 74ºN) with low nutrients.

Investigating the response of the biological pump to rising atmospheric pCO_2 using a Lagrangian model of sinking biogenic aggregates

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Aggregation and subsequent sinking of phytoplankton cells is a major pathway by which carbon is transported from the atmosphere to the deep sea, in a process called the biological pump. Climate change, due to rising atmospheric concentration of CO_2, is causing warmer and more stratified, nutrient depleted waters that affects phytoplankton physiology and recycling of organic matter. To understand the effect of environmental changes on the flux of organic carbon we have developed a particle-resolved model of aggregation and subsequent sinking of phytoplankton and detritus. Our model tracks a statistical sample of the particles throughout the water column. Briefly, coagulation and disaggregation occur stochastically according to probabilities calculated theoretically. The geometry of marine aggregates exhibit fractal properties; we use data on their fractal dimension to calculate porosity and thus density, and sinking velocity is then calculated using a modified Stokes equation. The model accounts for respiration of organic carbon and TEP due to bacteria and zooplankton. Organic carbon fluxes in the water column seem to require a slowing degradation rate with depth, which motivated us to implement multiple age groups with slowing degradation rate constants, as also observed more broadly in organic geochemistry. Minerals, $CaCO_3$ and opal, dissolve thermodynamically and $CaCO_3$ also dissolves biologically. Size spectrum data of suspended particles in the deep ocean suggest disaggregation is a major mechanism. We model disaggregation to be due to a combination of swimming zooplankton and the degradation of TEP.

The model is able to reproduce regional variations in organic carbon export efficiency to the sea floor by varying sea surface temperature, primary production and seasonality. It captures the decreasing export ratio with increasing temperature and the positive correlation between export and primary production as observed globally in the surface ocean.

The size and density of aggregates affect their sinking velocity which determines to a great extent the flux of organic carbon down the water column. We show the effects of changes in temperature, primary production, plankton calcification, bloominess and TEP production on the size, shape and sinking velocity of aggregates and the effects these have on the strength of the biological pump.

Oceanic element budgets: changing the paradigm

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Several recent publications – most of them based on isotopic budgets – suggest that continental sediments deposited along ocean margins are capable of releasing a significant proportion of their constituting elements to seawater. The oceanic distribution of neodymium (Nd) isotopes and concentrations suggest that ~3% of continental sediments deposited along ocean margins are involved in this releasing process *(Arsouze et al., 2009; Lacan and Jeandel, 2005)*, behavior consistent with observations made in estuaries and suggesting a sediment and/or suspended material source for Rare Earth Elements (REE) to the ocean (*Sholkovitz and Szymczak, 2000*). Off Papua New Guinea and the South African Coast, the heavy isotopic composition of dissolved iron (Fe) suggests that the process releasing Fe to the seawater could be a non reductive release of sediments, rather than the usually invoked reductive dissolution (*Radic et al., accepted, Labatut et al, this volume*). Although the release of Nd and other REE could also result from the dissolution of Mn and Fe oxides, the oceanic budget of Nd isotopes constrains the involvement of a detrital lithogenic end member in the release process *(Jeandel et al, submitted*). On the Kerguelen plateau, the δ^{30}Si composition of waters enriched in $Si(OH)_4$ is significantly lighter than those of nearby open ocean waters. These light values could reflect a significant contribution of the Kerguelen/Heard basalt alteration, representing about 10% of the mixed layer $Si(OH)_4$ concentration (*Fripiat et al., 2011*). Such field results raised the need to understand better which processes could release the elements from the lithogenic material.

Here we present results of batch experiments mixing riverine particulate matter and seawater indicate that between 1.5 and 27 % of strontium (Sr) is released from the riverine material within a year *(Jones et al., submitted)*. Similar experiments conducted on riverine, estuarine and shelf sediments from basaltic terrains also showed evidence for significant release of Nd isotopes and dissolved/particle REE exchanges as well as release of $Si(OH)_4$ from the particles to the dissolved phase. One of the factors driving these element release rates is the high surface area of riverine particulate material which typically range from 5 to 70 m^2/g. Chemical speciation of the particle surfaces, with a focus on the role of organic complexation and bacterial activity coul be another factor and will be investigated too.

Convergence of these experimental results with field observations confirms that consideration of the land-to-ocean fluxes should include the release of element from solids deposited along the ocean margins. The annual global river discharge of suspended particulates likely exceeds $19x10^{15}$ g/y *(Peucker-Ehrenbrink, 2009),* about 50 times the global dust input to the ocean ($0.425x10^{12}$ 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 biogeochemical cycles.

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Novel tracer applications of the cosmogenic isotope 7Be

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One of the stated goals of GEOTRACES is to create a unique opportunity for exploration and discovery by determining the distributions of novel TEIs that have received little attention to date. One such species, the radioactive isotope 7Be, will provide important biogeochemical rate information pertinent to the TEIs that will be measured during GEOTRACES and other programs. Many processes in the ocean cannot be directly observed and as such, tracers can provide important constraints to the rates and pathways of these processes. Be-7 is a tracer that, because of its half-life (53.3d), allows the study of processes occurring over seasonal timescales. This timescale is critically important to studies of biological production, nutrient regeneration, and atmospheric deposition, to name a few. However, it has been one that is difficult to approach because of the lack of oceanographic tracers suitable for integrating processes over this temporal range. As I will discuss, recent advances in sampling and analytical techniques, coupled with a better understanding of the behavior of 7Be in ocean biogeochemical cycles, present us with an opportunity to fully utilize this tracer.

Atlantic mercury emissions determined from measured elemental mercury sea-air disequilibrium

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A resent model study with the GEOS-Chem ocean-atmosphere model has shown that the ocean contributes the largest fraction to atmospheric mercury, but supporting measurements are sparse. For the determination of the Atlantic mercury emission, elemental mercury (Hg0) was measured in seawater and in the atmosphere on transects between Europe and South Africa and between South America and Europe in November 2008 and in April/May 2009, respectively. From the sea-air concentration difference the Hg0 gas exchange flux was calculated by application of a transfer velocity – wind speed relationship. A strong seasonal and regional variability of the Hg0 concentration was measured in surface waters. According to present knowledge the transformation of ionic mercury to volatile Hg0 depends on light supply, either by photochemical or by biotic transformation. The high accumulation of Hg0 in the tropics observed during our study was thus probably caused by intense solar radiation in combination with calm wind conditions in the doldrums leading to a shallow mixed layer and a sluggish Hg0 gas transfer, whereas in the mid-latitudes elevated Hg0 emissions were found in northern hemisphere in November and in the southern hemisphere in April. But also the tropics are subjected to episodic wind speed changes and thus to emission of the accumulated mercury. To obtain more realistic Atlantic Hg0 emissions, thus monthly mean wind speeds according to latitudinal belts were used to calculate monthly mean Hg0 fluxes. The emission pattern was principally different to the model results. But a final rough Atlantic mercury emission budget revealed similar integral emissions as the model.

Determination of the elemental mercury diffusion coefficient by means of molecular dynamics simulations and laboratory measurements

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Quantification of mercury exchange processes between the water phase and the atmosphere is important for understanding the biogeochemical mercury cycle. Soluble and particle reactive oxidized mercury is delivered to the sea by wet and dry deposition. In surface water ionic mercury is transformed to volatile elemental mercury (Hg) by photochemical or light dependent biotic processes and subsequently emitted to the atmosphere. The transfer of less soluble Hg between water and air is controlled by the waterside boundary layer and thus by the Hg diffusion coefficient (DHg). However, DHg is not established and is usually approximated by comparison with the diffusion coefficients (D) of other gases, i.e. by the dependency of D on molecular mass or molecular volume. This leads to deviating values for DHg and a considerable uncertainty of the flux calculation. We followed two approaches to better quantify DHg: first we used molecular dynamics (MD) simulations for the DHg determination, and second, we constructed a new diffusion chamber for its measurement. First measurements are in agreement with the results of the simulations. Applied methods and obtained results of both approaches are shown.

IPY – GEOTRACES: Dissolved Fe in the Arctic Ocean.

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The distribution of dissolved iron (Fe) is presented for the Arctic Ocean, a very scarcely sampled region for trace metal concentrations. Samples were taken with an ultraclean CTD sampling system [De Baar et al., 2008] during Polarstern expedition ARK XXII-2 within the framework of the IPY-GEOTRACES program. Shipboard analyses of Fe were done by flow injection and were successfully calibrated versus certified standard (SAFe) seawater [Johnson et al., 2007]. The simultaneous measurement of other chemical and physical parameters, improves the understanding of the processes determining the dissolved Fe distribution. In the upper Arctic Ocean, high ($>$2nM) concentrations of dissolved iron show a negative correlation with salinity. The contribution of (i) river runoff, (ii) Pacific derived water and (iii) sea-ice processes to the Fe concentration in the Arctic Ocean is estimated using δ18O, salinity and nutrients. This estimation clearly shows a very strong Fe input from (Siberian) rivers. In the deep Arctic Ocean, the hydrothermal activity above the Gakkel Ridge is a major input source of iron to deep waters as shown by a pronounced maximum of Fe and confirmed by anomalies of potential temperature and transmission and a pronounced maximum of dissolved manganese. The deep ($>$3000m) Amundsen and Makarov basins are marked by a high scavenging regime versus relatively little remineralization and the absence of other input sources. This dominant scavenging control leads to very low concentrations of iron and a positive relationship between dissolved Fe and Mn. At the Kara and Laptev seas, resuspension from continental slope sediment and the transport of particles from the shelves contribute to elevated dissolved iron concentrations.

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IPY – GEOTRACES: Dissolved Fe in the Southern Ocean

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Dissolved iron (Fe) is of major importance for phytoplankton growth in the Southern Ocean. Here, we present concentrations of dissolved Fe over three high resolution sections in the Atlantic Sector of the Southern Ocean, covering the prime meridian, Weddell Sea and Drake Passage. Samples were taken with an ultraclean CTD sampling system [De Baar et al., 2008], during Polarstern expeditions ANT XXIV-3 and ARK XXII-2 respectively, within the framework of the IPY-GEOTRACES program. Shipboard analyses of Fe were done by flow injection and were successfully calibrated versus certified standard (SAFe) seawater [Johnson et al., 2007]. The simultaneous measurement of other chemical and physical parameters, improves the understanding of the processes determining the dissolved Fe distribution. In the Southern Ocean, dust deposition causes locally elevated Fe concentrations, as confirmed by Al data over the same transect. South of the ACC, Fe input melting sea-ice and ice-berg melt are (local) sources of Fe. The NADW intruding from the North, causes elevated Fe at ∼2500 m depth. Above Bouvet Ridge hydrothermal input of Fe is observed. Within the Weddell Gyre and Drake Passage subsurface minima as low as 32 pM are observed where fluorescence values indicate high phytoplankton abundance. Also hydrothermal and sedimentary Fe input is recognized. Melting of sea-ice and the Antarctic continental ice-sheet affect the distribution of Fe in the Weddell Gyre, as confirmed by high resolution surface measurements. However, the continental margin appears to be less an Fe source compared to other regions in the world, most likely due to the ice-sheet well extending beyond the margin. The newly obtained dataset, together with existing data, enables us to present an overview of Fe concentrations within the Antarctic Circumpolar Current, at different depths ((i) Surface (mixed layer), (ii) subsurface(ML-300m), (iii) intermediate (300-1000m) and (iv) deep (>1000m)). Despite varying Fe concentrations in the Southern Ocean, a statistical significant difference between the Atlantic and the Pacific and Indian Sectors, in the (sub) surface waters indicates strong input of Patagonian dust and sedimentary sources in the Atlantic Sector. The Fe stabilizes with depth; deep water values show no differences between basins. In the Weddell Gyre, the dissolved iron is higher in the eastward return flow then in the westward flow more to the south, for all depths.

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De Baar H.J.W., Timmermans, K.R., Laan, P., De Porto, H.H., Ober, S., Blom, J.J., Bakker, M.C., Schilling, J., Sarthou,G., Smit, M.G., Klunder, M.B., 2008. Titan: A new facility for ultraclean sampling of trace elements and isotopes in the deep oceans in the international Geotraces program. Mar. Chem., 111, 4-21

Studying the Fe oceanic cycle in the western equatorial Pacific with Fe and Nd isotopes.

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There are large oceanic areas, as the eastern Equatorial Pacific Ocean, where major nutrients are not entirely used up by primary production (the so called High Nutrient Low Chlorophyll, HNLC, areas). In these remote areas, the hypothesis is that a lack of iron (Fe) is limiting primary production [*Martin*, 1990]. The Fe oceanic cycle therefore impacts the global carbon cycle and the climate. However, many aspects of the Fe cycle remain unknown. Recent analytical developments allow studying the Fe isotopic composition (Fe IC) in the ocean, including in Fe depleted HNCL waters [*Lacan et al.*, 2008, 2010]. Dissolved Iron (DFe) sources are characterized by specific isotopic compositions (δ^{56}Fe). Provided that these isotopic signatures are conserved within the ocean, they could enable us to trace the origins of the oceanic iron. However, several processes may modify the initial iron isotopic signatures by isotopic fractionation (e.g. oxidation, biological uptake, remineralization, precipitation and adsorption onto particles). In order to explore the properties of this new tracer and to investigate the Fe cycle in the western Equatorial Pacific, we have measured the concentrations and IC of dissolved iron and neodymium offshore Papua New Guinea (PNG) and in the western Equatorial Pacific. These measurements constitute an important contribution to this field, as only four points of DFe IC in the open ocean have been published so far [*Lacan*, 2008].

All the Fe IC data at 200m (depth of the Under Equatorial Current, EUC) display exactly the same value (δ^{56}Fe = +0.45 ± 0.10‰, 2SD, n=8, i.e. heavy iron) at 6 different stations, suggesting that the tracer is conservative within this water mass, over a distance of about 4000 km and a period of time of about 9 months and that the Fe found in the central equatorial Pacific does come from the PNG region. In addition, the invariance of the neodymium isotopic signature within the same waters supports the PNG origin of the Fe transported within the EUC. The heavy Fe isotopic signature of these waters (δ^{56}Fe= +0.45‰) suggest that the process releasing iron in this water layer is likely not sediment reductive dissolution (as frequently invoked in other areas, e.g. *Elrod et al.*, 2004), which would display a light isotopic signature, but rather sediment *non*-reductive dissolution. The DFe concentration does not increase at this depth along the PNG margin ([DFe] = 0.64 ± 0.019 nM in the Vitiaz Strait and 0.67 ± 0.019 nM downstream of the Sepik river). However, it is larger than typical open ocean values, suggesting that this layer is affected by Fe addition upstream from the studied area. Nd isotope data also suggest that the lithogenic inputs into these waters occur upstream of PNG.

Contrastingly Fe concentration increases along the PNG margin, at the surface (from [DFe] = 0.13 ± 0.004 nM to 0.89 ± 0.026 nM) and at intermediate depth (from [DFe] = 1.05 ± 0.03 nM to 1.46 ± 0.04 nM). This suggests significant Fe inputs along the PNG coast for these layers. Our data allowed estimating the Fe IC of this additional Fe: i) at the surface δ^{56}Fe$_a$ = +0.56 ± 0.09‰ (2SD), suggesting again that the DFe is provided by the non-reductive dissolution of lithogenic particles (either aeolian, or discharged by the rivers onto the margin), ii) in the AAIW (800m), δ^{56}Fe$_a$ = -0.38 ± 0.2‰ (2SD), a negative value which may reflect the contribution of both non-reductive and reductive dissolution of sediments, or/and hydrothermal inputs.

Along the equator, at depth, away from lithogenic inputs, the AAIW Fe IC remains almost constant despite significant Fe addition by remineralization and Fe removal (likely by scavenging). These data suggest that the Fe added by remineralization has a Fe IC close to that of the AAIW (around +0.15‰), and that the removal process is not associated to a significant Fe isotopic fractionation.

In the surface layer, the data were difficult to interpret because of the significant number of potential sources (aerosols, rivers, sediments) and processes (photo reduction, biological uptake, reductive and non-reductive dissolution, adsorption/desorption …), complex dynamic and probable large spatiotemporal variabilities.

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Iron isotopes in the ocean: new constrains on the Fe oceanic cycle

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Iron is an essential micro-nutrient. In large areas of the ocean (HNLC areas), iron limits phytoplankton growth and therefore impacts the carbon cycle. However many questions remain about its marine cycle. Dusts and sediments are considered as the main sources of iron to the surface open ocean. Because both sources display distinct iron isotopic compositions, iron isotopes in seawater were suggested as a promising new tracer of these sources. In addition, iron undergoes numerous exchange processes between the several physical and chemical forms coexisting in the water column. Some of these processes have shown isotopic fractionations through in vitro experiments. Iron isotopes in the water column could also help to clarify these processes.

Iron isotopes are now measurable with a good precision (δ^{56}Fe <0.08‰) in seawater, including in Fe depleted HNLC waters, both in the dissolved (<0.4µm) and the particulate phases [*Lacan et al.*, 2010]. Such data from four areas will be presented: the western Equatorial Pacific and the Papua New Guinea (EUCFe cruise, Kilo Moana, 2005), the Kerguelen area (KEOPS cruise, Marion-Dufresne, 2005), the subtropical southeast Atlantic Ocean and the Antarctic Zone along the Greenwich meridian (Bonus GoodHope cruise, Marion-Dufresne 2008) and the western North Atlantic (BATS, Geotraces intercalibration cruise 1).

The δ^{56}Fe variation range is larger in the dissolved phase, from -0.71 to +0.58‰, than in the particulate one, from -0.04 to +0.46‰. Relationships between Fe isotopes and concentrations in both phases, suggest significant dissolved/particulate interactions.

Because in situ isotopic fractionation – associated for instance to scavenging and remineralization processes - appear limited, the isotopic signatures of different water masses remain fairly stable over long distance (typically several thousands of km), which allows using the Fe isotopic signatures for tracing the Fe origin within the open ocean. For instance the Lower Circumpolar Deep Water (LCDW) is characterized by δ^{56}Fe≈-0.13±0.17‰ (2SD, n=2, data from the Bonus GoodHope and KEOPS cruises) and the core of the Pacific Equatorial Under Current (EUC) by δ^{56}Fe≈+0.36±0.14‰ (2SD, n=4, EUCFe cruise)

In the Antarctic Zone of the Southern Ocean (Bonus GoodHope), the dissolved oxygen minimum of the Upper Circumpolar Deep Water clearly coincides with a δ^{56}Fe minimum in the dissolved phase, underlying the importance of redox processes to the iron isotope oceanic cycle.

For several years, more and more attention is paid to the sedimentary source of iron. Whereas the involved process is usually proposed to be bacterial reductive dissolution, characterized by a significantly negative signature ($\Delta_{\text{diss-part}}$≈ -3 to -1‰), our results suggest the significance of a different process, the non reductive release of dissolved Fe from the sediments into seawater, displaying a mean fractionation of $\Delta_{\text{diss-part}}$≈ +0.2‰, releasing slightly heavy iron in the dissolved phase.

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Using C* to quantify entrainment into the Nordic Seas overflow water

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The quasi-conservative tracer C* [*Gruber et al., 1996*] is introduced as a tracer for the overflow waters from the Nordic Seas, and we show that this tracer can be used to identify and track Nordic Seas overflow water across the Greenland-Scotland Ridge (GSR) and into the North Atlantic. South of the GSR C* is significantly higher in the Iceland Scotland Overflow Water (ISOW) and Denmark Strait Overflow Water (DSOW) plumes than in the ambient water, and the difference thus provides a new angle for quantifying the amount of entrainment of ambient water into the overflow plumes relatively immediately downstream of the GSR in both the Iceland Basin and Irminger Sea. It is found that 34 % of ambient water is entrained into the Denmark Strait overflow in the Irminger Sea, while the same method in the Iceland Basin gives 45 % entrainment into the Iceland Scotland overflow. These estimates compare well with previously published calculations including many more source water masses and tracers [*e.g. Fogelqvist et al., 2003; Tanhua et al., 2005*].

Carbon and nitrogen isotopic compositions of particulate organic matter and biogeochemical processes in the western Arctic Ocean

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The Chukchi Sea is one of the Arctic marginal seas strongly influenced by the Pacific inflow, which is distinctive for the high biomass and the serious nitrogen limitation to primary production. These characteristics make the dynamics of nitrogen cycling distinctively different from previously studied marginal seas. Organic carbon and total nitrogen as well as stable carbon ($\delta^{13}C_{org}$) and nitrogen ($\delta^{15}N$) isotopic ratios were determined on suspended matter collected from the Bering Strait and Chukchi Sea during the summer period in 2008. The $\delta^{15}N$ and $^{13}C_{org}$ values ranged from 5.09‰ to 6.73‰ and from -24.10‰ to -20.69‰ respectively in the Bering Strait and adjacent area, while the $\delta^{15}N$ ratio was much heavier (up to 10.32‰) and the $^{13}C_{org}$ was much lighter (minimize value -26.00‰) in the central and north of the Chukchi Sea. The distribution pattern of $\delta^{15}N$ had a good correlation with nitrate concentration in the upper layer, suggesting the sedimentary $\delta^{15}N$ maybe a good proxy for reconstructing the paleo-nutrients cycle in the Chukchi Sea. The $^{13}C_{org}$ was influenced by the different solubility of dissolved inorganic carbon because of the wide range of temperature rather than the terrigenous matter in the euphotic zone. There were no significant changes for both of $\delta^{15}N$ and $^{13}C_{org}$ values during particle settling in the water column when the water depth less than 50 m. There was a lighter $\delta^{15}N$ signal jet below 20 m in the minimum ice zone (71°-72°), because of the influence of melt water. The $\delta^{15}N$ values increased with the water depth, especially in the water-sediment interface in the Chukchi Sea slope. The enriched $\delta^{15}N$ signal can be attributed to denitrification (or anammox) processes that will transfer ^{15}N-depleted of organic matter to N_2, which supported by the higher concentration of nitrite in this region. On the other hand, the $^{13}C_{org}$ values also increased in the water-sediment interface indicative that the influence of selective decomposition of organic matter will be another important factor for both of carbon and nitrogen stable isotope.

Determining the biological contribution to the high CO2 drawdown in the North Pacific through continuous estimates of carbon export and air-sea CO2 flux

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Much of the high air-sea CO2 drawdown in the North Pacific is focused in the region between the subarctic and subtropical gyres, called the North Pacific Transition Zone, which has a mean annual drawdown (4–10 mol C/m2 year) much higher than the ocean-wide average. Surface ocean pCO2 is controlled by both biological carbon export and temperature-determined solubility of CO2. To determine the contribution of biological carbon export to this region of high CO2 influx, we made continuous measurements of the ratio of dissolved oxygen to argon (O2/Ar) across the North Pacific using a shipboard membrane inlet mass spectrometer (MIMS). O2/Ar is a tracer of net community productivity (NCP), equivalent to the rate of organic carbon export. We compared our estimates of NCP to the air-sea CO2 flux determined by simultaneous underway pCO2 measurements. We report results of eight cruises crossing the North Pacific from Hong Kong to Long Beach, California on a volunteer observation container ship during fall, winter and spring 2008–2010. We compare our NCP estimates with results of a simple model estimating the influence of temperature and biological carbon export on the climatological annual cycle of pCO2 in the North Pacific.

Composition and distribution of U-Th-REE rich phases in marine sediments

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Particle-reactive tracers like Thorium (Th) and Neodymium (Nd), a Light Rare Earth Element (LREE), are widely used to study marine particle fluxes. ^{232}Th and Nd sources are exclusively derived from the continent while the ^{230}Th is also uniformly produced in the ocean by the radioactive decay of ^{234}U and rapidly scavenged on sinking particles (^{230}Th$_{xs}$). In sites with strong lithogenic inputs, 230Thxs is calculated subtracting a lithogenic term by using a crustal average U/Th ratio. We study U-Th-REE rich phases in marine sediments from the Mediterranean Sea (DYFAMED site) in order to (1) constrain the nature of the phases carrying Th isotopes and (2) determine the nature of the phases involved in the Boundary Exchange which is a key feature of the Nd cycle in the ocean.

Mineral separates of micron size-phases were obtained by density and chemical separation. Bulk samples and separated phases were used for systematic survey and quantitative analysis by scanning electron microscopy (SEM), for isotopic analyses by Thermal Ionization Mass Spectrometer (TIMS) and for concentration analyses by Inductive Coupled Plasma Mass Spectrometer (ICP-MS).

We have identified U-Th-REE rich phases of clearly lithogenic origin including zircon ($ZrSiO_4$), xenotime (YPO_4), monazite [$(REE,Th)PO_4$], florencite [$(REE)Al_3(PO_4)_3(OH)_6$], and allanite [$(REE,Y)_2(Al,Fe_3)_3(SiO_4)_3(OH)_6$]. The size distributions of these minerals were studied. Zircon grains have a large size (~1-25µm), monazite is intermediate (~1-15µm), and florencite is much smaller (~1-3µm). The inventory of these grains suggests that a large fraction of the ^{232}Th and U contained in the sediment could reside in monazite and zircon. Similarly, the main carriers of LREE are monazite and florencite. In addition, U/Th ratio (g/g) were measured by SEM. Results indicates that the average U/Th ratio in monazite (0.20±0.0.3) and florencite (0.33±0.07) are lower or close to the crustal average value (~0.3) whereas the average U/Th ratio in zircon (1.14±0.46) and xenotime (2.32±0.82) are much higher and also very heterogeneous among the crystal population.. The ^{230}Th/^{232}Th ratios measured by TIMS are consistent with U/Th ratios.

Concentrations and U/Th ratio in U-Th rich phases suggests that lithogenic U is significantly dependent on zircon, and ^{232}Th on monazite in sediment. Moreover, size distribution is a key factor when it comes to evaluate the content of U, ^{232}Th and Nd carried by these phases in sediment. Preferential settling of large zircon compared to smaller monazite during the transport from the Saharan to the DYFAMED site could produce a decrease of the zircon/monazite ratio and hence explain the large variability of the U/Th ratio in marine particles collected in the DYFAMED sediment traps [*Roy-Barman et al,* 1989]. It would also produce an increase of the Light REE

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(enriched in monazite and florencite). We will present data on filtered particulate matter following the same protocol to improve our previous results. The present work points out that the $^{230}Th_{xs}$ calculated using a crustal average value of U/Th ratio can generate biases in sites with strong lithogenic inputs. In such sites, measurement of uranium should lead to a better evaluation of the $^{230}Th_{xs}$.

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Development of a one-dimensional ecosystem model including iron cycle

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We developed a one-dimensional ecosystem model to study iron cycle in the Oyashio region of the western subarctic Pacific. The ecosystem model has 15 components including iron cycle. The parameters associated with iron cycle are optimized by assimilating the time-series observational data of monthly averaged 1) net primary production, 2) nitrate, 3) silicate and both 4) dissolved and 5) particulate iron within the mixed layer and two depths (200 and 300 m depth). The ecosystem model was driven by the vertical diffusivity obtained from a three-dimensional circulation model. The model successfully reproduced the observations and demonstrated the followings: 1) dissolved iron limits the phytoplankton production over an annual cycle or most period of a year, which is consistent with the iron stress in phytoplankton recently revealed by the immunological ferredoxin/flavodoxin assay results even in the spring bloom period around the site, and 2) the surface-mixed layer dissolved iron is mainly supplied from the subsurface water with high concentration of that by winter mixing. The simulated results of the dissolved iron were sensitive to the optimized parameters of stoichiometric ratio of iron to nitrogen in plankton and the scavenging coefficient for dissolved iron exceeding the prescribed ligand concentration of 0.6 nmol/l. The former is similar to the value expected from the observations. The latter is the parameter difficult to measure. Thus, the parameter should be constrained well using more relevant data, especially when embedding the model into a three-dimensional circulation model in the near future.

The Role of Ocean Mixing in Southern Ocean Iron-fueled Phytoplankton Blooms: Insight from Radium Isotopes

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An important feature of coastal margin and island systems in the high nutrient low chlorophyll (HNLC) waters of the Southern Ocean is greatly enhanced levels of productivity during the austral summer. This "island effect" has been hypothesized to be due to iron release from the island and shelf systems into the surrounding waters, thus allowing primary production to occur in these otherwise barren HNLC zones. The precise release mechanisms and the magnitude of dispersion and fate of any released Fe remains unclear. However, in terms of lateral dispersion and vertical mixing of Fe containing water into the euphotic zone, the use of natural radio-tracers represent a powerful tool to track these inputs and their transport to adjacent waters.

The large-scale input of radium isotopes along the coastline is akin to a purposeful tracer release, with the short-lived radium isotopes providing the rate of dispersion based on their decay as they mix away from the source. To this end we have used radium isotopes to identify the pathways and rates of supply of iron fueling phytoplankton blooms in three Southern Ocean environments: downstream of the Antarctic Peninsula and Crozet and Kerguelen Plateau regions. Our studies have generally focused on evaluating rates of vertical and horizontal Fe input. The vertical source is derived from deep water Fe mixed to the surface via enhanced mixing due to interaction of the Antarctic Circumpolar Current (ACC) or tidal flows with the shallow bathymetry of the plateaus. Horizontal sources include island runoff combined with diffusive input from plateau sediments carried by subsurface horizontal advection into the bloom region.

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Controls on hydroxide-speciated trace metals in the ocean

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Trace metals exhibiting hydroxide speciation in marine environments are particle reactive, resulting in short residence times and thus acting as valuable tracers of flux and water movement in the oceans. The aim of this work is to study scavenging of hydroxide-speciated trace metals sampled from environments of varying particulate abundance, controlled by physical and biological processes. Oceanic regimes influenced by eolian deposition, coastal upwelling, and variations in phytoplankton abundance provide a natural laboratory to determine influences on trace metal profiles. Observed concentration profile ratios of Al/Ga and Zr/Hf demonstrate fractionation from terrestrial ratios. Differential scavenging of such elemental pairs will be examined and compared to established tracers of particle flux and water mass transport. Ocean carbon cycling and flux will be investigated through assessment of scavenged trace metal behaviour within environments of contrasting particulate abundance. Additionally, sampling of low particulate environments will offer a unique opportunity to evaluate reversible scavenging mechanisms.

Evaluation of Crustal Deformation in Western, Eastern and Southern Margin of Caspian Sea

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In this research we are evaluated of crustal deformation in the western, Eastern and Southern margin of the Caspian Sea in Iran, by using earthquakes seismic data. Study area is divided into seven seismogenic zones and seismic strain tensors with symmetric and asymmetric components are calculated for each area. Referring to density of seismicity and seismic sources trend parallels with the faults criteria, all seismogenic zones have been selected. Scattered areas are such that the estimates do can be an image of the deformation zone show. In this research, we do this by dividing the total area under the smaller areas, turning special attention to host events in seismic zones; we have focused the attention on tasks that others are not. Our results show that the western margin of the Caspian Sea with the compression axis tilt 40 degrees Azimuth N75W almost perpendicular to the folding axis caused Caspian crust being pushed under the Azerbaijans mountain belt. This phenomenon, according to the rotation axis counterclockwise blocks north of the host also has to be interpreted. These blocks have opposite spin analogue clock is the vertical axis. Folding in the West side in southern Caspian Sea and the phenomenon of significant vertical axis is rotated counterclockwise. In Southern part of Caspian Sea (Central Alborz) using asymmetric tensor seismic vertical axis rotation of about 0.84 per million years was calculated. Compression axis (P axis) in this region, with Azimuth 43 degrees and tilt 17 degrees which causes it can be combined sinistral strike slip movement with East- West direction and reverse in North – South direction be interpreted. In the eastern fringe of the Caspian Sea, has a density axis oriented N18W with a dip or less neutral axis is almost vertical. In Eastern side of Caspian sea, shortening crust almost north - while the South East for the transition area, the compression axis to the north East side is divergent. Calculations carried out in Easter part of Caspian Sea shows along the East - West along with drooping vertical elongation is observed. In the northeast corner of the study area and adjacent common borders with Afghanistan and Iran, Tajikistan, P axis is the horizontal line is continually N39E. Comparison of the compression axis orientation in Eastern side of Caspian Sea transfer from West to East side indicates the rotation axis than along the North East side.

Heat Budget during the ice season in Hanko peninsula, Finland

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Hanko peninsula, which is located on the Finnish coast at the mouth of the Gulf of Finland, is the southernmost point of the mainland Finland. It belongs to the Seasonal Sea Ice Zone, therefore it is considered as a key area regarding the climate change. Three out of four winters the brackish waters offshore Hanko freeze over, in a process which has significant effects to both the physics and the ecology of the Gulf of Finland, while the inner archipelago is ice-covered every winter. A bilateral Finnish-Japanese experiment "Hanko-9012" has been performed in four winters (1999-2002) at the Hanko peninsula, not only with seasonal monitoring but also with intensive field campaigns. In this experiment, ice, oceanographic and meteorological data have been collected in order to investigate the structure and properties of the Baltic brackish ice, heat budget and solar radiation. Data from the aforementioned experiment are analyzed in this project for the estimation of the heat budgets during the ice season. This work is ongoing and it aims to cover the first two winter seasons of the experiment (1999-2001). The station data allows us to estimate the components of the ice – atmosphere heat exchange, mass and heat content of the ice sheet, and oceanic heat flux to the ice bottom.

Redox Speciation of Chromium in the Water Column of the Tropical Atlantic Ocean

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In the aquatic environment chromium is present as Cr(III) and Cr(VI). Depending on its redox state chromium can act as both micronutrient and microtoxin and therefore significantly controls the physiological state and the biochemical activity of marine organisms. Knowledge about the distribution of Cr species throughout the water column is required to evaluate the interactions of this metal with biota and possible environmental effects. Even though chromium isotopes are under discussion as proxies of paleo redox conditions [*Frei et al.,* 2001] and provide a tool to monitor Cr(VI) contaminations [*Ellis, Johnson and Bullen*, 2002], little is known about the biogeochemical cycling of chromium in the marine system. Chromium originates from both natural and anthropogenic sources. Weathering of rock constituents, wet precipitation, dry fallout from the atmosphere and riverine run-off make up the main contributions of chromium found in water systems [*Kotaś and Stasicka*, 2000]. Chromium is also linked to various industry processes. Anthropogenic Cr(III) results mainly from the tanning and the textile industry while Cr(VI) discharges are associated with electroplating, pickling and bright dipping [*Jaworsky*, 1980; *Geisler and Schmidt*, 1992].

As part of the GEOTRACES program water samples were collected at three stations in the tropical Atlantic Ocean during the RV Meteor cruise M81/1 in February 2010. The stations represent different settings ranging from a shallow shelf margin off the West African coast to two deep sea stations, one being off the coast of Brazil and one being further out in the tropical Atlantic Ocean. To avoid contamination the sampling of the water column was conducted with a trace metal clean CTD of the U.S. GEOTRACES program. Aliquots were filled in rigorously pre-cleaned LDPE bottles under class 100 clean laboratory conditions and immediately frozen to maintain the chemical speciation. Chromium redox speciation analysis is carried out using a catalytic adsorptive stripping voltammetric method with DTPA as a complexing agent and a hanging mercury drop electrode as working electrode [*Sander and Koschinsky*, 2000]. This method can distinguish between reactive and unreactive Cr(III) and Cr(VI). Based on CTD derived salinity and temperature data different water masses were characterized and clearly distinguished. At the respective stations South Atlantic Central Water and North Atlantic Central Water were found in the surface waters while Antarctic Intermediate Water, North Atlantic Deep Water and Antarctic Bottom Water were bound beneath the permanent thermocline [*Fischer*, 2010]. The distribution of chromium and its species with respect to these water masses will be investigated. Of particular interest is also the redox behavior of chromium across the oxygen minimum zone.

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The collection of trace elements and isotopes using a newly modified in situ pump – Radium as a case study

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Accommodating the sample needs of multiple PIs from a single sampling event is becoming a more common requirement on multi-disciplinary oceanographic expeditions. This mode of sample collection is advantageous because it generates a single, synchronous sample that is ideal for cross-comparison and data synthesis and also saves on ship time. On two recent cruises a newly modified *in situ* McLane large-volume pump was successfully deployed to sample for a wide range of dissolved and particulate trace elements and isotopes. The modified pump was equipped to filter seawater through two filter types: glass fiber and membrane, which are suited for organic and metal analysis respectively. The combined filtrate was then passed through a MnO_2 impregnated cartridge to scavenge dissolved thorium and radium isotopes. The typical total volume of seawater processed was 1300-1700 L during a four hour pump with a volume ratio of approximately 2.5:1 between the different filter heads. To demonstrate the pump's ability to address biogeochemical processes, preliminary measurements of radium isotopes from these two field campaigns will be presented. The first focused on the transport of organic carbon associated with intermediate and benthic nepheloid layers emanating from where the Deep Western Boundary Current skirts the North West Atlantic Margin. The second was part of the US North Atlantic GEOTRACES transect to investigate the horizontal and vertical distribution of trace elements and isotopes.

Poster presentation preferred.

Standardizing aerosol dust collection and analysis: results from the 2008/2009 GEOTRACES aerosol intercalibration study

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The GEOTRACES aerosol intercalibration initiative seeks to develop protocols for the collection and analysis of aerosols and rainwater emphasizing accuracy, precision and internal consistency. The broad scope of this intercalibration includes a comparison of equipment and filter types, sample collection approaches, and digestion and quantitation methods. Nearly twenty investigators analyzing for forty elements/isotopes of natural and anthropogenic importance are currently participating in two intercalibration projects, conducted at RSMAS/University of Miami (September 2008) and in the eastern North Pacific during the second GEOTRACES intercalibration cruise (May 2009).

The intercalibration results demonstrate that aerosol dust can be collected, digested and analyzed with great precision and minimal contamination. Despite variations in digestion and analytical methods used by the participants, bulk aerosol concentrations of Al, Fe, Mn and V agreed better than 20%, even for sample sizes of hundreds of micrograms. Similar agreement was observed for soluble trace elements and major anions extracted from the aerosol dust.

Currently, a few groups are participating in a second round of tests investigating modifications made since the first round of tests. Recent modifications include a new disk-filter arrangement for bulk aerosol dust collection as well as the development of a "consensus value reference material" dust.

Further details of the sampling equipment and collection methods will be presented, emphasizing the relative advantages of the various approaches. Many of the lessons learned from these intercalibration projects are being applied to the U.S. GEOTRACES North Atlantic Zonal Transect cruises (2010-2011). It is our intent that the current and future results of this intercalibration will continue to assist the community in establishing standard procedures for the collection and analysis of aerosol samples.

Oxygen, a tool for assessing ocean tracer transport models

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Various techniques are used by modellers in order to overcome difficulties inherent to the modelling of biogeochemical cycles over long time periods. Off-line modelling or asynchronous coupling are among the popular methods used for this purpose. In some other cases the numerical scheme used for the transport of tracers may differ from that used for the active variables (temperature T and salinity S) in order to guarantee positivity or conservation, or to get rid of spurious oscillations. These techniques imply that the different scalars in the model may be subject to slightly different numerical transport equations.

It is highly desirable that the chosen method be assessed as it might strongly affect the ocean ventilation rate as actually experienced by the tracers. However the available techniques allowing to test for the consistency of the chosen method suffer from strong limitation. A *salinity-tracer* essentially provides information about surface processes. Age tracers constitute interesting diagnosis tools but their use is impeded by the need of long-duration experiments.

In this work we show how a simple tracer, the *solubility oxygen*, offers an easy way of testing the coherency of the numerical model. It is straightforward to implement and provides at once informations on surface as well as deep ocean processes without calling for additional experiments. Due to the nonlinearity of O_2 solubility, mixing of different water masses may only result in a body of water slightly oversatured with respect to the final T and S. A *solubility oxygen* tracer, not affected by biological processes, is included in the transport model. This tracer obeys the same solubility equation as oxygen but its piston velocity is very large, so that surface waters in the model are at equilibrium with the atmosphere. By comparing the solubility oxygen distribution to the theoretical oxygen saturation obtained from the model temperature and salinity fields a clear diagnostic of the ability of the tracer model to correctly reproduce the ventilation scales of the OGCM may be drawn.

This procedure is applied to transport models forced by the outputs of different OGCMs. Reasons for departures are investigated and discussed. We then present a method based on age tracers which allow to improve the consistency between the OGCM and the tracer model ocean ventilation rates.

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Assessing the World Ocean ventilation timescales with simple analogs - the leaky funnel model

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The rate at which the ocean can sequester excess heat and carbon from the atmosphere is determined by its ventilation i.e. the renewal of interior waters by seawater that has been in contact with the atmosphere. Hence it is of importance to better assess this ventilation rate and its properties. Of use are numerical simulations and field measurements of appropriate tracer concentrations. However the intrisic complexity of water masses circulation and the huge amount of information provided by OGCMs make it difficult to extract the most relevant information on spatial and temporal scales characterising ventilation.

In [*Mouchet and Deleersnijder,* 2008] it is seen that an idealised model may suggest an appropriate scaling of the water age. A 1D advection-diffusion model is proposed in which the deep ocean is represented as a leaky pipe with decreasing section (i.e. a leaky funnel) - allowing recirculation of water and tracers toward the surface. The analytical solutions to the steady-state problem are readily obtained and yield expressions of the domain averaged-ages as functions of three independent numbers which determine the flow characteristic scales. A suite of experiences with a 3D OGCM allow us to calibrate and validate the leaky funnel representation. The agreement between the domain-averaged ages (water and radiocarbon) as obtained with the OGCM and with the leaky funnel is excellent. Further the parameters derived from this exercise have a clear physical meaning; the turnover time, the length scale of trajectories, and the diffusivity scale being consistent with our current knowledge of the World Ocean circulation.

The reasons for the excellent agreement between the 1D representation and the 3D OGCM remains rather elusive. Additional developments based on the age volume distribution function offer now the opportunity to revisit the leaky funnel model. These new developments provide for a supplementary and fully coherent validation of the leaky funnel representation. Eventually the age volume distribution suggests some interpretation of the deep ocean ventilation properties which result in the excellent correspondence between 3D and 1D domain-averaged ages.

This simple analog has a potential for applications in modelling studies. It may help in evaluating the relative importance, at the largest scales of motion, of advection and diffusion in 3D models. It also offers the opportunity to get an estimate of the numerical diffusivity even in the case of complex numerical schemes.

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Impact of climate and carbon sensitivities on the North Pacific ventilation in an Earth system model

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Under present-day conditions no deepwater is formed in the North Pacific. There is however evidence that a weakening of the Atlantic meridional overturning circulation (AMOC) consecutive to meltwater discharge during the deglaciation resulted in a switch of deepwater formation between the North Atlantic and the North Pacific [*Okazaki et al.,* 2010]. Earlier model studies already put in evidence a link between a weakened AMOC and the establishment of a Pacific meridional overturning circulation (PMOC) (e.g., [*Mikolajewicz et al.,* 1997]).

We address the potential establishment of a PMOC and its impact on biogeochemical cycles with the help of LOVECLIM, a global three-dimensional Earth system model of intermediate complexity[*Goosse et al.,* 2010]. In the present work, key physical or biogeochemical parameters of LOVECLIM are varied within their range of uncertainty in order to obtain an ensemble of parameter sets resulting in contrasted climate and global carbon cycle sensitivities. We then analyze the results of experiments in which the model is constrained with freshwater discharge in the North Atlantic.

While a weakening of the AMOC is obtained with each of the parameter sets the development of a PMOC only occurs with a few of them. The establishment of a PMOC leads to an enhanced ventilation with major changes in oxygen and radiocarbon deepwater content as well as in primary production. A significant increase in atmospheric CO_2 also occurs. The mechanisms leading to the different responses are examined and discussed.

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Biogenic trace gases CO2 and N2O in Tagus estuary

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Tagus estuary (Portugal), an important ecological and moderately productive system under considerable anthropogenic pressures, has been lately subjected to significant changes in its watersheds. In this work we compare biogenic trace gases carbon dioxide (CO2) and nitrous oxide (N2O) variability in the estuary under different hydrologic conditions. The estuary functions most of the time as a source of both biogases. Over 2006-2007, an average release of 40 mmol m-2 d-1 of CO2 and 2.7 μmol m-2 d-1 of N2O was estimated in the lower estuary (salinity 22-35). Dissolved inorganic carbon (DIC) and N2O display opposite behaviour as function of river discharge: DIC decreases (2.6 to 2.3 mM) simultaneously with a N2O increase (8.4 to 12.3 nM) up to discharges of 400 m3s-1, while DIC increases (up to 2.7 mM) and N2O decreases (down to 10.4 nM) under high river flow (800 m3 s-1). Thus, different driving factors operate under distinct river discharge. An attempt of determining the role of specific factors on the observed distribution patterns, as well as, identifying the respective underlying biogeochemical processes is undertaken.

Preindustrial North Atlantic δ^{13}C Distribution Reconstructed

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The carbon isotopic composition (^{13}C/^{12}C expressed as δ^{13}C VPDB) of fossil foraminifera is the primary tracer used to infer changes in past ocean ventilation and its variations are interpreted using the modern oceanic δ^{13}C distribution as a framework. However, since the industrial revolution this has been strongly overprinted by isotopically light anthropogenic CO_2, which confounds interpretation of downcore δ^{13}C variations. We will present a method to correct observed δ^{13}C for this C-13 Suess effect, which we published last year [*Olsen and Ninnemann*, 2010]. This has been used to reconstruct the preindustrial δ^{13}C in the North Atlantic, a much more appropriate reference for sedimentary δ^{13}C records than the present distribution, which has a richer and more detailed structure that is more clearly related to water mass distributions. Our results revise some fundamental perceptions regarding glacial-interglacial ocean δ^{13}C differences and allow paleo-δ^{13}C variations to be understood within the context of modern climate variability.

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Interchange of dissolved trace metals across sediment-water interfaces in a ria-type ecosystem (Ria of Ortigueira, NW Spain)

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In the intertidal areas of meso and macro tidal systems, covering and uncovering of sediments by tidal action implies changes in sediment chemistry due to shifts in equilibrium conditions between particles and pore water. Metal concentrations in river water, flooding and pore water at low tide and during short tidal inundation period were determined in the Galician ria of Ortigueira, NW Spain (43°43'N-7°53'W). These studies were preformed during spring (April) and summer (July) of 2008. Flooding waters were collected 1-cm above the sediment by means of pre-cleaned syringes with a polycarbonate filter (0.45 mm). Sediments were sampled at the air-exposed area before the arrival of the tide using a methacrylate core, and immediately sliced in 2-cm layers. Successive samples of flooding water and sediments were taken at 5, 10, 15, 20 and 50 minutes after tidal flooding inundation started. Pore waters were separated by centrifugation of the sediments, and then collected with plastic syringes and filtered through a 0.45 mm polycarbonate filter. Dissolved Co, Ni and Mn in flooding and pore waters were measured by ICP-MS in a Thermo-Elemental X-Series equipment. The accuracy of the analytical procedure was assessed by the analysis of certified reference materials. Pore water concentrations of dissolved metals ranged between 3-54 nM for Co, 84-377 nM for Ni and 526-6307 for Mn, whereas that dissolved metal concentrations in flooding waters were between 0.18-18 nM for Co, 8-287 nM for Ni and 62-1342 for Mn. Under air-exposure conditions depth profiles of metals were similar with a slight decrease with depth. Under air-exposure conditions depth profiles of metals were similar with a slight decrease with depth. Fluxes due to molecular diffusion and advective transport in the sediment-water interfaces were calculated. The results on a daily scale showed that advective transport by tidal flushing was always higher than fluxes resulting from molecular diffusion, which means that in this ria-type ecosystem, an export of metals occurs from intertidal sediments to the water column.

ACKNOWLEDGEMENTS

This communication was supported by CICYT under the project INTERESANTE (CTM2007-62546-C03/MAR), and to the Spanish-Portuguese Action ref. 2007PT0021.

Seawater neodymium isotope ratios in the Pacific sector of the Southern Ocean

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The South Pacific constitutes the largest sector of the Southern Ocean and accommodates major areas of intermediate and bottom water formation, making it an important end-member of the meridional overturning circulation. Yet, it is the least studied area of the circum-Antarctic ocean. Characterizing the concentration and distribution of chemical tracers in the South Pacific and in particular in intermediate and bottom waters formed in this part of the ocean is vital for the use of such tracers in the study of ocean circulation today and in the past. Moreover, defining the contribution of Antarctica to the chemical composition of the South Pacific is important for the understanding of global marine trace metal and isotope budgets.

Neodymium isotope ratios (^{143}Nd/^{144}Nd, expressed as ε_{Nd}) in seawater are an important tracer for the origin and transport of water masses, and the provenance of continental contributions to the ocean. Nd isotopes are therefore an ideal tool to study the chemical impact of Antarctica on seawater trace metal and isotope budgets and to trace the origin and advection of Antarctic Bottom Water (AABW) formed in the Ross Sea into the East Pacific. Here I present water column ε_{Nd} data from the Pacific sector of the Southern Ocean collected during expedition ANTXXVI-2 (*R/V Polarstern*) in Nov. 2009-Jan. 2010. The bottom water Nd isotopic composition shows ε_{Nd} values of -7 at 69°S (3850m water depth) and ε_{Nd} = -9 at 53°S (5190m water depth). The vertical seawater ε_{Nd} profile at 69°S exhibits a distinct change from ε_{Nd} = -7 at depth (3800-3000m) to ε_{Nd} = -8 at 2000m, and -9 at 1000m water depth, with a return to -8 near the surface. The upper water column ε_{Nd} is consistent with the isotopic composition considered characteristic of the Antarctic Circumpolar Current that reflects the mixing of Atlantic, Pacific, and Indian Ocean water masses. The more radiogenic bottom water ε_{Nd} south of the SAF, on the other hand, indicates contributions from radiogenic Antarctic sources. The distinct signature of AABW will therefore allow the tracing of this water mass away from its formation region in the Ross Sea and into the Pacific.

Towards the development of a numerical transport model for tracer dispersion in the Bay of Cadiz (southwest Spain)

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The Bay of Cadiz constitutes an environment of high ecologic value, including a Natural Park. It suffers a considerable anthropogenic stress, due to the population living along its shores, tourism, industry and the important port of Cadiz. The research project Radscavenging, between the universities of Cadiz, Huelva and Seville, is aimed at the determination of scavenging rates and sedimentation velocities using particle-reactive radionuclides in coastal waters; and their application to pollutant dispersion modelling. One scenario selected for the project is the Bay of Cadiz. Water and suspended sediment samples have been collected and several radionuclides (isotopes of U, Th and Ra among others) analyzed to determine transfer rates between the dissolved and solid phases. These rates are used in a radionuclide dispersion model, which is currently being developed. Tides are simulated using a 2D barotropic model, including a flood-dry scheme. Six tidal constituents have been included and the calculated amplitudes of tides, phases and currents have been compared with observations. Tidal residuals, as well as wind-induced circulation due to dominant winds, have been calculated. A sediment transport model has been developed, as the basis for a particle-reactive tracer dispersion model. It essentially consists of an advection/diffusion equation with some terms added, describing settling, erosion and deposition of particles on the seabed. The dispersion model includes the transfers of pollutants between water, suspended matter and bed sediments in a dynamic way. Some preliminary results are presented and discussed.

Radioisotopes and heavy metals as tracers of circulation in southern Iberian Peninsula coastal waters: a numerical modelling study

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Southern Iberian Peninsula coastal waters connect the Atlantic Ocean and the Mediterranean Sea, and have a high ecologic and economic value. Thus, it is relevant to know water and pollutant dynamics here. Two dispersion models have been developed for the Gulf of Cadiz (Atlantic) and Alboran Sea (Mediterranean). They consist of a hydrodynamic model, a sediment transport model and the dispersion model itself, which includes the interactions of isotopes and metals between the dissolved phase, suspended matter and bed sediments. Tides are solved in both domains using a 2D barotropic model. A 3D baroclinic model and a 2-layer model have been used for long term circulation in the Gulf of Cadiz and Alboran Sea respectively. Water-sediment tracer interactions are solved in a dynamic way. In the Alboran Sea, the model has been applied to simulate the transport of Cs and Pu introduced from atmospheric fallout. The effect of the Western Alboran Gyre has been studied and some characteristic times calculated. Also, fluxes of isotopes through the Strait of Gibraltar have been calculated and compared with previous estimations. Transport pathways of heavy metals discharged from three rivers draining a large mining area have been obtained for the Gulf of Cadiz. It has been found that these rivers constitute a source of trace elements to the Mediterranean through the Strait of Gibraltar. In both domains, calculated concentrations of isotopes and metals in the water column and bed sediments have been compared with measurements.

The geochemical behaviour of trace elements in coastal waters: a modelling study for the Huelva estuary

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The estuary of Huelva (SW Spain and formed by the Odiel and Tinto rivers) has been affected for decades by waste disposal from fertilizer plants. Simultaneously, both rivers drain a huge mining area and their acid waters carry significant amounts of isotopes of Ra, U and Th, which are maintained in solution due to the low pH of water. When river waters mix with seawater pH and salinity increase, precipitating elements in solution. The estuary constitute an excellent natural laboratory to study the geochemical behaviour of trace elements in coastal waters when significant changes in environmental conditions occur. These processes have been studied by means of numerical modelling. The model domain covers both rivers. Tides and the residual currents due to river flows have been simulated using a 2D barotropic model, since the estuary is shallow and well-mixed in the vertical. Seasonal pH and salinity distributions are simulated through an advection/diffusion equation for H^+ and Cl^- ions with appropriate boundary conditions. The dispersion of radio-isotopes of Ra and U is simulated during several years using seasonal pH, salinity and currents due to river flows. Simultaneously, real instantaneous tidal currents are considered. The exchanges of isotopes between the dissolved phase and bed sediments are simulated in a dynamic way using kinetic transfer coefficients. A new formulation has been developed to describe the effects of pH and salinity variations on these coefficients. Computed tide amplitudes and phases, as well as salinity and pH distributions, have been compared with measurements in the estuary. Also, calculated concentrations of ^{226}Ra and ^{238}U in sediments have been compared with measurements along the estuary for 4 sampling campaigns, one per season. There is a generally good agreement between model results and measurements, indicating that processes are adequately described. Finally, some numerical experiments have been carried out. They have revealed the significance of tides, in comparison to river flow induced currents, to maintain relatively lower levels of trace elements in the estuary. The relative importance of the different sources of isotopes (river inputs and leaching from a phosphogypsum pile located by the Tinto River) has been studied as well.

Arsenic transport through a river-estuary-ria system with arsenopyrites in the fluvial basin

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If The products of rocks and soil degradation and erosion are transported into surface waters towards the estuaries and the behaviour of arsenic in the estuarine environment has still received comparatively little attention. In the Galician Rias arsenic and its speciation was studied in marine sediments of a few rias while seawater dissolved arsenic concentrations were only measured in one. Although dissolved arsenic concentrations in open-ocean are relatively constant, the possibility of anthropogenic or geogenic additions of arsenic can result in higher arsenic concentrations in fresh water, which could increase the shelf levels of dissolved and particulate arsenic. It may be the case of the Ria of Laxe, affected by the local presence of arsenopyrite in the middle fluvial basin (Corcoesto zone). Therefore, the focus of this study is to research the river-ocean pattern of arsenic exportation through the continuum river-estuary-ria, with special attention to the role of estuary in the water and sediment transport.

In order to achieve the objective water and spm in fourteen sites distributed throughout the entire coastal system were monthly sampled from September 2005 to August 2006; moreover, thirty surface sediment samples were taken. Dissolved inorganic and, after UV oxidation, total arsenic concentrations were determined by means of hydride generation atomic fluorescence spectrometry while, after microwave digestion, arsenic in SPM and sediments was determined by means of AAS. Ultra-clean procedures were adopted during sampling, handling and analysis to avoid contamination and the analytical accuracy was checked using the CRMs.

Spatial variation of dissolved arsenic was observed from the river to the ria. In the upper river the trace element concentrations were lower than in the middle river zone (up to 4 $\mu g \cdot L^{-1}$). Here, granite and schist of Anllons upper basin have changed to quartz veins containing arsenopyrite enclosed in larger zones of silicification. Down at the river, in its estuary arsenic concentration decreased and were similar to the measured in the ria (1.5 $\mu g \cdot L^{-1}$). The annual average of inorganic dissolved arsenic increase in the Anllóns River due to arsenopirites influence is estimated in 2.1±0.5 times.

The concentrations of particulate arsenic in SPM in the Anllóns-Laxe system were between 21-181 $mg \cdot kg^{-1}$ in the river, 6-220 $mg \cdot kg^{-1}$ in the estuary and 3-40 $mg \cdot kg^{-1}$ in the ria. Arsenic richness in the SPM increased progressively for upper to the middle river section with highest values in the Corcoesto area: 181 $mg \cdot kg^{-1}$. Then, arsenic content in SPM decreased lightly until the estuary mouth (87±12 $mg \cdot kg^{-1}$); after, in the ria seawater, particulate arsenic levels fallen to 7 $mg \cdot kg^{-1}$.

Arsenic concentrations in the surface sediment of the Anllóns river-estuary increased slowly (17-23 $mg \cdot kg^{-1}$) in the upper river section as far as the Corcoesto area where increased to 47 $mg \cdot kg^{-1}$; a second significant rise occurred in estuarine area (up to 308 $mg \cdot kg^{-1}$). The highest concentrations of this coastal system were observed in the middle estuary where salinity changed from 0 to 10 in winter and from 0 to 25 in summer. In this fluvial zone alluvial deposits are accumulated and the fine fraction of sediment (12-41%) is the highest of the whole coastal system. After here, arsenic content in sediment decreased towards the mouth of the estuary (26 $mg\cdot kg^{-1}$) and likewise in direction of the ria mouth (10 $mg\cdot kg^{-1}$).

World studied systems can be divided into those in which the principal arsenic input is of marine origin and those in which the river is the major arsenic source. Continental contribution was the most important to the estuary of Anllóns. During the studied year the averaged Anllóns river flow was 10.2 $m^3\cdot s^{-1}$ and the fluvial contributions to the estuary were 13.3 and 9.4 $mg\cdot s^{-1}$ of dissolved and particulate arsenic, respectively. Whether or not arsenic behaves conservatively during estuarine mixing depends on the nature of the world system studied. Conservative pattern of dissolved and particulate arsenic in the Anllóns estuary varied along the year according to the inorganic dissolved arsenic concentrations in the river and the ria waters.

This communication is a contribution to the LOICZ-Spain program and it was supported by the project PGIDIT06RMA6040IPR financied by the ‘Xunta de Galicia’ in cooperation with the research project CTM2007-62546-C03-01/MAR (CICYT).

Dissolved and particulate trace metals in the Finisterre coastal waters. Is it a pristine environment?

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Lead is not an essential element from a biological point of view while copper is a bioactive element. The research of both trace metals is a question of general interest because its toxicity to marine biota in anthropogenic influenced areas. It may occur in coastal zones with high ship traffic as around Cape Finisterre. Then, it can be hypothesize that the Finisterre marine environment may not be pristine. So, the presence of metal contamination by Cu and Pb was researched in the Corcubión Sound. Sound is an 8 km arm of the sea forming a 90-50 m depth channel with a shallower inner zone that is made up of the small Cee and Xallas estuaries. The Corcubion Sound takes up and area of 90 km^2 bordered on the southern littoral of the Finisterre Cape.

To achieve the above mentioned objective three seasonal cruises have been carried out in the survey area on board the R/V *Lura*. During each cruise lead concentrations in the water column were measured in three stations along the sound axe besides the Xallas River, Cee water stream and Cee sewage treatment plant (STP): (1) Dissolved Cu and Pb using differential pulse anodic stripping voltammetry; (2) Particulate Cu and Pb in the suspended particulate matter (SPM) was analysed, after seawater filtration on policarbonate inside a laminar flow cabinet (class 100) and microwave digestion, by graphite camera atomic absorption spectrometry (GCAAS); (3) Aluminium, Cu and Pb concentrations were measured, after microwave digestion (3052 EPA procedure) in 15 surface sediment samples taken along the sound axe using FAAS and GCAAS. Clean techniques was used during all the sampling and analytical procedure checked with certificate reference material for water (CASS-4) and sediment (PACS-2) samples obtaining good agreement with the certified values.

Values of 0.1-0.9 nM of dissolved lead in seawater (0.2-0.8 nM in the rivers and 6-8 nM in the STP), 0.04-1.10 nM of particulate lead in seawater (0.6-8.3 nM in the rivers and 1-17 nM in the STP) for SPM and 12-145 mg·kg^{-1} in the sediment were found in this study to the Corcubión Sound area. Concentrations of 1-10 nM of dissolved copper in seawater (5-45 nM in the rivers and 80-100 nM in the STP), 0.1-0.4 nM of particulate copper in seawater (1-40 nM in the rivers and 10-420 nM in the STP) for SPM and 5-55 mgCu·kg^{-1} and 12-145 mgPb·kg^{-1} in the sediment were found in this study to the Corcubión Sound area.

Due to the different oceanic (outer) and continental (inner) influence, a division between both zones in the Corcubión Sound is made for a better discussion of the results. Levels of dissolved, particulate and sedimentary Cu and Pb are lower in the outer zone of the Sound indicating the continental inputs of these two trace metals to the coastal environment. High concentrations were measured in the freshwater contributions, and the spill from the sewage pre-treatment plant of Cee. Copper and Pb concentrations in the inner Sound zone are similar than those found in contaminated ria areas. On the other hand, trace metal levels in the outer Sound are in the order of those reported for open waters off Galicia. In the case of sediments, the values of Cu and Pb found in Corcubión inner zone reflects inputs of anthropogenic origins, with higher concentrations at locations close to contaminant sewage outflows.

Respect to copper and lead the outer Corcubion Sound, i.e. the southern coast of Finisterre, may be considered as a quasi pristine area and possible contamination was only observed in the innermost shallow zones.

This communication was supported by the project PGIDIT06RMA6040IPR financied by the ‘Xunta de Galicia’ in cooperation with the research project CTM2007-62546-C03-01/MAR (CICYT).

A tracer constrained inverse circulation model for estimating the ventilation rates of deep waters in the ocean

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Using a global inverse circulation model constrained from long-lived tracer observations we infer the ventilation properties of deep water masses in the ocean. We use the model to compute the mean time since water masses were last in the surface mixed layer where they could interact with the atmosphere and the mean time for deep water masses to be transported back to the surface where they can again communicate with the atmosphere. Apart from dynamical constraints, the inverse model uses gridded temperature, salinity, radiocarbon, phosphate and oxygen data to constrain the circulation.

Anthropogenic carbon changes in the North Atlantic Subpolar Gyre: what do we learn from $\delta^{13}C$?

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The North Atlantic Ocean, north of 50°N, is considered as one of the stronger anthropogenic CO_2 sinks, a consequence of the large heat loss and deep convection process during winter, as well as strong biological activity in summer and fall. However, anterior ocean CO_2 observations conducted in this region since 1981 suggest that the accumulation of anthropogenic carbon (Cant) is not steady and that Cant storage rates have been reduced since the mid-nineties [Perez et al., 2010]. This is likely associated to a large-scale climatic forcing, e.g. a shift in the North Atlantic Oscillation (NAO) in 1995-96. This is also coherent with a decreasing rate of air-sea CO_2 fluxes observed in the same region [e.g. Corbiere et al., 2007; Metzl et al, 2010]. In response to the increase in anthropogenic CO_2 emissions that are ^{13}C-depleted, the carbon isotopic composition ($\delta^{13}C$) of atmospheric CO_2 decreases by 0.02 ‰ yr^{-1}; consequently, the $\delta^{13}C$ values of dissolved inorganic carbon ($\delta^{13}C_{DIC}$) in sea water also decreases (so-called Suess Effect). Therefore, estimate of $\delta^{13}C_{DIC}$ changes in the ocean offers a companion information for understanding the anthropogenic CO_2 storage [e.g. Quay et al., 1992]. In this context we will first describe new $\delta^{13}C_{DIC}$ observations obtained in the North Atlantic Subpolar Gyre (OVIDE 2004, 2006) and compare the recent $\delta^{13}C_{DIC}$ distributions with historical data (TTO, WOCE). We will also explore the evolutions of the relationships between $\delta^{13}C_{DIC}$, DIC and Cant concentrations that could help in our understanding of where and why the Cant storage rate is decreasing since more than a decade.

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Tracking the fate of nutrients from different sources in the Baltic Sea food web

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In an ecosystem model for the Baltic Sea, ERGOM, we track the fate of nutrients entering the Baltic Sea from different sources. We extended the model by the possibility to mark nitrogen and phosphorous according to their source. Nitrogen isotope analysis in the sediments suggests that riverine nitrogen discharged into the Baltic Sea remains in the coastal area, whereas the inner basins are dominated by nitrogen from dinitrogen fixation. However, not much is known about the pathways or time scales of the spreading of the nutrients, as nutrients from different rivers are hardly distinguishable in an experimental way. Thus, numerical modeling appears to be an appropriate method to investigate spatial aspects of the nitrogen and phosphorous cycle. In the first run of our model, we marked thirteen element sources: Nitrogen and phosphorous from the rivers Oder, Vistula, Njemen, Daugava and Neva, and for nitrogen the fixation by diazotrophic cyanobacteria. The pathways of these elements can then be tracked both in three-dimensional space and in the phase space of the food web. Within the DFG project BEST (Baltic EcosySTem matter transport), the influence of the biology on the spreading of nutrients shall be investigated. Apart from passive advection with the currents, nutrients experience an active vertical transport by rising and sinking of particles. Also, sedimentation and resuspension alter their pathways. Additional to the marked-element tracers, we introduced an age tracer for time scale considerations. It denotes the average time since the considered element entered the ecosystem, and thus allows us to investigate residence times of nutrients as well as propagation velocities from one basin to another. Finally, attribution of the sources to the sinks of nitrogen and phosphorous gives us a complete overview of the fate of these nutrients supplied to the Baltic Sea ecosystem. For nitrogen and phosphorous, the timescales are totally different. Whereas most nitrogen is denitrified within the first two years and thus leaves the ecosystem, phosphorous residence time can be estimated to over 35 years.

Q-velocity model for Iranian Plateau

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In this study, we purposed first elastic and anelastic structure of the lithosphere and asthenosphere of the Iranian Plateau which is derived by means of tomographic techniques applied to local phase, group velocities and local attenuation coefficients of Rayleigh wave fundamental mode. We used commonly known as Hedgehog nonlinear inversion method to evaluate of the velocity structure. We improved Hedgehog to derive attenuation structure by using attenuation coefficients of Rayleigh wave fundamental mode. For this goal, we conducted a tomographic inversion of Rayleigh wave dispersion and attenuation coefficient to obtain, two-dimensional (2-D) phase, group velocity and attenuation coefficient tomographic images in the period range from 10 s to 100 s for the Iranian Plateau.Our results demonstrate that the Iranian Plateau is characterized by low crustal and uppermost-mantle group and phase velocities and high attenuation coefficient. Tomographic maps at high frequencies are well correlated with the upper crust structure and especially with sediments layers thickness.

Spatial and Temporal Distribution of Mollusks in North coast of Qeshm Island

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Qeshm Island is the largest island in the Persian Gulf, because of extensive coast line, high biodiversity and sensitive ecosystems like; Biosphere Reserve of mangrove forests, coral reefs and mud flats, is the one of sensitive coastal zones. For study of spatial and temporal distribution of coastal- marine mollusks in north of Qeshm Island, Laft port to Dargahan, sampling was conducted at August and December 2009. Samples were collected by quadrate 0.5 * 0.5 meter in intertidal zone and van Veen grab 0.025 m2 in marine stations. Therefore five transect with three stations in various levels of intertidal zone (supra tidal to sub tidal) and 2 stations at depths of 1.5 to 10 m, was determined. Samples were taken then fixed by formaldehyde, stained using Bangal Rose and separated and identified using certain identification keys. Water parameters such dissolved oxygen, salinity and temperature as well as total organic matter and grain size was analyzed. The biodiversity indices including Brillouin, Simpson and Margalef were determined. Finally, 35 species of gastropods and 20 species of Bivalves in winter identified. In winter 14 species of gastropods and 7 species of Bivalves in summer were found. The most dominant bivalves in winter was Tellina arsinoensis and the most dominant gastropods was Cerithidea cingulata. Also in summer Dosinia sp. was the most bivalve and Assimenia sp. determined as most abundant gastropod. All values of indices, except of Simpson, because of higher abundance and diversity in winter was higher than summer. Water parameters showed significant variation between seasons.

Influence of thorium small-scale spatial variability on export estimates

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Satellite images routinely demonstrate strong variability in ocean dynamics and biogeochemistry down to spatial scales of a few km. A question that arises is whether the intense spatial variability of organic matter observed at the surface persists deeper in the water column. Specifically, does sinking organic material share such patchiness? If so, how does this affect the robustness of point observations and our interpretation of them? Making observations of export that can resolve such fine spatial variability in the water column is not easy. The spatial resolution of direct sampling methods such as floating or tethered traps is too low. Indirect methods utilising Thorium deficiency could be more promising. Recent surface 234Th measurements show strong variability at the mesoscale (10-100 km, K. Buesseler pers. comm.), strongly suggesting the existence of significant small-scale variability of the particulate export. Motivated by these preliminary observations we couple an explicit model of Thorium dynamics to a high-resolution coupled physical-biogeochemical model, resolving the meso- and submeso-scale in the North Atlantic. The model supports the observations in displaying marked 234Th spatial variability. We use the model to quantify the contribution of the 3-D dynamics to the thorium budget, to estimate the errors on export estimates associated with the spatial and temporal undersampling of the 234Th variability and to test standard assumptions (e.g. steady-state) made when estimating export from Thorium deficiency.

Combined utilization of DGTs and bioindicators to trace chemical contamination threats on coastal ecosystems.

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Trace metal monitoring in marine organisms and their living habitats permit to trace chronic or acute contaminations of marine ecosystems due to human activities. While dissolved trace metal concentrations give us an overall and punctual view over biota contamination status, bioindicator species put their bioavailable and possible toxic fraction in an obvious. However, difficulties mainly inherent to metal measurements in seawater lead field ecotoxicologists to study marine pollution essentially through the use of bioindicators alone. The technique of diffusive gradients in thin films (DGT) for the measurement of trace metals in aqueous solutions was introduced in the mid-ninetieth by Davison and Zhang. This passive probe accumulates labile trace metal species in proportion to their bulk environmental concentrations by maintaining a negative gradient between the environment and an ion-exchange resin (Chelex). DGTs average natural water trace metal concentrations over the deployment period, concentrate them and avoid matrix interferences, notably due to dissolved salts in seawater. Their deployment in passive and experimental monitoring studies permits to reliably measure labile trace metal concentrations and, jointly analysed with bioindicators, to estimate their bioavailability to marine organisms.

This combined approach DGT-bioindicator was investigated in Calvi Bay (Corsica) through three monitoring studies. (1) DGTs were deployed in *Posidonia oceanica* bed, a Mediterranean seagrass forming dense meadows from the surface down to 40 meters depth, to study seasonal, spatial and bathymetrical variations of labile trace metal concentrations within this meadow. These concentrations were analysed jointly with *Posidonia* trace metal contents in order to quantify their bioaccumulation towards this primary producer, taking into account the seagrass biological cycle. (2) Portions of *Posidonia* meadow were also *in situ* experimentally contaminated with a mix of dissolved metals to study seagrass kinetics of pollutant accumulation and decontamination. Thanks to DGTs deployed inside contaminated mesocosms throughout experiments, *Posidonia* responses to known metal concentrations could be precisely quantified. (3) The blue mussel *Mytilus galloprovincialis* is widely used in trace metal monitoring programs. Mussels, stored in conchylicultural pouches, were transplanted for 3 months in contrasted stations of Calvi Bay (*e.g.* aquaculture farm, sewer, etc.) in parallel with DGTs. Such as for *Posidonia*, the complementary utilization of DGTs and mussels permitted to describe water contamination levels at the scale of the Bay, and their bioaccumulation towards mussels. These 3 studies demonstrate the usefulness of DGTs to monitor labile trace metals in an ecological and ecosystemic approach, in parallel with marine organisms, both indicators furnishing different and complementary informations about ecosystem functioning.

Dissolved Fe in the Western Atlantic Ocean: distribution, sources, sinks and cycling

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Iron (Fe) plays a key role in the regulation of primary production and dinitrogen fixation in large parts of the world oceans. Because there is an increasing urgency to understand the role of the oceans in global climate, it is paramount that we understand the biogeochemical cycle of bio-essential elements such as Fe. Despite this recognized importance there is still limited knowledge of the sources, sinks, chemistry and internal cycling of Fe. To fill this gap in our knowledge, the distribution and organic speciation of dissolved Fe (DFe) have been measured during three Dutch GEOTRACES cruises. Together, these cruises form a comprehensive, high resolution, full-depth section through the western Atlantic Ocean from Iceland to 58°S. In this presentation we will evaluate the distribution of DFe and its speciation using many other parameters such as dissolved inorganic carbon, total alkalinity, pH, dissolved oxygen, fluorescence, the macronutrients phosphate, nitrate and silicate and trace elements like dissolved aluminum (DAl) and dissolved manganese (DMn), to understand the processes that determine the distribution of DFe.

Storminess controls on Southern Ocean Ecosystems and Biogeochemistry

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It is well known that ocean ecosystems and biogeochemistry over the Southern Ocean are strongly influenced by the complex interplay between nutrient supply and mixed layer depth. It is also known that a common characteristic of IPCC AR4 models is a tendency towards increased storminess (by 20%-30%) over the 21st century under climate change scenarios. Given that storms are known to play an important role in sustaining mixed layer depths, it is important to understand how such dynamical changes may project onto ocean ecosytems and biogeochemistry, and whether there is an expected feedback on the carbon cycle, under climate change.

As a first step towards understanding the relationship between summertime storminess and ocean biogeochemistry and ecosystems, we have conducted a series of model perturbation studies where we have introduced changes in mixed layer depth in summer (in the absence of changes in the mean seasonal cycle of momentum and buoyancy forcing at the sea surface). The dynamical model used is NEMO, the biogeochemical model is PISCES, and the surface forcing is derived from the extended/interim ERA-40 reanalyis over 1958-2005. The relatively strong sensitivity exhibited by the model supports our contention that transient 21st century changes in storminess may be at least as important to perturbing Southern Ocean Ecosystems and Biogeochemistry as changes in eddy activity associated with changes in the mean strength of the Southern Ocean winds.

It is our intention that this modeling work be applied to the interpretation of GEOTRACES data, and relating this to measured seasonal variations in atmospheric O2.

Nd isotopes in the western equatorial Atlantic water masses: Amazon river and margin contributions.

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Neodymium isotopic composition (IC) of seawater has a strong potential for 1) tracing circulation and mixing of water masses in strategic places where salinity and temperature alone may not be sufficient [*Lacan & Jeandel*, 2004a 2004b] 2) exploring the role of continental margins in supplying and exchanging material with the ocean [*Lacan* and *Jeandel*, 2005; *Arsouze et al*. 2009].

The north Brazilian margin and Amazon estuary system may contribute significantly to the Atlantic ocean chemical signature due to it's considerable supply in fresh water and sediments that are in contact with major water masses (i.e. NADW, AAIW) and currents of contrasting origins and pathways (i.e. NBC WBUC).

Previously published dissolved Neodymium IC data were sampled during TTO/TAS and ANTXXIII/1 cruises and consist of a sample from the Amazon plume [*Goldstein & Jacobsen*, 1986], a profile at 7,73°N 40,70°E [*Piepgras & Wasserburg*, 1987] and a recently published set of surface and profile samples along a north-south transect in the east Atlantic [*Rickli et al.* 2009, 2010].

We present here results of Neodymium IC obtained in the framework of the AMANDES project. Nearly 60 samples were collected during AMANDES cruises (RV ANTEA) in October 2007 and February/April 2008 along the Amazon estuary salinity Gradient, on the French Guyana and Brazilian shelves, and further offshore. εNd values ranged from -8.9 +/-0.5 for the Amazon endmember to -13.8+/-0.3 for the Mid North Atlantic Deep Water. ADCP transects were also realised and ADCP moorings deployed, to identify fine circulation trends. Additionally a tidal model for the Amazon estuary and shelve were developed [*Le Bars et al.*, 2010]. The combination of the Nd concentrations, IC and physical oceanographic features allows us to quantify the margin and estuary system contributions on the equatorial Atlantic ocean Nd budget and infer the pathways of this contribution.

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Determination of sediment traps efficiency with $^{230}Th_{xs}$ in the Mediterranean Sea

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The evaluations of the biological pump of carbon and of the particulate fluxes of tracers strongly rely on sediment traps data. However, turbulence can prevent a significant fraction of the sinking particles from being collected. Therefore, it is critical to validate moored sediment trap data by the $^{230}Th_{xs}$ method. As $^{230}Th_{xs}$ is uniformly produced in the water column by radioactive decay of ^{234}U, the ratio between the flux of $^{230}Th_{xs}$ collected by the trap and the in situ production of ^{230Th} over the trap is a direct measurement of the trapping efficiency.

As part of the COMET project, we have determined the efficiency of sediment traps moored 200 m and 1000 m at DYFAMED (30 nautical miles off Nice) for the year 2005 and 2006. We first focused on these years because they are characterized by distinctively low mass flux. Th isotopes were measured on a Neptune+ MC-ICPMS. U concentration was measured by Q-ICPMS. The efficiency is calculated over a full year in order to cancel seasonal variations of the ^{230}Th flux and assume that there the longer-term steady state between production and removal of ^{230}Th. Determination of the sediment trap efficiency at the DYFAMED site is particularly challenging. In area with strong lithogenic inputs and/or at shallow depth, determining the $^{230}Th_{xs}$ requires an accurate knowledge of the lithogenic ^{230}Th (or "supported at secular equilibrium with ^{234}U and ^{238}U). Therefore, the average U/Th ratio of the continental crust cannot be used to determine the lithogenic ^{230}Th content of the trapped material. Direct measurements of the U content of the trapped material are required. However it is not sufficient because some of this U may be scavenged from the seawater. The lithogenic U content can be bracketed assuming (1) that all the U is lithogenic or (2) that all authigenic U is carried by organic matter and deducing the U content of organic matter from the "organic rich samples". However, it produces large uncertainties.

In 2005, the trapping efficiency is 136 % ± 47 % at 200 m and 96 % ± 10 % at 1000 m. In 2006, the trapping efficiency is 46 % ± 36 % at 200 m and 30 % ± 5

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% at 1000 m. The 2005 results are consistent with the trapping efficiencies determined at the same site and the same depth for 1999-2000 *[Roy-Barman et.al., 2009*]. The mass fluxes in 2005 were lower than in June1999-June2000, implying that the trapping efficiency determination is independent of the mass flux. In 2006, the trapping efficiency is significantly lower (particularly at 1000 m) than in 2005 and June1999-June2000. This can be related to strong convection associated to strong horizontal currents the occurred during the winter 2006 in the Ligurian Sea, probably leading to a low trapping efficiency over this period.

The large uncertainty at 200 m is directly related to the determination of the lithogenic U fraction. One way to reduce this uncertainty is to use the $^{234}U/^{238}U$ ratio of the trapped material, because this ratio is different in lithogenic particles and in seawater. Thus, efforts are underway to determine the $^{234}U/^{238}U$ in the trapped material by MC-ICPMS.

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Tracers of river inputs in the Transpolar Drift, Arctic Ocean during the Polarstern IPY expedition, 2007

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During Polarstern expedition ARK XXII/2 in 2007, GEOTRACES sections were made across the Eurasian Basin from the Kara Sea to the Alpha Ridge and from the Mendeleev Ridge to the Laptev Sea. Both sections crossed the Transpolar Drift. We show the distributions of 228Ra, 228Th, 234Th, 18O, Ba, Fe and Mn in surface waters. We use 18O, salinity and nutrients to derive the sources of the water masses, and discuss processes of uptake by plankton, scavenging, and radioactive decay and ingrowth. The study stresses the importance of this transport route of terrigenous inputs from Siberia over the central Arctic basin towards Fram Strait.

Highly productive coastal systems as important sources of complexed dissolved iron to open ocean waters.

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Iron is an essential nutrient playing an important role in the CO_2 cycle due to its limiting role in primary production in vast areas of the ocean *[Martin and Fitzwater, 1988*]. In the last decades it has become one of the main targets in biogeochemistry studies due to global warming and climate change. The limiting role of iron is a consequence of its low concentrations in seawater, due to its reactivity with sinking particles and low solubility *[Liu and Millero, 2002*]. Iron is mainly maintained in the dissolved form at concentrations that support primary production through formation of organic complexes.

The sources of iron to the surface ocean are numerous: they include: atmospheric, hydrothermal vents, sediment release, and riverine discharge. Among them, the atmospheric inputs (i.e. aerosols) has been traditionally considered to be the main one although concerns about its solubility and impact on primary production *[Boyd et al. 2010*]. However, there are signs that indicate that continental inputs (i.e. rivers and runoff) can export important quantities of iron, and what it is most important, in a complexed form (i.e. humic substances) [*Laglera and van den Berg, 2009*].

The Vigo Ria, is the southernmost of the Galician Rias located in the northwest of the Iberian Peninsula, with an oceanic climate that tends to be very dry in summer. Rias are estuarine-coastal systems formed by flooding of river valleys and are typical of world areas such as NW Iberia, SW England or SE Asia. Due to the presence of repeated upwelling events all along the year [*Prego and Bao, 1997]*, the primary production in the Vigo Ria is high. In a recent study [*Romera-Castillo et al., 2010*] it has been shown that an important percentage of dissolved organic carbon (DOC) is locally produced by the living phytoplankton. Due to the high biological productivity of the Iberian Atlantic coastal margin, Galician Rias produce 250,000 tons of mussels per year, representing about 50% of the European production [*Smaal, 2002*].

The first studies about iron concentration and cycling in the Vigo Ria (NW Iberian Peninsula) started in the 60´s [*López-Benito, 1969*] describing a decreasing concentration trend from the main river discharge towards the marine end member with seasonality presenting higher concentrations during summer. Due to lack of availability at the time, trace metal clean techniques were not used, leading to concentrations that seem to be too high (125-1250 nM). More recently, and with the use of clean labs and procedures, dissolved iron concentrations in the Vigo Ria and its exchange with ocean waters during typical winter conditions have been studied [*Prego et al., 2006*]. Levels oscillated between 150 nM in the fluvial end member and 15 nM in the marine end member with a nearly conservative behavior during the estuarine mixing. This is not the usual behavior in

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estuaries where dissolved iron concentrations decrease exponentially towards more saline waters [*Riso et al., 2007*] due to iron precipitation by both colloid formation and interaction with flocculates of organic matter, mainly humics *[Sholkovitz, 1978]*. *Prego et al. (2006)* observed a net export of dissolved iron to the ocean but the cause of this distinctive behavior remained unclear.

The objective of our study was to discover the cause of this conservative behaviour for iron in the Vigo Ria waters. Two sampling cruises were carried out in winter and summer 2009. The concentrations of dissolved iron agreed with *Prego et al (2006)* values (8-120 nM) showing the same conservative trend. In addition, the organic speciation was also studied finding high values of iron complexing ligands. In those waters, it was confirmed that concentrations of humics were not significant and that iron ligands, as the bulk of DOC, have a local phytoplanktonic origin. Those ligands are not subject to overwhelming flocculation as humics do explaining the distinctive response of iron to the saline gradient. The consequence is that the residence time of iron in the dissolved fraction is stretched significantly.

When these iron rich waters are exported outwards the estuary with the Ria water circulation, they will represent an important input of highly stable dissolved iron to coastal and oceanic waters. In the future, it would be interesting to monitor the stability of those ligands (subject to degradation and grazing) and carry out similar sampling cruises in the adjacent coastal area to follow the effect of Ria waters in the export of dissolved iron into the Atlantic margin.

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Sinking particles in a Western Galician Ria (NW Iberian Peninsula): Seasonal labile and total concentrations and fluxes of particulate metals to the sediment and post-depositional transformation.

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Sediments of estuaries and coastal areas receive metals through the water column with different origins. They are scavenged with the suspended particulate matter coming from runoff, rivers, sewages, atmospheric inputs and diffuse sources or by means of flocculation and coagulation processes. Once the particles are sedimented in the bottom of these systems and incorporated into the sediment, a series of diagenetic and postdepositional processes may occur.

The Vigo Ria, is the southernmost of the Galician Rias located in the northwest of the Iberian Peninsula. Rias are estuarine-coastal systems formed by flooding of river valleys and are typical of world areas such as NW Iberia, SW England or SE Asia. It has an oceanic climate and tends to be very dry in summer. Due to the presence of repeated upwelling events all along the year (Prego and Bao, 1997), the primary production in the Vigo Ria is high. It is the most industrialised and populated ria in Galicia with approximately 400,000 inhabitants, 80% of which are based at the southern margin (city of Vigo). Industrial and port activities have occupied the banks of this ria for decades, especially the Bouzas shipyard. Metal discharges into the Ria, through diffuse sources, occur from food factories and metal industries linked to shipyard and dock activities on the southern bank.

In order to study this transport of metals from the water column to the sediment and what happens during their storage, two sediment traps were located in the middle part of the Vigo Ria. The traps were anchored 5 meters above the bottom of the ria two times during one day in three different seasons (winter, spring and summer). In addition, three short sediment cores (15 cm) were sampled at the same dates in the central channel of the Vigo Ria.

The intrannual variation of the quantity and composition of the sinking particles in a Galician Ria has been studied. Levels of particulate metals (Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Ti, U, V and Zn) were determined both in the labile (HCl extraction) and in the total fraction. The levels and type of metals found in different seasons of the year depended upon oceanographic, physical, chemical and biological conditions but, in general, lithogenic type metals (Al, Fe, Ti, U and V) were more abundant during winter rainy campaigns when high quantities of SPM were recovered in the trap. However, the more biogenic metals (Cu, Pb, Zn) were more abundant in spring or summer associated to the higher quantities of organic matter found in the traps. The fluxes of these metals to the sediment were calculated being quite important. In special, the labile fraction, that once it reaches the sediment, it can suffer postdepositional diagenetic processes with the subsequent benthic fluxes of the dissolved form of the metals to the water column of the Ria.

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Impact of Anthropogenic Sources on Aerosol Iron Solubility: Comparative Study from Tropical Bay of Bengal and Arabian Sea

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The atmospheric supply of Fe associated with the mineral dust is an important source known to influence the ocean surface biogeochemistry. However, recent studies have highlighted the importance of combustion sources for the enhanced fractional solubility of aerosol-Fe. Our recent study reveals that the fractional solubility of aerosol-Fe over Bay of Bengal (range: 1.5 to 25%) is one to two orders of magnitude higher compared to that over Arabian Sea (<1%). This is attributed to the differences in the chemical characteristics of mineral dust entering the two oceanic regions. The Arabian Sea receives dust from Desert regions; whereas transport of alluvial dust from the Indo-Gangetic Plain represents a dominant source to the Bay of Bengal. The field-based data suggest that chemical processing of alluvial dust by atmospheric acidic constituents (H2SO4, HNO3) enhances the fractional solubility of Fe. In addition, the enhanced aerosol-Fe solubility over Bay of Bengal is attributed to the contribution from biomass-burning and fossil-fuel combustion sources. These results are important to constrain the existing uncertainties in the atmospheric source of soluble-Fe, associated with the high-dust events, and impacts on ocean surface biogeochemistry.

Atmospheric Deposition of Toxic Metals to Bay of Bengal: Implications to Ocean Surface Biogeochemistry

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Air-sea deposition of toxic trace metals is significantly important in the impact assessment studies of ocean surface biogeochemistry. In this context, first comprehensive data set on the concentrations of selected trace metals (Mn, V, Cu, Pb and Cd) in the ambient aerosols collected from the marine atmospheric boundary layer (MABL) of Bay of Bengal is reported here. The elevated concentrations, enrichment factors and dry-deposition fluxes, as summarized in the Table, suggest their dominant source from fossil-fuel combustion and biomass burning emissions. In general, enrichment factors of Pb and Cd are relatively high over the Southern Bay (south of 150N) and are associated with the continental outflow from south-east Asia. The atmospheric concentrations of trace metals in the MABL of Bay of Bengal are an order of magnitude higher than those over other oceanic regions. Furthermore, the anthropogenic origin of these toxic metals would lead to the enhanced solubility in sea water when compared to their supply via dry-deposition of mineral dust. As a consequence, toxicity levels in the surface waters could be significantly high during the downwind transport and deposition to the Bay of Bengal. This in turn would influence the marine biota (may inhibit the growth of specific phytoplankton community).

Element	**Conc. range (ng.m^{-3})**		**#EF$_{Avg}$**		**Dry-deposition flux***	
	2006	**2009**	**2006**	**2009**	**2006**	**2009**
Al	185-1892	205-3468	1	1	0.8	1.0
Mn	4.6-43	2.2-103	3	7	17	35
V	5.4-62	1.9-158	23	18	25	29
Cu	3.2-28	0.5-21	57	17	0.8	0.4
Pb	3.2-14	2.7-70	52	171	0.7	2.6
Cd	0.06-1.6	0.03-3	305	922	0.03	0.1

#EF : Enrichment factor w.r.t. Al. * Fluxes expressed in μg/m^2/day, except for Al is in mg/m^2/day.

Labile Fe(II) concentrations in the Atlantic sector of the Southern Ocean along a transect from the subtropical domain to the Weddell Sea Gyre

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Labile Fe(II) distributions were investigated in the Sub-Tropical South Atlantic and the Southern Ocean during the BONUS-GoodHope cruise from 34 to 57°S (February-March 2008). Concentrations ranged from below the detection limit (0.009 nM) to values as high as 0.125 nM. In the surface mixed layer, labile Fe(II) concentrations were always higher than the detection limit, with values higher than 0.060 nM south of 47°S, representing between 39 % and 63 % of DFe. Photochemical reactions as well as direct biological production were evidenced. At intermediate depth, local maxima were observed, with the highest values in the Sub-Tropical domain at around 200 m, representing more than 70% of dissolved Fe (DFe). Remineralization processes were suggested to be responsible of those sub-surface maxima. Below 1500 m, concentrations were close to or below the detection limit ($< 4\%$ of DFe), except at two stations (at the vicinity of the Agulhas ridge and in the north of the Weddell Sea Gyre) where values remained equal to 0.030-0.050 nM. Hydrothermal or sediment inputs may provide Fe(II) to these deep waters. Fe(II) half life times were estimated in the upper and deep waters and ranged from 1.2 to 17.8 min, and from 16 to 160 min, respectively. This study helps to considerably increase the Fe(II) data set in the ocean and to better understand the Fe redox cycle.

Solubility of iron in the Southern Ocean

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Presented is a dataset of Fe solubility and iron ligand concentrations from surface samples and upper ocean profiles taken during the FS $Polarstern$ expedition ANTXXIII$/$9 in the Atlantic and Indian sectors of the Southern Ocean. Fe solubility, capacity of seawater for soluble Fe, showed a clear decreasing trend from south to north in three different Southern Ocean zones (the Coastal Zone, the Antarctic Zone, and the Polar Frontal Zone plus the Subantarctic Zone). This decrease was at times but not always matched with an increase in temperature. Estimates for organic Fe solubility ($cFe_{S,org}$) in the samples, which were obtained by subtracting from total measured Fe solubility the solubility of inorganic species of Fe at the measurement temperature (20°C), representing an average of 30$\pm$11$\%$ of the concentration of ligands in the dissolved size fraction. Values of cFe_S (which was the total Fe solubility measured at 20°C) were mainly lower than the predicted value for inorganic Fe solubility at the $in\ situ$ temperature. Total $in\ situ$ Fe solubility ($cFe_{S,adj}$) was estimated by adjusting for inorganic Fe solubility at $in\ situ$ temperatures (between -2°C and +18°C). Because $in\ situ$ temperatures in the ACC were mostly lower than +3°C, such $cFe_{S,adj}$ values were generally more than twice as large as $cFe_{S,org}$. This adjustment relies heavily on model calculations of inorganic Fe solubility, but, if correct, indicates that the bulk of the solubility of Fe in the cold waters of the Southern Ocean is tied to the solubility of inorganic Fe rather than to Fe ligands in the soluble size fraction.

Using Isotopes to Reconstruct Glacial Nitrogen and Carbon Cycling

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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^{15}N) and carbon (δ^{13}C) 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 δ^{13}C 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.

Fe isotopes : a tool to trace biological processes in Antarctic sea ice.

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Iron limits primary productivity in more than 30% of the oceans, including the Southern Ocean. Antarctica is characterized by seasonal sea ice, which represents a significant source of Fe during its melting. Observed Fe concentrations in the sea ice can be up to 2 orders of magnitude higher in the sea ice and in the open ocean seawater. Biological activity varies geographically, seasonally and within the sea ice (surface, internal and bottom layers), and can be dominated by either autotrophic or heterotrophic activity. We hypothesized that these biological activities can play a crucial role in the cycling of Fe and can induce contrasted redox conditions within the brine pockets and channels, with impacts on both particulate and dissolved iron isotopic composition.

Dissolved and particulate Fe isotopic compositions of brines, seawater and sea ice have been determined on samples collected during ARISE (Sept-Nov 2003, 64-65°S/112-119°E), ISPOL (Nov 2004-Jan 2005, 67-68°S/54-55°W) and SIMBA (Oct 2007, 69-71°S, 90-95°E) cruises. Values of particulate δ56Fe up to +1.2‰ were observed in the bottom ice, where large diatoms dominate the microbial community (corresponding to Δ56Fep-d = +1.6‰). Lowest particulate δ56Fe down to −3.4‰ were obtained in brines where bacteria were dominant (corresponding to Δ56Fep-d = -2.1‰). These results appear to reflect the autotrophic and heterotrophic activities of the microbial communities and suggest that those activities play a pivotal role in the cycling of Fe in the sea ice.

A study of cyclonic eddy change and phytoplankton bloom induced by 10 typhoon cases in South China Sea

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We observe the 10 typhoons from year 1997 to year 2007 in South China Sea（SCS）act on cold-core eddy (CCE) areas. The pre-exist CCE play an important role in chlorophyll-a (chl-a) concentration increase in the CCE area by typhoon acting compare to the typhoon acting on the region without CCE. The changes of CCE acted by typhoons are described by kinetic energy (EKE) and available gravitational potential energy (AGPE), which are calculated by two- layer reduced gravity model. For the CCE change, the maximum ratio of post-storm EKE to pre-storm EKE reaches 5 and the maximum ratio of post-storm AGPE to pre-storm AGPE reaches 9. The maximum ratio of post-storm chl-a to pre-storm chl-a reaches 12.5 in CCE area. The change of chl-a concentration in CCE area is dependent on the ratio of post-storm EKE (AGPE) to pre-storm EKE(AGPE), and also is dependent on typhoon moving speed.

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Constraining the oceanic fixed N budget using xsP and nitrogen isotopes tracers

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Fixed nitrogen (N) is one of the major limiting nutrients throughout the global ocean. Its absence in sunlit surface waters prevents primary production and the biological sequestration of CO2 from the surface ocean and atmosphere to the deep ocean through sinking of detrital matter. Despite the nitrogen cycle's importance for ocean biogeochemistry, its major source and sink terms are regarded with considerable uncertainty. Specialized microorganisms capable of fixing dissolved N2 gas during growth provides the ocean with the majority of its fixed N, while fixed N is removed in low oxygen zones (O2 $<$ 10 uM) in the water column and sea-floor sediments via denitrification and anammox. All of these processes are likely sensitive to changes in climate, but whether they will have a net positive or negative feedback effect is still controversial. Global rates of N2 fixation and denitrification range between100-250 Tg N yr-1 and 200-450 Tg N yr-1, respectively, but are mostly based on local studies extrapolated globally using "back-of-the-envelope" calculations. In this study, we examine a coarse resolution (1.8x3.6 degrees) global ocean ecosystem-biogeochemical model and vigorously compare it to xsP (PO4 - NO3/16) and nitrogen isotope (d15NO3) observations locally where N2 fixation and denitrification occur, as well as on a global scale. Our simulations show that to best match the global distribution of xsP and d15NO3 global rates of N2 fixation, water column denitrification and benthic denitrification should be near 200, 75, and125 Tg N yr-1, respectively. These rates are on the high end for N2 fixation and on the low end for denitrification compared to previous estimates. This study highlights using global observational datasets of xsP and d15NO3 to qualitatively and quantitatively constrain model simulations, and thus improve our estimates of the global oceanic fixed N budget.

The Southern Ocean mixing layer south of Africa: Results from the IPY BONUS_GoodHope transect, other GoodHope recent cruises and Argo data

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The passage south of Africa is the largest Southern Ocean (SO) chokepoint. There, the SO plays a unique role in providing the export channel for North Atlantic Deep Water to the global ocean and by importing heat, salt and biogeochemical tracers from the Indian and Pacific oceans. This region is influenced by the largest turbulence ever observed and very efficient air-sea exchanges. Here the atmosphere and ocean are equally dynamic: the complex fronts, eddies and filaments in the ocean are matched by tight fronts, storm passages, and highly variable moisture contents in the atmosphere. Transfer of heat to the atmosphere from the ocean north of the polar front contributes to the dominance of cumuliform cloud types in this region. These local small-scale processes and the derived meridional fluxes constitute the major link between the Atlantic and the other ocean basins. Here we will discuss the regional dynamics and water masses as they have been observed during the BONUS-GoodHope cruise, other GoodHope cruises and ARGO data. We will in particular focus on the observed structure of the surface mixing-layer. The transition from warm, salty subtropical waters to cold, fresh polar waters occurs in a series of steps that coincide with the SO fronts. We will discuss differences on the mixed layer structure in the light of the observed particular intense expressions of oceanic mesoscale turbulence. This turbulence is responsible of properties exchange across frontal region with important consequence on heat and fresh water budgets, biogeochemical cycles and air-sea exchanges.

Iron speciation in the Talos Dome ice core

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In the oceans and in particular in HNLC(high nutrient low chlorophyl) areas , iron concentrations are able to limit phytoplankton production. Iron is an element of great interest for its role in primary production, oceanic carbon cycle regulation, and in the ocean capacity to bury CO_2. Environmental iron behaviour depends strongly on the oxidation state. For example, the iron solubility and capacity to form complexes depends upon chemical speciation. Distinguishing between the two iron species, Fe(II) and Fe(III), is interesting to estimate bioavailability, as Fe(II) species are more soluble and therefore readily available for phytoplankton uptake and growth. Here, we present iron speciation in the Talos Dome Antarctic ice core over the glacial/interglacial period (0-50 ky). We use a FIA-ICP-MS-ORC(Octopole Reaction System) with detection limits of 10 ppt (pg g^{-1}). Ni-NTA Superflow resin, that is able to separate Fe^{2+} and Fe^{3+}. At pH 2 the resin is capable of retaining Fe^{3+} with no retention of Fe^{2+}. After the initial separation we oxidize Fe^{2+} using H_2O_2, and estimate the Fe^{2+} concentration by the difference between the two measurements. However, Fe^{2+} species are unstable and rapidly oxidize. To minimize the oxidation of Fe^{2+} to Fe^{3+}, the samples were immediately analyzed after melting. Our initial results appear to show higher Fe^{2+} concentrations during glacial periods than during interglacial periods. These results suggest that more iron could be available for phytoplankton growth during a glacial maximum.

Ventilation, formation, and export rates of North Atlantic Deep Water

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The formation and transport of North Atlantic Deep Water (NADW) is subject to natural variability but may also be influenced by climate change. To investigate ventilation and southward export of NADW, the concept from Bolin and Rhode (1973) of transit time distributions (TTDs) for reservoirs is applied here. The TTDs for the different components of NADW (Labrador Sea Water and overflow waters) are computed as volume integral of pointwise TTDs, which are inferred from CFC data collected in the North Atlantic between 1994 and 2009. It will be discussed, in how far ventilation and formation of Labrador Sea Water, the import of overflow waters and the southward export of NADW can be derived from this method.

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Coastal upwelling off Mauritania inferred from helium isotope disequilibrium

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Coastal upwelling strongly affects local climate as well as biological productivity by bringing cold, nutrient rich water into the surface layer. As upwelling velocities are too small to be measured directly (in the order of 10^{-5} m/s), an indirect method using the helium isotope ratio is used here instead. This method is applied to a dataset collected during three cruises between 2006 and 2008 in the eastern tropical North Atlantic, including the upwelling region off Mauritania. In addition to CTD and helium data also microstructure shear measurements are available, which allow the estimation of the contribution of vertical mixing to the fluxes into the mixed layer. The upwelling velocities derived from the helium isotope method are compared with calculations based on the wind stress taken from the QuikSCAT SeaWinds scatterometer data.

Circulation of Abyssal and Deep Waters near the Hero and Shackleton Fracture Zones in the Drake Passage.

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Six expeditions were carried out onboard Russian research vessels ”Akademik Sergey Vavilov” and ”Akademik Ioffe” in 2003-2010 in the region of the Hero and Shackleton fracture zones in the Drake Passage. The CTD and ADCP measurements in the entire water column were executed during these expeditions. Properties and propagation paths of abyssal and deep waters in the Drake Passage are investigated on the basis of these measurements and WODB2009 database. It is shown that the Hero Ridge with Phoenix Rift and Shackleton Ridge are the obstacles essentially affecting the propagation paths and transformation of abyssal and deep waters. These ridges control the formation of several semi-enclosed abyssal circulations in the adjacent basins. Fresher and colder Weddell Sea Waters, flowing in the abyssal slope current along the northeastern side of the Shackleton Ridge reach the northern periphery of the Antarctic Circumpolar Current. In the Scotia Sea, this leads to a freshening of the abyssal and deep waters (Antarctic Bottom Water and lower layers of Circumpolar Deep Water) up to the northern side of the sea. Abyssal waters between the Hero Ridge with Phoenix Rift and Shackleton Ridge are also subject to freshening. This transformation is due to appear as a transfer of fresher water from the Slope Antarctic Current in a complex system of the abyssal circulation between the ridges, and overflow of the water from the aforementioned abyssal slope current through the gaps in the Shackleton Ridge.

Surface Nd isotopic distribution in the South Pacific Ocean and the Pacific sector of the Southern Ocean

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Heterogeneous distribution of the Nd isotopes in surface waters reflects multiple terrestrial sources of Nd and its transportation processes. In the North Pacific Ocean, Nd isotopic compositions are known to be more radiogenic than those in the Atlantic and the Indian Ocean, which indicates the important contribution of Nd derived from young oceanic islands and island arcs of the circum-Pacific. In the South Pacific Ocean, however, Nd isotopic composition and its concentrations in seawater have not been reported enough yet. In this study, we investigated comprehensive distributions of Nd isotopes and rare earth elements (REEs) concentrations in surface waters of the western South Pacific and the Pacific sector of the Southern Ocean. Seawater samples were collected on the latitudinal transects at 155^{o}E in the Coral Sea and the western Tropical South Pacific (2^{o}S to 25^{o}S) and 170^{o}W in the central South Pacific and Pacific sector of the Southern Ocean (10^{o}S to 67.5^{o}S). In the Coral Sea, the most radiogenic Nd was observed (-1.6 ¡ ϵ_{Nd} ¡ +0.4) compared with those in the central Tropical South Pacific Ocean (-3.6 ¡ ϵ_{Nd} ¡ -1.6). The margin of the Papua New Guinea have been recognized as radiogenic Nd source in the western Pacific in previous studies. In this study, the heterogeneous distribution of ϵ_{Nd} values in the Coral Sea suggests multiple basaltic sources such as islands of New Caledonia and Vanuatu. The Nd isotopic compositions in the Pacific sector of the Southern Ocean were unradiogenic (ϵ_{Nd} = ca. -9) and homogeneous, which is similar to those in the Atlantic sector. Around the Subtropical Front dividing water masses into Subantarctic Water and Subtropical Water, the ϵ_{Nd} values were between those in the Southern Ocean and Tropical South Pacific (-8.2 ¡ ϵ_{Nd} ¡ -0.9). However, anomalously high REEs concentrations were observed in the Suubtropical Water compared with those in Tropical Surface Water and Subantarctic Water. The high concentrations of REEs observed in the Subtropical Water could be resulted from the lateral transport of REEs from the east margin of the New Zealand.

Seasonal and depth-related variations of trace metals, organic, elemental carbon and molecular tracers in settling particles from the open Eastern Mediterranean Sea (NESTOR site)

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To understand the transfer mechanisms of both anthropogenic and natural materials to the ocean, as well as the possible link between atmosphere and seawater, time-series collection of sinking material was performed in the SE Ionian Sea, where the deepest part of the Mediterranean Sea is located (Calypso Deep; off Peloponnese). Two mooring lines, deployed from November 2006 to November 2008 at successive water column depths (700, 1200, 2000, 3200 and 4500 m; NESTOR 4.5), and (5200 m; NESTOR 5.2).

Sediment traps material analyzed for a variety of tracers of anthropogenic and natural sources; major and trace elements, organic and elemental carbon as well as molecular tracers such as Polycyclic Aromatic Hydrocarbons (PAHs) . Major and trace metals (Al, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Cd and Pb) were measured using ICP-MS, while organic (OC) and elemental carbon (EC) using a Sunset Laboratory OC/EC Analyzer. Molecular tracers (Polycyclic Aromatic Hydrocarbons, PAHs) were measured using GC/MS techniques.

Lithogenic material accounts for a significant part of sinking material in all traps ranging from about 30% in the upper ones to almost double in higher depths, due probably to lateral transport from the Peloponnese shelf. Significant correlations were observed between mass and lithogenic fluxes at all depths indicating rapid transfer of material to depth.

Concentrations and fluxes of trace elements and PAHs showed high seasonal variability. Mass flux was shown to be the most important driver of this variability while concentration was responsible for a smaller contribution to export processes. Higher fluxes for these tracers are mostly associated to lithogenic sinking particles, while interannual variability was also observed.

Delineation of the strong variability of vertical fluxes by time-series studies is essential for understanding pollutant fate and building pollutant budget in the Mediterranean Sea.

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Barium and Carbon fluxes in the Canadian Arctic Archipelago

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The seasonal and spatial variability of dissolved Barium (Ba) in the Amundsen Gulf, southeastern Beaufort Sea, was monitored over a full year from September 2007 to September 2008. Barium displays a nutrient-type behavior with the highest concentrations observed at river mouths. The water column maximum is located below the surface layer with lower concentrations above and below. The lowest concentrations are found in water masses of Atlantic origin, and Ba concentrations decrease eastward through the Canadian Arctic Archipelago. In the range of the subsurface Ba maximum, we observed supersaturation of Ba with respect to barite ($BaSO_4$), the remainder of the water column appeared undersaturated. A three end-member mixing model comprising fresh water from sea-ice melt and rivers, as well as upper halocline water, was used to establish their relative contributions to the surface waters of the Amundsen Gulf. Based on water column and riverine Ba contributions, we assess the formation of biologically bound Ba (bio-Ba) and the subsequent Ba depletion by particle sinking. From this we derive an estimate the carbon export production. In the upper 50 m of the water column of Amundsen Gulf, riverine Ba accounts for up to 15% of the dissolved Ba inventory, whereas up to 20% of the dissolved Ba inventory is depleted by bio-Ba formation and export. Since riverine inputs and Ba export occur concurrently, the seasonal variability of dissolved Ba is moderate. Assuming a fixed organic carbon to bio-Ba flux ratio, carbon export out of the surface layer is estimated at 2 mol C m^{-2} yr^{-1}. Finally, we propose a climatological carbon budget for the Amundsen Gulf based on recent literature data and our findings, the latter bridging the surface and subsurface water carbon cycles.

Evolution of dissolved inorganic radiocarbon in the eastern Atlantic sector of the Southern Ocean

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The Southern Ocean plays an important role in the Earth's climate system with its large productivity belt and vigorous circum Antarctic circulation patterns. However, our knowledge of temporal evolution of the Southern Ocean circulation including its carbon redistribution is poorly constrained by in situ observations in this vast remote region. Here, we used radiocarbon measurements of dissolved oceanic inorganic carbon (DIC) in order to provide powerful means to describe and quantify the movement of the water masses as well as the uptake of anthropogenic CO_2. We investigated the spatio-temporal variability of radiocarbon in the Southern Ocean during the last 40 years. Recent radiocarbon measurements were performed on DIC of five depth profiles off the Southwestern of Africa coast between 33.58°S 17.14°E towards 57.33°S 00.02°W obtained during Bonus-Goodhope cruise in 2008. We compare these results with those obtained from earlier cruises, GEOSECS and WOCE-France CIVA1. Within surface waters, observed ^{14}C gradients between north and south are consistent with previous observations. However, the absolute values of $\Delta^{14}C$ are slightly depleted compared to previous studies most likely reflecting the decrease of bomb ^{14}C in the atmosphere, the northward displacement of surface waters and replacement by old deep waters upwelled at the Antarctic Divergence. Our observation of arrival of deep waters is consistent with the observed oversaturation in CO_2 of subsurface waters compared to the atmosphere and the depleted $\delta^{13}C$ signature of DIC. In contrast, within the deep ocean, we observe a basin scale dramatic fall of $\Delta^{14}C$ values since the early 1970s, which may reflect strong invasion of ^{14}C depleted Pacific Deep Waters into the Circumpolar Deep Water (CDW). The origin of this remarkable replacement of water masses may be attributed to atmospheric climate dynamics over the last 40 years or may reflect other ocean interior processes.

Oceanic circulation changes in the Northeast Atlantic Ocean as documented by radiocarbon record over the last 40 years

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We present the first quasi-annual radiocarbon time series from the Northeast Atlantic Ocean (NEA) obtained from new ^{14}C measurements of mollusc shells and from synoptic hydrographic surveys to investigate changes in the sea surface Δ^{14}C over the last 40 years. These data were compared to hydrographic data and model ORCA results in order to explore changes of advection and mixing process and air-sea exchange. The NEA time series reveals rapid uptake of bomb radiocarbon compared to existing ^{14}C records of the Northwest Atlantic (Bermuda and Florida) consistent with simulations using the general ocean circulation model ORCA 2°. Following the bomb-peak a high ^{14}C variability is observed. Between 1972 and 1986, low Δ^{14}C values are correlated with surface salinity anomalies and most likely reflect a strengthening entrainment of Labrador Sea water into the North Atlantic current, i.e. an eastward expansion of the subpolar gyre into the northeast Atlantic sector. In contrast, we observe a very rapid decrease of Δ^{14}C during 1968 that cannot be explained by an advective mechanism. This event most likely reflects an increase of vertical mixing as suggested by a sensitivity test revealing inter-annual variability from simulations of the ORCA 2° model.

DERIVATION OF REMOTE-SENSING REFLECTANCE USING OPTICALLY ACTIVE MATTERS IN OCEANIC/COASTAL WATERS

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A bio-optical model is developed which predicts the remote sensing reflectance above the surface as a function of absorption by pure seawater, phytoplankton and detritus/gelbstoff particle concentrations for coastal Case 2 waters with consideration of elastic and non-elastic scattering (i.e., Raman scattering, fluorescence) respectively. The present model is based on simulation with the optical properties of seawaters; based on the results of in-situ measurements of inherent optical properties (IOPs) carried out during several cruise programs at different seas and oceans and data is complied by different researchers (i.e., NOMAD data sets). The input to the algorithms are the IOPs of the water (i.e., total absorption (a(lamda)) and total backscattering (bb(lamda)) with involved effect of the elastic and non-elastic scattering (Raman scattering). Furthermore, inverse modeling techniques is used to examine the contribution of water constituents to the remote sensing reflectance from the measured remote sensing radiance reflectance spectra. Moreover, the derived remote sensing reflectance spectra exhibit great variability in the shape and magnitude is due to variations in the optically active matters and apparent optical properties (AOPs).

Keywords: Inherent optical properties, Reflectance,Scattering, Chlorophyll

Oceanic transport of anthropogenic carbon in the changing climate

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We use a coupled climate-carbon cycle model to evaluate the role of ocean general circulation in transporting the anthropogenic carbon tracer in the ocean and its implications on the regional air-sea carbon fluxes. Here, long-term climate and carbon cycle responses are simulated based on historical and IPCC-SRES A2 emissions scenario. For the 1850-2099 period, the model predicts oceanic uptake of anthropogenic carbon uptake of about 538±23 Pg C. In the North Atlantic, the carbon uptake rate reduces considerable by the end of the 21^{st} century. We attribute this to the subsurface lateral influx of anthropogenic carbon from the low latitude oceans and the slow down in AMOC, which weakens the penetration strength of anthropogenic carbon into the deeper ocean. In the polar Southern Ocean, more than half of the anthropogenic carbon taken up is efficiently and steadily exported northward, predominantly into intermediate waters. Maximum northward transport is simulated in the western South Atlantic around 500m depth. This transport mechanism may be responsible for the increased future carbon uptake strength in the polar Southern Ocean region by the end of the 21^{st} century, where the uptake rate reaches 39.3±0.9 g C m^{-2} yr^{-1}, more than twice the global mean. Our study further emphasizes the key role of Southern Ocean in controlling long-term future carbon uptake.

Geochemical investigation of the bivalve *Adamussium colbecki*: potential high-resolution proxy to reconstruct Antarctic water properties

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In the framework of Polar DOVE (Polar Deep Ocean VEntilation) project of the Italian National Program of Antarctic Researches (PNRA), a controlled growth experiment of the Antarctic bivalve *Adamussium colbecki* (Smith, 1902) was carried out in Terra Nova Bay (Ross Sea). The *A. colbecki* is potentially a powerful climatic-environmental archive of the Antarctic water properties, in particular to investigate the High Salinity Shelf Water, that contributes to the Antarctic Bottom Water formation. The *A. colbecki* is, in fact, a long-lived bivalve that thrives in the nearshore environment in Antarctica and it is also found in the fossil record. Six specimens were selected to investigate the isotopic ($\delta^{18}O$ and $\delta^{13}C$) and elemental (Li, Mg, P, Mn, Sr and Ba) composition of the shell at high spatial resolution, using a Micromill sampling and a LA-ICP-MS technique. Our findings indicate that slow-growing specimens precipitate the shell in isotopic equilibrium with respect to seawater, whereas the fast-growing ones are strongly influenced by kinetic effects. Comparing the time series of $\delta^{18}O$ to the *in situ* temperatures with a Data Mining technique, we observed that the winter growth is very limited or almost zero, and that the mean temperature, derived from the $\delta^{18}O$-temperature equation [*Kim and O'Neil,* 1997] is equivalent to the mean summer seawater temperature. Due to the seasonal growth pattern of *A. colbecki*, its $\delta^{18}O$ signal can be considered a poor proxy for the seawater salinity, which varies mainly during the winter. The variation for the minor and trace elements along the shell transects is quite similar among the individuals for Li, Mn and Sr relative to Ca, whereas the Mg/Ca, P/Ca and Ba/Ca ratios show a certain variability along the transect and among the specimens. A principal component analysis shows that two components are sufficient to explain about 70-85% of the signal variance. Li, Mg, and partially Sr form the 1st component, whereas Mn, P and Ba the 2nd or 3rd ones, suggesting different uptake mechanisms: unlike Li and Mg, which seem to be incorporated into the calcitic structure of *A. colbecki* as a function of the environmental signals, most of the Mn, P and Ba variation is probably controlled by secondary mechanisms, likely related to physiological factors. The process regulating the uptake of Sr is not clear and it probably depends on both environmental and physiological factors. Our data suggest that the relationship between the elemental composition of the shell of *A. colbecki* and the environmental parameters is somehow modulated by "vital effects" that need to be quantified.

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Geographical distribution and chemical characterization of natural and anthropogenic substances in marine aerosols over the Pacific Ocean

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The Pacific Ocean, the world's largest (occupying about 30% of the Earth's total surface area) has several distinguishing biogeochemical features. In the western Pacific, dust particles originating from arid and semi-arid regions in Asia and Australia are transported to the North and South Pacific Oceans, respectively. Biomass burning aerosols emitted in the Southeast Asia are exported to the tropical Pacific, and anthropogenic substances flowing out from Asia and Eurasia spread both regionally and globally, affecting cloud and rainfall patterns, air quality, and the radiative balance of downwind regions. The deposition of atmospheric aerosols containing iron and other essential trace elements to the ocean surface is important for marine biogeochemical cycles because this source of nutrients helps sustain marine primary production and affects marine food-web structure. These effects in turn influence the chemical properties of marine atmosphere. Atmospheric concentrations of trace metals and other substances in marine aerosols are compiled from the several cruises conducted for aerosol measurements on shipboard over the Pacific Ocean. Marine aerosols over the open Pacific are characterized by the contribution of terrestrial, anthropogenic, seawater, and marine biogenic substances based on the trace elements. Mineral dust particles are low and uniformly distributed over the North Pacific during summer time as a background level concentration. The equatorial Pacific is one of major source regions for marine biogenic aerosols such as sulfates and organics. Although atmospheric deposition fluxes can be obtained based on their concentrations and deposition velocities, recycling components in marine aerosols (e.g., phosphorus) between atmosphere and ocean may cause overestimates of the net atmospheric deposition fluxes. To understand the important biogeochemical processes and interactions occurring over the open oceans, more long-term recurrent research cruises with standardized atmospheric shipboard measurements will be needed in the future.

Initial results of ^{14}C in GEOTRACES-NL

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The rare isotope of carbon, ^{14}C or radiocarbon, is a valuable tracer for various oceanographically relevant processes [**?**]. Among these are the formation, movement and mixing of abyssal water masses (using ^{14}C-derived watermass "age") and the ventilation of the thermocline (as derived from the rate of penetration of the "bomb-peak" of ^{14}C that was caused by atmospheric testing of nuclear weapons in the 1960s). Additionally, for ocean general circulation models the accurate reproduction of the distribution and evolution of ^{14}C in the oceans is considered a valuable metric of skill. During the 2010 GEOTRACES cruises of the Dutch R/V *Pelagia* in the western North Atlantic (Iceland-Bermuda, Bermuda-Fortaleza), samples for ^{14}C were collected from all depths at all stations for processing and analysis by accelerator mass spectrometry (AMS) at the Centre for Isotope Research at the University of Groningen [**?**].

Here we present initial results from a total of 28 samples from four stations. We compare these with results obtained during the WOCE programme in the 1990s. This comparison yields a (admittedly coarse) picture that shows a significant reduction since the 1990s of the surface water ^{14}C, and increased values between 800m and 1800m, reflecting the continued penetration of the atmospheric bomb peak into the ocean's thermocline and mode waters.

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Aluminium in a general circulation model. Optimising the model or the measurements?

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A model for aluminium is implemented in PISCES, the biogeochemical component of the ocean general circulation model NEMO. By comparing its results with the measurements done in the GEOTRACES project, free parameters in the model have been adjusted to fit the spatial distribution of the data. In this way a 3D picture of aluminium is obtained that best fits the data.

PISCES is the biogeochemical component of the ocean general circulation model (OGCM) Nucleus for European Modelling of the Ocean (NEMO). This component contains a number of biogeochemical tracers under which different forms of silicate, carbon and iron. Aluminium was not yet part of PISCES. Since the new measurements on aluminium might be further interpreted by means of an OGCM, aluminium has been included in the model. Two forms of aluminium (dissolved and particulate) have now been added to PISCES. For this model 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.

The measurements done on several cruises of the GEOTRACES project contain measurements on the aluminium concentration and increase the number of accurate measurements on this tracer enormously. Therefore the PISCES aluminium model can be assessed and values of the uncertain model parameters can be constrained.

Two parameters which are for a larger part unknown are the dissolution percentage of the dust, α, and the partition coefficient, k_d. A number of model runs for different combinations of these parameters have been performed to find out when the model output is most similar to the measurements. The implications and the validity of this approach are discussed.

Acknowledgments. The authors are grateful to Maarten Klunder and Steven van Heuven for stimulating discussions to use the data in a useful manner, and others who have been proved useful in discussion, among which Jack Middelburg, Laurent Bopp, Hylke de Vries and Sybren Drijfhout. Camiel Severijns, Bert Wouters, Geert Jan van Oldenborgh and Patrick Brockmann were very helpful in giving technical support in data processing and visualisation. We also want to thank our colleagues from the IMAU institute for their critical and useful feedback to the model configuration and output.

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Evidence of anthropogenic CO_2 in deep-water using discrete pCO_2 measurements.

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Increases in anthropogenic CO_2 in the world's ocean have been well established [e.g. Sabine et al., 2004]. The methods of quantifying these changes require a means to separate natural, or climate induced changes, in ocean inorganic carbon from that caused by penetration of anthropogenic CO_2 from the atmosphere. The inaccuracy of the data and methods commonly used to determine the anthropogenic CO_2 in the ocean make it difficult to quantify small changes in deep-water (depth $\approx$>2000−2500 m). Moreover, changes can be obscured by common procedures of normalizing disparate data, sometimes taken decades apart, to deep-water values by making the *a priori* assumption that the biogeochemical processes in deep-water have not changed over time. Determining if anthropogenic carbon has entered the deep ocean is of importance because of its volume [Garzoli et al. 2010], such that even small increases will have an appreciable effect on the total water column, and to better understand penetration pathways and storage patterns of anthropogenic CO_2 in the ocean. Moreover, on longer timescales the deep-water will be the major depository of anthropogenic CO_2.

There is increasing evidence of physical changes in the deep ocean attributed to increasing atmospheric CO_2 levels and associated climate change. In particular, there are small but clearly discernable changes in deep-water temperatures [e.g. Johnson et al., 2006]. Here we assess changes in inorganic carbon using the parameter "discrete pCO_2", that is the measurement of partial pressure of CO_2 at fixed temperature of individual sub-surface samples. The signal to noise of the measurement is five-to-eight fold greater than for the state variables, total dissolved inorganic carbon (DIC) and total alkalinity (TAlk) that are key parameters to determine anthropogenic CO_2. Changes in discrete pCO_2 in deep-water are not definitive indicators of anthropogenic CO_2 but together with other support parameters, such as chlorofluorocarbons (CFCs) and oxygen, and models, the discrete pCO_2 changes can indicate the source of CO_2.

Here we investigate changes in the deep ocean from observations in the Atlantic (sections commonly referred to as A16, and A13.5) and Eastern South Pacific based (line P18) using discrete pCO_2 measurements taken over a decade apart. Associated deep-water changes in oxygen, DIC and TAlk, which are within the uncertainty of the measurement accuracy of these parameters, and CFCs are used to speculate on the cause of the changes in discrete pCO_2. For the A16 section through the

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center of the Atlantic Ocean the evidence points towards changes due to penetration of anthropogenic CO_2. This includes deep-water changes in CFCs that are significantly above the uncertainly of the measurement accuracy. The attribution of observed changes in deep-water for the other sections is less clear, in part because of greater measurement inaccuracy of the support parameters. However, measureable CFCs levels along P18 south of about 40 ˚S and along much of A13.5 again point to penetration of anthropogenic CO_2 for much of these sections. An estimate of the total DIC deep-water change based on the pCO_2 measurements and assuming constant TAlk over time will be presented along with a speculative assessment of the possible upward revision of the anthropogenic CO_2 inventory in the ocean based on these changes.

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Biogeochemistry and distribution of Mn in the surface ocean and the influences of Saharan dust deposition.

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It is well known that the main external source for essential micronutrients like Manganese (Mn) to the surface ocean is via atmospheric dust deposition. Mn is a key metal for photosynthesis due to its unique role in photosystem II and it is also used in other redox enzymes such as superoxide dismutase. The residence time of compounds like Mn is conditioned by its chemical speciation and by a variety of biological processes. We will present work conducted in two different water masses which both represent low nutrient low chlorophyll areas and are strongly influenced by Aeolian dust deposition. In the first place we examined the temporal changes in the concentration of Mn in trace metal clean mesocosms after two additions of simulated Saharan dust plumes (mimicking a wet deposition of 10 g m-2) to the northwestern Mediterranean, close to the coast of Corsica (DUNE2). The second investigated area was the oligotrophic eastern Topical North Atlantic where daily shipboard measurements were conducted. We will present Mn depth profiles in the water column and daily cycles which were taken during a SFB754 (Climate-Biogeochemistry Interactions in the Tropical Ocean) cruise. This data will help to constrain the supply rate and the residence time of Mn in the ocean.

The response of a Gulf estuary plume and hypoxia to wind forcing

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The plume structure of the Perdido Bay Estuary (PBE), a typical bay on the Florida/Alabama coast along the Gulf, was simulated using an existing calibrated model (Xia et al., 2011). To better understand plume dynamics in the PBE and similar bay systems, idealized sensitivity experiments were conducted to examine the influence of wind stress on the 3-D plume signature. Results indicate that wind direction dominates plume orientation, while wind magnitude significantly influences plume size, width, length, and depth. The plume size was reduced under the effect of wind and increased wind forcing. A northerly wind could extend the plume length and duration at a lower wind speed (e.g 3 m/s), but its surface size will be smaller than with no wind forcing, but plume length and width will usually be decreased with the wind effect compared to no wind forcing. Bay-shelf salt flux and water flux were also investigated since they are important for the formation of a 3-D plume structure. Model simulation shows that water flux to the coastal ocean is stronger under a northerly wind, westerly wind, and easterly wind compared to that of a southerly wind at a given speed, and it could explain why the plume signature varied under the changing wind direction. With a high wind magnitude, the water flux typically increased compared to a no wind scenario or low wind magnitude scenario, but salt flux to the coastal ocean results in a relatively large amount of salt outflow so that the surface plume size is reduced. Thus, the surface plume appears to be significantly correlated with the combination of bay-shelf water and salt flux. A detailed understanding of this water and salt flux is essential to the study of plume dynamics. Additional particle transport analysis using variable wind forcing was conducted to validate the existence of the transport mode, which also determined the influence of the plume on particle movement. The results showed a consistency between the surface plume, salt flux, and particle transport.

In additional, hind casts of Perdido Bay bottom hypoxia is provided in response to local wind forcing. Observed average wind speeds of 3 m sec-1 during July were capable of redistributing hypoxia stressing the entire estuarine ecosystem. Easterly and westerly winds resulted in greater hypoxia near the shore, which put stress on near-shore habitats such as oysters and result in phenomenon like jubilees. Westerly and southerly winds resulted in significantly larger areas of anoxic conditions due to longer water-residence times that allowed continued surface primary production and subsurface microbial decomposition. Northerly and easterly winds, in contrast, promoted water transport toward the Gulf of Mexico, enhancing the freshwater discharge direction from Perdido River. Wind speeds over 3 m sec-1 were sufficient to enhance the advection of dissolved oxygen into bottom waters through vertical mixing and resulted in significant reductions in areal coverage of hypoxia. Therefore, periodic summer storms may alleviate hypoxic conditions within the estuary.