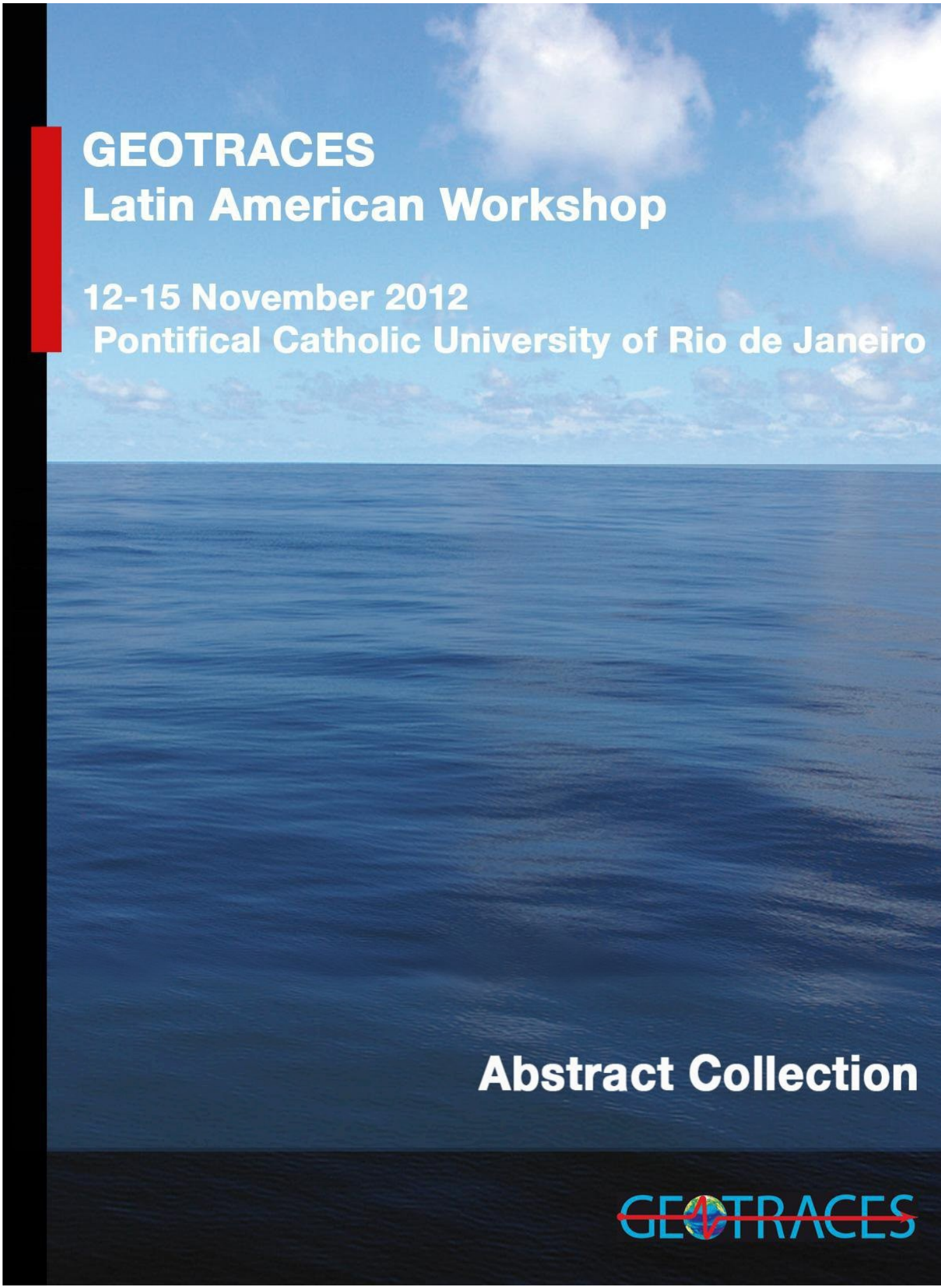
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GEOTRACES

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ABSTRACTS FROM INVITED GEOTRACES SENIOR RESEARCHERS

Supply and removal of trace elements at ocean boundaries

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Historical assessments of the biogeochemical cycles of trace elements in the ocean have often considered only rivers and the deposition of aerosols as the principal sources of these elements. However, recent studies have also invoked hydrothermal systems at mid-ocean ridges and the dissolution of sediments at ocean margins as significant sources of trace elements. The GEOTRACES program was designed to identify and quantify the major routes of trace element supply, as well as the primary processes removing trace elements from the ocean. The GEOTRACES global ocean survey is now underway, and we will present a limited selection of preliminary results from GEOTRACES cruises to illustrate the nature of the data being generated as well as the types of processes that influence the distributions of trace elements in the ocean. Using results from other groups as well as from our own, we will: 1) illustrate a new strategy using thorium isotopes to quantify fluxes of dissolved trace elements from continental mineral aerosols, 2) show that marine sediments and hydrothermal systems each serve both as a source and as a sink for trace elements, and 3) compare the "smooth" distribution in the Atlantic Ocean of Al, which reflects a strong influence by ocean circulation, with the "patchwork" distribution of Fe, which reflects its shorter residence time and multiple sources and sinks in the ocean.

Measuring the distributions of trace elements and their isotopes in the ocean reveals regions of active supply and/or removal. Perhaps the greatest surprise that is evident in the preliminary findings is the strength of the signal showing active removal of certain trace elements from near-bottom waters that is generally associated with resuspended sediments (nepheloid layers). Feature such as this will serve as targets for future process studies designed to examine supply and removal processes in greater detail.

The US GEOTRACES North Atlantic Transect: lessons learned and initial results

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On two research cruises of the R/V Knorr in late 2010 and 2011, the US GEOTRACES program collected trace element isotope samples (and supporting information samples) from a section going from Woods Hole Massachusetts to Bermuda to the Cape Verde Islands to Lisbon Portugal. A total of 36 stations were occupied, including x "full" stations (25-37 samples from the surface to the bottom, x "super" stations (full depth water column including additional casts for other properties, and x "demi" stations (13 samples in the upper 1000m). Contamination-prone trace metal samples were drawn from the ODU GEOTRACES GOFlo Carousel, while other types of samples were drawn from a Niskin Rosette samples. Large volume filtration samples were taken from McLane pumps mounted on a vectran cable with a new inlet baffle that eliminated particle disturbance during recovery. Aerosol samples were collected when underway winds were in-sector. In total, over 17,000 subsamples were collected during the expedition.

In these cruises we encountered several distinct environments that affect trace elements and their isotopes in different ways. For example: (1) Mediterranean Sea outflow (advective dispersal of water subject to strong aerosol and anthropogenic inputs), (2) North African upwelling and continental margin interactions, (3) Sahara dust input, (4) TAG hydrothermal plume, (5) BATS oligotrophic biota, (6) US continental margin bottom nepheloid layers and continental shelf inputs.

These samples have been/are being analyzed for a great diversity of trace elements and isotopes as well as conventional supporting properties such as salinity and nutrients. A few properties were measured on board as necessary (e.g. salinity, nutrients, CFCs, and some trace metals), but most were collected as samples for shore-based analysis. In this talk I will present some of the preliminary results of this cruise to demonstrate how having multiple trace elements and isotopes from the same samples especially illuminates the processes affecting these regions of the ocean. I will especially focus on MIT analyses of Pb and Pb isotopes. Pb has been put into the ocean dominantly by anthropogenic emissions that have evolved in time, in flux as well as isotopic composition. I will illustrate how these data illuminate processes that are common to many trace elements.

In particular for Pb, we see multi-decadal decline of Pb in the upper 2000m of the ocean in response to the phasing out of leaded gasoline, scavenging of Pb by hydrothermal vent particulates and Aftican continental margin nepheloid layers, and isotopic identification of advective sources of water masses.

Intercalibration, an essential component of the GEOTRACES Program

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Intercalibration is defined as, "the process, procedures, and activities used to ensure that several laboratories engaged in a monitoring program can produce compatible data. When compatible data outputs are achieved and this situation is maintained, the laboratories can be said to be intercalibrated." (Taylor, 1987) In other words, intercalibration is the active process of laboratories sharing their data and if disagreements exist, finding and fixing the causes. To achieve the major goals of GEOTRACES, trace element and isotope data must be as precise and accurate as possible, so intercalibration is an essential component of the Program. However, the scope of the science involved, the number of countries and labs participating, and the many sampling and analytical methods being used make intercalibration a difficult task. This presentation will explain the role of the Standards and Intercalibration Committee in GEOTRACES, and the intercalibration protocols that have been developed for the program. These protocols include the development and use of reference materials for analytical testing, and the occupation of crossover stations where multiple cruises sample at the same location and depths so the combined data sets intercalibrate all steps, from sampling to analyses. If a cruise cannot occupy a crossover station, then replicate sampling and analyses by different labs are conducted. Some of the intercalibration results to date will be shown to illustrate the protocols.

Submarine Groundwater Discharge: a potential source of TEIs to the ocean

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Submarine groundwater discharge has attracted the interest from the ocean scientific community over the past two decades for its (revealed?) impact on biogeochemical cycles in coastal ecosystems. Many studies have already demonstrated the significance of SGD-associated input of nutrients, TEIs, pollutants, pharmaceuticals and other chemical species into the ocean. SGDs include freshwater from geological formations and salt water that is either pumped or recirculated through intertidal and subtidal sediments or penetrates into depleted coastal aquifers. The GEOTRACES science plan highlights process studies to evaluate sources of TEIs and prioritize SGD as one of the main processes that should be studied. Although SGD studies have been conducted in many sites worldwide, South America is, nowadays, one of the less studied areas in the world. In this presentation, we would like to outline the importance of the SGD process to better understand the biogeochemical cycles in coastal areas. A review of the methods of estimating SGD based on radioactive tracers (i.e. Rn and Ra) is presented together with hydrogeological constraints.

Quantifying fluxes of essential micronutrients to the high productivity belt at 40ºS in the South Atlantic

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There is a prominent belt of high biological productivity spanning the South Atlantic and centred at 40ºS. This ocean region must be supplied with sufficient nutrients, including micronutrients such as Fe, to drive the high productivity. Surface water to the south of 40ºS are starved of Fe, and those to the north also have rather low Fe concentrations, so the Fe supply at 40ºS must be local. Possible sources include riverine and dust fluxes, particularly from South America, or upwelling of micronutrients from deep sources including slope sediments and mid-ocean-ridge volcanism.

The GEOTRACES Section – GA10 – was completed in January 2012 and sought to quantify the fluxes of Fe and other critical micronutrients (Zn, Cd, Co, Ni, Mn, Cu) into, out of, and within this 40ºS region. Direct aerosol measurements, together with surface ocean chemical tracers (Al, 232Th) allow an assessment of dust inputs. Lateral and upward mixing of micronutrients to the surface ocean are assessed using Ra isotopes, and by measurement of velocity and temperature microstructure. Fluxes to deeper waters from sediments are assessed through measurement on shallow sediment cores collected during the cruise. Biological removal of micronutrients will be assessed using 234Th measurements coupled to particulate trace-element data. The wide range of geochemical and other data collected during the cruise allow quantification of all significant fluxes of micronutrients in the surface ocean and thereby an assessment of the controls and limitation on productivity. In the east of the section, trace elements are at very low concentration, and waters are at least seasonally Fe limited. Fe limitation is relieved in the west, and preliminary data indicate that major micronutrient supply is on the western margin, and are then transported eastward in zonal surface currents to feed the ocean interior. The results point clearly to the importance of metal sources on the western margin and indicate the need for process studies in the South American coastal region.

The GEOTRACES Programme: What? Why? When? How?

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GEOTRACES is an international research programme focused on understanding the cycles of trace elements and isotopes (TEIs) in the global ocean. It seeks to assess and quantify the processes that govern TEI fluxes and distributions in seawater, and to do so sufficiently well that the response of these fluxes and distributions to global change can be predicted. TEIs that are of direct interest to the programme fall into four categories: those that are essential for life in the ocean (e.g. Fe, Zn, Co); those that trace processes in the modern ocean (e.g. Al, 234Th, 228Ra); those that are significantly contaminated (e.g. Pb, Hg); and those that are used as proxies to reconstruct the past (e.g. Cd, 231Pa/230Th, N isotopes).

Understanding of TEI cycles will be advanced through a series of ocean sections spanning the global ocean, and by a number of studies assessing processes in significant regions, particularly at ocean margins. The field phase of the programme formally launched in 2010 and has witnessed the successful completion of nine ocean sections (see map at http://www.geotraces.org/ for details). This field phase was proceeded by GEOTRACES work during the International Polar Year and by important (and continuing) work to ensure intercalibration of measurements and effective data management during the programme. The programme is a collaboration between scientists in many countries around the world, and actively seeks new participants with relevant expertise.

In this introductory talk, I will outline the justification for the GEOTRACES programme, and provide an overview of its activities and organisational structure. This talk will set the context for the talks that follow in the session outlining some of the early challenges and successes of the programme.

AMANDES: a multidisciplinary GEOTRACES process study on the Amazon shelf

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The main objective of the AMANDES French-Brazilian project was to better understand the physical and chemical fluxes, including geochemical tracers, from continents to the oceans, with a specific focus on the passive margin of the Amazon River estuary, characterized by an important continental influx, and a significant impact on Atlantic Ocean water masses. Three complementary tracks were followed 1) analytical developments in order to characterize the suspended matter trace element and isotopes as tracers for solid-solute exchange (REE, Nd, Ra, Pb, Be, Hg) 2) oceanographic expeditions on the Amazon shelf to deploy mooring and water column sampling during different seasons 3) development of a hydrodynamical model of the tidal dominated Amazon estuary, consistent with local forcing (river influx, eastern currents) and validated by in situ field (tides, currents) and remote sensing observations. Four cruises were realized on R/V ANTEA (IRD) between October 2007 and July 2008. Some main results of this GEOTRACES process study will be presented here:

The considerable improvement of the circulation model on the Amazon shelf: based on the hydrodynamic finite element model T-UGOm, we developed a precise and accurate regional tidal model. In our best simulation, the overall root mean square error on complex differences is reduced from 54 cm in a standard model to 27 cm. Such precise and accurate tidal modelling is a prerequisite for modelling particle transport, our next step.

What are geochemical tracers telling us? Based on the fine circulation description and the Rare Earth concentrations and Nd isotopes on the one hand and Ra isotopes on the other hand, all acquired in the salinity gradient and in the open ocean, we discuss and quantify shelf and estuary contributions to the ocean and infer their pathways.

The AMANDES project was supported by the IRD, CNRs and ANR in France and the CNPq in Brazil. International collaborations emerged from AMANDES with Brazil (Brasilia, Recife, Rio) and the UK (Bristol).

The US GEOTRACES aerosol and rainwater intercalibration and sampling program

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The primary goal of the US GEOTRACES atmosphere intercalibration program was 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 forty investigators analyzing for forty elements/isotopes of natural and anthropogenic importance participated in two intercalibration projects, conducted at RSMAS/University of Miami (September 2008) and in the eastern North Pacific during the second US GEOTRACES intercalibration cruise (May 2009). The sampling equipment has since been used on the US GEOTRACES North Atlantic Zonal Section cruises in 2010 and 2011.
We prepared and tested dual high-volume TISCH 5170-VBL aerosol samplers for inorganic trace elements and isotopes, major ions, organic material, and isotopes of nitrogen and oxygen. A third 5170-VBL aerosol sampler was equipped with a 5-stage Sierra-style slotted impactor to collect size-fractionated aerosols for similar chemical measurements. The aerosol samplers were operated at sea using wind speed and wind sector control to avoid contamination from ship's exhaust. Two N-CON automated rain samplers were configured with large (506 sq. cm) polyethylene funnels and receiving bottles to collect rain on an "event" basis (>1mm). Rainfall was filtered (within 30 minutes after collection).
Details of the sampling equipment and sample collection methods will be discussed, emphasizing the advantages of establishing consistent and reliable procedures for the collection and analysis of aerosol and rainwater samples. Data from the intercalibration experiments and from the US GEOTRACES North Atlantic Zonal Section will be presented.

Redox Conditions and metal transport along eastern boundaries

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Eastern boundary regions represent an important source of trace metals to the interior of the Pacific Ocean. Many of these regions have high productivity associated with upwelling which results in the formation of intense oxygen minimum zones. Redox gradients have an important influence on the geochemical cycling of redox active elements like iron and manganese, and also metals like copper, for which the effects of redox chemistry are less obvious. In this presentation, I will compare findings from five cruises carried out between 2005 and 2012 in eastern boundary regions off North and South America. Most of these have intense oxygen minima, where active denitrification processes occur that are closely coupled with iron redox cycling. One cruise was carried out along Line P (off the coast of British Columbia) where there is no active denitrification in the water column, and the behavior of Fe is quite different. The findings have important implications for the coupling of metal cycles with processes that are thought to contribute to the enhancement and strengthening of oxygen minimum zones worldwide. They also underscore the important connections between several transition metals and the nitrogen cycle, since key transformations within that cycle are catalyzed by metalloenzymes requiring these metals.

Applications of radium isotopes to studies of coastal ocean mixing and submarine groundwater discharge

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The four naturally-occurring radium isotopes each derive from decay of a thorium isotope. Because Th is only found attached to particles, the presence of Ra in sea water implies that the water was in contact with sediments on a time scale dictated by the half life of the Ra isotope. For example the presence of 224Ra (t1/2 = 3.66 days) in the coastal ocean requires the interaction of this water with sediments in the past 2 weeks. Coupling 224Ra measurements with the other Ra isotopes: 223Ra (t1/2 = 11.4 days), 228Ra (t1/2 = 5.75 yrs), and 226Ra (t1/2 = 1600 yrs), provides information on time scales of near-shore processes such as residence time of water in estuaries, ages of river plumes, and mixing rates and ages of coastal waters. With the critical information provided by Ra isotopes, fluxes of other dissolved components such as metals, carbon, and nutrients may be realized.

During studies of the short-lived Ra isotopes in coastal waters it was realized that there was far more 226Ra present than could be explained by conventional sources (rivers, sediments, upwelling). It was hypothesized that the excess 226Ra was supplied by submarine groundwater discharge (SGD). This hypothesis has been tested and proven correct at numerous locations on all 7 continents. These tests have further revealed that SGD is an important source of metals, carbon, and nutrients to coastal waters, in many cases exceeding riverine fluxes.

Coastal aquifers are being depleted due to over pumping. As freshwater in these aquifers is replaced with sea water, important chemical changes occur. The introduction of sulfate increases greatly the oxidation capacity of the water. The reaction products of degraded organic matter include both inorganic and organic forms of dissolved N, P, and C as well as sulfide. These conditions lead to reduction of metal oxides, increasing concentrations of Fe2+ and Mn2+ plus ions that were bound to the oxides. As this chemically-altered groundwater enters the ocean as SGD, it carries high concentrations of dissolved metals, carbon, and nutrients.

Instruments and supplies required to measure the short-lived Ra isotopes are relatively simple and inexpensive. Little training is required to conduct these measurements; the instruments can be set up easily in the field. Measurements of the long-lived isotopes require more complex and expensive instruments. In many cases it is better to partner with a lab that routinely makes these measurements.

The CARIACO Ocean Time-Series and the ANTARES Network: An effort to coordinate a continental-scale observatory of long-term changes in coastal ecosystems of the Americas

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Continental margins play an important role in the global carbon cycle, accounting for about 10-15% of the carbon produced in oceanic systems, and 40% of carbon deposition on the global ocean floor. To understand the biogeochemical and ecosystem processes that lead to one of the finest records of climate change in ocean sediments, the CARIACO Ocean Time-Series program has conducted monthly oceanographic cruises to the anoxic Cariaco Basin on the continental shelf off Eastern Venezuela since 1995. The program was established with support of the Venezuelan FONACIT and the US National Science Foundation. Hydrographic, bio-optical, and biogeochemical observations including primary productivity, microbial dynamics, dissolved inorganic carbon and nutrient concentration, and sediment flux observations are collected to build a robust long-term time series. The CARIACO time-series helps assess the variability of the carbon budget and hydrographic variables in the South-Eastern Caribbean from seasonal to decadal time scales. Marked changes have been observed over time in ecosystem state and biogeochemical cycles in the southeastern Caribbean Sea. These changes are caused by a decrease in coastal upwelling intensity, higher thermal stratification and a steady increase in sea surface temperature due to the weakening of the Trade Winds. These climatic changes are coincident with a northward migration of the inter-tropical convergence zone and therefore reflect large-scale changes which are then recorded in the sediment deposited in the basin.
CARIACO is an integral part of the ANTARES Network, a group of coastal time-series sites located around the Americas from Chile to Mexico. ANTARES investigators use in situ and satellite-derived data. One of the goals of ANTARES is to understand long-term changes in coastal ecosystems, to distinguish natural variability from anthropogenic effects, and to understand the potential socio-economic impacts of such changes. An important goal is to provide a network of support for scientists in developing nations, focusing on providing opportunities for capacity building as well as scientific and technical collaboration. The ultimate goal is to develop a continental-scale coastal biogeochemical observing network.

ABSTRACTS FROM PARTICIPANTS

On spatial patterns and regulation of primary production in the Rio de la Plata estuary

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Primary production in estuaries is a relevant process underlying biogeochemical patterns and fluxes between continental and marine systems. The Rio de la Plata is a large-scale estuary and the main point source of freshwater to the south Atlantic ocean. It is regarded as highly productive due to important fish populations which support industrial-scale fisheries by Argentinian and Uruguayan states. However, knowledge on fundamental ecosystem processes is still incipient; e.g., primary production rates (PP) and its spatial and temporal variability patterns are largely unknown with only few direct measurements of PP sensu stricto performed after year 2000. Here we present a review on recent and historical results on PP, phytoplankton biomass (chlorophyll-a), underwater light environment and macro-nutrients: dissolved inorganic nitrogen (DIN), phosphorous and silicates along the main salinity gradient. The goal was to explore potential regulation mechanisms for PP. Working hypothesis stated that regulation operates through a double and opposite horizontal gradient of light and nutrients as established for some northern hemisphere turbid estuaries. According to that hypothesis PP in riverine and oligohaline regions is mainly limited by light, while in the marine dominated region PP is limited by nutrients availability. Results indicated that underwater light climate was characterised by high turbidity in upper and middle reaches, and improved light penetration in the marine region; a sharp transition occurred in the oligo- to mesohaline range (salinity15 mM) and decreased towards the marine-dominated region (ca. 2 mM), with a main drop in the salinity range [20 - 25]. N:P molar ratio was always below the Redfield ratio and also decreased towards the marine area (1.92 in the salinity range [25 - 30]). PP varied between 20 and 55 mgC m-3 h-1, and peaked at intermediate salinities [10 – 20]. Those patterns are consistent with the hypothesised mechanisms, where PP is boosted at intermediate salinities seaward of a turbidity front, and is responsible for the assimilative loss of dissolved macro-nutrients. Further investigations are needed to confirm present results, which are based on a very limited number of PP measurements (n= 21), and to add temporal resolution for an ecosystem subject to significant seasonal and inter-annual (e.g., ENSO-driven) variability.

In search of context: remote sensing tools for GEOTRACES

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Sensors on earth-observing satellites have transformed our view of the ocean and given unique insight on distributions and processes since the late seventies. The temporal and spatial range of space observations depends on the number of relevant satellites and the characteristics of their orbit and sampling method. Ocean variables amenable to remote sensing are also limited, as the ocean is opaque to most sensing wavelengths. However, satellite derived information of environmental conditions affords an invaluable context for ship-based measurements. Here we discuss the most critical remote sensing tools for GEOTRACES, which aims to quantify the distributions of oceanographic trace elements and their isotopes (TEIs). While TEIs themselves lack a remote sensing signature, satellite-based observations of other variables, such as sea surface temperature, the concentration of chlorophyll, or aerosol loading, can characterize critical atmospheric and oceanographic processes that determine TEI distributions and cycling. Remote sensing also provides indicators of circulation, both in the atmosphere and ocean, to assist in interpreting cruise information. We will present an overview of remote sensing products that may be of particular interest to GEOTRACES researchers, including newly available variables such as sea surface salinity.

The Amazon River and other major rivers as sources of Zn complexing ligands to intermediate water masses.

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Using anodic stripping voltammetry and a novel interpretative mathematical approach, the concentration and binding strength of Zn and Cd complexing ligands has been studied in sections of the Equatorial and South Atlantic, the West North Pacific, the Chesapeake Bay and the North Persian/Arabic Gulf. The presence of strong Zn complexing ligands is linked commonly to phytoplankton that reputedly produce chelating agents to keep metals in solution and in a bioavailable form. Here we present evidence of links to organic matter originated more or less remotely from rivers. The influence of major global rivers in South America, North America, Africa, and Asia has investigated indirectly in open ocean sections, while direct studies in estuarine areas strengthen the hypothesis that riverine and continental shelf sources are important in defining the presence of Zn complexing ligands throughout the water column in the global ocean. More so, a study of discreet samples along the trajectories of specific water mass suggests that the ligands change concentration and binding strength as the water masses age. The potential ramifications of the chemical speciation and biolimitation of Zn after the eventual upwelling of these water masses is discussed.

Source apportionment of organic matter in the SE Brazilian continental margin as revealed by lipid biomarkers

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POSTER

Lipid biomarkers [fatty acids (FA), sterols and alcohols] and total organic carbon (TOC) were quantified in 215 surface sediment samples collected at depths ranging from 25 m to 3000 m along 10 cross-margin transects in order to investigate the processes related to the origin, transport and accumulation of organic matter (OM) in the studied region. The lipid biomarker composition suggested predominance of OM derived from primary and secondary producers in the water column, but significant spatial gradients in the quality and quantity of the sedimentary OM were observed. Lower concentrations with predominance of labile lipids were measured at the continental shelf (f and slope suggested the presence of bioavailable OM in the sediment, which in turn may have a major influence on the ecology of benthic communities.

Shale-normalized lanthanide signatures of the settling particulate matter and recent sediments of Alfonso Basin, La Paz Bay, Gulf of California

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Biogeochemical cycles of elements in the ocean lie at the center of our understanding of the functioning of ecosystems on different scales, whether global or regional. Some major, trace elements and lanthanides are known to be useful indicators of the origin of settling particulate matter and marine sediments, especially in contrasting environments with distinctive features such as active tectonics or environmental pollution.
The objective of this study is to characterize shale-normalized lanthanide patterns as well as trace element composition of settling particulate matter (SPM) and marine sediments of the Alfonso Basin, southwestern Gulf of California.
The SPM was collected with an automated sediment trap during 2002-2010 with a periodicity of 7-15 days near the bottom of Alfonso Basin. A recent sediment core was obtained with a box corer near the trap location. The major, trace element and lanthanide contents were determined using instrumental neutron activation analysis, aided with suitable standard reference materials. The core was dated using the Pb-210 method.
The trap material composition and sediment core analyses helped establishing fluvial supply, mostly during tropical cyclones (Sc and Fe), biogenic contribution (Ca, Ba and U), aeolian effect (Sc, Fe and As) and authigenic particle formation due to suboxic conditions of the water column or associated to organic matter (U and As). The shale-normalized patterns in SPM show an alternation between light and heavy lanthanides, as well as a typical negative Eu anomaly, which becomes positive during some events. The light/heavy (normalized La/Yb ratio) in the core, representing the time span between 1850 and 2008, showed the same alternation as the settling particles. Mostly the core has a negative Eu anomaly with rare positive Eu prominent peaks. The positive Eu anomaly in both cases is presumably related to hydrothermal activity of Gulf of California tectonics. Calcium values in the sediment core show an increase tendency after the year 1950 which seem to coincide with a superficial temperature reconstruction (NOAA ERSST v3b).

What controls sea-air CO2 fluxes in a pristine tropical estuary?

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The processes controlling the marine carbonate system and the sea-air CO2 exchanges along the Brazilian coastal area are, at date, poorly constrained. This study aims at establishing a carbon budget at the tropical Barra Grande Estuary (SE Brazil), as well as estimates of the sea-air CO2 fluxes in this area.

The Barra Grande Estuary is located at Vila Dois Rios, on the ocean-side of Ilha Grande, and characterised by the presence of dense mangrove forests on its margins. The whole island belongs to the Ilha Grande Regional Park, one of the best preserved Atlantic rain forest areas in Rio de Janeiro state (SE Brazil). A seasonal sampling programme over two years at a fixed estuarine station (hourly sampling during 2 tidal cycles = 25h), started on September 2012.

To achieve our results, we will measure two carbonate system parameters, pH and total alkalinity (TA), together with other physical and biogeochemical parameters in the study area (mangrove area, estuary, and coastal ocean). The other carbonate (DIC, pCO2) system parameters will be estimated using CO2calc software, using the available temperature, salinity, pressure, nutrients, pH and TA data. The results will also allow us to understand the seasonal variability in the sea-air CO2 exchange and determine whether the ecosystem acts as an atmospheric CO2 source or a sink. Concomitantly, the availability of carbon and physical/biogeochemical data should allow us to quantify the amount of dissolved anthropogenic carbon (C-ant) in the coastal ocean, and to determine the extent of the C-ant impacts to the ecosystem (e.g. enhancing a seasonal respiration-driven acidification).

Although carbon itself cannot be considered a trace element, this study relates to GEOTRACES Theme 1 - Continental Runoff by providing background information on the riverine fluxes of nutrients and the biogeochemical functioning of a coastal tropical ecosystem.

Distribution patterns of long-lived Ra isotopes in Bransfield Strait surface water – OPERANTAR XXIX and XXX expeditions

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POSTER

The Bransfield Strait in the Antartic Peninsula is a basin strongly influenced by processes occurring on its continental shelves. The modified shelf waters feed the polar surface layer or ventilate the subsurface layers of the interior basin and products of biogeochemical interactions within the shelf environment are transferred into surface and subsurface layers of the Southern Ocean. The overall goal of this study was to apply an isotopic tracer technique to investigate the rate of exchange between the Antartic Peninsula islands and the Brasnfield Strait interior. This technique was based on the measure of the surface water column ratio of two naturally occurring radium isotopes, 228Ra/ 226Ra. Because 228Ra is derived solely through input from shelf sediments, it is an unambiguous marker of water that has been in contact with shelves. Its relative distribution in shelf and basin water is therefore useful for assessing the degree of shelf-basin interaction. Seawater samples were collected between 8th March - 1st April 2011 (Operantar XXIX) and 13th October – 14th November 2011 (Operantar XXX) onboard the RV Ary Rongel, from Brazilian Navy. In March/11, 228Ra/226Ra activity ratios up to 4.0 were determined, the highest value being observed at station EB13, closest to the cost in Admiralty Bay. During October/11 226Ra activities ranged from 18 to 138 mBq 100 L-1, while 228Ra activities varied from or 228Ra, a linear gradient was observed and implies that mixing controls its distribution in the studied area.

Overview of Modern Dust Activity and in Southern South America

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The presence of dust in ice-cores and snow samples (East Antarctica) and in marine sediments (Atlantic and Indian sectors of the SO) as well as phytoplankton variability in the same area have been linked to dust sources located in Bolivia and Argentina. Yet this linkage is mostly based on modeling studies and a handful of in-situ studies in selected areas within the region. As a result , there is a notable lack of observations describing basic features such as of dust activity frequency, composition and geochemical fingerprinting in Southern South America's active and potential dust sources.

Since 2004, the authors have been carrying an an almost continuous survey of dust activity in the region with a major emphasis in the Patagonia desert. A ground based dust trap system has been operating at five sites at selected locations between Tierra del Fuego (54S) to northern Argentina (24S). Time series of horizontal and vertical dust transport have been created at monthly to weekly time resolutions enabling the study of year to year variability. An immense data base of soil and dust samples representative of known or potential dust sources have been collected. Textural , physical, chemical and isotopic analyses have been applied to a limited subset of samples. In addition and starting at 2004, daily and continuous satellite observations as well as monitoring of visibility reports at airport stations in Argentina have been carried out and a data base of observed dust events have been created. A few cases studies have been analyzed in order to determine the transport patters into the Southern Atlantic and to Antarctica.

This presentation will highlight modern dust activity features observed in the area of Patagonia, Central and North Argentina and Bolivia. It will present current efforts and status of the survey.

How many information can we get from 2ml samples? – Results of South Atlantic JC-057 Cruise

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POSTER

As part of the JC-057 cruise, 2 mL filtered seawater samples were collected from 18 stations at 24 different depth. The samples were analyzed for Ba, Mo and U applying a quadrupole ICP-MS after a simple 1:10 dilution.
The samples were also directly analyzed for δ(D) and δ(18O).using a L-1102i PICARRO water analyzer (cavity ring down spectrometer, CRDS). Each sample result represents the mean value of four different injections, and for a batch of each six samples a standard and a test sample were measured. Typical combined uncertainty is 0.7‰ for δ(D) and 0.2‰ for δ(18O).
Among Ba, Mo and U, better identification of the watermasses were obtained with Ba. Saturation index for barium sulfate was calculated for each sample and the calculated values shown a saturation gradiente from the surface to the botton, with unsaturation at the surface and saturation and higher depths.
The obtained results shown that light isotopes values are valuable tools to identify watermasses, presenting a good correlation to salinity and nutrients, as fosfate.

Anthropogenic impacts and fluxes of trace elements on tropical estuaries of northeast Brazil

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In this study, an evaluation of environmental impacts on the estuaries located at the Todos os Santos Bay, Bahia, Brazil, was performed using multiple lines of evidence. Fluxes of trace elements and suspended particulate material were also investigated in the main estuaries. This work is part of the long-term multidisciplinary research programme (BTS Project; http://www.btsinstitutokirimure.ufba.br), which started 5 years ago, together with the actions of the National Institute of Tropical Marine Environment (INCT AmbTropic; http://www.inctambtropic.org/).

Samples were collected during high and low flow conditions at ten stations in each estuary (Paraguaçu, Subaé, Jaguaripe, São Paulo, Mataripe and Camamu). For the fluxes study, hourly sampling during 2 tidal cycles was performed at the mouth of the estuaries. The organic and inorganic contaminant (trace and major elements) contents of biotic (bivalves and polychaetes) and abiotic (sediments and suspended materials) compartments and the structure of macrobenthic assemblages were determined.

There were significant differences among and within studied estuaries regarding contamination levels, fluxes and benthic assemblages. The estuaries located at the north part of the Todos os Santos bay (Subaé, Mataripe and São Paulo estuaries), where a large petrochemical and industrial complex is located, were the most impacted. On the contrary, Jaguaripe and Camamu present relatively well preserved conditions, which can be observed from the metal concentrations in sediments and SPM and the extensive mangrove, which occupies most of the estuarine margins and is an important source of organic matter in the system. Suspended particulate material transport varied from 1 x 103 and 100 x 103 kg. Total trace metal exportation varied between 10-1 and 10-5 kg/m of estuary section. The results suggest that studies in ecological systems with high variability must use integrated tools to improve the understanding of processes.

This study relates to GEOTRACES Theme 1 - River and groundwater fluxes from land to sea by providing information on the riverine fluxes of trace elements and the biogeochemical functioning of estuarine ecosystems.

Bahía Concepcion, western to Gulf of California: suitable natural laboratory for the marine biogeochemical studies of trace elements

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POSTER

The semi-closed, not deep and pristine Bahía Concepcion of the Gulf of California, which is almost inserted to semi-arid eastern Baja California Peninsula, outstands by its high biological productivity, geothermal hot springs, shallow-water gas-hydrothermal vents, and by the absense of permanent fluvial inputs. During a summer season the density stratification frequently causes the anoxic and hypoxic conditions in the water column. Due to all these reasons the Bahía Concepcion is an excellent natural reservoir to study biogeochemical cycles of trace elements (TEs) in coastal zone. We made there a first assessment of the influence of TEs coming up hot springs and shallow hydrothermal vents on adjacent marine environment. The TEs were determined in seawater, suspended particulate matter (SPM), sediments, and brown seaweeds. The dissolved elements Fe, Mn and Cu were analyzed by AAS after preconcentration with Chelex-100 resin, while dissolved Hg and As were analyzed according to standard EPA methods. The abundance of TEs elements in SPM, sediments and seaweeds were measured by ICP-MS and ICP-AES techniques.

The geothermal and hydrothermal fluids are distinguished by the highest concentration of the dissolved As (1.2-52.8 µg l-1), Fe (196-769 ng l-1), Mn (0.04-26.5 µg l-1) and mainly reactive dissolved Hg (18-171 ng l-1). The sediments of geothermal hot spring are enriched in As (111 mg kg-1), and Hg (25 mg kg-1). Similar trend was found in sediments of hydrothermal vents having high contents of As (207 mg kg-1) and Hg (143 mg kg-1). However, there is significant quick and drastic drop of TE concentration in the surrounding sea water with distance from the thermal apertures. Thus, dissolved mercury, occurring predominantly as the non-reactive (48 to 86 %), in the surrounding seawater samples dropped down to 11-34 ng l-1.The Fe is 99% in particulate form in the fluids and seawater, whereas As and Hg occur mainly dissolved in both water sample types (87-100% and near 100% correspondingly). The contents of both elements decreased rapidly in the sediments of the surrounding area. Sargassum sinicola brown seaweed specimens taken just over the hydrothermal site also presented elevated levels of As and Hg with maximum content of 640 mg kg-1 for As but further study is necessary to establish the primary-secondary relationship of those phenomena.

Platinum geochemistry in aquatics systems.

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POSTER

We were studied the influence of Amazon River over the dissolved platinum level and its interaction with the North Brazil Current into the Geotraces Program Background. There are not recent studies of the water column Pt distribution and the latest ones had opposite conclusions. One of the goals was to understand the platinum behavior in the Equatorial Atlantic Ocean. Geotraces Leg2 has been undertaken on board R/V Pelagia from the 11st June to the 8th July, 2011. Surface samples were collected at 21 stations and one station was sampled at different depths in the water column. We found that the Amazon River influences the platinum distribution in the stations close to the depth profile, mostly in the surface samples. We think that this fact should be due to a characteristic geochemical process in the North Brazilian Current during the summer. Therefore, our results show the platinum inputs from land to sea. The climatology hydrography information showed the influence of four water mass during this season: the North Atlantic Deep Water, Antarctic Bottom Water, Antarctic Intermediate Water and finally the South Atlantic Central Water.

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Spatial and seasonal differences in the geochemistry of suspended particulate matter of rivers and bottom nepheloid layers in the Cariaco Basin

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In order to better understand the connection between regional land and oceanographic processes and sediment transport from the shelf into the deeper Cariaco Basin (Venezuela), we obtained samples of suspended particular matter (SPM) from the four main rivers draining into the Basin (Manzanares, Neverí, Unare and Tuy) and from bottom nepheloid layers (BNL) on the shelf as part of the CARIACO Ocean Time-Series Program. SPM in the BNL were sampled during the peak of the rainy and upwelling periods (September 2008 and March 2009, respectively). River SPM was sampled only during March 2009 (low discharge). SPM was analyzed for particulate organic carbon (POC), major and minor trace metals. The Tuy River (largest in terms of discharge) had the highest SMP (97 ± 1.15 mg l-1), followed by the Unare River (second largest in terms of discharge; 38.3 ± 2.31 mg l-1). The Manzanares and Neverí rivers had the lowest SPM concentrations (7.18 ± 0.93 mg l-1; 5.25 ± 1.11 mg l-1, respectively). In general, BNL SPM concentration was higher ($p > 0.05$) during the rainy season (~1-7 mg l-1, as compared to 0.2-4.7 mg l-1 during March 2009), likely due to greater input of particles from rivers. %POC content of riverine SPM was relatively low (2-12%) compared to %POC measured within the BNL (2-30%). There was no significant difference in %POC content in BNL between seasons. Lithogenic element (Al, Ti, Fe and K) concentrations in the river SPM was directly related to SPM concentrations for each river, being highest in the Tuy (48.2 %Al; 2.6 %Ti; 28.0 %Fe; 8.2 %K) and lowest in the Neverí (2.1 %Al; 0.06 %Ti; 1.8 %Fe; 0.2%K). These rivers were also enriched in V, Cr, Cu, Zn and Pb, likely due to anthropogenic land-based processes, although some of these metals can originate in mafic-ultramafic formations which constitute part of the drainage basin of some of the rivers. Ca/Al and Sr/Al in BNL were highest during the upwelling season and attributed to enhance d biologic activity. BNL K/Al exhibited spatial variability in part due to differences in the lithology of source rocks and their degree of chemical weathering. There wasn't a significant seasonal or spatial difference in Ti/Al and Fe/Al ratios within BNL. This information is the first of its kind for the Cariaco Basin, and will provide a deeper understanding of sources and distribution of sediment in and around the Basin. Ultimately, these data may help better interpret the paleoceanographic record stored in the Basin's sediments.

Some IAEA-Environment Laboratories activities related to GEOTRACES and potential collaboration within the Latin-America GEOTRACES group

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The Environment Laboratories of the International Atomic Energy Agency has been over the years measuring and studying the behaviour of TEIs in the world's oceans. In the Latin-American region, during the last decade we have participated in a multidisciplinary oceanographic cruise in the SE Pacific measuring 234Th in the water column along a transect Talcahuano (Chile) - Easter Island - Tahiti. During this, we ascertained the striking differences in 234Th distribution in the water column of the several provinces sampled, associated to clear differences in the concentration of particles and carbon and their export from upper waters. During the first trimester 2013, we will be involved in a similar sampling programme off Peru on board of the German RV "Meteor", sampling 234Th and Ra isotopes along two transects perpendicular to the coast in an area with a marked minimum oxygen layer. Also, we participated in the GEOTRACES intercalibration studies of Thorium-234 in the water column and marine particles. Results and information on these actions will be presented.
Since one of the scopes of the workshop is to stimulate GEOTRACES activities in the region through facilitating integration and discussion, the synergy and momentum developed during the meeting could serve as a platform to prepare a concept proposal that could be fostered in the framework of the Technical Cooperation Programme of the IAEA. This could be a medium-term action having as scope to facilitate training and development of technical skills, which would catalyse activities in the field of TEIs studies.

Dissolved trace element concentrations and redox processes in the Orinoco River system, Venezuela

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Temporal and spatial analyses of pH, temperature, dissolved organic carbon (DOC), dissolved oxygen and dissolved Mn, Fe, Al, Zn and Ca concentrations were performed during fifteen months on the Orinoco, Apure and Caura river waters with the purpose to assess how the redox processes can affect the mobility of dissolved trace elements during transport. The reducing conditions promoted by microbial decay of submerged plants in the Apure River floodplain during the high discharge periods produce an enhancement in the binding capacity of Fe with DOC and the reduction of MnO2 content in the suspended material to dissolved Mn2+. Also, the high pH values of the Apure River promote the precipitation of Mn2+ to Mn(OH)2. The Zn solubility is controlled by the scavenging of Zn by Mn oxyhydroxides, whereas Al concentrations in the Apure River waters are correlated with DOC concentrations, suggesting the formation of Al-humate complexes. Owing to the Caura River showed high concentrations of dissolved oxygen during the whole hydrological cycle, there are no important temporal changes in the redox conditions in this blackwater river. This fact results in that Mn concentrations in the Caura waters were correlated only with pH, whereas the Al and Fe were correlated with DOC, suggesting that these elements are complexed by high molecular weight organic colloids. The relationship found between Al/Fe ratios and dissolved oxygen concentrations in the Orinoco River waters suggest an increase in the binding capacity of Fe with organic colloids when the concentrations of dissolved oxygen decrease. The Mn concentrations in the Orinoco River were inversely correlated with pH and dissolved oxygen. The enhancement of pH values in the Orinoco River after the Apure-Orinoco mixing zone decreases the Mn and Zn concentrations due to the precipitation of Mn(OH)2 and the scavenging of Zn by Mn oxyhydroxides, respectively. The comparison between waited and measured concentrations of Mn, Zn, Fe and Al in the dissolved phase demonstrates the non-conservative behavior of these elements after the Apure-Orinoco confluence. Overall, dissolved Fe concentrations in controlled by pH, redox processes and the DOC concentrations, dissolved Mn is a function of pH-dependent redox process, whereas Zn solubility is controlled by scavenging of Zn during the oxidation of Mn2+ to MnO2. Al is not dependent on redox processes because this element tends to form organometallic complexes with organic colloids.

Aquatic ecosystem responses to environmental events revealed by sediment tracers in the Southern Hemisphere

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Relevant ecological events both in space and magnitude have the power to be recorded in sediments. Most of the time radiogenic tracers are used to set a time frame to those events. Hundreds of studies around the world have used 210Pb as a geochronological tool in aquatic ecosystems. However little attention has been paid to the potential of this naturally occurring isotope as an environmental tracer of ecological events. Here we report instances in which 210Pb profiles measured on undisturbed sediment cores from lakes, rivers and fjords show us the potential of 210Pb profile as a tracer of natural and anthropogenic processes. The methodology used here is a suite of techniques combining biogeochemistry (micro-electrodes), paleomagnetism (susceptibility), Geotek parameters, sediment characteristics (LOI) and visualization (SPI and X-ray) applied to the interpretation of 210Pb profiles. We measured 210Pb profiles on sediments from a river, Cruces River (Chile), which recorded a clear shift in the water chemistry caused by a pulp mill effluent to the river. Here metal mobilization and remobilization of the tracer may be the cause of the observed profile. We also measured 210Pb profiles in sediment from two fjords of Southern Chile (Pillan and Reñihue), the sudden deposition change of fresh 210Pb with depth observed could very well be the result of bioturbation but it occurred in a seafloor area deprived of bioturbators. In this case, 210Pb recorded the onset of aqua- culture activities (fish farming) that took place two decades ago. Also 210Pb profiles measured in two lakes in the ‘‘pampa Argentina”: Epecuen and Venado showed a particular shape with depth. These profiles apparently registered a sudden depositional event with recent 210Pb material, probably related to strong shifts in precipitation and drought cycles in that part of the world. Finally we reported here the finding of mega earthquakes in the past 5000 years evidenced by a suite of geotechnical parameters on long cores collected in Patagonia in Southern Chile. These examples show that 210Pb profiles as well as other tracers can provide valuable information not only on geochronology, but also related to natural and anthropogenic short and long term processes, as shown here, but these are not always reported and well understood.

DISSOLVED INORGANIC NITROGEN (DIN) EXPORTS FROM 4 VENEZUELAN RIVERS: URBANIZATION AND AGRICULTURE IMPACT ON NITROGEN DELIVERY TO THE CARIACO BASIN AND COASTAL AREAS.

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The global nitrogen cycle has been altered dramatically over the past century by human influences such as burning of fossil fuels, agricultural practices, urbanization, forest fires and changes in land use leading to: (1) increasing the emission of gaseous nitrogen species (NH_3, N_2O and NO_x) relevant to climate change and atmospheric chemistry, (2) N losses by leaching and surface runoff with impacts on aquatic systems (3) changes in biological diversity and biotic interactions. Latin America (LA) has one of the highest world urbanization rates, but due to mostly unplanned urbanization, basic infrastructure services as sanitation are lacking, particularly in cities areas with economically deprived population. A direct effect of this urbanization development is the discharge of untreated sewage into water bodies. This causes both health problems and nutrients concentration (N and P) increases. Understanding changes in N loads for coastal ecosystems is crucial to determine changes in primary productivity, eutrophication, trace gases emissions and hypoxia scenarios in Latin American coasts in the future.

In this work we determined monthly concentrations dissolved inorganic nitrogen (DIN) from 4 Venezuelan watersheds during 3 years (August 2008 to September 2011). Three of these watersheds are mountainous rivers (Tuy, Neverí and Manzanares) and one is flat (Unare River) and they drain to the Cariaco Basin. The Tuy drains Caracas (> 4 million people), and is significantly impacted by untreated wastewater. The Neverí and Manzanares host small cities at their mouths (3-400,000 people). Wastewater from Cumaná, at the mouth of the Manzanares, is released offshore, reducing its impact on the river's nitrogen cycle. The Unare is a flat river draining an ecosystem dominated by agriculture and savanna. We found an order of magnitude larger DIN concentration values in the Tuy, which has the largest urban influence among the evaluated rivers. Most of the annual discharge for all rivers take place during the rainy season. Details about the implication of these results on nutrient delivery to the Cariaco Basin and the effect on coastal ecosystem will be addressed.

Assessment of Present-Day Levels of Heavy Metals in Marine Sediments from Santa Rosalía Copper Mining Region in Baja California Peninsula, Mexico

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Marine sediments from the coastal zone of Santa Rosalía are characterized by high contents of heavy metals due to ancient mining and smelting of copper ores. In order to find out the present-day levels of metals and specially due to the soon opening of the new mining and metallurgic company of “El Boleo”, 75 surficial sediment samples were collected in September 2011. The total contents of 50 elements in the sediments were measured by a combination of ICP-AES and ICP-MS instruments after concentrated strong acid digestion and heating at 250°C. “Mobile” metals in the sediments were determined after cold acid leaching.

The Principal Component Analysis with Varimax rotation was applied to the obtained dataset, which allowed distinguishing three associations of elements with high positive scores (> 0.5). The association I (Ag, Ba, Be, Bi, Cd, Co, Cu, Fe, In, Li, Mg, Mn, Mo, Ni, lanthanides, Pb, Sr, Tl, U, V, Y and Zn) presumably corresponds to the input of mineralized terrigenous material of ore deposits, naturally formed at first or modified during a smelting of ore minerals afterwards. The association II (Cs, Hf, K, Rb, Re, S, Se, Th and Corg) probably reflects the contribution of fine natural clayey material, enriched in organic matter. The association III (Al and Sc) is probably due to the supply of the terrigeneous aluminosilicates.

The enrichment factors (EFs) of Ag, Ba, Bi, Cd, Co, Cu, Mn, Ni, PB, Sb, U, V and Zn in sediments, calculated using Al as a normalizing crustal element, are higher than unity. With respect to the average EFs for the marine sediments with Cu content higher than the effect range-medium guideline value (ERM) of 270 mg kg-1, these enriched elements showed the following sequence: Cu (115) > Zn (29) > Co (27) > Mn (23) > Cd (12.6) > U (11) > Bi (10.9) > Pb (6.7) > Sb (5.0) > Ag (4.1) > Ba (4.0) > Ni (3.2) > V(2.6). All these elements are supplied to the marine sedimentary environment from sources related to the ore-forming mineralization in this mining district, or as the constituents of smelter slags.

The spatial distributions of total and acid leachable Cd, Co, Cu, Mn, Pb and Zn contents in the surface sediments delimit the principal “hot spots”, associated with the dumped smelting wastes. About 50% of the surface sediment samples exceeded the ERM guideline value of 270 mg kg-1 proposed for Cu, the principal pollutant of this specific environment.

Elements in Zooplankton of Northern Gulf of California in June 2008

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POSTER

The objective of this study was to determine the contents of elements in zooplankton from the Northern Gulf of California in June 2008, to characterize the associations of elements, as well as typical patterns of spatial distribution of concentrations of elements in zooplankton. The zooplankton samples were collected by Bongo nets (333 µm mesh, 60 cm mouth diameter) from near the bottom to the surface on shallow stations or from 200 m depth to the surface in the sites deeper than 200 m and immediately frozen until being processed in the laboratory. Defrozen samples were washed by deionised water, dried in the oven at 60°C and homogenized in an agate mortar. After total digestion of dried samples by a hot mixture of concentrated strong acids the concentrations of more than 50 major and trace elements were measured in final solutions using high resolution ICP-MS spectrometry. The obtained data set was processed with Principal Component Analysis (PCA) with Varimax rotation. The results of PCA allowed to distinguish several associations of elements of different origin (terrigenous, atmospheric, anthropogenic and marine biogenic). Typical spatial distributions of representative elements of each group were constructed and compared with spatial distributions of their contents of the surficial sediments of the Gulf of California. The terrigenous element Fe displayed accumulation in both zooplankton and the coastal sediments of the Baja California peninsula in front of Puertecitos, on the western coast of the Northern Gulf of California. Barium, being of marine biogenic origin, had its higher content in highly dynamic and very productive area between Angel de la Guarda and Tiburon islands. The lanthanides, being in the group of terrigenous elements, had different than North America Shale composite normalized pattern and displayed positive europium anomaly in most of the zooplankton samples.

MEASUREMENT OF LABILE CONCENTRATIONS OF COPPER AND ZINC BY DIFFUSIVE GRADIENTS IN THIN FILMS IN A MARINA AND PORT AREAS IN THE PATOS LAGOON, BRAZIL

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POSTER

Copper (Cu) and zinc (Zn) are the main inorganic elements in the composition of the new antifouling paints applied to vessel hulls. The aim of this study was to evaluate the labile Cu and Zn concentrations in estuarine waters, especially in marina and port areas in the southern area of the Patos Lagoon estuary (RS, Brazil), with the DGT technique. Seven locations in summer and winter (January and July/2010) were chosen to deploy the DGT devices in situ, immersed for 72 hours in each locations. The physical and chemical parameters (pH, salinity, temperature, dissolved organic carbon, particulate organic carbon and suspended particulate matter) in water were also quantified. Throughout the sampling period, weather conditions were under the El Niño influence (from July 2009 to January 2010) clearly observable because the constant low salinities (0 to 0.4). The labile Cu (0.45 ± 0.05 µgL-1) and Zn (9.96 ± 1.8 µg.L-1) concentrations were significantly higher ($p<0.05$) at one of the shipyards, that in the other locations. Differences in labile Cu and Zn concentrations found in the study areas are not only related to vessel activities but also to the hydrodynamics of each local and long periods of low salinity, a consequence of the El Niño effect. The results in the present study indicate similarities with the data of other marina in Australia densely occupied with leisure vessel.

Origin and fluxes of materials from an eutrophic system

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The Guanabara Bay in Rio de Janeiro, Brazil, is an outstanding example of anthropogenic impact in coastal systems due to various activities. In the present work the goals were to determine exchange fluxes of materials between the bay and the adjacent coastal waters and by using stable isotopes to characterize the process influencing the pool of carbon and nitrogen. For this we sampled water over 25 hours in winter and summer from three different depths at a single station strategically positioned in the bay. Measurements included CTD, nutrients, chlorophylls, DOC, POC, PON, carbon and nitrogen stable isotopes in particulate organic matter, among others. Ammonia is the most important species of dissolved nitrogen (8 – 46 μmol L^{-1}) and is significantly and inversely correlated with salinity in all depths. There is a marked and tidal independent trend to lower POC, PON, NH_4^+ in the bottom waters (28 m) as result of the high organic matter turnover rates in the surface waters. DOC is in general around 3 mg L^{-1} but very elevated values (up to 400 mg L^{-1}) were observed in certain periods. $\delta^{13}C$ and $\delta^{15}N$ varied in the range of 20.08-23.43 ‰ and 2.17-7.11‰, respectively. ^{13}C depleted organic matter was found principally in the bottom or in samples with lower Chl *a* concentration, while for ^{15}N the inverse was observed. For carbon this can be interpreted as resulting from degradation of algae material more than deriving from land inputs. The nitrogen isotopic signature seems to be strongly influenced by N derived from sewage in surface and mid depth waters since the ^{15}N depleted material is found associated with elevated OD and Chl *a*. C/N ratio varied from 5.3 to 7.3 and showed no correlation with N and C isotopes. The C/N range is typical for primary producers and in the lower range, of bacteria contribution (CAPES, FAPERJ).