



GEOTRACES
Mediterranean Planning Workshop
4-6 October 2010
Nice, France
Workshop Report

Written by the Workshop participants

Finalized on 09/06/2011

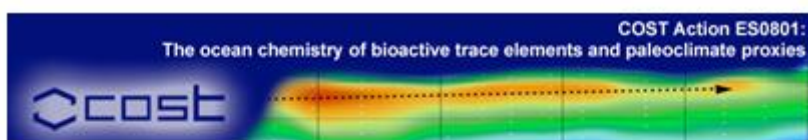


Table of contents

Introduction.....	2
Acknowledgements.....	3
Parallel Break-out Sessions A.....	4
I. TEI fluxes and processes at ocean interfaces	4
II. TEI as proxies for past change	8
Parallel Break-out Sessions B	10
III. TEI and particle cycles.....	10
IV. TEI and models.....	11
Parallel Break-out Sessions C.....	13
V. Mediterranean GEOTRACES section	13
VI. Western and Eastern Mediterranean process study/studies	15
Concluding discussions.....	16
Mediterranean GEOTRACES Sections	16
Mediterranean GEOTRACES Time-Series Sites	18
GEOTRACES Mediterranean activities map	20
Interaction with other programmes	21
GEOTRACES and the Black Sea	23
Mediterranean GEOTRACES Steering Committee.....	24
Appendices.....	25
Appendix I – Workshop participants	25
Appendix II – Extended abstracts	28

Introduction

Since the inception of the international GEOTRACES Program, a strong interest has been building in carrying out GEOTRACES-related activities in the Mediterranean Sea. This interest is well justified, due to the proximity and importance of the ocean-land-atmosphere domains, as well as the variety and intensity of exchanges between these domains.

During the Atlantic Basin Planning Workshop in September 2007, a breakout session was convened to briefly discuss bringing GEOTRACES to the Mediterranean and to sketch on a map (literally) a draft cross-basin GEOTRACES section. Informal discussions were launched and centered around coffee-break meetings during scientific conferences such as the January 2009 ASLO-TOS Aquatic Sciences Meeting in Nice, France, and aided by an unofficial web-site.

The materialization of a more formal discussion was made possible due to the inception of a GEOTRACES-inspired and COST-funded Action (ES 0801) titled “The ocean chemistry of bioactive trace elements and paleo-climate proxies.” It was during the third Management Committee Meeting of this Action (April 2009, Vigo, Spain) that the motivation and context of the implementation of GEOTRACES in the Mediterranean was definitively presented. At the next Management Committee meeting in December 2009, held in conjunction with the Action’s Data-Modeling Workshop in Paris, France, the Management Committee decided to allocate a generous fund for a Mediterranean Planning Workshop.

Navigating around a busy GEOTRACES year, the dates were set early in 2010 and planning began in earnest in March. Six months of preparation and planning later, and having met participation goals within budget, more than 50 participants (40 % of them early-career researchers and students) from 15 countries, met in Nice, France. For three days, they enjoyed the lovely Octobre-en-Provence weather, and discussed knowns and unknowns, cruise sections, process studies, methodologies, and logistics, while getting acquainted, creating friendships and forming a network worth the task ahead.

We hope that this Workshop report, as well as the upcoming implementation plan, reflects the success of the Workshop, as well as the much smaller distance now separating the international GEOTRACES programme and the Mediterranean.

The Organizing Committee,

Angelos Hannides
Laurent Coppola
Cécile Guieu
Catherine Jeandel
Pere Masqué

Acknowledgements

We would like to acknowledge the generous financial assistance of COST Action ES 0801, without which this Workshop would not have been possible. Funds from the Action paid a significant portion of the venue expenses as well as travel funding for three out of every five participants. The constant support of Gideon Henderson, Action coordinator, and Sara Tennakoon, his Personal Assistant, was invaluable.

We thank l'Observatoire Océanologique de Villefranche-sur-Mer for hosting the event and for generously providing supplementary funding for the venue, as well as for treating everyone to a wonderful ice-breaker cocktail party on the first night of the workshop.

Travel funding for participants from the U.S. was kindly provided by the U.S. National Science Foundation through the U.S. GEOTRACES programme. Special thanks go to Bob Anderson, not only for this sponsorship, but also for his constant support during the preparations.

The Scientific Committee on Oceanic Research, through a grant from the U.S. National Science Foundation, sponsored the much needed participation of colleagues from the South Mediterranean. Ed Urban's special assistance is particularly acknowledged.

We also thank the International Project Office (IPO) for its technical support in preparing and supporting the meeting material.

Finally, we would like to thank all the invited speakers and participants for their contributions and good will without which this workshop could not have been so productive and successful.

Parallel Break-out Sessions A

1. TEI fluxes and processes at ocean interfaces

Chair: Catherine Jeandel

Rapporteur: Pere Masqué

1) Characterization of surface active substances in the natural sea surface microlayers of the coastal Middle Adriatic stations, by S.Frka Milosavljević.

Frka Milosavljević briefly described the main characteristics of the SSM, highly enriched with organic matter, trace metals and organisms in the upper 30-300 μm of the ocean. The air-water interface favours adsorption of organic surface active substances (surfactants) where they form sea surface films. Organic compounds are the principal film forming components and they influence the presence of other constituents in this area. Thus, some trace metals can be highly enriched in the SSM due to complexing with particulate organic matter and surfactants. The chemical composition of natural organic films is largely unknown but they strongly impact different transport processes between the ocean and atmosphere. One of the key steps towards predicting a wide variety of exchange fluxes and processes across the air-sea boundary is to contribute to a better understanding of fundamental questions regarding chemical and physical characteristics of organic films at the sea surface. Sanya is using complex methodologies including electrochemical methods, monolayer studies (π -A isotherms), Brewster angle microscopy and fractal analysis. Future research plans foresee to look at the connections of the SSM with the aerosols in the atmosphere and the water column in terms of the distribution and cycling of organic and inorganic matter in the area of the central Adriatic. Two proposed localities at coastal middle Adriatic Sea are the Krka river estuary and eutrophicated saline Rogoznica Lake.

Landing asked about the sampling system and Frka Milosavljević showed a picture of the Garrett screen for organic samples, not suitable for trace metals. The glass plate method would be appropriate.

Guieu asked if there is previous work on aerosols and suggested that this will be a completely new kind of investigation in the east coast of the Adriatic Sea.

Murray commented on dust inputs, retaining and interaction with the SSM. Aluminium and titanium should both be measured when looking at metals, probably titanium a better tracer of terrestrial inputs.

2) Radium isotopes, seawater circulation and water ages in the Mediterranean coast of Northern Israel, by Y. Weinstein, Y. Shalem, Y. Yechieli, B. Burnett, P. Swarzenski, B. Herut

Weinstein presented results on ^{222}Rn and salinity showing the potential of Rn as a tracer of freshwater discharge, even at some distance (35 km) from the shore, indicative of discharge from deep aquifers at the continental slope. Radium would work better as a tracer of saline water discharge, with the added value of having 4 isotopes with different half-lives. This

allows (1) characterizing seawater circulation (e.g. deep/long vs. shallow/short), (2) investigating time-age of coastal water.

Together, Rn and Ra allow the investigation and quantification of the fluxes of nutrients and probably other TEIs to the sea by fresh groundwater and by recirculated water, while differentiating between the two sources.

Jeandel commented on the convenience to determine the resolution needed for the dynamical model to estimate water ages.

3) Early diagenesis and benthic fluxes in Adriatic and Ionian Sea, by F. Spagnoli, G. Batholini, P. Girdano

Spagnoli presented the study site and methods followed in this work which takes place in the Adriatic and Ionian seas. The various approaches used involve extracting pore water in a nitrogen atmosphere, measuring benthic fluxes by deployment of a benthic chamber or modelling of pore water profiles.

The Adriatic and the Ionian sea are characterised by different diagenetic environments, leading to different benthic fluxes. There is clearly a need to look at how organic matter mineralizes. Also, several elements/isotopes with potential relevance as proxies (such as $^{98/95}\text{Mo}$, ^{56}Fe , ^{74}Ge , ^{13}C , ^{15}N , ^{34}S) are affected by the early diagenesis and benthic fluxes .

There is planning underway to have a lander at 600 m depth operating by summer 2011, while there is already a benthic chamber available for work down to 100 m depth.

Open discussion

Questions:

- Importance of dust input versus solid river and margin sediment sources
- Impact of extreme events vs more continuous fluxes
- Submarine Groundwater Discharge (SGD) importance
- Dissolution processes: Bio-availability
- Dispersion within water masses (diffusion, circulation, time rates)
- Anthropogenic contaminants and impacts: What is the recent evolution of elemental distribution due to human activity?
- Identifying/differentiating aerosol to other inputs (river, margins): Potential TEIs to be studied: Ti, Sc, Nd, Th. Others?
- Hydrothermal activity – submarine volcanoes
- **Need for having 2 ships at a time for the Mediterranean section: Pelagia + Spanish ship? Italian ship?**
- Need for time series studies, including atmospheric inputs and moorings equipped with sediment traps. Logistics exist in the Western Mediterranean, but not yet in the Eastern Mediterranean(?).

Sampling should not be very close to mesoscale structures if we want to attain a snapshot of the “average” Mediterranean in terms of GEOTRACES. Discussion amongst the participants seems to suggest otherwise. There is a need for looking at both a snapshot picture and processes. There is also a discussion about the convenience of having two or more vessels at the same time/year in the Mediterranean to try to cover as many of the identified issues to be considered in Med-GEOTRACES. DeBaar stated that section cruises and process studies do not need to occur at the same time. He also pointed out the possibility of using the torpedo sampling system to obtain good water samples on small cruises not equipped with clean sampling systems.

Murray commented on the difficulty to choose a specific tracer in order to identify and differentiate river and aerosol inputs. Is there a strategy for temporal sampling on long term?

According to Guieu this is not simple. Also, there is a lot of scavenging, even of Al.

Landing states that Ti and/or Sc and a few others could be used as such a tracer. Data on sediment inputs by rivers should also be available. But we need to consider that not only large rivers are relevant in the Mediterranean, but also that indirect inputs from resuspension from the shelves/margins can be very significant

Jeandel suggested the possibility of using Nd. Scholten asked where in the Mediterranean are the rocks that would explain the radiogenic Nd signal. Jeandel answered that the Nile area is a likely possibility. The Nd signal is diverse depending of the source, even considering Saharan dust according to the origin area.

Scholten asked whether hydrothermal activity /submarine volcanoes should receive significant attention.

Guieu commented on the atmospheric measurements that will be carried out in Corsica within the frame of French programs that shall provide with a good plot of atmospheric fluxes. However, in the Eastern Mediterranean the on-going work is less intense and should be enhanced. Indeed, at several sampling sites in the Mediterranean (Corsica, Crete) there are continuous records of atmospheric fluxes that could be investigated to try to identify characteristic tracers of dust inputs. In some instances there could be accompanying information in the water column (i.e. sediment traps)

DeBaar pointed out the possibility of using the torpedo sampling system to obtain good water samples on small cruises not equipped with clean sampling systems.

Landing mentioned that daily high volume aerosol samples should also be collected, paired with dry deposition and automatic wet deposition samplers. Time-series sampling should be operative before the large sampling cruises. There is some consensus in that atmospheric sampling systems should also be placed onboard.

Several areas “near” the coast were mentioned in order to study the identified questions:

- The Nile “margin”: strong erosive processes in the Nile delta have been identified during the last few years: what is the fate of this material and associated TEIs? The Nile area is thought to also be a relevant site in terms of SGD
- Gulf of Lions – Ligurian Sea

- Adriatic Sea: transport of trace elements from the Adriatic to the Ionian Sea, anthropogenic contamination of TEs.
- Aegean Sea: importance of the outflow of water and impact in the Levantine

Hannides stated that there shall be further activities conducted by Cyprus in the Levantine basin to fill some of the gaps identified so far in the area.

Spagnoli proposed to measure benthic fluxes and to study early diagenesis of Fe, Mb, C, N and S isotopes in key areas and in hydrothermal vents.

II. TEI as proxies for past change

Chair and rapporteur: Marie-Alexandrine Sicre

Marine archives are used for reconstructing past ocean and climate changes as well environmental conditions beyond the instrumental period. Target variables/parameters for calibration are SSTs, IWTs, DWTs, salinity, ventilation, pH, productivity changes and anthropogenic inputs.

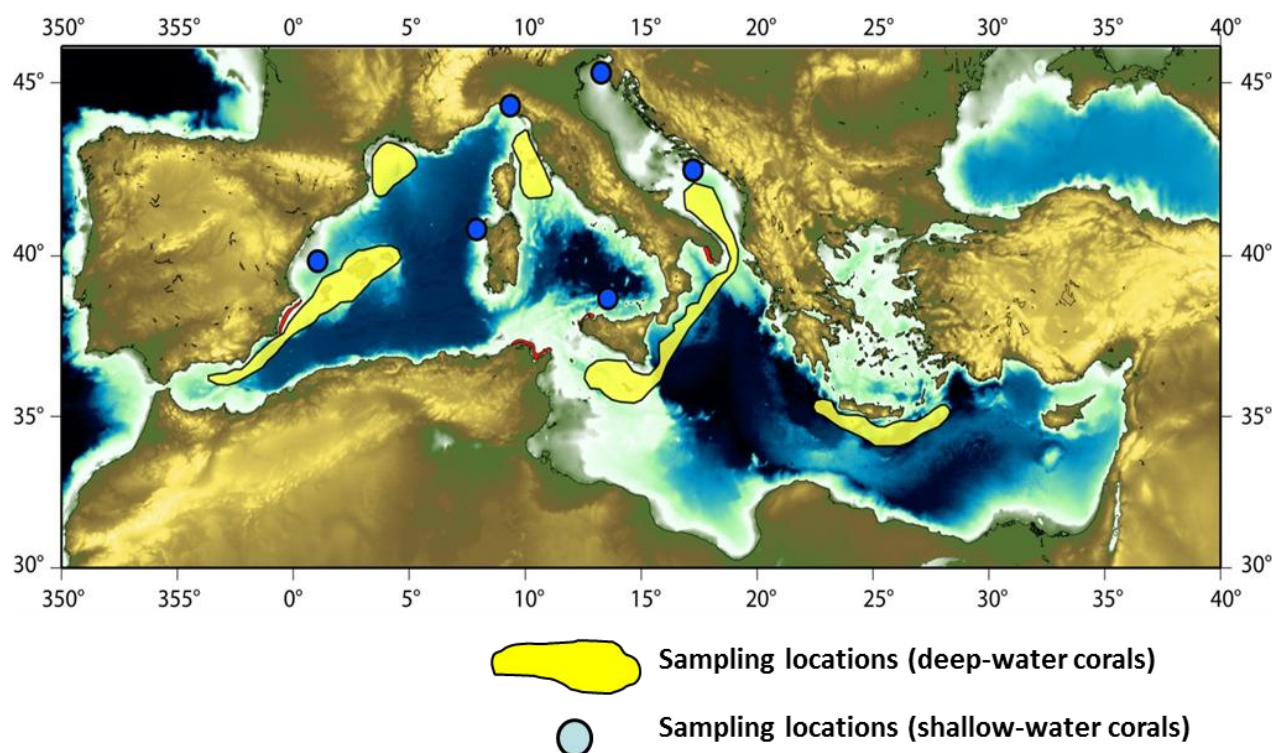
In paleoceanography, recent developments on corals living in shallow, intermediate and deep waters or bivalves, vermetids have shown a strong potential for documenting seasonal to decadal variability of temperature, pH, circulation, etc... over century to millennial time spans.

Apart from marine biogenic carbonates, there is a need to promote the study of high sediment rate marine sequences for reconstructing ocean variability at decadal time-scales (bays, contourites, coastal sediments, including lagoons...) using common used approaches in paleoceanography on foraminifera, biomarkers and sedimentary indicators.

Proxies to trace dynamical processes are Sr/Ca, O isotopes, Nd and ^{14}C , B isotopes, Cd isotopes, Sr/Ca on cocco for nutrient availability, ^{15}N , ^{30}Si nutrient uptake, Mo, traces metals for paleo-redox conditions. Anthropogenic proxies are also needed: Hg and Pb isotopes, water column and sediments.

In the GEOTRACES Mediterranean Sea context, a link can be established with the PALEOMEX action of MISTRALS.

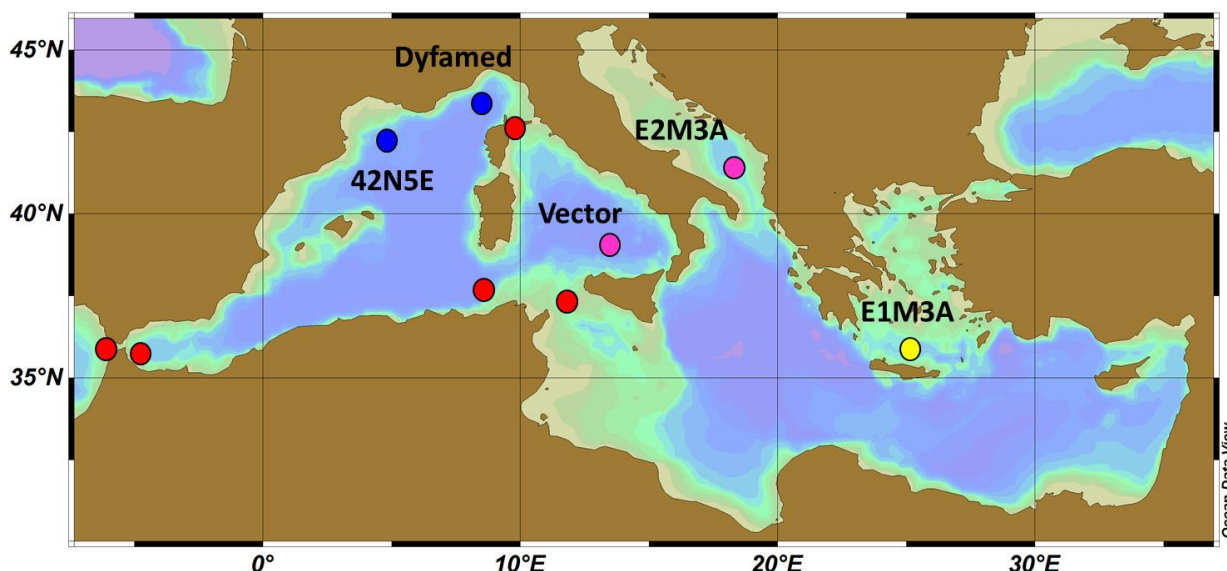
Map showing the on-going and future investigations in Mediterranean corals for paleoclimate reconstructions.



Tight links are now established with the Italian group of Bologna to participate to cruises aiming at collecting corals and sediment cores and develop a complementary approach on these two natural archives. Water samples will also be collected to perform calibration on relevant TEIs for time-series reconstructions. During our discussions, it has been emphasized that there is still a lack of census of coral and other marine biogenic carbonates in the Levantine basin.

Within the GEOTRACES Med Sea project, the proposed field strategy focuses on coral and modern sediments collection for calibration and independent validation on short time-series covering the last century for cross-comparison with instrumental observations. Complementary sampling for routine measurements of DIC, alkalinity, pH during hydrographic cruises and in sediment traps material (eg. MOOSE) should be a priority during cruises.

Map shows the present sites where time series is performed (mooring, traps). Temporal proxy calibration requires long time-series as well as opportunities for month or seasonal cruises.



Sampling for proxy calibration during the GEOTRACES Med Sea section may be on different legs or cruises or two ships because of cleaning constrains. A better synergy with the permanent station parameters should be also improved to conduct process study and evaluate proxy integrity.

Finally, there are links to modeling for improving calibration: Nd, Pa/Th, ^{14}C , He, river inputs.... For example: river inputs (damming, Suez channel opening for the Nile,...), paleo-dust measurements versus riverine inputs (Sr and Nd isotopes, Pb isotopes...).

Parallel Break-out Sessions B

III. TEI and particle cycles

*Chair: Laurent Coppola
Rapporteur: Stephanie Jacquet*

After a presentation by Cardinal on Si isotopes, we discussed particles issues in the ocean interior: transport and transformation processes (“internal cycling”) in the Mediterranean Sea. We were reminded of the particle processes as written in the GEOTRACES Science Plan: production vs. export (uptake and removal from surface waters), demineralization in subsurface and deeper waters, resuspension from cascading events and physical circulation (advection and convection). All these processes are relevant in the Mediterranean Sea and should be traced with appropriate isotopes (Th, Pa, etc.).

The discussion focused on tools useful to track the particles fluxes.

Sediment traps are necessary to estimate the export of the particles but the estimation of the trapping efficiency is crucial (as well as the particles’ composition). Some sites in the Mediterranean Sea are equipped with traps in the frame of time series (e.g., Dyfamed, 42N5E, E1M3A, Vector). For the GEOTRACES Mediterranean Sea, some specific sites might be equipped with new moored traps (?).

In situ pumps are also useful if we want to measure particle size of both settling and suspended particles (link with model). These pumps could be deployed in specific stations during the GEOTRACES Mediterranean Sea Section.

Finally, biological parameters are also crucial to determine the origin of the surface particles sinking to the deeper layers. This represents an interest to understand the uptake process vs. dissolution fluxes.

IV. TEI and models

Chair: Jean-Claude Dutay
Rapporteur: Miro Gacic

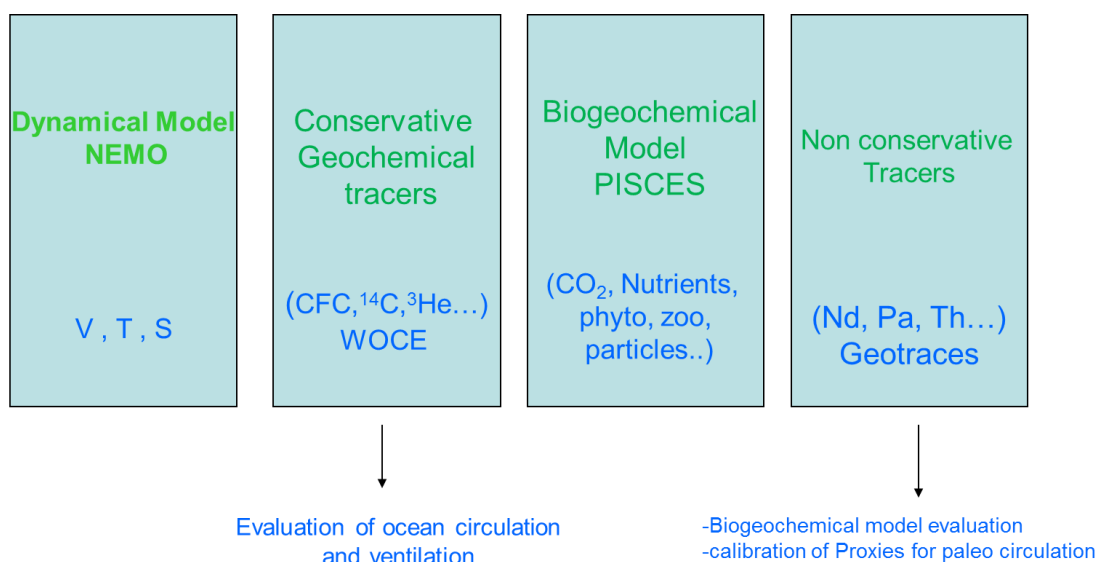
The session started with two presentations: one by Dutay (NEMO-MED12/PISCES model) and one by Petihakis (HCMR).

Existing models in the Mediterranean Sea:

A 1-D model flux-reservoir model of nutrient cycling (N and P) in the Eastern Mediterranean (M.D.Krom@leeds.ac.uk) which uses state-of-the-art nutrient measurements to model our new knowledge of how the Eastern Mediterranean Sea nutrient cycling functions. The model, which includes measured changes in inputs since 1950, predicts the changes in nutrient species and fluxes with time. It will be used to predict environmental and climate change on measurable nutrient species. It could be modified for other geochemical parameters.

OBGCM general circulation model coupled with biogeochemical model NEMO (Med12)/PISCES 8 km longitude, 6 km latitude CFCs, ^{14}C , ^3He , Nd, ^{231}Pa , ^{230}Th , Al, etc. (France). Some preliminary runs have been done in the Mediterranean.

POM 1D model coupled with the variant of the ERSEM (Greece) to understand, analyze and forecast the effects of atmospheric deposition through modeling work. Operational fully coupled physical – biogeochemical model for the Mediterranean, Eastern Levantine and Aegean Sea.



Existing physical and biogeochemical models for the Mediterranean Sea

In the implementation of GEOTRACES in the Mediterranean Sea, models should focus on:

- Incorporation of atmospheric deposition mechanisms in a model architecture (e.g. CHIMERE)
- Sensitivity runs to mechanisms and atmospheric inputs
- Scenarios on climate change
- Projections in the past
- Using 1-D model to test various parameter values for 3D models
- Provide a good in situ data for the model validation

Parallel Break-out Sessions C

V. Mediterranean GEOTRACES section

Chair: Pere Masqué

Rapporteur: Angelos Hannides

The session began with four short presentations.

Heimbürger presented a talk by Cossa et al. on the mercury cycle in the Mediterranean Sea. The talk advocated measurement of mercury isotopes and species during the transect cruises. The main challenge for sampling for these is the large volume needed (200 L), but this can be overcome using in-situ pumps. In the case of stable isotopes, deeper samples are needed, and – considering the time limitations during the cruises – two profiles would be conducted, one in the West Mediterranean and one in the East, perhaps on the *RV Pelagia* cruise. For the same time restrictions but also personnel requirements, sampling for mercury speciation will be conducted on the other transect cruises, with two scientists on board collecting and processing 1-L samples per depth of a deep profile along each transect.

Zeri and Kaberi reviewed current knowledge on TEI in the Aegean Sea and discussed questions relevant to GEOTRACES goals as those would be addressed in the region. Specifically, the questions they raised involve TEI mass –balance and cycling in view of deep-water enrichment in the North Aegean Sea, the role of particles in uptake and regeneration of TEI's in that region, and the extent of the effects of deep water formation there on the distribution of TEI's in the Cretan Sea and subsequently the Levantine. Based on their discussion, they recommended two short longitudinal sections at the western and eastern Cretan Straits, consisting of two stations each, as well as at two process study stations: E1M3A in the Cretan Sea and MNB1 in the North Aegean Sea.

Spagnoli discussed further the presentation by Spagnoli et al. given the previous day during Breakout Session I. Although it was deemed more appropriate for a process study, it was noted by the participants that perhaps the locations of the section stations in the Adriatic can be guided by sites where important SWI fluxes such as those discussed by Spagnoli et al. occur.

Hannides discussed the current level of biogeochemical oceanography operations in the Levantine Mediterranean by Cyprus institutions. He noted the usefulness of seaglider missions conducted by the Oceanography Center of the University of Cyprus in deciphering the intense and complex cyclonic activity usually evident in the region operation. Such information can help interpret section data in case such mesoscale features are crossed, and to direct in a more targeted fashion the investigation of their role in TEI cycling in case future GEOTRACES cruises in the Levantine are conducted.

The discussion that followed used the *RV Pelagia* section plans as a spring-board. De Baar clarified that his proposal focuses on contamination-prone TEI (e.g., Mn, Fe, Co, Ni, Cu, Zn, Ag, Cd, Pt, Pb and some others, at a total of 20). Only 20 scientists can be hosted on board, but at least 40 stations or 1 per day can be sampled and perhaps en-route surface sampling, assuming a focus on contamination-prone TEI. This would mean that super-stations (based on the needs for export calculation data, 10 of these may be needed), which involve many more hydrocasts, in-situ pumping, etc., must be conducted by the other vessel(s).

After discussion of various additional transects and excursions that the main GEOTRACES section should cover, the participants agreed that this section should focus on the deep Mediterranean stations to briefly cover adjacent basins. Based on the potential time and personnel availability, coverage of the Black Sea by the *RV Pelagia* does not seem feasible, and the same applies for the Aegean Sea.

Following the discussion regarding the second vessel to work in tandem with the *RV Pelagia*, the most likely option that emerged involved the joint MedSEA-GEOTRACES cruise operation in the West Mediterranean (the MedSEA project was presented by Ziveri et al. during the keynote talks on Day 1). Current planning for the MedSEA cruise in the region involves following a similar route as that proposed for the *RV Pelagia*, but after going through the Straits of Sicily to turn back, either between Sicily and Sardinia or between Sardinia and Corsica.

Coverage of the East Mediterranean by a second vessel in tandem with the *RV Pelagia*, was also discussed and, although not as much certainty exists as in the case of the West, a number of possibilities were mentioned: (a) an Italian vessel is very likely to be available; (b) the MedSEA project has a strong Greek participation, so the possibility of synergy between the two programmes is also a possibility; (c) the successor of the SESAME project is very likely to include a deep-basin cruise.

Another potential synergy that was mentioned involved the upcoming GO-SHIP cruise in 2011 (presented by Toste during the keynote talks on Day 1), during which certain TEI of interest to both programmes may be measured, including ^3H .

The often-discussed-in-GEOTRACES-workshops topic of simultaneous water-column and sedimentary sampling re-emerged in this break-out session. It was noted by the participants that, while it is very unlikely that this will happen in any GEOTRACES section (due to the logistical difficulty of switching between benthic sampling and ultra-clean water sampling systems), the Mediterranean is the case where it would be the most likely location that this could take place.

The initiative to collect microplankton samples during GEOTRACES cruises, dubbed BioGEOTRACES, was also put to the table. Although it is logistically possible for the science crew that would be on the *RV Pelagia* to accommodate sampling and storing for such analysis in the vessel's deep-freeze, it may be more feasible for the other ship to conduct this type of sampling.

VI. Western and Eastern Mediterranean process study/studies

Chair: Cécile Guieu

Rapporteur: Thibaut Wagener

The session began with 4 short presentations:

- Trace elements in different marine sediment fractions of the Gulf of Tunis: central Mediterranean Sea (Zaaboub)
- Distribution of redox-sensitive trace elements in the water column and sediments of seawater lake (Ciglenecki).
- Long term fluctuation of organic matter in the Northern Adriatic Sea: possible indicator of global changes (Vojdovic)
- Particulate aggregation during the DUNE mesocosm experiment (Bressac)

The beginning of the discussion was focused on the specificities of the Mediterranean Sea and in particular its short residence time of waters (30yrs). Consequently, the Mediterranean Sea has the same order of magnitude than anthropogenic changes.

The prerequisite to define a process studies area is to have the distribution of TEIs along the Mediterranean cruise track in particular on the potential TEIs inputs from shallow shelves (Tunisia, Sicilian strait, Gulf of Lions, etc.).

During the cruise(s), the process studies concerning the particle cycle can be done through leaching experiments both on collected aerosols and suspended particulate matter. On the Mediterranean Geotraces section, P should be considered as a key Trace Element (in particular speciation between organic and inorganic P). This parameter must be measured on board using clean protocols. Finally, it was decided that there will have no microcosm studies on board, but rather a comparison between mesocosm study between the Eastern and Western Mediterranean regions.

Some additional process studies have been also discussed. We should focus on SGD and inputs from pore waters in key areas. A short survey (high resolution) from coast to open waters following the TEIs gradient (6 – 7 surveys) has been suggested. Rogoznica lake (Croatia) has been mentioned has a good candidate for Redox process study in oxic/anoxic waters.

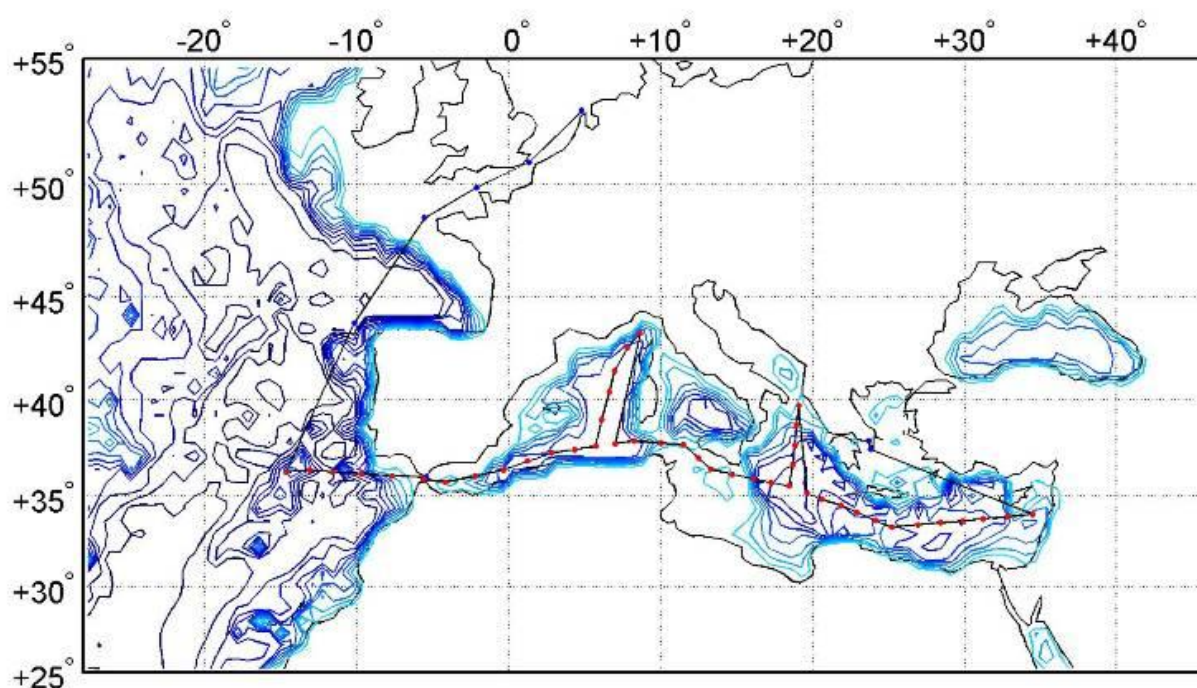
The use of tracers to track the Levantine intermediate water (LIW) formation and its transport in the Eastern Mediterranean has been evoked as an important process where TEIs should bring relevant information

Finally, the mesocosms experiments which are relevant for GEOTRACES in the Mediterranean Sea should be: aggregation processes, biota vs. TEI distribution and the microlayer process.

Concluding discussions

Mediterranean GEOTRACES Sections

The discussion focused on two main topics: the ideal Mediterranean GEOTRACES section, and the vessel or vessels necessary to cover it. A single specific proposal, which was presented by de Baar and Rijkenberg at various points throughout the workshop, was to carry out a trace metal-clean transect through the Mediterranean in the year 2013 aboard the RV Pelagia (a proposed cruise track is shown below).



In order to carry out the trace metal-clean sampling programme with adequate spatial coverage and the necessary GEOTRACES-compliant quality control safeguards in place, the RV Pelagia would have to forgo sampling for other crucial parameters. On that note, the discussion centered on the potential of carrying out a two-vessel cruise, where the RV Pelagia would carry the trace metal-clean sampling and the second vessel would sample for the remaining parameters. Several important points were made on this alternative plan:

- Cruise timing: Considering the lack of any other cruise proposals during the workshop, the likelihood that a second vessel would be available at the same time as the RV Pelagia is particularly low. In the case that sampling cannot be done simultaneously, it should be done as close as possible in time (at least the same year), and preferably during the best months for such a cruise: June or September. Many participants expressed strong reservations about the tandem use of data collected from two separate vessels at different time points, even if they are collected during the same year.
- Parameters measured on board on the different ships would have to be divided but some core parameters have to be done on all cruises (e.g., O₂, nutrients, hydrography, etc.).

- Intercalibration is of paramount importance. It is important for all participants in the GEOTRACES Mediterranean effort to perform the necessary intercalibration exercises in the framework of future cruises to receive the GEOTRACES-compliant label. Such intercalibration exercises should be done before the cruises. The fact that multiple groups may be working on the same parameters should be considered an advantage, since it lends more confidence in the results as it creates a peer-review quality-control system.

Regarding options for a second vessel, no offers emerged during discussion for a cross-Mediterranean cruise. Instead, a proposal that gained ground was that two vessels be used:

- 1) One Spanish vessel for a western Mediterranean transect (Ziveri). This was proposed because of the scheduled cruises in the framework of the MedSEA project.
- 2) One vessel for an eastern Mediterranean transect, which could be Greek (Ziveri) or Italian.

It was also clarified that transects covering the Adriatic and the Black Seas would probably require additional cruises.

The following table, drafted during discussion, identifies the parameters to be sampled (and methodologies to be used) by each ship, in case such a plan is carried out:

RV Pelagia	Second vessel
<p>Standard parameters:</p> <ul style="list-style-type: none"> - T, S, O₂, fluorescence - Nutrients (NO₃⁻ + NO₂⁻, PO₄³⁻, Si) - DOC - Hydrography <p>TEIs:</p> <ul style="list-style-type: none"> - Fe (total dissolvable, dissolved, colloidal, organic complexes) - Al, Mn, Ag (dissolved) - Pt - Co (total dissolvable, dissolved, organic complexes) - Zn, Cu, Cd, Hg (speciation) <p>Stable isotopes: Fe, Zn, Pb, Cd, Hg, Si, N</p> <p>CO₂ system: DIC-Alk, pH</p> <p>Additional sampling:</p> <ul style="list-style-type: none"> - CFC (?) - ¹⁴C/¹³C (?) - ³He 	<p>Standard parameters:</p> <ul style="list-style-type: none"> - T, S, O₂, fluorescence - Nutrients (NO₃⁻ + NO₂⁻, PO₄³⁻, Si) - DOC - Hydrography <p>TEIs: Ra, Th-Pa, Nd, Cs, B, P</p> <p>Isotopes: Pu and Np isotopes, any other stable isotopes, ²³⁴Th, ²¹⁰Pb-²¹⁰Po</p> <p>Additional sampling:</p> <ul style="list-style-type: none"> - In-situ pumping - Sediment? - Microplankton? - Aerosols, rain?

Mediterranean GEOTRACES Time-Series Sites

In the Mediterranean Sea, some sites record regularly oceanic and atmospheric core parameters in order to establish long time series dedicated to scientific research and observatories issues (climate change). Some of them have been created since JGOFS in 1988 (e.g. DYFAMED). The time series sites are mostly composed of a fixed platform (high frequency and continuous measurements) and regular vessel visits (CTD profiles, bottle collection, etc.).

Currently in the Mediterranean Sea, several networks of permanent and deep moorings operate through existing networks: M3A, HYDROCHANGES (CIESM) and recently the European projects ESONET and EuroSITES (2008-2011). Such mooring networks should be sustained in the future by different on-going projects like EMSO-ESFRI (deep sea observatories) as well as PERSEUS (WP3 and the integrated observatories systems).

These moorings are located in strategic areas dedicated to physical circulation, dense water cascading and particulate export. For that, all moorings present in such networks are equipped with physical sensors (CTD, currents) as well as biogeochemical sensors for some of them (O_2 , NO_3^- , Chlorophyll a, pCO_2 , pH) to collect a continuous record of hydrological and biogeochemical parameters.

Few of these moorings are equipped with sediment traps, which are the most relevant tool for GEOTRACES (particles, paleo proxies). Some of them exist since a long time and represent long time series of particle fluxes with a great interest for climate change and paleo studies, and they are described in the table below.

Site	Sediment traps (depths)	Collection frequency	Time series duration
Dyfamed (43°25N, 7°52E)	PPS5 200 and 1000 m	15 days	1988-present
42N5E (42°N, 5°E)	PPS3 1000 m	15 days	09/07- 04/09
Planier Canyon	PPS3 500 and 1000 m	1 month	1993-present
Lacaze-Duthiers Canyon	PPS3 500 and 1000 m	1 month	1993-present
E2-M3A (35°47N, 24°55E)	200 m	15 days	1994-present

In addition to the oceanic time series, the following atmospheric time series have been established through various programs (names of persons responsible are also shown):

- Cap-Ferrat, Nice (semaphore; C.Migon)
- Ile Rousse Corsica (semaphore, 42°39'N, 08°56'E, alt. ~25 m; Marie-Do Loye)
- Ostriconi Corsica (42°39'50"N, 9°04'24" E, alt 60 m)
- Galeria Corsica (42°26.5'N, 08°39.5'E, alt. ~160 m; K.Desboeuf)
- Frioul Corsica (semaphore; P.Raimbault)
- Cap Bear, Perpignan (43°31' N, 3° 09' E, alt. 170m)
- Can Llompart, Majorca (39°50'N, 03°01'E, alt. ~80 m; X. Querol)
- Finokalia, Crete (35°19'N, 25°40'E, alt. 250 m; N. Mihalopoulos).

Mediterranean GEOTRACES Process Studies

The following process studies were identified as important for GEOTRACES in the Mediterranean Sea:

1) Atmospheric deposition and particle cycling: use of the time series in specific sites

The time series of atmospheric deposition and sediment traps has to start one year before the section cruise. There is the potential for strong interaction with the CHARMEX community (contact person: Guieu).

2) Submarine Groundwater Discharge (SGD) and porewater inputs

A Mediterranean community studying SGD already exists and was well represented at the workshop. The importance of doing radon measurements during the 2011 GO ship cruise in order to have a first estimate of their significance was underlined. The budget of other TEIs must also be assessed (contact person: Garcia-Orellana).

3) Levantine Intermediate Water (LIW) formation and tracking

This may be part of the cruise section and not necessarily a specific process study. The ideal tracers for this process should be Ce and He isotopes. It is important to interact with existing work conducted by the physical oceanography community.

4) Importance of margins and sediment remobilization

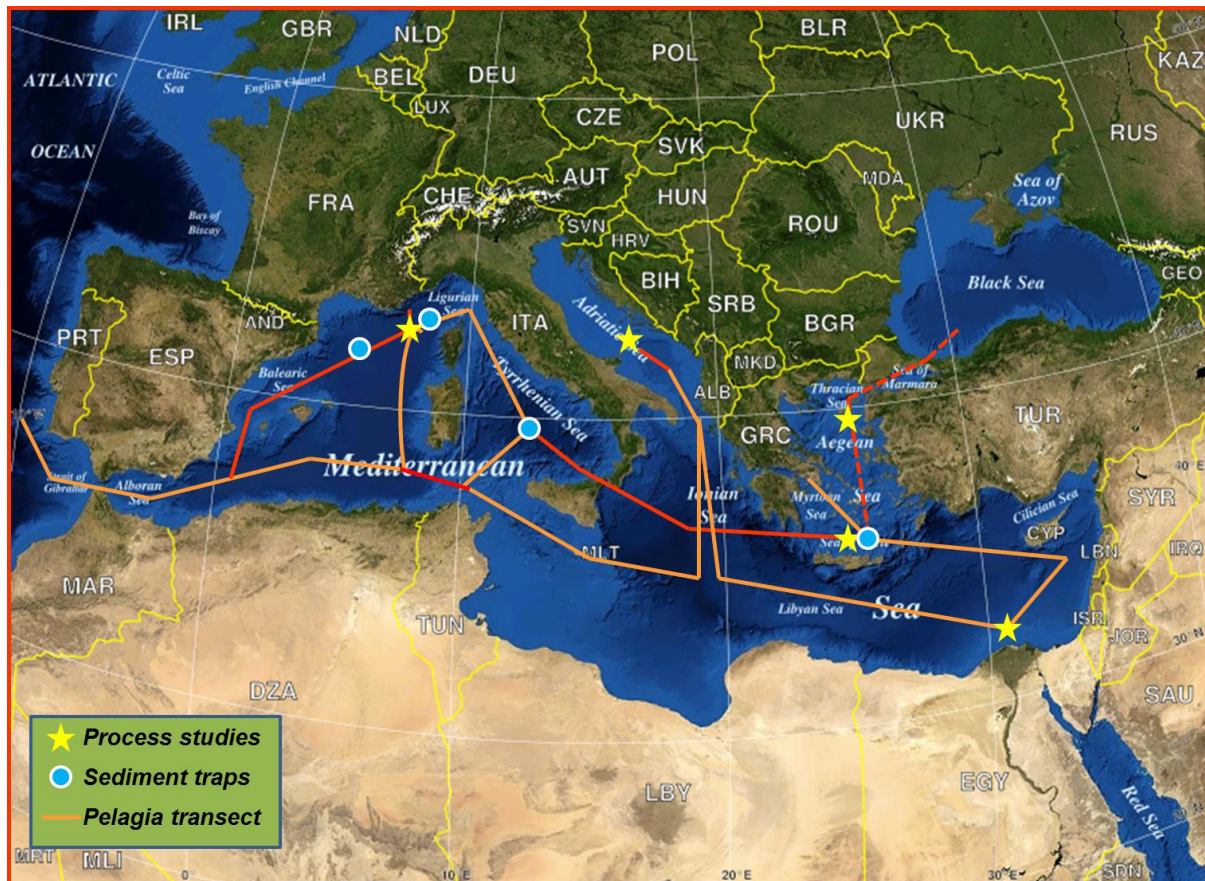
The data collected along the cruise section may help to assess the importance of the different continental margins (e.g., Gulf of Lions, Egypt, Adriatic Sea, etc.) on the supply of TEIs to the Mediterranean Sea (contact person for work in the Adriatic Sea: Spagnoli).

5) Mesocosms for comparative studies in the Western and Eastern Mediterranean

Mesocosms are a tool to study the impact of different processes on TEIs: dust deposition, interaction between biota and TEI cycling, etc. Experiments should be conducted in environments where the atmospheric and sediment traps time series are performed (contact person: Guieu).

GEOTRACES Mediterranean activities map

Based on the discussions described above, the map below illustrates the potential GEOTRACES Mediterranean section cruise, along with specific sites for process studies and sediment traps as oceanic time series stations.



Interaction with other programmes

MERMEX (PI C.Guieu, R. Sempéré, X. Durieu de Madron)

Marine Ecosystems Response in the Mediterranean Experiment (MerMex) <http://mERMEX.com.univ-mrs.fr/>. The objective of MERMEX is to study the response of Mediterranean marine ecosystems to climate change and anthropogenic pressure. These changes clearly influence the cycles of major biogenic elements, biodiversity, fisheries, invasive species and ultimately have socio-economic impacts. There is a need to develop a comprehensive and holistic approach to address particular questions at the proper spatial and temporal scales. The most relevant issues for the future of marine ecosystems in the Mediterranean and the proposed strategy have been detailed in a recent paper (*The MERMEX Group, Marine ecosystems' responses to climatic and anthropogenic forcings in the Mediterranean, Progress in Oceanography 2011 in press*). Several issues are very much linked with Geotraces (i.e. sources and sinks of chemical contaminants? dispersion/accumulation or dilution of carbon, nutrients, and pollutants from rivers? impact of Saharan dust? etc.). MERMEX questions require international, multidisciplinary, and large-scale research investigations at different temporal and spatial scales.

PALEOMEX (PI MA Sicre)

PaleoMex is an international coordinated effort that aims at documenting the Mediterranean climate over the Holocene along the following foci:

- Mediterranean hydrological cycle
- Ocean circulation variability
- Impact on paleoenvironments
- Impact on human societies.

PaleoMex is strongly multidisciplinary, and combines the expertise of climatologists, paleoceanographers, geochemists, archeologists, historians, etc.... It will promote a coordinated effort to document climate variability at highest possible temporal resolution from documentary and natural archives (proxy records) to extend records over centennial to millennial time-scales.

PaleoMex will put a strong emphasis on:

The past two millennia to investigate the links between climate and Mediterranean human societies and civilizations, their appearance, apogee and decline.

The Sapropel S1 (9000-7500 BP), a period of extreme alteration of the hydrological cycle of the Mediterranean.

MOOSE (PI P.Raimbault)

Mediterranean Ocean Observing System on Environment. This is a French project based on observatories in the NW Med Sea including fixed and lagrangian platforms and multidisciplinary parameters. The aim is to sustain long term time series and implement new biogeochemical parameters for observing impact of climate change and anthropogenic activities on the marine environment. This project is funded since 2009.

MEDSEA (PI: P Ziveri)

MedSeA is a medium-scale FP7 research project addressing ecologic and economic impacts from the combined influences of ocean acidification and anthropogenic warming. Increases of atmospheric CO₂ and associated decreases in seawater pH and carbonate ion concentration this century and beyond are likely to have wide impacts on marine ecosystems, including those of the Mediterranean Sea. MedSeA will forecast environmental changes and evaluate their socio-economical impacts driven by increases in CO₂ and other greenhouse gases, while focusing on the combined impacts of acidification and warming on marine shell building, productivity, and food webs. The project will involve an international partnership of 16 research groups. These experts will provide science-based projections of Mediterranean acidification under the influence of climate change as well as associated economic impacts. The scientific advances will enable the best advice to policymakers who must develop regional strategies for adaptation and mitigation.

BIOGEOTRACES

The participants strongly endorsed the facilitation of any BIOGEOTRACES-related activities during the GEOTRACES Mediterranean section cruise. It should be noted that as stated elsewhere in this report it is logistically possible for the crew on the *RV Pelagia* to accommodate sampling and storing for microplankton analysis in the vessel's deep-freeze.

PERSEUS (PI. V. Papathanassiou)

The overall scientific objectives of PERSEUS are to identify the interacting patterns of natural and human-derived pressures on the Mediterranean and Black Seas, assess their impact on marine ecosystems and, using the objectives and principles of the Marine Strategy Framework Directive as a vehicle, to design an effective and innovative research governance framework based on sound scientific knowledge. Well-coordinated scientific research and socio-economic analysis will be applied at a wide-ranging scale, from basin to coastal. The new knowledge will advance our understanding of the selection and application of the appropriate descriptors and indicators of the MSFD. New tools will be developed in order to evaluate the current environmental status, by way of combining monitoring and modelling capabilities and existing observational systems will be upgraded and extended. Moreover, PERSEUS will develop a concept of an innovative, small research vessel, aiming to serve as a scientific survey tool, in very shallow areas, where the currently available research vessels are inadequate.

In view of reaching Good Environmental Status (GES), a scenario-based framework of adaptive policies and management schemes will be developed. Scenarios of a suitable time frame and spatial scope will be used to explore interactions between projected anthropogenic and natural pressures. A feasible and realistic adaptation policy framework will be defined and ranked in relation to vulnerable marine sectors/groups/regions in order to design management schemes for marine governance. Finally, the project will promote the principles and objectives outlined in the "MSFD across the SES.

Leading research Institutes and SMEs from EU Member States. Associated States. Associated Candidate countries. non-EU Mediterranean and Black Sea countries, will join forces in a coordinated manner in order to address common environmental pressures, and ultimately, take action in the challenge of achieving GES.

GEOTRACES and the Black Sea

The participants received well the advocacy for GEOTRACES activities in the Black Sea. Notwithstanding the seemingly insurmountable logistical difficulties in accommodating such an effort in tandem with the GEOTRACES Mediterranean section cruise(s), the GEOTRACES Mediterranean effort should endeavor to support such an initiative in any which way it can should it arise in the future.

Mediterranean GEOTRACES Steering Committee

The participants decided to form a Mediterranean GEOTRACES Steering Committee that will oversee the drafting of an Implementation Plan for the Mediterranean, as well as all subsequent GEOTRACES activities in the Mediterranean Sea. The following individuals have consented to be members of the Steering Committee:

Section cruises liaisons	Micha Rijkenberg Patrizia Ziveri Helen Kaberi Pere Masqué
Time-series and process studies liaisons	Laurent Coppola Catherine Jeandel Nikos Mihalopoulos Jordi Garcia-Orellana Miro Gacic Marco Taviani Jean-Claude Dutay
Data management liaison	Catherine Schmechtig (from Dec 2011)
Intercalibration liaison	TBD
Links with SOLAS	Cécile Guieu
Liaison to GO-SHIP	Pino Civitarese
Liaison to MedSEA	Patrizia Ziveri

Appendices

Appendix I – GEOTRACES Mediterranean agenda

The GEOTRACES Atlantic Ocean Workshop - September 2007

During the Atlantic Ocean workshop in Oxford in September of 2007, a working group met to discuss potential GEOTRACES-related activities in the Mediterranean. Participants from seven countries met and discussed processes and features of interest in this marginal sea.

The ASLO Aquatic Sciences 2009 Meeting - January 2009

During the ASLO Aquatic Sciences 2009 Meeting in Nice, France, several interested individuals from five countries met informally and discussed GEOTRACES in the Mediterranean further. New individuals were informed of the international project, the developing effort for the Mediterranean, as well as of the relevant COST Action (ES0801), which had already been funded by the ESF.

The GEOTRACES Mediterranean Planning Workshop - October 2010

A special GEOTRACES Mediterranean Planning Workshop has taken place on 4-6 October 2010 in Nice, France. For more information, please see the workshop web-site and a summary for the motivation to carry out GEOTRACES activities in the Mediterranean.

Planned meeting: The GEOTRACES Mediterranean Implementation meeting – date not defined yet

A special meeting will take place in Toulouse (LEGOS) to plan the ship cruises in the Mediterranean Sea and others issues debated during the first meeting (intercalibration, processes studies, ...).

Appendix II – Workshop participants

[In alphabetical order by surname]

Wafa Abouchami	Max-Planck-Institut für Chemie	GERMANY	wafa.abouchami@mpic.de
Murat Ardelan	Norwegian University of Science and Technology	NORWAY	murato@nt.ntnu.no
Marie Boye	LEMAR, IUEM	FRANCE	marie.boyé@univ-brest.fr
Damien Cardinal	Université Pierre et Marie Curie	FRANCE	damien.cardinal@locean-ipsl.upmc.fr
Irena Ciglencečki-Jušić	Ruder Bošković Institute	CROATIA	irena@irb.hr
Guiseppe Civitarese	Istituto Nazionale di Oceanografia e di Geofisica Sperimentale	ITALY	gcivitarese@ogs.trieste.it
Christelle Claude	CEREGE	FRANCE	claudc@cerege.fr
Laurent Coppola	LOV, CNRS-UPMC	FRANCE	coppola@obs-vlfr.fr
Daniel Cossa	IFREMER	FRANCE	dcossa@ifremer.fr
Hein de Baar	Royal Netherlands Institute for Sea Research	NETHERLANDS	Hein.de.Baar@nioz.nl
Jean-Claude Dutay	LCSE, IPSL	FRANCE	jean-claude.dutay@lsce.ipsl.fr
Miro Gacic	Istituto Nazionale di Oceanografia e di Geofisica Sperimentale	ITALY	mgacic@ogs.trieste.it
Celine Gallon	University of California Santa Cruz	USA	gallon@metx.ucsc.edu
Jordi Garcia-Orellana	Universitat Autònoma de Barcelona	SPAIN	jordi.garcia@uab.cat
Cécile Guieu	LOV, CNRS-UPMC	FRANCE	guieu@obs-vlfr.fr
Angelos Hannides	University of Cyprus	CYPRUS	ahannide@ucy.ac.cy
Lars-Eric Heimbürger	LMTG, OMP	FRANCE	heimburger@lmtg.obs-mip.fr
Barak Herut	Israel Oceanographic and Limnological Research	ISRAEL	barak@ocean.org.il
Stef Jacquet	LOPB - UMR CNRS	FRANCE	stephanie.jacquet@univmed.fr
Catherine Jeandel	LEGOS	FRANCE	catherine.jeandel@legos.obs-mip.fr
Helen Kaberi	Hellenic Center for Marine Research	GREECE	ekaberi@ath.hcmr.gr
Azza Mohamed Mohamed Khaled	National Institute of Oceanography and Fisheries	EGYPT	azzakhaled_2004@yahoo.com
Michael Krom	Leeds University	UK	M.D.Krom@leeds.ac.uk
Bill Landing	Florida State University	USA	wlanding@fsu.edu
Karine Leblanc	LOPB - UMR CNRS	FRANCE	karine.leblanc@univmed.fr

Jacobo Martin	Marine Environment Laboratories, IAEA	MONACO	J.Martin@iaea.org
Pere Masqué	Universitat Autònoma de Barcelona	SPAIN	Pere.Masque@uab.cat
Christophe Migon	LOV, CNRS-UPMC	FRANCE	migon@obs-vlfr.fr
Sanja Frka	Ruder Bošković Institute	CROATIA	frka@irb.hr
Milosavljević			
Juan Carlos	Marine Environment Laboratories, IAEA	MONACO	j.c.miquel@iaea.org
Miquel			
Paolo Montagna	LSCE, CEA & Columbia University	FRANCE & USA	montagna@ldeo.columbia.edu
Jim Murray	University of Washington	USA	jmurray@ocean.washington.edu
George Petihakis	Hellenic Center for Marine Research	GREECE	pet@her.hcmr.gr
Elvira Pulido- Villena	LOV, CNRS-UPMC	FRANCE	pulido-villena@obs-vlfr.fr
Micha Rijkenberg	Royal Netherlands Institute for Sea Research	NETHERLANDS	Micha.Rijkenberg@nioz.nl
Matthieu Roy- Barman	LSCE, IPSL	FRANCE	mathieu.roy-barman@lsce.cnrs- gif.fr
Geraldine Sarthou	LEMAR, IUEM	FRANCE	Geraldine.Sarthou@univ- brest.fr
Jan Scholten	Marine Environment Laboratories, IAEA	MONACO	j.scholten@iaea.org
Marie-Alexandrine Sicre	LSCE, IPSL	FRANCE	Marie- Alexandrine.Sicre@lsce.ipsl.fr
Federico Spagnoli	Istituto di Scienze Marine	ITALY	f.spagnoli@ismar.cnr.it
Eleni Stathopoulou	University of Athens	GREECE	estath@chem.uoa.gr
Toste Tanhua	IFM-GEOMAR	GERMANY	ttanhua@ifm-geomar.de
Christina Theodosi	University of Crete	GREECE	c_theodosi@chemistry.uoc.gr
Marie Paule Torre	LOV, CNRS-UPMC	FRANCE	torre@obs-vlfr.fr
Thibaut Wagener	LOPB - UMR CNRS	FRANCE	thibaut.wagener@univmed.fr
Doug Wallace	IFM-GEOMAR	GERMANY	dwallace@ifm-geomar.de
Yishai Weinstein	Bar-Ilan University	ISRAEL	weinsty@mail.biu.ac.il
Nouredine Zaaboub	Institut National des Sciences et Technologies de la Mer	TUNISIA	nouri_zaaboub@yahoo.fr
Christina Zeri	Hellenic Center for Marine Research	GREECE	chris@ath.hcmr.gr
Patrizia Ziveri	Universitat Autònoma de Barcelona	SPAIN	Patrizia.Ziveri@uab.cat
Cheryl Zurbrick	University of California Santa Cruz	USA	Zurbrick@metx.ucsc.edu

Appendix III – Extended abstracts

The extended abstracts in the following pages are arranged alphabetically based on the last name of the lead author.

The workshop programme and many of the presentations are available on the GEOTRACES web-site at <http://www.geotraces.org/>.

Atmospheric and marine controls on the Non-Redfield N/P ratio in the Cretan Sea - a 1-D modeling study

S. Christodoulaki¹, K. Tsiaras², G. Petihakis², N. Mihalopoulos¹, M. Kanakidou¹, G. Triantafyllou²

¹ *ECPL, Dept. of Chemistry, Univ. of Crete, Heraklion, Greece*

² *Hellenic Center for Marine Biology, Heraklion, Greece*

Biological production in the sea water is affected by the levels of nutrients. Among the major nutrients for the marine ecosystems are nitrogen (N) and phosphorus (P) that present a roughly constant (Redfield) ratio N/P of 16 in most of the oceanic regions. However, the Mediterranean Sea shows a strong west to east gradient in these nutrients deficiency that result in a high N:P ratios and oligotrophic eastern Mediterranean basin. Atmospheric transport and deposition to surface is an important route for nutrients supply to the marine environment, especially in pelagic systems far from riverine influences, and may be the key source of ‘new’ nutrients supporting primary production. Especially for N, it has been realized that anthropogenic emissions to the atmosphere that have been strongly increased during the last century, led to greater atmospheric N deposition to the oceans providing a unique pool of N in excess of the canonical Redfield ratio N:P. In the present study, atmospheric deposition measurements of inorganic N and P over Crete island in the East Mediterranean are coupled with the sea water observations of nutrient availability and chlorophyll by the mean of a 1- dimensional ocean physical-biogeochemical model to evaluate the impact of the atmospheric deposition and its temporal variability on the marine primary production in the area. The marine ecosystem response to the atmospheric inputs of these nutrients and their role on the underlying biogeochemical and physical processes is investigated. The 1-dimensional ecosystem model taking into account the atmospheric inorganic N and P inputs and the physical mechanisms that may transport excess N from the ocean surface to the main thermocline, is tuned to simulate the sea water observations at the Cretan sea. The results are presented and thoroughly discussed.

**Distribution of redox-sensitive trace elements in the water column and sediments of
seawater lake (Rogoznica lake, Croatia)
a unique anoxic environment on the Adriatic coast**

Irena Ciglencečki*, Nevenka Mikac, Elvira Bura-Nakić

*Department of Marine and Environmental Research, Ruđer Bošković Institute, Bijenička 54,
10000, Zagreb, Croatia*

Rogoznica Lake or lake known under a name “Dragon Eye” is a typical example of anoxic saline lake. The lake is a small and shallow (10276 m², 15 m deep), naturally intensely eutrophicated and intermittently anoxic karstic seawater lake situated on the Eastern Adriatic coast close to Šibenik city (43°32'N, 15°58'E). A major physico-chemical characteristic of this lake is seasonal stratification with appearance of anoxic conditions below 10 m depth. During the thermohaline stratification (spring, summer) the surface water is well-oxygenated while anoxia is occurring in the bottom layer. Anoxic deep water is characterized by high concentrations of reduced sulfur species (up to 10⁻³ M, mainly in the form of sulfide); nutrients (NH₄⁺, up to 150 μM; PO₄³⁻, up to 22 μM; SiO₄⁴⁻, up to 400 μM) and DOC (up to 6 mg/l) as a result of the pronounced remineralization of allochthonous organic matter produced in the surface water.

Geochemical, mineralogical and sedimentological analyses have been made to view the difference between oxic and anoxic conditions in water column and sediment of the Lake. Due to relatively high accumulation rate of organic matter, and delicate exchange of water, the lake has almost permanent anoxic conditions below the depth of 12 m, and can be characterized as anoxic-sulphidic i.e. euxinic sedimentation environment. Changes in redox condition of the water column as well as sediments with depth affect the distribution and speciation of major redox-sensitive metals (Fe, Mn, Mo, V), reduced sulphur species (RSS) and dissolved organic C (DOC). In anoxic conditions enrichment of trace metals especially of those which accumulate in sulfidic environment (Fe, Mo) is observed. Regarding the sedimentary enrichment of Mo (up to 81 mg/kg) the Rogoznica lake can be characterized as a typical anoxic environment similar to well known anoxic systems like the Black Sea, Framvaren Fjord and Lake Pavin.

The existing observatories platforms useful for GEOTRACES in the Mediterranean Sea

L. Coppola¹, P. Raimbault², R. Lampitt³, K. Larkin³, V. Cardin⁴, G. Petihakis⁵

¹ *Laboratoire d'Océanographie de Villefranche-sur-Mer (LOV), CNRS-INSU-Université Paris 6, La Darse-BP 08-06238, Villefranche-sur-Mer Cedex, France*

² *Laboratoire d'Océanographie et de Biogéochimie (UMR 6535 CNRS), Centre d'Océanologie de Marseille, Université de la Méditerranée, Campus de Luminy, 13288 Marseille cedex 09, France*

³ *National Oceanography Centre, Southampton, United Kingdom*

⁴ *OGS, Trieste, Italy*

⁵ *Hellenic Center for Marine Biology, Heraklion, Greece*

In the context of GEOTRACES in the Mediterranean Sea, marine observatories offer the opportunity to benefit to long term time series of core parameters essential for the marine chemistry research. Such observation sites exist since several years in the Mediterranean Sea in key areas where processes, having a large impact of particles distributions, are observed (convection cell, atmospheric and river inputs, ...). Nowadays, fixed and lagrangian platforms are integrated in larger observation networks (e.g. MOOSE, Eurosites, Poseidon, ...) in order to measure simultaneously physical, chemical and biological parameters and to cover different spatial and temporal scales (minutes to decade and km to 100km). All dataset are available on public databases (Coriolis, SISMER, NOCS,...) in near real-time and delayed mode. Some specific sites (e.g. Dyfamed) benefit to old time series where measurements of TEI have been conducted, providing a reference for the next Geotraces Mediterranean section.

Revisiting the Mercury Cycle in the Mediterranean Waters coupling Speciation and Stable Isotopic Composition Approaches

D. Cossa¹, L.-E. Heimbürger², J. E. Sonke², C. Lamborg³ and N. Pirrone⁴

¹ *IFREMER, F-83507 La Seyne-sur-Mer, France*

² *LMTG-OMP, F-31400 Toulouse, France*

³ *WHOI, Woods Hole, MA 02543, USA*

⁴ *CNR-IIA, I-87036 Rende, Italy*

Mercury (Hg) is a globally distributed, redox active and highly toxic element because of the stability of naturally occurring bioaccumulating methylated species. The Mediterranean Sea is especially affected by Hg deposition, high recycling between atmosphere and sea-surface, and high methylation rates, which favours Hg hyperbiomagnification in marine food webs. Recent analytical developments in ultra-trace performances allow to perform high resolution vertical profiles of major Hg species speciation (HgT, HgR, DGM, Hg⁰, MMHg, DMHg). Moreover, recent discovery of both mass-dependent (MDF) and mass-independent fractionation (MIF) provide new insights into the Hg biogeochemical cycle. In addition, the MIF provides information about specific chemical pathways, such as photoreduction. However, no data has yet been reported for Hg isotope geochemistry in natural marine waters. We propose to revisit the Hg cycle in the major Mediterranean basins using these ultra-trace and stable isotope techniques.

GEOTRACES Deep Section from Mediterranean Outflow in East Atlantic across the Mediterranean Onboard RV PELAGIA in 2013 or 2014

H. de Baar, M. Rijkenberg, L. Gerringa, K. Timmermans, V. Schoemann, P. Laan, J. de Jong

Royal Netherlands Institute for Sea Research (NIOZ), Texel, Netherlands

The RV PELAGIA is provisionally scheduled to do a dedicated GEOTRACES deep section in 2013 or 2014 in the Mediterranean Sea.

This may comprise two Legs; firstly when approaching from the Atlantic there will be about five days dedicated for charting the Mediterranean outflow west of Gibraltar. After a bunker stop in Cadiz or Gibraltar there will be a second Leg of 26 days comprising an envisioned West to East section, the exact positioning of the section to be decided based on the information in the workshop.

Using the TITAN frame with 24 novel PRISTINE samplers of 27L each we aim for focusing on the contamination-prone trace elements and their isotopes Mn, Fe, Co, Ni, Cu, Zn, Ag, Cd, Pt, Pb and some others. At the workshop we seek an option for complementary cruise(s) by ships of other nations focusing on the elements and isotopes not requiring ultraclean sampling, that is the U-Th-decay series isotopes (^{234}Th , ^{230}Th , ^{231}Pa) and others.

Characterization of surface active substances in the natural sea surface microlayers of the coastal Middle Adriatic stations

S. Frka

Ruđer Bošković Institute, Bijenička 54, HR-10000 Zagreb, Croatia

Boundary layers between different environmental compartments represent critical interfaces for biological, chemical and physical processes. The sea surface microlayer (SSM) as the top 300 μm of the sea surface forms the boundary layer interface between the atmosphere and ocean. It plays a key role in the global biogeochemical cycling because all gaseous, liquid and particulate materials must pass through this interface when exchanging between the ocean and the atmosphere. The SSM represents a sink and a source for different compounds, as well as a very important driver enhancing air–water exchange processes. The chemical composition of natural films is largely undefined, although significant enrichment of many specific classes of compounds in the SSM has been demonstrated, particularly those that are surface active (SAS). The presence of organic compounds in the SSM facilitates enrichments in particles, organisms and dissolved material. Thus, some trace metals can be highly enriched by complexing with particulate organic matter (POM) and surface active organic material in the SSM, having values of enrichment factors similar to those of POM. The environmental significance of complex organic films is widely accepted, although there are still many gaps in our understanding of the morphology and chemical composition affecting the mechanisms of different exchange processes. Thus, one of the key steps towards predicting and modelling a wide variety of exchange fluxes across the air-sea boundary is to give contribution to better understanding the fundamental questions regarding source, formation, morphology, structural changes and build-up mechanisms of organic matter of the sea surface microlayer. Sea surface microlayer samples were collected in different seasons during a longer time period from the coastal area of the Middle Adriatic Sea including the locations of the seawater Rogoznica Lake and the semi-closed Krka River estuarine station. Complex methodology enables a new approach to the physicochemical characterization of natural surface microlayer.

Phase sensitive alternating current voltammetry was used for determination of the content of SAS in the natural SSM samples. Additional characterization of sea surface microlayers was carried out using electrochemical probe as an indicator of the permeability of different films adsorbed at the mercury electrode¹. Monolayer studies, particularly measurements of surface pressure-area (π -A) isotherms, have been applied for investigations of physical states of different microlayers. Furthermore, instead of analysing the chemical composition, it is possible to scale the SSMs π -A isotherms in terms of structural parameters (molecular weight masses, miscibility, elasticity) which appears to be a sensitive and quantitative measure of the film physicochemical composition of its film-forming components². Alongside, Brewster angle microscopy (BAM) was used for characterization and optical visualization of microlayers at the air-water interface without perturbing their structure and/or morphology. Application of fractal analysis to BAM images provides additional complementary means for characterization of materials, structures and dynamical processes at the interface giving information on (second order) phase transitions, interactions and aggregation mechanisms at the interface and structural changes under applied pressure³.

References

- ¹ S. Frka, Z. Kozarac and B. Čosović, *Est. Coast. Shelf Sci.* **85** 2009 555-564.
- ² Z. A. Mazurek, J. S. Pogorzelski and K. Boniewicz-Szmyt, *J. Mar. Sys.* **74** 2008 S52-S64.
- ³ Z. Kozarac, D. Risovic, S. Frka and D. Möbius, *Mar. Chem.* **96** 2005 99-113.

Biogeochemical changes following the damming of the Nile, is the South Levantine shelf still under changing conditions?

B. Herut¹ and A. Almogi-Labin²

¹ *Israel Oceanographic and Limnological Research, Haifa, Israel*

² *Geological Survey of Israel, Jerusalem, Israel*

During the last century a series of dams were built along the Nile (the first in 1902) and since the operation of the Aswan High Dam (AHD, 1965) almost all the discharge to the southeastern (SE) Mediterranean stopped, reducing drastically the input of freshwater, fine sediments and nutrients. In addition, the opening of the Suez Canal (1870) initiated a major transfer of Red Sea of relatively more saline and nutrient-poor seawater and of Indo-Pacific-origin organisms. During this period the southeastern Levantine Basin was exposed to the most dramatic change of such inputs in comparison to other Mediterranean sub-basins. The consequence of this drastic anthropogenic interference is evident by historic records of changes in the coastal seawater salinity and change in the sedimentary regime of the inner Israeli shelf. A series of short sediment cores taken along the Israeli coast, in the distal part of the Nile littoral cell, show sand content of >60% in post-AHD sediments compared to <10% in the pre-AHD sediments, due to the drastic decrease in fines, which completely changed the properties of the substrate and consequently might affect the benthic living ecosystem. In addition, a decrease in organic carbon and its stable isotope composition probably reflects the drop in nutrient input and hence phytoplankton intensity, consequently increasing hyper-oligotrophy of the South Levant. How such a shift, from mesotrophic towards oligotrophic conditions impacted the phytoplankton composition, nitrogen fixation rates and the nutrient dynamics needs to be assessed and may highlight the consequences of potential future shifts towards mesotrophy, attributed to anthropogenic sources.

It seems that the sedimentary regime in the distal part of the Nile littoral cell is still undergoing major changes and did not reach stabilization. What are the ecological consequences of such a change remains to be studied.

Sampling and analysis for atmospheric deposition: results from the US GEOTRACES Intercalibration Experiments

W. Landing, A. Milne, and P. Morton

Department of Oceanography, Florida State University, Tallahassee, Florida, USA

The GEOTRACES atmosphere 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 forty 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).

We have 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 is equipped with a 5-stage Sierra-style slotted impactor to collect size-fractionated aerosols for similar chemical measurements.

Formation of basin-wide bottom nepheloid layers in the western Mediterranean after major dense shelf water cascading events

J. Martin¹, P. Puig², X. Durrieu de Madron³, K. Schröder⁴, J. Salat⁵, J. L. López-Jurado⁶, G. P. Gasparini⁴, A. Palanques², M. Emelianov⁵, A. P. Karageorgis⁷, A. Theocharis⁷

¹ *Marine Environment Laboratories, IAEA, Monaco*

² *Departament de Geologia Marina, Institut de Ciències del Mar, Barcelona, Spain*

³ *CEFREM, University of Perpignan, Perpignan Cedex, France*

⁴ *ISMAR, CNR, Pozzuolo di Lerici, La Spezia, Italy*

⁵ *Departament de Oceanografia Física, Institut de Ciències del Mar, Barcelona, Spain*

⁶ *Instituto Español de Oceanografía, Centro Oceanográfico de Baleares, Palma de Mallorca, Spain*

⁷ *Institute of Oceanography, Hellenic Centre for Marine Research (HCMR), Anavyssos, Greece*

The analysis of a compilation of deep CTD cast conducted in the western Mediterranean from 1998 to 2010 have documented the role that dense shelf water cascading off the Gulf of Lions plays in transporting suspended particulate matter from the coastal regions down to the basin. Deep CTD casts revealed that after the 1999 and 2005-2006 major cascading events the Western Mediterranean Deep Water (WMDW) was characterized by the presence of a thick bottom nepheloid layer that scaled in thickness with a thermo-haline anomaly generated by the mixture of dense waters formed by deep convection at open sea and by cascading. This nepheloid layer can be hundred-meters thick, last for several years and cover the entire western Mediterranean basin. The aim of this talk is to highlight the fact that the WMDW can be periodically modified by the arrival of suspended particles generated by resuspension processes during major cascading events, being a key process that could significantly affect the trace-element cycles in the western Mediterranean.

Neodymium isotopes in biogenic carbonates from the Mediterranean Sea: reliable archives of water mass circulation

P. Montagna^{1,2}, S. Goldstein², M. Taviani³, N. Frank¹

¹ LSCE-IPSL, CEA, Gif-sur-Yvette cedex, France

² Lamont-Doherty Earth Observatory, Columbia University, Palisades, New York, USA

³ ISMAR, CNR, Bologna, Italy

Neodymium isotopes are increasingly employed to trace provenance and water mass mixing in the past, not being fractionated by biological processes in the water column and having a residence time in the order of 500-1000 years. In the modern ocean the different water masses ultimately derive their $^{143}\text{Nd}/^{144}\text{Nd}$ value through continental weathering, erosion and particle-seawater interactions. This geochemical tracer has been successfully applied to the dispersed authigenic ferromanganese oxide fraction in marine sediments, ferromanganese crusts, foraminiferal shells, fossil fish teeth and only very recently to scleractinian deep-water coral skeletons sourced from various sites and depths in the Atlantic ocean (van de Flierdt et al., 2006; Robinson and van de Flierdt, 2009; Colin et al., in press; Copard et al., in press).

These aragonitic corals have the great advantage of being precisely dated by U-series, potentially providing century-long records of intermediate and bathyal zone variability at sub-decadal resolution. Motivated by these recent findings we have investigated the Nd isotopic compositions of living specimens of deep-water corals and other calcifying organisms collected in two key locations of the Mediterranean Sea. In particular, several specimens of the deep-water coral *Desmophyllum dianthus*, *Lophelia pertusa*, *Madrepora oculata*, the temperate coral *Cladocora caespitosa*, the bivalves *Glans aculeata* and *Karnekipia brunei*, and the polychaete *Serpula vermicularis* were retrieved from the Strait of Sicily and the Southern Adriatic Sea at different water depths. Ten seawater samples from three new profiles were also collected at the same locations and depths, offering a unique opportunity to compare the Nd isotopic composition of biogenic carbonates directly with the surrounding ambient seawater. The Mediterranean Sea is particularly suited for this comparison exercise since it is characterized by water masses displaying a large δNd isotopic range, from -10.5 in the Western Mediterranean to -4.8 in the Eastern Mediterranean.

Nd isotopes in the modern biogenic carbonates analyzed thus far from the Mediterranean Sea match the surrounding seawater. Unless diagenesis has a major later impact, we expect that these calcifying organisms can serve as reliable archives for past water mass circulation.

References

- Colin C., Frank N., Copard K., Douville E. *Quaternary Science Reviews*, in press.
Copard K., Colin C., Douville E., Freiwald A., Gudmundsson G., De Mol B., Frank N. *Quaternary Science Reviews*, in press.
van de Flierdt T., Robinson L.F., Adkins J.F., Hemming S.R., Goldstein S.L. (2006) *Paleoceanography*, **21**, doi:10.1029/2006PA001294.
Robinson L.F., van de Flierdt T. (2009) *Geology*, **37**, 195-198.

Tracers for Redox Environments: GEOTRACES in the Black Sea

J. W. Murray

School of Oceanography, University of Washington, Seattle, Washington, USA

The Black Sea contains well documented oxic, suboxic and anoxic (sulfidic) zones. It is often mentioned as an analog for modern and ancient redox environments. A thorough study of the concentrations and speciation of the suite of elements and isotopes included in GEOTRACES would provide essential data for evaluating tracers for these environments. This study should include elements susceptible to redox change (e.g., Mn, Fe, Co, Cu, As, I, V, Cr, U, Pb) and sulfide formation (e.g., Fe, Ni, Co, Mo, Ag, Cu, and Cd plus Pb and Po isotopes). The study should include proposed tracers for terrestrial detrital material (e.g., Al, Ti and Nd and Th isotopes) and biological production (e.g., Cu, Ba, ^{13}C , ^{15}N and others). With the GEOTRACES community mobilized to study the Mediterranean the Black Sea study would best be done as a separate leg.

This study would address the GEOTRACES Themes as followed:

1. Fluxes and processes at ocean interfaces

oxic/suboxic/anoxic (sulfidic) interface

2. Internal Cycling

redox sensitive cycling +

euphotic zone versus chemosynthetic biology

3. Development of proxies for past change

tracers for redox environments

Particle cycling/circulation/margin interactions in the distribution of particle-reactive tracers

M. Roy-Barman

LSCE-IPSL, CEA, Gif-sur-Yvette cedex, France

One of the challenges of GEOTRACES is to improve our understanding of the behaviour particle-reactive tracers such as thorium, neodymium, iron, lead... Among the processes controlling these elements, their preferential removal of these elements at the ocean margin (boundary scavenging) has been recognized since several decades and studied though ^{210}Pb in the Gulf of Lion for example. More recently, it was shown that balancing the budget of Th and Nd isotopes in the Mediterranean Sea requires a significant dissolution of the lithogenic material stored on the Mediterranean margins. These observations (with many other) contributed to the emergence of the boundary exchange concept.

Water-particle interactions at the basin margins could strongly compete with the water-particle interactions in the local water column. However, we do not have a clear and quantitative view of the processes driving boundary exchange and boundary scavenging, that would allow a prognostic modelling of the tracers in the Mediterranean Sea. These uncertainties have also direct impact on our ability to constrain key parameters of the carbon cycle such as the biological pump. For example, it is the case for the determination of the sediment trap efficiency at the DYFAMED station that can be potentially complicated by convection and boundary scavenging. Resolving these issues implies to have a good physical and geochemical insight on many transient processes that occurs primarily at the margins such as sediment resuspension, nepheloid layer formation and spreading, winter convection. This will strongly impact the sampling strategy during GEOTRACES-Med sea.

Submarine Groundwater Discharge: Contributions to GEOTRACES

J. Scholten¹, J. Garcia-Orellana² and P. Masqué²

¹ *Marine Environment Laboratories, IAEA, Monaco*

² *Grup de Física de les Radiacions, Facultat de Ciències, Universitat Autònoma de Barcelona, Bellaterra, Spain*

Understanding the marine biogeochemical cycling of trace elements and isotopes (TEIs) requires the source of TEIs to be well determined. One of the less constrained sources of TEIs is submarine groundwater discharge (SGD). SGD is defined as any subsurface flow of water across the seabed to the coastal zone and the inner shelf shoreline. SGD may be of terrestrial (freshwater), marine (recirculated seawater), or composite origin. Because seepage of groundwater through sediments will occur anywhere an aquifer with a positive head is hydraulically connected to a surface water body, almost all coastal zones are subject to such flow. Certain types of geologic settings are especially conducive to SGD, e.g. karst, volcanic terrains, and areas with highly permeable sediments. Estimates of the volume of SGD vary considerably between 5-10% of global freshwater runoff to the ocean and up to 160 % of the river flux if the total (freshwater plus recirculated seawater) SGD flux is considered. Based on a water balance model the freshwater SGD flux to the Mediterranean Sea was calculated to be as much as 24% of the river flux. This comparably high freshwater flux is caused by high mountainous relief at most of the Mediterranean coasts, relatively high precipitation and, most importantly, a widely developed karst which allow for a focused flow of freshwater towards the sea.

Compared to surface waters SGD often carries relatively high dissolved matter content, thus even a small SGD flux may have considerable effects on the coastal environment. For instance, high dissolved N:P ratios in coastal groundwater relative to surface waters could drive the coastal ocean towards P-limitation. Some data show that SGD may be a major pathway for micronutrients such as iron to the coastal ocean and is important for the oceanic budget of trace elements like e. g. molybdenum, mercury, neodymium, and strontium.

This presentation will summarize our current understanding of SGD and possible contributions to a GEOTRACES programme in the Mediterranean Sea.

Early diagenesis and benthic fluxes in Adriatic and Ionian seas

F. Spagnoli ¹, G. Bartholini ¹, and P. Giordano ²

¹ *Istituto Scienze Marine, CNR, Ancona, Italy*

² *Istituto Scienze Marine, CNR, Bologna, Italy*

Various research projects studied early diagenesis processes and benthic fluxes in Adriatic and Ionian seas from eighties: IGM-CNR Bologna projects, MAST, EUROMARGE, PRISMA1 and VECTOR. In these projects early diagenesis have been investigated by pore water analyses while benthic fluxes were determined by direct measurements (benthic chamber deployments and on deck incubations) or pore water modelization. From the integration of these researches different diagenetic environments have been distinguished; they resulted from different particulate and dissolved continental inputs, different distances from main sediment sources (mainly the Po River), different bottom sediment composition (carbonatic or silicoclastic), different organic matter (fresh marine and old continental organic matter), different depths (more or less resuspension events, increasing pressure with depth), different oxygenation of water column.

As regard the Northern and Central Adriatic Sea it is possible to discriminate: 1) the area on the North of the Po River, characterized by carbonate sediments, low upward or downward phosphate fluxes, due to authigenic apatite precipitation, low ammonia fluxes and downward DIC fluxes for low reactive organic matter inputs and carbonate precipitation. In this area, sediments in front of main rivers are higher in organic matter content producing slowly higher fluxes of phosphate and DIC by oxic and suboxic organic matter degradation; 2) the proximal area in front of the Po River, characterized by high ammonia, phosphate and DIC fluxes for the high organic matter and silicate inputs. In this area, when bottom waters reach anoxic conditions, also Fe, Mn and phosphate fluxes increase for dissolution of Fe and Mn oxy-hydroxide surface layer; 3) the distal costal area South of the Po River, where lower fresh organic matter and silicate inputs originate weaker early diagenesis processes and nutrient benthic fluxes; 4) the Mid-Adriatic Depression area, characterized by oxic conditions in uppermost centimetres consequent to very low inputs of fresh organic matter and low sediment accumulation rates; this produces low upward fluxes of all nutrients with the exception of nitrate flowing into the sediment.

As regard the Southern Adriatic and the Ionian basins some regional differences can be highlighted: the Southern Adriatic basins, more distant from main sediment sources and at greater depths of the northern areas, are characterized by oxic and suboxic-non sulphidic organic matter degradation. The most intensive degradation processes occur in the Otranto Channel sediments. In the Ionian basin the sediment remineralisation processes takes place mainly by means of oxic reactions. This means that inputs of reactive organic matter are lower for the lower productivity of the basin, for the greater water column depth and for the higher distance from river inputs.

Calculated benthic fluxes reflect the early diagenesis processes, they show a northern-southern and shallow-deep trend characterized by lowering of remineralisation processes, this generate weaker oxygen fluxes into the sediments and DIC fluxes outside the sediments. Furthermore, in very low accumulation rate or erosion areas DIC fluxes are towards the sediment. Ammonium and nitrate fluxes are complicated by the nitrification/denitrification processes occurring in the oxic zone. Trace element stable isotopes ($\delta^{98/95}\text{Mo}$, $\delta^{74}\text{Ge}$, $\delta^{56}\text{Fe}$) and also other stable element isotopes ($\delta^{13}\text{C}$, $\delta^{15}\text{N}$, $\delta^{34}\text{S}$) related to early diagenesis and associated fractionation studies are completely lacking in the Mediterranean so investigation in this field could be very interesting.

Interaction between GEOTRACES and GO-SHIP in the Mediterranean Sea: report on a GO-SHIP Med-section in 2011

T. Tanhua

Leibniz Institute of Marine Sciences (IFM-GEOMAR), Kiel, Germany

Despite numerous technological advances over the last several decades, ship-based hydrography remains the only method for obtaining high-quality, high spatial and vertical resolution measurements of a suite of physical, chemical, and biological parameters over the full water column. Ship-based hydrography is essential for documenting ocean changes throughout the water column, especially for the deep ocean below 2 km. The Global Ocean Ship-based Hydrographic Investigations Program (GO-SHIP) brings together scientists with interests in physical oceanography, the carbon cycle, marine biogeochemistry and ecosystems, and other users and collectors of ocean interior data to develop a sustained global network of hydrographic sections as part of the Global Ocean / Climate Observing System.

The last few decades has seen dramatic changes in the circulation of the Mediterranean Sea. This is manifested amongst others as a shift of deep water formation from the Adriatic to the Aegean Seas. Furthermore, the characteristics of the Mediterranean Sea are such that it has the potential to sequester large amounts of anthropogenic CO_2 , C_{ant} , (i.e. high alkalinity and temperature and an active overturning circulation). In fact, the column inventories of C_{ant} are higher in the Mediterranean than anywhere else in the world ocean, and the C_{ant} storage in the Mediterranean is a significant portion of the anthropogenic emissions of CO_2 . However, few carbon data exist in the Mediterranean Sea, and very little is known about how the recent changes in circulation has affected the storage rate of C_{ant} .

Here I will report on anthropogenic carbon content in the Mediterranean, and I will discuss the cruise track of a hydrography section through the Mediterranean that is scheduled for April 2011 on the German research vessel Meteor. It is my hope that this will lead to interaction between GEOTRACES and GO-SHIP activities in the Mediterranean and elsewhere. Since no WOCE or CLIVAR sections have been made through the Mediterranean Sea, the section through the Med is not a "core section" in the GO-SHIP program. However, the large inventory of anthropogenic carbon as well as the observed dramatic changes in circulation motivates the inclusion of the Mediterranean section in the GO-SHIP program.

The significance of atmospheric inputs of dissolved and particulate trace metals to the Eastern Mediterranean seawater

Z. Markaki and N. Mihalopoulos

Department of Chemistry, University of Crete, Heraklion, Greece

Atmospheric deposition is a potential source of trace metals of continental origin to oceanic areas. Trace metals speciation (Fe, Al, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Cd and Pb) was studied in atmospheric deposition (wet and dry) collected at Finokalia (35°20'N, 25°40'E), a remote coastal site in the Northeast part of Crete, in the Eastern Mediterranean over a two year period (January 2005–December 2006). Sediment traps were moored for seven years in the Southern Cretan Sea (along 45°06'E, 500m and 1715m depth) and samples were collected from 1999 until 2005, on a two-week basis. An acid microwave digestion procedure followed by Inductively Coupled Plasma Mass Spectrometry was applied to measure metal concentrations in sediment trap and deposition samples.

Partitioning of atmospheric deposition between soluble and insoluble fractions demonstrated that Fe, V, Cr and Pb are mainly in the particulate form. For Cd, Zn, Mn and Cu, the dissolved fraction represents 60-68% of the total atmospheric input. Mean solubility for all metals is decreasing with increasing pH values and increasing dust mass. Cr, Mn and Cu are removed from the Eastern Mediterranean atmosphere by dry deposition, while Zn and Fe almost equally by wet and dry deposition whereas the rest of the studied metals via wet deposition.

In sediment traps, a significant correlation was observed between mass fluxes at 600m and 1715m indicating a quite good homogeneity in our system. Total mass flux presents two maxima: The first during spring, while the second one during autumn. Both are due to the increase in productivity and deposition of atmospheric dust. Similar seasonal trend was observed for Fe and Pb, elements characteristic of crustal and anthropogenic sources respectively, indicating similarity in transport mechanism independent of the trace metals origin. Dust is the main component of the sediment material as it accounts for about 40-44% of the mass. In addition a coherence between marine and atmospheric dust fluxes was observed. Annual deposition of atmospheric dust and dust in sediment traps are equal, in terms of fluxes, suggesting that atmospheric dust can be transferred in full down to 600 and 1715m.

Regarding the trace metals, our results suggested that atmospheric deposition is sufficient to balance their levels in the water column, indicating the predominant role of atmospheric deposition as external source of these elements in the area. Indeed DSRFe levels deposited were sufficient to account for the dissolved iron levels in seawater, therefore dissolved iron in the Mediterranean Sea could be exclusively attributed to atmospheric deposition. Cr, Mn, Fe, Zn, and Pb atmospheric deposition supplies 57- 84% of the amount collected in sediment traps. Total atmospheric depositions of Cu, Ni and Cd are equal to the fluxes from sediment trap deployment.

Long-term fluctuation of organic matter in the Northern Adriatic Sea: possible indicator of global changes

V. Vojvodić, B. Ćosović, and J. Dautović

*Department of Marine and Environmental Research, Ruđer Bošković Institute, Bijenička 54,
10000, Zagreb, Croatia*

Dissolved organic carbon (DOC) in the ocean is one of the Earth's largest reservoirs of organic matter which provide a substrate for life, and it is a source for nutrient regeneration, ion exchange capacity, and light and heat absorption and so on. Increased precision of measurements enabled detection of deep-sea concentration gradients and basin-scale differences, opening the use of DOC as a new geochemical tracer. Marine organic carbon represents a dynamic component in the global carbon cycle and is recognized now as an important component of the biochemical system and possibly an indicator of global change.

The shallow northern Adriatic Sea is characterized by marked seasonal and long-term fluctuations of oceanographic and biological conditions, mainly due to atmospheric forcing, Po River eutrophic freshwater discharges from the western coast, advection of oligotrophic central Adriatic seawater along the eastern coast, and a very variable and complex circulation pattern.

In the last fifteen years in the northern Adriatic the formation of massive organic aggregates reported as "mucilage phenomenon" occurred with increased frequency (1,2). The intensity of this phenomenon varied over the years: (1988, 1991, and 1997, 2000-2004) > 1998, 1999. In the period 2005-2009 mucilage phenomena did not occur.

In the period 1998-2009 we have studied seasonal and spatial distributions of the content of dissolved organic carbon and concentrations of the reactive part of organic matter with surface active properties (3).

Distribution patterns of DOC and SAS over the whole period of investigation showed that the maximum values were found in 1998 after mucilage events of very high intensity in summer 1997, followed by a decreasing trend until 2006 (down to 43% and 72% of the mean values for DOC and SAS, respectively). In the same interval significant reduction of the nutrients and chlorophyll a concentrations were detected, corresponding to the decrease of the Po River discharge, pointing also to the existence of oligotrophication in the north Adriatic Sea (4,5).

However, an increasing trend of DOC and SAS concentrations during the period 2007-2009 may indicate a new cycle of the organic matter accumulation which, accompanied with other favourable conditions may lead towards eutrophication of the northern Adriatic Sea, as found in the period 1997-2004.

References

- 1 Giani, M., Savelli, F., Berto, D., Zangrando, V., Ćosović, B., Vojvodić, V., 2005. *Sci. Tot. Environ.*, **353**, (1-3), 126-138.
- 2 Giani M., Degobbis, D., and Rinaldi A., 2005. *Sci. Tot. Environ.*, **353**, (1-3), 1-2.
- 3 Ćosović B. and Vojvodić V., 1998. *Electroanalysis*, **10**, (6), 429-434.
- 4 - Zanchettin, D., Traverso, P., Tomasino, M., 2008. *Climatic Change*, **89**, 411-433.
- 5 - Mozetic, P., Solidoro, C., Cossarini, G., Socal, G., Precali, R., Francé, J., Bianchi, F., De Vittor, C., Smolaka, N., Fonda Umani, S., 2010. *Estuaries and Coasts* **33**, 362-375.

Radium isotopes, seawater circulation and water ages in the Mediterranean coast of Northern Israel

Y. Weinstein¹, Y. Shalem¹, Y. Yechieli², B. Burnett³, P. Swarzenski⁴, and B. Herut⁵

¹ *Department of Geography and Environment, Bar-Ilan University, Ramat-Gan, Israel*

² *Geological Survey of Israel, Jerusalem, Israel*

³ *Department of Oceanography, Florida State University, Tallahassee, FL, USA*

⁴ *Coastal Marine Geology Program, U.S. Geological Survey, Santa Cruz, CA, USA*

⁵ *Israel Oceanographic and Limnological Research, Haifa, Israel*

Two geological units are exposed at Dor bay, southern Carmel Coast. The first is Pleistocene calcareous sandstone (locally called 'Kurkar'), and the second consists of Holocene loose sands, which cover the Kurkar. Both radon activities and $^{224}\text{Ra}/^{223}\text{Ra}$ activity ratios (AR) are very different in groundwater of the two units. Radon is one order of magnitude higher in the Kurkar water as compared with groundwater in the sand (350-450 and 10-90 dpm/l, respectively), while AR is significantly higher in the loose sand (average ratios of 12.5 and 3.5, respectively).

ARs in saline water discharging from the bay floor (via seepage meters) are very similar to those in the loose sand (average AR=13.1), implying that circulation of seawater is shallow and confined to the loose sand. This is also supported by the low radon activity in the discharging saline water. AR in bay water is somewhat lower (8-11), which implies that the average age of recirculated water (the water that recycled in the sediment) in the water column is 2.7 days. Using this water age and average ^{224}Ra activities in seepage meter water and bay water (104 and 6 dpm/100L, respectively), we calculated the fraction of recycled seawater in the bay as 10% (^{224}Ra is assumed zero in open seawater). The exact value could be slightly lower, since there is also a minor component of radium input by fresh water discharge.

ARs found in the offshore water (up to 1.3 km from shore and ca. 17 m deep) are very similar to those found in the bay (8-11). Activities of ^{224}Ra in the offshore water are also pretty similar to those found in bay water (3.3-3.8 compared with 6.4 dpm/l). Taken together, those observations imply that the radium in the shallow offshore water is supplied by local sandy sediments and not by cross-shore currents from the coast.

Further north, at the western Galilee, where the aquifer consists of carbonates, seawater AR at the coastline is 5.2, while significantly lower (1.2-1.5) in offshore water (ca. 800 m from the coast). This suggests that offshore water in this area does not circulate in the seafloor, which consists of similar carbonates. It also implies that the offshore shallow water in this area is relatively 'old' (10-11 days) with respect to its radium source.

Trace elements in different marine sediment fractions of the Gulf of Tunis: central Mediterranean Sea

N. Zaaboub^{1*}, W. Oueslati², S. Abdeljaoued², F. J. Huertas³, and A. López-Galindo³

¹ *National Institute of Science and Marine Technology, Salamboo, Tunis, Tunisia*

² *Science University of Tunisia, Manar, Tunis, Tunisia*

³ *Instituto Andaluz de Ciencias de la Tierra. CSIC – UGR.18002 Granada, Spain*

* *nouri_zaaboub@yahoo.fr*

In the North of Tunisia the major wind period is marked by strong and frequent North West direction. This wind engenders littoral currents, gyrating current anticlockwise forms in the centre of the gulf, forming weak current in the central part. Sediment dynamics along a littoral zone is closely dependent on the direction and the intensity of the littoral currents. The Gulf of Tunis (Fig.1) is connected to two principal water flows, the Mejerda River and the Ghar el Melh lagoon. The Mejerda River catchments area was characterized by mining activity (tailings, mine waste) putting dumps mainly from Pb, Zn, and Ba mines in the outlet of Mejerda River for many decades.

The Concentration of major and trace elements (Al, Ti, P, K, Mg, Na, Ca, S, Fe, Cl, V, Cr, Co, Ni, Cu, Zn, Ga, Br, Rb, Sr, Y, Zr, Nb, I, Ba and Pb) are determined in different three fractions of surficial sediments. Grain size distribution of fine fractions (<2 µm, 2-20 µm, 20-63 µm) reveals that clay and fine silt fraction are dominant 75-95% in the deeper estuarine region. Regarding clays, the dominant phases are dioctahedral smectite, illite and kaolinite. Chlorite and interstratified illite-smectite are also present. The total organic carbon (COT) content in surface sediment of the gulf of Tunis varies between 0.08 and 1.37 %. The determination of total nitrogen permitted to calculate the C/N ratio with an average~7. The C/N indicates a marine origin of the organic matter, only in front of the outlet of Mejerda River and Ghar el Melh lagoon where the organic matter has a mixed origin. The use of “Principal Component Analysis” statistical method, helped to establish which organic and/or inorganic phases concentrate the trace element. There is a significant correlation between COT and trace element Cu, Zn..., in the fine fraction <2 µm. This correlation is weak with clay minerals. The correlation of, Fe₂O₃, MnO₂ and P₂O₅ with traces element, mainly in the fraction < 2µm, reveals that amorphous iron Fe and Mn are among the most active scavengers of dissolved metals mainly in continental environments (Mejerda River).

The cluster analysis, using the similarity matrix with the ratio matching, supplements the results obtained for the metals of the fractions of the sediment (<63 µm). This test allows classifying the sediments of the study area in terms of their inter-metallic ratios. That is, sediment samples that are similar in origin tend to associate in one group, whereas sediments that are affected by some factor, such as transport pattern of sediment or their closeness to point sources of contamination, tend to separate into independent groups. The cluster analysis between sites is applied with data of different grain size fractions of the sediment. The dendrogram suggests a separation of five different groups. The most important groups are in the fraction < 2µm and in the fraction between 2-20µm. In the fine fraction (< 2µm), we note the highest average metal concentrations Pb, Zn, Ni and Cr. The Group 5 contains sites with the low average concentration of Zn, Cr, Zr, Br and Ba (Table: 1). In coarser grain size sediment (2-20µm) in Group 1 that contains the sites considered as potential sources of metals in the region mainly Zn, Cu and Pb. The representation of higher trace element (Fig2), according the cluster analysis classification of the surface sediments in terms of their inter-metallic and composition ratios shows that:

- a) In the fraction $< 2\mu\text{m}$, Group 1 is characterized by a relatively highest average metal concentrations Fe, Pb, Zn, Ni and Cr. Most of the sites of this group are in front of Mejerda river.
- b) In coarser grain size sediment ($2-20\mu\text{m}$), Group 1 contains an extended area of potential sources of metals contaminants in the region, mainly Zn, Cu and Pb.
- c) The Group 2 in fraction grain size fraction between ($2-20\mu\text{m}$) present a dominance of clay fraction mainly smectite (average 34%). These sites have high concentrations for most of the metals measured, mainly high levels of Pb. The Group 4 is marked by high Content in quartz, representing the distribution of continental sediment discharge in costal area (Table: 2). In grain size fraction between ($20-63\mu\text{m}$) Groups 2 and 5 forms two areas respectively, northern area and southern one. The sites of the Group 2 is characterized by a low average of metal except of Fe and Zr and high average of smectite and the sites of the Group 5 are characterized by a high average of metal mainly for Cr, Br and Ba with a low average of smectite (Table: 3).
- d) Grain size distribution is influenced by littoral currents, gyrating current anticlockwise forms in the centre of the gulf, forming weak current in the central part of the golf. Trace element are differently associated to geochemical phases in grain size fractions $<2\mu\text{m}$, $2-20\mu\text{m}$ and $20-63\mu\text{m}$. In different fractions, traces elements are associated to hydrogenous fraction from water source outlet, ferromagnesian oxyhydroxide, only Pb is associated to smectite in the tow coarser grain size fraction.

Trace Elements and Isotopes in the Aegean Sea: Baseline Information

C. Zeri and E. Kaberi

Institute of Oceanography, Hellenic Centre for Marine Research (HCMR), Anavyssos, Greece

The Aegean Sea is a very dynamic area due to important water mass exchanges with Black Sea through the Dardanelles Straits in the north, and with the Eastern Mediterranean basin through the Cretan Straits in the south. Previous results have shown that the surface low salinity waters of the North Aegean Sea are enriched in dissolved TEI's (Delfanti, 2005; Zeri & Voutsinou Taliadouri, 2003). Within this mixed surface layer dissolved TEI's distribution vs salinity follows a conservative mixing pattern (Figures 1, 2). Because ^{137}Cs has its major source to the Chernobyl accident, coupling the mixing line of ^{137}Cs with those of other TE's clearly shows that BSW carry increased amounts of TEI's into the North Aegean Sea. Deep basin enrichments of TEI's have been recorded in the North Aegean Sea and have been linked to deep water formation events. This again is further supported by the ^{137}Cs redistribution in the N. Aegean water column in 2001 (Figure 3). Since surface waters in the N. Aegean are enriched to ^{137}Cs relatively to those in the Cretan Sea, one would expect that the formation events in the two sub-basins would result in different ^{137}Cs profiles with lower ^{137}Cs concentrations in the Cretan Sea. The picture recorded in the Cretan Sea during 2003, however, revealed equally high ^{137}Cs deep water concentrations between the North and South Aegean (Cretan Sea) (Figure 3). This implies that deep water formation taking place in the north contributes to the deep water masses of the Cretan Sea. Other TEI's and especially the more conservative ones are expected to follow this pattern.

So the questions raised are: How are the enrichments observed in the North Aegean balanced? What is the role of particles in the North Aegean Sea in uptake and regeneration of TEI's. To what extent deep water formation, taking place in the North Aegean, influences the distribution of TEI's in the Cretan Sea and subsequently the Levantine?

In order to provide answers to these questions we propose within the Geotraces strategy to study TEI's distribution along two longitudinal sections at the western and eastern Cretan Straits as well as at two process stations: E1M3A in the Cretan Sea and MNB1 in the North Aegean Sea.

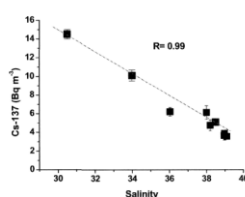


Figure 1
(Delfanti et al, 2005)

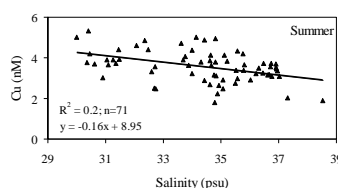


Figure 2
(Zeri & Voutsinou-Taliadouri, 2003)

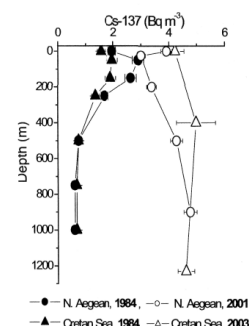


Figure 3
(Delfanti et al, 2005)

References

- Delfanti, R, Tsabaris, C., Papuci, C., Kaberi, H., Lorenzelli, R, Zervakis, V., Tangherlini M., Georgopoulos D. 2005. *IAEA CN118/5*, pp. 89-92.
Zeri C. and F. Voutsinou-Taliadouri, 2003. *Continental Shelf Research*, **23**, 9, 919-934.