**CRUISE: MedSeA**
Geotraces Section: GA04
PI: Patrizia Ziveri (MedSeA EU Project) and Jordi Garcia Orellana (Geotraces)
Departure date: May 5th 2013
Arrival date: June 1st 2013
Number of stations: 22

In May 2013 a cruise in the Mediterranean Sea took place on-board the *R/V Ángeles de Alvariño* (Fig. 1). This cruise was embraced within as an essential part of the European project Mediterranean Sea Acidifcation in a changing climate (MedSeA) and the GEOTRACES program, which aims to improve the understanding of biogeochemical cycles and large-scale distribution of trace elements and their isotopes in the marine environment. The cruise is part of the Geotraces program to cover the section GA04, in combination of NIOZ cruise on board of the *Pelagia*. Both cruises will take samples to determine the distribution of the GEOTRACES TEIs and many other trace elements. While *Pelagia* will cover a trace element that necessitates trace metal clean sampling, *Ángeles Alvariño* will collect those samples that required large volume of water such as, among others, artificial radionuclides.

**Fig. 1:** R/V Ángeles de Alvariño.

# Cruise Personnel

| | Leg | Name | Institute | email |
|---|---|---|---|---|
| PI | 1 | Patrizia Ziveri | UAB[1] | Patrizia.Ziveri@uab.cat |
| PI | 2 | Jordi Garcia-Orellana | UAB | Jordi.Garcia@uab.cat |
| Geotraces | 2 | Núria Casacuberta | ETH[2] | ncasacuberta@phys.ethz.ch |
| ST | 1 | Muntsa Roca | UAB | Montserrat.Roca.Marti@uab.cat |
| ST | 1-2 | Maxi Castillejo | UAB | Maxi.Castillejo@uab.cat |
| ST | 1-2 | Abed El Rahman Hassoun | UPVD[3] | abedhassoun@gmail.com |
| | 1 | Eva Krassakopoulou | HCMR[4] | ekrasekras@hcmr.gr |
| | 2 | Tatiana Tsagaraki | HCMR | tatakltatiana@hcmr.gr |
| | 1-2 | Eva Mayol | IMEDEA[5] | emayol@imedea.uib-csic.es |
| | 2 | Mauro Celussi | OGS[6] | mcelussi@inogs.it |
| ST | 1-2 | Gianmarco Ingrosso | OGS | gingrosso@inogs.it |
| | 1 | Michele Giani | OGS | mgiani@inogs.it |
| | 1-2 | Uxue Tilves | ICM[7] | tilves@icm.csic.es |
| | 1-2 | Elissar Gemayel | UPVD | elissargemayel@hotmail.com |
| | 1 | Barbara d'Amario | UAB | Barbara.DAmario@uab.cat |
| | 2 | Ramiro Mata | UAB | Ramiro_mata@alumni.brown.edu |
| | 1-2 | Marina Sanz Martín | IMEDEA | marinaotri@gmail.com |

1. UAB: Universitat Autònoma de Barcelona
2. ETH: Eidgenössische Terchnische Hochschule Zürich
3. University of Perpignan
4. Hellenic
5. Instituto Mediterráneo de Estudios Avanzados
6. Istituto Nazionale di Oceanografia e Geofisica Sperimentale Trieste
7. Institut de Ciències del Mar

# Cruise Objectives

The main objectives of the cruise related to MedSeA EU project were:

- To refine the climatological maps of the distribution of carbonate species in the Mediterranean Sea (pH, $pCO_2$, $CO_3^{2-}$, $C_T$, $A_T$, $\Omega_a$, $\Omega_c$).
- To determine the distribution of anthropogenic carbon in the Mediterranean Sea and constrain their uncertainty.
- To determine the effects of carbon chemistry in carbonated and non-carbonated planktonic organisms of the Mediterranean SeA.
- To determine the synergistic effects of acidification, global warming and nutrients in major pelagic organisms of the Mediterranean Sea.
- To identify and quantify the responses of the key biogeochemical processes in the Mediterranean Sea due to acidification and global warming.

The main objectives of the cruise related to Geotraces programme were:

- To study the concentration of $^{137}Cs$, $^{90}Sr$, Pu-isotopes, $^{237}Np$, $^{236}U$ and $^{129}I$ in different profiles collected along the Mediterranean Sea
- Constrain the sources of these radionuclides in this sea (i.e. global fallout, Chernobyl accident, nuclear and nuclear reprocessing plants)
- Trace oceanographic processes by combining them.
- Complete the set of $^{228}Ra$ samples to estimate the influence of submarine groundwater discharge in the Mediterranean Sea.
- Determine the protactinium-thorium ($^{231}Pa$ /$^{230}Th$) distribution in the Mediterranean Sea in order to study particle flux-derived processes such as sedimentation rates and distribution, particle export and ocean productivity.
- Determine the distribution of Rare Earth Elements (REE) in seawater in order to evidence interactions between lithogenic material and the water masses.
- Deuterium distribution on the sampled stations in order to compare the results with those obtained in the Ducht cruise.

# Sampling Stations

| Station | Date | Time | Latitude | Longitude | Depth (m) | Nº of cast |
|---|---|---|---|---|---|---|
| 1 | May/2/2013 | 23.15 | 36 02.09 N | 006 38.53 W | 556 | 3 |
| 2 | May/3/2013 | 12.00 | 35 56.89 N | 005 33.71 W | 557 | 3 |
| 3 | May/4/2013 | 9.30 | 36 07.46'N | 04 11.04'W | 1336 | 3 |
| 4 | May/7/2013 | 5.30 | 37 29.02' | 1 26.820' E | 2776 | 3 |
| 5 | May/8/2013 | 8.30 | 38 31.399' N | 5 32.720'E | 2844 | 5 |
| 6 | May/9/2013 | 18.30 | 38 15.937'N | 8 41.232 E | 2237 | 3 |
| 7 | May/10/2013 | 20.30 | 37 7.08'N | 12 40.553 E | 263 | 1 |
| 7a | May/10/2013 | 1.45 | 37 3.284'N | 13 11.142'E | 469 | 3 |
| 8 | May/11/2013 | 15.25 | 36 2.723'N | 15 13.544' | 140 | 1 |
| 9 | May/12/2013 | 11.25 | 35 6.871' N | 18 17.640' E | 3774 | 5 |
| 10 | May/14/2013 | 10.51 | 33 48.784´N | 24 15.986 E | 1845 | 3 |
| 11 | May/15/2013 | 11.44 | 33 30.149´N | 28 0.091´E | 2865 | 5 |
| 12 | May/17/2013 | 3.45 | 33 12.929´N | 32 0.119´E | 1647 | 3 |
| 13 | May/17/2013 | 16.20 | 34 13.450´N | 33 13.502E | 2042 | 3 |
| STOP IN HERAKLION | | | | | | |
| 14 | May/21/2013 | 6.00 | 35º 41.75´N | 23º 25.31´E | 619 | 2 |
| 15 | May/21/2013 | 21.30 | 36º24.13 N | 20º48.48 E | 2925 | 1 |
| 16 | May/21/2013 | 1.00 | 40º14,05 N | 18º50,26 E | 808 | 2 |
| STOP IN BRINDISI | | | | | | |
| 17 | May/23/2013 | 14.30 | 41º50.19N | 17º15.27E | 970 | 2 |
| 18 | May/25/2013 | 20.00 | 37º42,40' N | 18º31,12' E | 3061 | 3 |
| 19 | May/27/2013 | 13.00 | 39º49.76'N | 12º30.94'E | 3061 | 4 |
| 20 | May/29/2013 | 14.45 | 41º19.02'N | 5º39.94'E | 2561 | 4 |
| 21 | May/30/2013 | 8.21 | 40º04.41'N | 05º56.85'E | 2834 | 4 |
| 22 | May/31/2013 | 13.00 | 40º57.05'N | 3º19.15'E | 2274 | 6 |

# Stations map

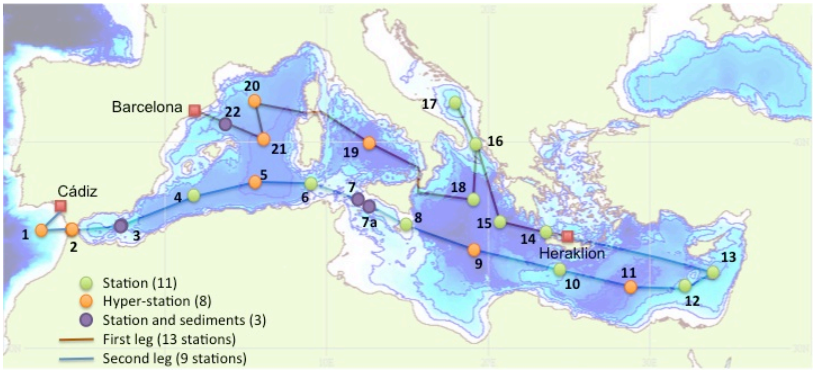


**Fig. 2:** Location of the sampling stations in the MedSeA cruise.

# Particulate trace metals

*Scientist in charge: Maxi Castrillejo*[1]
*Not on board: Maeve Lohan*[2] *and Pere Masqué*[1]

[1]*Universitat Autònoma de Barcelona (UAB), Institut de Ciència i Tecnologia Ambientals (ICTA) and Department of Physics*
[2] *Plymouth University*

## *1. Introduction and objectives*

Iron (Fe) has been shown to be the prime limiting micronutrient in high-nutrient-low-chlorophyll waters. Some other bioactive trace metals (zinc, cadmium, etc.) are also vital for biological productivity as they are often involved in enzymatic activity or become part of proteins. Yet, little is known about the processes by which these elements are supplied to the oceans (aeolian dust, resuspension of continental shelf sediments, upwelling, etc.) and which mechanisms govern scavenging/uptake, solubility, mineralization or remineralization in the water column. Recent studies suggest that marine particles could be an important source of bioactive trace metals for the phytoplankton. Determining the particulate trace metal (Fe, Mn, Co, Cd, Ni, Zn, Cu, Pb, Ba) distributions will therefore help fill this gap and allow inferring and quantifying the processes which are controlling primary productivity, biogeochemical processes and supply and removal of trace metals in Mediterranean waters.

The main objective on board was to obtain uncontaminated trace metal samples using in-situ pumps.

## *2. Methodology*

Particulate samples were collected from 6 stations. Particles were collected using Challenger in-situ pumps deployed at the base of the euphotic zone and 100 below the euphotic zone. Each pump was equipped with a filter holder equipped with 53 µm and 1 µm nylon mesh filters (Nytex, SEFAR) which were soaked in 10 % v/v HCl (Fischer Scientific Trace metal grade) for 3 days and the in Milli-Q water (>18.2 MΩ cm) till a pH of ~ 7 was achieved. Parts of filter holders which were in direct contact with the sample (O-rings and polypropylene support mesh) were acid cleaned with the same HCl solution. Acid and Milli-Q water baths were changed regularly. Filter holders were kept in plastic bags before and after the deployment to avoid the contamination from the ship. On recovery, the filter housings were placed in a Class-100 laminar flow hood for removal of the nylon mesh. A clean ceramic blade was used to cut a quarter (typically equivalent to 100 L of pumped seawater) of the nylon mesh, which was then rinsed with Milli-Q water into a clean plastic jug. This water was then filtered over a acid cleaned 25 mm PES filters (0.2 µm, Supor, Pall Gellman) housed in a clean filter holder (Swinnex, Millipore) using an all polypropylene syringe attached to the top of the filter holder. Residual water was forced through the filter using air from within the flow hood, the filter was then folded in half and placed in acid clean 2 mL LDPE cryogenic vial. Filter and sample handling was always done under the laminar flowhood and using trace metal clean techniques.

Digestion of PES filters and determination of trace metals by ICP-MS techniques will be done at the University of Plymouth.

# Artificial Radionuclides ($^{137}$Cs, $^{90}$Sr, Pu-isotopes, $^{237}$Np, $^{236}$U and $^{129}$I)

*Scientist in charge: Núria Casacuberta[1] and Jordi Garcia-Orellana[2]*
*Not on board: Pere Masqué[2]*

*[1] ETH-Zurich, Ion Beam Physics*
*[2] Universitat Autònoma de Barcelona (UAB), Institut de Ciència i Tecnologia Ambientals (ICTA) and Department of Physics*

## *1. Introduction*

During the last 60 years, artificial radionuclides (e.g. $^{14}$C, $^{3}$H, $^{99}$Tc, $^{137}$Cs, $^{90}$Sr, Pu-isotopes, $^{236}$U, $^{129}$I, $^{137}$Np) have been released to the environment, and in particular to the World's oceans. The three main sources of anthropogenic radionuclides to the oceans include the global fallout from the atmospheric weapon tests, nuclear accidents such as Chernobyl and Fukushima and dumping of wastes from nuclear reprocessing plants (i.e. La Hague and Sellafield). Other minor sources are nuclear submarine accidents and loss of nuclear weapon and radioactive sources. Cs-137 is so far one of the better-constrained radionuclide in the oceans. The ocean inventory of $^{137}$Cs in 2000 was of 700 PBq due to global fallout, about 40 PBq from the releases of La Hague and Sellafield, other 16 PBq from Chernobyl, and so far a maximum of 22 PBq had been estimated as a result of the Fukushima nuclear power plant accident. Average concentrations in surface water of the World's oceans and seas of $^{137}$Cs range from 0.1 (Antarctic) to 61 Bq·m$^{-3}$ (Baltic Sea).

Once incorporated in the marine environment, these anthropogenic radionuclides are used in oceanography as powerful tools that allow quantifying oceanic processes like water mass mixing, deep water formation rates, or determining the age of water masses. Over the recent past, significant progress has been achieved in the development of both, new analytical tools (e.g. mass spectrometric techniques) and innovative laboratory methods (e.g. sequential extraction techniques). New tracers are evolving (e.g. $^{236}$U) and more traditional tracers (such as $^{137}$Cs, $^{90}$Sr, $^{129}$I, Pu-isotopes and $^{237}$Np) are becoming available at higher precision.

Not many data on artificial radionuclides is available for the Mediterranean Sea. A cruise performed in 1997 onboard R/V Deneb showed that average values in surface waters of $^{137}$Cs, $^{90}$Sr and $^{239+240}$Pu (decay corrected at year 2000) were of 2.6, 1.7 and 0.014 Bq/m$^3$, respectively.

## *2. Objectives*

The aims are:

-To study the concentrations of $^{137}$Cs, $^{90}$Sr, Pu-isotopes, $^{237}$Np, $^{236}$U and $^{129}$I in several profiles collected along the Mediterranean Sea;

-To constrain the input functions (i.e. global fallout, Chernobyl, nuclear reprocessing plants) of these radionuclides in the Mediterranean Sea;

-To test the potential of $^{236}$U as a new oceanographic tracer;

-To trace oceanographic processes by combining the results obtained with the different artificial radionuclides.

These aims are embraced within the GEOTRACES program.

## *3. Methodology*

*3.1 Sample location*

10 deep profiles for the determination of the distribution of artificial radionuclides were collected during the MedSea cruise (stations #2, #4, #5, #6, #9, #11, #19, #20, #21 and #22). Samples were generally collected at surface (4.5 m), 25, 100, 250, 500, 1000, 1500, 2000 and 3000 meters depth.

*3.2 Volumes*

30 L of seawater were collected for the analysis of $^{137}$Cs, $^{90}$Sr, Pu-isotopes and $^{237}$Np. A sequential method extraction will be applied to these samples at the Universitat Autònoma de Barcelona.

6.5 L and 0.5 L of seawater were collected for the analysis of $^{236}$U and 129, respectively. These samples will be analyzed in ETH-Zurich.

# Protactinium-Thorium ($^{231}$Pa /$^{230}$Th)

*Scientist in charge: Matthieu Roy-Barman[1] and Jeanne Gherardi[1]*
*On board: Núria Casacuberta[2], Maxi Castrillejo[3], Montserrat Roca-Martí[3] and Jordi Garcia-Orellana[3]*

*[1]Laboratoire des Sciences du Climat et de l'Environnement (LSCE)*
*[2] ETH-Zurich, Ion Beam Physics*
*[3]Universitat Autònoma de Barcelona (UAB), Institut de Ciència i Tecnologia Ambientals (ICTA) and Department of Physics*

*1. Introduction*

$^{231}$Pa and $^{230}$Th with half-lives of 32.5 kyr and 75.2 kyr respectively, are formed at a constant rate by $\alpha$ decay of uranium. While uranium is generally conservative in the ocean, protactinium and thorium are particle reactive thus they are readily removed from the water column. Therefore, long lived $^{231}$Pa and $^{230}$Th have been used to study particle flux-derived processes such as sedimentation rates and distribution, particle export and ocean productivity. $^{230}$Th is preferentially removed to $^{231}$Pa, thus $^{231}$Pa has a longer residence time and is affected more strongly by advection processes, which makes the $^{231}$Pa/$^{230}$Th pair an important tool to investigate ocean circulation processes. Only few $^{230}$Th water column data are available in the Mediterranean Sea and no $^{231}$Pa data exists.

*2. Objectives:*

The aims are:

-To study the concentrations of $^{231}$Pa and $^{230}$Th in different profiles collected along the Mediterranean Sea;

-To constrain the settling rate of marine particles in the different basins of the Mediterranean Sea. These settling rates will be relevant for other particule-reactive tracers;

- To constrain the impact of advection on $^{231}$Pa and $^{230}$Th distribution.

The aims are embraced within the GEOTRACES program.

*3. Methodology*

A total of 71 seawater samples (5 L each) were collected at stations 2, 3, 5, 7a, 9, 11, 14, 19, 20 and 21. Samples were acidified immediately after sampling and stored

with double plastic bags. Additionally, particles (size fractions of >53 μm and 1 to 53 μm) were collected at 4 depths (up to 2000 m) using in-situ pumps at stations 3, 5, 9, 11, 19 and 21. These samples will be processed at the Laboratoire des Sciences du Climat et de l'Environnement (France).

# $^{228}$Ra distribution in the Mediterranean Sea as a tracer of Submarine Groundwater discharge

*Scientist in charge: Valentí Rodellas[1] (not on board) Jordi Garcia-Orellana[1]*

*[1]Universitat Autònoma de Barcelona (UAB), Institut de Ciència i Tecnologia Ambientals (ICTA) and Department of Physics*

## *1. Introduction and objectives*

The main objective of our participation in the cruise MedSeA-GA04S was determining the concentration of $^{228}$Ra in the Mediterranean Sea in order to estimate the Submarine Groundwater Discharge along the Mediterranean Basin.

Submarine Groundwater Discharge (SGD) is defined as any flow of water at continental margins from the seabed to the coastal ocean, regardless of fluid composition or driving force. The flux of submarine groundwater discharge has been considered to be a pathway for enriching coastal waters in essential nutrients, trace metals and carbon. Much of the chemical composition of SGD is the result of reactions occurring in the subterranean estuary, where meteoric groundwater mixes with intruding seawater. The composition of SGD differs from that predicted by simple mixing because biogeochemical reactions in the subterranean estuary modify its chemistry. In this context, Ra isotopes have been proven to be a very powerful tool to estimate submarine groundwater discharge fluxes. Because Ra isotopes are highly enriched in salty coastal groundwater relative to the ocean, small inputs of SGD can be recognize as a strong signal.

Our strategy for determining the submarine groundwater discharge to the Mediterranean Sea derives from the fact that radioactive decay is the primary sink for $^{228}$Ra in the Mediterranean. To maintain a steady state, these losses must be balanced by fresh inputs of $^{228}$Ra to the Mediterranean Sea. If other sources can be evaluated, the $^{228}$Ra flux that must be sustained by SGD can be determined. By using the $^{228}$Ra content of groundwater in coastal aquifers, the $^{228}$Ra flux can be converted to an SGD flux to the Mediterranean Sea.

## *2. Methodology:*

### *2.1 Sampling*

During the cruise track, 10 stations of surface waters (circa 350 L) were collected from the membrane pump of the vessel (4.5 m depth). In 3 stations, two samples of 120L were collected at two additional depths in order to characterize the $^{228}$Ra content in LIW and in deep waters.

These large volumes of water were passed through columns loaded with $MnO_2$-impregnated acrylic fiber (hereafter Mn-fiber) at a flow rate lower than 1 $L \cdot min^{-1}$, which quantitatively extracts Ra isotopes. In order to check for complet Ra uptake, 29 samples were filtered through two Mn-fiber columns connected in serie.

*2.2 Future analytical work*

All the samples (Mn-fiber) will be analyzed to determine the concentration of $^{228}$Ra in water samples, following two different approaches. The comparison of two different approaches will allow us to test the different methods but also achieve more accurate results.

-*Measurement of $^{228}$Ra via gamma spectrometry:* the Mn fiber will be ashed and transferred to hermetically sealed counting vials to determine $^{228}$Ra (and also $^{226}$Ra) using a well type Ge-detector.

-*Measurement of $^{228}$Ra via MC- ICPMS:* The multicollector inductively coupled plasma mass spectrometry (MC-ICPMS) is used to determine $^{226}$Ra and $^{228}$Ra concentrations and the $^{228}$Ra/$^{226}$Ra isotopic ratio. After the gamma measurements, the Mn fibers are prepared for purification of Ra using two ion exchange columns. These measurements will be conducted at Bar-Ilan University (Israel).

# Nd in the Mediterranean Sea

*Scientist in charge: Ester Garcia Solsona[1]*
*On board: Maxi Castrillejo[1], Montserrat Roca-Martí[1], Núria Casacuberta[2] and Jordi Garcia-Orellana[1]*
*[1]Universitat Autònoma de Barcelona (UAB), Institut de Ciència i Tecnologia Ambientals (ICTA) and Department of Physics*

*1. Introduction and objectives*

Concentrations of Rare Earth Elements (REE) in seawater are used to evidence interactions between lithogenic material and the water masses given that competition between REE solubilization/removal exchanges causes fractionation between light and heavy REE. Indeed, they allow identifying which marine process could have modified their distribution in seawater. On its turn, the isotopic composition of Nd ($\varepsilon_{Nd}$) of a water mass in the ocean is ultimately controlled by the continental imprint via weathering, erosion and particle-seawater interaction. Its ocean residence time (200-2000 y) gives it the character of a water mass mixing tracer. Close to the continent, Nd is no further conservative and continent/ocean interactions may also play a role in the global Nd budget. Understanding the sources and sinks of these trace elements in the oceans has important implications for quantifying their global geochemical cycles, their application as paleoceanographic tracers, and in discerning the geochemical reactions that mobilize, sequester, and fractionate REEs in the environment.

*2. Methodology*

A total of 19 seawater samples were taken at 3 stations covering the Northern and Central Alguero-Balear, and Catalano-Balear regions. A stainless CTD equipped with OTE bottles was used to take samples from 100 m till the bottom depth. Sample manipulation was done following clean trace metal techniques and an enclosed tubing system was used to take the seawater from the OTE bottles straight into the cubitainers minimizing the contact of the sample with the environment. Samples were then filtered (0.2 um pore size) using a trace metal clean pump and acidified with ultrapure grade acids.

# Deuterium

*Scientist in charge: Jose Marcus Godoy*[1]
*On board: Jordi Garcia-Orellana*[2]
[1]*Pontifícia Universidade Católica do Rio de Janeiro*
[2]*Universitat Autònoma de Barcelona (UAB), Institut de Ciència i Tecnologia Ambientals (ICTA) and Department of Physics*

*1. Introduction and objectives*

Both delta(D) and delta(O-18) depend on the past "history" of a water mass like: where and how long it was at the surface. Therefore, it is well correlated with the salinity and the temperature. Leaving the surface, for intermediate or deeper depths, the water is no longer affected by air–sea exchange; the delta parameter is thus conservative and its distribution follows the circulation pattern of the water masses. Due to the actual achieved precision and the observed larger delta values, better resolution is obtained applying delta(D) than delta(O-18). The main objective of this sampling is to compare the results with those obtained in the Ducht cruise.

*2. Methodology*

Samples are collected on 2 mL chromatographic vials, each samples in injected 8 times on Water Isotope Analyzer PICARRO, being the last four measurements used for the mean value calculation, for each batch of six samples a standard is measured as well as a known test sample. The delta values are normalized the Vienna Standard Mean Ocean Water (VSMOW).