JOINT SEA STUDIES OF THE IAEA & EUROPEAN UNION

MEDITERRANEAN PARTNERSHIP

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The Mediterranean Sea is a unique body of water from both a cultural and socio-economic standpoint. As an integral part of the cradle of western civilization, it has long served as a life support system for the human population in terms of both nutrition and as a vehicle for commerce and trade. Today it is home for the millions of people permanently inhabiting its coastlines, and a playground for the millions more that crowd its shores at various times of the year for the purpose of recreation.

Such human activities and pressures have inevitably resulted in environmental stresses and pollution that can potentially impact the functioning of this critical marine ecosystem.

Several oceanographic and geographic features of the Mediterranean Sea render it particularly vulnerable to the potential effects of anthropogenic pollutants. The sea is a relatively shallow, semi-enclosed body of water with only limited water exchange taking place at the Straits of Gibraltar and through the Bosphorus. Less saline Atlantic surface water enters at Gibraltar and slowly circulates counter clockwise around the Mediterranean basin. There it gradually becomes warmer and more saline due to insolation and intense evaporation. The weak coastal current systems and general lack of tides combine to reduce dispersion of pollutants entering its coastal waters. Furthermore, recent construction of dams on some major rivers have substantially reduced spring runoff which tends to cleanse the shelf region of deposited contaminants.

Besides these unique physical features of the Mediterranean Sea, much of its water is very low in nutrients and generally impoverished in sea life. *(See map)* Hence, significant perturbation of its limited potential productivity could cause long-term detriment to the ecosystem.

Given the Sea's special geographical setting and potential sensitivity to human activity, it is not surprising that over the last decade much effort has been put into studying its biogeochemical structure and functioning. Furthermore, the Sea's restricted size affords marine scientists the opportunity to study, on a reduced scale, processes typical of the world's oceans. Recent trends in oceanography have shown that the degree of our understanding these processes significantly improves when the questions to be answered are addressed in a multidisciplinary way.

Recognizing this fact, the European Union (EU) has mounted various large-scale multidisciplinary marine programmes, several of which have focused on the Mediterranean Sea. Because of its long history of collaborative work in the Mediterranean, the IAEA's Marine Environmental Laboratory (MEL) in Monaco has been invited by several EU partner institutes to contribute to these programmes, usually in the area of employing nuclear techniques to study key oceanic processes. These EU-supported programmes have been instrumental in broadening MEL's extra-budgetary funding base, which is often necessary to fulfil approved IAEA regular programmes dealing with marine environmental questions.

In this respect, MEL has been very active in the 1990s studying oceanic processes in the Mediterranean Sea that are crucial to understanding the transport and fate of radionuclides and other contaminants. This article highlights the main actitivities MEL has undertaken.

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TRACKING POLLUTION'S HISTORY

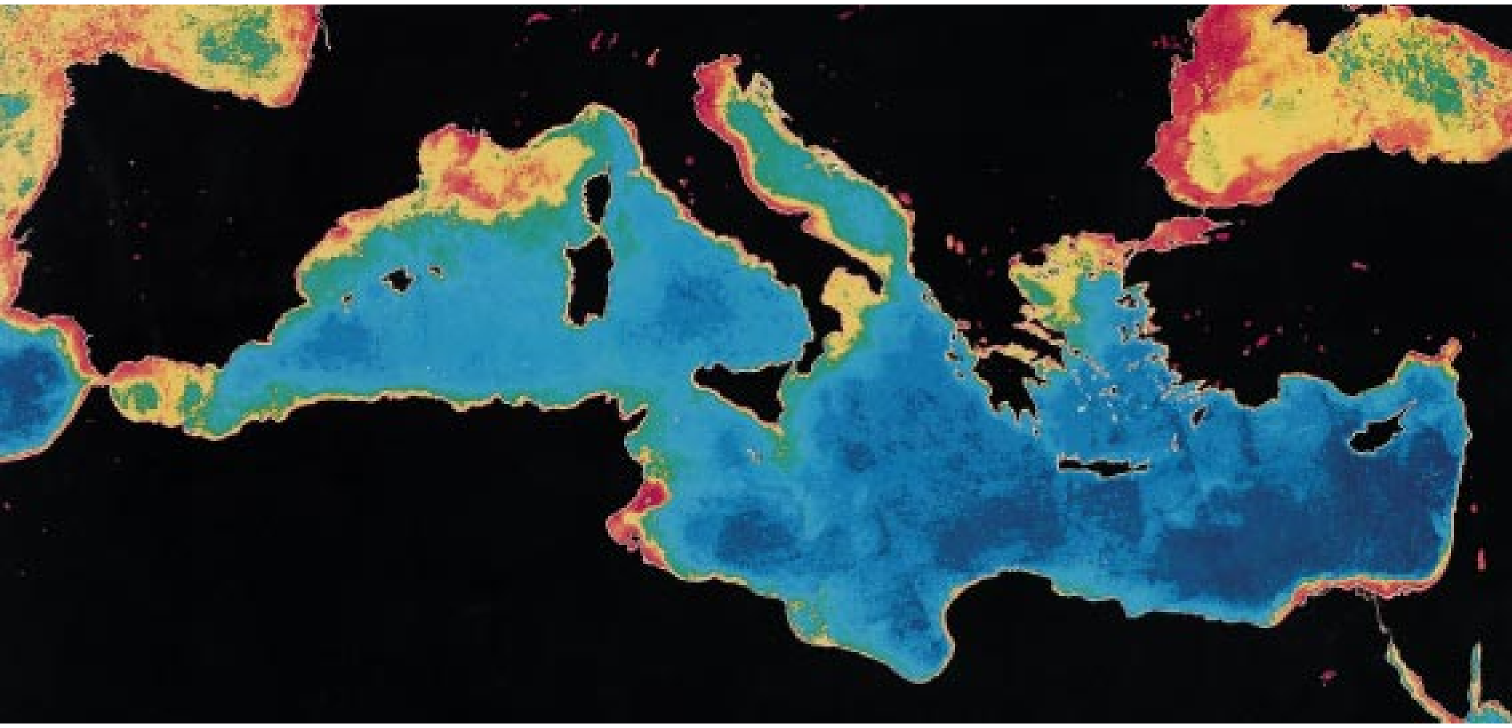
One area of study has engaged MEL's expertise in the EU-sponsored ELNA programme (Eutrophic Limits in the Northern Adriatic). One of MEL's tasks was to establish the pollution history of various contaminants in the polluted, northern Adriatic region.

The method chosen was to date sediment cores using nuclear techniques, and then relate the derived sedimentation rates to the contaminant levels measured in the different sediment layers which are deposited over time. The nuclear technique most often used in these geochronology studies is to follow the decay of atmospheric-derived lead-210 after its deposition in the sediments. The primary assumption with this technique is that only radioactive decay of the deposited lead-210 (physical half-life of 25 years) is responsible for its decrease in concentration with depth. The lead-210 in sediments is actually computed through the direct measurement of its radioactive granddaughter, polonium-210. From the dry mass accumulation rate, a sedimentation rate in centimeters per year can then be calculated through knowledge of sediment porosity and density.

Mercury and PCB pollutants. Off the mouth of the Po river in Italy, sedimentation rates were found to be relatively high, which is indicative of this coastal area. Because the Po river outfall is known to be a major source of land-derived contaminants to the northern Adriatic, the sediment core from off the Po was analyzed for two key pollutants in the Mediterranean, mercury and PCBs.

Photos: Above, scientists deploy an automated sediment trap in the Adriatic Sea. Below, colour scanner images of the Mediterranean Sea indicate areas of high productivity (orange and yellow) and low productivity (blue) during the spring season.

(Credits: Miquel/MEL; NASA Goddard Space Flight Center)



The profiles of common PCB mixtures show maximum values deposited between roughly 20 and 27 years earlier. This timeframe corresponds closely to the period of maximum PCB sales which occurred during 1969-70. Furthermore, PCBs have only been produced commercially since 1929. The profiles also show a rapid drop-off in PCBs by the 18 to 20 centimeter horizons. This corresponds closely to the time when one would expect to see these compounds first entering the environment.

In the case of mercury, absolute concentration is often related to the organic content of the sediment. A profile was obtained for the same Po outfall sediment core of methyl mercury concentration normalized to the particulate organic carbon (POC) content. Such profiles are complex and difficult to interpret; however, two clear maxima in concentration appear at depths between 8 to 10 centimeters and between 20 to 22 centimeters.

There is a general lack of information on methyl mercury in the Adriatic. Noteworthy from MEL measurements is that both total and methyl mercury concentrations peak in depth horizons of 20 to 22 centimeters, which corresponds to approximately 77 to 85 years before the core was collected. This relationship suggests that these maxima closely correspond to the year of maximum mercury production (1913). At that time, the Idria mine on the neighboring Isonzo river produced twice the average amounts of mercury as in any other year.

Such multidisciplinary studies — using what are assumed to be largely undisturbed sediments — demonstrate that the use of the physical time clock of a natural radionuclide deposited in the seabed can be a powerful tool for describing the historical record of sea pollutants linked to human activities.

UNDERSTANDING MARINE PROCESSES

Since 1996, MEL has been collaborating in the EU-MAST (Marine Science and Technology) project in the eastern Mediterranean basin entitled "Hydrothermal Fluxes and Biological Production in the Aegean Sea".

The Aegean Sea is an area of high seismic and geothermal activity. The island of Milos is noted for having some 35 km^2 of geothermally active seabed in surrounding shallow waters where large volumes of free gas as well as phosphate and manganese are vented.

The geochemical cycling and biological production based on chemosynthesis in these shallow vents is still largely unknown, particularly the importance of vents in the production and export of particulate organic material.

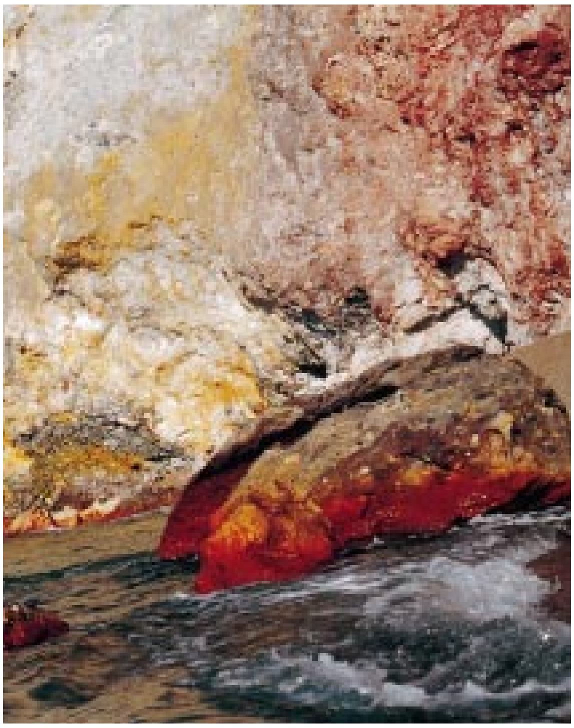
One of MEL's main objectives in the programme was to characterize and quantify the export of particulate organic carbon from the euphotic zone in the vicinity of the hydrothermal vents. This was accomplished through long-term studies of sedimenting particulate material, water column measurements, and bottom sediment analyses.

Field trips near the Milos Islands. During 1996-97, three field trips were organized to the south coast of Milos Islands to sample settling particles and sediments, and to deploy and recover moored arrays containing sediment traps and current-meters. The "time-series" sediment traps collected particles fluxing through a depth of 60 meters during summer at three sites along a transect from a vent zone to an area free of any major vent influence.

At the three sites, eight sample cups sequentially collected particles, each for a 12-day period. Particle fluxes at some distance from the vent site were clearly different from fluxes in the vent area. During most of that time, one or two orders of magnitude more particulates were produced and exported at the vent site than at the control and intermediate sites. Fluxes were comparable at all stations only during a brief period in mid-summer. In periods of highest sedimentation, organic material was 30 to 100 times more important at the vent site.

Sediment traps were deployed within a total distance of only 3.5 nautical miles during summer 1996. Yet the settling particles differed between sites not only in quantity but also in their composition.

Most of the samples were primarily composed of zooplankton debris (bits of animal carcasses, exoskeletons and a large variety of fecal pellets). But September samples from the vent site were completely different from all other samples and were largely composed of tiny elongated, dark brown fecal pellets which were very homogeneous in size and shape. The final sample



collected was composed almost exclusively of this kind of fecal material. Marine bacteria were also present in all samples but were more abundant in the particulates from the vent site. Their contribution to carbon flux was minor (<1%), except in mid-summer when mass fluxes were very low.

Hydrothermal vent-associated thermophilic bacteria were identified by DNA analysis only in samples from the vent sites. Thus, the production of carbon and subsequent export to the sediments at the vent site was significantly more important than in the surrounding areas sampled. Particles were largely of pelagic origin and carried a clear bacterial marker of hydrothermal origin.

Particle transport processes. During the same set of field experiments in the Aegean Sea, the differing chemistries of the natural radionuclide pair, polonium-210 and lead-210, were used to study particle transport processes in a shallow water hydrothermal vent zone. Polonium is present in the marine environment primarily as a result of the decay of lead-210 following atmospheric deposition and by the outgassing of radon from sediment and sub-marine vent formations. If the vents are acting as a source of hydrothermal waters enriched in polonium-210 and its grandparent lead-210, then particles in the vent field might also be expected to be enriched in these radionuclides. Therefore particles were collected at shallow depth (60 meters) on four different occasions during summer 1996.

There was no evidence from the trap data that the sulfur-rich environment observed in the vicinity of vents was affecting polonium-210 concentrations in settling particles. Polonium-210 concentrations were of the same order as the Po concentration previously reported for sediment trap material collected during summer in the coastal northwestern Mediterranean, far from any vent influence.

Likewise, lead-210 showed no enhancement in particulate matter originating in the vent zone. In fact, particles from the "control site" tended to contain more lead-210 than those in the vent zone.

Photos: Along the shores of Milos Island, iron (brown) and sulphur (yellow) deposits are evident in an area of geothermal activity. In shallow hydrothermal fields of the Aegean Sea, an underwater camera captures rings of chemical precipitates and bacterial mats in one area, and, in another, shows scientists that gas (mainly CO_2) is rising from the bottom sediment. (Credit: Miquel/MEL)

The behaviour of polonium-210 in the ocean is different from that of lead-210, especially because of the former's higher affinity for organic matter. Thus, the nature and the fluctuations of the relative proportion of organic and inorganic fractions of sinking particles may have a greater influence on polonium-210 and lead-210 levels than the venting dynamics themselves.

The vertical fluxes of polonium-210 and lead-210 were also compared for the two sites. It is evident that the ranges of vertical particulate fluxes of these two radionuclides are on average higher in the vent zone. This is not due to high radionuclide concentrations in the settling particles near the vents, but rather to the higher particle flux in the vent zone. Clearly, productivity and resultant biogenic particle fallout are enhanced near the vents, which, in turn, increases the downward radionuclide flux. Therefore, vents can indirectly regulate the radionuclide flux by affecting the types and amounts of particles produced locally, for example in hydrothermal vent areas.

In the unique ecosystem of Milos, high sulfur-reducing and sulfur-oxidizing regimes are associated with the vents. Given the similar chemical characteristics of sulfur and polonium, such sulfur-rich vents might be expected to be highly enriched in polonium. This would be expected to lead to a potential enhancement of polonium levels in biota feeding in the adjacent areas.

In fact, bacterial flocs were abundant around the vents, and marine snails were often found to be grazing on the whitish bacterial mats that were present in the shallow waters. Polonium-210 and lead-210 were measured in the soft parts of these organisms to determine a possible enhancement of their respective levels, and to evaluate the resulting marine food-chain transfer of these important natural radionuclides.

Interestingly, the polonium-210 and lead-210 contents were similar to the median values based on several hundred data from the literature for non-vent organisms, and more specifically, they were lower than the concentration measured in deep water hydrothermal vent worms that had ingested sulfide mineral particles enriched in polonium-210. Thus, the ingestion of bacteria associated with the Milos mineral mats does not appear to have any major influence on the polonium-210 and lead-210 concentrations in these gastropods.

MEL studies described here represent the first attempts in the Mediterranean Sea to quantify vertical fluxes and the cycling of materials, and the natural radionuclides associated with shallow hydrothermal vent fields.

ASSESSING POLLUTION'S IMPACTS

MEL also actively participated in the European River-Ocean System (EROS 2000) programme, sponsored by the European Union MAST. It aimed to assess the impact of riverine and land-based sources of pollution in the ecosystems of the European shelf.

A sampling cruise on the French vessel *Marion Dufresne* was undertaken between the central portion of the northwestern Mediterranean basin and the region off the Ebro river in Spain. One objective was to measure sedimentation rates of biogenic (carbon, nitrogen, faecal pellets, intact organisms) and non-biogenic materials (radionuclides, rare earth and other elements) using both moored and floating sediment traps. Various water column measurements including suspended phytoplankton and zooplankton detritus were also made. This was done in order to relate sediment trap collections to open ocean processes that regulate the vertical flux and composition of particulate matter.

Using four automatic sediment traps moored in the open northwestern Mediterranean basin at depths from 200 to 2000 meters, and sampling at intervals of two weeks, the settling of a phytoplankton bloom to the deep-sea floor was detected during the month of May. Trap collections during this period consisted predominantly of two phytoplankton species. Most likely, the bloom, which utilized nutrients mixed upward by strong winds during mid-April, sedimented following nutrient depletion in the surface waters. Trap results demonstrated a rapid sinking (>140 meters/day) of carbon-rich particulate material throughout the water column down to the sea floor. During this "pulsed" sedimentation in May, particle flux at 200 meters was three to four times higher than in the preceding or following periods. This pulse became even more significant at depth, with particle fluxes six to ten times higher during the peak sedimentation period, and 10 to 30 times higher for carbon flux.

In the same samples, zooplankton faecal pellets, another important transport vehicle, were analysed by a computerized image analysis system. The total number of sedimenting pellets began to increase during the period of the maximum phytoplankton abundance in the water column, but was highest two weeks later when zooplankton biomass peaked. During that period, zooplankton faeces were found to contribute up to 25% to 40% of all sedimenting carbon. The delay between the maximum phytoplankton abundance and faecal matter sedimentation is related to the life-cycle of zooplankters (e.g., microscopic crustaceans, worms, and fish) and their interactions in the open sea food web.

The composition of rare earth elements (REE) — some of which are stable elements or analogues of key artificial radionuclides — was examined in the sinking particles from the four depth horizons measured with time-series sediment traps.

During the sedimentation pulse, particles from the deepest traps were characterized by REE patterns similar to those in the upper 200 meters. This indicated that little, if any, additional REE scavenging by particles occurred during the sedimentation event. In contrast, after the sedimentation pulse, particles from deep waters showed an enrichment of light-REE (LREE) relative to heavy-REE (HREE) and a positive cerium anomaly.

The differences in REE patterns in particles from the upper water column (200 meters) with those from depth (1000 and 2000 meters) during and following the sedimentation pulse were compared. The comparson indicated that time is a key factor in determining REE scavenging by sinking particles. This is particularly evident for the preferential scavenging of cerium, which is most pronounced in the finer, slowly sinking and presumably older particles. These findings are consistent with REE patterns in seawater from the northwestern Mediterranean, which show a strong negative cerium anomaly and gradual enrichment of REE with increasing atomic number. The enrichment of LREE relative to HREE in particles from deep waters results in either preferential scavenging of LREE on particles, analogous to the enrichment of cerium, or selective dissolution of HREE in association with particle remineralization processes, or both.

Knowledge gained about the marine behaviour of cerium, europium, and other particle-reactive REE has proven very useful in understanding the cycling and transport of analogue radionuclides, such as radiocerium and americium-241 in oceanic systems.

BENEFITS OF COOPERATION

Increased cooperation during the 1990s between the IAEA and the European Union in the area of applied marine research in the Mediterranean Sea has been mutually beneficial.

MEL researchers have profited by being able to work closely with scientists from other Member States in large-scale multi-disciplinary projects. This work has focused on marine problems of worldwide interest, and employed state-of-the-art oceanographic instrumentation and methodologies that are not normally available to MEL staff. This is particularly important regarding regular access to oceanographic vessels which are costly to rent or maintain. Free access to national research ships and their shipboard instrumentation has proved to be vital in carrying out the regular marine programmes of the IAEA in a cost-effective manner.

In return, MEL has placed its sophisticated array of nuclear and isotopic techniques at the disposal of other scientists in the programme to better understand the processes that are controlling the bio-geochemistry of key elements in the Mediterranean Sea.

The recent move of MEL to its new expanded facilities on the port of Monaco will allow the Laboratory to enhance its assistance to collaborating scientists in both the areas of analytical training and sample analyses. It is therefore hoped that such cooperative endeavours between the IAEA and the European Union will continue to grow well into the 21st century. Both organizations thus can better achieve their specific goals in striving to maintain the health of the oceans. ❑