GLOBAL CHANGE AND ECOSYSTEMS
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Coordinator: Hellenic Centre for Marine Research, Greece

Pressures on the Black Sea Environment: an Overview from IASON SSA (WP4)

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Nutrient Inputs from Land-based Sources

Based on available scientific assessments and findings of the Black Sea Transboundary Diagnostic Analysis, the overall yearly input of nutrients from human activity amounts to 647,000 tons of nitrogen and 50,500 tons of phosphorus. (Mee, L., Ed. (1998) Black Sea Pollution Assessment). These estimates included also the river discharges.

Tab.1 The Estimated Input of Total Nitrogen into the Black Sea

Country	Inputs, thousand tons per year			
	Domestic	Industrial	Riverine	Subtotal
Bulgaria	2.5	71.0	19.2	92.7
Georgia	0.9	44.4	132.0	177.3
Romania	9.5	31.0	36.3	78.6
Russian Federation	0.4	0	62.3	62.7
Turkey	1.6	0	0.0	1.6
Ukraine	5.4	0.6	32.0	38.0
Other countries				198.3
Subtotal	20.3	146.9	281.8	647.3

Tab.2 The Estimated Input of Total Phosphorus to the Black Sea

Country	Inputs , thousand tons per year			
	Domestic	Industrial	Riverine	Subtotal
Bulgaria	0.7	0.0	1.9	2.6
Georgia	0.3	0.3	11.111.6	
Romania	2.6	1.7	5.79.9	
Russian Federation	0.5	0.0	6.16.6	
Turkey	0.4	0	00.4	
Ukraine	2.2	0.1	3.6	5.9
Other countries				13.6
Subtotal	6.7	2.0	28.2	50.5

The input of nutrients and other pollutants from land-based sources as reflected in sets of data presented for the period 1996-2000 shows a steady decline in the discharges of wastewaters and individual pollutants and nutrients in the territorial waters of the Black Sea countries. The reasons for such reduction might be attributed partially to the economic difficulties in those countries with transitional economies. At the same time, the Black Sea coastal states made profound progress in developing and enforcing legislative and regulatory tools.

Priority Point Sources of Pollution

The Black Sea Transboundary Diagnostic Analysis, 1997, as well as the National Black Sea Environmental Studies (Turkey, 1998, Ukraine, 1998) specifically studied and ranked pressures on the Black Sea environment from land-based sources and indicated the most dangerous of them, the so called "hot spots" that required particular attention and urgent actions.

The total number of priority point sources of pollution in the Black Sea coastal state was 49. In all the Black Sea coastal states, industries are, as a rule, connected to the municipal wastewater treatment systems, therefore mixed discharges from municipal sources that enter the marine environment are typical for the region. For this reason, the priority point sources of pollution, sometimes referred as "hot spots" and described in Black Sea Transboundary Diagnostic Analysis, are presumably presented by wastewater treatment plants or port treatment facilities. As follows from the national reporting the loads of nitrogen, phosphorus, suspended solid, and BOD decreased or were stabilized in 1996-2002.

In **Bulgaria** nine priority point pollution sources were identified as follows:

Name	Type	Nature of Investment
Rosenets	Oil Terminal	WWTP Construction
Varna	Port	WWTP Extension
Burgas	Port	WWTP Extension
Asparouhovo	Domestic	WWTP Extension
Balchik	Domestic	WWTP Extension
Sodi	Soda Ash	WWTP Construction
Tsarevo	Domestic	WWTP Extension
Neftochim	Refinery	WWTP Construction
Sozopol	Domestic	WWTP Extension

Georgia

The decreasing trends in pollution loads from "hot spots" also reflects an improvement of the national regulatory and enforcement mechanisms.

Name	Type	Nature of Investment
Kutaisi	Domestic	WWTP Reconstruction
Batumi	Domestic	WWTP Reconstruction
Chiatura	Manganese	WWTP Construction
Poti	Domestic	WWTP Reconstruction
Zestaponi	Metallurgy	WWTP Construction
Tskhaltubo	Domestic	WWTP Reconstruction
Zugdidi	Domestic	WWTP Reconstruction

In **Romania** fluvial discharges, municipal waste waters discharges, industrial wastewater discharges, maritime traffic and offshore oil activities influence the water quality and environment of the Romanian coastal waters. Decreasing trends are evident in the overall loads of nutrients, pollutants and concentrations of these substances in the Romania coastal waters, following rehabilitation and modernization of WWTP. None of the direct industrial discharges or untreated discharges enters into Romanian marine waters.

Name	Type	Nature of Investment
Fertilchim	Fertilizer	WWTP Rehabilitation
Petromedia	Petrochemistry	WWTP Rehabilitation
Constanta North	Domestic	WWTP Extension
Eforie South	Domestic	WWTP Extension
Mangalia	Domestic	WWTP Rehabilitation
Constanta South	Domestic	WWTP Rehabilitation

In the Russian Federation five " hot spots " were reported for the Black Sea and three "hot spots for the Sea of Azov, namely:

Name	Type	Nature of Investment
Rostov-on-Don	Domestic	WWTP Extension
Taganrog	Domestic	WWTP Extension
Sheskhoris	Oil	WWTP Rehabilitation
Azov	Domestic	WWTP Extension
Tuapse	Port	WWTP Construction
Anapa	Domestic	WWTP Extension
Gelendzhik	Domestic	WWTP Extension
Dzhoubga	Domestic	WWTP Extension

The overall reduction of inputs of total nitrogen, phosphorus, BOD, suspended solids and detergents was reported for the wastewater treatment plants in Anapa and Drouzhba. The loads of the same substances from the wastewater treatment plant in Gelendzhik increased slightly. A rising trend was also reported for ballast water treatment plant "Sheskharis" in Novorossiysk. No impacts were observed in the vicinity of the "hot spots" except for the ballast waters treatment plant in Novorossiysk.

Turkey

Name	Type	Nature of Investment
KBI Samsun	Copper	WWTP Rehabilitation
TUGSAS Samsun	Fertilizer	WWTP Rehabilitation
Trabzon	Domestic	WWTP Construction
KBI Murgul	Copper	WWTP Rehabilitation
Samsun	Domestic	WWTP Construction
Zonguldak	Domestic	WWTP and Sewerage
Giresun	Domestic	WWTP Construction
Ordu	Domestic	WWTP Construction
Bafra	Domestic	WWTP Construction

Eregli	Domestic	WWTP Construction

A number of projects for the improvement or construction of wastewater treatment facilities are continuing or are in the planning stage.

In Ukraine ten hot spots were identified including 7 municipal water treatment plants, two industrial and one port waste water treatment facilities, namely:

Name	Type	Nature of Investment
Pivdenni	Domestic	WWTP Construction
Pivnichni	Domestic	WWTP Construction
Balaklava	Domestic	WWTP Construction
Yevpatoria	Domestic	WWTP Construction
Sevastopol	Domestic	WWTP Construction
Yalta	Domestic	WWTP Construction
Gurzuf	Domestic	WWTP Construction
Kamish Burunski	Iron ore	WWTP Construction
Illichevsk	Port	WWTP Construction
Krasnoperekopsk	Brom	WWTP Construction

The operation of existing wastewater treatment facilities improved or stabilized in 1996 – 2000 resulting in decreasing trends of pollutant loads for most of the indicated “hot spots” in Ukraine. The concentrations of monitored pollutants in the impact areas did not show any meaningful trend in most cases and were in compliance with national water quality standards.

Inputs from Diffuse Sources of Pollution.

The greatest sources of diffuse pollutions are related to agricultural activities, to households not connected to sewer systems, and to atmospheric depositions. Inadequate land use and the excessive application of mineral and organic fertilizers result in high nutrient inputs into the rivers and ultimately into the Black Sea.

The quantities of inorganic fertilizers used in those Black Sea states with transitional economies was drastically reduced. Additional improvement arises from the enforcement of the nitrates directive in the EU countries and from the transposition of this directive in the accession countries. As a result, improvement of water quality the in Bulgarian and Romanian coastal waters were reported.

There are estimates that atmospheric inputs of total nitrogen to the Black Sea amount to 400 thousand tons per year and is comparable in magnitude to the total input of this nutrient from rivers, domestic and industrial sources (647 thousand tons per year). If these estimates are correct, the air emissions are significant sources of nitrogen input into the marine environment. Adequate policies and measures have to be introduced by the Black Sea coastal states in order to control emission sources.

Inputs from Other Pollution Sources.

The intensive marine traffic and offshore exploration of oil and gas constitute additional sources of marine pollution. Incidental oil spills pose particularly high risks for the Black Sea due to its isolated position. The general trend indicates a reduction of incidental oil spills. At the same time, an expected increase of oil transport will poses an additional threat from oil pollution.

Dumping of the dredged spoils, originating from routine operations in harbors, creates additional sources of trace metals and oil pollution.. The concentrations of these pollutants at dumping sites could exceed the background values. The current number of dumping sites for dredged spoils is about 12-15 and will grow with increasing intensity of marine traffic. The volume of dredged spoils dumped exceeds 2000 th.m3 per year.

Pollution Levels

The Transboundary Diagnostic Analysis (1995) and a number of other reports that focused on the issues related to the state of the environment of the Black Seas ranked the environmental problems as follows:

- eutrophication;
- oil pollution;
- reduction of fish stocks;
- invasion of exotic species;

Excessive input of nutrients provoked the development of the eutrophication phenomena that in turn affected Black Sea biota and biological resources. Black Sea new comers favored the eutrophic conditions and their populations, in the absence of natural enemies, greatly multiplied. Recent data shows some lessening of past ecological problems although the situation is still unstable. An irreversible collapse of the Black Sea ecosystem may result with additional pressures.

Nutrients.

The elevated concentrations of nutrients are recognized as the main cause of eutrophication in the Black Sea and cause severe environmental pressure on the Black Sea ecosystem. During the last decade, the available scientific and monitoring data provide evidence of an overall reduction of nutrients in the marine environment. National monitoring systems reported lower concentrations of nutrients for impact areas in the vicinity of hot spots in the national coastal territorial waters of the Black Sea costal states.

For the coastal waters of Bulgaria there is no evidence of increasing pollution over the few past years.

In Romanian coastal waters a slight decrease in the concentrations of nitrogen was supported by the analysis of valid monitoring data. It is obvious that the more likely causes of the decrease are the low application of fertilizers and the effective enforcement of the EU Nitrate Directive in the countries of the Danube basin.

Fig. 1 Mean Annual Concentrations and Fluxes of Nutrients in the transitional waters of Romania, 1988-2001. Sulina (NIMRD data)

(Mihnea, R., Cociasu, A.. Romania. National reporting to the Black Sea Commission for the years 1999-2000: Pollution Monitoring and Assessment)

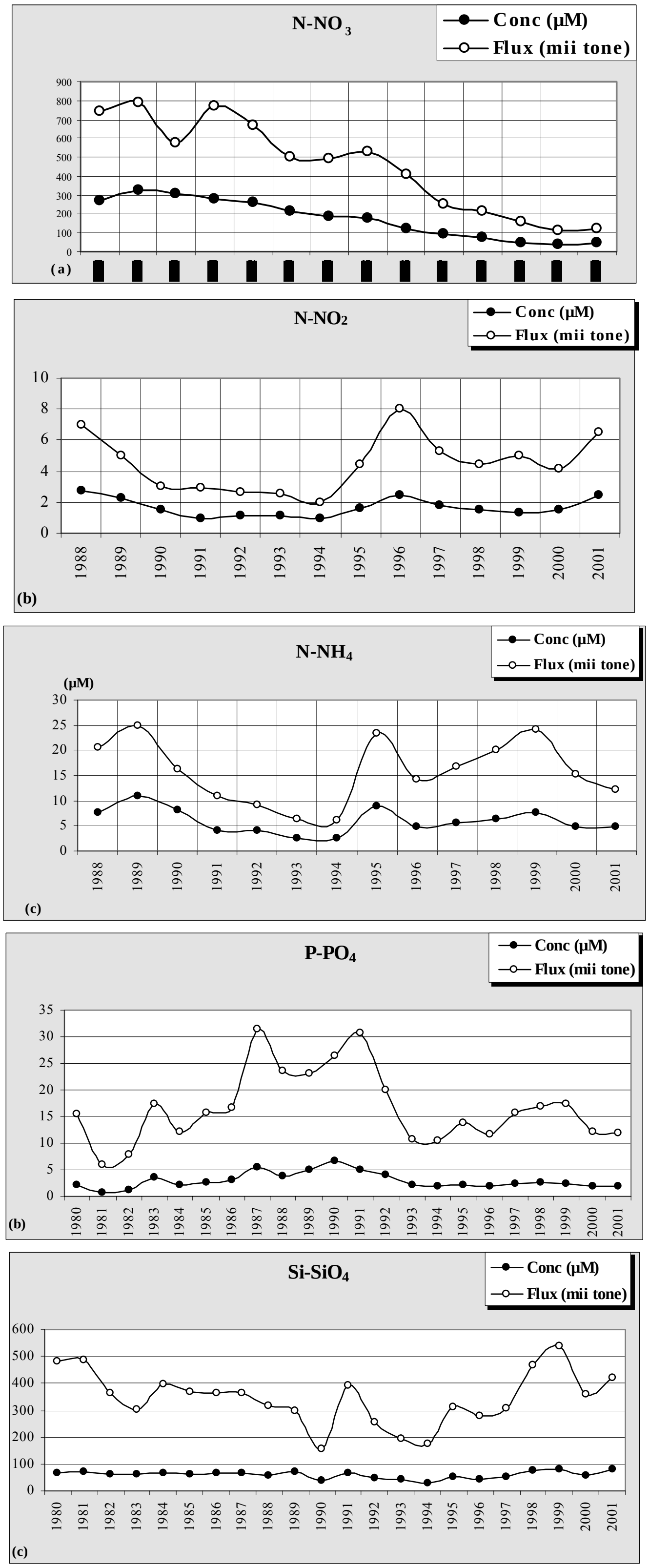
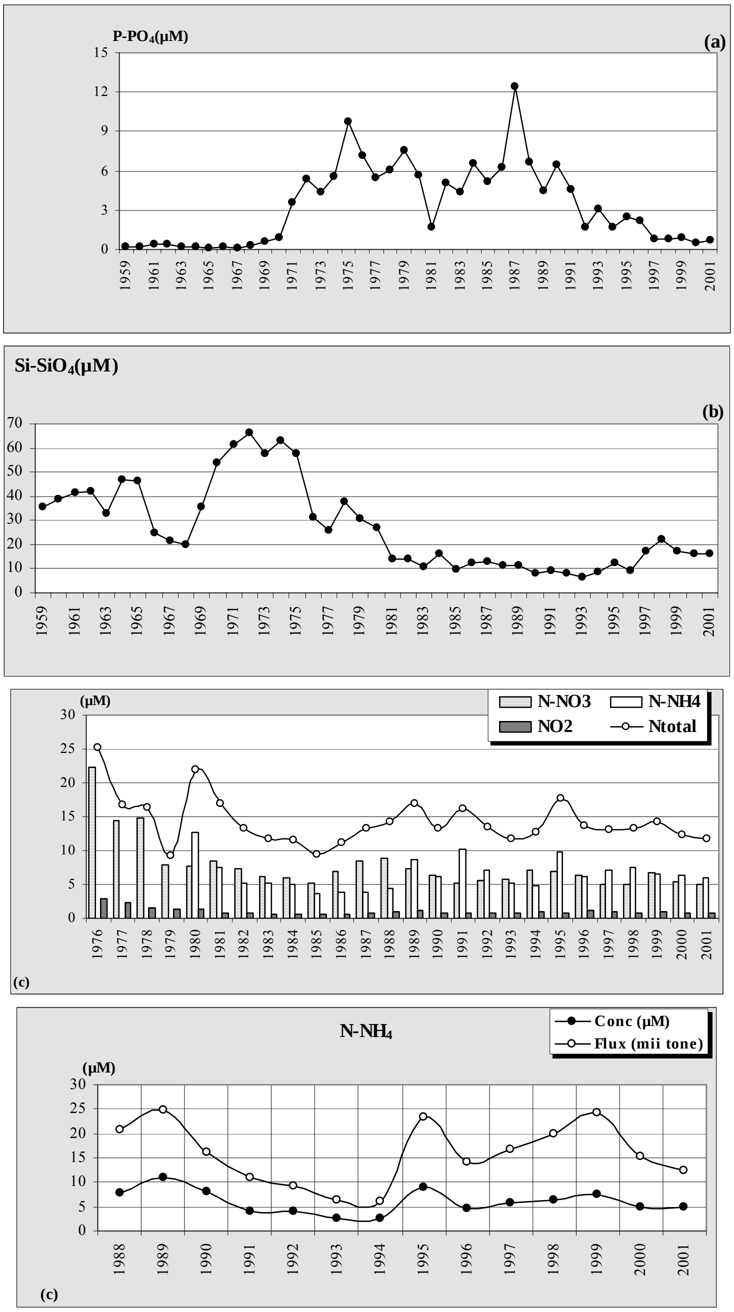


Fig.2 Mean Annual Concentrations and Fluxes of Nutrients in the coastal waters of Romania, Constanta ,1988-2001. (NIMRD data)

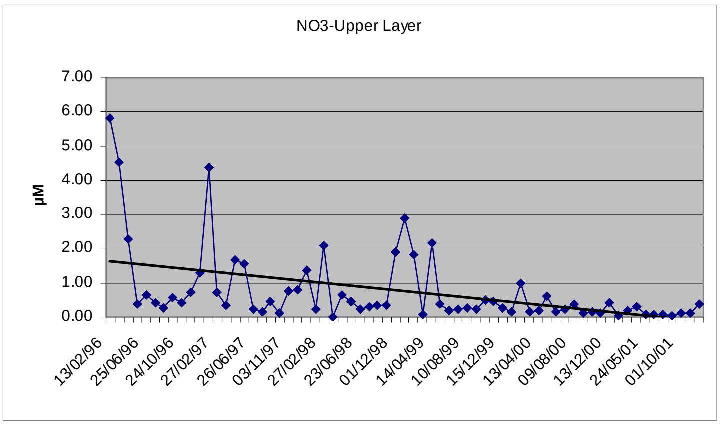
(Mihnea, R., Cociasu, A.. Romania. National reporting to the Black Sea Commission for the years 1999-2000: Pollution Monitoring and Assessment)

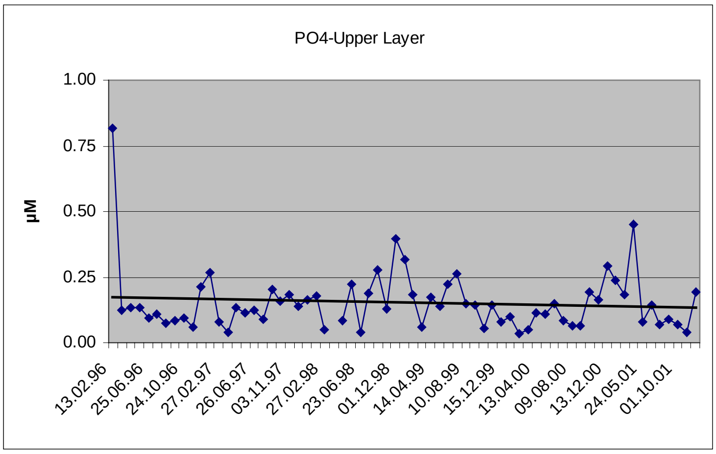


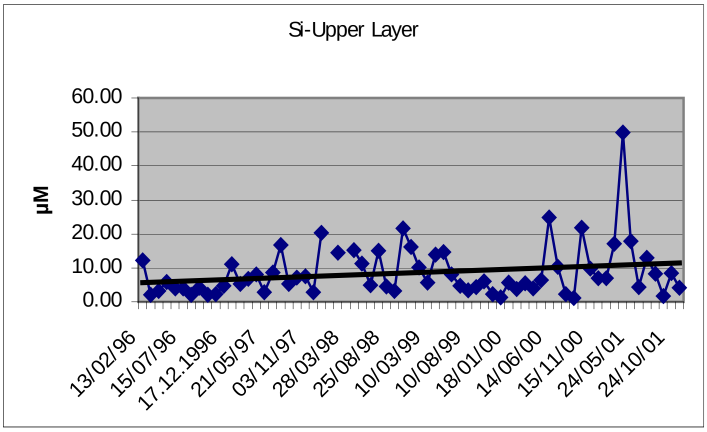
In the Russian Federation no increase of dissolved inorganic nitrogen and phosphorus were observed and reported for its territorial waters. Compared to the data before 1996, no increase in the pollution of coastal waters was observed in these years.

The data from Turkish confirm a steady decline of nitrogen at the entrance of Bosphorus while the concentrations of phosphorus decreased somewhat less. As a positive signal of the shift to recovery, a slight increase of silicates was reported.

Fig 3 Concentrations of Nutrients in the Territorial Waters of Turkey
(Entrance to the Bosphosrus strait), 1996-2001



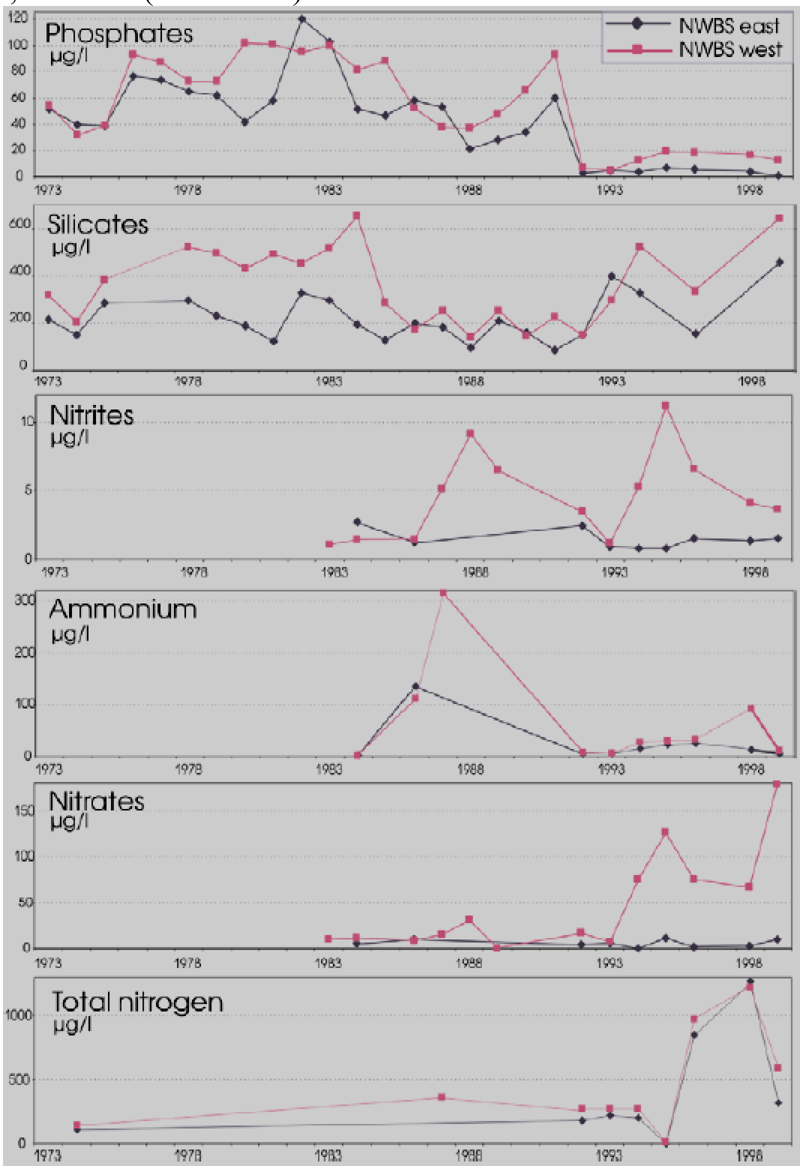




Considering that NW part of the Black Sea shelf is affected by the some of the largest European rivers such as the Danube and Dnipro, and by some of the smaller but equally important rivers such as the Dnister and Southern Bug, the reduction of nutrient fluxes is not so obvious in this area. Data of the Ukrainian Center of the Sea Ecology shows that during the past couple years some increased levels of nitrogen and phosphorus, clearly connected with high water flows from the rivers, were observed. In addition, the very hot summers strongly influenced the processes of mobilization of nitrogen and phosphorus accumulated in the bottom sediment and increased biosedimentation rates. An increase of nitrogen, organic matter, and silicates were reported for the last two years when water levels were high in the rivers discharging into the Black Sea.

Fig.4 Average Annual Nutrient Concentrations in the Surface Layer of the North Western Shelf of the Black Sea (Ukrainian territorial sea), 1959-2001

(Mikhailov, V. et al. (1996-2000). State of the Environment of the Black Sea. Ukraine)



One of the most negative consequences of the elevated inputs of nutrients and the subsequent eutrophication is a disturbance of the oxygen regime with further hypoxia and anoxia. Development of hypoxia phenomenon, the level of eutrophication of water, river discharge, and hydrodynamic, hydro chemical, hydro biological, and hydro-meteorological conditions, as well as the physical and chemical processes in sediments etc. are all interrelated. Beginning in the 70's, hypoxia developed annually in the northwestern shelf of the Black Sea. It usually covered progressively larger areas though there are fluctuations connected with flow of the rivers and climatic factors. In the year 2000, the total area exposed to hypoxia reached 14 thousand km2 (38 % of the northwestern shelf). This is three times less when compared to 1983 figure - when more than 50 % of the northwestern shelf of the Black Sea was exposed to hypoxia.

Biological Oxygen Demand, used to monitor the input of organic substances in the Black Sea, had been reduced or stabilized in the period between 1996 – 2001. However, it may increase significantly in recreational waters in high seasons as was reported for some countries.

The observed trends, derived from reported national sources, were further supported by the data from the NATO project for the Black Sea open sea area.

Available historical scientific data show that the two to three fold increase in nitrate concentrations and the shifting maximum nitrate concentrations from 15.7-15.9 to 15.3-15.5 occurred between 1969 and 1991. This was due to structural changes of the phytoplankton community and to the dominating nitrogen and silicate cycles in the upper layer of the Black Sea. A scientific assumption explains that the variation of basic chemical properties in the water column of the Black Sea is caused by this increase in nutrient inputs due to a more intense flux of particulate organic matter to the depth thereby causing a temporal increase of nitrate fluxes from late 1960s to the early 1990s. As most of the sinking particulate organic matter is oxidized in the oxycline, the temporal changes seem to be more profound at the upper boundary of the oxic/anoxic transition zone. Furthermore, it has been estimated that the residence time of nitrate in the layer of the main pycnocline is fairly short and small changes in the fluxes could result in substantial changes in nitrate concentrations over a period of years. Phosphate concentrations were slightly lower in the upper layer than in the deeper layer resulting in a shifting from a nitrogen limitation of primary production to a phosphorus limitation in 1990s.

Assessment of the temporal variations of nutrients in recent years showed that depletion of NO_3, occurred after mid 1990s and that NO_3+NO_2 and PO_4 reached their lowest levels in 2000-2001. This followed an increase of both NO_3+NO_2 and PO_4 in the first half of 1990s with stronger increase for in NO_3+NO_2 and reduction of in (NO_3+NO_2)/PO_4 ratio. Thus, the PO_4 and nitrate stocks of this layer dropped to its lowest level of the last decade.

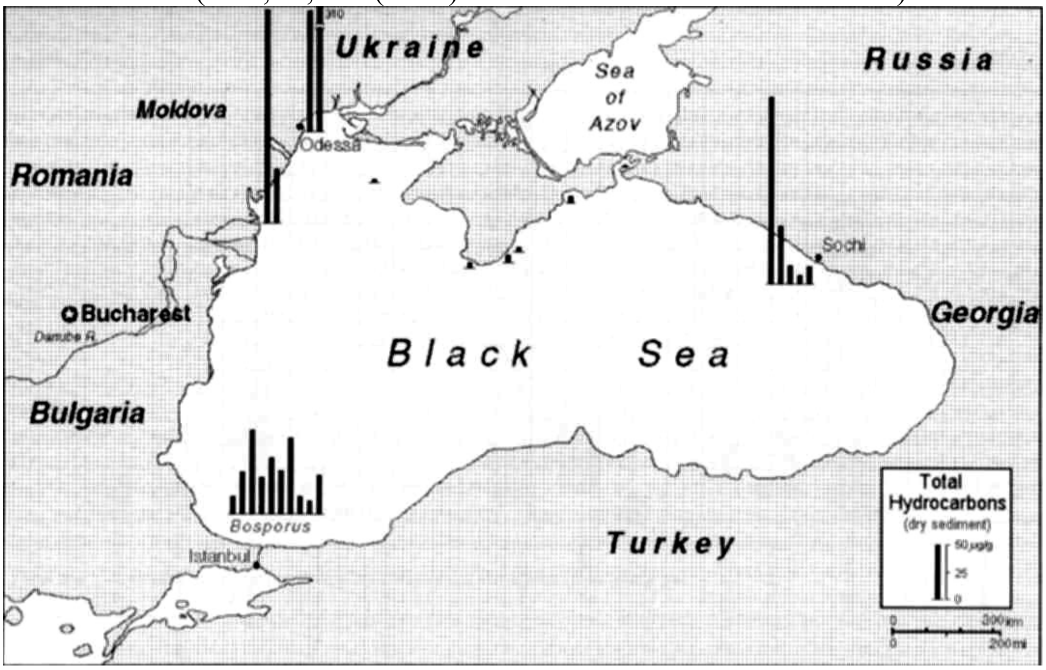
Trace Metals.

Quite a large amount of reliable data has been gathered on the concentration of heavy metals in the Black Sea. This data has been analyzed in such a manner as to distinguish natural sources of metals from anthropogenic (human-induced) ones. From this analysis, it is quite apparent that the Black Sea is not generally polluted by heavy metals. There are some areas where elevated concentrations may occur (near "industrial hot spots") and it will be important to complete a more detailed survey of coastal sites.

Oil Pollution.

Currently overall decreasing trends are reported for oil related pollution in marine waters of all Black Sea coastal states.

Fig 5. Concentrations of Hydrocarbons in the Bottom Sediments in the Black Sea (Mee, L., Ed. (1998). Black Sea Pollution Assessment)



In harbors and near the petrochemical plants pollution levels are especially higher. Oil pollution is a concern for the Black Sea environment in particular due to increasing risk of accidental spills that may result from the expected twofold increase of oil transit by tankers. It should also be noted that an increase of oil transportation would proportionally enhance the uncontrolled flow of isolated ballast into the central part of the sea, thus bringing a threat of different exotic species and pathogenic organisms to the Black Sea ecosystem, and probably additional pollution.

Persistent organic contaminants (polychlorinated biphenyls and organochlorinated pesticides)

The concentrations of PCBs in bottom sediments are low in comparison with other inner seas of Europe. The highest concentration of PCBs (24.3 ng/g) was found in a sample from the Constanta Port harbor. Elevated concentrations of lindane and other isomers of HCH along Romanian and Ukraine coasts influenced by the Danube River indicate the application of this pesticide in the Danube River basin. Low ratios of DDT and DDD along with their elevated concentrations in bottom sediments (especially in sediments in the Odesa area and areas influenced by Danube) indicate recent inputs of this pesticide. Considering the existing ban on application of DDT in all Black Sea coastal states, possible sources of this pollutant could be inappropriate storage of accumulated expired pesticides.

Fig. 6 Concentrations of Polychlorinated Byphenils in the Bottom Sediments of the Black Sea, 1995
(Mee, L., Ed. (1998). Black Sea Pollution Assessment.)

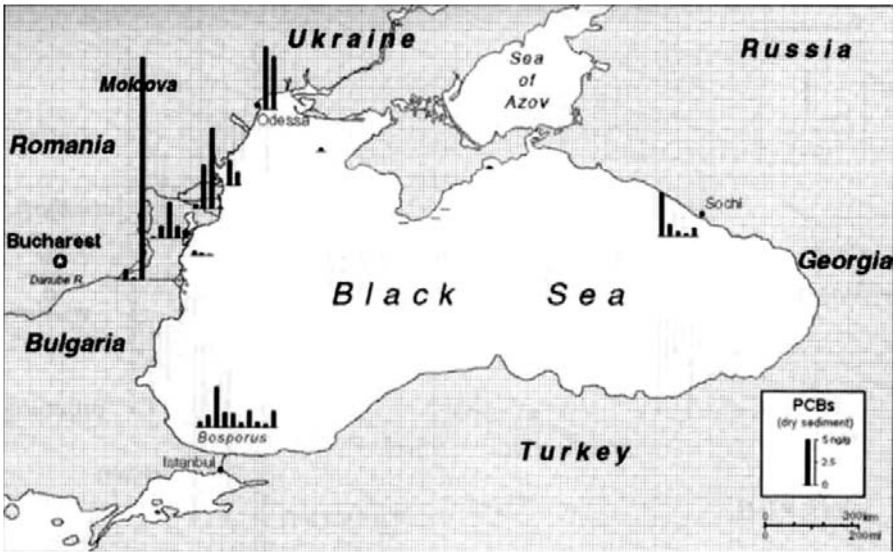


Fig. 7 Concentrations of Lindane and HCH Isomers in Bottom Sediments of the Black Sea , 1995
(Mee, L., Ed. (1998). Black Sea Pollution Assessment)

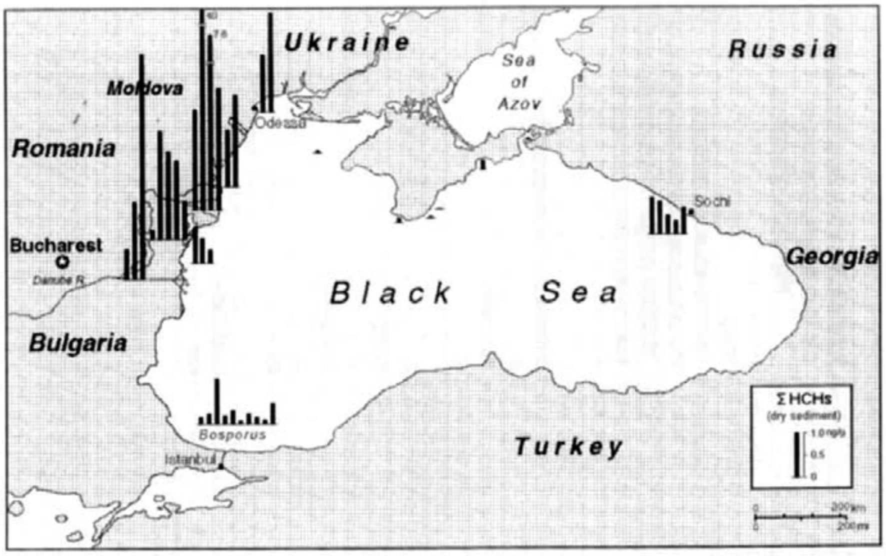
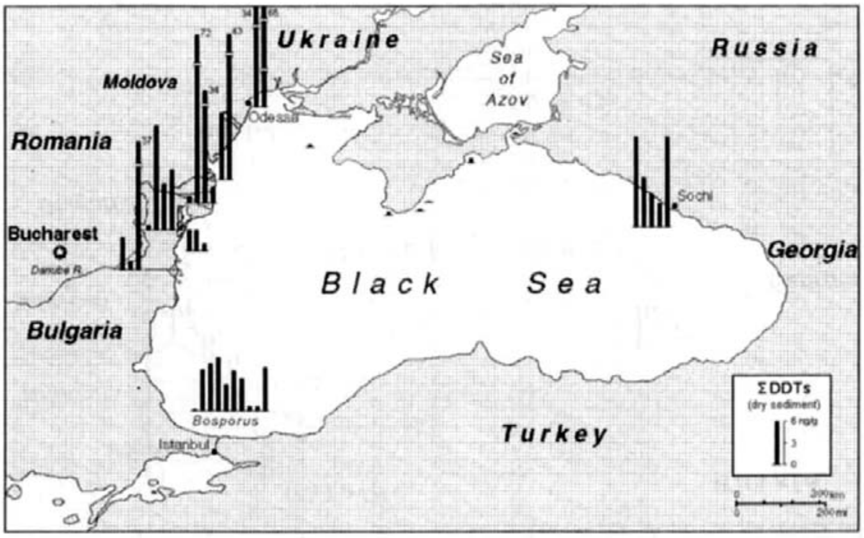


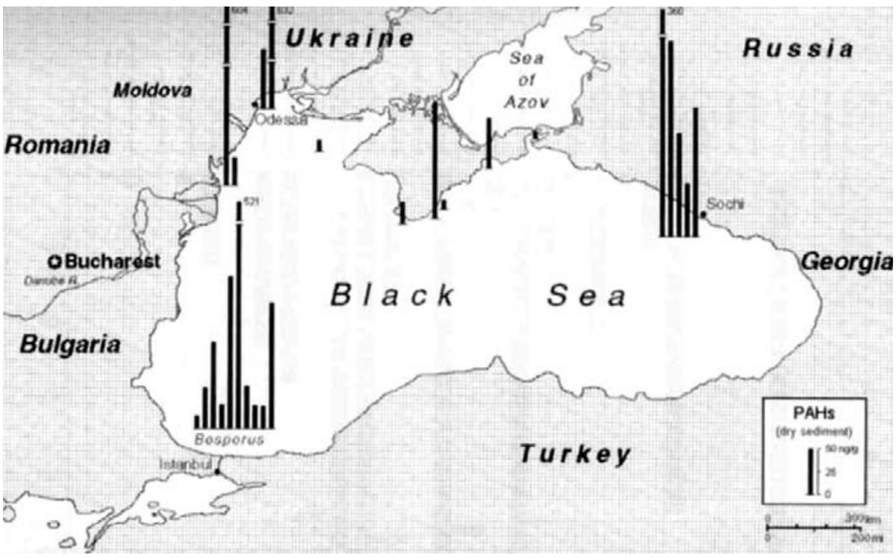
Fig. 8 Concentrations of DDT in Bottom Sediments of the Black Sea, 1995
[Mee, L., Ed. (1998). Black Sea Pollution Assessment]



Polyaromatic Hydrocarbons

Polyaromatic hydrocarbons (PAHs) constitute a critical part of oil pollution having proven carcinogenic and mutagenic effects. In bottom sediments, the highest levels were detected near Odessa, the Danube coastline and in Socchi.

Fig. 9 Concentrations of Polyaromatic Hydrocarbons in the Bottom Sediments of the Black Sea, 1995 [Mee, L., Ed. (1998). Black Sea Pollution Assessment]



This pollution in mostly related with port activities. In the ports with long histories of operation, the concentrations of polyaromatic hydrocarbons could reach rather high levels. The pollution of mussels by oil components is rather high. The elevated concentrations of oil were revealed in the Phylopora from Zernov's field.

Radionuclides.

Levels and trends of radionuclide pollution do not present a threat to human health and biota. Since Chernobyl accident, the radioactivity is gradually decreasing and currently has almost reached the previous values although, in general, the background values in the Black Sea are twice as high compared to the Mediterranean. The preliminary results of the "Marine Environmental Assessment of the Black Sea Region" IAEA project, show that radioactivity levels have no significance in terms of human health and environmental safety.

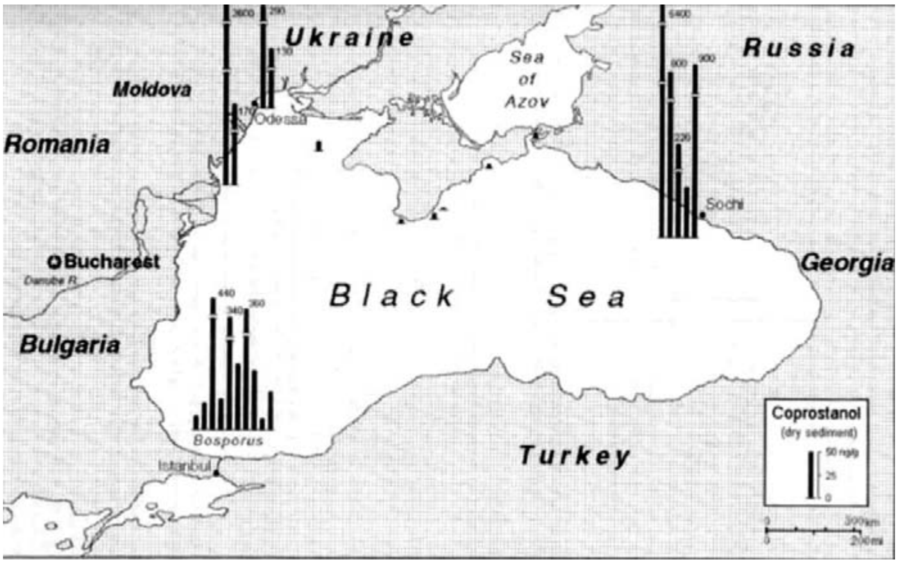
Litter.

The littering of beaches and ultimately marine waters is illegal in all Black Sea Costal States. Nevertheless, in some cases, due to a poorly developed tourist infrastructure and the illegal disposal from marine transport and households, the problem exists. The scope of the problem and an assessment of the impact of litter on marine life were never studied.

Microbiological pollution

Microbiological pollution of bathing waters creates an imminent threat to human health. Echerihia colli, Streptococus facaelis, and other pathogenic bacteria are widely used for assessment of microbiological pollution. From the chemical point of view, corpostanol is one of the important indicators of faecal pollution in bottom sediments. The highest levels of this pollution were found near the Danube delta and in Sochi in 1995 (IAEA, 1995).

Fig. 10 Concentrations of Coprostanol, an Indicator of Faecal Pollution in the Bottom Sediments of the Black Sea [Mee, L., Ed. (1998). Black Sea Pollution Assessment]



Overall improvement in the conditions of bathing waters is progressing in the Black Sea countries, especially in the accession countries. In Bulgaria none of beaches were closed due to chemical or microbiological pollution in the period from 1996-2001. In Romania the EU Directive for Bathing Waters is being transposed. Evident improvement of bathing water quality was observed in the period from 1996-2000. Turkey promotes the Blue Flag Program for beaches.

Impact on biology and biodiversity

The water layer supporting biological life and the biodiversity of species is so thin and fragile that the effects of pollution or destruction of habitats and landscape result in the ecological changes of great economic and social impacts. Those areas affected, depending on exploitation or use of living marine resources or their aesthetic values include fisheries, tourism, and other sectors.

Bacteria of the Black Sea

As Black Sea eutrophication evolved, the number of saprophytic bacterial plankton sharply increased particularly the cocci and bacilli. This is a result of the higher levels of dissolved and particulate organic matter that is a source for nutrition of saprophytic microorganisms. Bacteria populations, particularly pathogenic organisms have reacted to changing marine conditions particularly in the increase of organic matter in the water column and in bottom sediments with a sharp increase in numbers and diversity

Phytoplankton and Zooplankton

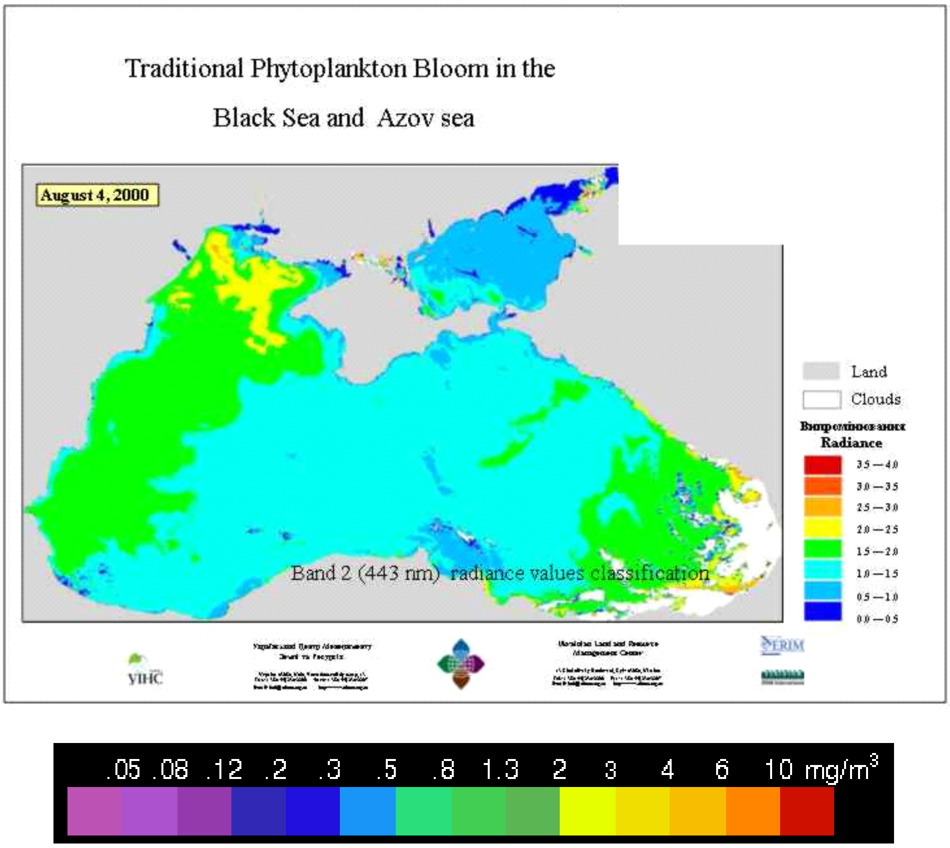
The structure and abundance of the phytoplankton species were heavily affected by eutrophication that has been progressively developing from the late seventies to the nineties when, after the collapse of the former Soviet Union, there was pressure against polluting and the inputs of nutrients were reduced due to the economic crisis.

Eutrophication, pollution, and climatic changes affected the phytoplankton communities and resulted in a number of processes with very adverse effects on the Black Sea ecosystem.

The main manifestation of these changes in the phytoplankton communities include:

- Increase in the total biomass
- More extensive and more regular alga blooms
- Increase in the number of mass species
- Decline in the population of previously abundant species
- Growth in numbers of species of brackish and freshwater origin
- Changes in the correlation between different taxa of alga

Fig. 11 Traditional Phytoplankton Bloom in the Black Sea and Azov Sea



Zooplankton

Changes in phytoplankton lead to the corresponding changes in zooplankton. Some zooplankton species that were abundant before the 1970s have become sparse or have even disappeared. As a general rule, large species of crustacean zooplankton were replaced by smaller species. Another drastic change in the zooplankton communities was an outburst in the number of gelatinous species, including the largest Black Sea jellyfish *Rizzhosstoma pulmo*, and the moon jellyfish - *Aurelia aurita.*

The invasion of the exotic ctenophore - *Mnemiopsis leidyi* and its outbreak in the late 1980s - is another example of a gelatinous plankton outburst in eutrophic marine waters. The highest Mnemipssis biomass was recorded also for the northwestern shelf of the Black Sea. The new comer - *Beroye ovata* - that feeds on *Mnemipsis leidyi* seems to be a useful exotic species able to control the development of the Mnemiopsis. The data from Romania and the Russian Federation show a significant decline in the abundance of the predator Mnemiopsis.

Benthic Communities

Benthic Macroalgae.

Since the 1970s, insufficient insolation became a limiting factor for macro algae growth at a depth of 25 m and more in the offshore areas, and at a depth of 8m and more in the coastal zone. The sharp reduction of the famous Zernov's *Phyllophora* field (a submerged meadow of algae harvested for agraroid), located in the central part of the northwestern shelf occurred.

The Black Sea brown alga - *Cystoseira barbata* - that inhabits rocky coasts, began disappearing from the coastal waters of Ukraine and Romanian in the 1980s. This large perennial alga, unable to endure the eutrophic costal waters, was replaced by filamentous green and red algae. Due to a recent reduction of pollution pressures on coastal waters, a reoccurrence of the *Cystoseira barbata* was reported.

Benthic Animals

The development of large-scale eutrophic phenomena and the resulting depletion of oxygen occurred due to decay of massive quantities of dead algae and due to sedimentation on benthic communities. This provoked frequent occurrences of hypoxic and anoxic conditions at the Black Sea shelf. First observed in 1973, oxygen poor zones were frequently observed every year in summer and autumn. The mass mortality of benthic animals was caused by this phenomenon. In recent years, in many areas the biological diversity of benthic communities showed an increase and the quantitative structure recovered slightly..

Ichthyofauna

The Black Sea ichthyofauna is considered rather poor compared to that in the other European Seas. The major changes occurred in the fish species composition, including the number of fish in specific populations. For many fish species, these changes were so drastic that their commercial value was completely lost and they dwell in the Black Sea only as representatives of the species.

There are a few reasons for the decline of fish stocks and for the structural changes of ichthyophauna. Over-exploitation has affected fish stocks. Some valuable species have practically disappeared. Of the 26 commercial fish species in the period from 1960 to1970, only five were left by 1980.

Key Commercial Conservation Status

Pelagic fishes

Sprat - the sprat stock is rather high, especially in the northwestern part of the Black Sea. In 2001, both the average number and the abundance of sprat eggs have been higher than in the previous years in Romanian waters; and the situation was even better concerning larva, both the distribution and the average number.

Anchovies – some recovery of sprat stocks occurred but was restricted by uncontrolled exploitation. In the period analyzed, the abundance of eggs larva and juveniles was increasing. The biomass of the spawning fishes that reached 20000 tons, reflects conditions of recovery of the anchovy stocks.

Horse mackerel – some recovery of stocks occurs; but the situation would improve if Mnemiopsis leydyi could be controlled by its predator. In Romanian waters the abundance of eggs has decreased every year. The horse mackerel juveniles were recorded in the higher abundance in September 1999. The year 2001 was an exceptional year for the horse mackerel juveniles, it

appeared in a majority of the samples. The horse mackerel catch has decreased from a few hundred tons in 1982, to 1-3 tons in 1999. This increased to 17 tons in 2000-2001 in Romania.
Demersal fishes

Turbot stocks are severely depleted due to the poor environmental quality of shelf waters that prevents recovery of these species, unsatisfactory fishing practices (fishing gears) and illegal fishing. Until a regional estimate of the actual state of the stock, turbot fishing, at least in the spawning period, should be prohibited.

Spiny dogfish stock has declined in most areas, although relatively immune to Mnemiopsis leydyi. Commercial fishing should not exceed a sustainable level, and the migration routes should be protected.

Anadroumous fish
Sturgeon – some species, such as the giant sturgeon, are endangered, while others are depleted. Their stocks are maintained due to the operation of hatcheries especially where spawning rivers are unusable.

Shad stocks are recovering. The shad population depends on the water quality in the Danube River. In the Romanian waters, there is an increasing trend for the number of the specimens with lengths of over 100 mm. This indicates good conditions for these species although the catches have decreased from over 1000 tons in the years 1986 and 1987, to 45 tons in 1997 and 22 tons in the year 2000.

Pomatomus saltatrix (blue fish) stock, again recorded in the Romanian waters from 1994, has a tendency toward population recovery; its reappearance in the northwest part of the Black Sea is related to the improvement of the quality of environmental conditions in this area.

Exotic species
Intensive marine traffic results in large quantities of discharged ballast waters and the consequent introduction of alien species that compete for food with the indigenous species or, in the absence of the natural enemies, develop an intensive biomass.

Among the newly introduced exotic species, 34 % have been imported for aquaculture and 66 % have entered the Black Sea as pelagic larvae in ballast waters and/or fouling organisms on ship hulls. The number of introduced species is continuously increasing

Key habitats.

Fish nursery and spawning grounds.

The commercial stocks of fish strongly depends upon availability of wintering and forage resources and undisturbed spawning and nursery grounds. The wintering and main feeding areas of the Black Sea commercial fish species depends upon particular fish species, nevertheless the Black Sea shelf and in particular Ukrainian Black Sea shelf is of the greatest value.

The quality of nursery and spawning grounds plays a crucial role in the reproduction of fish stocks. Construction of dams and hydraulic structures kept the anadromous species like sturgeons from their natural spawning grounds in the estuaries of Danube and Dnipro Rivers. Therefore, these anadromous fish species currently depend on industrial breeding. Fishing activities during spawning period are strictly prohibited in all Black Sea states. However, illegal fishing is common in the current economic conditions and damages the success of breeding efforts, in particular in cases of sturgeons and turbots. Most of them need special protection and remedial measures in order safeguard the successful replenishment of fish stocks in the Black Sea.

Protected Areas.

An exhaustive description of the protected areas in the Black Sea coastal states is given in the “Biological Diversity in the Black Sea. A Study of Decline and Change”, 1997. A large number of wetlands with rich biodiversity and a recognized value for migratory waterfowls continue to be the focus of environmental conservation. The coastal wetlands occupy large areas and serve as a buffer zone between huge catchment areas and the Black Sea itself. The Black Sea wetlands include marsh reeds, forest dominated river flood plains, inland lakes and lagoons, deltas, marine lagoons, etc.

Conclusions.

Owing to natural factors, the diversity of species of Black Sea fauna is approximately three times lower when compared with that of the Mediterranean. Specific features of the Black Sea make it very vulnerable to disturbances of its environment and ecosystems.

Eutrophication, pollution, and irresponsible fishing resulted in an overall decline of: biological resources, the diversity of species and landscapes, and of the aesthetic and recreational values of the Black Sea, thereby bringing its ecosystems to the edge of collapse.

National efforts and regional - international cooperation in the framework of the Convention on the Protection of the Black Sea Against Pollution expressed in the concerted actions of the Strategic Action Plan for Rehabilitation and Protection of the Black Sea brought the first signs of recovery to the Black Sea.

These optimistic signals shall not hinder the pursuit of existing problems:

- The above changes are still in the early stages, are unstable and still far from the strategic target: that is to bring the conditions of the environment back to those that were observed in the 1960s. With any additional pressure, they can revert and the environment of the Black Sea would be endangered.
- The Black Sea is still a sea in trouble. Algae blooms are still heavy, pollution, although localized, affects biological communities. Fish stocks of commercially valuable species, such as sturgeons and turbots, suffer from illegal fishing, pollution and destruction of their habitats.
- The process of the recovery of the Black Sea will take a long time and will require implementation of all measures provisioned in the Black Sea Strategic Action Plan .
- There are gaps and lack of scientific knowledge and information on many processes and phenomena that are needed for policy and decision-making.
- The sustainable development of societies and the well being of the coastal population shall be priorities for the governments of the Black Sea Coastal States.

Source of information:

The Black Sea Commission Report "State of the Environment of the Black Sea: Pressures and trends 1996-2000", Istanbul 2002.

http://www.blacksea-commission.org/

Pollution in the Mediterranean Sea: an overview from IASON SSA

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⇒ Introduction

The IASON (International Action for Sustainability of the Mediterranean and Black Sea EnvirOnmeNt) Specific Support Action, among other issues, aims at identifying anthropogenic pressures exerted upon the functioning of the ecosystems of the two seas (Fig. 1/1). Marine pollution is a major multifaceted problem, which produces, in the long term, strong environmental impacts, particularly on the coastal environment. This review lies within the activities of WP2 (Information Management: to compile bibliographical information and assess the existing data on available meteorological, physical, biogeochemical, land use, coastal and marine resource, and socioeconomic information) and WP4 (Pressures on the Coastal Zone: to assess the current state of the system's coastal zone) focusing on pollution. Pollution problems can be classified in four categories: (1) eutrophication; (2) heavy metals; (3) organic contaminants; and (4) radioactive substances. This document describes the current state of the Mediterranean Sea environment on the aforementioned categories.

⇒ Regional setting

The Mediterranean Sea (Fig. 1/1) is the largest semi-enclosed basin in Europe (2.500.000 km^2) and is separated in smaller basins (Alboran Sea, Ligurian Sea, Tyrrhenian Sea, Adriatic Sea, Ionian Sea, Aegean Sea, Levantine Sea). The average depth is 1.500 m, whilst the deepest basin exceeds 5.000 m, offshore Peloponnese. The northern margin receives freshwater from a few big rivers (Ebro, Rhône, Po) and smaller (Axios, Strymon, Nestos, and Evros). The largest Mediterranean river is the Nile, which flows in the southeastern sector (Egypt). Riverine waters deliver into the sea large amounts of anthropogenic substances, which, together with atmospheric deposition, are the main sources of pollutants.

Figure 1/1: The Mediterranean Sea (source IFREMER)

⇒ Driving forces and pressures

The long civilization (>8.000 yr) and urbanization (more than 300.000.000 inhabitants) exert severe pressures on the marine environment. According to EEA (1999) the main human activities and pressures identified are: (1) population growth; (2) tourism; (3) agriculture; (4) fishing and aquaculture; (5) industry; (6) maritime traffic; (7) discharge from sewage outfalls; and (8) discharge via rivers. Domestic, industrial and agricultural activities are considered to be the three main pollution sources.

Nutrients in the Mediterranean Sea

Introduction

In the Mediterranean Sea, nutrients are important tracers of biological cycles, new production, natural and anthropogenic inputs and transfer processes (Bethoux *et al.*, 1998). The Mediterranean nutrient concentrations are very low, much lower than those of the Atlantic (Mc Gill, 1961, 1965; Coste *et al.,* 1988). These low nutrient levels generally cannot support a large biomass. Besides the oligotrophic properties of the open Mediterranean Sea, recent observations of high nutrient levels in the Gulf of Lions and the northern Adriatic Sea have raised the question how the increasing anthropogenic inputs from land and river discharge and from rainfall may influence the nutrient concentrations and lead to a critical eutrophication (Denis-Karafistan, 1998).

The inverse estuarine circulation of the whole Mediterranean basin determinates a negative budget for nutrients at the Gibraltar Strait (Bethoux, 1998). The nutrient-poor waters are imported in surface from the Atlantic Ocean and the relatively nutrient-rich deep waters are exported to the ocean in the deep layer (Schink, 1967; Mc Gill, 1969; Coste *et al.*, 1988). The nutrient deficit in the Strait of Gibraltar is compensated by riverine and atmospheric inputs (UNESCO 1988; Turley, 1999). It has been reported that river outflows are the most significant source of phosphate supply, whereas, inorganic nitrogen deriving from the atmosphere is also important (Bethoux *et al.*, 1998; Moutin *et al.*, 1998; Migon *et al.*, 2001; Sanz *et al.*, 2002). The Rhône River in southern France is considered to be a significant source of nutrients to the Western Mediterranean Basin affecting the nutrient levels in the Gulf of Lions (Moutin *et al.*, 1998; Durrieu de Madron *et al.*, 2003). It is noteworthy, that its mean flow is ~three times higher than the sum of that of the Ebro, the Arno and the Tiber rivers (Martin and Saliot, 1992). River discharge of freshwater into the Mediterranean Sea varies spatially. For example, river discharge from North Africa is low, whereas, the average discharge from Ebro and Rhone rivers is quite significant. (Martin and Milliman, 1997). The biological N_2 fixation plays an important role in the nitrogen budget of the Mediterranean reinforcing the unusual high N/P ratio (Bethoux and Copin-Montegut, 1986). In general, the phosphate is considered to be the limiting nutrient for primary production in the Mediterranean Sea, especially in the Eastern Basin (Krom *et al.,* 1991). The N:P molar ratio of the Mediterranean deep waters is ~22, in the Western Basin and ~ 24 in the Eastern Basin, instead of 16 in the ocean (Bethoux *et al.*, 2002). The degree of phosphorus limitation increases from west to east (Moutin and Raimbault, 2002). In order to explain the high N:P ratio, several hypotheses have been proposed in the literature. Bethoux and Copin Montegut (1986) suggested nitrogen fixation by cyanobacteria; Coste *et al.*, (1988) have tried to connect the high ratio to internal processes in the basin; and the hypothesis of Krom *et al.* (1991) is based on phosphate removal by the absorption of Saharan dust particles rich in iron oxides in the eastern Mediterranean Sea. Ridame *et al.* (2003) performed radio-labelled phosphate adsorption experiments and showed that Saharan particles do not represent a significant sink for seawater phosphate in the western Mediterranean Sea.

Spatial Distribution

The inflowing Atlantic water carries in Mediterranean Sea low amounts of nutrients which are directly available for photosynthesis. Estimations of the inorganic forms in the inflowing waters showed ranges from 0.05 to 0.20 μM for phosphate, 1 to 4 μM for nitrate and nearly to 1.2 μM for silicate (Coste *et al.*, 1988). Important density gradients develop in the lower part of the inflowing Atlantic waters thereby preventing the exchange with nutrient-rich subjacent basin waters. The nutrient content of the surface water is reduced along its propagation in the Mediterranean Sea, due to the mixing with nutrient-poorer basin water and the biological activity.

Deep water nutrient distributions are mainly determined by the water masses circulation. The outflow to the Atlantic Ocean of a mixture of Western Mediterranean Deep Water (WMDW) and Levantine Intermediate Water (LIW) of the basin, over the Gibraltar Sill, constitutes a permanent loss of nutrients and reduces their accumulation in the deep layers.

The deep waters of the different sub-basins in the Mediterranean are separated from each other through the existence of successive sills. McGill (1965) first discussed the considerable depletion of nutrients from the western to the eastern part of Mediterranean Sea. The nutrient concentration in the Aegean Sea is twelve times lower than in Atlantic Ocean and eight times lower than in Alboran Sea. The oxygen and nutrient data collected in the eastern Mediterranean Sea during the past decade, through national and international research programs, confirmed the above observations and showed a depletion of nutrients, of the same order of magnitude as that of McGill 1965, in the following order : Levantine > Ionian>Aegean (Fig. 4/1) (Souvermezoglou, 1989; Stergiou *et al.*, 1997).

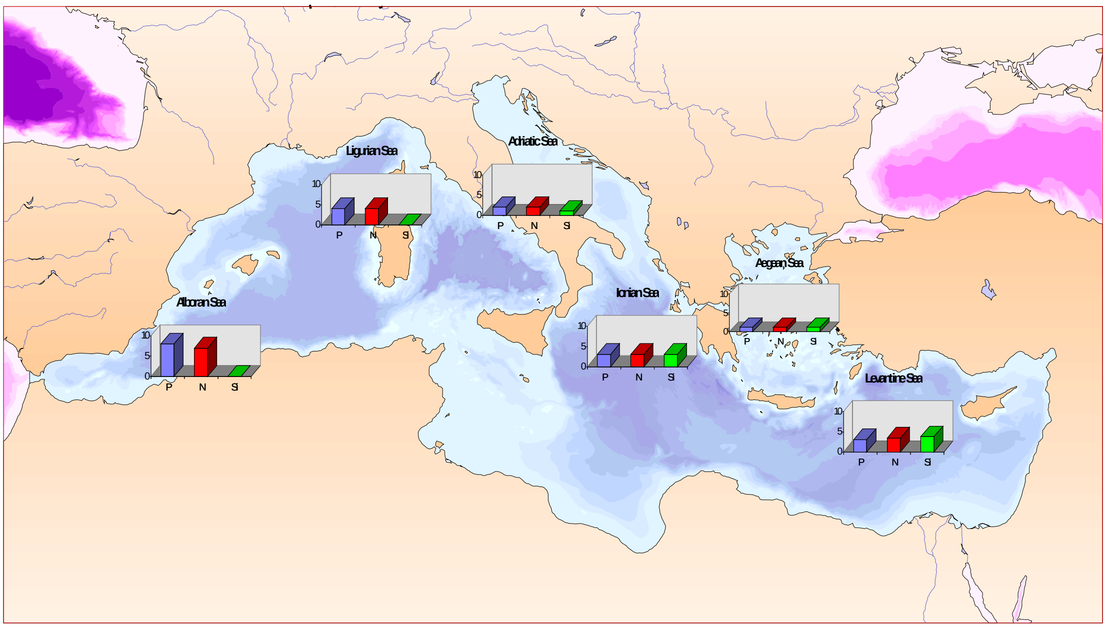

Figure 4/1: Relative concentrations of nutrients in the deep basins of the Mediterranean Sea compared to the Aegean Sea. The nutrient concentration in the Aegean Sea are assumed to be 1.

Besides the oligotrophic character of the open Mediterranean Sea, elevated nutrient data indicating eutrophication problems occur in some coastal areas of the Mediterranean.

Eutrophication problems have been reported along the east coast of Spain, due to both air pollution and riverine outfalls (Sanz *et. al.*, 2002). The Ebro River, in the eastern coasts of Spain, enriches the marine environment in phosphate and nitrate. Agricultural non point sources account of the 64% of nitrate loads in the Ebro river while the industrial point sources are responsible of 88% phosphate loads (Torrecialla *et. al.*, 2005).

High nitrate and nitrite values have been reported in NW Mediterranean along the Catalan-Balearic Sea. Some high nitrate+nitrite concentrations of 8-12 μM have been reported at the surface waters suggesting high nitrogen inputs (Lucea *et al.*, 2003). In regions of the Western Mediterranean Sea with permanent geostrophic fronts, new primary production has been often associated to the turbulent transport of nitrate from deeper waters. The high nitrate concentrations, observed at the Catalan Sea, during winter due to the vertical convection of the mixing layer, causes phytoplankton blooms. The blooming phytoplankton rapidly depletes nitrate in the surface layer. (Bahamon, *et.al*., 2003).

Eutrophication problems with elevated nitrate values have also been reported in the Gulf of Lions (Denis-Karafistan *et al.*, 1998; Durrieu de Madron *et al.,* 2003). Terrestrial sources of nutrients from sewage treatment plant, runoff and rivers, bring significant amounts of nitrate and ammonium into the Gulf (Diaz et. al., 2000). Significant discharges of treated sewage inputs occur at Marseilles. The Gulf of Lions receives water discharges from about ten rivers. The Rhône River, in the north-western part of the gulf, is considered to be the most important one, which delivers into the gulf about the 90% of the total riverine water inputs. Rhône River is one of the largest Mediterranean rivers. It has been calculated that the nitrate and ammonium input by the Rhône River into the Mediterranean Sea is ~ 92-96 kt per year and ~6.5 kt per year, respectively. The annual input of orthophosphate is ~3.0 kt per year. It is noteworthy, that a large part of the phosphorus input is in the particulate form (Moutin *et. al*., 1998).

In the Gulf of Lions, nutrient maximum is observed at 500 m depth related to the Levantine Intermediate Water (LIW) layer. Bellow 500 m depth, abnormal high nutrient concentrations (nitrate ~8.0 μmol/L; phosphate 0.40 mmol/L; silicate 8.5 μmol/L) have been observed, result from the terrestrial inputs and the oxidation of the organic matter precipitating from the euphotic zone (Manca *et al.*, 2004).

In the Algerian Basin, the highest nitrate and phosphate values were also found at 500 m depth, and were higher than the ones in the Tyrrhenian Sea and the Gulf of Lions, corresponding to the oxygen minimum, which was more pronounced in the Algerian Basin, because more time is needed for the LIW to flow into Algerian Sea after its recirculation in the Tyrrhenian Sea (Manca *et al.*, 2004). The surface layer also showed significant spatial variation, with the highest nutrient values to be observed at the Gulf of Lions, whereas, in the Algerian and Tyrrhenian Seas, the surface layer is nutrient depleted.

Several areas along the Apulian coasts, in Italy, which are influenced by anthropogenic activities (ports, industrial wastes, aquaculture activities), are enriched in nutrients. Dissolved Inorganic Nitrogen shows significant seasonal variation, within a range of concentrations from 1 to 5.4 μM, with the highest concentration during the cold period (Dell Anno *et al.*, 2002; Sabetta *et al.*, 2005).

The Adriatic Sea is considered important for the whole Mediterranean: it contains one of the most eutrophic regions (the Northern Adriatic) of the Mediterranean; moreover, the Adriatic Sea is the site of convective processes generating cold, dense and oxygenated deep waters, which feed, through the Strait of Otranto, the deep layers of the Eastern Mediterranean. Relative to the Mediterranean, the Northern Adriatic has the largest shallow-shelf system and the largest single river discharge. The external seaward nutrient supply is minimal and ~85 % of its nitrogen derives from land runoff. The Western Adriatic Current (WAC) is the primary mechanism for exporting mass and information from the Northern Adriatic system. The amount of fresh water per water column indicates the degree of mixture of river water within the system, and consequently the nutrients. The distributions of Fresh Water Content (is defined as the amount in centimeters of fresh water added to a reference salinity in order to produce one meter of an observed salinity) clearly show a gradient pattern with FWC contours strongly increasing towards the Italian coast.

Several smaller-scaled patterns also demonstrate: the tendency for fresh water to accumulate south of the Po Delta an area of minimum values in the southern central portion; greater accumulations along the northern shore, particularly in the Gulf of Trieste. (Hopkins, 1996; Souvermezoglou and Krasakopoulou, 1999a).

Recently several investigators have pointed out the increasing eutrophication of the northern Adriatic (Souvermezoglou *et al.*, 1999). Justic (1987) demonstrated trends in summer oxygen data for 1911 to 1984 showing a mean decrease of a mean decrease of 1.1 cm^3 O_2 /dm^3 in the bottom values. Degobbis (1989) showed that periodically, near-anoxic conditions can occur at the water-sediment interface in late summer or early autumn as a result of heavy organic matter loads and/or minimal water exchange with the central Adriatic Sea.

The Ionian Sea is almost nutrient depleted at the surface layer (Manca *et al.*, 2004). Kalamitsi and the Sea of Kerkyra, in the Ionian Sea are considered to be unpolluted areas with nutrient concentrations much lower than those observed in Amvrakikos Gulf (Phyllidou *et al.*, 1997).

Amvrakikos Gulf receives nutrients through Arachthos and Louros Rivers, both draining agricultural areas (Frilligos *et al.*, 1997). Amvrakikos Gulf, which is mainly influenced by agricultural runoff and high fertilizer applications in the catchment area of the rivers, is characterized as a high polluted area with high nitrate, silicate and phosphate concentrations of ~1.6 μM for nitrate, 0.50 μM for phosphate and 16 μM for silicate.

Argolikos Gulf, in the northeastern Peloponnese, is affected predominantly by agricultural runoff and effluents from industrial activities. The area is characterized as an intermediate polluted area. Mean nitrate concentrations of 0.82 μM have been reported. It seems that the material exchange with the open sea is a significant factor that regulated the nutrient distribution in the Argolikos Gulf (Archonditsis *et al.*, 2001).

Eutrophication has also influence the water quality of the Saronikos Gulf which is affected by the Athens municipal treated sewage outfall. High nutrient concentrations have been recorded near the Sewage Treatment Plant, showing a significant decreasing shift with distance from the sewage plant to the south (Pavlidou *et. al.*, 2004).

Pagassitikos Gulf is greatly influenced by human activities especially around the industrial town of Volos (Inner Pagassitikos Gulf). The scattered farmlands along the coastline, some rather distant sources (e.g. Lake Karla) and the domestic and/or industrial effluents (sewage outfalls), enrich the marine environment in nutrients. Relatively higher nutrient concentrations characterize the Inner Pagassitikos Gulf as well as the area where the sewage effluents discharge (Pavlidou *et al.*, 2005)

Thessaloniki Bay and the northern Thermaikos Gulf are influenced by both industrial-domestic effluents from Thessaloniki and riverine inputs. Data for the period 1995-2002 have revealed eutrophication problems in the area. Nutrient concentrations are 2-6 times higher than the corresponding oligotrophic area (Dassenakis *et al.*, 2000). Low N to P ratios indicates that during the last ten years nitrogen was developed towards the limiting nutrient in the area. (Pavlidou and Psyllidou, 2004; Pavlidou *et al.*, 2005).

In Strymonikos Gulf, the principal environmental load of nutrients is provided by agricultural activities. Strymon River enriches the marine system in nutrient, indicating a eutrophic environment near the mouth of the river (~40 μmol/L for DIN at the surface layer near the mouth of the river). As mixing with offshore waters progressed, nutrient levels declined dramatically (Pavlidou *et al.*, 2002).

The North coasts of Greece (Macedonia) receive pollutants from point sources, such as Nea Karvali (industrial area of Kavala with industry of fertilizers), the sewage effluents of Kavala City and riverine waters. The influence of the riverine water remains within a few hundred meters from the coast of Macedonia. Nutrient surface distribution demonstrates high values near the mouth of Nestos River and near Nea Karvali (Pavlidou *et al.*, 2001; Pavlidou *et al.*, 2005).

In the Aegean Sea, there are coastal areas with eutrophication problems related to anthropogenic activities, sewage outfalls, riverine outflows etc. Agriculture is a significant activity on the coasts of the Aegean Sea. It has been reported that the loads of nitrogen and phosphorus transferred into the Aegean Sea from the coasts of Greece and Turkey have been estimated at 5000-15000 t P/y and 30000-130000 t N/y for Greece and 25000-60000 t N/y and 6000-8000 t P/y for Turkey (Dassenakis *et al.*, 2000).

In the Gulf of Gera, in Lesvos Island, the flux of nutrients from non-point sources (agricultural run-off) is considerable, especially during the winter period, when the contribution to the total inorganic nitrogen stock (the limiting nutrient in the area) varies between 40 to 60%. The most important point discharges are untreated domestic wastewater and effluents from the local industrial activities, especially olive oil processing by-products. The input of nutrients and organic matter from the surrounding watershed and the low renewal rate result to the development of eutrophication crises during the year. During the warm months of the year (April to October), the physical conditions allow the entrance of oligotrophic water masses from the Aegean Sea into the gulf and influence the nutrient levels (Archonditsis et. al., 2000).

In most of the polluted Helenic coastal areas, the limiting factor for the phytoplankton growth is nitrogen (Pavlidou *et.al*., 2005).

According to the mean nutrient concentrations and the water quality indices for the Hellenic coastal zone (Karydis, 1999), the Hellenic coastal areas have been classified into four main categories:

unpolluted areas, rather unpolluted, intermediate polluted and polluted (Fig. 4/2) (Pavlidou *et.al*., 2005).

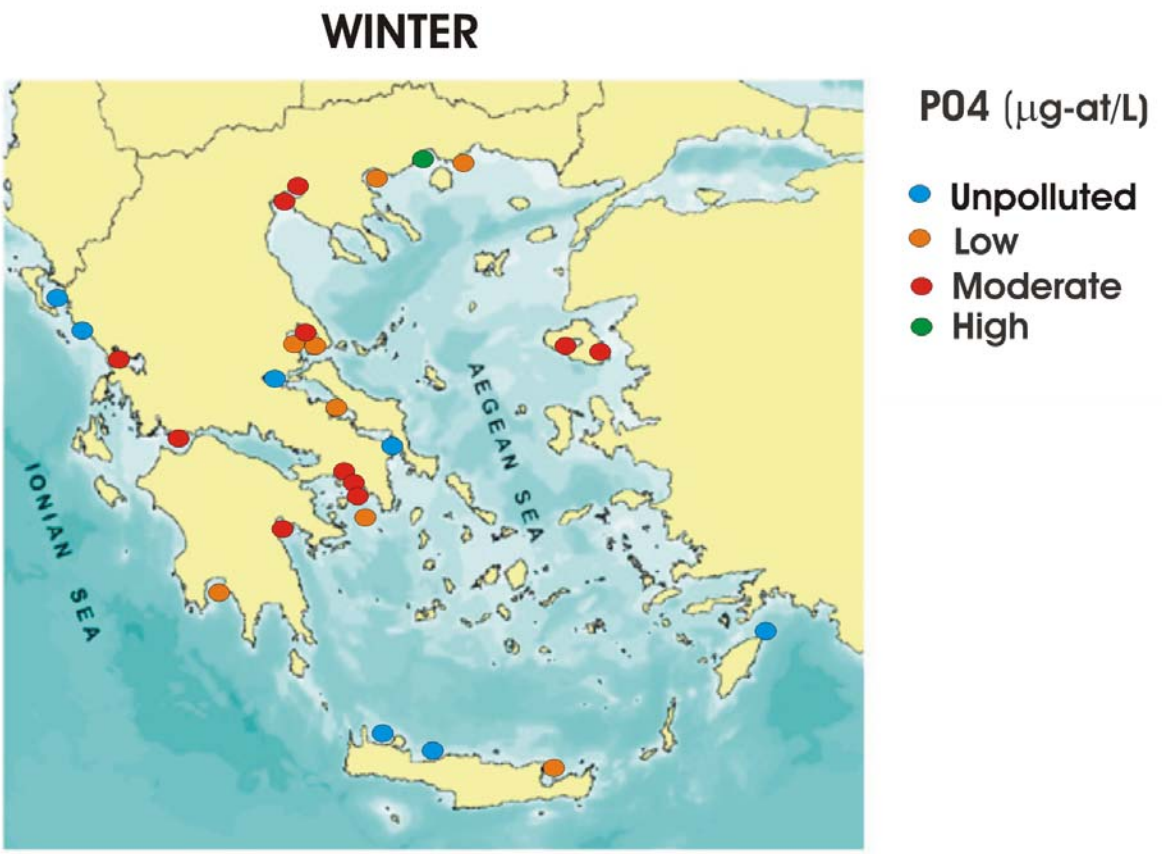

Figure 4/2: Ecological quality of coastal areas based on winter phosphate concentrations. Source: Pavlidou *et.al*., 2005.

High terrestrial inputs result to the increase of nutrient values in the Izmit Bay (Dassenakis *et. al*., 2000). The mean nutrient concentrations showed ranges of 0.01-0.19 and 0.01-10 μM for phosphate, 0.10-1.8 and 0.12-27 μM for nitrate+nitrite, and 0.30-5.8 and 0.43-39 μM for silicate in the outer and middle-inner bays, respectively. The limiting element is nitrogen resulting to the appearance of diatoms and dinoflagellates during all the year (Kucuksezgin *et al*., 2006).

Before the emplacement of the High Dam at Aswan, Nile carried waters to the Eastern Mediterranean Sea. After the damming, nutrient-rich waters from seasonal flooding rarely reached the sea.

The results obtained during the last years showed that although the Mediterranean in whole is oligotrophic, locally and temporary high planktonic biomasses can be found. In the cyclonic regions where the nutricline ascends to the base of the euphotic zone, the phytoplankton biomass and primary production is higher than in the anticyclonic regions where the nutricline is situated at greater depths, limiting the nutrient input to the surface waters during the winter mixing (Salihoglou *et al.*, 1990; Souvermezoglou and Krasakopoulou, 1999b).

The Levantine basin is the second largest basin of the Eastern Mediterranean Sea. The meteorological and hydrological conditions in the Levantine Sea are often favourable for the convergence and the convective sinking of high salinity waters.

The Rhodes gyre is a large permanent cyclonic eddy covering a large area centred upon the Rhodes basin. The domed pycnocline of the Rhodes gyre favours on the one hand the formation of Levantine Intermediate Water (LIW) and on the other hand the development of increased primary production and zooplankton abundance. The homogeneous water column formation in the Rhodes cyclonic gyre due to the strong overturning during 1992, 1993 and 1995 winters resulted uniform profiles down to at least 1000m (Yilmaz and Tugrul 1998; Souvermezoglou and Krasakopoulou, 1999b). The surface nutrient concentrations reached up to the deep water concentrations *e. g.* 0.16 μM, 4.7 μM, 7.8 μM for phosphate, nitrate and silicate respectively. The efficient nutrient pumping from aphotic to euphotic zone in the Rhodes Gyre centre and its peripherals caused unusually high biomass accumulation and an increase in primary production rates.

Temporal variation

The extensive study of the nutrient regime in Mediterranean Sea showed no significant seasonality. However, the influence of riverine discharge and coastal runoff is significant throughout spring due to snow melt (Migon *et al.*, 2001).

The combination of the chemical and physical oceanography data revealed the important chemical signature of the physical processes, the circulation features and dynamics. The nutrient pattern is affected by the presence of mesoscale cyclonic and anticyclonic gyres in the Mediterranean Sea.

In the deep and intermediate water formation areas the vertical mixing of the water column during the cold period, transports nutrients to the surface layer, whereas, in warm period, the surface layer is not fed by deep water nutrients, due to the strong stratification of the upper layer.

The nutrient distributions in the Gulf of Lions manifest seasonal variations. In winter, the upper column is enriched in nutrients, due to deep convection and the homogenization of the water column. Nitrate values of ~2.1 μmol/L have been found in the upper layer of the Gulf of Lions, during winter period, whereas, nutrient depletion in the upper layer has been reported in summer and autumn (Manca *et al.*, 2004).

It has been reported that in Western Mediterranean Sea, from 1960 to 1994, the phosphate and nitrate concentrations in deep waters increased (Bethoux *et al.*, 1992; Raick *et al.*, 2005). Bethoux, *et al.* (2002) tried to relate this augmentation to increasing agricultural, industrial and urban activities since the 1960s. The growing human impact on the Mediterranean watershed has brought increasing phosphate and nitrate inputs to the sea. However, due to the differences in the residence times of deep waters in the Western and Eastern Mediterranean Basins, an increase of phosphate and nitrate has been observed in the Western Mediterranean, whereas, in the Eastern Mediterranean, phosphate, silicate and nitrate concentrations have not dramatically changed.

Intensive research during the past decade revealed an unusual evolution of oxygen and nutrients in the deep and bottom layers of the eastern Mediterranean Sea. The hydrographic surveys showed that after 1987 the Adriatic Sea ceased to be the dominant source of the Eastern Mediterranean Deep Water (EMDW) and Cretan Deep Water (CDW) became an important contributor (Roether *et al.*, 1996). The CDW flows towards the Levantine and Ionian seas though the deeper straits of the Cretan Arc, sinks and occupies layers below 1000-2000 m displacing upwards the old EMDW of Adriatic origin (Souvermezoglou and Krassakopoulou 1999b). Furthermore, after 1994 a new nutrient-rich and oxygen-poor intermediate layer was formed in the Eastern Mediterranean. In the Cretan Sea the concentrations of nutrients in this layer were sometimes twice those found during previous years.

Heavy metals

Introduction

Heavy metals in the marine environment originate in the weathering of terrestrial and underwater rock formations, and also from anthropogenic activities (domestic and industrial effluents, and agriculture). The latter are transported predominantly by rivers and atmospheric fallout, but could be also injected directly into the sea through sewage pipelines, thus constituting significant pollution point sources. Industrial residues (e.g. from metallurgy) or dredging materials are often dumped at sea by barge boats, with similar effects.

Heavy metal levels are traditionally measured in river and marine waters (dissolved and particulate forms) and biota. However, these data are fairly variable over time, whilst sediment analysis provides a long-term estimate of heavy metal enrichment; thus, this analysis will focus on the sediment heavy metal content.

Reviewing the currently available peer-reviewed literature and NGO's Reports (EEA, UNEP/MAP, FAO, and others), we identified the scarcity of data for the southern Mediterranean sector, neighbouring the African coast. Conversely, numerous papers exist for the NW Mediterranean Sea, followed by fewer for the Adriatic, Ionian and Aegean Seas (Table 5/I). In any case, these studies focus mainly on shallow coastal or river delta areas, whilst open sea sectors have been studied to a much lesser extent. On the other hand, available data on sediment heavy metal content are often difficult to compile on a common basis, due to differences in sampling and/or analytical techniques. For example, several research groups select for analysis only the fine fraction of the sediment (usually <63 μm, but often <20 or <5 or <2 μm), in order to minimize grain-size effects, whilst others analyze the bulk sediment. Similarly, some scientists rely on sequential extraction methods (many variations) to assess the portion of anthropogenic-related heavy metals, which are more easily remobilised; others undertake bulk heavy metal determination (total digestion or X-ray Fluorescence methods). Heavy metal contents are reported without any correction, or quite often on a carbonate-free or salt-free basis, thus obstructing a direct comparison. More confusing is the expression of heavy metal abundance as loads ($t\ yr^{-1}$) or fluxes ($g\ m^{-2}\ yr^{-1}$), which gives a better quantitative approach but is more difficult to determine, because more data are required (e.g. water discharge, sedimentation rates). To compensate these limitations, we have decided to use ranges and/or mean heavy metal contents for comparison purposes and to state the sediment fraction and analytical method employed, wherever this was possible.

Table 5/1. Heavy metal contents in surface sediments from the Mediterranean Sea (mean, max, mean, and median values in μg/g). EF: enrichment factor.

Area	Metal							remarks	reference
	Cr	Co	Cu	Ni	Zn	Pb	Cd		
Barcelona									Puig *et al.* 1999
min	17.2		5.08	14.7	53.0			Bulk	
max	167		82.6	54.6	278			ICP	
mean									
EF	2.5		3.4	1.6	3.7				
Barcelona									Guevara-Riba *et al.*, 2004
min								Bulk	
max	110		530	34	1130	589	2.7	XRF	
mean								ICP (Seq. Extr.)	
EF									
Tyrrhenian									Leoni and Sartori, 1996
min	18	3	14	29	18	17		Bulk	
max	269	25	44	118	130	58		XRF	
mean	31	23	27	113	121	51			
EF	1.9		3.7		4	8.2			
Po									Fabri *et al.*, 2000
min								Bulk	
max								AAS	
mean	91		14	50					
EF									
Adriatic									De Lazzari *et al.*, 2004
min	3	4	2	12	27	10	0.04	Bulk	
max	247	26	86	205	162	50	0.97	AAS	
mean	96.1	10.9	16.5	59	80.8	27.3	0.2		
EF									
Albania									Çelo *et al.*, 1999
min	146		13.5	110	16.6	9.8	0.08	<250 μm	
max	812		624	413	355	51.1	0.24	AAS	
mean									
EF									
Kerkyra									Voutsinou-Taliadouri, 1998
min	35	2	3	31	21	7		<1 mm	
max	257	28	30	192	94	24		AAS	
mean	154	17	18	132	67	16		leaching with 2N HCl	
EF									
Amvrakikos									Voutsinou-Taliadouri, 1998
min	27	4	2	33	12	7		<1 mm	
max	177	30	31	188	80	21		AAS	
mean	125	18	24	131	62	12		leaching with 2N HCl	
EF									
Patraikos									Voutsinou-Taliadouri, 1998
min	55	11	16	60	43	11		<1 mm	
max	119	23	43	132	88	20		AAS	
mean	100	19	35	110	72	16		leaching with 2N HCl	
EF									
Saronikos									Voutsinou-Taliadouri *et al.*, 1989
min	60	7	20	70	60	30	0.1	Bulk	
max	390	12	230	120	1680	400	2.5	AAS	
mean	130	9	100	90	760	210	0.8	leaching with 2N HCl	
EF	6.5	1.5	8.1	1.3	28.9	12.7	17.9		

Area	Metal							remarks	reference
	Cr	Co	Cu	Ni	Zn	Pb	Cd		
S. Evvoikos									Karageorgis *et al.*, 1997
min	20		1	15	7	7		Bulk	
max	342		91	301	102	59		XRF	
mean	138		12	110	55	22			
EF									
N. Evvoikos									Voutsinou and Varnavas, 1993
min	10.6		20.9	370	69			<63 μm	
max	2360		115	3610	471			AAS	
mean	445		43.7	1295	147			leaching with HCl	
EF	19.6		3.24	2.6	2.65				
Pagasitikos									Karageorgis *et al.*, 2002
min	334		49	113	147	27		<2 μm	
max	526		117	233	226	112		XRF	
median	389		62	180	165	50			
EF									
Thessaloniki									Karageorgis *et al.*, 2005
min	147	15	18	57	96	42		Bulk	
max	458	44	108	407	429	265		XRF	
mean	256	25	44	152	177	82			
EF	1.8	6.1	1.5	0.2	0.7	2.7			
Thermaikos									Karageorgis *et al.*, 2005
min	152	9.7	2.9	42.9	33	16.5		Bulk	
max	453	30	47.9	250	124	48.6		XRF	
mean	250	22.2	24	157	86.9	32.7			
EF	3.7	1.3	1.3	1.5	1.4	1.3			
Saros									Sari and Cagatay, 2001
min								Bulk	
max								AAS	
mean			19	60	73	22			
EF									
Mytilene									Aloupi and Angelidis, 2001
min	40		5.34		12.9	20.7	0.03	Bulk	
max	154		86		230	93	0.50	AAS	
mean									
EF			3.3		3.2	2.2			
Rhodes									Angelidis and Aloupi, 1995
min	19.4		31.5		59	36.6	0.03	<63 μm	
max	118		101		242	230	0.17	AAS	
mean									
EF	0.82		4.33		6.04	20.9	0.52		
Iskenderun									Ergin *et al.*, 1996
min	67	6	9	179	30	10		Bulk	
max	694	99	39	808	117	61		AAS	
mean	246	56	23	444	74	26			
EF	2.8	4.1	4.4	4.7	3.9	6.5			
Strymonikos									Stamatis *et.al.,* 2002
min	29.2		5.3	9.1	24.3	23.4		Bulk	
max	213		51.2	74.5	159	130		AAS	
mean	149		27.1	53.9	111	92.1			
EF									
Israel Coast									Goldsmith *et al.*, 2001
min			28.7		83.1	18.4	0.18	<63 μm	
max			57.6		137	37.4	0.36	AAS	
mean			42.7		107	24.4	0.25		
EF			1.3		1.1	1.1	1		

Area	Metal							remarks	reference
	Cr	**Co**	**Cu**	**Ni**	**Zn**	**Pb**	**Cd**		
Aegean Sea									Friligos *et al.*, 1998
min	55.4		15.2	70.2	68.8	22.7	0.13	<63 µm	
max	129.6		47.1	216	140	30.4	0.22	AAS	
mean	84.2		32.2	117	95	26.2	0.16		
EF									

Spatial distribution

In Spain, the Ebro, Besòs, and Llobregat Rivers are mainly responsible for the transfer of anthropogenic metals into the sea. In the Llobregat prodelta (south of Barcelona), metals produce significant anomalies of chromium (×2.5), copper (×3.4) and zinc (×3.7) in the surface sediments (Puig *et al.*, 1999). In the Besòs prodelta (north of Barcelona) sediments accumulated during the 18th and 19th centuries were already affected by a moderate heavy metal contamination. This contamination increased drastically in the sediments accumulated during last decades (Palanques *et al.*, 1998). Heavy metal contamination has been also reported for the port of Barcelona (Guevara-Riba *et al.*, 2004).

In the Northern Tyrrhenian/Eastern Ligurian Seas, offshore the Arno and Serchio River mouths, Pb, Zn, Cr and As, followed by Cu and V appeared to be enriched in surface sediments, due to intense industrialisation of the coastal plain (Leoni and Sartori, 1996). Danovaro (2003) reported that coastal sediments offshore the Arno River exhibit Cd contents up to ×20, than background levels in pristine areas of the Ligurian Sea.

The gulf of Trieste in the northern sector of the Adriatic Sea has been contaminated by mercury (×25), supplied by the river Isonzo, making this shallow basin one of the most contaminated marine areas in the length of time and amount of metal accumulated (Covelli *et al.*, 2001). Mercury originates in cinnabar ore, which has been mined intensively since the 16th century (Idrija mine in Slovenia). Minor enrichment was reported for zinc (×1.5), nickel (×1.4), and copper (×1.1).

The sector of the Adriatic Sea offshore the Po R. delta was studied by Fabri *et al.* (2000). Fe, Mn, Cu, and Ni contents were found generally to be constant against depth, whilst a decreasing trend was observed from the north to the south, owing to the influence of the rivers Po, Adige and Brenta. Relatively elevated chromium content was attributed to effluents from leather industries. The most striking feature was the clear enrichment of sediments in mercury, which ranged from ×3 to ×11. Possible Hg sources are (1) the Po R., where high levels of Hg were measured in suspended matter; (2) the Gulf of Trieste, which displays the highest concentrations of Hg in the Mediterranean basin, delivered through the Isonzo River from the mercury mining region of Idrija; (3) the Gulf of Venice, where waste materials from the industrial processing of zinc minerals were dumped; (4) disposal sites where dredged materials containing mercury have been discharged; and (5) coastal sites whose sediments are heavily contaminated by mercury utilised in industrial activities, like Marano Lagoon (chlor-alkali plant) and Ravenna Lagoon (mercury used as catalyst in the production of acetaldehyde and vinyl chloride).

De Lazzari *et al.* (2004) reported that sediment contents in Zn, Pb, Co, Cr and Ni in the Northern Adriatic decreased from the Italian to the Croatian coast. In the Central Adriatic, Zn and Pb were homogeneously distributed at concentrations well above the total mean. Co, Cr and Ni in the Central Adriatic were higher than in the north and decreased going from west to east. Cu was heterogeneously distributed throughout the study area, with higher values in the Central Adriatic. Vanadium in the Northern Adriatic significantly decreased from west to east, whereas in the Central Adriatic concentrations were homogeneously higher.

Nearshore sediments of the Adriatic Sea in Albania exhibit significant heavy metal enrichment due to industrial activity (chlor-alkali plant in Vlora Bay; mercury ×43), harbour activities (Durres Port; cadmium ×9, lead ×3) and the Mat and Ishem Rivers discharges, possibly related to natural erosion and/or industrial activities inland (copper ×24, chromium ×4) (Çelo *et al.*, 1999).

Sediments in the Ionian Sea (Kerkyra Strait, Amvrakikos Gulf, Patraikos Gulf) exhibits generally low heavy metal contents both in the open sea and the coastal areas, probably due to a general absence of large industrial units in western Greece (Voutsinou-Taliadouri, 1998).

Saronikos Gulf, situated in the southeastern part of the Greek mainland, is the main receptor of the industrial and municipal effluents of the heavily populated metropolitan area of Athens. Due to the heavy loads of discharges, the inner Saronikos Gulf is ranked in the first group of priority in UNEP's priority pollution "hot spot" areas of the Mediterranean (UNEP, 1999). Surface sediments in this part were found enriched mainly in Zn (×28.9), in Pb (×12.7), in Cd (×17.9), Cu (×8.1) and Cr (×6.5) (Voutsinou-Taliadouri *et al.*, 1989). Elefsis Gulf, near Athens has been identified as an area heavily polluted by industrial/shipping activities. According to Scoullos (1986), significant amounts of Pb have accumulated in the upper 5-10 cm of the sediments there, whereas Pb sediment content in a few cases is 10-50 times higher than the natural background levels. Recent studies using biological effect methods have shown that Elefsis Gulf suffers from significant ecological stress due to the polluting activities (Cotou *et al.,* 2002).

Sediments of south Evvoikos Gulf have been enriched in Ni, due to the natural weathering of ultra-mafic formations in Central Evvoia Island and/or the activity of laterite-processing factory for aluminium production, in Aliveri (Karageorgis *et al.*, 1997). Dassenakis et al (2003) have reported sediment enrichment factors for Cu and Zn of about ×0.15-1.4 and ×0.29-4.1, respectively.

North Evvoikos Gulf has been a dumping site for metallurgic residues from the nickel factory of 'Larko' for several decades. Voutsinou-Taliadouri and Varnavas (1993) have found that surface sediments were markedly enriched in Ni, Cr and Mn, compared to the Aegean shelf sediments, mainly due to weathering of mafic and ultramafic rocks present on the Evvoia Island.

High Pb, Cu, and Zn contents were found in the clay fraction in the northern part of Pagassitikos Gulf. This enrichment was attributed to the discharge of raw domestic and industrial effluents of Volos city and port (Karageorgis *et al.*, 2002).

The Antikyra Bay in Korinthiakos Gulf receives tailings from the alumina factory of 'Pechiney'.

The Bay and Gulf of Thessaloniki, as well as the northern Thermaikos Gulf have been influenced by industrial and domestic effluents and the discharges of the Axios, Loudias, and Gallikos Rivers. Sediments exhibited high contents for Cu, Zn, As, Cd and Pb (Anagnostou *et al.*, 1998; Karageorgis *et al.*, 2005). The Axios River and the northern Thermaikos Gulf sediments were compared against the Direct Exposure SALs Standards for residential use; criteria were violated for As and Cr (Karageorgis *et al.*, 2003).

The Ierissos and Stratoni Bay in northern Aegean Sea have been influenced by mining operations and the discharges of Strymon River. The most polluted area for Pb, Zn and Cu in both gulfs is the sector located near the load-out facility of the mining operations ('flotation') in Stratoni Bay. In particular, the inshore northwest sector of Ierissos Gulf is one of the most polluted coastal ecosystems of the east Mediterranean by Pb and Zn (Stamatis *et al.*, 2002).

Minor pollution by Cd, Cu, Pb and Zn has been reported for the Mytilene harbour in Lesvos Island (Aegean Sea), where the domestic sewage outfall is located (Aloupi and Angelidis, 2001). Sediments of the gulf of Gera, in Lesvos Island, were found to be enriched in Cr and Ni, due to the natural weathering of ultra-mafic rocks, and tannery installations inland (Anagnostou *et al.*, 1998). Port activities in the Lakki Bay (Leros Island, Aegean Sea) are probably responsible for elevated contents for Pb, Cu and Zn in the pelitic fraction of the surface sediments (Sioulas *et al.*, 1998). Sediments of Rhodes Island harbours (Aegean Sea) studied (Angelidis and Aloupi, 1995), revealed a contamination by copper (×4), lead (×21) and zinc (×6), and were attributed to sewage outfall of the city, discharging in Mandraki harbour. In the gulf of İskenderun (Aegean Sea, Turkish coast), high Pb contents were measured in sediments from the northeastern part of Gulf, close to the discharge areas of industrial and domestic effluents. The overall high Pb contents of fluvial sediments of the Ceyhan River could be, in part, due to anthropogenic activities, as well (Ergin *et al.*, 1996).

The Gulf of Saros in the northeastern Aegean Sea (Turkey) is a relatively unpolluted marine environment, since almost no industry and only small settlements exist in the surrounding region (Sari and Çağatay, 2001).

In the coast and slope of Israel, a sector of the eastern Mediterranean Sea influenced by the Nile River discharges, sediment metal content exhibited a south-north increase in Pb, Cd, Zn and Cu. It was suggested that Pb contamination was from the atmosphere, whilst Zn, Cd, and Cu were input mainly from land based point sources (sewage outfall, power plants) and the rivers Yarqon, Alexander and Hadera (Goldsmith *et al.*, 2001)

Heavy metal pollution assessment

Heavy metal pollution in the Mediterranean Sea, as recorded in the sediments, appears to be a well-documented phenomenon. In most of the cases, pollution is related to (1) nearshore industrial, mining, and harbour activities; (2) domestic sewage effluents, released though pipelines; and (3) river discharges impacted by anthropogenic activities in the catchment area. However, these problems are clearly confined near the coast and part of the continental shelf, whilst slope and open sea sediments seem to be influenced in a minor degree. At this point, we should outline the scarcity of comprehensive data sets for the open sea. In addition, data from the north African coast are virtually absent. It is possible that such information could be discovered in reports and local conference proceedings, therefore the collaboration with scientists from the north African countries could facilitate data mining.

Apart from the identification of 'environmental hot spots' along the Mediterranean coastline, a deep insight into the level and potential hazards pertaining to heavy metal pollution, is difficult to achieve. This is because available data are pretty much inhomogeneous, preventing a straightforward ranking method to be applied. The inherent limitations deriving when analysing different fractions of sediment and employing different analytical methods, cannot be overridden. Therefore, a direct comparison of heavy metal contents between different locations of the Mediterranean Sea seems to be useless. However, several scientists have stressed significant effort to assessing heavy metal background values, and subsequently to estimate enrichment factors. When this procedure uses local unpolluted sediment as a reference (and maybe statistics), it is probably the best way to assess pollution levels. Conversely, the very often used average shale or mean crustal values could be very misleading. Geochemical background values for heavy metals were found to be highly variable across the Mediterranean, due to differences in lithology and local metal-ore occurrences.

Pollution from organic contaminants in the Mediterranean Sea

Organochlorinated compounds

Introduction

Organochlorinated compounds are by far the most important group of the persistent organic pollutants (POPs), as they are characterised by high resistance to photolytic, biological or chemical degradation. The list of organochlorinated compounds consists of more than one thousand substances. Approximately 20% of these substances are pesticides while the rest of them are miscellaneous compounds used, produced or by-produced by industries.

The organochlorine contaminants typically measured in the Mediterranean marine and coastal environment are polychlorinated biphenyls (PCBs), DDT and its metabolites (DDE, DDD), hexachlobenzene (HCB), heptachlor and the pesticides aldrin, dieldrin and endrin. PCBs were introduced industrially in 1929 and manufactured in many countries, including some Mediterranean ones: France (6557 tons/yr), Italy (1479 tons/yr) and Spain (1241 tons/yr) (UNEP, 1990). PCBs are chemically stable and heat-resistant, and were used worldwide as transformer and capacitor oils, hydraulic and heat-exchange fluids, lubricating and cutting oils, and as plasticizer in joint sealants. By the late 1970's, evidence of the extreme persistence and adverse health effects of PCBs had resulted in bans on their manufacture in most countries. The most influential force leading to these restrictions has probably been a 1973 recommendation from the Organisation for Economic Co-operation and Development (OECD), (WHO, 1993). Although they are no longer manufactured or imported into many countries, they remain sizeable quantities in storage. In addition, PCB fluids are present in many older transformers, fluorescent lighting fixtures, and other electrical devices and appliances. These are vulnerable to release into the environment, as older components can leach. Other sources of PCB contamination come from improper disposal or incineration of PCBs and PCB-containing waste sites. It has been estimated that total European emission of PCBs decreased from 1325.6 tons/yr in 1982 to 143.4 tons/yr in 1990. The contribution of the Mediterranean countries is about 25% of the total emission, which is an amount of 35.8 tons/yr (UNEP, 2001, Tolosa *et al.,* 1997).

DDT is the most known and widespread chlorinated organic pesticide. It was introduced as an insecticide in 1945 and since then it has been used in large amounts to control disease-carrying insects and especially mosquitoes. It is estimated that during 1948-1993 the global production and usage of DDT exceeded 1500000 tones. After environmental impairments caused by the extensive use of DDT were manifested, some legislative restrictions were imposed and in 1979 DDT was banned in most Western European countries, whereas some Eastern Mediterranean countries

(Cyprus, Egypt, Israel, Libya and Turkey) do not use chlorinated pesticides since 1985. It is still used in other parts of the world, especially in tropical climates, areas from which it is subject to long-range transport.

The most important source of organochlorine compounds in both the coastal environments and in the open marine ecosystems appears to be atmospheric deposition occurring either as wet or dry deposition or as vapour phase adsorption. PCBs emitted and deposited during the years of intensive production and use are still a diffuse source to the global environment. Evaporation of PCBs from polluted soils and waters is a significant source to the atmosphere. Once in the atmosphere, PCBs enter the global circulation and can travel long distances either as molecules in the gas phase or adsorbed on particles and suspended in aerosols. As a result of PCB banning since 1970s riverine inputs of PCBs or direct inputs from industrial and municipal outfalls, waste waters or sewage sludge are low compared with aerial inputs but they can be locally damaging. It is estimated that for PCBs the 80% and for DDTs the 98% of the total marine inputs are the atmospheric ones (Clark, 1997, Caparis, 2001).

In the Mediterranean region, monitoring activities initiated in the 1970s as a result of the implementation of the Barcelona Convention led to the recognition of point sources. Organochlorine compound levels have been reported for river and marine waters, marine biota and sediments. However, water concentrations are usually close to the detection limits of the analytical methods used, as a consequence of the very low water solubility of these compounds, whereas data on biota present high variability due to biological and biochemical factors. Moreover, organochlorinated compounds being highly lipophilic have a strong tendency to bind to suspended particles and to finally accumulate to marine sediments, which are considered as the ultimate sink for these compounds. For these reasons this report will focus on marine sediments.

Current knowledge on the environmental levels of organochlorinated compounds in Mediterranean sediments is restricted to the vicinities of point pollution sources and major river estuaries, while open sea areas have been studied much lesser. Moreover it is often difficult to compare the reported levels in different marine areas, due to differences in analytical techniques and to poor intercalibration practices. For PCBs, the main problem when comparing and interpreting the available data is that different scientists measure and report varying numbers of PCB congeners. The reported sum of PCBs can correspond to as little as seven or as many as 60 congeners or even to technical mixtures equivalents such as arochlors.

Organochlorine compounds in the Mediterranean marine sediments.

The reported data on the PCBs and DDTs levels in the Mediterranean marine sediments are presented in Table 6/I.

Northwestern Mediterranean surface sediments have been extensively studied by Tolosa *et al.* 1995. According to this study, Rhône River seems to transfer significant amounts of organochlorine compounds. In the Rhone prodelta surface PCBs concentrations (sum of 10 congeners) ranged between 38.3 and 228.5 ng/g and DDTs between 62 and 675 ng/g. These values correspond to mean annual fluxes of deposition 750 μg/m^2/yr for PCBs and 2060 μg/m^2/yr for DDTs. In Ebro prodelta organochlorine concentrations were much lower (PCBs: 3.2-33.6 ng/g, mean annual flux 84 μg/m^2/yr, DDTs: 3.5-11.5 ng/g, mean annual flux 200 μg/m^2/yr). Relatively high values were also measured in the area offshore Barcelona (PCBs: 57.3 ng/g, DDTs: 76.2 ng/g), whereas in gulf of Lions organochlorine values were low (<10 ng/g). In deep-sea sediments organochlorine concentrations reflect the integrated deposition via the atmosphere. In the northwestern Mediterranean, the higher concentrations reported in the western basin (the Catalan Sea) (PCBs: 2.6-5.8 ng/g, DDTs: 3.1-5.4 ng/g) compared to the eastern basin (between the Balearic islands and Corsica) (PCBs: 1.2-1.9 ng/g, DDTs: 1.4-2.5 ng/g).

The only systematic study on PCBs in coastal sediments from the southwestern Mediterranean basin was performed in 1977 (Tolosa *et al.* 1997). Low levels were detected in sediments from Tunisia and Algeria (0.5-7 ng/g), although some localized acute contamination was found off Oran in Algeria (323 ng/g). Low PCBs concentrations (<12 ng/g) were also found in sediments collected from the Tunisian coastal zone close to the city of Sousse in 1995 (Pavoni *et al.,* 2000). The differences in PCB levels between northwestern and southwestern sectors reflect the different degrees of industrialization and population densities existing in these two coastal areas.

In the Ligurian coastal zone an extensive study on organochlorine levels and distribution was performed in 1999 by Bertolotto *et al.,* 2004. Surface sediment samples were collected from 25 locations along transects at 500, 700 and 1000 m from the shoreline. PCBs concentrations varied from 9.6 to 227 ng/g and the most contaminated locations were the industrialized zones of Genova Punta Vagno, Polcevera and Riva Trigoso. DDTs concentrations ranged from 2.5 to 25 ng/g and the highest values were recorded at Arma di Taggia, Albisola Marina and Sanremo.

In sediments from the Gulf of Naples in Southern Italy close to the Bagnoli industrial area, relatively high PCBs values were recorded ranging between 4 and 100 ng/g (Romano *et al.,* 2004)

In Central and Northern Adriatic open sea sediments the reported organochlorine concentrations were low (PCBs: 0.9-14.7 ng/g, DDTs: 0.03-11.3 ng/g) (De Lazzari *et al.,* 2004). However, high PCBs levels were recorded in coastal sediments collected in 1997 in the area of Zadar and Krka estuary (6-2203 ng/g, mean value 181 ng/g) (Picer, 2000). DDTs in the same areas were relatively low (0.2-35.0 ng/g, mean value 3.7 ng/g). A lot of work has been performed in Venice lagoon (Frignani *et al.,* 2001, 2004, Moret *et al.,* 2001, Secco *et al.,* 2005). According to this, significant quantities of PCBs were found in sediments (44-2049 ng/g) due to the high industrialization of the area. However, a notable improvement in the sediment quality regarding PCBs levels was observed from 1987 to 1998, attributed to the improvement of the depuration systems of the industrial plants in Porto Marghera.

Table 6/I. PCBs and DDTs concentrations in the Mediterranean surficial sediments

Area	PCBs (ng g^{-1})	DDTs (ng/g)	Year of survey	References
Rhône River prodelta	38.3-228.5	62-675	1987-1991	Tolosa *et al.* (1995)
Ebro River prodelta	3.2-33.6	3.5-11.5	1987-1991	Tolosa *et al.* (1995)
Barcelona coastal area	57.3	76.2	1987-1991	Tolosa *et al.* (1995)
Gulf of Lion	4.1-8.9	3.5-11.5	1987-1991	Tolosa *et al.* (1995)
Catalan Sea	2.6-5.8	3.1-5.4	1987-1991	Tolosa *et al.* (1995)
Tunisian coastal zone	0.1-12.5		1995	Pavoni *et al.* (2000)
Ligurian sea coastal zone	9.6-227	2.5-25	1999	Bertolotto *et al.,* 2004
Gulf of Napoli	4-100		2000	Romano *et al.,* 2004
Open Adriatic sea	0.9-14.7	0.03-11.3	1990	DeLazzari *et al.,* 2004
Ktka estuary, Adriatic Sea	6-2203	0.2-35.0	1997	Picer (2000)
Venice Lagoon	44-2049		1994	Moret *et al.* (2001)
Kalamas estuaries, Ionian sea	0.04-1.0	0-6.2	1999	Lelekis *et al.* (2001)
Gulf of Thessaloniki	1.8-88	1.4-23	1995	Hatzianestis *et al.* (2001)
Thermaikos Gulf	0.4-1.4	0.8-3.1	1999 - 2000	Cotou *et al.* (2005)
Strymon estuaries, Aegean Sea	0.1-3.0	0.6-48.0	1997-1998	Pavlidou *et al.* (2002)
Nestos delta, Aegean Sea	0.2-1.8	0.2-10.2	1997-1998	Hatzianestis and Sklivagou (2000)
Saronikos Gulf	0.2-5.3	0.2-2.1	2004	Hatzianestis and Botsou (2005)
Elefsis Bay	20-71	4.1-7.8	2004	Hatzianestis and Botsou (2005)
Psyttaleia, Saronikos Gulf	19-73	13.4-442	2004	Hatzianestis *et al.* (2003)
Egypt coastal areas	23-231	32-223	1989-1991	Abdallah and Abbas (1994)
Alexandria harbour	0.9-1211	0.3-885	1998	Barakat *et al.* (2002)

In Ionian Sea data exist only for Kalamas River estuaries and the Gulf of Igoumenitsa (Lelekis *et al.,* 2001). The sediment samples were collected in 1999 and the recorded values for the organochlorine compounds were very low (PCBs: 0.04-1.0 ng/g, DDTs: 0-6.2 ng/g).

In Saronikos Gulf relatively high PCBs concentrations (19.0-70.7 ng/g) were found only in Elefsis Bay and in the area close to Athens sewage outlet in Psyttaleia, while in the rest gulf PCBs values were low (<5 ng/g) with a decreasing trend from the urban coastal zone to the outer parts of the gulf (Hatzianestis and Botsou, 2005). Extremely high DDT concentrations (>400 ng/g) were measured in the area northeast of the sewage outlet indicating recent inputs of DDT in the area

In Thermaikos Gulf organocholine levels and distribution in sediments were studied in 1995 (Hatzianestis *et al.,* 2001) and in 1999 (Cotou *et al.,* 2005). Increased values were recorded only in the inner part of Thessaloniki Bay with PCBs up to 88 ng/g and DDTs up to 23 ng/g. In the other parts of the gulf organochlorine levels were very low similar to the background ones.

Strymon River in Northern Aegean Sea seems to be an important source only for DDTs, as values up to 48 ng/g were recorded in sediments collected in front of the river mouth (Pavlidou *et al.,* 2002), while PCBs at the same location were very low (<3.2 ng/g) reflecting the absence of industrialization in the greater area. In contrast with Strymon River, Nestos River cannot be considered as a major organochlorine supplier as minor pollution for both PCBs and DDTs has been reported in its deltaic area (Hatzianestis and Sklivagou, 2000)

For the southern and southeastern sectors of Eastern Mediterranean, very limited data regarding organochlorines have been published. In a study performed during 1989-1991, significant pollution has been reported for Abu-Quir and El-Mex bays in Egypt (PCBs: 23-231 ng/g, DDTs: 32-223 ng/g) (Abdallah, 1992, Abdallah and Abbas, 1994), while extremely high values (PCBs up to 1211 ng/g, DDTs up to 885 ng/g) were recorded in 1998 in Alexandria harbour (Barakat *et al.,* 2002).

Although the available data on the organochlorine contaminants levels and distribution in the Mediterranean marine sediments are rather restricted and despite the analytical uncertainties, an assessment of these data shows that a decline in PCBs and DDTs concentrations has taken place during the last 20 years, in accordance with the regulatory restrictions on the use of these chemicals. However these compounds remain an important class of contaminants in some coastal areas of the Mediterranean Sea, where localized, chronic pollution continues to exist.

Polycyclic aromatic compounds
Introduction

Polycyclic aromatic hydrocarbons (PAHs) have received special attention since they have long been recognized as hazardous environmental chemicals (NAS, 1975), and are included in priority pollutant lists (e.g. United States Environmental Protection Agency (USEPA) list). Because various PAHs have been shown to be carcinogenic and genotoxic, a detailed investigation of the carcinogenic fraction of the large number of PAHs in environmental samples is desirable.

PAHs are formed mainly as a result of pyrolytic processes, especially the incomplete combustion of organic materials during industrial and other human activities, such as processing of coal and crude oil, combustion of natural gas - including heating - vehicle traffic, cooking and tobacco smoking, as well as in natural processes such as carbonization. The compositional pattern of pyrolytic PAHs (dominance of parent PAH with M.W>202), is characteristic of PAH mixtures formed during high temperature combustion (pyrolysis) of fossil fuels (Laflamme and Hites, 1978; Sporstol *et al.*, 1983). On the other hand, unburned fossil fuels contain mainly low MW PAHs (1-3 rings) and their alkylated derivatives as their most abundant constituents (Neff, 1979). The latter compounds are known to degrade more severely than the high-molecular weight, mostly pyrolytic PAHs, through physical-chemical and microbial processes. As a consequence, an apparent predominance of pyrolytic PAHs is commonly observed in the marine sediments, unless outstanding petroleum-related inputs have occurred.

PAHs enter the marine environment by both aquatic and atmospheric pathways, the latter consisting in dry and wet deposition. The relative importance of the two main input pathways for a given environment depends on the geographical setting of the later (Prahl *et al.*, 1984; Lipiatou and Albaiges, 1994; Gogou *et al.*, 1996; 2000). Coastal sewage dumping, continental runoff, river outflows and accidental oil spills are the expected contributors of PAHs in the coastal sites, while the atmospheric route is considered to be the main pathway for their transport to the open marine sites. Furthermore, sea transportation appears to be one of the main sources of PAHs pollution into the Mediterranean. It has been estimated that about 220.000 vessels of more than 100 tons each, cross the Mediterranean each year and about 250.000 tons of petroleum hydrocarbons are discharged due to shipping operations such as de-ballasting, tank-washing, dry-docking, fuel and bilge oil, etc. (UNEP/IOC, 2002). This is assuming, tentatively, a concentration range of 3-5 ring PAHs in crude oils from 1.3 μg/g in light oils, and up to 0.2% in heavy oils (as the ones spilled in the Eureka accident). Aside from anthropogenic sources, hydrocarbons have also several natural ones, such as terrestrial plant waxes, marine phytoplankton and bacteria, biomass combustion and diagenetic transformation of biogenic precursors.

As a result of the variety of their sources, hydrocarbons occur as complex mixtures in environmental samples. Their sources and their physical-chemical properties largely control transport and fate of hydrocarbons in the marine environment. Thus, bioavailability/ biodegradation rates of PAHs in the marine environment can differ drastically (Mackay *et al.*, 1992;

Schwarzenbach *et al.*, 1993). Association with fast sinking particles (such as fecal pellets and marine snow) is considered as the major mechanism of hydrocarbon transport from the surface to the deep-water column and accumulation in sediments (Prahl and Carpenter, 1979; Baker *et al.*, 1991).

More than twenty-five individual PAHs have been determined in the Mediterranean sediments, comprising three- to six-ring unsubstituted compounds along with several alkyl-substituted homologues. The sum of parent PAHs with MW 202, 228, 252, 276, 278, 300 has been used to represent pyrolytic PAHs. Furthermore, several diagnostic ratios between specific PAHs have been used to assess the different sources and origins of PAHs (Tolosa *et al.*, 1996; Gogou *et al.*, 2000). Nevertheless, their use in sediments can be significantly biased due to modifications occurring from emission of the PAHs to their deposition on sediments. Despite this, characteristic ratios between PAHs of the same MW and with different reactivity can still enable recognition of major transport pathways. Some of the characteristic concentration ratios are those of: benzo[a]anthracene and chrysene/triphenylene (BA/BA+CT) and benzo[e]pyrene and benzo[a]pyrene (BeP/BeP+BaP) (Grimmer *et al.*, 1983). Finally, petrogenic PAHs can be recognized within the dibenzothiophene and phenanthrene series by considering the concentration pattern of the phenanthrene and its alkylated homologues, namely methyl- and dimethyl-dibenzothiophene and –phenanthrene (Tolosa *et al.*, 1996; Gogou *et al.*, 2000).

Polycyclic Aromatic Hydrocarbons in the Mediterranean marine sediments

While a large body of hydrocarbon data sediments has been published during the last two decades in the Western Mediterranean (Albaiges *et al.*, 1984; Grimalt *et al.*, 1984; Lipiatou and Saliot, 1991, 1992; Bouloubassi and Saliot, 1991, 1993a,b; Tolosa *et al.*, 1996; Lipiatou *et al.*, 1997 and references therein), there are only few studies in the Eastern Mediterranean Sea (Gogou *et al.*, 2000; Hatzianestis and Sklivagou, 2002a,b; Tsapakis *et al.*, 2005). Fustheromore, previous studies are largely focused in the northern parts of the Western and Eastern Mediterranean sub-basins and mainly in coastal areas.

In the North Western Mediterranean Sea, concentrations of total PAHs in sediments have been reported in coastal areas, off the Rhône and Ebro rivers, near major urban and industrial centers, while few data have been published in the open sea (reviewed by Lipiatou *et al.*, 1997; Table 6/II). In polluted coastal areas, PAHs occur at concentrations up to 1 $\mu g\ g^{-1}$, while sediment concentrations off the Rhône and Ebro Rivers may exceed 3-5 $\mu g\ g^{-1}$. On the other hand, open sea sediments exhibit total PAHs concentrations from 0.1 to 1 $\mu g\ g^{-1}$.

Another review study by Tolosa *et al.* (1996), presented the concentrations and relative contributions of PAHs in the Western Mediterranean sediments depending on their sources: pyrolytic, fossil and diagenetic. According to this, the highest concentrations of pyrolytic and fossil PAHs were found in sediments from the Rhône prodelta and offshore Barcelona, whereas 1 order of magnitude lower levels were encountered in the Ebro prodelta and other coastal sites far from urban/industrial inputs, which exhibit values comparable to the ones reported in nonpolluted areas of the Adriatic Sea and the Spanish and French coasts (Tolosa *et al.*, 1996).

Table 6/II. Total PAH concentrations in the Western Mediterranean surficial sediments (modified, after Lipiatou *et al.* 1997)

Area	PAH concentrations (ng g^{-1})	Water depth (m)	References
Northwestern Mediterranean	620, 750	2500, 1700	Ho (1982)
Coastal shelf between Monaco and Rhône Delta	128-238	–	Mile *et al.* (1982)
Rhône Delta	376-6364	4-95	Milano *et al.* (1986); Lipiatou and Saliot (1991a); Bouloubassi and Saliot (1993b)
Western Mediterranean central cyclonic gyre	179	2970	Lipiatou and Saliot (1991a)
Ebro Delta	50-6500	10-1000	Albaiges *et al.* (1982); Tolosa *et al.* (1996)
Ligurian Sea off Monaco	599-723	250	Burns and Villeneuve (1983)
Adriatic Sea	12-174	29-252	Marcomini *et al.* (1986)
North Adriatic coast	20-500		Guzzella and De Paolis (1994)
Morocco Mediterranean coast	10 - 550		Pavoni *et al.* (2003)
Sfax bay, Tynisia	1865		Louati *et al.* (2001)
French Riviera	103-8525		Narbonne *et al.* (1991) ; Raoux and Garrigues (1993)
Gulf of Lions shelf, slope, fan	182-763	69-2200	Lipiatou and Saliot (1991); Tolosa *et al.* (1996)
Balearic/Catalan Sea	10-500	1000-1500	Tolosa *et al.* (1996)
Coastal area near urban centers of Barcelona/ Valencia	1396-2313	10-25	Grimalt *et al.* (1984)

In the Eastern Mediterranean Sea, a study on PAH levels and distribution surface sediments from the Aegean Sea was performed during 1997-2000 (Hatzianestis *et al.,* 1998, Hatzianestis & Sklivagou, 2002a,b; Table 6/III). Total PAH concentrations varied between 25.3 and 282 ng/g in the north Aegean and between 19.4 and 120.0 ng/g in the south Aegean Sea. These values are generally considered as low and are comparable with those found in relatively unpolluted locations in other seas. In Nestos delta the concentrations found were slightly elevated (141.1 - 422.3 ng/g), whereas high values were measured in Strymonikos gulf (133.3 - 837.6 ng/g) and even higher in Evros estuaries (932-1025 ng/g). However these values are lower than those reported in Rhone and Ebro delta in Western Mediterranean (reviewed by Lipiatou *et al.*, 1997). Pyrolytic PAH predominated in all cases although Strymon and Evros rivers also transfer significant amounts of terrestrial biogenic compounds. In Thermaikos Gulf, PAH concentrations higher than 1 μg/g were measured only in the inner parts of Thessaloniki Bay, while in the outer gulf PAH levels are similar to those in North Aegean Sea (Hatzianestis *et al.*, 2001, Cotou *et al.*, 2005).

Table 6/III. Total PAH concentrations in the Eastern Mediterranean surficial sediments

Area	PAH concentrations (ng g^{-1})	Year of survey	References
North Aegean Sea	25.3-282	1996 - 2000	Hatzianestis *et al.* (1998), Hatzianestis & Sklivagou (2002a,b)
South Aegean Sea	19.4 - 103.2	2000	Hatzianestis & Sklivagou, (2002b)
Cretan Sea	14.6-161.5	1994, 1998	Gogou *et al.* (2000)
Nestos delta	20.6-422	1998	Hatzianestis & Sklivagou, (2000, 2002a)
Srymonikos Gulf	133-838	1998	Pavlidou *et al.* (2002)
Evros delta	932-1025	1999	Hatzianestis & Sklivagou, (2002a)
Gulf of Igoumenitsa	167-1127	2000	Lelekis *et al.* (2001)
Acheloos delta	36.4-560	2000	Hatzianestis & Sklivagou, (2002a)
Acherontas delta	131-530	2000	Hatzianestis & Sklivagou, (2002a)
Kalamas estuaries	83.1-188.9	2000	Lelekis *et al.* (2001)
Asopos estuaries	155-156	2000 - 2001	Zenetos *et al.* (2004)
Outer Thermaikos	37.4 - 291	2000 - 2001	Cotou *et al.* (2005)
Gulf of Thessaloniki	217-1410	1998 - 2001	Hatzianestis *et al.* (2001)
Saronikos Gulf	64.6-838	1999 - 2000	Hatzianestis *et al.* (2003)
South Evoikos	25.6-196	2000 - 2001	Zenetos *et al.* (2004)
Elefsis Bay	1807-5087	1993 - 2000	Sklivagou *et al.* (2001), Hatzianestis et al (2003)
Israel coasts and rivers	2760 - 7760	1995	Zimand (2002)
Psyttaleia, Saronikos Gulf	2936-17090	1999 - 2000	Hatzianestis *et al.* (2003)

In Saronikos Gulf, Elefsis Bay is highly contaminated due to the industrial zone along the northern coast (PAH: 1.8-5.1 μg/g), while extremely high values up to 17 μg/g were recorded in the marine area around Psyttaleia receiving the effluents of the Athens sewage outlet. In the rest gulf PAH concentrations are significantly lower (64.6-838 ng/g) with a decreasing trend with distance from the North and Northeast coastal zone (Sklivagou *et al.,* 2001, Hatzianestis *et al.,* 2003)

In the Ionian Sea, PAH values above 1 μg/g were measured in Igoumenitsa and Argostoli Gulfs, while in estuaries Acheloos, Acherontas and Kalamas rivers no pollution from PAH was recorded (PAH concentrations <0.5 μg/g) (Lelekis *et al.,* 2001).

Gogou *et al.* (2000) presented a study of the composition of PAHs in the Cretan Sea sediments, along two transects from the coast (100 m) to the open sea (1700 m). Total PAHs ranged from 14.7 to 161.5 ng/g. These values are considerably lower than those reported in NW Mediterranean areas located near the outflow of the Rhône and Ebro rivers, where Total PAH concentrations reached values up to 6500 ng/g (Lipiatou and Saliot, 1991; Bouloubassi and Saliot, 1993b; Tolosa *et al.*, 1996). Also in the vicinity of urban centers, e.g. Barcelona, Valencia the Total PAHs concentrations were measured in levels up to 2313 ng/g (Grimalt *et al.*, 1984). Total PAH concentration levels in the Cretan Sea sediments fall in the range of those reported in open sea areas in the Mediterranean, such as the Adriatic Sea (12-174 ng/g, Marcomini *et al.*, 1986) and the open NW Mediterranean Sea (100-500 ng/g, Tolosa *et al.*, 1996). The concentration of PAHs measured in this study falls in the same range of corresponding concentration (ca. few hundred ng/g) measured at open sea worldwide (Boehm and Farrington, 1984; Barrick and Prahl, 1987; Venkatesan *et al.*, 1987; Wakeham, 1996). Pyrolysis and combustion processes appear as the major sources of PAHs encountered in this area. Pyrolytic PAH concentration were found in significantly lower levels compared to the Western Mediterranean coastal and open sites, varying from 11.4 to 99.6 ng/g and accounting for 63-79% of the total PAHs. On the other hand, total phenanthrene concentrations, indicative of petrogenic inputs were significantly lower, accounting for less than 15% of the total PAHs.

In both the Western and Eastern Mediterranean sites, the relative abundance of pyrolytic compared to petrogenic PAHs was slightly elevated at the deep sampling sites compared to the shallow ones (Tolosa *et al.*, 1996; Gogou *et al.*, 2000). Such a trend has been previously observed in several marine environments and most likely results from: I) the preferential preservation of PAH released from combustion processes which are known to resist to degradation during atmospheric transport and sedimentation (Baker *et al.*, 1991; Behymer and Hites, 1988; Wakeham, 1996), II) the preferential association of pyrolytic PAH with fine particles, which can be transported along long distances from the coast (Boehm and Farrington, 1984; Readman *et al.*, 1984), and III) finally, this trend suggests that the atmospheric deposition could be the major source of pyrolytic PAHs in the open marine sites. The latter statement is further supported by the distribution profiles of PAHs in background aerosol samples, collected over the Mediterranean Sea (Simo *et al.*, 1997; Gogou *et al.*, 1996), which are similar to the one observed for the majority of the open Mediterranean Sea sediments.

Radioactive Substances

Radionuclides (radioisotopes) have similar chemical characteristics with stable elements. Therefore, their biochemical behaviour in the marine environment depends on their chemical properties. They undergo various environmental processes taking place in situ, such as dissolution, precipitation, sorption, complexation, biological ingestion and excretion, etc. in a manner similar to those of stable isotopes.

The *natural radionuclides* had already existed at the beginning of the universe and since then they have always been present in the environment. More than 60 radionuclides are known to occur naturally in the environment and are classified into two groups according to their origin: terrigenous (three primordial actinide parent nuclides, ^{232}Th, ^{235}U, ^{238}U and their descendant products) and cosmogenic (principally ^{3}H and ^{14}C).

The *artificial radionuclides* have been present in the environment since the 1940s. Their major sources are: (i) the nuclear weapons explosions and testing, with ^{14}C, ^{90}Sr, ^{137}Cs and Pu isotopes being the most significant residual species and ^{241}Am produced by decay of fallout ^{241}Pu; (ii) the nuclear power production, where mining and milling of uranium results in the release of ^{222}Rn to the atmosphere, whereas the reprocessing activities of the spent nuclear fuel, which contains large quantities of 235U and ^{239}Pu, discharges significant quantities of ^{137}Cs and $^{239,241}Pu$; (ii) the accidents involving reactors and other nuclear facilities; (iv) the waste disposal from a variety of civilian and military operations; and (v) the underground disposal of the solid radioactive waste.

Pathways for their introduction to the Mediterranean marine environment are: the atmospheric fallout, the river run-off, the exchange with the Black sea via the Dardanelles strait and the exchange with the Atlantic Ocean via the Gibraltar strait.

Spatial distribution

Anthropogenic radionuclides have been used as tracers of the rates and mechanisms of a range of environmental processes due to their characteristic time-dependent decay. Thus, most of the scientific work in the marine environment refers to this kind of studies, whereas there are a relatively limited number of pollution studies, with the exception of a period right after the Chernobyl accident. Furthermore, most of the literature refers to the western and central part of the Mediterranean region since there are more nuclear plants in the western countries (France, Spain, Italy) than in the eastern part (UNEP, 1987). According to the EEA report (1999), the total inventory of radionuclides in the Mediterranean Sea is declining. In surface waters the levels of ^{137}Cs and $^{239,240}Pu$ show decreasing trends. Nevertheless, it was estimated from 1991-1994 data that the ^{137}Cs inventory in the Mediterranean water column was increased after the Chernobyl accident by approximately 25%. In marine organisms used for human consumption, ^{137}Cs concentration is very low (less than 1 Bq/kg), far below the limit (600 Bq/kg) fixed by the EU as the maximum permitted level in food.

From the analysis of plutonium and americium in vertical profiles in the vicinity of the Strait of Gibraltar, it was clear that inflowing Atlantic waters had lower concentrations than outflowing Mediterranean waters (León Vintró *et al.*, 1999). On the other hand, the inflow of Black sea water enriched in ^{137}Cs through the Dardanelles strait strongly influences ^{137}Cs concentrations in surface and intermediate waters of the north Aegean Sea (Florou *et al.*, 1995; Delfanti *et al.*, 2004).

Nuclear facilities in the Mediterranean basin are mainly located along rivers and their effluents are subjected to riverine geochemical processes that delay, to a considerable extent, output to the sea. The contribution from these installations into the sea is usually low and limited to confined areas, which are regularly monitored by national authorities. In the case of the surface waters of the Ebro river basin, contamination from nuclear power plants located along the river was not detected (Pujol and Sanchez-Cabeza, 2000).

Radionuclide concentrations in sediments are usually highest on the continental shelf and near the river mouths, whereas, they reached the lowest values in deep-sea sediments. Recent data indicate that ^{137}Cs in the sediments of the Western Mediterranean, at water depths of about 1000 m is in the order of 230 Bq.m^{-2}, corresponding to 5-10% of the cumulative fallout deposition (EEA, 1999). In deep-sea environments Pu inventories were as low as a few Bq.m^{-2}, whereas, in the area affected by the Palomares accident, ^{239,240}Pu inventories were in the range of 200-1500 Bq.m^{-2} (Anton *et al.*, 1995).

In the Spanish Mediterranean coast, results obtained from 1987 to 1991 showed an enhancement of ^{137}Cs levels in seawater after the Chernobyl accident by 33±2 %. The ^{137}Cs activity incorporated by *Posidonia oceanica* from the Catalan coast after the Chernobyl deposition over the Mediterranean Sea has shown an increase of 100±40% one year after the accident (Molero *et al.*, 1999). The Spanish continental shelf, accounting for just 1% of the total Mediterranean Sea floor surface, accumulates 4% of plutonium, 3.5% of americium and 1.4% of caesium (Gascó *et al.*, 2002).

In surface sediments of the Ligurian Sea Pu concentrations were found ten times higher than in the adjacent river sediments. The integrated inventory of ^{239,240}Pu in a sediment core was calculated to be 3.5 mCi.km^{-2}, nearly twice the average input from fallout at these latitudes, apparently because Pu is removed from seawater by scavenging onto particles (Jennings *et al.*, 1985).

Delfanti *et al.* (1995) reported ^{239,240}Pu concentrations in surface sediments of Taranto Gulf to be in the range of 0.5-1.0 Bq kg^{-1}; in the sediments of La Spezia Gulf Pu inventory was higher than that calculated by the overall fallout deposition. The ^{239,240}Pu vertical profile from a core collected in an abyssal plane of the Western Mediterranean Sea (Algeria) at 2880m depth, Pu concentrations were very low, ranging from 0 to 0.21 Bq kg^{-1} (Delfanti *et al.*, 1995). In surface sediments from the Gulf of Ghazaouet, on the western coast of Algeria, the $^{239,240}Pu$ range was 0.3-0.6 $Bq.kg^{-1}$, and ^{137}Cs 6.9-8.5 $Bq.kg^{-1}$. The concentrations of these radionuclides were similar to the one reported in the literature for the pre-Chernobyl sediments, revealing a single source of radioactive contamination i.e. global fallout (Noureddine and Baggoura, 1997).

Frignani and Langone (1991), in the study of the sediment accumulation rates off the Po River delta and the Emilia-Romagna coast in the north western Adriatic Sea, reported surface ^{137}Cs concentration ranges of 4.33-16.5 $Bq.kg^{-1}$, and ^{137}Cs inventories ranging from 617-6680 $Bq.m^{-2}$.

Accordingly, Radakovitch *et al.* (1999) studied the ^{137}Cs accumulation in the Rhone river delta sediments; the ^{137}Cs inventories ranged from 1100 to 40000 $Bq.m^{-2}$, with the higher values close to the river mouth.

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