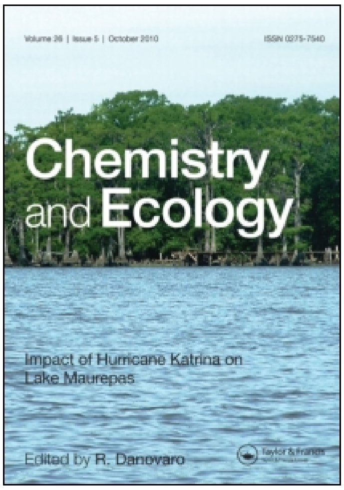

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POLLUTION THREATS IN THE MEDITERRANEAN SEA: AN OVERVIEW

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This overview summarises the present knowledge on major sources of pollution, which are of concern for the Mediterranean Sea. Eutrophication, red tides, organic loads, hydrocarbon spills, heavy metal contamination and their biological effects are described on the light of the ecological characteristics of the Mediterranean. In particular special attention is paid to the "new pollution" processes; *i.e.*, the introduction of novel substances with biological activity that might have synergetic effects with "classical pollutants". Different compartments and marine ecosystems are considered and compared. The degree of anthropogenic impact and its apparent trends are discussed. Possible monitoring plans and remedial actions for a sustainable management of coastal zones subjected to increasing pollution are also suggested.

Keywords: Marine pollution; Eutrophication; Harmful blooms; Organic wastes; Oil spills; Heavy metal contamination; Ecological response

1 DEFINING POLLUTION

The Convention in Barcelona on the Mediterranean introduced a new concept, leading to new perspectives in environmental conservation, defining marine pollution as: "any natural or anthropogenic input or subtraction of energy and material that causes a persistent change of the chemical, physical or biological characteristics of a system, altering the functioning of the marine ecosystems and affecting the possibility of human exploitation of the natural resources including the use of the coastal areas for recreational purposes".

Pollution is increasingly becoming synonymous with damage and disease. As such some authors tend to define pollution only as the introduction by man of substances or energy. The multiple nature of pollution should also be stressed: macroscopic effects are becoming increasingly evident, including not only direct human introduction of pollutants but also climatic changes (from green house effects to UV radiation etc.).

Coastal ecosystems are clearly subjected to increasing anthropogenic impact. Most pollutants and/or substances having biological effects, are released in huge amounts in coastal areas often without adequate treatment or control (Tab. I; from Della Croce *et al.*, 1997, quantities released annually).

In addition, in the Mediterranean the development of urban centres, agriculture and industry has been often geographically interdependent so that pollutants, generally collected by rivers

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TABLE I Elements and Compounds Delivered Annually into the Mediterranean Basin.

Nitrogen	1×10^6 t
Hydrocarbons	0.3–0.5 $\times 10^6$ t
Phosphorus	0.3–0.4 $\times 10^6$ t
Pesticides	90.000 t
Detergents	60.000 t
Organic loads	2.5×10^6 t
Zinc	25.000 t
Mercury	130 t
Lead	3.800 t
Chromium	2.400 t
Phenols	12.000 t
Industrial discharge	10×10^6 t

are concentrated along limited coastal areas, thus increasing their negative consequences. For such a reason it is often difficult to discriminate between sewage dump and industrial/agricultural discharge and diffused pollution that is characterised by synergetic effects.

However, for practical reasons we will present here different "kinds" of pollution that might be of particular concern and their potential consequences. It should be pointed out anyway that this synthesis does not want to be exhaustive rather its aim is to focus on certain aspects (eutrophication and harmful algal blooms, hydrocarbon pollution, mariculture impact, heavy metal contamination etc.) that have to be directly approached for a correct management of the coastal waters. It is omitted for brevity reasons the treatment of environmental problems related to the fisheries and to the introduction of alien species.

2 VULNERABILITY OF THE MEDITERRANEAN SEA

The Mediterranean covers an area of about 3 million km^2 (*vs.* Baltic and North Sea that together cover about 1 million km^2). It is a semi-enclosed system, characterised by large continental shelf surface (about 20%), low average depth (*ca.* 1400 m; compared to *ca.* 3850 m of the other oceans world-wide) and extended continental shelves, especially in the Adriatic Sea. Mediterranean marine ecosystems present an idiosyncratic combination of characteristics, which make them very different from north European conditions. Critical points for potential impact of pollutants in the Mediterranean coastal systems are:

High temperatures: Annual minimum of 12 °C, reaching up to 25 °C during summer, that induces high metabolic rates, thus affecting both the production and the activity of living communities.

Microtidal regime: tidal range is typically less than 50 cm reducing the potential for dilution and dispersion of solutes and particulate wastes particularly in enclosed bays were wind-driven currents are relatively weak.

Oligotrophy: low nutrient content, low primary production, and low phytoplankton biomass are typical of most Mediterranean marine ecosystems, particularly in the Eastern Basin (Bethoux, 1981; Azov, 1986). Low phytoplankton biomass induces high transparency of the water and light penetration deeper in the waters thus allowing photosynthesis at a greater depth (Ignatiades, 1998).

Primary production (PP): PP is phosphorus limited (Krom *et al.*, 1991) as opposed to nitrogen limitation in the Atlantic and in most of the world's Oceans. In this context, eutrophication would be expected only when phosphate is released in adequate quantities.

Freshwater inputs: The Mediterranean is a evaporation basin in which the limited water exchange through the Gibraltar strait and the limited freshwater input results in low water masses turnover rates.

Coastal morphology: Coastal morphology of bays is also very different from that of Scottish lochs and Norwegian fjords. They are typically not associated with permanent freshwater supply nor do they have a sill impeding the subsurface exchange of water masses.

Biodiversity: High biodiversity of the ecosystem (*i.e.* the fauna and flora), particularly in the coastal zone and consists of a large proportion of endemic species (Fredj *et al.*, 1992) as a result of the dynamic geological past of the Mediterranean. Benthic assemblages are typified by low abundance and biomass as a result of the prevailing oligotrophic conditions (Karakassis, 2000; Karakassis and Eleftheriou, 1997).

Anthropogenic pressure: About 300 million people inhabit the Mediterranean basin or discharge their end-product into the Mediterranean and about 100 million tourists "use and live" Mediterranean waters during the summer.

All these factors make the Mediterranean Sea particularly susceptible to the impact of most pollutants introduced anthropogenically.

3 EUTROPHICATION OF COASTAL AREAS

When inorganic nutrient load is limited there is a strong competition between phytoplankton species and between phytoplankton and heterotrophic bacteria (Danovaro, 1998). When nutrient loads increase phytoplankton becomes successful over bacteria in such competition and their growth can stimulate an algal bloom. Phytoplankton blooms maybe the result of an increase in cell number of either many species or can determine the selection of few species. For instance high P:Si and N:Si ratios have been proved to limit diatom growth (that specifically need silicates) while increasing dinoflagellate or other phytoplankton species.

The term eutrophication was coined in 1937 by Weber to indicate "a nutrient enriched water body in which primary production was enhanced". In fact, the prefix "eu", is from Greek "nice/good". Eutrophication can be referred to an ecosystem characterised by a high primary production sustained by high nutrient concentrations. However, it should be clarified that eutrophication is not a state of a marine ecosystem, rather a process of progressive enrichment of its trophic conditions.

In this synthesis we will distinguish between eutrophication, dystrophy/mucilage production and red tides/harmful blooms. In fact all these phenomena are directly or indirectly related to algal development, but their "triggering" mechanisms and ecological consequences are different.

Eutrophication can be identified in different ways: in terms of inorganic nutrient concentrations (primarily nitrogen and phosphorus), increased primary production, increased vertical fluxes or increased organic inputs to bottom sediments. Often such process, that can also be the result of natural (*i.e.*, non anthropogenic) phenomena, are connected with degradation of ecological conditions, and might precede the occurrence of dystrophy (phenomenon that will be discussed later). Enclosed marine ecosystems might become eutrophic by "aging" as they have been historically identified as optimal reservoirs for human activities, such as extensive aquaculture and particularly shelf fish cultures. Coastal waters and especially semi-enclosed systems, in which nutrient discharge already exists (domestic, agricultural and industrial), are generally characterised by strong changes in nutrient concentration with time. Phytoplankton blooms generally start in late winter-early spring as a result of higher nutrient availability combined with light, transparency, temperature, salinity needs and competition among species.

3.1 Ecological Consequences of Eutrophication

The negative impact of algal bloom can be directly due to the algal production of certain toxines (see below) or to the creation of altered environmental conditions. In this context we will point out just the effects of eutrophication in terms of reduction of oxygen availability due to the decomposition or large amounts of primary organic matter. In the northern Adriatic, such consequences are closely coupled with the reduced coastal water circulation, which is limited especially in summer when the anti-clockwise circulation is reduced and the river Po plume extends for several miles creating vertical and horizontal (frontal) stratification of the water column. In these conditions any biological effect is exacerbated by the limited mixing and oxygen diffusion. At the end of the bloom, senescent and dead algae settle to the sea floor and are attacked by microbes for their degradation. This process reduces oxygen level in bottom waters to create sub-oxic/hypoxic or even anoxic conditions.

An interesting "chronistory" of the mucilage phenomena in the Adriatic Sea is reported by Solazzi and Boni (1989). Briefly: in 1968 and 1969, for instance, phytoplankton blooms caused a large mortality in benthic organisms, that were subsequently deposited along the seashore causing hygienic problems too. Similarly in September 1980 a *Gonyaulax polyedra* bloom (16×10^6 cells per litre) in the Bay of Le Kastela determined a strong mortality of fish and molluscs (Marasovic and Vukadin, 1982). The same happened in May 1982 due to a *Glenodinium lenticula* bloom and in June–July a *Gonyaulax polyedra* bloom caused anoxic conditions over an area of *ca.* 1000 Km^2 along the Romagna coasts (Montanari and Rinaldi, 1983). Another summer bloom in 1984 *Gonyaulax*, *Gymnodinium* and *Massarthia*, caused anoxic conditions along 200 Km from the Po to Ancona, together with mortality of benthic organisms.

Eutrophication is not only due to phytoplankton blooms, but can be also the result of an anomalous development of macroalgal species. This is particularly evident in the Venice lagoon, where benthic macroalgae of the Ulvacee (defined also "nitro-philic algae") produced large quantities of *Ulva* and *Enteromorpha* which caused a general concern for possible consequences on public health due to the bacterial development and to the formation of hydrogen sulphide.

Death of benthic organisms has been also described in the Gulf of Trieste in 1983 (Stachowitsch, 1984), but in this case without any apparent major bloom, it is possible that it was simply caused by the strong water column stratification. Therefore, caution must been used when hypoxic phenomena are indicated as a direct consequence of eutrophication events.

3.2 Threatened Areas of the Mediterranean

The Adriatic Sea is the most endangered area; with a surface of about 132,000 km^2, corresponding to about 1/20 of the entire surface of the Mediterranean, but equivalent to 1/125 of its volume, it can thus be assimilated to a macro-lagoonal system. The Adriatic Sea receives a large freshwater input from the river Po (more than 1500 $m^3\,sec^{-1}$) equivalent to about 30% of the total Mediterranean river inputs. About 85% of this freshwater input is delivered in the Northern Adriatic, where the average depth is 40 m. Organic loads from 25 million habitants is brought into the Adriatic by the rivers Po, Adige, Brenta and Isonzo that collect rain precipitation from about 120,000 km^2 (*ca.* 40% of the Italian surface). These characteristics make the northern Adriatic highly susceptible to eutrophication. Phytoplankton in the Adriatic is composed of various taxa including Diatoms, Dinoflagellates, Coccolitoforids, Silicoflagellates, Cloroficeans, Euglenoficeans and Criptoficeans. 150–200 species, largely dominated by Diatoms and Dinoflagellates (*ca.* 90–95%; Solazzi and Andreoli, 1971; Marzocchi *et al.*, 1979), have been identified so far. Phytoplankton density ranges from

1000 to 600,000–700,000 cells per litre, depending upon location. But in eutrophicated areas bloom cell densities can reach hundreds of millions per litre.

The first bloom, with green-red coloured waters, has been described in 1954 from a coastal area close to the Po delta and was due to algal organism typical of fresh-/mixo-aline waters (*Chromulina rosanofii* -Crisomonadina- and *Oscillatoria tenuis* -Cyanophicea). In 1968 and 1969 dinoflagellate blooms (*Peridinium depressum*) were also observed (Mancini *et al.*, 1980). From 1975–79 along the northern Adriatic coasts eutrophic events appeared every summer with blooms (up to 21 million cells per litre) dominated by dinoflagellates (*Ceratium ssp* in 1975, *Prorocentrum micans* in 1977, *Gymnodinium corii* in 1979).

From the constant monitoring of the Adriatic coasts it appears evident that such events are becoming more frequent. Dinoflagellate blooms are always anticipated and/or alternate with Diatom blooms. Some authors hypothesise that also the introduction of vitamins B12 and other growth factors through waste waters could have induced certain algal blooms.

Such events are evident, even though to a lesser extent in the eastern Adriatic coast. In the Gulf of Trieste and Slovenian coasts intense algal blooms of *Peridinium ovum* have been reported since 1973 causing death of several benthic specimens (particularly the shell-fish *Pecten jacobaeus*). Other dinoflagellate blooms (*Scrippsiela jáeróense* and *Gonyaulax polyedra*) have been observed since 1983 (Fonda Umani, 1985), and repeatedly described for several years (Cabrini *et al.*, 1988). In other Italian coasts eutrophication arises mainly from human discharge. The western coasts are characterised by much higher hydrodynamic and nutrient dilution but in some areas (estuary of the rivers Teber and Arno) and in the Gulf of Naples a pronounced eutrophication is evident.

The French coast is mostly affected by the Rhône river discharge that delivers five million tons of suspended solids, 76,000 tons of inorganic N and 8400 tons of P per year. Blooms of diatoms and dinoflagellates occur in favourable conditions (low hydrodynamism, high temperatures, high stratification). The problem does not affect the French and Italian Riviera due to the cyclonic circulation from the Ligurian Sea.

The Spanish coast is characterised by both natural enrichment due to upwelling and an induced eutrophication caused by human discharge. The high productivity of the Alboran Sea appears to be related to the upwelling generated by the anticyclonic circulation generated by the flow of Atlantic waters entering the Mediterranean through the Gibraltar strait. Highly eutrophicated areas appear to be coastal areas close to Valencia and the Ebre delta.

The Eastern Mediterranean is generally characterised by highly oligotrophic conditions. Coastal Greek waters, especially in bays and estuaries appear rather endangered. Algal blooms have been described in the Gulf of Salonikos, and Thessaloniki. The same applies to the Lebanon coasts, while in Egypt eutrophication has been largely observed in coastal waters as a result of the large nutrient input (though the Nile input was reduced by 90% in the last decades), such as in Alexandria and in some places nitrogen limitation and hydrogen sulphide production is observed.

4 DYSTROPHY AND MUCILAGE PRODUCTION

When eutrophication processes reach extreme conditions, such as those reported in the semi-enclosed northern Adriatic, the reduced summer hydrodynamism often drives this system towards dystrophic conditions.

It is therefore possible that the occurrence of sticky mucilaginous masses (also known as "mare sporco"). Part of the material is floating on the sea surface and is deposited on the beaches by winds and currents, reducing the suitability of bathing and threatening tourism.

The size of this mucilage (up to 4 m in length) and the dimension of the phenomenon is such that they might cause serious problems to fisheries.

Mucilage production generally occurs in peculiar physical conditions (*i.e.* highly stratified waters, low-turbulence and developed pycnocline) typical of late spring-summer season, after the decay of spring phytoplankton blooms.

Mucus aggregates have been described in the form of stringers (elongate, comet-shaped aggregates), macroflocs (subspherical, irregular, whitish aggregates), or dense clouds (large, elongate to subspherical aggregates), that are transported horizontally and vertically in the water column. They are composed of gelling of polysaccharide exudates including phytoplankton cyanobacteria heterotrophic bacteria and other plankton and display a generally high C:N ratio and a low protein content. Polysaccharides are thought to play an important role in formation of larger organic aggregates, by producing transparent exopolymeric particles, which are thought to represent the nuclei for organic matter aggregation. Large-scale gelatinous mucus aggregations observed in the Adriatic Sea mainly consist of polymeric carbohydrates, produced by algae especially in response to environmental/nutritional stress (Posedel and Faganelli, 1991) and produced toward the end of blooms when particle aggregation is pronounced (Myklestad *et al.*, 1989). Aggregates might have a relatively long life (1–3 months) and once organisms have been embedded they become progressively less dependent on processes in surrounding waters. Primary and secondary production, indeed, in these aggregates is extremely high indicating that they might be self-sustaining.

Mucilage phenomenon is of natural origin, but its intensity and duration are particularly marked in the northern Adriatic. The causes of the mucilage phenomenon have not yet been explained, but several hypotheses have been proposed:

Environmental changes. These include changes in the freshwater input from the Po river leading to an increased nutrient availability, especially during spring; the extremely reduced vertical and horizontal mixing and increased radiance; changes of the environmental conditions at the interface of the Po river plume/oligotrophic waters; change in the nutrient ratios and generally drastic nutrient limitation (when phosphorus is no longer available for nucleic acid synthesis). In addition to nutrient limitation, high temperatures and irradiances might increase stress in metabolic rates. All these factors have induced large excess of carbohydrate production and high exudation rates.

Change in grazing pressure. Grazing could play an important role in the development of mucilage. When copepod stock is too low to control algal development, grazing pressure can be further reduced by the deterrent effect of exudates produced. Naupliar copepod populations are affected by mucus and adult copepods are unable to feed on marine snow.

Bacterial contribution to exudate production. Bacteria can contribute to exudate production in conditions of nutrient exhaustion, which can impede bacterial growth. Their ability of degrading the exudates might also be limited by unbalanced C:P and N:P ratios.

Virus infections. Virus infection and phytoplankton cell lysis are also considered as causes of DOM production and polysaccharide accumulation. Experimentally this has been demonstrated with the formation of marine snow after addition of concentrated virus-like particles.

Aggregation mechanisms. A recent hypothesis links gradual aggregation processes of marine snow in the pycnocline layer with gelatinous mass formation, which include intermediate stages of stringers, clouds and creamy surface. Large stringers and clouds might be also formed directly by coagulation of gel-like dispersed substances accumulated in unusual quantities. A possible role of Zeolite A (allumino-silicates) and carboxilic acids-polycarboxylates as nuclei for mucilage aggregation has been proposed. Zeolite has gradually substituted polyphosphate in detergents in Italy during the eighties (*i.e.*, immediately before mucilage appearance). Zeolite would also stimulate diatom production of exudates. During the summers of 1988, 1989, 1991 and 1997 floating gelatinous aggregates appeared in large areas of the northern Adriatic basin, causing anoxia and mechanical threats to the benthic system (Welker and Nichetto, 1996). The appearance of mucilage aggregates along the Adriatic coasts during the summer of 1997 coincided with evident changes in biochemical features of the benthic system.

The most evident changes in the biochemical composition of the sedimentary OM are related to the decrease in the protein to carbohydrate ratio and to the significant increase of the lipid content during mucilage appearance. Biochemical indicators, such as the RNA:DNA ratio, indicated altered metabolic activity induced by mucilage accumulation (Manini *et al.*, 2000).

5 HARMFUL ALGAL BLOOMS AND RED TIDES

There might exist different types of algal bloom, having different consequences: toxic blooms that discolour the water, blooms of non toxic species that harmlessly discolour the water or toxic blooms without causing discoloured waters. In recent years, harmful algal blooms (HAB) have been reported along an increasing number of the Mediterranean coasts. Toxic algae can become dangerous when they are present at certain densities (few hundreds per litre) and are concentrated by filter feeders (such as the common mussel) that are subsequently ingested by humans. Among organisms that concentrate these algae, highest toxicity is generally observed in mussels, followed by other shellfish such as the *Pecten*, and is practically negligible in oysters.

So far 52 species dinoflagellates, endemic of the Mediterranean have been identified, which are able to produce Diarrethic Shellfish Poisoning (DSP; Volterra and Premazzi, 1993). Eight species have been identified in the whole Adriatic (5 in the central Adriatic: *Dinophysis acuta*, *D.caudata*, *D. fortii*, *D. rotundata*, *D. tripos*; Honsell *et al.*, 1990), though no records have been registered in the last 3 years. Several DSP-producing dinoflagellates (*Dinophysis ssp.*) have been also encountered along Spanish coasts.

Among the different possible diseases caused by toxic algae, only DSP toxicity cases have been reported in the Mediterranean. Since 1989 along the Adriatic coasts (from Friuli to Abruzzo), several cases of DSP provoked by the dinoflagellate *Dinophysis* have been observed. No PSP (Paralytic Shellfish Poisoning) cases have been reported as of yet, but this does not mean that the Mediterranean is safe. In fact, PSP-causing species, such as *Alexandrium minutum*, *A. catenella*, *A. tamarense* and *Gymnodinium catenatum*, have been consistently reported in Catalunya and Egyptian coastal waters. Often these species are found in ports, which are considered important potential starters of HAB. Besides the obvious concern for human health, ecological consequences of HAB include fish mortality, induced by *Gyrodinium corsicum* blooms, reported in the Delta de l'Ebre bays.

The concern caused by such events induced several organisations (NSF, NOAA) to deal with these problems with a co-operative approach creating a scientific agenda called ECOHAB (Ecology and Oceanography of harmful algal blooms), and international programmes (such as GEOHAB, Global Ecology and Oceanography of Harmful Algal Blooms) which have been started with the support of the European Community.

The harm caused by these algal blooms is very different depending on the species and the effects of the toxin present. The expression of these toxins can be influenced by several factors and the production of algal toxins appears modulated by co-occurring bacteria. Some species cause harm at low densities, while others become dangerous only at high densities. In some species (*e.g.*, *Alexandrium*) the quantity of toxins appears nutrient limited. Relating HAB to eutrophication is ecologically not correct, as eutrophication does not means necessarily harm.

In this regard, noxious blooms can not be predicted on the basis of nutrient concentrations. This is consistent with observations of all algal blooms that they cannot be studied independently of their abiotic and biotic context. Most algal blooms represent a stage of natural plankton succession and toxic and non-toxic species obviously interact and compete for nutrients. Since the relevance of a certain species among an assemblage depends on several factor regulating its growth and metabolism, the knowledge of their ecology is an essential pre-requisite for coastal monitoring that could help in predicting the possibility of blooms given certain environmental conditions. For instance the identification of the potential grazers of toxic species could be imagined in the future as a potential tool for controlling noxious algal blooms.

Moreover, as many species are known to produce cysts and "disappear" from the water column for years, the detection and quantification of cyst banks in surface sediments should be, for instance, an obvious target for coastal monitoring. This obviously requires a taxonomic approach to identify potential harmful species throughout their life cycle.

Finally coastal oceanography and the knowledge of the hydrodynamic conditions (currents, up-welling, plumes etc.) and their interaction with atmospheric conditions are needed to predict the expansion and progressive contamination of coastal areas, starting from local restricted blooms.

Although all algae require nutrients for their growth, toxic blooms have nothing in common with eutrophication. Recent studies have demonstrated that nutrients brought to the sea by rivers do not affect the growth and development of *Dinophysis* (Delmas *et al.*, 1992). Highest densities of *Dinophysis acuminata* observed in the Tyrrhenian Sea coincided with very low nutrient content, and similar results have been reported from the Atlantic coasts. HAB are neither related to dystrophic events; in fact, in the Adriatic, during normal blooms or during mucilage production no toxic algae are found. From these data it has been also hypothesised a competition of DSP-producing dinoflagellates with other phytoplankton species (*e.g.*, *Skeletonema costatum*) would reduce the development of harmful species. As for HAB, the presence of red tides is not synonymous with eutrophication (Viviani, 1992). In the Venice lagoon the first "coloured tide" has been reported in spring 1970 and 1971 and was caused by the diatom *Skeletonema costatum* and by the Euglenoficean *Eutreptiella pascheri*. The same phenomenon happened again the following year. In 1975 and 1977, red tides have been observed in several Adriatic bays including the eastern coast. The dinoflagellate *Noctiluca miliaris*, reached 48×10^6 cells per litre, but their bloom disappeared in few hours due to the presence of strong winds. Red tides due to *Gonyaulax polyedra*, *Gymnodinium adriaticus* and *Noctiluca miliaris* have been described in these years along the Yugoslavian waters (Maretic *et al.*, 1978).

In march 1981, a red tide caused by *Glenodinium lenticula*, and "green tides" caused by *Gymnodinium* have been observed (Viviani *et al.*, 1985). This species was accompanied by another species similar to the toxic *Gonyaulax tamarensis*. Summer red tides are also increasingly observed along the Costa Brava (Spain).

6 DOMESTIC WASTES

During the seventies most coastal areas of the Mediterranean were found to discharge untreated sewage to the sea and the rest usually gave only minimal treatment. The worst affected areas were obviously those of the northern Mediterranean coasts subjected to higher anthropogenic pressures. The Riviera coast from the Ebro in Spain across the French Riviera to the Italian Riviera and the Arno estuary were found to be the most polluted coasts (but these appear to be those areas investigated in detail). The Israeli and Greek coasts were found in similar conditions.

A vigorous attack to the problem was carried out especially in Italy, France and Spain and later on in Greece. The results are becoming evident only in the last 10 years due to the creation of sewage treatment plants (more than 20 alone in the Italian Riviera from Genoa to Ventimiglia), but the problems still remain in those small villages that during summer become tourist hot spots (such as the Romagna Coast in Italy, the Costa Brava and Costa Dorada in Spain and part of the French Riviera) which have not catered for the increase in domestic sewage inputs. Another problem is related to the actual functioning of these treatment plants that often are not in activity of have a reduced efficiency. Besides the obvious damage from tourist activity and for aesthetic reasons, one of the main consequences of domestic sewage pollution is a threat for human health with some cases of cholera in southern Italy where shellfish is generally consumed crude (such as in Naples, Bari and Taranto).

7 ORGANIC LOADS AND MICRO-POLLUTANTS: THE MULTIFACETED IMPACT OF INTENSIVE AQUACULTURE

Aquaculture is a relatively new and promising industry. Theoretically, fish farms are a good thing, as they provide much needed food, while taking some of the pressure off dwindling fish population in the wild. In practice, fish farms, especially if mis-managed, can have a severe impact on the surrounding environment. The increase in the number of intensive fish-farm plants on the continental shelf of the Mediterranean Sea during the last twenty years is causing increasing concern for their possible environmental impact, especially in the light of the possible synergistic effects with other well established pollution sources. In fact, whilst the Mediterranean fisheries harvests are declining (for *ca.* 10% from 1995 to 1996), aquaculture production is increasing (5% in the same period; FAO 1999). Fish farming has increased 10-fold over the last ten years (FAO 1998) and a substantial growth of aquaculture is anticipated in the Mediterranean Sea during the next several years.

Fish farm feeding stocks, organic loads and bio-deposit production are proportional to the fish biomass. Food surpluses not eaten by the fish and medicines excreted within faeces reach the bottom around the cages. The most evident effects of the fish cages on bottom sediments are the accumulation of organic matter and the progressive transformation of the substrate into a flocculent anoxic environment (Holmer, 1991; Wu, 1995). Previous studies have clearly demonstrated that disturbance induced by increasing organic loads in coastal areas might determine also a strong reduction of the benthic biomass, changes in the community structure, functioning and biodiversity of the natural assemblages (Brown *et al.*, 1987; Pocklington *et al.*, 1994), and in some extreme cases might even result in azoic sediments (Frid and Mercer 1989; Weston 1990). Such changes in the physical and chemical characteristics of the sediment have strong inherent impacts on the biogeochemical cycling, the transformation of key elements including noxious, damaging or harmful micro-pollutants.

Calculations have indicated that 70–80% of the drugs used in fish farming end up in the water and in the sediment beneath the fish farms reaching high concentrations (Samuelsen *et al.*, 1992a). The environmental fate of the antibiotic agents in the sediments is of great concern as persistent antibacterial substances may enhance unfavourable environmental effects and decrease benthic bacterial density by 50% (Lunestad *et al.*, 1995). Several months after treatment, in the vicinity of fish farms, acute toxic effects of furazolidone have been reported on crustaceans and in both wild and cultured shellfish (Samuelsen *et al.*, 1992b). Most drugs (such as oxytetracycline chloride and quinolones) are extremely persistent in the sediments (Hektoen *et al.*, 1995).

In the aquaculture industry, the administration of hormones (including protein hormones, peptides and steroids) is a common practice and most, if not all, diets used in fish culture contain non-negligible amounts of steroid and steroid-like compounds (Pelissero and Sumpter 1992). Because manufactured fish food is a complex mixture of many ingredients, amongst which fish meal represents the main animal ingredient (up to 40% of the total weight), the type and amount of steroids present in fish food are often unknown, and only few steroids (androstenedione and 17α,20β dihydroxy-progesterone) in fish diets have been assayed (Feist and Schrenk 1990). The main steroid-like compounds are likely to be phyto-estrogens originating from the vegetable part of the diet as these have been found in a variety of vegetable foods (Stob 1983). Soya (Eldridge 1982) and alfalfa (Knuckles *et al.*, 1976), commonly used as the basis of the vegetable component of fish diet (Cho *et al.*, 1974), are known to contain high amounts of phyto-estrogens.

Cultivation of fish in floating cages has a strong impact on the sediment biogeochemical cycles. This is basically because a large amount of the supplied food is not eaten by the fish and settles to the seafloor. Together with non-ingested food, faecal pellets produced by the dense fish shoals in the nets also fall to the sediment beneath and around the cages. High sedimentation rates associated with metabolically very active sediments, exhibiting rapid exchanges of nutrients and gasses have been reported in fish farm areas (Kaspar *et al.*, 1988; Holby *et al.*, 1991). A 10-fold increase in benthic metabolism below the cages and demonstrated a stimulation of anaerobic mineralisation rates as for benthic oxygen uptake rates these were 12 to 15 times higher than those measured in adjacent pristine areas. White mats of *Beggiatoa* are generally observed on the sediment surface. The sediment below the cages is black, highly reduced and containing large amounts of water and organic matter. Porewater sulphate is almost depleted and sulphide concentrations are very high (10 to 13 mM), with gas bubbles (mainly methane) released by the sediment during late summer and fall.

The impact of fish farming on sediment processes depends on several factors:

(a) the amount of organic matter load settling to the seafloor, which depends on the external input, the assimilation efficiency by the fish and local water currents;
(b) the extension of the area affected by this input depends on hydrodynamics and bottom topography;
(c) the sediment response depends on site-specific features.

Despite mass balance calculations which show a loss of up to 20 and 50% of the supplied P and N, respectively, to the water column, the pelagic environment appears to be relatively unaffected. This is likely due to the fact that at most sites all wastes are rapidly diluted. The sediment can be monitored more easy than the water column and the extent of organic matter input can be followed by examining the sediment below the cages and along transects downstream of the fish cages. Nutrient regeneration, sediment anoxia and stimulation of anaerobic conditions at the expense of aerobic processes in the sediments beneath the cages can enhance water column production, but may have negative impact on the benthic infauna and the pelagic organisms, which have part of their life cycle close to the sediment surface. The time period needed for recovery of sediments is determined by numerous local factors. Different sediment types have distinct recovery times which must be evaluated when planning the installation of a fish farm and in turn to determine the schedule for the cage displacements.

All the above mentioned studies reported a strong impact of fish farms on the sediment biogeochemistry. Only 17–19% of the supplied P is recovered in the fish harvest, whilst 78–82% is lost in the environment; of this 59 to 66% is accumulated in the sediment and 4 to 8% of the sedimented P returned to the water column through benthic fluxes.

The environmental P load for each ton of fish produced is around 20/22 Kg; this means that local eutrophication problems maybe enhanced in sensitive areas. There is a serious risk of enhanced eutrophication in coastal ecosystems hosting fish farms due to direct supply of both organic and inorganic (particulate and dissolved) nutrients from the fish food and due to the shifts in dominant microbial processes in the sediment which promoted N-recycling over N-losses via denitrification.

The early identification of stressful conditions in both benthic and farmed organisms may be detected by the use of appropriate biological responses which potentially represent important tools for the sustainable management of economic activities and environmental protection (Collier *et al.*, 1998); however the use of biomarkers has not been standardised in the Mediterranean for comprehensive assessment of the impact of anthropogenic activities.

8 HYDROCARBON AND OIL SPILL POLLUTION

In the Mediterranean Sea about 600–800 $\times$ 10^6 tons of hydrocarbons are transported per year (equivalent to about 30% of the world maritime transport of crude oil). Oil spills are still one of the major sources of organic contamination of the marine environment. Refinery wastes are a secondary but important source of chronic oil pollution. Off-shore extraction activities further contribute to the release of hydrocarbons at sea as about 300,000 tons of crude oil is dispersed in the Mediterranean every year. A ban on the discharge of oily wastes (in 1976) proved to be effective and the quantity of tar in the Mediterranean decreased drastically; in the Eastern Mediterranean, for instance oil concentration decreased from 37.0 to 1.2 $\mathrm{mg\,m^{-2}}$ in twenty years (Clark, 1998).

The actual impact of oil on the structure and functioning of natural ecosystems is far from complete. Benthos is the optimal domain for studying the effects of oil disturbance on the environment as it has been demonstrated that soft bottoms represent "retentive systems" able to record biological processes occurring in the entire ecosystem. In the past 20 years macrobenthic community structure was extensively studied and utilised in the assessment of the pollution impact, but recent studies have stressed the importance of considering the response of smaller size communities. Micro-benthos (*i.e.* microphytobenthos, bacteria and protozoa) and meiofauna appear adequate for pollution studies because of their high sensitivity, short generation time and, consequently, short response to disturbance events.

Few field investigations have been carried out on the effects of hydrocarbons on benthic microbial and meiofaunal assemblages, and most of them have been intensified after the *Amoco Cadiz* oil spill (Bodin 1988; Atlas and Bronner 1981; Bonsdorf 1981, Elmgren *et al.*, 1983; Fleeger and Chandler 1983, Fricke *et al.*, 1981, Gee *et al.*, 1992, Heip *et al.*, 1980, Renaud-Mornant *et al.*, 1981). Despite these studies, a general discussion of the effects of oil spills on benthic community structure and functioning is complex because oil impact can vary as a consequence of many factors, including the toxicity of the spilled oil, the time of the year, the degree of exposure of the affected area, the quantity of oil dispersed, the methods used to clean up the oil and the environmental characteristics (*i.e.* temperature, salinity, hydrology).

All these factors, influence the duration of the recovery period and therefore oil spill in the Mediterranean cannot be compared with other cases occurring in the Baltic or Bering Sea. Moreover the interpretation of the field results on the effects of oil pollution is complicated by the limited knowledge (or lack of information) on *pre-pollution* conditions.

The first consequence of the release of oil at sea is the creation of an emulsion coupled with oil adsorption on suspended matter with subsequent deposition on the seabed. The presence of rough sea conditions increasing the formation of emulsions but also the resuspension of oiled sediments. Depending on the quantity of oil released, the bathymetric depth and the distance from the shore, crude oil may accumulate in the sediments, reaching high concentrations. An increase of about 200 $\mu g\,g^{-1}$ of bunker equivalents crude oil was observed in the Gulf Marconi (NW Mediterranean) at 10-m depth, about 80 km far from the accident between *Agip Abruzzo* and *Moby Prince*.

The main effects of increased oil levels in the sediments may be summarised by reduction in oxygen levels and changes in sediment properties (including changes in RPD-Redox Potential Discontinuity-layer depths). Generally, sediment hypoxia or anoxia are present only temporarily in areas very close to the oil spills. A reduction of the redox-potentials in sediments contaminated by oil have been observed with concentrations above 1000 ppm (Christie and Berge 1995). However, oil emulsion and tar particles may affect sediment structure and related sediment characteristics. In fact, while hydrocarbon in water column is diluted and dispersed, sediments are a hydrocarbon sink, so that benthic organisms are surrounded by petroleum contaminated sediments. Oil contamination influences sediment particle aggregation with consequences in the porosity and interstitial sedimentary space and at the same time affect benthic fluxes reducing solute exchanges at water-sediment interface.

Oil toxicity changes obviously in relation to its composition (percentages of saturates, *n*-alkanes aromatics and insoluble), but is also affected by the use of dispersants (such as organic solvents: phenol, propane, furfurole; and other substances contained in standard decontaminants such as Prodesolv 128/D, Albisol BPS, TC6). Such substances may increase the toxicity of hydrocarbons with important consequences on benthic communities. Most of the oil is, under normal conditions, removed by physical forces (tidal movements, evaporation, dispersion adsorption on particles, photo-degradation) that rapidly reduce hydrocarbon concentrations so that sedimentary oil levels may recover pre-pollution conditions after few weeks. Bioturbation of infauna (*Capitella capitata*) can stimulate biodegradation of oil for about 15% increasing the oxygen concentration in deeper sediment layers (Zhang and Li, 1993). However, a large fraction of the oil might be buried in the sediments where microbial degradation plays an important role, unless oil reaches the deeper anaerobic layers, thus remaining un-degraded for years.

Acute and long-term effects might have different consequences: while acute spills might be initially toxic, both field (*Tsesis* oil spill) and experimental studies (Elmgren and Frithsen, 1982) on phytoplankton response to long term-low level oil contamination demonstrated that phytoplankton diversity and biomass increased and species composition changed. It is possible that the increased concentrations of dissolved organic material from both oil and its degradation contributed to the available nutrient supply of the benthic diatoms (some of which are known to grow hetero-trophically; Elmgren *et al.*, 1980).

Immediately after the *Agip Abruzzo* oil spill in the Ligurian Sea (April 1991), microphytobenthic biomass increased significantly, but the sudden increase in phaeopigment concentrations in oiled sediments also indicated a possible algal (phytoplankton?) death. An alternative explanation of the increased microphytobenthos densities is the diminished ingestion by sediment-feeding macrofauna and decreased grazing by meiofauna which were severely reduced by the spill.

Immediately after oil contamination the acute effects of the spill generally show a marked initial decrease in bacterial number (Danovaro *et al.*, 1996). This short-term effect on benthic bacteria has been generally reported only in presence of high oil concentrations ($>3000\,\mu g\,g^{-1}$). After few days, following a reduction of oil concentration and toxicity, bacterial number increased for up to two orders of magnitude, thus revealing a highly opportunistic behaviour. After increased oil concentrations in coastal sediments of the Ligurian Sea foraminifer density was found to decrease by about 70% (Danovaro *et al.*, 1995b). However, their density recovered rapidly back to pre-pollution conditions and subsequently increased rapidly towards values exceeding that of non-oiled sediments. It seems that protozoa are not very sensitive to oil disturbance and this apparently is the case also in the Mediterranean.

Pollution effects on benthic fauna seem to be dependent on spill size and habitat characteristics (Fleeger and Chandler, 1983), as well as taxonomic grouping (Heip *et al.*, 1988). Meiofaunal density decreases immediately after the oil spill (Grassle *et al.*, 1980). Direct microscopic observations of the polluted samples, reveal the presence of a significant number of dead organisms associated to the presence of tar particles. Crude oils are generally less toxic to meiofauna than refined oils and nematodes, the numerically dominant taxon (50–90% of the total density), appear in many cases sensitive to increased oil content of the sediment, whilst copepods appeared highly tolerant (Danovaro *et al.*, 1995). Experimental oil-tolerance studies from the Venice lagoon showed for some species a great sensitivity, and for others a high tolerance (Dalla Venezia and Fossato, 1977). A possible explanation of the copepod survivorship is that they were dominated by epibenthic forms able to swim over the bottom thus avoiding oil contamination and possible oxygen reduction or by opportunistic species (Sandulli, 1986).

After the *Agip Abruzzo* oil spill kinorhynchs, turbellarians and ostracods showed reduced densities, displaying sensitivity to hydrocarbon contamination. Meiofaunal response to oil-spill disturbance is generally rapid. In many oil spill cases the structural characteristics of meiobenthic assemblages recovered after a few weeks and were practically indistinguishable from pre-pollution conditions after a few months, thus indicating a high resilience, although the spill size does appear to be the determinant in the recovery process. Ecological studies following oil spills in the Mediterranean are extremely scarce. Two examples are reported here:

The *Patmos* oil spill. In March 1985 the collision between two tankers (the *Patmos* and the *Castillo de Monte Aragon*) resulted in the oil spill of over 1000 tons of crude oil about 900 m distance from Punta Mezzo (Calabria, Italy). Due to the high hydrodynamism and oil dispersion, no evident changes were observed in the structure of the benthic assemblages as well as on the microbial component (Crisafi *et al.*, 1989).

The *Agip Abruzzo oil spill*. On April 10th, 1991 about 30,000 t of crude oil were released in front of Leghorn (Ligurian Sea, NW Mediterranean) as a consequence of an accident that occurred between the large oil tanker *Agip Abruzzo* and the ferry–boat *Moby Prince*. The initial effects of the oil spill caused an alteration in microbial assemblages and a significant reduction of the meiofaunal density.

9 HEAVY METAL CONTAMINATION

Heavy metals are generally brought to the sea by river input and/or industrial discharge. Their concentrations are generally directly correlated to the organic matter content, so that problems of waste disposal are generally associated to heavy metal contamination. These problems are exacerbated in coastal sediments where heavy metals are known to accumulate especially near population centres, river outflows and industrial outfalls.

In the Mediterranean Sea, the distribution of dissolved zinc, copper, lead and cadmium is primarily controlled by marine circulation, surface source dynamics and biological new production. The present relatively high content of these metals in the surface layer is due to non-steady-state cycles as a result of source increases probably following increases in industrial, agricultural and urban activities around the Sea since 1960. Unlike the open ocean, for which the deep water response time to perturbations is of the order of 1000 years, the Mediterranean response to environmental disturbances are perceptible in two decades. Comparison of surface with bottom concentrations permits an estimation of the growth of dissolvable anthropogenic discharges and a forecast of the biogeochemistry of this continental sea (Bethoux *et al.*, 1990).

In general, although the data base is skewed towards the NW Mediterranean, the available information suggests that this region is under the greatest pollution stress (Fowler 1985), with concentrations up to 15 times higher than in ocean waters (Albaigés *et al.*, 1984). Egypt coastal waters are considered as one of the most polluted areas in the Mediterranean Sea as far as heavy metals are concerned. About 5 to 14 tons of Hg are discharged annually to the coastal waters. Hg and Pb are accumulated in organisms from regions affected by chlor-alkali, textile and dyes industries. These metals are toxic casing several adverse effects on the mussel *Mytils edulis* (FAO-UNEP 1992). Similarly high heavy metal concentrations have been reported from Greek coasts (especially Saronikos Gulf and Elefsis Bay; Voutsinou 1981). Cd concentrations in coastal sediments facing the River Arno estuary are up to 20 times higher than background levels in pristine sites of the Ligurian Sea. Such high levels are likely related to the industrial discharge through river input, and have been reported to cause a decrease bacterial density and activity in sediments directly influenced by the river plume (Fabiano *et al.*, 1994). Large accumulation of heavy metals has been observed in sediments facing the Besos and Llobregat river deltas (Spain; Palanques *et al.*, 1998; Puig *et al.*, 1999). By contrast analysis of dissolved Cd, Cu, Ni and Zn in the Adriatic Sea indicate that overall the zone is not contaminated with these metals and concentrations are similar to values reported in open ocean and other coastal systems (Tankere and Statham 1996).

It is known that heavy metals bio-accumulate in organism tissue during their growth and are bio-magnified along the trophic chain so that determining their levels into various organisms is essential to infer on their potential toxicological effects. Among primary producers, the phanerogams *Posidonia* and *Zoostera* reported high accumulation of Hg and Cd. Cd and Zn have been found to accumulate in seagrass leaves of *Posidonia oceanica* and Pb in its roots. Concentrations in these phanerogams reflect the environmental contamination as they were similar to those reported in the sediment (Sanchiz *et al.*, 1999). However, different levels of heavy metals have been observed to accumulate in algae (*e.g.*, *Padina pavonia*) collected together with the seagrass indicating that they are dependent upon differences in physiology rather than in environmental contamination. *Posidonia* scales do not decay and their cycling permit retrospective dating (lepidochronology); analyses on these scales revealed that heavy metal contamination in the NW Mediterranean had increased in recent years (*i.e.*, from 1982 to 1992; Romeo *et al.*, 1995). An exception is represented by Pb concentrations that, due to anti-pollution policy, decreased abruptly in the Mediterranean in the last 10 years (Nicolas *et al.*, 1994).

The determination of the heavy metal content of 5 species of deep-sea benthic fauna (3 crustaceans and two fish species) in the south-eastern Mediterranean Sea revealed Hg and Cd levels comparable or higher than those in near shore species indicating that the deep sea is not safe or free from increasing impact (Kress *et al.*, 1998).

The determination of the concentration heavy metals (Hg, Cd and Pb) in Mediterranean marine turtles (*Chelonia mydas* and *Caretta caretta*) revealed levels similar to those reported in turtles from other areas (from Haway to Japan), except for Pb concentrations that in *C. caretta* are at levels that are known to cause sub-clinical toxic effects in other vertebrates (Godley *et al.*, 1999).

Trace elements in striped dolphins (*Stenella coerruleoalba*) analysed in specimens from both Spanish and Italian coasts revealed higher Hg levels in muscle of dolphins stranded along the Italian coasts, probably related to Hg pollution from natural weathering of cinnabar in central Italy. Se and Cd levels had the same accumulation patterns of those of Hg (Monaci *et al.*, 1998). These data are consistent with observations on certain pelagic fish that displayed higher Hg concentrations in the Mediterranean than in the Atlantic (Fowler 1985).

A comparison of heavy metal content in sea urchins (*Paracentrotus lividus*) from the Egypt, Ireland and United Kingdom revealed similar concentrations at all sites with the exception of Cu and Zn that displayed highest concentrations in gonads from Mediterranean urchins.

Finally, heavy metals concentrations determined at different levels of a Mediterranean food chain (phyto- zooplankton, nektonic crustaceans) indicated lower contamination in predators than in prey, but tuna, bonito and conger revealed higher Hg concentrations than the lower trophic levels indicating that the problem of Hg contamination in the Mediterranean remains.

10 CONCLUSIONS AND PERSPECTIVES

The Mediterranean sea is in danger? The Mediterranean appears, as a whole, a large lagoon (or a semi-enclosed micro-ocean), which responds rapidly to any change in "anthropogenic pressure", but despite its sensitivity the pollution impact on the Mediterranean open sea does not seem to be much different from the pollution reported in other oceans. Sewage and oil still pose the greatest and most evident problems. The Mediterranean certainly suffers from the enormous coastal urbanisation and major industrialisation along its shores, but this is apparently not (anymore) directly related to increasing pollution levels. By contrast, for certain pollutants (such as heavy metals, particularly lead) specific policy measures at European level have already produced clear effects. Neither the water nor the organisms in the Mediterranean appear to be seriously contaminated by heavy metals and other persistent chemical contaminants are apparently subjected to de-magnification. Also tar ball pollution is clearly decreasing in the last years. In the present overview it has been clearly pointed out the potential role of incoming new pollutants. Future research should be focused on these novel substances (whose effects have still to be tested) and to their synergetic or cumulative effects with "classical pollutants" (particularly chemical pollutants such as fertilisers, pesticides, detergents-, industrial wastes, heavy metals and hydrocarbons). It is likely, indeed, that in the coming years the anti-pollution policy at the European level will enhance the control and the management of the Mediterranean Sea and will reduce the impact of the classical pollutants. However, the potential impact of the "novel chemical pollution" (*i.e.*, substances that have potentially important biological effects) is still to be evaluated and the subtle impact could remain hidden for a long time before becoming apparent. As the main risk for Mediterranean health is the synergetic effect of different environmental variables/pollutants, systemic studies in targeted areas (*vs.* pristine controls) are recommended in the future.

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