Review

Marine ecosystems' responses to climatic and anthropogenic forcings in the Mediterranean

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ABSTRACT

The semi-enclosed nature of the Mediterranean Sea, together with its smaller inertia due to the relative short residence time of its water masses, make it highly reactive to external forcings, in particular variations of water, energy and matter fluxes at the interfaces. This region, which has been identified as a "hotspot" for climate change, is therefore expected to experience environmental impacts that are considerably greater than those in many other places around the world. These natural pressures interact with the increasing demographic and economic developments occurring heterogeneously in the coastal zone, making the Mediterranean even more sensitive. This review paper aims to provide a review of the state of current functioning and responses of Mediterranean marine biogeochemical cycles and ecosystems with respect to key natural and anthropogenic drivers and to consider the ecosystems' responses to likely changes in physical, chemical and socio-economical forcings induced by global change and by growing anthropogenic pressure at the regional scale. The current knowledge on and expected changes due to single forcing (hydrodynamics, solar radiation, temperature and acidification, chemical contaminants) and combined forcing (nutrient sources and stoichiometry, extreme events) affecting the biogeochemical fluxes and ecosystem functioning are explored. Expected changes in biodiversity resulting from the combined action of the different forcings are proposed. Finally, modeling capabilities and necessity for modeling are presented. A synthesis of our current knowledge of expected changes is proposed, highlighting relevant questions for the future of the Mediterranean ecosystems that are current research priorities for the scientific community. Finally, we discuss how these priorities can be approached by national and international multidisciplinary research, which should be implemented on several levels, including observational studies and modeling at different temporal and spatial scales.

Contents

1. Introduction

1.1. Present perspectives on Mediterranean biogeochemistry

Since 2007, French oceanographers studying biogeochemistry have debated the issue of the responses of Mediterranean marine ecosystems to likely changes in physical, chemical and socio-economical forcings induced by climate change and by growing anthropogenic pressures. This debate, which is summarized in the present review, has focused on the current understanding of the effects of key natural and anthropogenic forcings on ecosystems (from coastal zones to open ocean, from pelagos to benthos) and organisms (from viruses to fishes and mammals). It has further aimed to identify knowledge gaps and to contribute to the emergence of a large integrated research project, the Marine Ecosystems' Response in the Mediterranean Experiment (MERMEX, http://mermex.com.univ-mrs.fr/; PIs: Xavier Durrieu de Madron, Cécile Guieu and Richard Sempéré).

This initiative complements other actions (Hydrological Cycle in the Mediterranean Experiment: HYMEX, and Chemistry-Aerosol Mediterranean Experiment: CHARMEX) that jointly aim at studying the water cycle and dynamics of atmospheric aerosols in the Mediterranean basin, considering the coupling between compartments (continent, ocean, atmosphere), the roles of extreme events (precipitation, heat waves, Saharan dusts), and the impacts on regional climate and marine systems.

1.2. Attributes of the Mediterranean Sea

Physically, the Mediterranean is a semi-enclosed sea surrounded by continents and is characterized by very short ventilation and residence times (~ 70 years) when compared to the other oceans (200–1000 years). It is worth noting that this relatively short residence time is of the same order of magnitude as the duration of the industrialization era, meaning that the whole Mediterranean is in contact with anthropogenic pressures.

Like in the global ocean, thermohaline circulation takes place in the Mediterranean basin and is driven by Atlantic spreading in the basin as well as surface water convection in some sub-basins. The main external sources of water in the Mediterranean basin are Atlantic water spreading through the Strait of Gibraltar, contributions by rivers and the Black Sea.

Freshwater inputs, mostly discharged by northern rivers, play a unique role in the Mediterranean Sea because they significantly enhance primary productivity at local scales and play a major role in balancing the water budget with the Atlantic.

Because of its weak cloud coverage, the Mediterranean Sea is also subject to stronger solar radiation in comparison with oceanic areas of similar latitude, causing a limitation of photosynthesis by algae and plants, a higher level of photoreception potentially damaging phytoplankton, and stronger photochemical reactions in the photic layer. The low trophic state together with increased light is a relevant forcing for the algal community structure and composition.

Biogeochemically, the Mediterranean has long been known as an impoverished area with relatively low-nutrient concentrations and is characterized by a general west-to-east gradient of increasing oligotrophy. The elemental stoichiometry in all compartments (i.e., particulate and dissolved, inorganic and organic) reveals an excess of carbon, a deficiency of phosphorus relative to nitrogen, and a sporadic deficiency of silicate (Béthoux et al., 2002a). Macro-nutrient concentrations mainly depend on the exchanges through the Straits of Gibraltar and Bosphorus, atmospheric depositions, and river discharges. Continental inputs are characterized by strong variability and dominated by extreme events (i.e., large river floods and Saharan dust deposits) due to the climatic specificities of this region.

The Mediterranean exhibits rich biodiversity and an elevated proportion of endemic species. Despite its small surface area (0.82% of the world's ocean surface) and relative oligotrophy, the Mediterranean hosts from 4% to 18% of the world's marine diversity depending on the phylum considered. The Mediterranean harbors one of the few warm deep-sea basins in the world and contains key geomorphological structures – such as sub-marine canyons, seamounts, mud volcanoes, hypersaline anoxic environments, and deep trenches – that have a distinctive effect on deep-sea biodiversity (WWF/IUCN, 2004). Another important issue is the relative isolation of deep-sea communities, not only with respect to those of the Atlantic, but also between those in the eastern and western Mediterranean, separated by the Sicily Channel.

Demographically, the Mediterranean is subject to strong human pressures that threaten marine ecosystems. The countries bordering the Mediterranean currently have a combined population of about 450 million people, and the Mediterranean's 26,000 km of coast support an estimated population of 132 million as well as intensive farming and industrial activities. The population increases sharply during the summer tourist season as the Mediterranean is the world's leading tourist destination, with about 200 million arrivals per year. Land-based (farming, domestic, commercial and industrial) activities generate large volumes of waste water that supply nutrients, organic matter, toxicants and pathogens that impact coastal marine environments. Growth of populations and changes in traditional and recreational fishing practices along the coasts have led to the expansion of sea fishing and increased landings. The gradual depletion of the most prized fish populations has resulted in the exploitation of new and/or less sought-after species. The oligotrophic nature of the Mediterranean makes it more sensitive to bioaccumulation processes because the "biodilution" of contaminants by organic carbon is reduced. The rapid turnover at the bottoms of the food webs may also be a key factor in the contaminants' biomagnification.

All of these characteristics make the Mediterranean a unique ocean region undergoing many climatic and anthropogenic forcings. This region is predicted to be particularly sensitive to current and future trends of these forcings.

1.3. Aims of the paper

This paper aims at synthesizing the current understanding of marine ecosystems' responses to natural and anthropogenic forcings and at envisaging changes induced by global change and growing anthropogenic pressures. This synthesis is organized around the main variables that may have significant impacts on the biogeochemical fluxes, ecosystem functioning, and biodiversity (Fig. 1). It takes into account the whole continent-coastal zone-open sea continuum in relation to the atmospheric and sediment compartments. First, we considered the single effects of the main natural and anthropogenic forcings, namely hydrodynamics, solar radiation, temperature and acidification, and chemical contaminants. In this deconvolution exercise, we summarized for each forcing the current knowledge about its characteristics and impact on marine ecosystems and then the expected changes in light of their likely evolution. Second, we addressed synergistic effects. Indeed, recent studies have repeatedly showed that ecosystems' responses to different constraints imposed by climatic and anthropogenic forcings cannot be deduced from mere knowledge of the effect of each of the constraints. Ecosystems often have an important ability to alleviate a single constraint, but the addition
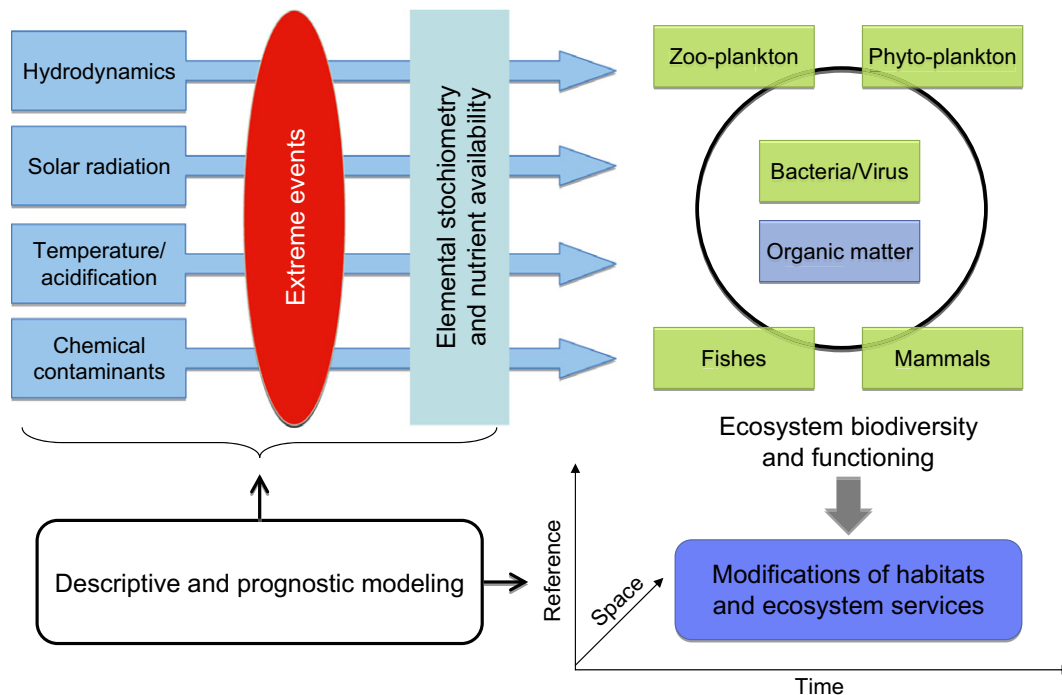
Fig. 1. Schematic of the key forcing variables influencing the marine ecosystems' diversity and functioning, and use of modeling as an integrative tool at the intersection of the different objects considered in this synthesis.
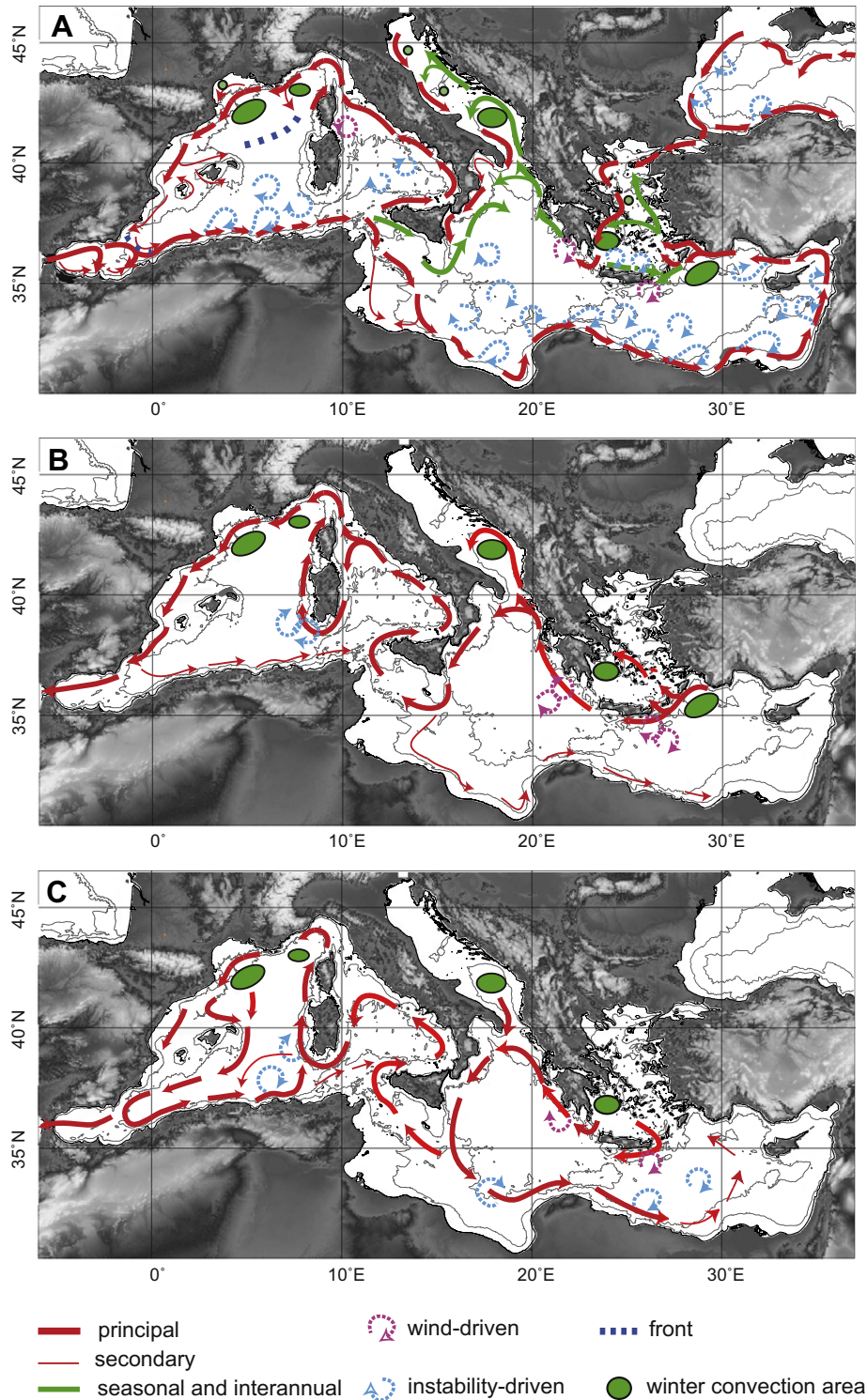
Fig. 2. (A) Circulation of surface water masses, redrawn from Millot and Taupier-Letage (2005a). (B) Circulation of intermediate water masses, and (C) represents circulation of deep water masses. The thin lines represent the 1000-m and 2000-m isobaths.

of new constraints often provokes a faster or larger response by ecosystems. It is essential to identify and study the combined effects of several factors, even though this requirement greatly complicates the task. The vulnerability of marine ecosystems to multiple forcings is illustrated here through the impacts of nutrient sources, stoichiometry and extreme events. Expected changes in biodiversity resulting from the combined actions of the different forcings are proposed. Finally, the capabilities of and requirements

for modeling, which can be used as an integrative tool to investigate the question of how climate change and anthropogenic activities impact the cycle of biogenic elements and marine ecosystems, are presented.

This multi-disciplinary overview complements recent works, such as that of Danovaro and Pusceddu (2007) that focused and synthesized the most important factors (habitat destruction, over-fishing, contaminants, eutrophication, introduction of alien

species, and climate change) potentially affecting benthic biodiversity and ecosystem structure in the Mediterranean.

2. Influence of hydrodynamics

The Mediterranean thermohaline circulation drives the transport of the water masses and biogeochemical elements in the different basins and sub-basins and, via the Strait of Gibraltar, controls the exchanges with the Atlantic Ocean. Due to the specific orography and topography of the basin (an enclosed sea with very patchy bathymetry), the basin-scale circulation can be split into regional (sub-basin-scale) patterns bounded by shelf-slope exchanges, which are affected by (sub-)meso-scale activity in addition to atmospheric-driven seasonal overturning (Lacombe and Tchernia, 1972; Robinson et al., 2001).

At basin and inter-annual scales, the thermohaline circulation controls the "background" dispersal of biogeochemical elements, thereby directly affecting the distribution and the seasonal cycle of phytoplankton that, in turn, determines the trophic inputs to secondary and upper-levels. Sub-basin and meso-scale circulations, shelf-slope exchanges, and atmosphere-driven seasonal overturning additionally modify the regional distribution of biogeochemical elements and affect the vertical exchanges. The resulting picture is that the large-scale distribution of the biogeochemical elements (mainly driven by the thermohaline circulation) is additionally, and relevantly, modified by regional and small-scale physical processes.

Consequently, the Mediterranean shows, more than other regional oceanic areas, a strong imbrication of physical processes that act on a large spectrum of spatial and temporal scales (Fig. 2) to impact the ecosystem dynamic directly (but not linearly). Hereafter, we aim at sketching out these interactions according to spatial scales (i.e., basin scale, sub-basin-scale, coastal scale, and meso-scale). Each section of this chapter first describes the main features of a specific physical scale and then addresses their documented and hypothesized impacts on marine ecosystems.

2.1. Basin-scale circulation

2.1.1. Current knowledge

The Mediterranean has a negative water budget, i.e., evaporation exceeds the sum of precipitation and river runoff. The freshwater budget estimates (for review, see Ribera d'Alcalà et al., 2003) yield a net negative value ranging between ~0.5 and 1 m year^{-1}. The loss of water is compensated at the Strait of Gibraltar by an inflow (~0.5×10^6 to 1.0×10^6 m^3 s^{-1}) of surface Atlantic water (AW). The overturn period of these waters, circa 20–50 years, is relatively short. AW is warmer and fresher than the residing waters (schematically the Mediterranean waters: MWs; for a detailed review of the horizontal circulation of the water masses in the Mediterranean Sea, see Millot and Taupier-Letage, 2005a; Taupier-Letage, 2008). Being less dense, AW constitutes the surface circulation (Fig. 2a), which describes a counter-clockwise circuit along the continental slopes through both basins. During winter, intense episodes of dry and cold northerly winds occur on the northern parts of both basins, causing dense water formation in some specific areas of the basin: severe cooling and evaporation of the surface water in the Levantine basin increase the density of AW, which sinks to intermediate levels (about 300–400 m) to form a distinct intermediate water mass (Levantine Intermediate Water: LIW) (Fig. 2b). During the most intense winters, mixing involves AW and the underlying MWs (Fig. 2c): the convection reaches deep layers, and the water masses that are formed can reach the bottom. More specifically, dense water formation is recurrently observed in the Rhodes gyre, the Northern

Aegean, the Southern Adriatic, and the northern part of the western basin (mainly the Gulf of Lions).

Like the global ocean, Mediterranean Deep Waters then feed a basin-scale thermohaline circulation. The presence of the Sicilian Strait (at about 400 m depth) prevents deep water exchange, decoupling the deep circulation of the eastern and western Mediterranean basins (see Fig. 2c). Consequently, only intermediate waters formed in the Levantine basin (Lascaratos et al., 1999) can flow westward across the Sicilian sill. Part of these Mediterranean deep and intermediate waters that originated from both basins ultimately outflows at Gibraltar and cascades into the Atlantic (see Millot, 2008, and references therein).

As a result, the waters that remain trapped in the deepest parts of the (sub-) basins, until newly formed, denser waters arrive, have longer residence times compared to the overlying waters. The new deep water then uplifts the older water masses, allowing them to overflow either through the Sicily Channel towards the western basin (cascading in the Tyrrhenian sub-basin) or through the Strait of Gibraltar towards the Atlantic.

2.1.2. Impacts on biogeochemistry and ecosystems

The Mediterranean is considered an oligotrophic sea. Satellite ocean color observations indicate that the two basins display different ecological behaviors (Bosc et al., 2004), which are likely related to the physical dynamics of the basins. In the eastern Mediterranean, the increased thermal stratification may prevent effective and diffuse vertical uptake of nutrients. Furthermore, it is also probable, as suggested by Crispi et al. (1999), that (i) nutrients are used first in the southern part of the western basin and only the most superficial fraction can cross the Sicily Channel and that (ii) some of the nutrients that are regenerated in the eastern basin are exported to the western basin at depth through the Sicily Channel. The stronger stratification and the limited availability of nutrients are believed to induce a deepening of the deep-chlorophyll maximum and a relative increase of the regenerated production. On the other hand, in the western basin, the more energetic air–sea exchanges and convection are believed to induce a more effective nutrient refueling of the euphotic zone. Schroeder et al. (2010) recently confirmed the role of the eastern basin as a source of nutrients for the western basin and showed the significant evolution of the geochemical footprints of the deep water masses of the western basin due to recent formation of new deep waters.

The two basins import nutrients mostly in their organic form from the surface water of the adjacent basin and export inorganic nutrients within the intermediate water flux, suggesting that the western and the eastern Mediterranean can be considered sites of mineralization for the Atlantic Ocean and the western Mediterranean, respectively (Béthoux et al., 1998). Although exchanges of total nitrogen and phosphorus (dissolved and particulate organic and inorganic components) through the Sicily Strait and Strait of Gibraltar are nearly balanced, the net flux of Si across the straits are highly unbalanced in favor of a net export from both the eastern basin and the whole Mediterranean (Durrieu de Madron et al., 2009).

2.2. Sub-basin-scale circulation

2.2.1. Current knowledge

Upon entering the Mediterranean, AW generally describes in the Alboran sub-basin two clockwise gyres, constrained by the bathymetry, and reaches the Algerian slope near 0° longitude. Part of the flow proceeds to the eastern basin along the Tunisian slope, and part of the flow reaches northern Sicily and circulates along Italy. The veins from each side of Corsica join and form the Northern Current that flows from the Ligurian to the Balearic slopes,

essentially skirting the shelf edge. This along-slope circulation and the north-Balearic front to the south form the counter-clockwise northern gyre that delimits the area of convection and deep-water formation in the northwestern Mediterranean. AW closes its western gyre southeast of Spain, close to Almeria, where it encounters the newly entered AW: it delimits a strong gradient along the jet that reaches the Algerian slope (the Almeria–Oran front). Further east, upon exiting the Sicily Strait, AW generally splits into several veins. Part of the flow proceeds eastwards off Libya and Egypt, with a path that is still debated (see Hamad et al., 2005). In any case the general circuit is counter-clockwise at basin-scale, and the counterpart of the aforementioned northern gyre is the Rhodos gyre, where convection occurs, leading mostly to LIW but also episodically to Levantine deep water). Another part of the AW flow leads to a complex circulation in the Ionian; the signature of AW is still debated because , since surface circulation it shows a decadal variability leading to either anticlockwise or clockwise circulations (see Malanotte-Rizzoli et al., 1997; Hamad et al., 2006). Through the Strait of Otranto, a flow of Ionian AW enters the Adriatic Sea, where the surface circulation is cyclonic in all seasons. Part of that water flows northward along the Balkans and returns as a southward flow along the Italian coast. Most of the water does not penetrate north of 43°N but instead turns immediately west and re-circulates along the Italian coast, forming the permanent southern Adriatic gyre, which is the principal site of Adriatic deep-water formation

2.2.2. Impacts on biogeochemistry and ecosystems

The general oligotrophy of the Mediterranean is essentially provoked by the different localizations of the physical (the winter mixed layer) and nutrient (the nutricline) vertical interfaces, which are both determined by the large-scale circulation. Satellite observations (D'Ortenzio and Ribera d'Alcalà, 2009) have revealed the intrinsic relationship between sub-basin-scale cyclonic physical structures and the occurrence of surface phytoplanktonic blooms in the northwestern Mediterranean, South Adriatic, and Rhodos Gyre. Similarly, frontal systems, like those of the Atlantic inflow in the Alboran Sea or the Northern Current in the Ligurian Sea, exhibit vertical motions that induce significant exchanges of properties between the surface layer and the deeper layers (Prieur and Sournia, 1994; Fielding et al., 2001; Niewiadomska et al., 2008) and affect the prokaryotic mineralization (Sempéré et al., 2003) and the input of biogenic material under the photic zone and ultimately to the sea-floor (Sanchez-Vidal et al., 2005).

The relatively weak winter convection prevents an efficient uplift of mineralized nutrients in the photic layers, except in areas where recurrent physical structures facilitate the deepening of the mixed layer. The vertical motions associated with these physical structures have an important role in the heterogeneity of nutrient inputs in the mixed layer and in the photic zone. These inputs trigger localized phytoplankton blooms (e.g., Lévy, 2003), with a consequent biological response in the upper trophic levels (e.g., mesozooplankton, Pinca and Dallot, 1995; macrozooplankton such as salps, Licandro et al., 2006, and euphausiids, Warren et al., 2004; larger predators, such as squid, small fish, and fin and sperm whales, Panigada et al., 2005).

Sub-basin physical features in the Mediterranean Sea are essential to induce the necessary vertical motions, which can support phytoplankton growth and, consequently, the upper-level ecosystem dynamic.

2.3. Coastal dynamics

2.3.1. Current knowledge

The shelf regions are peculiar environments characterized by intricate processes (river plume dynamics, wind-driven meso-scale circulation, coastal eddies, shelf dense water formation and transport) that control the exchanges of water and biogeochemical elements from the enriched coastal areas to the interior of the basin. Freshwater discharges from large rivers (e.g., Rhone, Po) produce nutrient-rich, highly stratified buoyant flows, which, by interacting with meso-scale circulations generated by the wind but mostly by current instabilities, spread over and sometimes beyond the shelf.

The northern continental shelves (Gulf of Lions and Northern Catalan shelf, the Northern Adriatic Sea and the Northern Aegean) are sites of intense vertical mixing and dense water formation during winter due to the intense and persistent continental winds and moderated depth (Vilibíc and Supíc, 2005; Durrieu de Madron et al., 2005a). The dense coastal water eventually overflows the shelf and cascades down the slope, mainly through sub-marine canyons. This process can be enhanced by concomitant storms that flush the shelf water or hindered by intense freshwater discharge (Ulses et al., 2008c).

2.3.2. Impacts on biogeochemistry and ecosystems

High values of primary production associated with the Rhone River's rich nutrient outflows have induced rich zooplankton production in the Gulf of Lions (Diaz et al., 2008) and along the Catalan coast (García and Palomera, 1996; Sabatés et al., 1989). Similarly, high organic carbon input stimulates prokaryotic degradation in the coastal area of the Rhone River (Sempéré et al., 2000). Moreover, in the Catalano-Balearic Sea, phytoplankton and zooplankton production are associated with a front parallel to the Catalan coast (Estrada and Salat, 1989) and Ebro outflows (García and Palomera, 1996). Several planktivorous fish (anchovies, sardines, pilchards, round sardinella) feed on mesozooplankton aggregated in these structures.

Dense shelf water formation appears to be concomitant with high planktonic production. Hence, during the cascading of these dense water masses off the shelf, significant quantities of nutrients and organic matter, including living phytoplankton, are transported to the intermediate or deep-water layers on the slope (Canals et al., 2006; Vilibíc and Supíc, 2008) and probably fuel the deep ecosystems (Danovaro et al., 1999).

2.4. Meso- and sub-meso-scale dynamics

2.4.1. Current knowledge

The circulation patterns and associated impacts reported in the previous paragraphs may be regulated by atmospheric fluxes over seasonal and shorter periods and consequently can be significantly modulated by the so-called meso-scale activity that directly influences momentum and thermohaline fluxes. Significant vertical motions like eddy pumping, upwelling and subduction are associated with meso-scale features (Van Haren et al., 2006).

In the southern Mediterranean, meso-scale features dominate (Millot and Taupier-Letage, 2005a). Triggered by the instability of the Algerian and Libyo-Egyptian currents, anticyclonic eddies can range from 50 to 150 km in diameter (up to ~250 km), extend vertically over several hundreds to thousands of meters (down to the bottom, ~3000 m), and span several months or even years, with associated currents that usually reach ~50 cm s^{-1} in the upper layer (Puillat et al., 2002; Hamad et al., 2005). Their self-consistent dynamics allow unconstrained pathways and thus interact with other circulation structures or bathymetry, which generates sub-meso-scale phenomena like upwelling cells, filaments or shear cyclonic eddies. In some cases, such large eddies can strongly perturb the circulation, dispatching water masses from the surface, intermediate and deep layers and even blocking the basin-scale circulation or reversing it down to the bottom (Bouzinac et al., 1999; Testor et al., 2005; Millot and Taupier-Letage, 2005b). In the northern part of both basins, there is a clear seasonal signal of

atmospheric fluxes, meso-scale activity of the currents, and events of vertical mixing. In the northwestern Mediterranean, these meso-scale structures are ∼30–70 km in size and propagate westward at a speed of a few kilometers per day (Sammari et al., 1995; Flexas et al., 2002). In the Levantine basin, several recurrent eddies are observed either due to the wind (that generates the clockwise Pelops and Ierapetra eddies, see Fig. 2a) or to the bathymetry (e.g., the clockwise eddy over the Erathostenes Seamount).

Frontogenesis generated by the deformation of the geostrophic field or other ageostrophic sources (such as a local wind burst) can force secondary circulations associated with intense sub-meso-scale vertical motions (Zakardjian and Prieur, 1998) and increase the primary production in an oligotrophic area (Prieur and Sournia, 1994; Niewiadomska et al., 2008). At the shelf edge, meso-scale perturbations of the adjacent circulation system may strongly influence the renewal of coastal waters by intruding into continental shelves (Petrenko et al., 2005), with repercussions on the whole shelf circulation.

The generation of (sub-)meso-scale eddies by instabilities promotes vertical motions that affect the mixed layer dynamics. Whereas the local doming of isopycnals associated with cyclonic (anticlockwise) eddies enables the winter mixing to go deeper, anticyclonic (clockwise) eddies help to maintain the stratification. The preconditioning effect of cyclonic eddies is important for deep convection. Subsequently, post-convection spreading of newly formed deep waters over the whole basin is driven by long-lived sub-meso-scale deep eddies (Testor and Gascard, 2006).

2.4.2. Impacts on biogeochemistry and ecosystems

Horizontal and vertical (sub-)meso-scale circulations influence the spatial distribution of biogeochemical elements (Lévy, 2003) and induce a strong patchiness in plankton, larva and fish distributions (García Lafuente et al., 2002; Sabatés et al., 2004). This patchiness is not always easy to interpret because various processes, including stirring and turbulent diffusion, are at play (Gorsky et al., 2002; Maynou et al., 2006; Riandey et al., 2005), and the rotation directions of eddies lead to contrasting effects. The doming of isopycnals associated with cyclonic (counter-clockwise) eddies locally brings nutrient-rich water close to the surface that impacts the development and onset of phytoplanktonic blooms. Conversely, surface anticyclonic eddies are favorable to phytoplankton biomass in two ways. First, they generate sub-mesocale phenomena like upwelling cells, filaments and shear cyclonic eddies, and second, during spring the mixed layer's depth can reach several hundreds of meters due to the eddies' homogeneous central zone, allowing a thick phytoplankton bloom to develop (e.g., Yacobi et al., 1995; Taupier-Letage et al., 2003). Long-lived eddies (up to several years), which are generally anticyclonic (clockwise), form dynamic barriers that isolate water in their cores from the surrounding waters. This retention enables biogeochemical elements and organisms to be transported by the eddies over long distances (several hundreds of kilometers).

The (sub-)meso-scale activity of boundary currents around the shelf break leads to strong patchiness of the nutrient and primary production distributions (Diaz et al., 2000). Interactions of the boundary current with sub-marine canyons produce topographically-controlled up- and down-wellings that affect the cross-slope transfers of particulate and biogenic matter (Durrieu de Madron et al., 1999; Palanques et al., 2005). Sub-marine canyons are further known to possess a large density and diversity of benthic and pelagic fauna (e.g., Gili et al., 1999 revealed the presence of singular hydromedusae populations in northwestern Mediterranean canyons) and represent a preferential recruiting ground for some fish species (Stefanescu et al., 1994) and feeding habitat for cetaceans (David, 2000).

2.5. Expected alterations

The description of the large-scale thermohaline circulation is usually based on the assumption that the Mediterranean is a stationary system. This point was disproved as significant changes in the deep waters of the eastern basin were observed during recent decades (the Eastern Mediterranean Transient, EMT, Roether et al., 2007 and the references therein) and reached the western basin later (Schroeder et al., 2008; Millot, 2008). The EMT was a climatological event in the early 1990s; the circulation of the eastern basin experienced a dramatic change in the deeper layers when deep water of Aegean origin replaced the resident Eastern Mediterranean Deep Water of Adriatic origin. By inducing the uplifting of the existent deep waters, the EMT significantly modified the characteristics of the water masses flowing through the Sicily Strait, while the remarkable presence of salty Cretan Intermediate Water in the Ionian Sea enhanced the salt export from the eastern basin to the western basin after 1999. Moreover, the deep waters of the western Mediterranean have been observed to show a rather constant trend towards higher salinity and temperature since the 1950s. The acceleration of this tendency was initially attributed to the effect of the propagation of the signal of the Eastern Mediterranean Transient from east to west. However, recent observations performed in the deep western basin have evidenced a drastic change with the appearance, and dispersal throughout the basin, of highly saline and warm new deep water simultaneously with saltier and warmer Levantine Intermediate Water, which has substantially renewed the resident deep water (Schroeder et al., 2008). This new deep water possibly originates from massive deep-water formations that developed in the northwestern Mediterranean during the winters of 2005 and 2006 and significantly affected the biogeochemical properties of the deep water masses (Schroeder et al., 2010). In the Strait of Gibraltar, Millot (2008 and references therein) showed that the Mediterranean exchanges through the strait underwent large compositional changes. The outflow shows a trend towards more saline waters in relation to the EMT, and the inflow shows that the AW entering is warmer and more saline (Millot et al., 2006). This latter point is of the utmost importance because it used to be accepted that changes in the Mediterranean waters' properties were only related to local Mediterranean forcing. The rapid change in deep-water properties in the western Mediterranean as a response to a dramatic event in the eastern Mediterranean only one decade earlier and to strong local climatological events exemplifies the instabilities in the thermohaline circulation and demonstrates how different sub-basins interact on short time-scales (<10 years). However, the effects of the EMT on the ecosystems dynamic of the Mediterranean are not still well understood: if an uplift of the isopycnes (and, consequently, of the nitracline depth) induces an increase in primary production, the available data do not highlight any important modification of the surface chlorophyll stock of the Mediterranean. Changes, however, could be occurring in the sub-surface layers, far from the depths accessible from space, where in situ observations are less constant and frequent (at the DYFAMED station; for example, the maximal concentration of integrated chlorophyll-a in 15 years of monthly observations was observed in April 2006 (Marty and Chiaverini, 2010). The EMT is an example of the difficulties of addressing the impact on ecosystems of even dramatic modifications of the physical dynamic.

Numerical exercises indicate that, during the 21st century, the Mediterranean Sea might experience extensive warming and salting as well as a weakening of its thermohaline circulation (Somot et al., 2006). Herrmann et al. (2008) suggested that the magnitude of dense shelf formation and export to the slope will be drastically reduced by the end of the 21st century. The frequency of severe cyclones is also supposed to decrease, but those that form will be more intense (Anagnostopoulou et al., 2006), thereby intensifying

wind forcing and mixing on the oceanic upper layers. Gaertner et al. (2007a) detected a risk of tropical cyclone development over the Mediterranean Sea for a future climate change scenario.

The impact on the decadal and longer term changes of the circulation on the ecosystems could be major. Modifications of the water budgets of the Strait of Gibraltar and the Sicily Strait could substantially alter the exchanges of nutrients with the Atlantic and between the eastern and western basins, directly impacting the absolute and relative concentrations (i.e., Redfield ratios) of the deep nutrient reservoir.

Modifications of the coastal and open sea dense water formation magnitudes, derived by the expected changes in the atmospheric forcing, could have relevant repercussions for the vertical redistribution of nutrients and carbon in the water column. In the Mediterranean, areas of dense water formation coincide with areas of major phytoplankton blooms (Bosc et al., 2004). Although the interactions between the two processes are not yet entirely elucidated (Levy et al. (2000)), changes in the dense water formation could directly and/or indirectly affect the magnitude and occurrence of the biomass-enhancing events that are crucial for ecosystem functioning.

The mixed layer's evolution could change as a result of the expected changes in the characteristics of surface water (saltier and warmer) and in the atmospheric forcing (stronger and more frequent winds). The two processes act on the mixed layer's evolution in contrasting ways, so the changes are difficult to estimate. In any case, phytoplankton will respond through changes in physiological properties, growth and division rates, and/or modification of their succession pattern in the community, all of which are processes affecting the primary productivity rate of the area.

The expected changes in biomass, which could affect the seasonal cycle, vertical distribution (i.e., depth of the deep-chlorophyll maximum), and magnitude and occurrence of the annual peaks, could entirely reconfigure the functioning of the ecosystems in the basin. The basin could shift from its several contrasting trophic regimes (i.e., D'Ortenzio and d'Alcala, 2009) toward a more intense oligotrophy (e.g., if blooming areas lost their capacity to accumulate nutrients during winter) or toward a diffused augmentation of primary production (e.g., if the enhanced wind forcing deepens the winter mixed layer). The first hypothesis would lead to increased dominance of small algal cells with large consequences for matter transfer into food webs. The second would favor the growth of large opportunistic species.

All of the above predictions indicate that the specific configuration of the Mediterranean induces the cohabitation of several trophic regimes (and thus gradients) in the limited area of the Mediterranean. In addition, the evolution of these gradients is not linear when important changes in the circulation occur (i.e., EMT). The mechanisms behind Mediterranean biogeography are still undefined, but it is clear that:

- the strong interplay of the physical (or ecosystemic) processes acting at different temporal and spatial scales on the distribution of nutrients on the water column relevantly affects the Mediterranean eco-regions (ecologically and geographically defined areas with distinct environmental conditions and biological dynamics) and ecotones (transition area between two adjacent ecological regions);
- the relative depths of the two horizontal interfaces of the Mediterranean, the halocline and the nitracline, directly affect the response of autotrophs and, consequently, of the whole ecosystem.

The first point, which is the result of all of the processes discussed previously in this text, is relatively well documented, although it is crucial to identify the scientific tools for monitoring this evolution in a context where EMT-like scenarios could become more and more frequent. The second point is much less documented and requires a dedicated experimental effort.

3. Influence of solar radiation

3.1. Solar radiation in the Mediterranean basin atmosphere

3.1.1. Current knowledge

Solar radiation plays a vital role for life on Earth by providing the energy (photosynthetically available radiation; PAR) for photosynthesis in plants and algae, upon which virtually all food webs ultimately depend. However, solar ultraviolet radiation (UVR) is also an important part of incident light and can have deleterious effects on terrestrial and aquatic ecosystems as well as on human health. At the earth's surface, the relative solar spectral distribution is 1–5% UVR (280–400 nm), 46–52% PAR (400–700 nm) and 43–53% infrared (IR: 700 nm to 1 mm). UV-B (280–315 nm) and UV-A (315–400 nm) represent 1–5% and 95–99% of the total UVR flux, respectively (Whitehead et al., 2000). The main factor influencing the intensity of solar radiation at the earth's surface is the solar zenith angle (SZA), which leads to a strong dependence of solar irradiance on latitude, season and local time, followed by cloud cover. Other factors, such as stratospheric ozone (O_3) concentration (mainly for UV-B), surface albedo, altitude, aerosols and air pollution, may also have significant impacts on the intensity of solar radiation reaching the earth's surface. The Mediterranean basin is characterized by relatively high solar radiation levels due to its weak cloud cover (Vasilkov et al., 2001; Cristofanelli and Bonasoni, 2009). During the period of 1958–2001, the annual average total solar radiation flux reaching the whole Mediterranean Sea was 168 W m^{-2}, with values of 162 and 172 W m^{-2} for the western and eastern basins, respectively (Ruiz et al., 2008). These fluxes showed a strong seasonal cycle and a significant north–south gradient (Ruiz et al., 2008). In the framework of the European Light Dosimeter Network (ELDONET) program, Häder et al. (2007a) reported mean irradiances in the PAR, UV-A and UV-B ranges at several coastal stations of the western Mediterranean Sea based on 5 years of monitoring (1998–2003). Under clear skies, mean PAR, UV-A and UV-B irradiances reached 414 ± 13, 62 ± 3 and 2.0 ± 0.3 W m^{-2}, respectively, in summer and 219 ± 14, 28 ± 3 and 0.5 ± 0.1 W m^{-2}, respectively, in winter. The cumulative daily PAR, UV-A and UV-B doses during 3-month periods in summer and winter (irrespective of cloud cover) could be as high as 975, 129 and 3 MJ m^{-2} and 299, 45, and 0.5 MJ m^{-2}, respectively (Häder et al., 2007a).

It is known that solar radiation in the Mediterranean basin is strongly affected by air pollution, especially through the formation of photochemical (tropospheric) O_3 and by aerosol loading, with a dimming effect of both anthropogenic (urban/industrial and biomass burning) and natural (Saharan dust) aerosols (see below). In addition, several studies have demonstrated the influence of cloud cover on the biologically effective UV irradiances, such as the erythemal or DNA damage effective irradiances, over the Mediterranean basin (Vasilkov et al., 2001).

3.1.2. Photochemical ozone over the Mediterranean basin

The summertime atmosphere in the Mediterranean Sea makes it one of the world's most polluted systems in terms of photochemical ozone (tropospheric O_3). Indeed, the elevated solar irradiance resulting from the sparse cloud cover, combined with meteorological conditions favoring the accumulation of primary pollutants (such as nitrogen oxides and volatile organic compounds) in the low atmosphere, enhances the formation of secondary gases and aerosols (Marmer and Langmann, 2005). O_3 is one of the key agents determining the oxidation capacity of the troposphere (Crutzen,

1974; Logan et al., 1981; Gauss et al., 2003), and it has been recognized as the third most common greenhouse gas in terms of additional radiative forcing in the free troposphere (Forster et al., 2007). Also, due to its chemical properties, it is considered a dangerous secondary pollutant causing harm to human health (Conti et al., 2005) and terrestrial ecosystems (Scebba et al., 2006). Consequently, there has been great scientific interest in studying the influence of photochemical O_3 on climate. The average tropospheric O_3 concentrations over the Mediterranean basin have increased by a factor of 5 since the 19th century (Nolle et al., 2005) even though emissions of O_3 precursors in the European Union have declined by about 36% since 1990 because of the introduction of catalytic converters in cars and new laws to reduce air pollution (EEA, 2007).

Although the processes influencing O_3 formation may vary greatly within the Mediterranean region, two major formation areas have been identified in the western and eastern basins (Millán et al., 2000). Millán et al. (2000) observed that the complex layout of the coast and mountains surrounding the western Mediterranean basin favored the development of meso-scale atmospheric recirculation patterns and the formation of ozone reservoir layers above the coastal areas and the sea. Ribas and Peñuelas (2004) measured ambient O_3 at a coastal site of the northwestern Mediterranean Sea and found high concentrations exceeding the European protection thresholds for humans ($110 \mu g\ m^{-3}$, 8-h average) and plants ($65 \mu g\ m^{-3}$, 24-h average) during 54 and 297 days per year, respectively. Dueñas et al. (2002) and Castell et al. (2008) also reported elevated O_3 concentrations at different stations in Spain, with average values in summer of 90 and $120 \mu g\ m^{-3}$, respectively. During summer 2003, in the urban area of Marseille (France), O_3 concentrations frequently exceeded $150 \mu g\ m^{-3}$, with a maximal recorded value of $250 \mu g\ m^{-3}$ (Tedetti et al., unpublished). Koronakis et al. (2002) showed that a buildup of O_3 and nitrogen oxides inside the urban Athens (Greece) plume during cloudless and windless warm days could cause global UV irradiance depletion of between 5% and 14%, diffuse solar irradiance enhancement of up to 38.1%, and global solar irradiance attenuation ranging up to 6%. Although O_3 concentrations have been recorded over the Mediterranean basin, the photooxidative impact of O_3 on the surface waters of the Mediterranean Sea remains largely unknown, thus needs to be studied in the near future.

3.1.3. Attenuation of solar radiation by aerosols in the Mediterranean basin

Tropospheric attenuation of solar radiation by anthropogenic or natural aerosols, or 'dimming', is well known to modify the radiative budget and decrease primary production at local scales (Mallet et al., 2009 and references therein). Because the Mediterranean atmosphere is regularly modified by storm events from the Sahara desert to the south, from biomass burning (mainly from Greece, Spain, France, Italy) and from anthropogenic aerosol inputs due to industrial activity to the north, significant variability in the incoming radiation budget can be expected. Concerning Saharan dust, measurements on the island of Lampedusa discriminated events with Aerosol Optical Depth, (AOD, integration of the aerosol extinction for the whole atmospheric column) of close intensity on July 14, 2002 (0.23) and July 16, 2002 (0.26) and one significantly larger event on May 18, 1999 (0.51). Radiative transfer computations for these events denote a significant attenuation of the radiation (integrated over the spectral range of 290–800 nm) at the seawater surface, with respective instantaneous surface "forcings" of $-24\ W\ m^{-2}$ (July 16, 2002), $-13\ W\ m^{-2}$ (July 14, 2002) and $-70.8\ W\ m^{-2}$ (May 18, 1999). The larger seawater surface forcing observed on May 18, 1999 is due to the larger AOD. In parallel, di Sarra et al. (2008) indicated that for May–November of 2003 and 2004 on Lampedusa Island, the seawater surface forcing of dust was much larger than for the other aerosol classes, with daily means at the summer solstice and equinox of -30 and $-24\ W\ m^{-2}$, respectively. Over the coastal French Mediterranean region, Saha et al. (2008) documented a dust event that took place on June 19, 2006, characterized by an AOD of 0.80 (440 nm). Authors indicated a mean daily surface forcing (integrated from $0.3 \mu m$ to $3.0 \mu m$) of $-61.8\ W\ m^{-2}$. Finally, over Spain, Cachorro et al. (2008) reported instantaneous surface forcings of -140 and $-107\ W\ m^{-2}$ at Palencia and El Arenosillo, respectively, during a dust event (July 23, 2004). It should be mentioned that dust AOD values as large as 1 have been measured at Lampedusa (di Sarra et al., 2001), and comparatively larger seawater surface forcing may occur. Furthermore, Antoine and Nobileau (2006) have shown an increasing trend in dust transport over the Mediterranean basin for the 1998–2004 period using SeaWiFs observations, thus indicating that the dust effect on the sea surface radiative budget could intensify in the near future.

Concerning the direct surface "forcing" by anthropogenic aerosols (including those from urban, industrial and biomass burning sources), Mallet et al. (2006) reported a decrease in surface fluxes of about $34\ W\ m^{-2}$ (integrated from 200 nm to 4000 nm) from studies undertaken during the ESCOMPTE campaign, which took place in southeastern France during the summer of 2001. Surface radiative forcing due to anthropogenic aerosols has also been reported by Horvath et al. (2002) at Almeria (south Mediterranean coast of Spain), showing a surface forcing (integrated from 400 to 800 nm) of $-23.1\ W\ m^{-2}$. During summer 2006 and over the coastal Mediterranean region (Toulon), Saha et al. (2008) reported a daily surface forcing (integrated from 200 nm to 4000 nm) of about $-25\ W\ m^{-2}$ due to the presence of urban aerosols. In addition, the surface radiative forcing of "aged" anthropogenic aerosols over the eastern Mediterranean was documented during the MINOS experiment. Markowicz et al. (2002) indicated that aerosols, mostly of anthropogenic origin, led to a diurnal average reduction of $17.9\ W\ m^{-2}$ (integrated from 280 nm to 2800 nm) at the seawater surface. Finally, two cases (25 and 27 May 1999) of "aged" anthropogenic aerosols originating from Europe were documented by Meloni et al. (2003) at Lampedusa, showing a daily decrease in surface illumination of about $20\ W\ m^{-2}$ (integrated from 300 to 800 nm).

At present, few studies have investigated the surface radiative effect of aerosols derived from biomass burning over the Mediterranean region. Calculations performed during the STAAARTE-MED experiment conducted in August 1998 in the Eastern Mediterranean. Formenti et al. (2002) indicated that, over the sea, the shortwave (integrated between 280 and 4000 nm) radiative forcing is up to $-64\ W\ m^{-2}$ at the surface (daily mean). Meloni et al. (2006) reported AODs that ranged between 0.3 and 0.8 (at 415 nm) at Lampedusa from 5 to 22 August 2003, a period corresponding to intense active fires in Southern Europe, but did not perform radiative calculations. Such large AODs suggest that larger sea surface forcings may occur compared to those reported by Formenti et al. (2002). In parallel, Cachorro et al. (2008) reported instantaneous forcing of $-78\ W\ m^{-2}$ during a smoke event (July 28, 2004) observed at Palencia (Spain). Results for attenuation by anthropogenic or natural Mediterranean aerosols are similar to those reported for the North Indian Ocean during the dry season (Ramanathan et al., 2001), over the Atlantic Ocean (east coast of the United States; Russell et al., 1999) and over the Pacific Ocean (Bush and Valero, 2003).

3.2. Attenuation of solar radiation in the Mediterranean Sea water column

3.2.1. Current knowledge

Modeling the penetration of UV and visible radiation in the water column, in a remote sensing context or in an ecosystem

model, necessitates knowledge of the seawater's inherent optical properties (IOPs). These can be considered as the individual components that contribute to the overall seawater apparent optical properties (AOPs) and include contributions from the water itself (absorption (aWAT) and diffusion (bbWAT)), backscattering from particles (bb), chromophoric dissolved organic matter absorption (aCDOM), phytoplankton absorption (aPHYTO) and absorption by non-algal particles (aNAP). If in open ocean, aNAP and aWAT are small compared to CDOM absorption, in coastal areas where terrestrial riverine inputs are the main chromophoric dissolved matter (CDM) contributor compared to autochthonous primary production, aNAP is a significant contributor to the CDM absorption. CDOM is a major factor that determines the optical properties of natural waters, particularly in the blue and UV regions of the spectrum, and directly affects both the availability and the spectral quality of light. CDOM absorption of sunlight causes various photo-reactions that affect its chemical, physical, and biological properties and eventually leads to its degradation (Moran and Zepp, 1997). It is stressed that an accurate description of aWAT is highly relevant for quantifying the attenuation of UV and blue radiation in clear waters that are typical of a large part of the Mediterranean basin where the absorption coefficient by pure seawater is significant relative to aCDOM.

Different parameterizations (Bricaud et al., 1995; Pope and Fry, 1997; Morel et al., 2007) and additional inputs provided by remote sensing (i.e., aPHYTO and the sum aNAP+aCDOM) have allowed a complete determination of the IOPs in the Mediterranean Sea surface mixed layer. Extending this information along the vertical requires specific parameterizations like that of Longhurst et al. (1995) for phytoplankton. Satellite-derived IOPs can be obtained with algorithms such as that of Lee et al. (2002), the uncertainties of which have been analyzed by IOCCG (2006) and Mélin et al. (2007). This semianalytical approach can be prone to large uncertainties stemming from variable spectral shapes for aPHYTO, particularly in the UV region, and a lack of knowledge of the vertical structure of other IOPs. The principal component analytical (PCA) approach of Fichot et al. (2008) allows a direct empirical estimation of UV attenuation and aCDOM without a defined dependence on the spectral shapes or distributions of other IOPs. With regard to both approaches, it is clear that the current modeling framework can be improved and further tuned for Mediterranean waters.

The satellite-derived distribution of aNAP+aCDOM (at 443 nm) for Mediterranean waters is illustrated in Fig. 3a (showing data for two representative months, March and September 2001). This distribution is very useful as a primary determinant of UV and blue light penetration. The full time-series and similar maps for aPHYTO
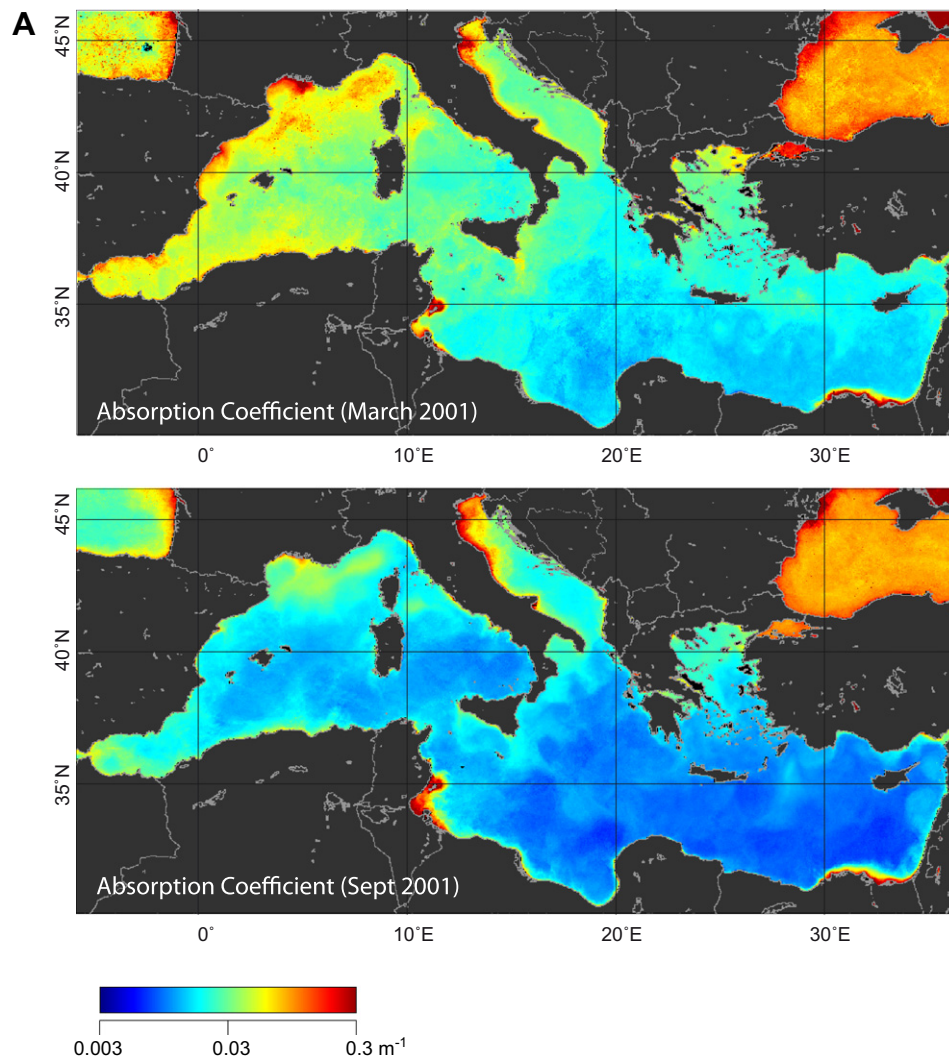
Fig. 3. (a) Maps of absorption coefficients due to DOM and non-pigmented particles derived from SeaWiFS for March (top) and September (bottom) 2001. (b) Maps of the depths of UV-A penetration Z1% (1% irradiance level) for March (top) and September (bottom) 2001.
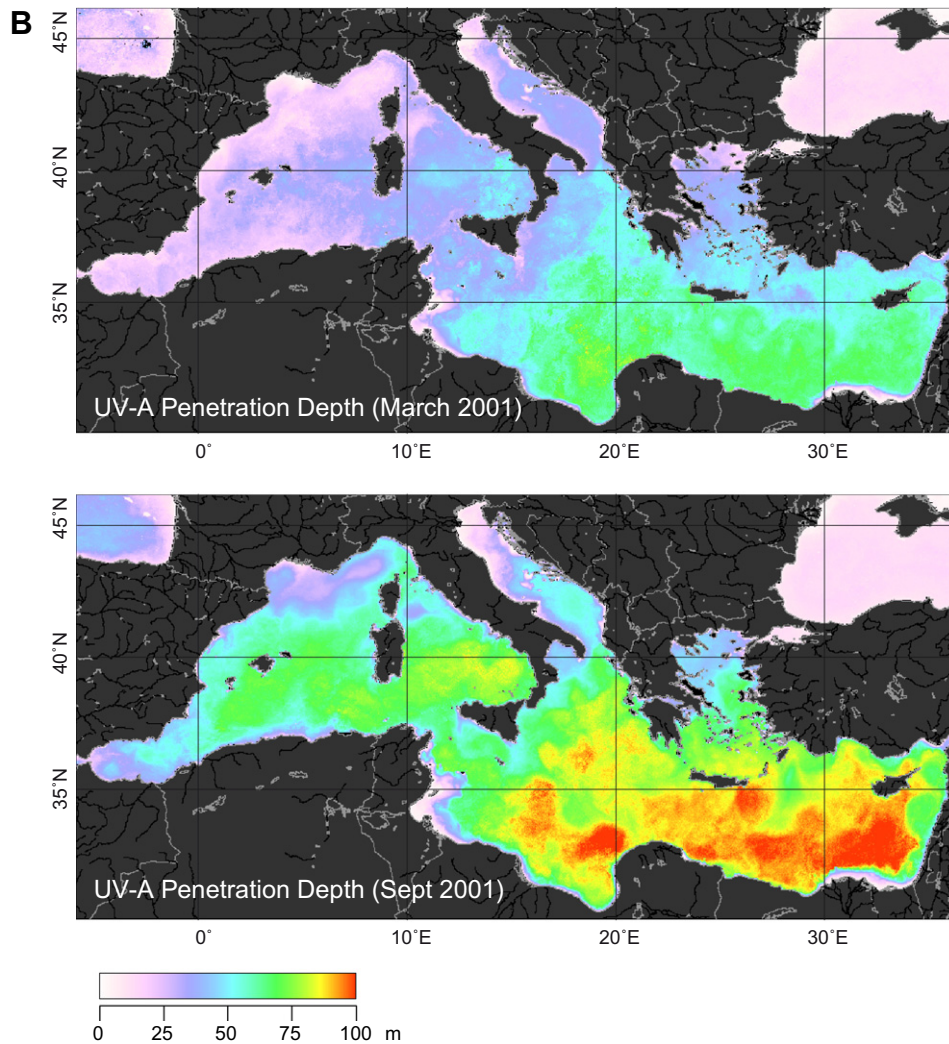
Fig. 3 (*continued*)

show that aNAP+aCDOM usually accounts for more than 50% of the total absorption coefficient in Mediterranean waters, a result confirmed by Berthon et al. (2008). Rather high values are found to be coincident with the large phytoplankton bloom in the Ligurian Sea and coastal regions in March. The amplitude of aNAP+aCDOM is much lower at the end of the summer season, even in the oligotrophic waters of the central and eastern basins. The relative contributions to total absorption of aNAP+aCDOM and aPHYTO are variable. Climatological values of the ratio of aPHYTO to aNAP+aCDOM averaged for the Ligurian Sea reached a peak (∼0.5) in March–April associated with the spring bloom. Interestingly, the ratio of aNAP+aCDOM to total absorption in oligotrophic waters like the Ionian or Levantine basins shows a maximum in January–February (∼0.58) and decreases through the summer to values close to 0.44. Such variations might be linked to photobleaching or to enhanced bacterial abundance and activity in summer. Field measurements of IOPs in different seasons and Mediterranean regions are essential to assess the accuracy of satellite-derived distributions.

3.2.2. Application to depth of penetration and absorption budget

In situ measurements have shown that in the open Mediterranean Sea, the depth of the euphotic layer generally varies from 40 to 60 m in the western basin (Marty et al., 2008), although its depth can reach 80 m in some areas (Strait of Sicily, Brunet et al., 2006, 2007) and even 90 m in the South Tyrrhenian Sea (Brunet et al., unpublished results). Maximum values of 100 m have been reported in the eastern basin (Moutin and Raimbault, 2002).

However, although data related to the penetration of visible radiation are available, there are very few UV-B and UV-A measurements for the Mediterranean Sea. Table 1 presents all of the available in situ measurements of the diffuse attenuation coefficient [Kd (λ) m^{-1}] for UV radiation. With a simple approach that uses the model of Gregg and Carder (1990) extended for UV and a correction for cloud cover in the radiative transfer model calculations can be performed on large (satellite) data sets with the IOP parameterizations introduced above. The resulting maps of penetration depths for UV-A (320–400 nm) are shown in Fig. 3b for the same months of March and September 2001. Comparable spatial patterns are obtained for PAR (400–700 nm) and UV-B (300–320 nm), with obvious smaller values for UV-B (i.e., the color scale range for UV-B is about 3–4 times smaller). The depth of penetration, Z1%, is defined as the depth level where the irradiance in the specified spectral interval is 1% of its surface value. Clearly, Z1% (Fig. 3b) has an inverse relation with absorption values (Fig. 3a), showing depths of penetration exceeding 75 m in September over a large part of the basin, mainly in the eastern part. Conversely, shallow depths of penetration are found in the northern Adriatic

Table 1
Values of diffuse attenuation coefficient (K_d) in the UV spectral domain for different locations and dates in the Mediterranean Sea.

Location	K_d (UV-B) (m^{-1})	K_d (UV-A) (m^{-1})	Instrument	Date	Source
Open sea					
Eastern Mediterranean	0.14 (310 nm)	0.05 (375 nm)	Photoelectric method	–	Jerlov (1950)
Mediterranean Sea	0.25 (312 nm)	–	Robertson meter	–	Smith and Calkins (1976)
Northern Adriatic Sea	0.57 (305 nm)	0.35 (340 nm)	PUV-500	July 1996	Sommaruga et al. (1997) and Herndl et al. (1998)
Northern Adriatic Sea	0.92 (305 nm)	0.38 (340 nm)	PUV-500	Aug. 1995	Brugger et al. (1998)
Northern Adriatic Sea	0.88 (305 nm)	0.35 (340 nm)	PUV-500	Sept. 1995	Kaiser and Herndl (1997)
South Aegean Sea	0.25 (305 nm)	0.12 (340 nm)	PUV-500	Sept. 1997	Obernosterer et al. (1999)
North Aegean Sea	0.57 (305 nm)	0.25 (340 nm)	PUV-500	Sept. 1997	Obernosterer et al. (1999)
Northwestern Mediterranean Sea	0.52–1.19 (305 nm)	0.31–0.92 (340 nm)	PUV-500	May 2006	Joux et al. (2009)
Northwestern Mediterranean Sea (MOLA)	0.43–0.51 (305 nm)	0.19–0.29 (340 nm)	PUV-500	June 2004	Jeffrey and Joux (unpublished data)
Coastal waters					
Cabo de Gata (Southern Spain)	0.34–0.57 (305 nm)	0.10–0.18 (380 nm)	PUV-500	Sept. 1996, February 1997	Figueroa et al. (2002)
Bay of Marseille (SOFCOM)	0.33 (305 nm)	0.21 (340 nm)	SAtlantic MICRO-PRO	Feb. 2008	Para et al. (unpublished data)
Bay of Marseille (SOFCOM)	0.61 (305 nm)	0.39 (340 nm)	SAtlantic MICRO-PRO	June 2008	Para et al. (unpublished data)
Bay of Marseille (SOFCOM)	0.42 (305 nm)	0.25 (340 nm)	SAtlantic MICRO-PRO	July 2008	Para et al. (unpublished data)
Northwestern Mediterranean Sea (SOLA)	0.50–0.59 (305 nm)	0.28–0.32 (340 nm)	PUV-500	June 2004	Jeffrey and Joux (unpublished data)
Rhône Estuary	0.40–0.84 (305 nm)	0.21–0.26 (340 nm)	SAtlantic MICRO-PRO	May 2008	Para et al. (unpublished data)

Sea and the Ligurian Sea in March. The values of Z1% for the Mediterranean Sea appear at the high end of values reported for other marine systems (e.g., for UV, Tedetti and Sempéré, 2006; Morel et al., 2007; Tedetti et al., 2007a). The possible overestimation observed here might be related to the simplistic radiative transfer scheme adopted here or from remaining uncertainties in our current ability to accurately predict all IOPs.

Mediterranean waters present a clear anomaly for defining optical trends. Empirical relationships relating the euphotic zone depth (Z_{eu}) to either surface or integrated chlorophyll concentrations, which were developed for typical oligotrophic waters such as those in the South Pacific, predict shallower values than those measured in the Mediterranean waters. Morel et al. (2007) suggested that this situation might relate to the significantly different bio-optical states of these two oceanic regions. They reported that in Pacific waters, phytoplankton seem to dominate the attenuation in the PAR spectral domain, whereas in the Mediterranean Sea, additional substances compete with algae for PAR photons. These results revealed that, in late summer, Mediterranean waters are "greener" than expected from their surface Chl*a* concentration (Claustre et al., 2002). It was suggested that this anomaly could be associated with the presence of Saharan desert dust or to a higher level of aCDOM as well as non-algal detrital particles (Morel et al., 2007). Consequently, regional algorithms dedicated to Mediterranean waters have been established for a more accurate retrieval of Chla from ocean color remote sensing (Bricaud et al., 2002).

There is a general lack of knowledge about optical properties in Mediterranean coastal waters, which are largely influenced by river inputs that provide dissolved and particulate matter as well as CDOM to the coastal zone (Para et al., 2010 and references therein). The impacts of particulate matter on optical properties are poorly constrained due to a lack of data on solid fluxes carried by Mediterranean rivers at the interface between land and ocean (river mouths) and along river margins. These poor optical constraints also derive from the physical dynamics of coastal waters within river mouths and plumes, the complexity of flocculation and the formation of aggregates from terrestrial mineral particles and or-

ganic matter, as well as from the mixing of autochthonous and allocthonous organic matter (Doxaran et al., 2002).

3.3. Impact on chemistry

3.3.1. Current knowledge

Although it contains clear waters favorable to the strong penetration of solar radiation (UVR and visible), several coastal zones in the Mediterranean Sea are subject to high nutrient injection from rivers (Ludwig et al., 2009) and a large input of terrigenous dissolved organic carbon (DOC) compared to the global ocean (Sempéré et al., 2000). Note that DOM likely includes a large, albeit uncharacterized, quantity of photoreactive CDOM and that NO_3^- efficiently absorbs UV-B radiation to produce the highly reactive hydroxyl radical (OH) (Qian et al., 2001). Therefore, it is very likely that in coastal zones, occurrence of radical precursors and strong solar radiation induce direct cellular damage to organisms as well as important photo-oxidation reactions involving DOM. In order to fully account for the impact of solar radiation (more specifically UVR) on DOM near the coast, it will also be crucial to account for the combination of factors (e.g., O_3, CO, SO_2, NO_x, smoke; i.e., anthropogenic pollution) that can lead to local alteration of the solar radiative flux often observed close to urban sites (tropospheric extinction) (Kazantzidis et al., 2005; Ribas and Peñuelas, 2004). Similarly, as a low-nutrient, low-chlorophyll system (LNLC), the open Mediterranean Sea allows deep penetration of solar radiation and therefore contains significant photochemical reaction rates throughout a much deeper surface layer that has not been satisfactorily quantified over a large-scale.

3.3.2. Effects on dissolved organic matter

Sunlight-induced degradation of DOM, which is considered to be a major sink of riverine DOM, takes place in the oceans through two processes: (1) an abiotic oxidation process involving the direct production of carbon monoxide (CO) and CO_2, and (2) a sequential process of abiotic and biotic reactions involving the photochemical alteration of the biological lability of organic substrates followed

by their DOC assimilation by bacterioplankton and conversion to biomass and CO_2 via respiration (Mopper and Kieber, 2002). Recent studies suggest that the fluxes of CO and CO_2 generated by the direct photodegradation of DOM represent between 16 and 36 Mt C year^{-1} for CO (Stubbins et al., 2006) and 3–12 Gt C year^{-1}for CO_2 and for the global ocean, although a minor fraction of the order of 10–20% of oceanic CO is also produced by biotic processes (Gros et al., 2009). Similarly, the UV-induced photodegradation of DOM and particularly of its carbonyl-bearing components (Riemer et al., 2000) leads to the formation of reduced light hydrocarbons (alkenes) of ∼5–10 Mt year^{-1}globally (Plass-Dülmer et al., 1995). Although these abiotic processes could represent 5–20% of the global carbon fixed by phytoplankton photosynthesis (Mopper and Kieber, 2000; Johannessen et al., 2000), very little is known about this topic for the Mediterranean Sea. Concerning sequential abiotic/biotic reactions, the irradiation of DOM from terrigenous or deep oceanic origins (i.e., mostly biorefractory DOM) will produce labile substrates like monocarboxylic acids and carbonyl compounds, which stimulate a 30–500% increase in bacterial production and respiration (Obernosterer et al., 1999; Mopper and Kieber, 2002; McCallister et al., 2005). For instance, a recent experimental study demonstrated the production of dicarboxylic acids during solar irradiation of a fatty acid solution enriched with NO_3^- (Tedetti et al., 2007b). Others reports suggest that NO_3^- photolysis, via the formation of OH radicals and some selective free radicals derived from bromide and bicarbonate/carbonate ions, may be a potentially important pathway for dimethylsulfide (DMS) photodegradation in marine waters (Bouillon and Miller, 2005) and pesticides (Richard et al., 2007).

These studies strongly suggest that the high levels of solar radiation encountered in the Mediterranean Sea combined with the high levels of photosensitizers like CDOM and NO_3^- discharged by Mediterranean rivers will enhance photochemical oxidation reactions in coastal areas.

Photochemical damages to phytoplanktonic cells are not created only by UVR and dissolved organic compounds. In fact, due to the presence of chlorophylls (which are very efficient photosensitizers (Knox and Dodge, 1985)), numerous organic components of phytoplankton are susceptible to PAR photodegradation during senescence. It was demonstrated recently that irradiation of senescent phytoplanktonic cells by the light used for their growth resulted in the photodegradation of most of their unsaturated lipid components (Rontani, 2001, 2008). The detection of relatively high amounts of lipid photoproducts in the particulate matter and recent sediment samples collected in the northwestern Mediterranean Sea (for a review, see Rontani, 2005) attests to the importance of photodegradation processes by visible solar radiation in this zone. Most of the photoproducts detected clearly originated from visible light-induced degradation of lipid components of senescent or grazed phytoplanktonic cells. The high levels of photoproduct biomarkers observed in regional samples are not surprising, given the fact that the overlying waters of the Mediterranean are subject to high irradiance (up to 1900 μmol of photons m^{-2} s^{-1} at solar noon in the Ligurian Sea; Cuny et al., 2002). Assuming a surface daily irradiance of 60 mol of photons m^{-2} (PAR) (a value representative of mid-latitude waters under a clear summer day; Nelson, 1993), it appears that most of the phytoplanktonic lipids (half-life doses ranging from 1 to 350 mol photons m^{-2}) (Rontani, 2001) may be significantly photodegraded in the upper portion of the euphotic zone during senescence or during herbivore grazing. Isoprene (2 methyl, 1-3 butadiene), a hydrocarbon of biotic origin frequently observed (Bonsang et al., 1992; Broadgate et al., 2004), is emitted by phytoplankton organisms under PAR radiation. Its production is linked to their photosynthetic activity and to the synthesis of terpenoid compounds, which are known to have many important biological and physiological func-

tions. As for terrestrial plants, isoprene emission by phytoplankton seems to be light dependent (Shaw et al., 2003; Bonsang et al., 2010) and could be the result of photo-protection mechanisms (Demers et al., 1991) to protect their thylakoid membrane against light stress (Harvaux, 1998).

In the northwestern Mediterranean Sea and the Ionian and Cretan Seas, DMS concentrations paradoxically peak in the summer, when Chl *a* concentrations reach their lowest levels (Kouvarakis et al., 2000; Belviso et al., 2003; Vila-Costa et al., 2008), as in the Sargasso Sea (Dacey et al., 1998). Although the seasonality of dimethylsulfide (DMS) is certainly determined by the interplay between numerous physical and biogeochemical processes and parameters, Vallina and Simó (2007) showed that sea surface DMS concentrations are highly positively correlated, both locally and globally, with the mixed layer solar radiation dose (SRD, i.e., the average solar radiation intensity experienced by phytoplankton in the mixed layer). Recent re-examination of this relationship at a global scale by Derevianko et al. (2009) seems, however, to indicate that when using minimal aggregation methods, SRD accounts for only a small fraction (4 – 14%) of the total variance in DMS concentration. At local scales, data show that DMS and SRD can be correlated, but slopes and intercepts display little consistency in the Atlantic Ocean and the Mediterranean Sea (Belviso and Caniaux, 2009; Miles et al., 2009). Nevertheless, it has been suggested that in highly irradiated waters typical of summer conditions, stronger stratification of the water column would favor high sulfur-producing phytoplankton. Moreover, high UV irradiances in shallow mixed layers generate high UV radiation doses for plankton that may inhibit the consumption by heterotrophic bacteria of DMS and of its precursor dimethylsulfoniopropionate (DMSP) and enhance the antioxidative responses of phytoplankton (i.e., intracellular OH radicals are removed by reaction with DMS and/or its photooxidation products), all resulting in higher DMS production than consumption (Toole and Siegel, 2004; Vila-Costa et al., 2008). Hence, the influence of solar radiation on the cycling of DMS is certainly less straightforward than its influence on the regulation of carbonyl sulfide (OCS) and CO concentrations (Pos et al., 1998).

3.4. Impact on marine organisms

3.4.1. Effects of solar radiation on bacterioplankton

Heterotrophic marine prokaryotes are responsible for the majority of the transfer of organic carbon from the dissolved to the particulate phase (bacterial biomass production, BBP) and the biogenic production of CO_2 (bacterial respiration, BR; Azam et al., 1983). Recent results in the coastal western Mediterranean Sea showed that DOM phototransformation may change the community structure of bacteria (Abboudi et al., 2008), while having contrasting effects on bacterial production and respiration that depend on the water's origin (Obernosterer et al., 1999, 2001; Mopper and Kieber, 2002; Tedetti et al., 2009). In surface waters, bacteria are exposed to damaging solar ultraviolet radiation that may cause distinct but overlapping kinds of damage. UV-B leads to direct damage of DNA by inducing dimerization of DNA bases and blocking DNA transcription and replication, while UV-A, and to a lesser extent visible light (400–700 nm), causes indirect damage by generating reactive oxygen species (ROS) that damage DNA, proteins and lipids. UVR could be particularly deleterious for bacteria because they have simple haploid genomes with little or no functional redundancy (Giovannoni et al., 2005) in addition to their small size, which precludes effective cellular shading and protective pigmentation (Garcia-Pichel, 1994). In fact, the deleterious effects of UVR on bacteria have been observed in a wide range of eutrophic and oligotrophic aquatic ecosystems (Häder et al., 2007b), as demonstrated by measurements of DNA damage and

inhibition of BBP, exoenzymatic activity and BR (Jeffrey et al., 2000).

UVR certainly affects bacterial processes in near surface waters, but it also has consequences at significant depths in the water column. Few studies have attempted to quantify this significance for bacteria compared to phytoplankton, and most have focused only on coastal waters (Conan et al., 2008 and reference therein). Recently, Joux et al. (2009) determined that UVR affected bacterial production down to 8 m depth in the open waters of the Gulf of Lion. These data support the need for expanding studies to other regions of the Mediterranean Sea, especially into the clear waters of the eastern part, and into different seasons, to get a better idea of the global impact of UVR on BBP and BR.

Indeed, the response of bacteria to UVR is certainly not only a function of the radiation levels received but also depends on a number of other environmental (e.g., temperature, nutrient status, mixing) and biological (e.g., specific sensitivity, photoacclimation capacity) factors. The interactive effect of nutrient limitation and UVR on aquatic bacteria has been less studied compared to the same effect on phytoplankton. Kaiser and Herndl (1997) observed that BP inhibition induced by UV-B was higher in freshly collected seawater than in aged seawater where bacteria were less active, but recovery under photoreactivating UV-A was also greater for the more active bacteria present in freshly collected seawater. Other studies have reported that the sensitivity to UVR of phosphorous-deficient bacteria is reduced by an increase of inorganic P availability (Medina-Sanchez and Villar-Argaiz, 2006; Pausz and Herndl, 1999). Recently, Joux et al. (2009) observed that bacteria growing faster after stimulation by nutrients in the NW Mediterranean Sea were more sensitive to direct solar radiation. However, the nutrient addition increased the recovery of bacteria after UV stress because nucleotide excision repair ("dark repair") mechanisms require energy and because the use of the small organic molecules from DOM photodegradation may be facilitated in the presence of inorganic nutrients added to the samples (Reche et al., 1998). These results demonstrate the complex interaction between UVR and nutrients, which needs to be clearly elucidated because bacterial production is often strictly limited by phosphorus availability in the Mediterranean (Thingstad et al., 2005; Pinhassi et al., 2006).

UVR not only affects global bacterial activities but may also inhibit specific microbial functions due to the sensitivity of the species harboring these functions. For instance, the impact of UVR on nitrification activity (i.e., the microbial oxidation of ammonium to nitrate via nitrites), and on the diversity of the microbial community associated with this process, is an important issue to consider in the context of global changes in the Mediterranean Sea. The latter might particularly affect terrestrial nutrient input, water stratification and light intensity. It was recently shown that nitrification is not only carried out by some ß- and γ-proteobacteria but also by certain Crenarchaeota (Wuchter, 2006). Such nitrification occurs at significant rates at the surface of the oceans and can potentially fuel primary production in well-lit waters (Yool et al., 2007). The production of ammonium by photomineralization of DOM has been measured in many aquatic environments, including the oligotrophic Mediterranean Sea (e.g., Kitidis et al., 2006), where this process could support the activity of the ammonium-oxidizing bacteria and archaea. Recent studies in DOM-enriched coastal productive waters suggest that a significant proportion of primary productivity could be fueled by in situ ammonium regeneration and nitrification (Fernández et al., 2009), while previous efforts have highlighted the role of ammonium in the euphotic zone of the western Mediterranean Sea (Diaz and Raimbault, 2000). It is therefore important to explore the interaction between photomineralization, recycling of DOM and bacterial activity within the euphotic zones of contrasting environments because they fuel a fraction of primary production that has yet to be accurately determined.

Also importantly, UVR could directly inhibit the oxidizing ammonium activity of certain nitrifying proteobacteria that seem to be particularly sensitive to this stress (Guerrero and Jones, 1996a,b). It is important to note that while laboratory studies have proposed differential responses to PAR and UV among the bacterial nitrifying community, differences have also been detected in their recovery capacities. Under simulated conditions, it was proposed that responses of NH_4^+ and NO_2^- oxidizing bacteria depend on factors such as time of exposure, cell density and wavelength (with an overall increased sensitivity of ammonium oxidizers in the blue region of the spectrum). However, it was also observed that photoprotection by increased substrate concentration may occur among ammonium oxidizers but remain absent in nitrite-oxidizing bacteria (Guerrero and Jones, 1996a,b). The importance of light response and recovery among nitrifying assemblages is gaining particular importance since the realization that archaeal nitrification can be highly significant in the euphotic zone of open ocean and oligotrophic waters. However, nothing is yet known about the UV or full-sunlight sensitivity of ammonium-oxidizing archaea, a task that is further complicated by the existence of only one cultured representative of this group (N. maritimus; Könneke et al., 2005).

3.4.2. Effects of solar radiation on phytoplankton

Light is probably the most variable environmental factor in the water column, determining the high variability that is observed in primary productivity. This variability is due to the fact that visible radiation can either enhance photosynthesis or, conversely, inhibit photosynthetic activity by causing photodamage to cells. Therefore, microalgae must develop photoacclimative strategies to accommodate the continuous changes in light of the diel cycle, turbulence, cloud cover, vertical or horizontal advection and cell migrations (see Brunet and Lavaud, 2010). Thus, both atmospheric and water column forcing might strongly affect photosynthesis and growth of phytoplankton (Dimier et al., 2009a). Enhancement or depression of these biological functions have great implications for the competitive ability and species succession of phytoplankton at different spatial and temporal scales, which, in turn will modify the primary production budget of the water column. Spatial and temporal succession of phytoplankton depend on, among other factors, the capacity of regulating photosynthesis (Brunet and Lavaud, 2010). Recently, Dimier et al. (2009b) highlighted the ecophysiological properties of low-light acclimated, variable-light acclimated and high-light acclimated microalgal species in relation to the environmental properties of their ecological niches, including both the upper-mixed layer and the deep-chlorophyll maximum layer. In the former niche, photosynthetic rate is determined by the amount of light penetrating the upper layer, UV radiation (which can damage some cell components and function), the depth of the mixed layer (which affects the daily integrating light dose), self-shading in the case of algal blooms, the mixing rates in the upper layer, and the species'/groups' capacity to react to light variations. The role of CDOM in the UV effects on phytoplankton activity is also crucial. Indeed, Arrigo and Brown (1996) demonstrated that primary production in the upper 30 m of the water column was enhanced by the presence of CDOM, which absorbed damaging UVR, although it contributed to reducing the level of PAR.

UV-B radiation can reach 30 m in depth in open ocean waters (Tedetti and Sempéré, 2006) and potentially damage phytoplankton (e.g., Vincent and Roy, 1993), causing microalgal cell death (Llabres and Agusti, 2005; Agusti and Llabres, 2007).

Other than DNA changes, one of the most severe forms of damage impacts photosynthetic activity through damage to photosystem II. Whether because of enhanced high-light defense

processes in algae and cyanobacteria (e.g., the xanthophyll cycle, Zudaire and Roy, 2001, or production of mycosporine-like amino acids, Balskus and Walsh, 2010) and/or light-filtering mechanisms involving production and synthesis of mycospirine amino acids by some algal species, these features reduce the photosynthetic quantum yield and thereby the photosynthetic rate.

3.4.3. Effects of solar radiation on zooplankton

While it is widely recognized that zooplankton responses to changes in solar radiation (composition and intensity) are directly related to the effects observed on phytoplankton, there is also increasing evidence of specific responses among zooplankton groups to sunlight. It has been recently stated that increased UV-B radiation can have negative effects on zooplankton dynamics (e.g., Lacuna and Uye, 2000; Yu et al., 2009). In fact, nauplii and copepodite stages of *S. inopinus* (Copepoda) were observed to have high sensitivity to UV-B radiations resulting in increased mortality. Effects were also observed in adults in terms of ingestion rates and fecundity (Yu et al., 2009). The modification of ingestion rates can be related to the direct damage of skin and tissue or the indirect effect of modifications in trophic interactions. Therefore, although mechanisms for photoprotection might be at work among zooplankton (such as antioxidant enzyme production and even vertical migration, Hylander and Hansson, 2010), it is not clear whether enhanced UVR would change copepods' community composition in a future climate scenario. Many laboratory or mesocosm studies have shown that zooplankton are able to escape UV radiation by migrating vertically (e.g., Rhode et al., 2001). Hansson et al. (2007) demonstrated that to adapt to changes in UV radiations, zooplankton use migration together with protective pigments. Diel vertical migrations of zooplankton have recently been thoroughly studied in the Mediterranean Sea (Minutolli and Gugliemo, 2009). Increasing UV might thus lead to a decreasing presence of zooplankton on the surface layer and/or to a selection of species/groups that are able to migrate along the water column.

If zooplankton are distinguished into the two functional groups of protozooplankton and metazooplankton, some further results about the effect of increased UV-B radiations on zooplankton and the food web structure can be determined. Protozooplankton (mainly, heterotrophic flagellates and ciliates) prey on bacteria and small phytoplankton, whereas metazooplankton (e.g., copepods) prey on large phytoplankton, such as diatoms. Previous studies show that UV-B radiations increases in the absence of large metazooplankton severely affects the ciliate communities, which induces a trophic impasse by trapping carbon in small organisms. Therefore, the plankton food web can shift toward the less productive microbial food web (Mostajir et al., 1999; Ferreyra et al., 2006). However, recent studies show that a moderate but realistic UV-B radiations increase (Nouguier et al., 2007) in the coastal Mediterranean food web did not affect the protozooplankton community as seriously as was reported in the previous study in the presence of metazooplankton (Vidussi et al., 2011). In other words, the coastal Mediterranean food web, including zooplankton, would be somehow more resistant to a moderate UV-B radiation increase.

3.5. Expected alterations

3.5.1. Solar radiation

While it was previously thought that the destruction of the stratospheric O_3 layer and the resulting increase in the UV-B irradiance were linked specifically to the emission of chlorofluorocarbons (CFCs) (Molina and Rowland, 1974), it was recently discovered that there are very complex interactions between UVR, stratospheric O_3 and climate change (Weatherhead and Andersen, 2006). Indeed, UVR might also be affected by a variety of direct and indirect effects of climate change, such as changes

in cloud cover, changes in atmospheric dust caused by changing precipitation and wind patterns, the cooling of the stratosphere, the emission of greenhouse gases or even urban pollution (McKenzie et al., 2003; Kerr et al., 2003). As a result, the UV surface irradiance may be modified in the coming years to a much larger degree than previously estimated by only taking into account the evolution of CFC concentrations (which have been in constant decline since the Montreal Protocol). Therefore, the effect of increased irradiance may be significant not only at the poles but also in the mid-latitudes (WMO, 2006).

3.5.2. Dimming

It should be mentioned that in a future warmer climate, large-scale heat waves, such as the one observed in the summer of 2003 (Hodzic et al., 2007), and large concentrations of anthropogenic and biomass-burning aerosols are expected to appear more frequently over the European Mediterranean region (Moriondo et al., 2006). Because episodic injections coming from Sahara dust events, biomass burning, or fuel combustion-derived products along the coastal Mediterranean Sea are predicted to increase during the 21st century, future work on understanding atmospheric and marine optics together with the corresponding impact of solar radiation on marine systems in terms of light availability for marine organisms is warranted. A recent study by Mallet et al. (2009) strongly suggests that such effects play a significant role, at the very least, on the intensity of primary production. Therefore, studies going farther in connecting direct and indirect solar radiative effects on atmosphere/ocean biogeochemical cycles will provide a critical background for the interpretation of future climate scenarios.

3.5.3. Stratification

Mixing intensity and mixed-layer depth changes will expose micro-organisms to variations in daily light doses that may exacerbate an increase of visible light penetrating the water column and UV-B damage in cells (Neale et al., 2003). This is a crucial parameter when considering the relationship between light (visible and UV) and the biological compartment, as it has been noticed on bacteria (Huot et al., 2000; Van Wambeke et al., 2009) or phytoplankton (Brunet et al., 2008). For instance, Van Wambeke et al. (2009) showed that the depth of the mixed layer had a great impact on the daily underwater UV doses received by heterotrophic bacteria in the surface ocean. They also found a negative linear correlation between the UV-B/UV-A tri-hourly dose ratios and bacterial production (BP), suggesting that changes in the balance between DNA damages and photorepairs might have a significant influence on the diel variability of BP in the surface oceanic waters. Intensifying solar radiation, and thus stratification, might be the cause for increasing the dominance of high-light-adapted cells, such as *Synechococcus* (Casotti et al., 2003) or some pico- or nano-eukaryotes (Brunet et al., 2006, 2007; Dimier et al., 2009b). On the contrary, an increase in stormy events will lead to an occasional deepening of the mixed layer that would select more opportunistic species as greater cells (diatoms for instance), capable of a low-light acclimation strategy and efficient photoprotection (Brunet and Lavaud, 2010). The worst-case scenario for algal photosynthetic efficiency would be a decrease of visible light, in terms of daily light harvested by algae, while UV-B increases, as UV-B effects would be potentially more damaging.

Increasing water column thermal stratification through Mediterranean warming might increase the deleterious effects of UVR on organisms present in the surface mixed layer. Conversely, stronger winds and more frequent storms that deepen the mixed layer would also alter overall biological exposure to damaging UVR in the surface ocean. In any case, the climatological prediction from current models is an increase in stratification expected in the

Mediterranean Sea during the 21st century (Somot et al., 2006), and this will certainly modify the exposure of organisms and organic compounds to solar radiation and favor photochemical oxidation reactions. A better understanding of the quantitative links between photochemical and photobiological processes and mixing depths currently requires further work for the appropriate modeling of biogeochemical cycles.

4. Influence of temperature and acidification on the Mediterranean Sea solubility and biological pumps

4.1. Warming in the Mediterranean

4.1.1. Current knowledge

Since the end of the 19th century, the global average temperature on the earth's surface has increased by 0.6 °C and is predicted to increase by another 1–6 °C by the end of the present century, according to different scenarios of greenhouse gas emissions (IPCC, 2007). Representing more than 1000 times the caloric capacity of the atmosphere, the ocean undoubtedly plays a crucial role in global climate fluctuations. Levitus et al. (2005) showed a significant increase of the global ocean heat content (0.06 °C; 0–700 m) between 1957 and 2004. This temperature increase in sea surface temperature has also been demonstrated worldwide, both at regional and local scales.

The Mediterranean Sea is a largely enclosed sea, with high temperature and salinity, and decreasing freshwater due to dams and river diversions. In the western basin, the surface temperature ranges from 12–13 °C in winter to 26 °C in summer, while in the eastern basin, the surface temperature is approximately 16–17 °C in winter and 27 °C in summer. During the summer, the surface waters are characterized by a thermocline, whose depth, temperature gradient and duration increase slowly from the western to the eastern basin. The deep Mediterranean waters (from 250 m to a maximum depth) are very homogeneous, with a temperature of about 12.8 °C and a salinity of about 38.2.

4.1.2. Expected alterations

The temperature increase observed in recent decades in the ocean, both at the global but also at the local/regional scale, has also been observed in the Mediterranean Sea. Indeed, Moron (2003) has analyzed the long-term (1856–2000) variability of Mediterranean Sea surface temperatures (SST). Although no clear linear trend can be established over the whole period, two warming periods have been observed. The first one occurred between 1910 and 1940, which, according to the author, can be attributed to an increase in solar radiation and a decrease in volcanic activities. The second period, from 1970 to 1975, can be attributed to both an increase in solar activity and an increase in the concentration of greenhouse gases in the atmosphere. This increase in Mediterranean SST in recent decades has also been shown by Lelieveld et al. (2002) and Rixen et al. (2005), based on models forced by *in situ* measurements (1930–1998) and amounts of ~0.5 °C between 1980 and 2000. Significant warming trends have also been observed in the western Mediterranean basin shelf in the 1990s at six of eight stations analyzed by Vargas-Yanez et al. (2008); warming rates ranged from 0.039 to 0.167 °C year^{-1}. Satellite observations provide interesting datasets for the last two decades. Studies that have made use of these data reveal a significant warming trend for Mediterranean SST (0.03–0.15 °C year^{-1}) but also a noticeable seasonal variability in these warming trends that has not been highlighted previously (Nykjaer, 2009 and references therein). Regarding intermediate and deep waters, significant warming trends have also been pinpointed. According to Béthoux and Gentili (1996), Western Mediterranean Deep Water (WMDW)
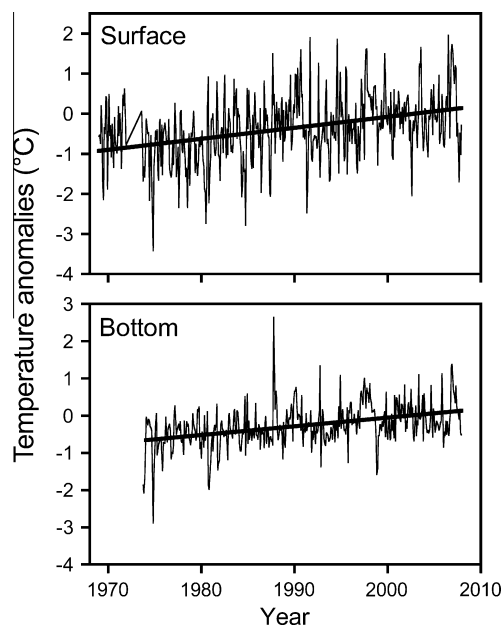
Fig. 4. Temperature anomalies at the surface and bottom (80 m) at l'Estartit Oceanographic Station, Spain. Data at 80 m are shown in Vargas-Yanez et al. (2008). The l'Estartit Oceanographic Station is operated by the Instituto de Ciencias del Mar (Consejo superior de investigaciones científicas; ICM/CSIC) and the Mediterranean Group on Climate Change (GCC; Instituto Español de Oceanografía; www.ma.ieo.es/gcc).

has increased its temperature at a rate of 0.0035 °C year^{-1} in the period 1957–1997. The temperature increase of the Levantine Intermediate Water (LIW) in the same period was 0.0068 °C year^{-1}. The reasons for these trends are still unclear, and it has been shown recently that warming trends are not a linear or constant process (Vargas-Yanez et al., 2008) with warming accelerations at the surface, such as the one observed in the 1990s. The scarcity of data also makes trend estimation very sensitive to analysis methods, demonstrating the importance of systematic sampling for studying long-term changes (Vargas-Yánez et al., 2009). A recent analysis of daily to biweekly temperature time series (1975–2004) from three coastal stations ca. 400 km in the northwestern Mediterranean showed consistent surface warming rates of 0.026–0.033 °C year^{-1} and fairly similar monthly to multi-decadal variability, demonstrating that the warming was driven by regional phenomena rather than local conditions (Bensoussan et al., 2009). Looking at the effects of this warming trend on stratification on the Catalan coast (Spain), Coma et al. (2009) showed enhanced stratification with a ca. 40% lengthening of summer conditions since 1974. According to Vargas-Yanez et al. (2008; Fig. 4), several hypotheses have been proposed to explain these non-linear temperature increases: (1) changes in the freshwater budget induced by damming in the eastern Mediterranean and damming of the rivers draining into the western Mediterranean, (2) changes in the ocean–atmosphere heat exchange linked to global warming and (3) a continuous positive trend of the North Atlantic Oscillation (NAO) index since the early 1960s towards a maximum positive phase in the early 1990s. In the eastern basin, although fewer long-term data series are currently available, there is some evidence that between 1987 and 1991, the eastern Mediterranean Deep Water (EMDW) became warmer and saltier due to the switch of its source water from the Adriatic to the Aegean (Gertman et al., 2006), most likely related to changes in the heat and freshwater flux anomalies in the Aegean Sea.

To conclude, as for the global ocean, the Mediterranean Sea has experienced a positive trend in both sea surface and deep-water

temperatures, which has affected the outflow of water into the North Atlantic at Gibraltar. More long-term data series are needed to carefully assess warming rates, especially in the eastern basin where data are currently lacking, as well as to clarify the reasons for such a warming process. This increase in temperature is highly susceptible to having severe impacts on the role of the Mediterranean Sea in the global carbon cycle, through changes of both the solubility and biological carbon pumps (see next section). Moreover, changes in species distributions and modifications of Mediterranean habitats are presently occurring and will undoubtedly occur in the next decades (see Chapter 7).

4.2. Acidification in the Mediterranean

4.2.1. Current knowledge

Human activities are responsible for a 36% increase in atmospheric CO_2 since the beginning of the industrial era (1800). This increase is due to the CO_2 emissions that come from the combustion of fossil fuels (coal, oil and natural gas), cement production, as well as deforestation. The atmosphere's level of CO_2, measured as the partial pressure (pCO_2), rose from 280 μatm before the start of the industrial era to 381 μatm in 2006 (Canadell et al., 2007). Only 45% of the CO_2 emitted by human activities during the industrial era has remained in the atmosphere. Approximately 30%, or 118 (±19) billion tons (Gt), of carbon were absorbed by the oceans between 1800 and 1994 (Sabine et al., 2004). Nowadays, oceans trap CO_2 that dissolves in the surface water and reacts with the water molecules (H_2O), forming carbonic acid (H_2CO_3). Most of this acid dissociates into hydrogen ions (H^+), bicarbonate ions (HCO_3^-) and carbonate ions (CO_3^{2-}), and the increase in concentration of H^+ ions reduces pH (pH = $-\log_{10}[H^+]$). Oceanic pH has already declined by approximately 0.1 unit since the beginning of the industrial era and is expected to decrease by an additional 0.4 unit by the end of this century (Haugan and Drange, 1996). This pH decrease will potentially have impacts on the physiology and metabolism of marine organisms through a disruption of inter-cellular transport mechanisms. Moreover, as this decrease of oceanic pH causes a shift of the carbonate system equilibrium toward more dissolved CO_2 and less CO_3^{2-} (Fig. 5), other impacts are expected. Indeed, on the one hand, the increase of CO_2 is expected to be beneficial for primary producers, while, on the other hand, the decrease in CO_3^{2-} concentration will potentially threaten marine calcifiers, which grow their shells/skeletons (calcium carbonate: $CaCO_3$) from calcium (Ca^{2+}) and CO_3^{2-} (see following sections).

Because pCO_2 is very sensitive to a temperature increase (it rises by ~4.3% per °C increase), a decrease in the ocean buffer capacity of surface waters is expected due to global warming and has already been shown by Le Quéré et al. (2007) in the Southern Ocean as well as by Schuster and Watson (2007) and Watson et al. (2009) in the North Atlantic and by Thomas et al. (2007) in the North Sea. Temperature change affects ocean carbonate chemistry because both the apparent dissociation constants and the CO_2 solubility vary with temperature. Nevertheless, McNeil and Matear (2007) reported from a coupled climate-carbon cycle simulation (IS92a scenario) that while the effects of climate change on surface ocean pH will be negligible, the saturation state of seawater with respect to calcium carbonate will be buffered by 15% due to the temperature increase by the end of the century. Similar conclusions have been found by Cao et al. (2007), who concluded that future changes of the oceanic pH are largely independent of the amount of climate change.

The assessment of the role of the Mediterranean Sea with respect to CO_2 exchange with the atmosphere suffers from a clear lack of data. Although some data associated with the air–sea exchange of CO_2 have been published in the recent years, most of these data are restricted geographically to the western basin, with very few data in the eastern basin (Krasakopoulou et al., 2009), and also restricted temporally, as even fewer studies have covered an annual cycle. Basin-scale estimates of air–sea CO_2 fluxes in the Mediterranean are thus very uncertain, and indirect methods have been used (Copin-Montégut, 1993). Based on satellite-driven modeling of the upper-mixed layer, D'Ortenzio et al. (2008) estimated that the Mediterranean Sea, as a whole, acts as a small-to-medium sink for atmospheric CO_2 (0.24 Gt C year^{-1}), with opposite behaviors occurring in the two basins, the western basin acting as a sink of 8.64 Gt C year^{-1} and the eastern basin acting as a source of 8.4 Gt C year^{-1}.

As a consequence of its high salinity, the total alkalinity (A_T) of the Mediterranean Sea is also high (~2600 μmol kg^{-1}). The major inputs of A_T in the system are the rivers and the Black Sea, while the main outputs are the sedimentation of $CaCO_3$ and exchanges with the Atlantic Ocean. As pointed out by Touratier and Goyet (2011), the eastern basin is clearly characterized by an A_T > 2600 μmol kg^{-1}, while the A_T of the western basin is always <2600 μmol kg^{-1}. The distribution of the total dissolved inorganic carbon (C_T) shows opposite trends, with the highest concentrations generally found in the western basin. With increasing depths, the rising levels of C_T are a direct consequence of the CO_2 released by respiration of organisms and the decomposition of organic matter. As the Mediterranean Sea is relatively more alkaline than the open ocean, it can theoretically absorb relatively more anthropogenic CO_2 than the open ocean and has been shown to act as a significant source of C_T for the Atlantic ocean (Ait-Ameur and Goyet, 2006). This has been questioned recently by Huertas et al. (2009); however, this study used the inappropriate approach of Gruber et al. (1996) to estimate the level of anthropogenic CO_2 in the inflowing Atlantic surface waters.
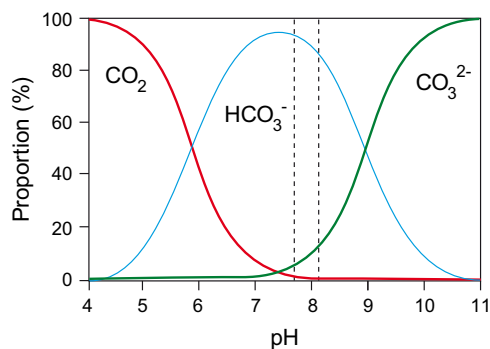

Fig. 5. Proportion of the different dissolved inorganic carbon species in seawater as a function of pH. Vertical dotted lines refer to the present global ocean pH (~8.1) and the level projected for the end of this century (~7.8).
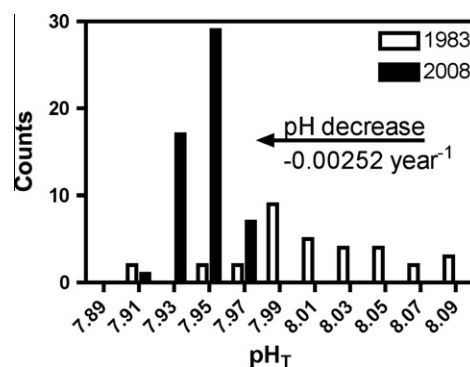

Fig. 6. The evolution of the pH of the dense cold winter water mass (NAdDW) in the northern Adriatic Sea between 1983 and 2008 (Luchetta et al., 2010).

4.2.2. Expected alterations

As mentioned above, long-term data series of the carbonate properties are very scarce throughout the Mediterranean Sea, and this precludes making an accurate evaluation of the degree and rate of acidification in this region. However, a modeling exercise from Louanchi et al. (2009) suggests that the Mediterranean Sea has been transformed from a source of 0.62 Gt C year^{-1} for atmospheric CO_2 in the 1960s to a net sink of -1.98 Gt C year^{-1} in the 1990s. This study also suggested that changes of surface pH in the Mediterranean Sea were not significant over this period. Touratier and Goyet (2009), by using anthropogenic carbon (C_{ANT}) estimations at the DYFAMED site (northwestern Mediterranean) between the 1990s and 2000s, have demonstrated that the temporal trend of C_{ANT} is decreasing, although C_T is increasing, and have suggested that pH may have already increased by 0.15 pH unit since pre-industrial times. A recent estimate provided by Touratier and Goyet (2011) indicates that all water masses in the Mediterranean Sea are already acidified (-0.14 to -0.05 pH unit). Waters from the eastern basin (especially those located in the intermediate layer) appear to be less contaminated than those from the western basin. When compared to the typical value of -0.1 for the surface waters of the world ocean, the Mediterranean Sea appears to be one of the regions that are the most impacted by acidification. On a more local scale, Luchetta et al. (2010; Fig. 6) studied the variation of dense cold winter water mass (NAdDW) pH level between 1982–1983 and 2007–2008. They reported a significant pH decrease between these two periods of -0.063, corresponding to an acidification rate of 0.0025 pH unit year^{-1}. This value is higher than the ones measured at station ALOHA (central North Pacific Ocean; 0.0019 year^{-1}; Dore et al., 2009) and similar to the one measured in the Iceland Sea (0.0024 year^{-1}; Olafsson et al., 2009). To the best of our knowledge, no estimates of future acidification rates in the Mediterranean Sea have been carried out. Upcoming research efforts will need to provide an accurate assessment of the actual and future acidification level in the Mediterranean Sea (CIESM, 2008b). This can only be achieved by increasing the number of medium to long-term monitoring stations and by adding pH and other variables of the carbonate system as key parameters to be included in existing monitoring actions, hopefully providing enough high-quality data for predictive modeling purposes.

4.3. Impacts on primary production

4.3.1. Current knowledge

Phytoplankton growth depends on temperature and the availability of light and nutrients. Most of this nutrient supply to the surface ocean comes from the mixing and upwelling of cold, nutrient-rich water from below. Surface seawater warming increases stratification, inhibits mixing and reduces the upward nutrient supply and therefore decreases productivity (Doney, 2006; see Chapters 1 and 5). However, it must be stressed that most papers dealing with the effect of global change on photosynthesis have focused on the importance of thermal stratification for light supply and nutrient availability without disentangling those effects from direct temperature effects. Indeed, temperature increase is known to provoke an acceleration of physiological rates. Although the organic matter production of light-limited phytoplankton appears to be less responsive to temperature than heterotrophic processes, this parameter is suspected to affect the magnitude, timing and composition of phytoplanktonic blooms. In the North Atlantic, the bloom peaks of different phytoplanktonic species have advanced by up to several weeks compared to the late 1950s, with associated changes in zooplankton seasonal distribution (Edwards and Richardson, 2004). Increasing water temperature leads to an elongation of the phytoplanktonic growing season, which may allow sub-tropical and temperate species to bloom earlier. Recently,

Hare et al. (2007) studied the effect of a 4.7 °C increase in SST of the Bering Sea and found not only a significant increase in photosynthetic rates (2.6–3.5 times) but also a shift of the community away from diatoms towards nanophytoplankton. These modifications of the phytoplanktonic community structure have also been shown by Feng et al. (2009) using shipboard continuous culture experiments during the North Atlantic spring bloom, following perturbation scenarios consisting of both temperature and pCO_2 increases. Although higher production rates might help mitigating climate warming by increasing the capacity of the ocean to store anthropogenic CO_2 by phytoplanktonic production, this shift from large to small species might have severe effects on the overall productivity of this ecosystem, the transfer of carbon and energy towards higher trophic levels and the capacity of the ecosystem to export organic matter. In the latter case, increased primary production rates' effects on air–sea CO_2 fluxes might be countered by increased mineralization rates in the mixed layer (see next section). Such an increase in primary production rates was not found by Sommer and Lengfellner (2008) in Baltic Sea mesocosms. These authors reported no effect of a 2, 4 and 6 °C temperature increase on the timing of the phytoplanktonic spring bloom (determined by light availability) but observed significant decreases in phytoplankton peak biomass and also a shift from diatoms to nanophytoplankton. These authors explained the decreased peak biomass as an effect of more efficient grazing and recycling (see Hoppe et al., 2008; next sections) and suggested a future decrease of the biological pump under warming scenarios. In the benthic compartment, temperature is also affecting photosynthetic rates of macroalgae (Yokohama, 1973) and seagrasses (Bulthuis, 1987), with primarily higher rates at higher temperature. N-fixing organisms play an important role in oligotrophic areas of the ocean. Breitbarth et al. (2007) showed a dependency of *Trichodesmium* production rates on temperature and suggested future increases of the nitrogen inputs to oligotrophic waters such as the Mediterranean Sea in the coming decades. Finally, nitrifying organisms are chemoautotrophs and use carbon dioxide as their carbon source for growth. Nitrification is a key process of both the carbon and nitrogen cycles and consists of the biological oxidation of ammonium with oxygen into nitrite, followed by the oxidation of nitrite to nitrate. This process may provide a significant amount of nitrate for regenerated production. To the best of our knowledge, nothing is known about the potential effect of global warming on nitrification activities in the ocean in the coming decades.

While the effects of CO_2 enrichment on terrestrial plants have been intensively studied since the 1990s, relatively little is known about these effects on marine primary producers. In seawater, RUBISCO carboxylation is *a priori* not optimal at the current environmental CO_2 concentrations. However, many species developed several mechanisms to overcome this low environmental CO_2 and to increase CO_2 concentrations at the site of carboxylation. Therefore, it seems logical that many species do not benefit from an increase in seawater pCO_2, as this is the case for diatoms and for the prymnesiophyte *Phaeocystis globosa* (see review from Riebesell et al., 2007). In contrast, several coccolithophorids species as well as nitrogen-fixing species such as *Trichodesmium* (see later) show increased production rates at higher CO_2 levels. This suggests that some species will benefit from elevated CO_2 conditions, while others will not, precluding changes in community production and composition as well as potentially related nutritive values (increase of particulate organic matter C:N ratios) and export capacities (decrease of the inorganic/organic particulate ratio, see thereafter; Feng et al., 2009; shift from heavy cells to nanophytoplankton, Hare et al., 2007). Not only the production but also the fate of this organically fixed carbon is expected to be altered at high CO_2 levels, which might lead to major changes in the food-web dynamics and export rates. For instance, the production of

dissolved organic matter (exudation) has been shown to be sensitive to CO_2 availability (Engel, 2002), with an increase in Transparent Exopolymeric Particles (TEP) production at high pCO_2 potentially leading to substantial modifications of particle-sinking velocities and export productions (see next section). While primary production from coccolithophorids seems to be positively influenced by ocean acidification, calcifying species from this group will most likely suffer from this perturbation through an alteration of their calcification process (see review from Zondervan, 2007). Indeed, although a very recent study suggested enhanced calcification rates of *Emiliania huxleyi* at high pCO_2 (Iglesias-Rodriguez et al., 2008), most of the studies to date showed an alteration of this process at a low pH that might have adverse effects on the competitive fitness of this group. As mentioned earlier, N-fixing organisms play an important role in oligotrophic areas of the ocean, and several studies have revealed a significant dependency of diazotrophy on pCO_2 levels, which might enhance the productivity of N-limited oligotrophic areas of the ocean and drive some of these areas into P-limitation. Among these studies, Hutchins et al. (2007) showed enhanced N-fixation and growth rates under severely limiting P conditions. Concerning nitrification, Huesemann et al. (2002) reported a significant dependency of marine nitrifiers to elevated pCO_2 with a 38% rate decrease for a 0.5 pH unit decrease. It must be stressed that the potentially associated overall effect on the functioning of the planktonic communities and biological pump is presently unknown. With respect to the benthic compartment, a positive effect of CO_2 enrichment on photosynthesis has been found in macroalgae (Gao et al., 1993) and seagrasses (Zimmerman et al., 1997). In contrast, calcareous coralline algae and corals, which were the first organisms to be studied in the context of ocean acidification (e.g., Gattuso et al., 1998), show no apparent or limited effects on primary production and an alteration of calcification rates for the vast majority of the studied species for a review on corals, see Marubini et al., 2008.

The Mediterranean Sea contains one of the most nutrient-poor waters in the world (Dugdale and Wilkerson, 1988), with a trophic status varying from mesotrophic in the northwestern Mediterranean to extremely oligotrophic in the eastern basin. Average values of primary production amount to 158 and 109 g C m^{-2} year^{-1} for the western and eastern basins, respectively (Antoine et al., 1995). Both nitrogen and phosphorous have been shown to be potentially limiting nutrients for phytoplankton and bacterial growth (Béthoux et al., 1992). In the western basin, thanks to the winter mixing of surface waters with nutrient-rich deep waters, the development of the winter-spring phytoplankton bloom is one of the most coherent features of the Mediterranean ecosystem (Goffart et al., 2002), with mostly the presence of diatoms and, to a lesser extent, flagellates and coccolithophorids. The contribution of picophytoplankton to primary production ranges from 31% to 92%, being more important in oligotrophic offshore waters (Magazzú and Decembrini, 1995). In the Mediterranean Sea, benthic primary producers play important roles, such as the endemic seagrass *Posidonia oceanica*, which covers about 35,000 km^2 (Pasqualini et al., 1998) and is the basis of a highly diverse and productive ecosystem. Calcareous primary producers such as coralline algae and four symbiotic scleractinian corals, e.g., *Cladocora caespitose*, are also present in the Mediterranean and create important biodiversity hotspots.

In the Mediterranean Sea, specific studies assessing the effects of both ocean warming and acidification on planktonic and benthic primary production are particularly scarce. However, several studies have investigated the separate effects of these stressors. For instance, Goffart et al. (2002) showed changes in the development of the winter-spring bloom and a drastic reduction of phytoplankton biomass in a bay of Corsica, related to a modification of the water column vertical stability and a decrease of nutrient replenishment

as a consequence of surface waters warming. Changes in the phytoplanktonic community structure due to seawater warming have been shown by several studies (Tunin-Ley et al., 2009 and references therein), most of them showing a shift towards small-sized species (picophytoplankton and nanoflagellates) and a decline of diatoms. This reduction in phytoplankton biomass was not observed by Marty et al. (2002), who even showed a general increase in total phytoplankton biomass between 1991 and 1999 at the DYFAMED site (NW Mediterranean). These authors concluded that this increase was mainly due to small-sized phytoplankton as a specific response to the lengthening of the summer stratification period, a period favoring the growth of species supporting the regeneration production. According to Bosc et al. (2004), a comparison of ocean color data acquired for the periods 1978–1986 and 1998–2001 revealed conspicuous differences in the northwestern sub-basin, such as the reduction of the deep convection zone, the earlier start of the spring bloom and the quasi disappearance of the autumn bloom. Recently, Vidussi et al. (2011) have conducted mesocosm experiments at the Mediterranean platform for Marine Ecosystem Experimental Research (MEDIMEER, South of France) to assess the effects of ultraviolet radiation and warming on coastal spring planktonic assemblages. The authors showed a significant increase in net oxygen production, suggesting increased primary production rates, under warmer conditions. To the best of our knowledge, the only studies that investigated the combined effects of seawater warming and acidification have been conducted on benthic species. These stressors have been shown to be deleterious for Mediterranean calcareous primary producers, such as coralline algae (Martin and Gattuso, 2009) and scleractinian corals (Rodolfo-Metalpa et al., 2005), and some species have already exhibited signs of demise or reached extinction in some sites of the Eastern Mediterranean (M. Fine, pers. com.).

4.3.2. Expected alterations

Considering its oligotrophic nature, it is unlikely that seawater warming will have significant effects on photosynthetic rates in the Mediterranean Sea, and we expect that the strengthening of the water column stratification (see Chapter 1) will even exacerbate these nutrient-limiting conditions (see Chapter 5) and decrease primary production rates, as suggested by Behrenfeld et al. (2006) for the world ocean, although this will undoubtedly require more investigation. Nevertheless, it seems clear now that seawater warming will induce a shift in dominant species toward small-sized cells. This will have impacts on the capacity of the surface water ecosystems to provide organic matter for higher trophic levels and the deep-sea (see next section).

Ocean acidification is expected to occur in the same direction and to provoke a shift to smaller species and an associated decline of export capacities, although, to the best of our knowledge, no data are currently available for the Mediterranean Sea. As mentioned earlier, ocean acidification will potentially have impacts on calcifying organisms, such as coccolithophorids, which are important planktonic primary producers in the Mediterranean. However, it is too early to state whether these species will suffer from ocean acidification in the Mediterranean, as no data are currently available in this specific region. As nutrient concentrations play an important role in limiting primary production rates, and considering that the speciation of macro- and micro-nutrients is dependent on pH, ocean acidification and associated changes in nutrient availability are expected to alter biological productivity as well as ecosystem structure and functioning. As diazotrophy is an active process in the Mediterranean (Garcia et al., 2006), the potential increases in nitrogen fixation rates as a consequence of seawater warming and acidification have the potential to increase primary production rates in the N-limited regions of the Mediterranean Sea and to drive the latter into P-limitation. As nitrification

has been shown to provide up to 66% of phytoplankton nitrogen requirements in the northwestern Mediterranean (Bianchi et al., 1999), an alteration of this process by increased temperature and acidification may have important consequences on the nutrient supplies for primary producers. However, the clear lack of data with respect to this process does not allow the drawing of any conclusions on the evolution of this process in the Mediterranean Sea.

In the benthic compartment, significant effects of warming and acidification are also expected in the coming decades. As mentioned earlier, both perturbations are expected to be beneficial for macroalgae and seagrasses. On the one hand, in general, it seems that photosynthetic, non-calcifying species, such as green and brown algae and the plant *Posidonia oceanica*, which form one of the most important and rich ecosystems in the Mediterranean Sea, might directly take advantage of warmer and acidified conditions by increasing their photosynthetic rates. For instance, this species has recently been found to benefit from high CO_2 concentrations released from a natural volcanic CO_2 vent in Italy, at the expense of calcareous species (Hall-Spencer et al., 2008). On the other hand, it has been reported that high temperature episodes might constitute a source of stress for the plants and cause high mortality (Diaz-Almela et al., 2009), either directly (physiological disruption) or through external mechanisms, such as increasing anoxia in the sediment. As mentioned previously, Hall-Spencer et al. (2008; Fig. 7) reported a total absence of calcifying organisms at the proximity of a natural CO_2 vent (low pH) and suggested that future pH conditions in the Mediterranean will negatively affect calcareous primary producers and significantly affect community structure.

To conclude, both seawater warming and acidification are expected to significantly affect primary production rates in the Mediterranean as well as the structure of the planktonic community, with most likely a shift from heavy to small-sized cells. This shift will potentially affect the capacity of the Mediterranean surface waters to provide organic matter to higher trophic levels, directly affecting fisheries, and to the deep ocean, affecting the capacity

of surface waters to pump atmospheric CO_2. More data are needed to carefully assess these impacts, especially on the future role of N-fixing species in the planktonic community of this oligotrophic area of the world, under potentially modified N and P availability. In the benthic compartment, seawater warming and acidification will most likely benefit seagrasses and macroalgae, although they might be threatened by repeatedly hot summers, and will be detrimental for calcareous species. Nevertheless, as for planktonic primary producers, the available information is, at the moment, insufficient to carefully assess the impacts of these two perturbations on the distribution of benthic primary producers and the high biodiversity they shelter.

4.4. Impacts on remineralization and organic matter export

The organic matter produced in surface waters is either respired by autotrophic and heterotrophic organisms or exported by sedimentation to deeper layers. The capacity of the ocean to store anthropogenic CO_2 depends mainly on this process, which is known as the biological pump (Volk and Hoffert, 1985). Microbes utilize 10–50% of carbon fixed by photosynthesis (Azam et al., 1983) and therefore play an essential role in controlling the organic matter fluxes in the ocean and strongly affect global climate.

4.4.1. Current knowledge

The metabolism of micro-organisms is based on enzymatic reactions, which follow the Arrhenius law and are therefore influenced by temperature. However, due to the co-variation of biotic and abiotic forcing, it is difficult to extract the direct effect of temperature on heterotrophic bacterial activities of a natural bacterial consortium. For instance, variations can be attributed to changes in bacterial community structure and/or to organic matter supply. The latter is a more important factor in carbon-limited ecosystems, compared to temperature, which becomes primordial in eutrophic systems. In temperate waters, optimal growth rates can be observed in the case of no carbon limitations. Published work has shown that the Q10 of community respiration is close to the one of gross production in permanently cold waters (Robinson and Williams, 1993), whereas in temperate waters, the Q10 value for community respiration is significantly higher (Lefevre et al., 1994). According to this observation, in temperate waters, a 3 °C temperature increase will theoretically enhance production by 23%, while respiration will be increased by 51%, therefore increasing the net heterotrophy of the surface ocean. Recent work carried out in Baltic Sea mesocosms simulating the succession between phytoplanktonic bloom and post bloom showed that the transfer to the bacterial compartment increased during the bloom phase due to the increase in temperature, implying a tighter coupling between phytoplanktonic spring bloom and bacterial degradation, leading to less organic matter available for the post bloom stage (Hoppe et al., 2008). However, it must be stressed, as mentioned by the authors, that the increased ratio between bacterial degradation and phytoplanktonic production in warmer conditions was mainly due to a decrease of primary production, which was probably supported by changes in phytoplankton species composition (see above; Sommer and Lengfellner, 2008). Therefore, this does not imply a net increase in the amount of recycled products in surface layers. On top of this tighter coupling between production and degradation, the authors observed a decrease in bacterial growth efficiency (BGE), implying a faster mineralization of organic matter, with ultimate effects on the CO_2 exchange between the ocean and the atmosphere, decreasing the biological pump efficiency and acting as a positive feedback to global warming. Indeed, if warming positively affects the rates of bacterial production and respiration, but respiration rates increase more abruptly than production rates, BGE will decline with increasing temperatures, and a higher

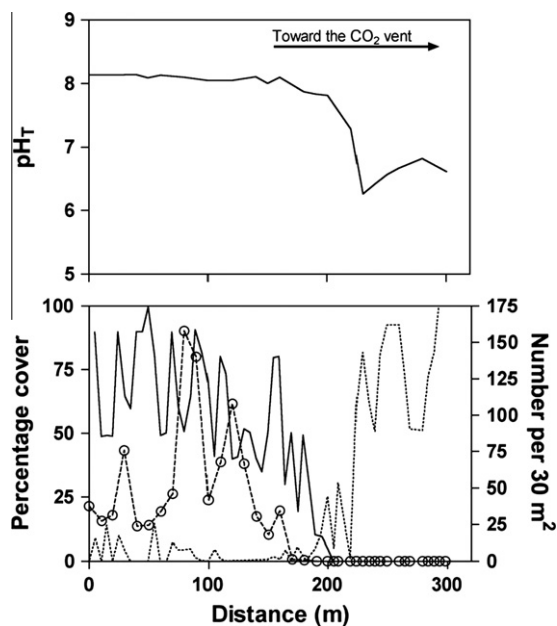**Fig. 7.** (Top) Variation of pH along a transect toward a CO_2 vent south of Castello d'Aragonese (Ischia, Italy). (Bottom) Along the same transect, the abundances of key species of this ecosystem. The percentage cover (left axis) of calcareous (solid line) and non-calcareous algae (dotted line) as well as the abundance (right axis) of sea urchins (dotted line, open circles) are shown. Data are from Hall-Spencer et al. (2008).

proportion of the carbon demand will be respired (Rivkin and Legendre, 2001), implying that more of the organic carbon consumed is remineralized to CO_2. As proposed by Laws et al. (2000), warming the surface waters of the ocean will decrease export rates in the more productive parts of the ocean and particularly in the temperature range 10–20 °C, although in relatively warm oligotrophic regions, export rates might actually increase, but under any conditions, the export ratios (ratio of export production to net primary production in surface waters) in such regions would be low, i.e., 0.10–0.15. It is interesting to note that the exact opposite situation (decreased mineralization rates) during interglacial-glacial transition periods (temperature decrease) has been proposed as a major process driving the decrease of atmospheric pCO_2 (Matsumoto et al., 2007).

Although it has been shown for terrestrial ecosystems that high pCO_2 levels lead to increased bacterial numbers and activities, related to increased photosynthetic exudates, very few data are available regarding this effect in aquatic environments (see the review of Liu et al., 2010). For instance, Grossart et al. (2006) reported increased bacterial abundances and activities (as measured by protein production) at higher pCO_2, which were related to increased dissolved organic carbon (DOC) production by phytoplanktonic cells readily degradable for bacteria. More recently, a second experiment in high CO_2 mesocosms revealed that changes in pCO_2 led to significant changes in the community structure of free-living but not attached bacteria, which were more tightly correlated to phytoplankton dynamics (Allgaier et al., 2008). This study also revealed a dependency of bacterial production on the C:N ratio of newly produced organic matter, which was modified at high CO_2 levels (see previous section). The results of Rose et al. (2009), from shipboard continuous culture experiments led during the North Atlantic bloom, suggested that both increasing pCO_2 and temperature will have effects on the microzooplankton community structure and metabolism, although the changes were mainly attributed to changes in the phytoplanktonic community (Feng et al., 2009) rather than to direct effects. However, recently, the study of Piontek et al. (2010) has revealed that ocean acidification has the potential to significantly alter the fate of produced organic matter. Indeed, their study showed that following a decrease in pH to ∼7.8, the degradation of polysaccharides by bacterial extracellular enzymes was significantly accelerated. As polysaccharides are a major component of marine organic matter, and especially of TEP, for which production is expected to increase at a lower pH, these increased bacterial activities have the potential to reduce carbon export and to enhance respiratory CO_2 production in the future ocean. Amongst the mechanisms controlling the vertical export of organic carbon, the formation of marine snow aggregates is one of the most important. TEP play a central role in aggregation and sedimentation processes by promoting aggregation and by regulating sinking characteristics of aggregates via alteration of their density. We already mentioned that ocean acidification is believed to enhance TEP production by phytoplanktonic species. However, it has recently been shown that the decrease in pH also leads to a diminution of the sticking properties of these TEP, therefore inhibiting the downward flux of organic matter and acting as a positive feedback to climate change (Mari, 2008). Similarly, in the previous section, we mentioned that coccolithophorids will most likely suffer from ocean acidification via an inhibition of their ability to produce coccoliths. As the calcium carbonate produced in the surface ocean, by not only these organisms but also by foraminifera and pteropods, is believed to play a very important role in favoring the sinking of organic matter to the deep ocean (ballast effect), a decrease in its production would lead to a decrease in the sinking rate of organic matter and therefore a decrease in the biological pump (positive feedback to the increase of atmospheric CO_2). However, because calcium carbonate production is a CO_2-producing

process, it must be stressed that a decrease of calcification rates in surface waters will first act as a negative feedback to the increase of atmospheric CO_2.

It has been recognized that heterotrophic bacteria can be strong competitors of phytoplankton for inorganic nutrients (Thingstad and Rassoulzadegan, 1995), and bacterial processes appear to be P-limited in the oligotrophic waters of the Mediterranean Sea. Highly significant positive relationships have been shown between primary and bacterial productions in both western and eastern basins, indicating that primary production is a source of DOC for bacterial production in both areas, although the nature of the relationships is significantly different between the two basins. Bacteria play a major role in organic carbon flow in both basins, but this role is greater in the East, where micro-heterotrophs totally dominate the food web. In the western basin, the relatively smaller importance of the microbial food web leads to an accumulation of DOC produced from photosynthesis during the summer. There is therefore a substantial West–East decrease in vertical export fluxes. For instance, carbon export from the euphotic layer to a 1000 m depth has been estimated to be about 10% in the Gulf of Lions and 2–3% in the Cretan Sea (Berline et al., in press). Surface water pCO_2 has been simulated to range between 350 and 500 µatm in the eastern basin and, therefore, generally oversaturated with respect to the atmosphere, while lower values were simulated in the western basin because of the inflow of low pCO_2 Atlantic waters and by a significantly higher export ratio than in the eastern basin. The biological pump seems to be an active process in the western basin, partly responsible for the uptake of 8.64 Gt C year^{-1} in this region. As detailed earlier, due to the role of the eastern basin as a source of CO_2 to the atmosphere, the whole Mediterranean acts as a weak CO_2 sink of 0.24 Gt C year^{-1} (D'Ortenzio et al., 2008).

4.4.2. Expected alterations

Modifications of the organic matter fate in the Mediterranean Sea through alterations of bacterial abundance and metabolism are expected in the coming decades due to both seawater warming and acidification. As for the global ocean, very few data are available to assess the sensitivity of microbes to these perturbations and the associated modifications of the Mediterranean carbon cycle. To the best of our knowledge, the only study that has focused on the effect of future seawater warming on microbes in the Mediterranean Sea is that of Vasquez-Dominguez et al. (2007). These authors showed, on the contrary to what Rivkin and Legendre (2001) suggested (see above), a concomitant increase of bacterial production and respiration over an annual cycle in a Mediterranean coastal site, considering a 3 °C increase in temperature. This study suggests no effect of the projected temperature increase in the next decades on BGE but implies that more carbon will be consumed and used by microbes, with most of this carbon ending-up as CO_2 and therefore acting as a positive feedback to the increase in atmospheric CO_2. This study was performed at a coastal site that is fueled by organic matter originating from land. As BGE is mainly determined by substrate quality (del Giorgio and Cole, 1998), more data are needed in oligotrophic open Mediterranean waters to carefully assess the future of the microbial loop in these regions. It must be stressed that La Ferla et al. (2005) already showed that BGE in the central Mediterranean is not correlated to primary production and temperature, and therefore, they highlighted the considerable complexity of the dynamics of bacterial metabolism in this region.

As for temperature, nothing is known about the effect of increasing CO_2 on bacterial abundances and metabolism. As phytoplankton and bacteria seem to compete for phosphorus in the Mediterranean Sea, and as the theoretical speciation of phosphorus nutrients show defined shifts with changes in pH (Zeebe and

Wolf-Gladrow, 2001), there is a possibility that the future decrease in pH will further limit bacterial production in this oligotrophic region of the world. Modifications of TEP productions and properties (stickiness for instance) will most likely modify the sinking rates of particles and the biological pump strength in the Mediterranean, especially in the western basin where the TEP pool has been shown to be high and represents an important component of the carbon cycle (Beauvais et al., 2003). Finally, as it has been mentioned previously, calcareous planktonic species, such as coccolithophorids, pteropods and foraminifera, are present in the Mediterranean and are responsible for a basin $CaCO_3$ sedimentation of about 11.4 Gt C year^{-1} (Schneider et al., 2007). A decrease of calcification rates with decreasing pH will undoubtedly cause a decrease of the previously mentioned ballast effect and a decrease of organic matter sinking velocities. No data are, so far, available to confirm or reject these expectations in the Mediterranean Sea.

To conclude, both mineralization and export rates from the euphotic layer will, most likely, be altered in the coming decades due to seawater warming and acidification. Very little is known about these potential modifications in the Mediterranean Sea and their associated impact on the role of the Mediterranean Sea in the global carbon cycle. Both laboratory and *in situ* community perturbation experiments are necessary to assess both indirect (potential increase of dissolved phytoplanktonic production, see above) and direct effects of the future warming and acidification of surface Mediterranean waters.

4.5. Impacts on higher trophic levels

As it has been detailed in the previous section, primary production rates and the composition of the photosynthetic community are supposed to be modified under warmer and more acidified conditions, with indirect effects on higher trophic levels. In the present section, we will deal with the direct effects of these two perturbations on the metabolism of higher trophic levels.

4.5.1. Current knowledge

For the life of marine invertebrates, temperature is a major environmental entity, affecting both the physical–chemical characteristics of their habitat and their biological processes. Temperature determines the rate of biochemical reactions and thus of metabolism and activity, particularly in poikilotherms. Metabolism comprises all processes that use and convert material and energy for maintenance, growth, reproduction and repair, while activity is the result of the integrated metabolism and involves respiration, locomotion, fighting, courting and mating. Because increasing temperature enhances the metabolic rates of organisms, the growth rate of species is faster at higher temperatures but drops considerably above an optimal temperature, until the critical maximal temperature is reached. For instance, according to Huntley and Lopez (1992), temperature explains more than 90% of variance in the growth rate of marine copepods, independent of species and body weight, via its effect on metabolic activity. It has often been observed that body size increases with increasing latitude, as slower growth rates result in larger individuals with a prolonged growing period, late attainment of maturity and long life span. Effects of temperature on upper trophic levels may be strongly mediated by zooplankton size, which is a key determinant of food quality for planktivorous fish. Thermal requirements for reproduction often are restricted to a quite narrow temperature window, separating the vegetative from the reproductive temperature range, and may additionally differ between gonad growth, gamete maturation, spawning and embryonic development (reviewed in Kinne, 1970). In many species, sex ratio is also known to be temperature-dependent. The biological effects of a given temperature pattern may differentiate populations of the same species, different life stages or sexes and may reflect the temperature history of the individual. Animals may react directly to a change in temperature or show adaptation, i.e., genetic or non-genetic adjustments to thermal alterations that increase their survival, reproduction and competition capacity. Thermal tolerance is species-specific but can even gradually change during ontogeny (Sulkin and McKeen, 1994). Phenology, or the timing of life cycle events in species, is directly linked to climatic cues, such as temperature, precipitation and sunshine. Species-specific responses to temperature change may affect the phenological coupling of trophic relationships within a food web. As sea temperature is an important trigger of the outburst of the resting phase and therefore affects the development of planktonic population, the timing of peak abundance of zooplankton will be sensitive to climate warming, and this can have effects that resonate to higher trophic levels (Edwards and Richardson, 2004).

"Our current knowledge of CO_2 effects ranges from effects of hypercapnia on acid-base regulation, calcification and growth, to influences on respiration, energy turnover and mode of metabolism" (Pörtner et al., 2004). As mentioned above, ocean acidification will potentially modify the C:N:P ratio of the newly formed organic matter, and this ratio determines the food quality for herbivores (Anderson and Hessen, 1995); therefore, this would alter the pathway of organic matter through the food chain and have consequences on the dynamics of secondary producers. Besides this indirect effect, several studies focused on the direct effect of increasing pCO_2 on higher marine organisms and significant impacts of hypercapnia have been evidenced for both planktonic and benthic organisms (Ishimatsu et al., 2004). However, several of these studies considered pH levels far below the ones predicted for the next 300 years (-0.7). While being relevant for estimating the environmental effects of CO_2 sequestration in the deep ocean (as a mitigation procedure), they do not suggest any significant effect of short-term exposure to CO_2 levels expected for the next centuries in the upper ocean, and more data are still needed to carefully assess the effect of the projected pH decrease on marine higher organisms. An important concept relevant to the understanding of fish physiology is that of thermal windows (Pörtner et al., 2005), where species have developed an ecological and physiological niche to a particular environment. Stenotherms are animals that prefer a narrow temperature range and have increased energy efficiency over a narrow range that supports growth performance. However, within a thermal window, it is oxygen consumption that limits growth. The additional increase in CO_2 reduces available oxygen and adds an additional stress. To date, very few studies have focused on these combined effects, which will deserve extensive examination in the coming years. Among heterotrophic organisms, species that secrete important calcareous structures, such as, for instance, foraminifera, pteropods, bivalves and echinoderms, are likely to be severely impacted by ocean acidification (see review from Doney et al., 2009). Indeed, several studies report significant impacts on most of these organisms (Ries et al., 2009 and references therein). Very few laboratory studies have focused on this issue for Mediterranean species. Among these, Michaelidis et al. (2005) studied the effect of long-term (100 days) moderate hypercapnia on *Mytilus galloprovincialis* (the Mediterranean mussel), the most important cultivated species in the Mediterranean. They showed a significant reduction in shell growth accompanied by a significant reduction in metabolic rates at low pH. Recently, Hall-Spencer et al. (2008; Fig. 7) studied the effects of acidification from a natural volcanic CO_2 vent on biological entities of a coastal ecosystem located off Ischia Island (Italy). As mentioned earlier, they found that calcareous organisms (calcareous algae, sea urchins, mollusks, and epiphytes on seagrass leaves) progressively disappear with decreasing pH. Larval stages of benthic organisms are believed to be more sensitive to environmental stresses than adult

stages (Raven et al., 2005). As for adult stages, significant impacts of decreasing pH have been highlighted for several species (e.g., mollusks and echinoderms; see Kurihara, 2008 for a comprehensive review). Finally, sediments play a key role in major nutrient cycling, especially in coastal and shelf sea ecosystems. Within the sediments, microbial activities may be impacted by global change (see previous section), but multicellular organisms living on top or within the sediment are also important for sediment reworking and nutrient fluxes. Particularly important are the organisms that build and irrigate permanent burrows. For instance, by studying a burrowing polychaete and associated nutrient fluxes under high pCO$_2$ conditions, Widdicombe and Needham (2007) suggested that ocean acidification may have a significant impact on nutrient fluxes as a result of changes in the structure and function of bioturbating communities. Very recently, several meta-data analyses on the effect of ocean acidification on marine organisms and biodiversity have been conducted (Dupont et al., 2010; Hendriks et al., 2010; Kroeker et al., 2010; Nisumaa et al., 2010). The very different conclusions that have been drawn from these different analyses show the extreme complexity of interpreting laboratory data. Furthermore, there is still a huge gap to fill before making a realistic extrapolation of *in vitro* data to *in situ* conditions considering the numerous interactions between species and the potential capacity of the organisms to acclimate or adapt to their new acidified environment.

For a surface area representing 0.82% of the world ocean, the Mediterranean Sea shelters between 4% and 18% of the world's marine species (Bianchi and Morri, 2000). Despite this high biodiversity index, the Mediterranean Sea may be one of the most degraded marine ecosystems worldwide, as it has been inhabited and influenced by human civilization for millennia (Coll et al., 2008). Ecological changes that have occurred include proliferation of species and invasions, changes in species distribution, harmful algal blooms and eutrophication. Common indicators of ecological degradation in marine ecosystems are the depletion of biomass at high trophic levels, the simplification of food webs, and shifts in biomass and productivity towards lower trophic levels. Human induced pressures are numerous and include over-fishing, habitats alteration and, of course, climate change.

4.5.2. Expected alterations

Both warming and acidification are expected to significantly alter higher trophic levels in the Mediterranean. The warming observed in recent decades in this region has already impacted species distribution. It is beyond the scope of this chapter to detail the numerous examples of species geographical shifts that occurred in the Mediterranean over this period, and one is invited to read CIESM (2008a), Lejeusne et al. (2010) as well as Chapter 7 of the present paper, for comprehensive reviews on this subject. Briefly, direct consequences of warming in the Mediterranean Sea may be: (1) a further meridionalization (increase in abundance of eurythermal species and decrease of cold stenothermal species), (2) a northward shift of species and (3) mass mortalities during

unusually hot summers. In addition to direct temperature effects, modification of higher trophic levels' community composition can be severely altered via impacts on primary producers. For instance, a shift in the dominant phytoplanktonic species can induce phenological changes in copepods' abundance, which will ultimately affect fish recruitment and fisheries; these indirect effects are presently very poorly documented. As mentioned earlier, acidification of Mediterranean waters will have severe effects on biological calcification rates. Planktonic mollusks producing a calcareous shell, such as pteropods and some heteropods, are abundant in Mediterranean waters and are significantly and negatively affected by ocean acidification at both larval and adult stage levels (Comeau et al., 2010 and pers. comm.). Calcareous ecosystems, such as coralligenous and vermetid (gastropods) reefs, cladocora banks and deep-water corals, are theoretically very sensitive to both warming and acidification. As they usually shelter very important species richness, their disappearance would undoubtedly lead to a decline of the Mediterranean biodiversity. Unfortunately, very few data are available thus far to confirm or reject these predictions. However, as it has been discussed, naturally acidified environments that can be found in the Mediterranean Sea have the potential to provide interesting insights on the future state and dynamics of Mediterranean ecosystems under these anthropogenic pressures. These natural laboratories are essential, as they provide interesting information on the long-term effects of ocean acidification and on the potential cascading effects from lower to higher trophic levels, and will deserve strong research efforts in the coming years.

To conclude, human-driven seawater warming and acidification in the Mediterranean have already and will undoubtedly alter Mediterranean ecosystems in the coming decades. While the direct effects of temperature (acute and chronic) have received some attention in recent years, with many documented on-going impacts such as species extinctions, migrations and replacements, virtually nothing is known with respect to indirect effects, e.g., modifications of lower trophic levels' composition and dynamics. These potentially cascading effects will definitely need to be investigated in the near future. Concerning acidification, natural Mediterranean CO$_2$ vents provide very interesting laboratories to study the effects of this perturbation on an ecosystem from end-to-end.

5. Influence of chemical contaminants

The Mediterranean is a semi-enclosed sea surrounded by continents with intense human activities, which constitute sources of chemical contamination and may cause degradation and serious damage for the coastal and marine zones (EEA, 1999).

In the future, coastal areas are expected to face increasing anthropogenic pressure, especially from emerging chemical contaminants (e.g., hormones, drugs, pesticides, and plastic particles), agriculture, over-fishing, aquaculture, urbanization, tourism, maritime transport, with their consequences on ecosystems (e.g.,

Table 2
POP inputs to the Mediterranean Sea (Dachs et al., 1996; Mandalakis et al., 2005; Tsapakis et al., 2006). Sinking marine fluxes are derived from sediment traps deployed between 186 and 2837 m. Negative flux denote movement from the seawater to the air.

Compounds	Wet deposition (μg m^{-2} year^{-1})	Dry deposition (μg m^{-2} year^{-1})	Air–sea exchange (μg m^{-2} year^{-1})	Sinking marine fluxes (μg m^{-2} year^{-1})	Reference
Western Mediterranean					
ΣPCB	8.3	14.7	–	4.4–6.9	Abad et al. (2007)
ΣPAH	11–26	15–35	–	80.3–87.6	Abad et al. (2007)
Eastern Mediterranean					
ΣPCB	0.79 ± 0.18	0.18 ± 0.12	−1.91 ± 1.03	0.1–0.4	Abad et al. (2007)
ΣPAH	165.7	58.0	706.4	22.7–28.2	Achterberg and van Den Berg (1997)

dystrophies, eutrophication, and toxic algae). However, because of the particular importance of the atmospheric inputs and the air–water exchanges in the Mediterranean, the open waters are also greatly affected by chemical contamination, especially through the bioaccumulation process and the trophic transfer. On the one hand, recycling and thermo and photochemical transformations at the air–water interface may alter the net input of contaminants to the water column, depending on the climatic changes (e.g., wet vs. dry deposition, irradiation, and temperature). On the other hand, the oligotrophic nature of the open Mediterranean (and its possible changes) makes it more sensitive to the bioaccumulation processes because the "biodilution" of contaminants by organic carbon is reduced. In addition, the rapid turnover at the base of the food webs may also be a key factor for contaminant biomagnification.

Like many seas in the world, the Mediterranean is affected by inputs of various chemical contaminants (CC), including trace elements, artificial radionuclides and organic substances with POPs (persistent organic pollutants), biocides, hormones, and drugs. Our knowledge of concentration levels, fluxes, behavior within the water and sediment columns or toxicological impacts for the ecosystem is very different, depending on the group of contaminants. Some, such as ^{137}Cs or Hg, have been studied in different research projects and locations, but for most of them there are relatively few studies, from which it is difficult to infer the extent and consequences of the contamination. This section presents the state-of-the-art and the expected alterations in the future of examples taken within three major groups of chemical contaminants: (i) stable trace elements, (ii) artificial radionuclides and (iii) organic substances.

5.1. Trace elements and their organic compounds

5.1.1. Trace element inputs in the Mediterranean Sea

Owing to its reduced dimensions as well as numerous and intense land-based emission sources along its densely populated shores, the biogeochemical cycling of trace elements (TEs) in the Mediterranean Sea is largely governed by atmospheric inputs (Migon et al., 2002), which are characterized by a European background signature (natural and anthropogenic) upon which Saharan dusts are superimposed (e.g., Guerzoni et al., 1999). Mediterranean climate and meteorology strongly determine the partition (dissolved or particulate) under which these atmospheric TEs enter the sea surface (Nicolas et al., 1995) and thus their involvement in marine biogeochemical cycles. For the particle inputs, the lability of TEs is related to the atmospheric solubilization processes that occur during aerosol transport (mainly driven by pH variations) and especially at the origin of the incoming air mass, which governs the nature of aerosol particles. Crustal metals are mainly deposited in particulate form (e.g., >90% of the total deposition of Al and Fe; Guerzoni et al., 1999), while anthropogenic metals are much more soluble. However, even for metals whose cycling is essentially controlled by wet events (e.g., Cd, Zn), dry deposition prevails because of the dominance of this deposition mode, particularly during the long Mediterranean dry season (~3 months in winter and three months in summer; Nicolas et al., 1995).

Atmospheric fluxes, estimated at the Cap Ferrat sampling station (Ligurian Sea shore, northwestern basin) since 1986 (Migon and Caccia, 1990), have revealed an increase in the anthropogenic influence for Zn and Cu, while the opposite is true for Pb, due to the progressive banning of leaded gasoline. In spite of a decrease in Cd concentrations in Cap Ferrat aerosols between 1998 and 2008 (Heimbürger et al., 2010a), no clear decreasing trend over the past 20 years was observed in Cd deposition (Guieu et al., 2010). According to the same authors, Zn deposition is slightly higher in the western Mediterranean basin than in the eastern basin,

whereas Pb and Cd fluxes are similar in both basins. In contrast to these metals, the case of mercury is very particular and requires more research to clarify mass balances and the anthropogenic contribution. Indeed, even if the atmospheric Hg deposition onto the Mediterranean Sea is substantial, its evasion from the surface is at least three times higher and may constitute a source of mercury for the surrounding continent (Cossa and Coquery, 2005; Andersson et al., 2007).

In spite of the epicontinental characteristic of the Mediterranean, the main routes for dissolved metal inputs to the open Mediterranean is *via* the atmosphere and the exchanges through the straits. Particularly, anthropogenic metals input at Gibraltar has been documented (e.g., Elbaz-Poulichet et al., 2001). Obviously, the influence of rivers is greater in coastal zone areas and constitutes the major source for particulate metals on some continental shelves. For the Gulf of Lions shelf, which receives the Rhone river inputs, Elbaz-Poulichet (2005) estimated that all atmospheric inputs dominate those from rivers, except for Cu and Ni, but these atmospheric fluxes are, however, negligible when particulate fraction alone is concerned (Radakovich et al., 2008). Throughout the entire western Mediterranean basin, Martin et al. (1989) calculated that particulate atmospheric inputs of Pb, Cd and Cu were two to three times higher than those from rivers, and Guieu et al. (1997) and Guerzoni et al. (1999) obtained similar factors for Cd, Zn and Pb for the northwestern basin. In the case of Hg for the entire Mediterranean, Rajar et al. (2007) estimated the annual river inputs to be 65 kmol, while atmospheric deposition was estimated to be twice this amount. Riverine particulate inputs have to be more precisely estimated for all the TE, especially regarding flood events, which are characteristic of the Mediterranean climate and can transport 80–90% of the yearly average flux (Radakovich et al., 2008). Some atmospheric inputs will also require a better estimation, especially Zn, for which the high variability observed by Guieu et al. (1997) might be due to an underestimation of the aerosol concentration (possibly due to the existence of a significant gaseous contribution) or an overestimation of the flux. Other and poorly quantified inputs of TE in the Mediterranean Sea include sub-marine volcanoes, cold seepage, sub-marine freshwater inputs in the coastal zone, as well as inputs from large coastal cities, industries and maritime traffic, limited to the antifouling compounds, which remain a real contamination problem for organotin, even offshore (Michel and Averty, 1999).

5.1.2. Dissolved trace elements distributions in Mediterranean waters

The dissolved TE distributions in the Mediterranean Sea are atypical compared to other areas of the world ocean, as the distributions of nutrient-like metals Cd, Cu and Ni (as well as Cr) are dominated by lateral advection and vertical mixing rather than by biogeochemical cycling (Achterberg and van Den Berg, 1997). Early measurements of TEs, for example by Copin-Montegut et al. (1986), indicated that Cd had a fairly homogeneous vertical distribution, but a sub-surface cadmium-rich layer was observed in the Alboran Sea, related to the presence of Winter Intermediate Water (formed in the northwestern coastal sector of the western Mediterranean Sea), with a possible anthropogenic component (Riso et al., 2004). Mn, Co and Pb distributions are closer to those found in the world ocean, with a more or less continuous decrease with depth (Copin-Montegut et al., 1986). For Pb, the effects of the ban of Pb additives to gasoline were evidenced by the decreasing concentrations from 1983 to 1995 over the whole water column of the Ligurian Sea (Migon and Nicolas, 1998). Finally, several measurement campaigns were conducted for mercury (see Cossa and Coquery, 2005 for review; Cossa et al., 2009), from which it was concluded that air–water exchanges and organic matter regeneration processes are the main processes for establishing the vertical distributions and the methylation of this element
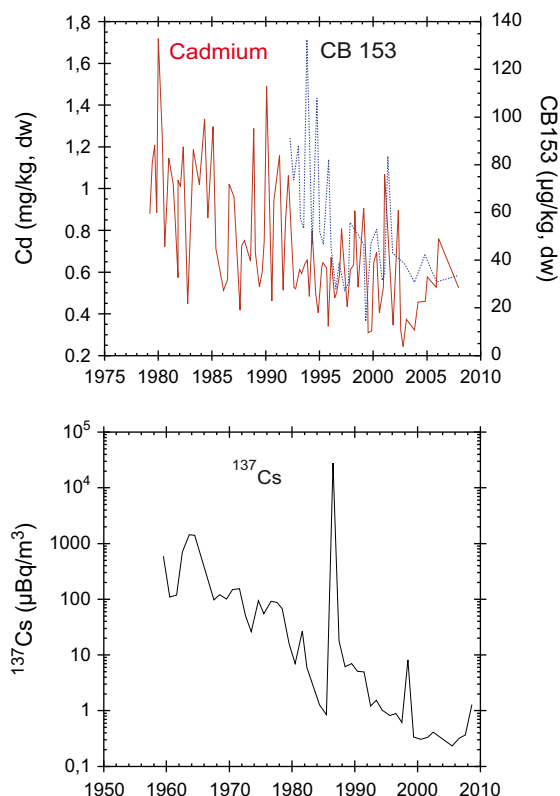
Fig. 8. Time-series of Cd (mg kg^{-1}, dw) and CB153 congener concentrations (μg kg^{-1}, dw) in the soft tissue of the blue mussel (*Mytilus galloprovincialis*). Samples were collected in the Thau lagoon (northwestern Mediterranean, RNO) and near the mouth of the Rhone River for PCB. Temporal evolution of ^{137}Cs (average of the French territory stations, IRSN data) in aerosols sampled in France from 1959 to 2004. Peaks in 1962 are related to atmospheric tests; in 1986 to the Chernobyl accident; and in 1998 to the Algeciras incident.

(methylmercury being the bioamplified and toxic form of this metal). Cossa and Coquery (2005) suggested that the "Med-Hg anomaly" (high mercury concentrations in the muscle of open sea fish), which appeared 30 years ago (Aston and Fowler, 1985), are more likely from biological than geochemical origins.

5.1.3. Trace element distributions in Mediterranean sediments and organisms

Trace element concentrations and distributions in the sediments of the Mediterranean Sea have been reported in many papers on the contamination of coastal areas (e.g., lagoons and harbors) and paleoceanographic work. Such data sets are very difficult to discuss on a large-scale for two reasons: most of these studies refer to local anthropogenic sources, and the parameters necessary to compare concentrations between various sites (e.g., grain size or organic matter content) are generally not reported. More constructive information on the chemical contamination of the near-shore coastal areas can be obtained from monitoring programs based on international expertise that use quantitative biological indicators and/or surface or sediment cores (e.g., GESAMP, ICES, ICEMS, and MEDPOL). Such biological indicator scan be compared and have the capacity to integrate the temporal changes of contaminants, concentrations or fluxes over various time-scales. The MEDPOL and several French programs (e.g., RNO/ROCCH and RINBIO) have used this approach, and a 25-year-long time-series (Fig. 8) examining wild mussels on the French Mediterranean coast is now available for Cd, Cu, Pb, Hg, Zn, Cr, Ag, V, PCBs, pesticides and PAHs (http://www.ifremer.fr/envlit/region/reg10paca/index.htm#). In addition, transplanted mussels have been used for approximately

10 years to characterize water contamination, even in locations where no native wild bivalves are available (http://www.ifremer.fr/envlit/region/reg10paca/rlm.htm#RINBIO). This project succeeded in assessing the natural background contamination of the NW Mediterranean (Andral et al., 2004).

Recently, the MYTILOS project (http://mytilos.tvt.fr/) has sampled across the whole western Mediterranean Sea (Fig. 9). The results have identified hot spots at the mouths of rivers (e.g., the Rhone and Ebro) and near urban areas (e.g., Barcelona, Marseille, Naples and Algiers), as expected. Geochemical background levels for trace elements (TEs) revealed some differences between basins, and this constitutes the most exhaustive dataset for TEs in Mediterranean organisms.

Tributyltin compounds (TBT), now prohibited, have been widely used as antifouling agents in ship paint, and their deleterious effects on shellfish reproduction and on the sex ratio of several marine organisms have been extensively reported (e.g., Chiavarini et al., 2003). This has resulted in TBT being prohibited from all ships entering the ports of the European Union and the banning of all organotin compounds in antifouling preparations.

Some TEs, which are called "bioactive," are involved in the Redfield model of organic matter synthesis and deep remineralization. During photosynthesis, phytoplanktonic organisms assimilate nutrients and TEs in proportions following a Redfield ratio of: C:N:P:Fe:Zn:Cd, Cu, Mn, Ni = 106:16:1:0.005:0.002:0.0004 (Bruland et al., 1991). This ratio is an approximation, and the relationships between TEs and macronutrients could vary regionally, but such a value has never been evaluated for the Mediterranean Sea.

Bioactive TEs are likely to limit the growth of phytoplankton and heterotrophs at low concentrations in seawater, but their potential toxicity may also inhibit biological development. Potentially toxic metals, even when they have a biological role, are likely to produce environmental harm through their assimilation by planktonic species at high concentrations. Experimental studies (e.g., Wang and Fisher, 1998) have been carried out concerning the transfer of TEs up the food chain and their accumulation in marine organisms. In the case of the Mediterranean Sea, field studies have shown significant accumulation in various species, from numerous planktonic and nektonic organisms (Fowler, 1977, 1986; Roméo et al., 1992) up to higher trophic level species at the end of the marine food chain, such as dolphins and whales (Augier et al., 1993; Frodello and Marchand, 2001). The earliest baseline data for zooplankton that were obtained from several areas of the open and coastal Mediterranean Sea during the 1970s demonstrated that TE concentrations were highly species dependent (Fowler, 1986). For any given trace element, the concentrations in mixed microplankton samples varied little between regions. Furthermore, the comparison of the levels in microplankton as well as certain individual planktonic species with the data reported for similar species from other oceanic areas suggested that the TE concentrations in open ocean plankton and nekton were no higher in the Mediterranean than elsewhere at that time. However, as similar basin-wide data from earlier years did not exist for the same pelagic species, it was not possible in that study to assess temporal trends for TE concentrations in these Mediterranean organisms. Given that reliable field data on TE concentrations in Mediterranean planktonic species remain sparse, new surveys will be needed to make any sort of state-of-the-art comparison of the levels in the Mediterranean with those in similar species from other regions as well as establishing temporal trends.

In contrast to plankton and other lower trophic level pelagic organisms, more studies are being carried out on the contamination of species under threat, such as cetaceans from the Red List of the International Union for Conservation of Nature (http://www.iucn.org/). The concentrations of TEs found in whale
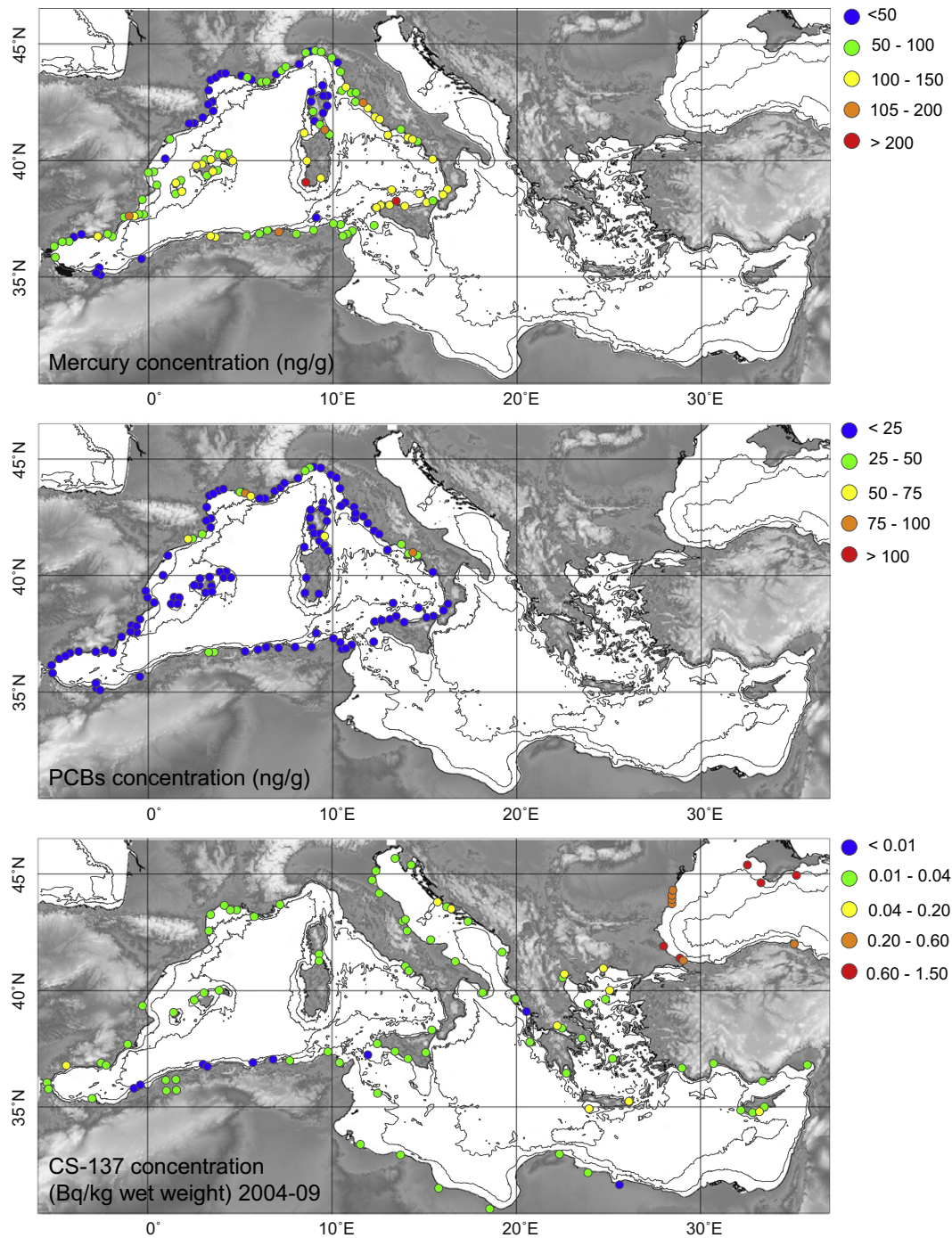
Fig. 9. Maps of the concentrations of mercury (in µg g^{-1} dry weight) and PCBs (sum of 7 PCBs in ng g^{-1} dry weight), and ^{137}Cs (Bq kg^{-1} wet weight) in mussel flesh along the western Mediterranean coasts. (^{137}Cs distribution is updated from Thébault et al., 2008).

stomachs suggest that their food source is responsible for significant metal contamination in whales (Frodello and Marchand, 2001). Mercury (Hg) concentrations in certain Mediterranean fish are twice those found for the same species living in the Atlantic Ocean, and most of the mercury content in the fish muscle is present as methylated species. However, the exact reasons for the higher total Hg levels observed in these Mediterranean fish species remain unclear (Aston and Fowler, 1985). Recent results for fish (Harmelin-Vivien et al., 2009) have confirmed these findings, and the occurrence of higher metal bioaccumulation in planktonic organisms in oligotrophic environments has been suggested. This suggestion that the key cause for the "Med-Hg anomaly" probably

originates from the higher bioaccumulation of methyl mercury (MeHg) at the base of the food chain, especially in phyto and bacterioplankton (Harmelin-Vivien et al., 2009), needs to be rigorously examined, particularly in view of earlier data which indicate that Hg levels in small pelagic organisms from the Mediterranean are no higher than those reported for other areas of the world ocean (Aston and Fowler, 1985; Fowler, 1986). A high Hg methylation rate in the Mediterranean water column has already been suggested (Cossa et al., 1997). Recent results by Heimbürger et al. (2010b) show that the mercury methylation within the water column of Ligurian Sea would be favored by micro-organisms associated with the degradation of pico- and nano-plankton (Fig. 10).
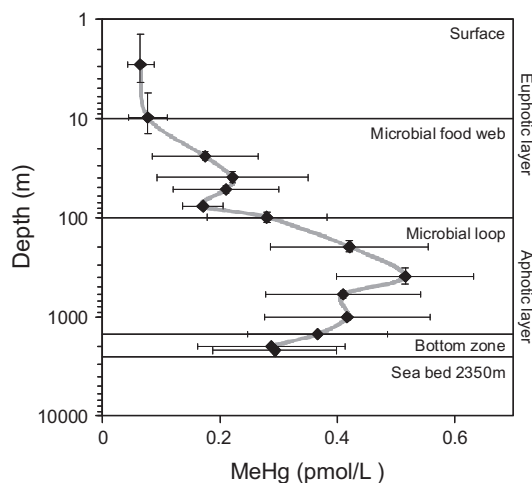
Fig. 10. Methylmercury (MeHg) abundance in the water column of the Ligurian Sea (from Heimbürger et al., 2010b).

5.1.4. Expected alterations

Various scenarios may be developed concerning changes in TE fluxes in Mediterranean environments. First, in addition to the variations in emissions due to the evolution of industrial processes and the effects of regulations, climate change should introduce modifications in the input-output budgets for elements *via* water budget changes. River as well as air-borne materials could be subject to more extreme flushing events.

Second, any changes in water circulation and stratification could induce changes in the bioavailability of TEs for organisms. Circulation modifications, especially the expected decrease of vertical mixing, will affect the dynamics of TEs and their residence times in the various basins. Changes in summer oxygen concentrations on the shelves may become more numerous, with consequences for the mobilization-remobilization of deposited metals and, in the case of mercury, possible changes in its methylation rate. An increase in stratification will permit contaminants to remain in the euphotic zone, increasing their availability for adsorption and uptake by phytoplankton and consequently their transfer within food webs. On the other hand, while oligotrophy favors higher metal bioaccumulation at the base of the trophic web, the possible increase in primary production may constitute a dilution of the elements within the biota. In addition, possible changes in the structure of food webs will have consequences on bioaccumulation and bioamplification processes, especially in the case of Hg, but also for other of TEs and chemical contaminants in general. This issue should be a priority research subject in the coming years.

Third, air and water temperature changes will modify the rates of thermochemical reactions, and changes in UV should alter the rates of photochemical reactions (e.g., iron, mercury and chromium reductions). Consequently, the recycling at the air–sea interface and the net deposition flux to the sea could change. Finally, if the numerous microbiological mechanisms that govern biogeochemical cycles are affected (see other chapters), the bacterial activity involved in the cycle and speciation of certain metals (e.g., Hg, Cd, and Zn) will also be subject to change (e.g., methylation/demethylation for Hg).

Fourth, new anthropogenic sources of TEs could affect the Mediterranean ecosystem due to new industrial processes or new uses. Seawater desalination plants, for example, will surely increase along the Mediterranean coastline and could cause inputs of metals such as Cu or Ni due to corrosion. Because of their wide range of applications, organotin compounds like TBT and TPT may now con-

stitute a(n) (re)emerging threat for marine ecosystems. For example, Borghi and Porte (2002) have suggested that the presence of TPT in deep-sea fishes from the northwestern Mediterranean is likely due to its use as a fungicide in agriculture or as an algaecide in rice fields. Finally, the expected increases in the sizes of large coastal cities could have local impacts on direct discharges from sewage treatment plants or surface runoff from urbanized soils. Such potential changes in trace element types, concentrations and distributions could be identified by undertaking basin-wide bio-indicator surveys of pelagic and benthic species and comparing the results with the baseline data produced from earlier basin-wide studies.

5.2. Artificial radionuclides inputs to the Mediterranean

A variety of practices and activities introduce radioactivity into the marine environment: military activities, nuclear fuel cycle operations and the use of radioisotopes by research centers, hospitals and industry. The main sources of man-made radionuclides into the Mediterranean Sea are the atmospheric fallout arising from both past above ground nuclear bomb testing and the Chernobyl accident, the wash-out of the river catchment basins contaminated by this fallout and routine discharges from the nuclear industry.

5.2.1. Atmospheric inputs

Various radionuclides are associated with the testing of nuclear weapons, and the resulting deposition from the atmosphere has caused significant temporal variation. Global fallout began in the early 1950s in the northern hemisphere, with intensive yield from programs during 1954–1958 and 1961–1963. In 1963, a partial ban of this practice was agreed upon, and atmospheric testing ceased completely after 1980. Atmospheric fallout is still a significant pathway for inputs onto land and into the ocean, but fission products in the stratosphere are constantly being reduced by radioactive decay. Thus, the present inputs of concern are intermediate (^{3}H, ^{90}Sr, and ^{137}Cs) and long-lived radionuclides (mainly plutonium isotopes). The Mediterranean Sea received substantial amounts of fallout from the Chernobyl accident (April 1986), but making a precise estimate of the total input is difficult because the deposition pattern was patchy and depended on the plume trajectories. The radioactive contamination resulting from this accident was dominated by cesium isotopes and did not contribute significantly to plutonium inputs.

Atmospheric fallout is controlled mainly by wet deposition, which removes more than 90% of radionuclides from the atmosphere. Lee et al. (2003), for example, have shown that the deposition of anthropogenic radionuclides over the northwest Mediterranean basin has occurred mainly in the spring and autumn, seasons of heavy rainfall, but these authors have also estimated that a significant fraction of annual atmospheric input has come with Saharan dust, up to 34% for ^{239,240}Pu and 29–37% for ^{137}Cs.

Fig. 8 shows the progressive decrease of ^{137}Cs in aerosols from 1959 to 2004. The present mean activity levels of ^{137}Cs measured at Toulon (French Mediterranean coast) are currently very low: 5×10^{-4} mBq m^{-3} in comparison with 4.5 and 0.8 mBq m^{-3} for natural ^{7}Be and ^{210}Pb. However, the mean annual airborne ^{137}Cs level at this station has not diminished since 2000. This indicates that the atmosphere is mainly fed by soil resuspension mechanisms such as wind erosion or wildfires (Johansen et al., 2003). This also explains the influence of Saharan dust events.

5.2.2. Land-based sources

Nuclear sites surrounding the Mediterranean Sea are all located in the northern countries and mainly in France, Spain and Italy. The

Rhone River (France) in particular has been a major source of man-made radionuclides since 20 reactors were established on its banks between 1956 and 1986. However, the majority of inputs came from the releases of the only spent fuel reprocessing unit on the Mediterranean Sea (Marcoule), which was created in the 1950s and shut down in 1997. In addition, each river represents a point source because of the wash-out of river catchment basins contaminated by previous atmospheric fallout.

5.2.3. Spatial and temporal distribution of ^{137}Cs and $^{239+240}$Pu in the Mediterranean Sea

The isotope ^{137}Cs can be considered as a conservative parameter in marine waters because its distribution is mainly controlled by physical processes such as water mass advection and convection. In contrast, the distribution of plutonium isotopes is also governed by its chemical speciation and its strong association with particles, which causes it to be more effectively removed from the water column. Both nuclides have decreased over time in Mediterranean surface waters (Papucci et al., 1996; León Vintró et al., 1999; Fowler et al., 2000). In the case of ^{137}Cs, it tends to increase with time in deep waters due to its conservative behavior. Papucci et al. (1996) thus observed an increase from an average of 1 mBq l^{-1} below a depth of 1000 m from 1970–1982 to a mean value of 2 mBq l^{-1} in 1986–1992 in the western basin. For $^{239+240}$Pu, Fowler et al. (2000) reported a 62% decrease in concentrations in surface waters of the northwestern Mediterranean Sea between 1990 and 1999. Residence time estimates for plutonium in the western Mediterranean Sea range from 2.5 year in the Lacaze-Duthiers canyon in the Gulf of Lions to 15–30 year in the open water (Fowler et al., 1990, 2000; Papucci et al., 1996). In the case of the more particle-reactive transuranic nuclide, ^{241}Am, it has a much lower residence time (5–10 year) in open Mediterranean surface waters, which is likely due to its greater binding affinity than plutonium to aluminosilicate particles that frequently enter these waters via Saharan dust events (Fowler et al., 2000).

Concentrations of ^{37}Cs and $^{239+240}$Pu have been measured in the sediments of various parts of the Mediterranean Sea, including deep basins, and they have been found in the uppermost centimeters of the sediment (e.g., Garcia-Orellana et al., 2009). Their concentrations and inventories in coastal environments are generally higher because, in specific places, the contribution of land-based sources can exceed atmospheric inputs (for example, near the Rhone river mouth or in the vicinity of Palomares; Gascó et al., 1992). Furthermore, ^{137}Cs has a high affinity for particles in freshwater, and part of the cesium that is strongly fixed in clay lattices does not desorb into saline waters. This process, as well as the flocculation and aggregation at river mouths, has led to an accumulation of radionuclides drained by fluvial systems into deltaic areas. For the Rhone River, Charmasson (2003) calculated that the ^{137}Cs inventory in the sediment over a 480-km^2 area near the mouth reached 19.6 10^{12} Bq in 1990, with 40% trapped in a very small area (30 km^2) in the vicinity of the mouth (compared to an amount of 49.10^{12} Bq stored over 11,000 km^2 in the watershed). At least 50% of this ^{137}Cs originated from nuclear liquid releases, and plutonium isotopes are also efficiently stored in this area (Lansard, 2005). Such preferential accumulation around river mouths has also been shown for the Danube, Dniepr, Po and Ebro rivers (Delfanti et al., 1997; Sanchez-Cabeza and Molero, 2000; Gulin et al., 2002).

Studies on anthropogenic radionuclides in marine organisms in the Mediterranean Sea also underscore that the radionuclide levels are constantly decreasing due to modifications of the inputs (Papucci et al., 1996; Charmasson et al., 1999; Catsiki and Florou, 2006). The most exhaustive data for any organism has been obtained by the Mediterranean Mussel Watch monitoring program in the Black Sea and the Mediterranean Sea. The mussel *Mytilus galloprovincialis* is an excellent bioindicator that has been analyzed since 1984 along the French Mediterranean coast, and the most recent results for the 2004–2006 period have allowed for the first comprehensive mapping of ^{137}Cs concentrations in mussels on a basin-wide scale (Fig. 9c Thébault et al., 2008). Levels are less than 1.5 Bq kg^{-1} fresh weight, which is very low, and the mapping effort clearly shows the residual contamination due to the Chernobyl accident in the Black Sea compared to the other basins in the Mediterranean.

In comparison, very little work has been done to examine the trophic transfers of man-made radionuclides. Recent studies conducted on the ^{137}Cs content in hake (*Merluccius merluccius*) and their prey in the Gulf of Lions have revealed that the ^{137}Cs content shows a clear trend for an increase with hake size and a lower contamination in females due to their higher growth rates (Charmasson et al., unpublished). The content of ^{137}Cs in hake and their prey also shows a tendency to increase with δ^{15}N, which can be considered as a proxy for trophic level, and the observed bioamplification of ^{137}Cs between prey and hake remains less than a factor of 5. In contrast to ^{137}Cs, very little plutonium is assimilated in marine organisms, and Pu does not bioamplify between prey and predator. Higgo et al. (1977), when analyzing plankton from northwestern Mediterranean waters, found that $^{239+240}$Pu concentrations in euphausiids (*Meganyctiphanes norvegica*) were one order of magnitude lower than the corresponding concentrations in their microplankton prey. Furthermore, they showed that the majority of the ingested plutonium is not assimilated and is egested in plutonium-rich fecal pellets that contribute greatly to the downward vertical transport of this radionuclide in the Mediterranean and elsewhere. The same biological mechanism was also found to be largely responsible for the rapid removal of the Chernobyl radioactivity that entered the surface waters of the northwestern Mediterranean as a single pulse and its subsequent transfer to a depth of 200 m in a matter of days (Fowler et al., 1987).

5.2.4. Expected alterations

A general decrease in the total inventory of both ^{137}Cs and ^{239,240}Pu in the Mediterranean Sea is expected due to the absence of relevant input sources, the natural biogeochemical processes occurring in the upper water column, loss through the straits of Gibraltar (Pu) and physical decay (Cs). However, in the future several southern Mediterranean countries are expected to build nuclear power plants along their coastlines, which could potentially cause some contamination. Although the authorized releases from nuclear power plants do not lead to significant amounts of contamination, potential accidents in the nuclear industry remain a matter of justified concern. In addition, climatic changes that involve increases in the frequency and intensity of wildfires or wind erosion could result in rising activity levels over a short period of time and contribute to perpetuating a residual activity level of ^{137}Cs in the atmosphere, a potential source term for marine waters.

5.3. Organic chemical contaminants (OCCs)

The essential laws and principles governing the biogeochemical behaviors, fates and modeling of organic chemical contaminants (OCC) in terrestrial and aquatic systems have now been gathered in reference works such as Schwarzenbach et al. (2003), and a global contamination of the oceanic and continental ecosystems by persistent organic pollutants (POPs) is now well documented (Lohmann et al., 2007). The ocean is the main receptor environment for POPs (Dachs et al., 2002), and these compounds may attain dangerous concentration levels in marine organisms because of bioaccumulation and biomagnification processes in food webs, especially concerning the top predators, including marine mammals.

With the improvements of analytical techniques, the identification and determination of many previously undetected

anthropogenic organic compounds in the environment have increased dramatically in recent years, including the polybrominated diphenyl ethers (PBDEs), perfluorochemicals, perfluorooctane sulfonates (PFOSs), perfluorooctanoic acid (PFOA), alkylphenolic compounds (nonyl- and octyl-phenol), many pesticides (ex., Triazine), phenyl urea herbicides, veterinary and human pharmaceuticals, biocides, bactericides and, finally, phthalate esters (e.g., Tronczyski et al., 1993; de Boer et al., 1998; Mackintosh et al., 2004). Moreover, it has been found that the detection of certain of these "novel/emerging" contaminants might indeed be of environmental concern because they have been shown to be mobile, persistent, and toxic, and some are bioaccumulative. A few studies have also shown that the levels of some of these chemicals have increased over recent decades and that their presence in the environment is widespread (e.g., PBDEs; Johansson et al., 2006). Finally, the scientific community has also gathered growing evidence of their biochemical reactivity and a potential for biological effects in animals, including humans. Recently, for instance, the endocrine disrupting effects of some OCCs have been recognized as having a major impact on wildlife (Escher and Hermens, 2002).

5.3.1. Inputs to the Mediterranean Sea

The Mediterranean Sea is influenced by riverine inputs and air masses from northern Europe that contain POPs. Recently, elevated polychlorinated biphenyl (PCB) levels were detected in the Rhone river waters and sediments and are related to an industrial waste chemical treatment plant close to Lyon. Today, the high levels of PCBs in this river may constitute a significant source for the Gulf of Lions, but this is difficult to evaluate because the only available estimate of the PCB flux from the Rhone River is dated. The riverine inputs of OCCs to the Mediterranean Sea are in fact unknown.

Two main processes must be distinguished concerning atmospheric sources: (i) dry/wet deposition, which is a net input, and (ii) exchange processes at the atmosphere-ocean interface, which can act both as inputs and exports (Jurado et al., 2004). Air-borne POPs are delivered to the sea by dry and wet depositions and by diffusive exchanges at the air–sea interface. The mean annual PCB concentration in the lower troposphere of central Europe is estimated to be 800 pg m^{-3}, with two times lower concentrations in coastal areas and in the open Mediterranean (UNEP/MAP/WMO, 2001). Atmospheric PCBs can be transported over long distances (i.e., from central Europe to the eastern Mediterranean basin; Mandalakis and Stephano, 2002), but they did not show significant seasonal variation, in contrast to polycyclic aromatic hydrocarbons (PAHs), due to their source from fossil fuel combustion and their pyrolytic fingerprint. Indeed, PAH concentrations in the marine atmosphere of the western Mediterranean were found to be around 2 ng m^{-3} in spring, but increased significantly in winter (Mandalakis and Stephano, 2002). According to Lipiatou and Albaigés (1994), the total atmospheric deposition for PAHs is within the range of 28–61 μg m^{-2} year^{-1}. Thus, in comparison to the Rhone River input, the atmospheric deposition of PAH represents 15-30% of the total input in the Gulf of Lions, whereas it is the dominant source for the whole northwestern Mediterranean Sea. Organic contaminant concentration values for the eastern Mediterranean basin are scarce. Recent data concerning marine aerosols of the eastern Mediterranean underscore the dominance of PAHs in their gaseous phases over their particulate phases (Tsapakis et al., 2003). An overview of the POP inputs to the Mediterranean is given in Table 2.

Estimates of air–sea diffusive exchanges were computed from several measurements of OCC concentrations in their atmospheric gaseous phases and their marine dissolved phases at a site on the Catalan coast (NW Mediterranean). The strong temporal variability of these concentrations leads to a highly variable air–water exchange, both in intensity and direction, which may cause overestimates in air–water exchange calculations (Pérez et al., 2003).

5.3.2. OCC dynamics in the water column

The air–water exchange of OCCs to the ocean is driven by the marine cycle of organic carbon (Dachs et al., 2002). Primary production and particle settling shift the partitioning of OCC between surface waters, deep waters and sediments. The first series with monthly readings of PAH flux data in the deep western Mediterranean basin show relatively high levels and efficient transfers toward the deep layers, which appear to be a large sink of chemical contaminants with a significant temporal variability (Bouloubassi et al., 2006). Moreover, the data suggest that the levels and fluxes of PAHs are the result of complex interactions between sources/emissions and biogeochemical processes (linked, in particular, to the carbon cycle). Our understanding of the fates and sinks of OCCs in the Mediterranean Sea is still hindered by the lack of temporal surveys of their concentrations in surface and deep particles. In the North Atlantic, the flux of OCCs that is associated with deep-water formation is higher than the flux of pollutants driven by particle sedimentation (Lohmann et al., 2007). This kind of estimate is not available for the Mediterranean Sea, but the impact of deep-water formation in the northern areas of the Mediterranean Sea clearly have to be taken into account.

5.3.3. OCC distributions in waters and sediments

The contents of OCCs and POPs in the Mediterranean Sea have been the subject of many studies, most of them dealing with coastal regions, especially in France and Spain. A recent detailed survey of the existing literature by Albaigés (2005) indicates that most of the available data concern living organisms and that few studies deal with the water columns and sediments in oceanic environments. Moreover, these rare data concern only a few combustion PAHs and some PCBs.

Bouloubassi and Saliot (1991) have shown that dissolved PAHs in the Mediterranean Sea can account for up to 92% of total PAHs, with dissolved PAH concentrations in the western basin varying between 0.4 and 0.9 ng l^{-1} in the open sea, around 2 ng l^{-1} in coastal areas and up to 31–50 ng l^{-1} in the Rhone delta. More recent data on dissolved PAHs show higher concentrations in the southwestern Black Sea and eastern Mediterranean than in the western Mediterranean, reflecting different pollutant loads, trophic conditions and cycling rates (Berrojalbiz et al., in press). Since sediments integrate PCBs and PAHs over time, analyzing coastal sediments allows for the detection of major continental inputs and the evaluation of their magnitude. All large-scale surveys have demonstrated that the northern Mediterranean is subject to much higher anthropogenic inputs; therefore, much higher PCB levels are present in these sediments (Albaigés, 2005). The concentrations of PCBs in coastal sediments from the French monitoring network averaged between 0.3 and 396 ng g^{-1} dw (the sum of 11 congeners), with the area of Marseille as a hotspot (RNO, 1998). Further "hotspots" are generally found near sewage outfalls and river deltas, such as those of the Rhone and the Ebro Rivers. Concerning PAHs, coastal areas, and continental shelves and slopes are dominated by petrogenic PAHs, whereas the deep basins of the northwestern Mediterranean Sea are characterized by high amounts of pyrogenic PAHs. Furthermore, the similar distributions of PAHS in deep-sea sediments (Albaiges et al., 1991) and aerosols (Simó et al., 1991) account for the prevailing dominance of atmospheric inputs, and the mean PAH fluxes for the northwestern basin are comparable with estimates of atmospheric deposition (3–16 ng cm^{-2} year^{-1}) (Lipiatou and Albaigés, 1994). The total PAH concentrations in the NW Mediterranean surficial sediments range from several ng g^{-1} at the open sea sites to several μg g^{-1} in coastal environments, especially near the Ebro or Rhone River mouths or near

the industrialized and densely urbanized zones of the French Riviera (e.g., Lipiatou et al., 1997). According to Gómez-Gutiérrez et al. (2007), who present a review of sediment contamination, the chemical contamination by POPs in the Mediterranean area is associated with urban/industrial activity and river discharges and particularly affects harbors and coastal lagoons. The northern coast is the main area of concern for POP pollution. A general decline in concentrations has been observed over time, more evident for DDTs than for PCBs. However, for emerging POPs, such as PBDE, information is lacking. Moreover, there is also a lack of data for the southern and eastern parts of the Mediterranean Sea.

5.3.4. POP bioaccumulation and biomagnification

The RNO database provides evidence for contamination of coastal Mediterranean waters by various xenobiotics. For example, it appears that after a sharp decrease in PCBs during the 1990s, a significant background concentration remains in filter-feeding mussels (Fig. 9b). The retrospective analysis of "classic" (PCBs, PCDDs, and PCDFs) and "novel" (PBDEs) POPs in the archived samples of marine mussels collected over the past 24 years within the RNO-Network has provided a more quantitative estimation of their temporal trends (Johansson et al., 2006; Munschy et al., 2008). The trends can be explained by simple linear regressions or exponential curves, which show the same decreasing trend for PCDFs, PCDDs and PCBs but an increase in PBDEs (Johansson et al., 2006). However, the time-scales for the decreases in PCDD/F and PCB concentrations differ by a factor of two in the Mediterranean lagoon Thau (12 and 8 years, respectively; Munschy et al., 2008), which could be related to the somewhat various dynamics and contamination histories of the two POP groups.

In a basin-wide scale survey carried out with caged mussels, Andral et al. (2008) found consistent distributions of PCBs, PAHs and DDT in the entire western Mediterranean basin. Concentrations were significant (e.g., CB153: 0.5–41.3 ng g^{-1} d.w.), but lower than along the French coasts (e.g., CB153: 2–593 ng g^{-1} d.w.), and new hot spots were detected. The average value of the sum of PCB compounds was 14.6 ng g^{-1}, with a median of 9.0 ng g^{-1} at the scale of this study (Fig. 9b). The results show that the presence of the sites that are impacted by PCBs correspond to large cities (Barcelona, Marseille, Napoli, Algiers) and industrialized sites (the naval base of La Maddalena in the Tyrrhenian sub-basin) or, at a lesser degree of contamination, large rivers like the Ebro (20.37 ng g^{-1}) and Rhone (37.80 ng g^{-1}).

The contents of PCBs in the Mediterranean have received scientific attention for over 30 years owing to their health risks and tendency to accumulate up the trophic chain (e.g., Fowler, 1987; UNEP/MEDPOL, 1989). An early survey of PCBs in plankton and nekton from the central and eastern Mediterranean basins carried out in 1977 found that the concentrations in the macrozooplankton and nekton were not significantly different from the PCB levels in similar species from other seas (Fowler and Elder, 1980). In contrast, the survey indicated a trend toward slightly lower PCB levels in mixed microzooplankton samples. Recently, Bodiguel et al. (2009) explored the mechanisms of PCB bioaccumulation within the food web of hake (*Merluccius merluccius*) from the northwestern Mediterranean basin. Muscle tissues of these fish exhibited a greater contamination level than those from the Atlantic (Bay of Biscay), and this initial study of classic and novel organohalogen contaminants (PCBs and PBDEs) in hake tissues (liver and muscles) also demonstrated a very high variability in concentrations. Furthermore, these results suggest that fish size is not the only factor acting on contamination levels and that the difference in contaminant concentrations between males and females could be due to the decontamination of females during spawning. Furthermore, this phenomenon may be magnified by the lower growth rate of males, and the growth dimorphism between sexes

suggests that age is probably a more important factor than body size for PBDE and PCB bioaccumulation. The observed inter-individual variability of contaminant levels may also have been related to differences in fish environmental habits, possibly leading to greater dissimilarities in dietary exposure levels. Finally, other factors, such as variations in the physiological conditions (e.g., reproduction, diet status, and overall fitness) of individuals have also been identified as being able to influence POP contamination in fish.

For other emerging organic contaminant compounds, more data are needed, especially in the vicinity of sources (e.g., estuaries, lagoons, and large cities) and in all environmental compartments. For these compounds, significant geographic gaps exist (particularly in the southern part of the Mediterranean), and discontinuous data series make their temporal assessment difficult.

5.3.5. Expected alterations

Several climatically related changes may significantly affect the fate and behavior of OCCs in Mediterranean waters. Even in the absence of changes in economic practices that affect the utilization of OCCs, their inputs will be affected by climatic variations in factors such as temperature, UV radiation and rates of soil wash-out, which are governed by the size and frequency of floods and precipitation. The effect of changes in primary production on the transfer of OCC to marine sediments requires a better understanding of the role of bacterioplankton, phytoplankton and zooplankton in the removal of POPs from the water column before any precise predictions can be made (e.g., see Elder and Fowler, 1977). We can *a priori* expect that an increase in primary productivity in coastal zones could strengthen the air–sea exchange and the incorporation of OCCs into sediments. The eutrophication of some near-shore areas will possibly lead to an increase in OCC removal. In contrast, the oligotrophization of other Mediterranean areas would favor an increase in OCC stocks in the atmospheric gaseous and marine dissolved phases. Thus, a comprehensive budget of the contamination by OCCs will be required to link their study to the carbon, phosphorus and nitrogen biogeochemical cycles. More generally, the dynamics of marine particles constitutes a critical domain to better understand the fate of OCC to the deep-sea. The post-depositional mobility and general diagenetic behavior of POPs should also be documented in this particular marine environment. This would permit the prediction of possible changes in the bioaccumulation and biomagnification processes of POPs in food webs and permit the estimation of the health risks for seafood consumers. At the least, a better knowledge of the concentrations, partitioning and speciation of emerging organic contaminants (including more hydrophilic compounds) is required to predict their fates, mainly on the basis of changes in their degradation rates (microbiological and photochemical), and to assess the resulting risks for different ecosystems.

6. Influence of nutrient sources and stoichiometry

6.1. The role of nutrients in pelagic ecosystems

The concept and relevance of the 'Redfield ratio' (276O:106C:16N:1P; Redfield, 1934), or the 'extended Redfield ratio' when considering all biogenic elements in aquatic systems, has been largely debated over recent decades (e.g., Takahashi et al., 1985; Geider and La Roche, 2002) to the extent that it has achieved nearly canonical status. Despite a perceived uniformity, it is known that the elemental composition of biotic and abiotic compartments can widely vary with environmental conditions (e.g., light, temperature) and/or growth rates of organisms. The degree to which organisms maintain a constant chemical composition relative to
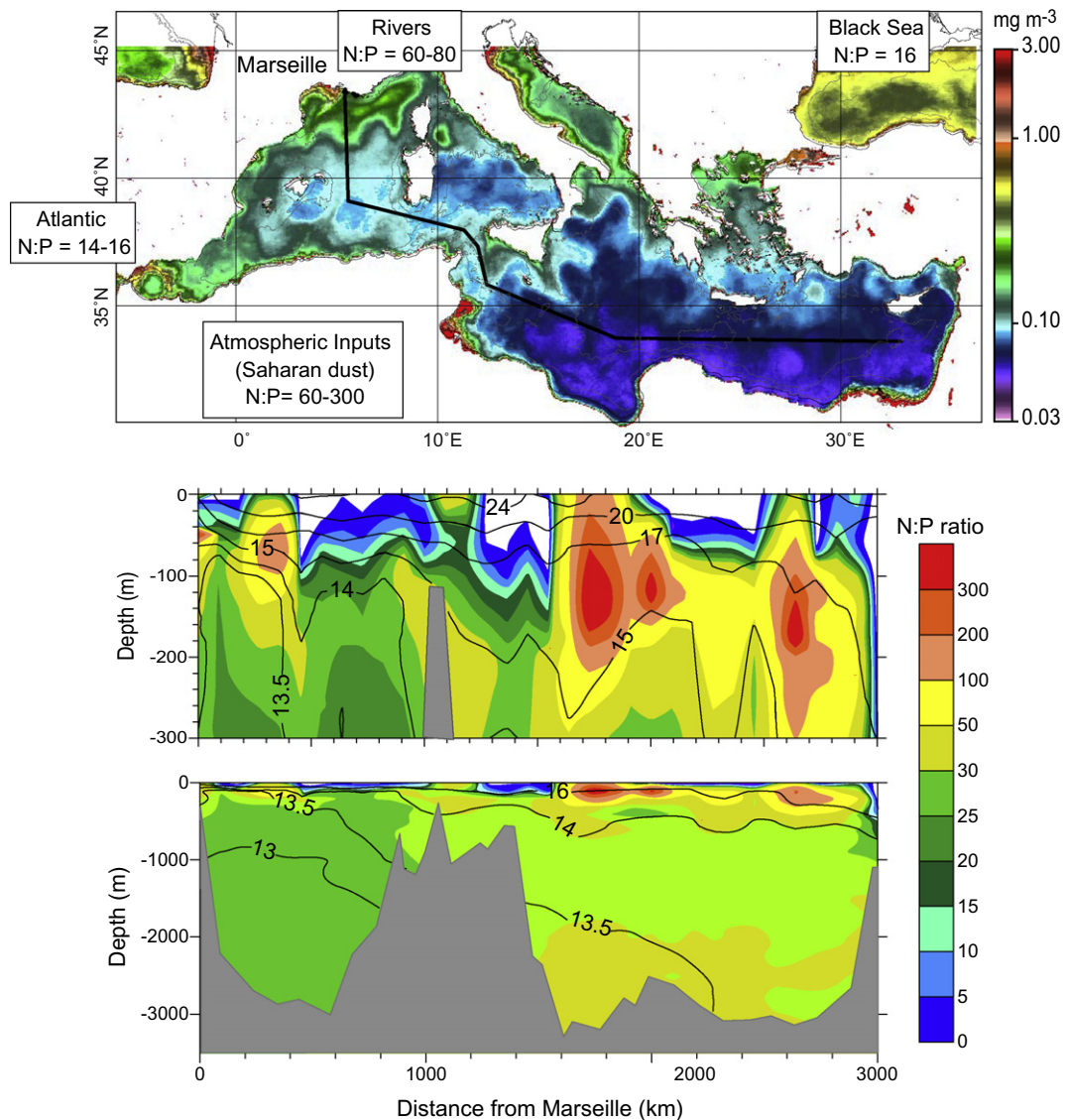
Fig. 11. (A) Satellite map of the mean chlorophyll concentrations in summer 2007 for the Mediterranean Sea with the nitrate to phosphate ratio ($NO_3:PO_4$) in the main external sources of nutrients (††: ratios with large uncertainties) (Aqua-MODIS Satellite data provided by the ocean color processing team (oceancolor.gsfc.nasa.gov), final data treatment and mapping by E. Bosc). The black continuous line is the sampled transect during the BOUM cruise in July 2008; http://www.obs-vlfr.fr/proof/boum/), (B) Vertical distribution of the $NO_3:PO_4$ ratio and temperature (black line, °C) during the BOUM cruise in the 0–300-m layer. (C) As in (B) but for the whole water column (0–3500 m). The white areas correspond to ratios where nutrients are undetectable by conventional methodology.

the variations in their environment is referred to as 'stoichiometric homeostasis'. One of the major hypotheses in the functioning of marine pelagic ecosystems, "the light-nutrient hypothesis" related to "the bottom-up vs. top-down ecosystem control", states that the importance of the microbial food web relative to the grazing impacts by macro-zooplankton and the nature of the relationship between algae and bacteria (competition or commensalism) are affected by the balance of light and nutrients experienced by phytoplankton (Conan et al., 2007; Elser et al., 2007; Thingstad et al., 2008). Nutrients may originate from allochtonous and/or autochthonous sources. The first are mainly abiotic (e.g., upwelling, convective overturning, advection, continental inputs, ground water discharges, and atmospheric inputs), whereas the second are mainly biotic (e.g., excretion and mineralization) sources. At various scales, there is then a continuous recycling of particulate organic matter (POM) and dissolved organic matter (DOM) to dissolved inorganic matter (DIM) and back again through various microbial processes.

Aquatic ecosystems respond differently to nutrient enrichment and to altered nutrient ratios along a continuum from fresh water through estuarine, coastal and marine systems (Davidson and Howarth, 2007; Elser et al., 2007). In principle, the elemental ratios in the oceans can only change on time-scales comparable to the residence times of the major nutrients ($\sim 10^4$ years for NO_3 and PO_4, Falkowski and Davis, 2004), although it is now evident that human activities alter theses ratios at decadal time-scales (Turley, 1999). This is particularly relevant for the Mediterranean Sea, which is characterized by short ventilation and residence times (~ 70 years) when compared to other oceans (500–1000 years). By affecting biological activity and diversity, nutrient cycles control the efficiency of the biological carbon pump, and thus, any change in nutrient stoichiometry is expected to modify carbon sequestration by the ocean.

The aims of this chapter are: (i) to synthesize the current state-of-the-art information on nutrient availability in the Mediterranean Sea and (ii) to discuss the predicted changes in major abiotic

sources of nutrients, with specific attention paid to feedback mechanisms.

6.2. Nutrient availability in Mediterranean pelagic ecosystems

6.2.1. Current knowledge

The Mediterranean Sea has long been known as a relatively low-nutrient concentration basin (McGill, 1965; Krom et al., 1991), although it exhibits increasing oligotrophy from west-to-east (Fig. 11). The stoichiometry of the DIM, POM and DOM pools reveals an excess of C and a deficiency in P relative to N across the whole area throughout the year (see, for example, Fig. 8 in Marty et al., 2002). Another Mediterranean characteristic is its relatively low silicate concentration (Lucea et al., 2003), as a result of the negative exchange budget at the Strait of Gibraltar and the damming of a number of the major Mediterranean rivers (Béthoux et al., 2002a). In fact, changes in the Mediterranean Sea nutrient status can directly result from a change in the total input rates and/or from an alteration of the nutrient stoichiometry. Macro-nutrient concentrations in the NW Mediterranean Sea mainly depend on: (i) river and groundwater discharges, (ii) atmospheric deposition and (iii) exchanges through the Straits of Gibraltar and Bosphorus (Fig. 11a). According to Béthoux et al. (1998), 70% of the surface phosphate inputs in 1994 originated from atmospheric and terrestrial inputs, while less than 30% were of Atlantic origin.

While several hypotheses have been proposed over the last 20 years to explain the stoichiometrically anomalous N:P ratio in the Mediterranean Sea (see the review of Krom et al., 2010 for details), it still remains an open issue for the oceanographic community. In one hypothesis, the anomalous N:P ratio is due to the strong influence of continental and atmospheric sources, all providing nitrogen in excess relative to phosphorus (e.g., Markaki et al., 2010; Krom et al., 2004). Consequently, the total nutrient budget in terms of N and P shows that the biologically available N load to the basins is significantly higher than the 16:1 Redfield ratio of biologically available N:P (Fig. 11a). This characteristic is clearly illustrated when considering the nutrient values and the gradients of the $NO_3:PO_4$ ratios from the east to west and from the surface water (Fig. 11b) to deep water (Fig. 11c) in the Mediterranean Sea.

A second hypothesis argues that high N:P ratio is due to intense dinitrogen (N_2) fixation, the reduction of atmospheric N_2 into bioavailable ammonia, providing a source of 'new' N and increasing the seawater N:P-ratios. It has been hypothesized that fixation by diazotrophs could be a significant source of new nitrogen to the Mediterranean Sea: indirect evidence based on nutrient budgets (Béthoux et al., 1998) and on N stable isotope studies (Sachs and Repeta, 1999) suggest significant N_2 fixation rates in the present and recent geological times. Pantoja et al. (2002) even proposed an eastward increase in the contribution of N_2 fixation to the total N water column budget (from ~20% in the western basin to 90% in the eastern basin) based on their analysis of $\delta^{15}N$ variations in the PON, chlorophyll *a* and deep-water nitrate. However, several recent studies have reported direct N_2 fixation measurements across the entire Mediterranean Sea. Except the high and controversial (Krom et al., 2010) fluxes reported one isolated station by Rees et al., 2006) in the Levantine basin, direct measurements show that diazotrophy is extremely reduced in the eastern Mediterranean Sea during the stratification period (<3 µmol N m^{-2} d^{-1}; Ibello et al., 2010; Bonnet et al., 2011; Yogev et al., 2011) and increases in the western Mediterranean basin (10–200 µmol N m^{-2} day^{-1}; Garcia et al., 2006; Bonnet et al., 2011) to reach fluxes commonly encountered in sub-tropical gyres. Interestingly, the highest N2 fixation rates across the Mediterranean basin were not measured in nitrate-depleted waters, but rather in water masses exhibiting micromolar nitrate concentrations (in the Rhone river plume during the summer stratification or during late spring and fall (Garcia et al., 2006; Capone, Comm. Pers.), when the stratification breaks down and surface waters are enriched in nutrients. The increasing gradient of N_2 fixation from West to East is in disagreement with previous estimates based on geochemical tracers ($\delta^{15}N$), but Mara et al. (2009) and Krom et al. (2010) have pointed out that the N stable isotopic studies cited above did not take into account the high atmospheric deposition of nitrate (highly $\delta^{15}N$-depleted) in their mass balance calculations. By including atmospheric deposition, the unusually low $\delta^{15}N$ in the eastern Mediterranean basin is explained without the contribution of N_2 fixation. To conclude, it is clear that further research is necessary to precisely determine the role of diazotrophic organisms along the year cycle in the control of Mediterranean N:P stoichiometry.

In addition to the disequilibrium in the main nutrient sources (Fig. 11) and N_2 fixation, other internal processes have been proposed to explain the deviation of the Mediterranean Sea elemental stoichiometry from the Redfield ratio. These include, among others, the short residence time of deep waters (~70 years), leading to the incomplete remineralization of the semi-labile pool of organic matter, and phosphate removal through adsorption onto iron oxide-rich Saharan dust particles (Krom et al., 1991). This last process is negligible according to Ridame et al. (2003). Consequently, with respect to this specific elemental stoichiometry, the phosphacline is frequently located deeper than the nitracline and the thermocline, inducing abnormally high DIN:DIP ratios (>300) in sub-surface waters, at least at the end of summer stratification (Pujo-Pay et al., 2010). This pattern suggests incomplete nitrate utilization by phytoplankton due to the lack of phosphate at the bottom of the photic layer (Diaz et al., 2001). Bacterial denitrification could also be an important sink for nitrate, although Krom et al. (2004) reported no denitrification or low denitrification rates in the eastern Mediterranean basin. On the other hand, the nitrification process could be a source of nitrate, both in sediments and in the water column (Bianchi et al., 1999). Another factor controlling the C:N:P stoichiometry in autotrophs is irradiance. High intensities of photosynthetically active radiation (PAR) increase C:P-ratios, whereas exposure to ultraviolet radiation can reduce cellular C:P- and N:P-ratios in phytoplankton (Hessen et al., 2008). The net outcome of these opposing effects will depend on the optical properties and mixing depth in the water column.

Concerning the role of nutrients in the functioning of ecosystems, it is well known that the growth and reproduction of autotrophs, as well as large-scale ecosystem primary production, are frequently limited by supplies of nitrogen and/or phosphorus (see the review by Elser et al., 2007). It is generally considered that N is the primary limiting nutrient in terrestrial and marine ecosystems, whereas P is the main limiting nutrient in lakes and in the Mediterranean Sea. A large and diverse set of geochemical and ecological factors can influence the nature of N- and P-limitations; the diversity of habitat-specific climatic, edaphic and ecological influences on N and P availability makes it difficult to obtain a broad picture of the relative importance of nutrient limitation in the biosphere. Previous studies have questioned these generalizations across terrestrial, aquatic and marine ecosystems (Kress et al., 2005; Thingstad et al., 2005), calling attention to complex relationships, equivalences in N- and P-limitation in lakes and streams and the frequent occurrence of P-limitation in the ocean (Ammerman et al., 2003). For example, changes in the availability of reduced N (mainly NH_4^+) and the N:P-ratios in inorganic and organic forms could be important factors in the control of bloom succession and ecosystem organization (Pujo-Pay et al., 2006). In this way, a P fertilization experiment carried out in the ultra-oligotrophic eastern Mediterranean basin (CYCLOPS) unexpectedly caused a decrease in chlorophyll and increases in bacterial abundance and copepod egg production (Thingstad et al., 2005). The authors propose two,

non-exclusive, pathways for the transfer of P to copepods via the microbial food web: a "trophic bypass" whereby added P bypasses the phytoplankton compartment through a predatory food chain from heterotrophic bacteria and a "trophic tunneling" in which phosphate disappears through rapid luxury consumption into phytoplankton and bacteria, thus changing the stoichiometry, but not the abundance, of prey organisms. Predicting the effects of altered nutrient loading requires an understanding of if, where and to what extent these key nutrients limit primary producers and successive trophic levels.

6.2.2. Expected alterations

A number of predicted effects associated with climate change (see Table 5.1 in UNEP-MAP, 1999) are expected to play a prominent role in modifying nutrient availability and nutrient dynamics in the Mediterranean Sea. The winter deep convection events allow the replenishment of nutrients in the surface layers and, in this sense, support phytoplankton productivity (Schroeder et al., 2010). Recent observations and models indicate a tendency for a decrease in phytoplankton productivity in oceans. This decrease in productivity would be linked to an enhancement in upper stratification and slower deep-water formation as a response to warming climate (see Chapter 1 'Influence of hydrodynamics'). However, this warming trend could be partly counterbalanced by a salinity increase due to long-term changes in the freshwater and heat fluxes of the Mediterranean Sea in relation to climatic/anthropogenic changes (Béthoux et al., 1999; Millot et al., 2006; Ludwig et al., 2010). Indeed, the frequency of extreme events (high mixing, high nutrients and high biomass) has increased in recent years, resulting in an increase in phytoplankton biomass in the NW Mediterranean Sea (Marty and Chiaverini, 2010), following a trend that has been observed since 1991 (Marty et al., 2002). These results suggest an increase in productivity, not the decrease predicted by general models.

From a chemical point of view, the predicted increase in pCO_2 means that the ocean will become more acidic, more stratified and less oxygenated (see Chapter 3 'Influence of temperature and acidification on the Mediterranean Sea solubility and biological pumps'). Elevated CO_2 can potentially affect many processes in marine biogeochemistry, and each of these affects will be at least non-linear and potentially complex with both positive and negative feedback mechanisms. Even if large uncertainties remain, in particular concerning hydrodynamic changes (see Chapter 1 'Influence of hydrodynamics') and impacts on ecosystem structure and functioning, a change in ocean carbon chemistry will undoubtedly affect marine organisms directly by acting on their physiology and/or indirectly by altering the food web. Integrating the net effect of these processes at regional and basin-scales is a future outstanding challenge. Three untested hypotheses concerning ocean acidification and nutrient availability can be put forward.

(i) *Enhanced oligotrophy* resulting from the combination of reduced nitrification (Huesemann et al., 2002) and elevated denitrification in sediments. This combination will accelerate the removal of NO_3^- from overlying waters (Widdicombe and Needham, 2007).

(ii) *Further P-limitation* may occur as a result of an increase in the N:P stoichiometric ratio, which may result from a shift in the $NH_4^+ : NH_3$ equilibrium and be exacerbated by increases in prokaryotic N_2 fixation (e.g., Hutchins et al., 2007). This may be a function of, or enhanced by, an increase in the availability of trace metals that are essential for the activity of metalloenzymes.

(iii) *Reduced productivity and carbon export* resulting from a decrease in the $NO_3^- : NH_4^+$ ratio that is partly due to inhibition of nitrification. In surface waters, this will impact the rates of new and regenerated production, increase production of transparent exopolymer particles (TEP; Engel et al., 2002) and, ultimately, may lower the rate of carbon export and the quality (C:N:P ratio) of exportable organic matter (Grossart et al., 2006; Riebesell et al., 2007) with direct impacts on productivity (including fisheries) and the sequestration of C in the deep ocean through modifications in the C:N:P:Si export ratios of POM and DOM. In fact, the question of whether primary production and the efficiency of carbon sequestration is likely to increase or decrease in response to predicted environmental changes is a question still open to debate (Antoine et al., 2005; Vasquez-Dominguez et al., 2007).

It is, however, obvious that a number of these potential impacts may counteract each other or compound with each other with a degree of synergy that cannot be described from experimental observations alone. Moreover, preliminary results underscore the importance of biologically driven feedbacks in the ocean to global change. Models currently provide the only tool by which we can interrogate the multifaceted relationship between these processes to investigate future changes in ecosystem functioning.

6.3. Impact of river and groundwater discharges on coastal ecosystems

6.3.1. Current knowledge

The generalized conceptual model of continental water inputs considers a variable buoyant plume in which surface turbidity decreases while light penetration increases with distance from the river mouth because large suspended particles sink out of the plume. Phytoplankton and bacteria take advantage of this high nutrient environment (Conan et al., 1999) and 'bloom', while other trophic levels (small and large zooplankton, fish and even marine birds and mammals) congregate and utilize this highly productive region. Benthic ecosystems also take advantage of these allochthonous and autochthonous inputs. As riverine particles are deposited and recycled on the continental shelf and slope, they contribute to the biogeochemical cycles at the river-shelf intersection. This productivity occurs in a highly dynamic and variable physical environment (e.g., in terms of winds, currents, waves, and tides). In spite of these generalities, however, each river-shelf system has unique attributes that cause the ultimate fates of river-borne nutrients to vary.

Rivers and other continental water sources (i.e., groundwater; Buddemeier, 1996) inject about 300 km^3 $year^{-1}$ of water into the Mediterranean Sea (half of this value is introduced by the 10 biggest rivers) and are an important source of nutrients and other chemicals, including contaminants (Ludwig et al., 2010). Nutrient data are incomplete with respect to the spatial and temporal variability of riverine nutrient loads, but a general extrapolation of the average global budgets for the nitrogen and phosphorous inputs into the Mediterranean Sea gives concentrations of 1.25 mg N–NO_3 l^{-1}, 0.1 mg P–PO_4 l^{-1} and 0.25 mg TP l^{-1} (Total Phosphorus) (UNEP-MAP, 2003). Rivers also carry small rock fragments and minerals, including clays, which are produced in weathering reactions. These particles contain numerous elements such as Al, Fe, Si, Ca, K, Mg, Na and P among others. Anthropogenic inputs to watercourses are generally diverse and include industrial waste, outflows from sewage plants and runoff from agricultural regions. For example, the fluvial loading of total organic carbon (TOC) into the Mediterranean Sea comprises 0.08–0.3% of the standing stock of TOC in the whole Mediterranean basin, which is much higher than the average reported for the World Ocean (Smith and Hollibaugh, 1993), and highlights the main role played by the rivers in the Mediterranean carbon cycle (Sempéré et al., 2000). The Rhone and the Pô are the two greatest rivers, accounting for about one

third of the average total freshwater input to the Mediterranean Sea (Ludwig et al., 2010). It should be noted that the construction of dams since the end of the second World War has resulted in drastic changes in water, particulate and dissolved matter discharges from the affected rivers (Turley, 1999). For example, a 10-fold decrease in the sediment load was observed for the Rhône River (Pont, 1997).

One of the most productive areas of the Mediterranean Sea is the Gulf of Lion, which is influenced by large inputs from the Rhône River. On an annual basis, ∼50% of the primary production in the Gulf of Lion can be attributed to continental nutrient inputs (Lefèvre et al., 1997; Pujo-Pay and Conan, 2003; Pujo-Pay et al., 2006). With a $NO_3:PO_4$ ratio of 65–80 (Ludwig et al., 2009, 2010), the Rhône River contributes to the relative P deficit of the Mediterranean Sea. For the period from 1987–1996, the annual fluxes of dissolved and particulate organic carbon (DOC and POC) were estimated to be 1.1 ± 0.2 and $1.6 \pm 0.5 \times 10^{10}$ moles C year^{-1}, respectively, whereas the total suspended matter flux was estimated to be $9.9 \pm 6.4 \times 10^6$ T year^{-1} (Sempéré et al., 2000). The latter roughly corresponds to 80% of the total riverine particulate flux entering the Gulf of Lion (Roussiez et al., 2005) and thus a large fraction of that entering the western Mediterranean basin. The Rhône River accounts for 3–14% and 10–12% of the overall total organic carbon and total inorganic carbon river inputs, respectively, to the Mediterranean Sea (including the Black Sea).

Few detailed data sets exist for the rivers flowing into the eastern Mediterranean basin. The most detailed studies concern the northern Adriatic, fed by the River Pô and adjacent catchment areas (e.g., Degobbis et al., 2000 and citations therein). An estimate of the total dissolved N and P introduced by rivers into the northern Adriatic is $\sim 20 \times 10^9$ mol N year^{-1} and $\sim 1 \times 10^9$ mol P year^{-1}. Of this value, the Pô River itself contributes about 50% of the total nutrient transport into the basin (Degobbis and Gilmartin, 1990).

6.3.2. Expected alterations

Even if the nutrient concentrations in Mediterranean rivers are about four times lower than those in western and northern European rivers, increased concentrations of dissolved nutrients and modified nutrient ratios will impact the biogeochemical processes in coastal areas in a variety of ways. Moreover, the frequency and magnitude of extreme events (floods, low-water levels) will probably increase in the future (HYMEX, 2008) and hence alter the inputs of nutrients, subsequently impacting ecosystems in river-dominated coastal seas. We already know that eutrophication can lead to the massive growth of nuisance and toxic algal blooms, benthic algae and submersed and floating macrophytes (Turley, 1999). Coastal waters can, in this way, become discolored, murky and unsightly, impairing local fisheries, navigation and recreation by tourists.

In recent decades, anthropogenic factors in the drainage basins of many rivers have resulted in numerous changes to the dissolved and particulate properties of the river water entering into the Mediterranean Sea (Ludwig et al., 2009). These changes reflect the impacts of climate change, and dam construction. The decreases in water discharge, already clearly visible during the last 50 years, are predicted to continue in the future. By 2050, the Mediterranean may have lost more than one-fourth of its freshwater river inputs compared to 1960 (Ludwig et al., 2010; HYMEX, 2008). In fact, a reduction in freshwater discharge of about ∼20% has already been observed between 1960 and 2000 (Ludwig et al., 2009). In contrast, there is no similar pattern for river discharges into the Black Sea. A decrease can also be expected in the flux of dissolved silica, in contrast with the fluxes of N and P, which have increased by more than a factor of 5. To be more precise, while the N flux still remained at elevated levels in 2000, the P flux only increased up to the 1980–1990s and then rapidly dropped down to about the values of the
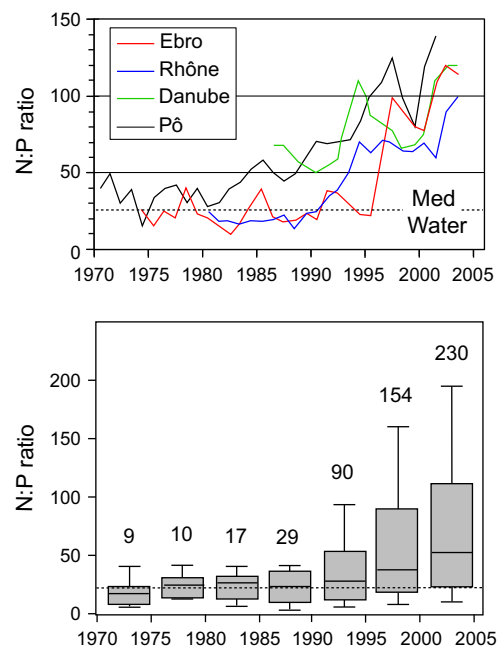
Fig. 12. Long-term evolution of N:P ratio in the large rivers around the Mediterranean and Black Seas. The dashed line is the present mean N:P ratio of Mediterranean water. Figure extracted and modified from Ludwig et al. (2009).

1960s because of the regulation of phosphorus used in detergents. Consequently, the DIN:DIP ratio in rivers has increased by a factor of 6 between 1980 and 2000 (Fig. 12). During the same period, the average Si:N ratio was 0.88 between 1980 and 1998 and 0.66 in 2000–2001, with a current trend of a continuing decrease. These stoichiometric ratios have thus been deeply modified, and many coastal management practices exacerbate these perturbations.

It is important to learn from our recent past. In the last two decades, several studies have reported increasing dystrophy in coastal waters that appears to be linked to riverine inputs (see, for example, the review of Jickells, 1998). A decrease in the Si:N ratio has been observed in Adriatic coastal areas as a result of the damming of the Pô river. A long-term time-series (1960s–1990s) in the western Black Sea has revealed an increase in phosphate and nitrate levels, a decrease in silicate and changes in the summer oxygen concentration on the shelf that are associated with the damming of the Danube River. As a result, the Si:N ratio fell by a factor of 15, leading to a shift in phytoplanktonic from diatoms to coccolithophorids and flagellates (i.e., a shift toward more non-siliceous phytoplankton blooms) that likely impacts the food web structure, the water chemistry and fluxes to sediments. Moreover, it seems that the amount of nutrients regenerated from shelf sediments and/or upwelling have increased substantially (Yunev et al., 2007).

6.4. Impact of atmospheric deposition on pelagic ecosystems

6.4.1. Current knowledge

The Mediterranean Sea receives a noticeable flux of dust (Dulac, et al., in preparation), mainly derived from Sahara Desert, in the form of strong pulses (i.e., Guerzoni et al., 1999). Organic carbon deposition by wet and dry deposition into the Mediterranean Sea ranges from 10 to 20×10^{10} mol C year^{-1} (Loÿe-Pilot et al., 1990; Copin-Montégut, 1993). Moreover, the Mediterranean basin continuously receives anthropogenic aerosols from industrial and domestic activities in populated areas around the basin and other parts of Europe (e.g., Migon and Sandroni, 1999), as well as seasonal inputs from biomass burning. Both natural and

anthropogenic atmospheric deposition can be a source of dissolved macronutrients and micro-nutrients such as P (Ridame and Guieu, 2002; Pulido-Villena et al., 2010) and Fe (Bonnet and Guieu, 2006) to Mediterranean surface waters. Atmospheric deposition can also be a source of other elements with key roles in plankton dynamics such as Zn, Cu and Co (e.g., Morel et al., 2003).

During the stratification period, atmospheric inputs can be the main external nutrient supply to offshore surface waters (Bartoli et al., 2005; Guieu et al., 2010), and episodes of Saharan dust deposition can enhance primary production (Ridame and Guieu, 2002), impact the phytoplankton community structure (Bonnet et al., 2005) and increase bacterial abundance and respiration (Pulido-Villena et al., 2008). In the eastern Mediterranean Sea, atmospheric inputs have a N:P ratio of 117:1 and can account for 60–100% of the bioavailable-N and for 30–50% of the bioavailable-P (Krom et al., 2004). Recent results by Markaki et al. (2010) indicate that the DIN:DIP molar ratio of the atmospheric bulk deposition decreases from the eastern (105:1) to the western (60:1) Mediterranean basin, similar to the decrease observed in the seawater column. Atmospheric inputs may thus contribute to the anomalously high N:P-ratios of the Mediterranean Sea (Fig. 11), as suggested for other oceanic areas (Fanning, 1989).

6.4.2. Expected alterations

Current climate change models predict a mean reduction of precipitation by about 20% (IPCC, 2008), implying enhanced dust export due to an increase in aridity (Moulin and Chiapello, 2006). In western Mediterranean, an increase of the frequency of rainfall loaded with such dust (red rain) in the last decades has been evidenced (Avila and Peñuelas, 1999). Moreover, due to the enhanced demographic pressure around the Mediterranean basin, anthropogenic atmospheric inputs are also expected to increase. More droughts in the Mediterranean region as well as changes in land use should also increase fire frequencies, an important source of Fe-rich aerosols (Guieu et al., 2005). The widespread use of chemical fertilizers in agricultural practices increases inputs of both N and P from air-borne particles because of enhanced soil uplift by winds. The same consequences are expected from the increased number of urban incinerators, especially in the northern Mediterranean countries (Migon et al., 2001). Major consequences on planktonic ecosystems can be expected from changes in natural and anthropogenic atmospheric inputs of nutrients, particularly for the oligotrophic and ultra-oligotrophic areas of the Mediterranean Sea. In addition, the expected increase in the thermal stratification of the surface layer will reduce the supply of nutrients to the photic layer through vertical transport, enhancing the role of external nutrient sources. The global response of these ecosystems to varying atmospheric inputs still needs to be assessed on a larger temporal/spatial scale.

6.5. Impact of exchange through the straits on basin-scale ecosystem structure

6.5.1. Current knowledge

The nutrient fluxes through the Straits of Gibraltar and Bosphorus vary widely over annual and longer time-scales. Exchanges through the Strait of Gibraltar have received significant attention because of its strategic location and because it is a key issue for the Mediterranean environment and global ocean circulation and climate variability studies (Bryden and Kinder, 1991). The Atlantic surface waters entering the Mediterranean Sea at the Strait of Gibraltar have higher concentrations of organic forms and lower concentrations of mineral forms (0.05–0.20, 1–4 and 1–2 µM for PO_4, NO_3 and $Si(OH)_4$, respectively) than the deeper outflowing Mediterranean waters (Dafner et al., 2003). These surface Atlantic waters generally induce an increase in productivity in the Alboran

Sea (Lefèvre et al., 1997), but these exchanges result in sum in an estimated Mediterranean net "deficit" of 10% for N and P and of up to 50% for Si. The N:Si:P ratio in Atlantic waters increases along the strait from the western entrance to the eastern exit (from 14:12:1 to 24:29:1; Dafner et al., 2003). Both physical and biological processes account for the observed spatial variability (for 16% and 84%, respectively). They also contribute to the overall P-depletion and Si-depletion of the Mediterranean Sea. The TOC input varies from 0.28 to 0.35×10^{12} mol C year^{-1}, which is 2–3 orders of magnitude higher than that reported for the Bosphorus Strait and the mean Mediterranean river input (Sempéré et al., 2002). Considering this positive budget for carbon and negative budget for nutrients, the Mediterranean basin is a "mineralization basin" for carbon according to Copin-Montégut (1993).

The Atlantic waters, entering through the Strait of Gibraltar, flow on to form the Algerian current that flows along the North African coast and arrives at the Strait of Sicily where it initiates the beginning of the Atlantic Ionian Stream, at the border between the western and eastern Mediterranean basins. The Strait of Sicily contains a two current system with the Atlantic inflow from the west at the near surface Strait region and the salty Levantine outflow from the eastern basin, located at depth. It is characterized by systematic seasonal changes in both water flux and the depth of the upper layer (the flux is higher and deeper in winter than in summer). Although the composition of the nutrient budget is quite different on an annual basis, the water flow is similar between eastern and western parts (~0.5 Sv). As for the Strait of Gibraltar, the water that flows into the eastern basin is water with surface characteristics, whereas the flow out of the eastern Mediterranean basin is intermediate and/or deep water, characterized by an abnormally high N:P ratio (Fig. 11b and c). Despite a chronic lack of nutrient data for this area, Krom et al. (2004) took into account the seasonality of water flows and nutrient distributions and estimated net fluxes from the eastern to western Mediterranean of 142×10^9 mol N year^{-1} and 4.4×10^9 mol P year^{-1}.

Water exchange between the Mediterranean and the Black Sea occurs via the Dardanelles and the Bosphorus Straits, across the Sea of Marmara. In the northern basin of Aegean Sea, fresh water (Poulos et al., 1997) and mainly organic-rich brackish water from the Black Sea (100–1000 km^3) are injected into surface layer. The net mass transfer from the Black Sea to the Aegean Sea has been estimated to be $11–12 \times 10^{10}$ mol C year^{-1} (Polat and Tugrul, 1996; Sempéré et al., 2002), but the Black Sea coastal waters transported toward the Bosphorus regions are severely polluted by large inputs of nutrients and organic matter discharges. The polluted Black Sea surface inflow is further contaminated by waste discharges into the Bosphorus from the city of Istanbul by numerous industries and about 6 million people before spreading into the upper layer of the Marmara Sea (Polat and Tugrul, 1996).

6.5.2. Expected alterations

On longer time-scales, the elemental stoichiometry of the bottom waters will impact pelagic ecosystems through modifications to their surface community structure. In the western basin, the hydrological and biogeochemical properties of the deep water masses are conditioned not only by the water masses at the surface during their formation phases but also by the properties of the water masses originating from the eastern Mediterranean basin with an estimated time lag of ~30 years. As an example, the signal of the eastern Mediterranean transient (EMT) has recently been evidenced in the waters exiting Gibraltar (Millot et al., 2006; Millot, 2009).

In fact, further alteration of the mass budget through the Straits largely depends on how the elemental composition of the nutrient sources will change and on how hydrodynamic processes will drive the surface to deep water distribution of nutrients in the

Mediterranean Sea. It is obvious that the changes in the elemental stoichiometry and nutrient availability in marine ecosystems are strongly dependent on the changes in water circulation in and across the Mediterranean basins and Straits and the degree and depth of water column stratification.

7. Influence of extreme events

The repeated occurrence of episodic disturbances constitutes one of the fundamental features of coastal ecosystems. These disturbances, namely atmospheric (dust events and heat waves), hydrologic (river floods) or hydrodynamic events (sediment resuspension and mixing of the water column), generally result in a relative enrichment in organic matter and nutrients. The effects of these individual events on the first levels of pelagic and benthic trophic networks are largely unknown; however, these events are quantitatively important in the transfer of material in or to

the sea. Describing the modifications (physical, chemical and biological) of the environment quantitatively, their recurrence and their controls constitutes a growing need in order to understand ecosystem functioning. Extreme events are one end member of disturbances and refer to the extreme value theory of statistics, which describes the extreme deviations from the median of a probability distribution. The most common example of an extreme event is the centennial river flood, i.e., it has an average return time of a century.

In this section, we explore the consequences of intense events that are of large importance in shaping mass transfers to the Mediterranean Sea and its ecosystems. Some of these events have return times of 1–10 years and may not be considered as "extreme" in a statistical sense. In reality for the ecosystems, they are extreme in the sense that they deeply modify the ecosystem functioning/viability by the intensity of transfers and habitat alterations generated by the event. Furthermore, they last a short time,

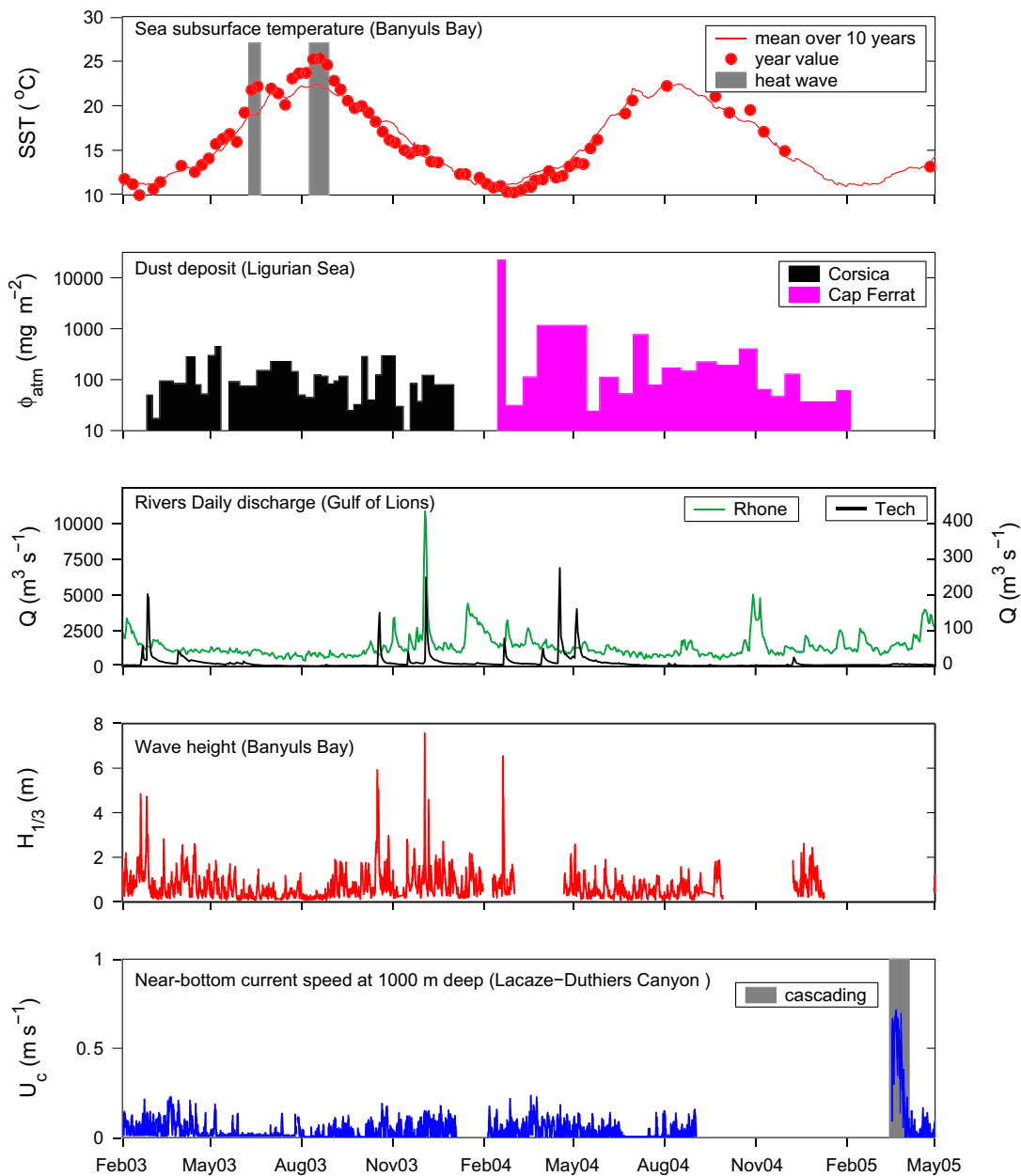**Fig. 13.** Time-series between 2003 and 2005 (top–bottom) of seawater surface temperature in the Banyuls Bay, dust deposition, Rhone River and Tet River water discharges, wave height and currents in the Lacaze-Duthiers Canyon. The series show the extreme events, including a heat wave (August 2003), extreme dust event (February 2004), storm (December 2003), flood (December 2003) and dense water cascading (April 2005).

occur infrequently and have no known periodicity, which is an additional feature of extreme events. In this paper, we use the term "extreme" with this meaning, rather than regarding the statistical theory.

We will cover five different types of events (Fig. 13):

– River floods and their consequences on the continental margin.
– Storms and the resuspension and transport induced in the coastal domain.
– The impact of episodic events (dense water cascades and other sediment gravity flows) on continental slope and deep-sea ecosystems.
– Extreme atmospheric inputs: Saharan dust storms, biomass burning and intense rains in the open waters of the Mediterranean Sea.
– Heat waves.

7.1. River floods and their consequences on the continental margin

7.1.1. Current knowledge

Large variations in river flow are a major characteristic of Mediterranean rivers. The extreme example is located on the Southern bank of the Mediterranean Sea with the "Oueds," which are typically non-permanent rivers with extreme flash floods that occur after rain events. Even the permanent rivers display very large floods, as demonstrated during the last two decades in the Rhône River in Southern France (e.g., Vaison-la-Romaine, September 1992; Gard, September 2002 and December 2003), in the Po River in Italy (Tesi et al., 2008; Oct 2000) and the Medjerda River in Tunisia (Bouraoui et al., 2005). As an example of these large Mediterranean rivers, the Rhône discharge is still subject to important short-term variations (Pont et al., 2002) that result mainly from localized storms of Mediterranean origin. Moreover, while the mean annual flow rate of the Rhone has been rather constant since the beginning of the 20th century, the flood frequency is highly variable. The 1960–1990 period had only a few exceptional events in comparison with the 1990–2003 period, which was characterized by six major floods of a >50-year return time (Antonelli, 2002). These floods are a major carrier of particles to the sea and, consequently, of sediment-bound carbon and pollutants. Although these events are still poorly understood due to the lack of experimental sites and long-term hydro-meteorological data with adequate spatial and temporal resolutions (Gheith and Mohamed Sultan, 2002), they are believed to represent a large proportion (around 80%) of particulate inputs to the Mediterranean Sea by large rivers (Radakovich et al., 2008; Antonelli et al., 2008) and thus a crucial input to Mediterranean ecosystems.

7.1.2. Impact on ecosystems

Understanding the influence of extreme floods on ecosystems and biogeochemical cycling in the Mediterranean Sea is still in its infancy. Although such events undoubtedly shape the shelf ecosystem by causing habitat alterations and providing particulate inputs to the ecosystem of sediment-bound carbon and contaminants, the fate of particulate material delivered during floods is largely unknown. The main areas that have been investigated with regards to floods and their consequences on mass transfer are the Gulf of Lions and the Adriatic shelf. Compared to the oligotrophic Mediterranean Sea, higher rates of biological productivity (Pujo-Pay et al., 2006) were recorded in the Gulf of Lions due to the influence of the largest rivers of the western Mediterranean in terms of freshwater and particulate discharges (Ludwig et al., 2003). At least 80% of the riverine input of total suspended solids (TSS) into the Gulf of Lions comes from these rivers (Durrieu de Madron et al., 2000). The remaining part is delivered by small coastal streams, mainly in the form of intermittent pulses triggered by flash floods. Recent work has highlighted the significant contribution of floods on the reuptake/translocation of Rhone riverbed sediments that were contaminated over the past 40 years by nuclear production/reprocessing to the Mediterranean Sea (Eyrolle et al., 2004; Eyrolle et al., 2006). The contribution of Rhone floods to the transfer of polyaromatic hydrocarbons (PAHs) can also be very important, with about 77% of the annual delivery of particulate PAHs transferred in a few days during an extreme flood event of November 1994 (Sicre et al., 2008). The Rhône River and the Po River are also major sources of particulate carbon to the ecosystem located near the river mouth (Darnaude et al., 2004; Tesi et al., 2008). Their influence vanishes rapidly with distance from the shoreline, as evidenced by the recycling rate in surficial sediments or the terrestrial organic matter content of the sediment (Lansard et al., 2009; Tesi et al., 2008). However, the specific impacts of floods on carbon burial and mineralization and benthic ecosystems have been rarely studied. Cathalot et al. (2010) showed that flood deposits could cause a slowdown in mineralization activity in the sediment during a short period (<6 months, Fig. 14). Tesi et al. (2008) found that the quality of the organic matter deposited during a flood of the Po River contained less lignin than regular river deposits, indicating that more soil organic matter was brought to the shelf during the flood. Depositional conditions may thus constrain the ratio of recycling to burial. It has been known for years that sediment accumulation rates correlate positively with carbon preservation efficiency (Hedges and Keil, 1995 and references therein) because of physical protection of the organic load from degradation and shorter period of exposure to oxygen (Hartnett et al., 1998). Therefore, flood deposits should actively promote the preservation of organic matter if deposited in thick layers with relatively refractory organic matter, although opposite processes may act to promote mineralization, i.e., secondary transport of unconsolidated sediments, foraging of benthic fauna and deposition of fresh terrestrial organic matter. Floods can destroy benthic habitats by depositing thick layers of sediment (>10 cm, Miralles et al., 2006), and floods may favor opportunistic species vs. endemic species adapted to their average habitat because the food supply is largely enhanced.

Rivers also fuel the continental shelf with nutrients in the river plume. Floods obviously increase the nutrient input, but also produce turbid waters in the river plume that decrease the availability of light to phytoplankton. Floods thus shift the maximum production zone toward the shelf edge for large rivers and potentially modify the type of plankton in turbid waters to which flagellates are better adapted than macro-phytoplankton (Harmelin-Vivien et al., 2008). In smaller stream-connected coastal zones, functioning may be different during flash flood events and lead to increased primary production (Guizien et al., 2007), which can represent about 20% of the annual production of phytoplankton biomass in the near-shore zone (SOMLIT survey). On the continental shelf, up to 4.7×10^{10} moles of organic carbon produced by primary production and delivered by the Rhone River could be exported off the shelf (Sempéré et al., 2000), thus escaping burial or bacterial degradation in shelf sediments.

For large and small rivers, the carbon balance is a competition between in situ production based on new nutrients inputs from the rivers and the burial of carbon of both riverine and marine origin. In this respect, deltaic sedimentation (sedimentation rates of up to 30–50 cm year^{-1} have been determined close to the Rhône river mouth; Charmasson et al., 1998) and the subsequent burial of particles or their transport to the open shelf play a major role. Their relative importance is highly dynamic and affected by the combination of several processes, such as sediment delivery by floods, their temporary storage in the delta, their remobilization during storms and their deposition in proximate and distal sedimentation zones (Guillén et al., 2006, Ulses et al., 2008b). Floods
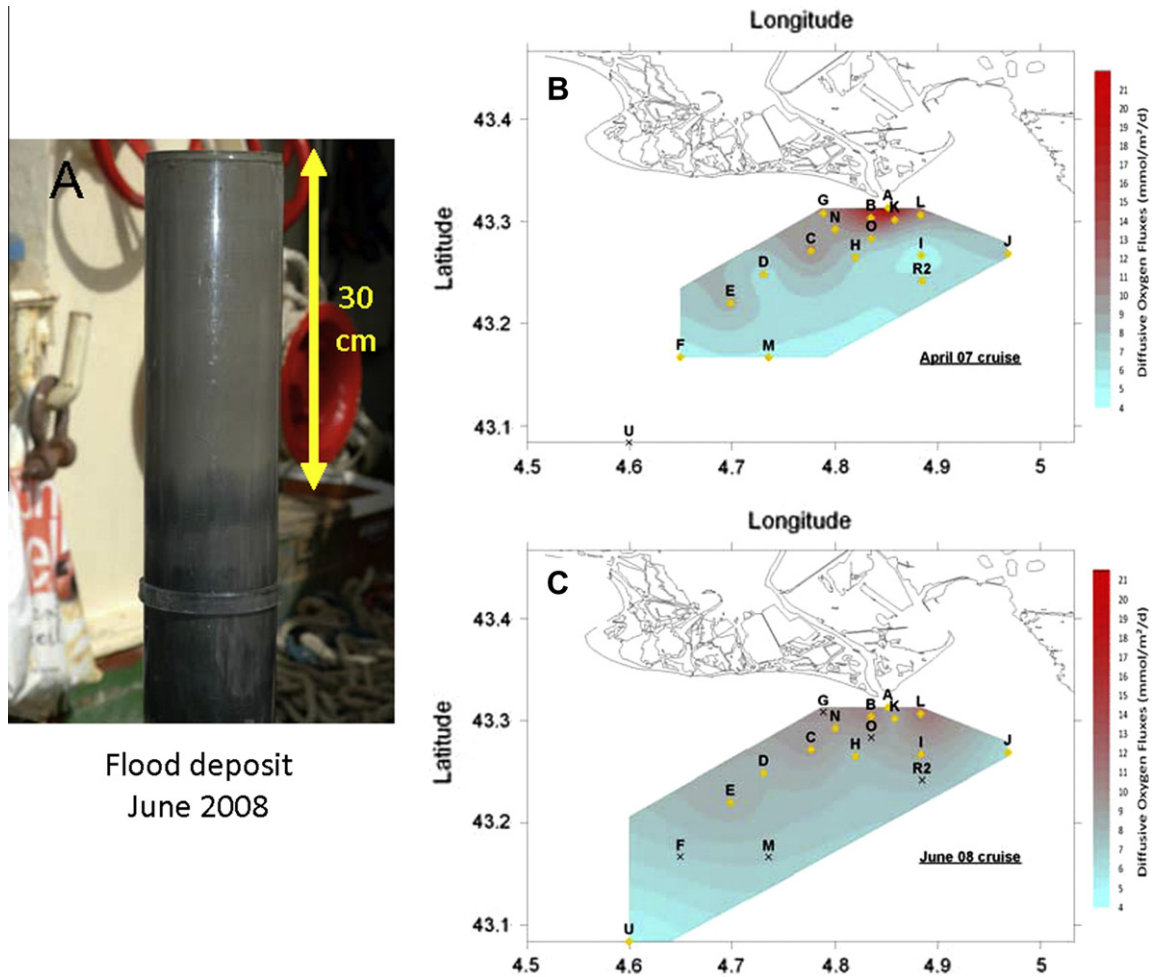
Fig. 14. Flood deposition and its effect on benthic recycling. (A) Core photographs showing a 30-cm thick deposit after a Rhone flood in June 2008 at a 45-m depth. Benthic recycling illustrated by the diffusive oxygen uptake (DOU) before the flood in April 2007 (B) and immediately after the flood in June 2008 (C). A large decrease is visible near the river mouth (the red zone in B) from 20–25 to 10–15 mmol m^{-2} day^{-1}, while the rest of the shelf is unaffected (redrawn from Cathalot et al. (2010)).

may thus change the carbon balance by modifying the export of particulate material from the shelves to the open Mediterranean Sea and changing the location and delivery of nutrients and the primary production associated with these nutrients.

7.1.3. Expected alterations

Assessing the potential impact of a future change in the occurrence of extreme events first requires an understanding of the response of material transfer and ecosystems to extreme events, such as storms, floods and other dynamic processes that are part of the "natural" functioning of the environment. As noted in the above paragraph, this is largely unknown in the present stage of our research.

Second, this assessment requires an understanding of the consequences of climate change on the occurrence and intensity of these events; these consequences are the focus of several major research programs (WCRP, GEWEX, IGBP, GICC, IMFREX). Most model scenarios on future climate change predict increasing summer droughts and wetter winters in the Mediterranean region (Somot et al., 2008). The French program IMFREX, for example, predicted an increase of severe winter precipitation in the northern half of France and a general increase of floods during winter and spring. According to Hertig and Jacobeit (2008), a shorter but wetter wet season is predicted for the western and northern Mediterranean regions, including precipitation increases in winter and decreases in the transitional seasons for the period 2071–2100 compared

to 1990–2019 (Déqué, 2007). Boberg et al. (2008) predicted that extreme precipitation would increase in the Mediterranean area despite the general decrease in precipitation foreseen for the region. This is partially confirmed by the intense precipitation events over the southeastern part of France predicted by the CYPRIM project using coupled regional climate models and new statistical-dynamical methods (La Météorologie, special issue, to be published). A new model analysis based on hydrological projections (Boé, 2007) predicts that the variability of the Rhône River flow in winter should increase, but that extreme events (intensity in the 99th quantile) should remain the same or slightly decrease during the 21st century. As Boé pointed out, these simulations of intense events are still preliminary, and a large variation between models is observed. Indeed, Quintana Segui (2008) shows an opposite result, with a decrease of the mean river runoff accompanied by an increase of the flood frequency at the end of the 21st century. Therefore, the evolution of the river flood frequency and intensity remains uncertain at present, and more work is needed on this topic to refine these scenarios.

7.2. Storms and induced resuspension and transport in the coastal domain

7.2.1. Current knowledge

In the coastal domain, waves act as sediment-stirring agents; once resuspended, the current can then transport sediment. In
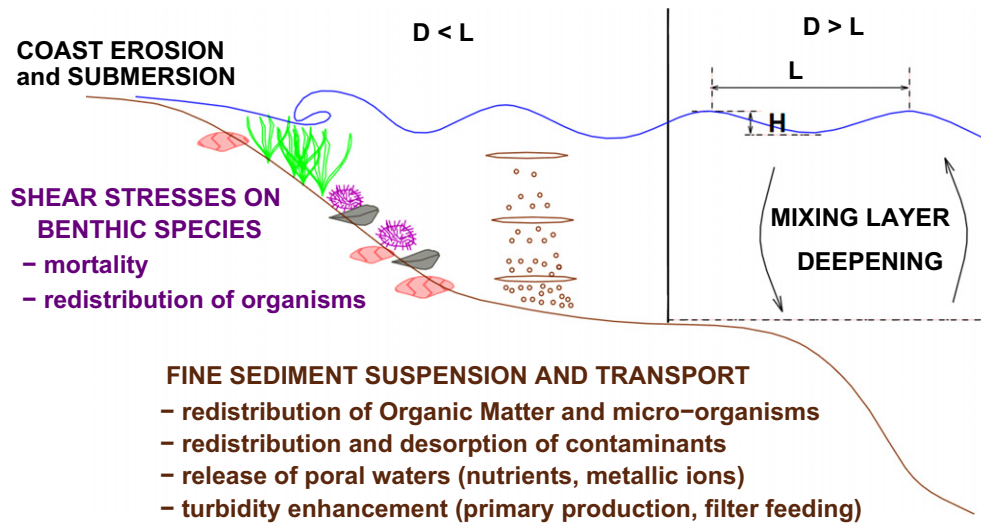
Fig. 15. Diagram showing the processes linked to sediment resuspension and its effect on ecosystems.

particular, storm swell (i.e., long energetic waves) are known to induce a large resuspension of particulate material (Fig. 15). Sea waves are described by two parameters: their period and height. While the height is a measure of the wave energy, the wave period allows for a typology of gravity sea waves based on comparing the wavelength to the water depth between short and long waves. As a consequence, waves with a long period will affect the sediments deeper in the coastal area. For example, waves with periods of 7, 10 and 15 seconds (s), respectively, will disturb a water column up to 9, 19 and 43 meters (m). Thus, only the longest swell will affect the ecosystem along a broad cross-shore gradient, with damped energy from the shoreline to offshore. In this section, we present the influence of storm swells on ecosystems and biogeochemical cycles after defining their frequency and intensity.

In the Mediterranean basin, wave measurements are rather recent and were initially motivated by risk management demand in relation to coastal erosion and increases in flood damage due to waves at the coast (Eurosion EC project, Beachmed EC Interreg IIIc project). Wave buoys were moored in the 1980s along the northwestern Mediterranean coasts (1985 in Spain, 1988 in France and 1989 in Italy) and were only recently developed in meshed networks. In the eastern basin, one wave buoy has been maintained along the Israeli coast since 2005. The scarcity of the data limits statistics on extreme swell events to a few locations, although these data already provide a general picture of wave activity in the Mediterranean: in Sete (27 m water depth, Gulf of Lions, France), the longest wave period recorded was 14.4 s, and swells (mean period larger than 7 s) represent only about 5% of the observations, 50% of which had a height larger than 3 m (Guizien, 2009).

7.2.2. Impacts on ecosystems

Because of scarcity of such swell events and wave damping in deep waters, storm swell effects on ecosystems have been poorly studied. Two kinds of impacts on shallow benthic ecosystems have been considered: wave-induced bed shear stresses may either directly affect benthic organisms (fauna and flora) or indirectly disturb their habitat and food quality through the induced sediment dynamics. In the Mediterranean basin, it has been suggested that these direct effects control the spatial distribution of some species along the cross-shore gradient (*Pinna nobilis* in Garcia-March et al., 2007), control the population dynamics of other species (*Paracentrotus lividus* in Hereu et al. (2004), the emblematic *Posidonia oce*

anica in Balestri et al. (2006), *Ditrupa arietina* in Labrune et al., 2007) or stress nutrition activity (Stramonita haemastoma in Rilov et al., 2005). As far as indirect effects are concerned, storm swells provide the energy for the physical transfer of riverine, fine-grained sediment from the inner shelf to the mid-shelf (Guillén et al., 2006). However, the effects of fine-grained deposits after a resuspension event on benthic ecosystems may not be positive: indeed, Pusceddu et al. (2005) showed that although enriched in organic matter, sediment in suspension (caused either by swells or trawling) had a lower nutritive quality for benthic fauna. Additionally, contaminants are often adsorbed on these fine-grained sediment fractions (Radakovich et al., 2008) and can be released under swell agitation (plutonium in Lansard et al., 2006), which would facilitate its trophic transfer to filter feeders (PCB in Charles et al., 2005).

Other impacts of sediment disturbance under swells should be expected on the pelagic ecosystem, as evidenced by experimental controlled trawling studies performed within the INTERPOL EC Program (pore water nutrient release, Durrieu de Madron et al., 2005b; enhanced bacterial carbon production, Polymenakou et al., 2005; changes in viable dinoflagellate cyst distribution in the sediment, Giannakourou et al., 2005). Finally, the stirring effect of waves in the upper part of the water column would destabilize or inhibit thermo-haline stratification and affect primary production from shallow to deep waters. However, in shallow waters near the shore, swell effects are often combined with fresh and nutrient-rich water inputs that complicate the assessment of the swells' contributions to the biogeochemical cycles based on observations (Grémare et al., 2003). Thus, modeling appears to be a necessary tool to discriminate between concomitant forcings and to integrate opposite effects of a single forcing. Progress on ecosystem and sediment transport modeling in relation to storm swell forcings is reviewed later in this paper (Chapter 8 on Modeling, section on sediment transport models).

7.2.3. Expected alterations

Swell predictions are not a direct product of General Circulation Models (GCM). Thus, to infer the evolution of extreme swell events, a reliable proxy based on GCM outputs is required. Swells result from the dispersive evolution and propagation of wind waves, which build up by the growth of sea surface perturbations caused by winds applied over a fetch. Long fetch and strong winds (intensity or duration) create highly energetic wind waves, allowing the

emergence of large swells. However, wind is also not a direct GCM output, but it is closely related to pressure gradient fields, which are described in GCM. In this respect, Lionello and Sanna (2005) described the Mediterranean wave climate variability over the 1958–2001 period according to two main wind regimes (northerly Mistral/Etesian and southerly Libeccio/Sirocco) and found seasonal correlations between the average significant wave height and large-scale windstorm track indicators (NAO and Indian Monsoon). However, their study underlined the difficulty in reconciling climate studies with trends in the occurrence of extreme events. Their large-scale study over the whole Mediterranean basin limited the mesh resolution, which tends to underestimate wave predictions. Additionally, their wave climate modeling was assessed on monthly averaged values, which are not good indicators for short-lived swell events (less than 2 days, Grémare et al., 2003). Nevertheless, intense cyclone occurrence is a prerequisite for the occurrence of large swell events. As a consequence, the trend in cyclone frequency and intensity predicted by GCM should indicate an alteration of the storm swell occurrence. Pinto et al. (2007) examined possible changes in the storm track and cyclone activity over the Northern Hemisphere based on simulations of recent climate conditions (1960–2000) and future climate conditions (2060–2100). For the Mediterranean basin, they concluded that more intense cyclones should decrease by 22–37% (depending on the scenario) over the extended winter (October–March). Leckebusch et al. (2006) also predicted a decrease in cyclone activity in Southern Europe by comparing four GCM predictions for the 21st century. This should lead to reduced storms over the Mediterranean in the future.

7.3. Impact of dense water cascading on slope and deep-sea ecosystems

7.3.1. Current knowledge

Dense water formed over the continental shelf and cascading down the slope is responsible for shelf-slope exchanges in many parts of the world ocean (Ivanov et al., 2004). A number of northern Mediterranean shelves in the NW Mediterranean Sea, Adriatic Sea, and Aegean Sea are known to be regions of dense water formation during winter due to the evaporation and cooling of shelf water by strong and cold northern winds (Ivanov et al., 2004; Durrieu de Madron et al., 2005a and the reference therein). The quantity of dense water formed over and exported from the shelf is highly correlated with atmospheric conditions. During years that are colder than average, most of the dense water is formed over the shelf cascade into the deep ocean, whereas during warmer years, dense water is mainly consumed by mixing with lighter surrounding water, and only a small quantity escapes the shelf, flowing along the coast without sinking. The overflowing and cascading of these dense shelf waters on the slope during the coldest years represent major mechanisms of matter and energy transfer from the surface to the deep ocean (Canals et al., 2006; Heussner et al., 2006). The frequency of such events is poorly known, but it is believed to be characterized by a sub-decadal recurrence (Béthoux et al., 2002b; Herrmann et al., 2008). For example, since 1993, three extreme cascading events have been observed in 1999, 2005 and 2006 in the Gulf of Lion (NW Mediterranean). During the 2005 event, the volume of shelf water exported to the deep slope and basin amounted to 2270 km^3 and represented about 80% of the dense water formed on the shelf (Ulses et al., 2008a). By comparison, this volume is equal to twice the volume of the shelf, or about 40 years of the average Rhone river water discharge. Transfer pathways from the shelf to the slope are generally localized because submarine canyons that drain and speed up the bottom flow largely control cascading. Meanwhile, the effect can be felt at a much lar-

ger scale, as it eventually spreads over a large distance and can be traced over the entire deep basin (Béthoux et al., 2002b).

7.3.2. Impacts on ecosystems

The impacts of extreme cascading events on ecosystems are multiple and contrasted, as they can induce abrupt physical and chemical changes of the slope and basin environments.

On the one hand, the concomitance of the late winter phytoplanktonic bloom with dense shelf water formation on the shelf allows the rapid transport of large quantities of fresh, highly nutritive organic matter on short time-scales to the slope and the basin, which may have a profound impact on the fueling of deep benthic ecosystems (Canals et al., 2006). For instance, there is evidence that the modification of the physical–chemical conditions that occurred between 1992 and 1994 in the Cretan Sea (eastern Mediterranean) caused a significant shift in faunal abundance and diversity (Danovaro et al., 2004).

On the other hand, a strong bottom current (up to 1 m s^{-1}) associated with intense cascading events has the potential to erode and transport large quantities of sediment both on the shelf (Bourrin et al., 2008) and slope (Puig et al., 2008) environments. The impact can be locally catastrophic but ecologically significant in terms of population dynamics. As such, hydrodynamical and sedimentological conditions can disrupt the existing populations, remodel the sea-floor and expose new surfaces for colonization. For instance, in the NW Mediterranean basin, there is evidence that the major events that occurred in 1999 and 2005 provoked the disappearance of deep-sea shrimp, *Aristeus Antennatus*, populations from their fishing grounds, producing a temporary fishery collapse. Despite this initial negative effect, the transport of particulate organic matter associated with cascading appears to enhance the recruitment of this species in the following years (Company et al., 2008). These events can thus promote high levels of deep-sea biodiversity both through the creation of a mosaic of different topographic conditions and by offering new opportunities for colonization and speciation. Finally, it is noteworthy that the massive flushing of sediments also transports pollutants, thus cleaning the shallow coastal environments while also contaminating deep, sensitive areas. Studies indicate a contamination of the deep organisms by extremely toxic pollutants has occurred (e.g., organotin, Borghi and Porte, 2002).

7.3.3. Expected alterations

Recently, Herrmann et al. (2008) investigated the impact of atmospheric inter-annual variability and climate change, under IPCC A2 scenario forcings, on dense water formation over the Gulf of Lions shelf. These numerical modeling experiments suggested that dense water formation over the shelf in the future would be strongly reduced due to the stronger stratification of the water column, and cascading would practically disappear because most of the dense water formed is consumed over the shelf by mixing, and a very small part escapes the shelf, mainly in the surface layer.

The reduction of the frequency of the most intense episodes of dense shelf water formation implies a severe reduction of the injection of organic matter into the deep ecosystems as well as the environmental perturbations that might affect deep-sea biodiversity.

7.4. Saharan dust, deposition from biomass burning and intense rains

7.4.1. Current knowledge

The Mediterranean Sea is submitted to contrasting atmospheric inputs from natural (mainly from the Sahara) and anthropogenic (numerous sources all around the basin) origins, and it has been shown in the past decade that these inputs represent an important source of new nutrients to the system (see Chapter 5, Influence of

nutrient sources and stoichiometry). Among these atmospheric inputs, some can be qualified as extreme events because they are associated with sudden and massive inputs of material to the surface waters and can affect an important percentage of the entire Mediterranean Basin. Intense wet and dry deposition of dust particles provides significant amounts of new nutrients and pollutants to the surface mixed layer. These events are relevant to the biogeochemistry of the Mediterranean Sea. When occurring during the 6-month stratification period, such events can also provoke profound changes in the physical structure of the surface mixed layer. It also has been shown recently (Ternon et al., 2010) that strong POC fluxes can result from a combination of forcings (winter mixing or Saharan events, particularly in extreme cases), biological (zooplankton) activity, and organic-mineral aggregation, inducing a ballast effect. For example, the extreme Saharan event of February 2004 exported ∼45% of the total annual POC compared to an average of ∼25% for the bloom period that year. This emphasizes the role played by more extreme Saharan events in the carbon export efficiency in the NW Mediterranean Sea, as such events are more efficient in transferring POC to the deeper layers than the spring bloom itself. Although specific experimental approaches have shown its importance (see, e.g., Pulido-Villena et al., 2008, 2010; Bonnet et al., 2005; Ternon et al., 2010), the understanding of the atmospheric contribution to the global biogeochemical functioning of the Mediterranean Sea has been hardly been taken into account in models, and the particular question of extreme events has been almost totally ignored.

Three types of extreme atmospheric events can be relevant to the biogeochemistry of the Mediterranean Sea.

First, strong Saharan events can bring large amounts of particulate matter (Fig. 16) and associated nutrients (phosphorus and iron) to the ocean surface in a few hours. It has been demonstrated that dust deposition in the Mediterranean basin is dominated by events of high magnitude and low-frequency (Loÿe-Pilot and Martin, 1996); only few events are responsible for the annual deposition of dust over the whole Mediterranean (estimated to be 40×10^6 tons year^{-1}, Guerzoni et al., 1999), and some extreme dust events bring the same amount of dust in a few hours as the cumulated amount over several years of low deposition (a good example is the dust fall that occurred on February 20th, 2004 in the northwestern Mediterranean, which represented a dust flux

of up to 22.2 g m^{-2} in some locations in Corsica and the French Riviera (Bonnet and Guieu, 2006; Ternon et al., 2010), compared to the average annual dust flux of 12 g m^{-2} year^{-1} established from a 12-year series (Loÿe-Pilot and Martin, 1996). Such extreme events are often associated with strong winds but not necessarily with important rainfall. Remarkably, those events do affect large areas of the basin; according to satellite images, plumes measuring as large as half of the basin are observed (Fig. 16), but there are uncertainties about how much of the dust actually deposits in the open sea.

Second, intense summer storms that occur after long periods of drought can trigger the wash-out of the atmosphere over several thousand meters in a short time; large rainfalls with low pH cause strong inputs of pollutants and anthropogenic species, including nitrogen. For example, some summer storms can deliver up to 6000 µmol event^{-1} of inorganic nitrogen (Martin et al., 1989; Loÿe-Pilot et al., 1990, Loÿe-Pilot unpublished values) and 17 µmol event^{-1} of inorganic phosphorus (Migon and Sandroni, 1999) in a few hours. The inputs to the open waters of the Mediterranean are even more important in the case of mixed events when Saharan dusts are mixed with anthropogenic components (Loÿe-Pilot and Morelli, 1988; Ternon et al., 2010), as illustrated in Fig. 16. In such a case, in addition to bringing bioavailable nitrogen, acid anthropogenic components can alter the dust particles and increase the release of biogeochemically active elements (such as Fe, P). Those mixed events require specific attention, as very little is known about their specific inputs.

Thirdly, "pyrogenic events" are linked to huge forest fires that frequently occur in the summer in the Mediterranean region: recent examples are the fires that occurred in 2003 during the heatwave that hit Europe, particularly France, and the fires that occurred in Greece in the summer of 2007, in which 2% of the total surface of the country burned (Boschetti et al., 2008). Such fires produce large amounts of gases and particles from biomass burning and soil particles lifted during the fires. When transported offshore, which is often the case with the Mistral wind in France, these events represent a source of nutrients for the marine ecosystem. Pyrogenic emissions represent a significant source of dissolved iron (DFe) to the surface waters at the regional scale; Guieu et al. (2005) showed that the 2003 fires were responsible for 85% of the DFe increase observed at that time in the surface
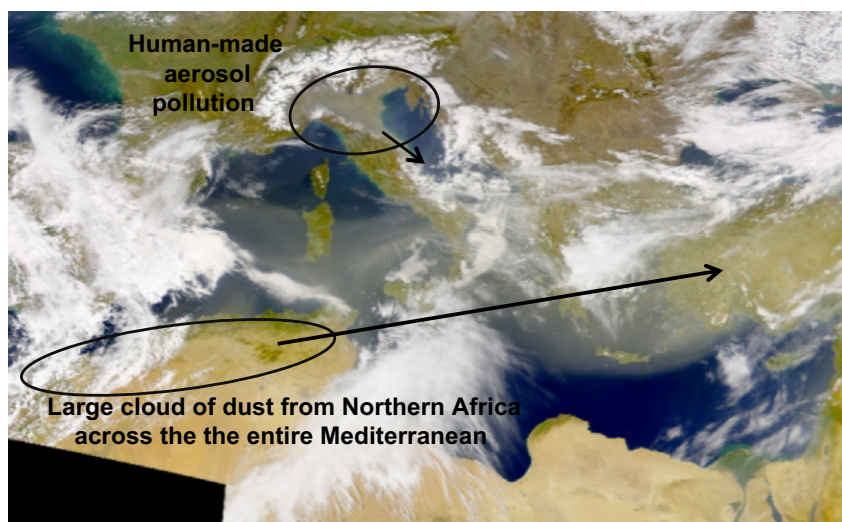
Fig. 16. Illustration of a large-scale dust event in the Mediterranean region. On March 4, 2002, SeaWiFS observed from space this large cloud of dust blowing from northern Africa across the Mediterranean Sea and southern Italy, Albania, Greece, and Turkey, i.e., all along the Mediterranean's northeastern shoreline. This event also illustrates well the mixing of those natural particles with anthropogenic aerosol. This confluence is clearly visible south of the Italian Alps and over the Adriatic Sea. (Image courtesy the SeaWiFS Project, NASA/Goddard Space Flight Center, and ORBIMAGE).

mixed layer in the Ligurian Sea. It should also be the case for dissolved phosphorus and nitrogen, as N and P are major components emitted from biomass burning; organic components are mineralized during fires, producing different, easily soluble components emitted as gas (N) or aerosols (N, P).

7.4.2. Expected alterations

The forcings in our case are as follows: (a) the chemical composition of the atmosphere and (b) meteorological conditions. They can be modified by global climatic change and/or the increase of the regional anthropogenic pressure (such as desertification and increase of the population in coastal areas).

The evolution of climate conditions (i.e., changes in the rain regime, an increase in temperature, and an increase in heatwave occurrence) clearly indicates a dryer and warmer summer climate in the Mediterranean basin (Somot et al., 2008; Déqué, 2007; Hertig and Jacobeit, 2008). This may have profound implications on the atmospheric fluxes and deposition type (dry vs. wet; particulate vs. dissolved), which directly impact the bioavailability of elements reaching the seawater. However, the on-going scenario of a warming atmosphere and surface water (Somot et al., 2008) might increase the stratification of the surface waters in the Mediterranean Sea. Therefore, the biogeochemical impact of extreme deposition events might be more pronounced in the future, particularly during the stratification period.

The temporal pattern of Saharan inputs (cf. Loÿe-Pilot and Martin, 1996; Guieu et al., 2010; Ternon et al., 2010) displays a high inter-annual variability. This variability may perhaps display some decadal periodicity; in recent years, the occurrence of events with extremely strong fluxes ($\geqslant 20\,t\,km^{-2}\,event^{-1}$) was significantly higher than in the 1990s. The reasons for those fluctuations are not well understood. An increase in Saharan dust transport over the past decade was reported from satellite monitoring (Antoine and Nobileau, 2006), but thus far, no obvious scenario of an increase vs. decrease can be proposed by the current models, and this is a question that is usually considered in the context of CHARMEX (Dulac, et al., in preparation).

The Mediterranean surface receives anthropogenic aerosols from industrial and domestic activities from populated areas around the basin and other parts of Europe. Due to increasing demographic pressure, atmospheric fluxes from anthropogenic sources (such as emissions from incinerators) are expected to increase rapidly (Lionello et al., 2006). Pyrogenic inputs are predicted to increase in relation to forest fires linked to heat waves and generalized summer drought. We may thus expect a scenario in which atmospheric inputs are increasing. Increasing reactive nitrogen from anthropogenic activities mixing with Saharan dust might have a positive fertilization effect on biota by bringing bioavailable-N and -P to the Mediterranean surface waters, particularly during the stratification period.

7.5. Heat waves and their consequences

7.5.1. Current knowledge

Temperature is an important control on marine ecosystems. Both the physiology of marine organisms and the functioning of the ecosystem (production vs. respiration) are affected by temperature. The alterations of hydroclimatic conditions, such as heat waves and marine water warming, may promote deep impacts on marine ecosystems, particularly because they occur on short timescales in comparison with average species evolution rates. Predictions for future changes in biodiversity are particularly difficult due to the complexity of the marine biodiversity and connectivity between species (Harley et al., 2006). For instance, heat stress can induce direct alterations of organism physiology, but indirectly, it may also favor the growth of virulent pathogens,

which may thereafter weaken individuals presenting less defense capacities (Bally and Garrabou, 2007). In addition, summer heat waves often occur when food availability is low. Furthermore, for several species, they occur just after the extensive energetic effort invested in reproduction during late spring, which synergistically drives drastic metabolic constraints (Coma and Ribes, 2003). Finally, ecosystem modifications most often do not occur on a linear (gradual) scale but rather in sudden phase shifts, which correlate with species replacement or even mass mortalities. A better understanding and definition of the critical points corresponding to ecological thresholds, as well as global synergisms in the marine web, represent crucial steps toward better long-term biodiversity management and protection.

7.5.2. Impacts on ecosystems

The recent climatic trends with warming of the marine waters in the Mediterranean Sea are inducing significant responses by the marine ecosystems at various levels all along Mediterranean coasts (Francour et al., 1994). First, because global warming modifies both the food web and the biological cycles of several pelagic species, it affects pelagic productivity, with major concerns for some fish populations, which are already under high anthropogenic pressure. Second, temperature alteration leads to shifts in the species' geographical distributions, drawing new patterns in community composition or migration (Chevaldonné and Lejeusne, 2003; Rosenzweig et al., 2007). Indeed, to escape thermal stress, a frequently observed comportment is shifts in distribution areas towards higher latitudes or depths. Moreover, temperature increases also favor the arrival of new so-called tropicalized species, particularly those entering through the Lesseps channel (Bianchi, 2007). Finally, the culminating impact of environmental changes certainly concerns fixed living species, such as sponges or conidarians. Indeed, even when a free-living phase exists at early stages of development, juvenile and, thereafter, adult individuals have to settle at a site where environmental parameters are favorable to development throughout their lifetimes. This raises many concerns when considering the survival, in a rapidly changing environment, of such long-lasting animals, which can grow over several decades. To face new environmental conditions, fixed organisms have to modify their physiology (e.g., in terms of metabolic rates, nutrition, and defense systems). When such acclimatizing processes are overcome, there is a direct risk of mortality. In this situation, the entire population can only rely on reproductive dissemination of future generations in more favorable areas to survive. However, in case of insufficient reproductive effort (either in terms of mass or dissemination distance), there is a risk of mass mortalities and even of total species extinction.

Several episodes of such mass mortalities of rocky benthic macro-invertebrates (mainly gorgonians and sponges) have been observed in the last few years, illustrating the complexity of ecological responses. In the case of the summer of 1999, mortality was not correlated with a maximum peak in seawater temperature but was linked to an abnormal duration of the heat wave (Garrabou et al., 2009), which drove the thermocline significantly deeper than usual (below 40 m). Both shallow and deeper populations were impacted with unprecedented intensity, rapidity and geographic distribution. Even after several years, different impacted populations did not show a complete resilience (Cerrano et al., 2005). During the summer of 2003, a new extensive mass mortality event was observed for the entire northwestern Mediterranean region but primarily impacted shallow populations. Indeed, during that summer, sea surface temperatures reached unprecedented maximum values for short durations (2 weeks), which did not significantly alter deeper bathymetries (Garrabou et al., 2009). These two examples, both directly connected to particularly low wind
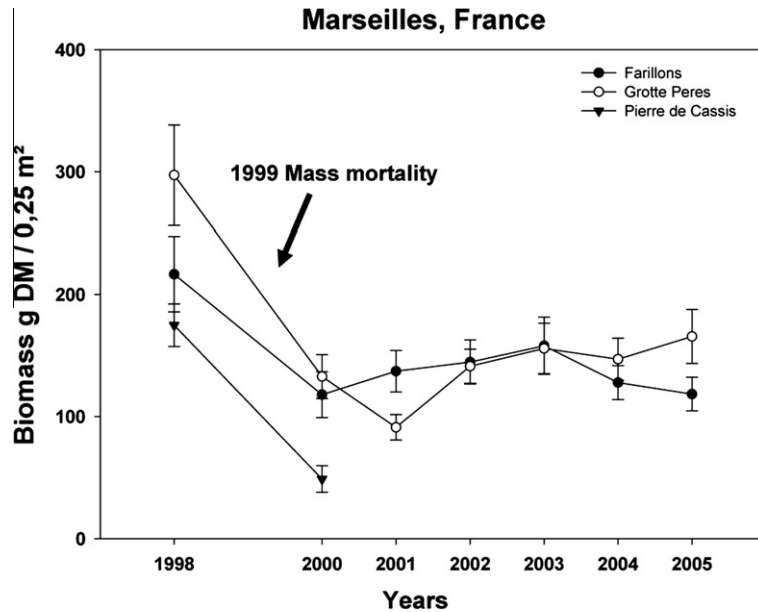
Fig. 17. Time-course evolution of *Paramuricea clavata* biomass from three populations at 20-m depth between July 1998 and September 2005 from the Marseilles area of France. Values are mean ±SE in g of dry mass (DM) per 0.25 m^{-2}. The size was used to estimate biomass using the relationship reported by Coma et al. (1998): $B = 0.002\,H^{2.61}$, where B is biomass of DM in g and H is the colony height in cm. Corrections for biomass loss caused by injury were introduced to calculations by subtracting the percentage of biomass equivalent to the percentage of colony surface affected by injury. This figure clearly displays the 1999 mass mortality event (indicated by the arrow), which was correlated with anomalous summer warm temperatures and which affected both shallow and deep (to −40 m) populations of *P. clavata*, as well as many other sessile invertebrates (see Pérez et al., 2000). The impact of the 1999 mortality resulted in a biomass decrease of approximately 50% from initial values (1998). Populations did not show any sign of recovery of biomass at the end of the study (2005). The studied populations were not affected by the 2003 mass mortality, which affected shallower depths in the Marseilles area (see Garrabou et al., 2009). This figure, which corroborates the reports of Linares et al., 2005, Linares, 2006 and Cupido et al., 2008, clearly illustrates that the resilience of such long-lived gorgonian populations is very low. It further shows that the risk of extinction depends not only on the intensity but also the frequency of mass mortality events associated with summer heatwaves (redrawn from Boury-Esnault et al., 2006).

regimes, illustrate that several modalities of thermal stress can end with extensive mass mortalities.

7.5.3. Expected alterations

A part of hydroclimatology research aims to better analyze how past, actual, and future trends in climate systems can influence seawater temperatures both at a global or very local scale. The few available works concerning the northwestern Mediterranean Sea clearly demonstrate a global positive increase of mean water temperatures, even for deep bathymetries (Béthoux et al., 1999). This roughly corresponds to a +1 °C increase over the last century but with a clear acceleration during the last three decades (Romano, 2003). This trend accompanies both an increase in heatwaves (both in frequency and amplitude) and a decrease of cooler episodes. Modification in species' geographical distribution will result in a significant redrawing of community composition patterns. Optimistic points of view may argue that such changes will result in new equilibriums, offering ecosystem renewal and reorganization. However, several past and present examples demonstrate that global ecosystem regime shifts can also initiate an avalanche of extinctions and irreversible habitat degradation (Thomas et al., 2004). For instance, when gorgonians massively die in a certain region, this represents a loss of biodiversity per se. However, gorgons are also important structuring agents of the coralligenous ecosystem, offering both the protection of egg deposition and the protection of juveniles of several fish species (including some of commercial interests). In addition, when the coralligenous habitat is highly impacted, it becomes extremely vulnerable to macroalgal proliferation, which thereafter renders the anchoring or growing of new individuals even more complicated (Ballesteros, 2006). Consequently, the most catastrophic scenario (i.e., mass extinctions) has to be accounted for, particularly in the Mediterranean context of high anthropogenic and climate pressure.

In conclusion, the direct links between expected increasing heatwaves and marine Mediterranean ecosystem degradation remain a nearly complete terra incognita, requiring extensive studies both in the field and in laboratory experiments to significantly extend our knowledge from molecular activation pathways to metapopulation dynamics (Fig. 17).

8. Ecosystem response to changes in the Mediterranean Sea

The Mediterranean is globally considered an oligotrophic sea and represents 0.82% of the world oceans. However, despite its small extension, it presents considerable heterogeneity and gathers from 4% to 18% of the world's marine diversity depending on the phylum considered (Bianchi and Morri, 2000; UNEP-MAP-RAC/SPA, 2008). The actual biodiversity has appeared quite recently and is linked to the opening of the Gibraltar strait after the Messinian crisis more than five million years ago (Bianchi and Morri, 2000), after which the hypersaline areas were recolonized by Atlantic species. Is the Mediterranean Sea going to face another crisis related to biodiversity, and how will this influence the geography of species habitats and resources of this basin? What are the driving forces, and how can we estimate the role of anthropogenic impacts? Since global warming accelerated in the late 1980s, northward advances of southern species and retreats of northern species have been recorded worldwide in both pelagic and benthic species (Beaugrand et al., 2002) and appear to be largely temperature-controlled. Invasive species represent a recognized threat to diversity and the abundance of native species as well as a threat to the ecological stability of the infested ecosystems. The warming of the Ligurian Sea favored the penetration of warm-water species, such as the ornate wrasse Thalassoma pavo, which from 1985 onward established large and stable populations

(Francour et al., 1994). In the Mediterranean Sea, in contrast to the North Atlantic Sea, there are few large-scale studies or even time-series on zooplankton, nekton or benthic communities aside from studies of exploited fishes. Nevertheless, the few time-series reported have highlighted changes in these ecosystems. For example, analyzing copepods over a long time series, from 1967 to 1993, at Point B in the Bay of Villefranche, Molinero et al. (2005) identified a cascade of links between the large-scale climate pattern playing out in the North Atlantic and the local climate variability governing the NW Mediterranean. The chain of events appeared driven by the long-term temperature anomalies that, in turn, played a key role in the top-down control of copepods by jellyfish.

The concern is now to understand how the Mediterranean biodiversity will react to this changing environment. How will species, communities and production vary in space and time in response to the abiotic and biotic changing factors? What are the consequences of human perturbations, from the local scale to the global scale, of the Mediterranean?

To answer these questions, we have to understand the spatial and temporal distribution of species ecophases and their importance in biogeochemical processes. The species ecophase habitat can be related to the ecological niche, as defined by Hutchinson (1957). This definition includes the geographical, physical and chemical features of marine areas and also biological interactions in species assemblages, which sustain marine populations throughout their full life cycle. The habitat can be defined by its structure (spatial arrangements of patches), function (connectivity between patches) and changes that are alterations of its structure or function (e.g., fragmentation or human use). Comparing species habitats will help to draw ecosystem boundaries to define eco-regions. Eco-regions will need to be defined in terms of structure (species or ecophase diversity) and function (trophic web or productivity) in connection with abiotic or anthropic forcings.

In some cases, the use of an indicator or "sentinel" species might help to address these objectives: Posidonia oceanica (Pergent-Martini et al., 2005), gorgonians, micronekton and top predators, for instance, are sometimes pertinent to modifications of the ecosystem. In other cases, the indicator should be at the level of a group such as echinoderms and fishes in the coastal zone or a community, when looking at pelages. As Pergent-Martini et al. (2005) stated, a "good descriptor at the Mediterranean scale must (i) provide reliable information about the quality of the environment; (ii) be used by most people and (iii) provide answers to the actual questions of stakeholders and managers.

8.1. Impact on coastal and shelf ecosystems

8.1.1. Current knowledge

Coastal and shelf zones encompass different ecosystems depending mainly on the type of substrate. Posidonia oceanica is an endemic marine phanerogam species that is protected in France (Mediterranean Action Plan of Marine Vegetation; UNEP). It forms seagrass meadows from the littoral to 30–40 m depth, indicating a stable environment (Francour et al., 1999). These meadows stabilize the sediment, are involved in nutrient recycling and are habitats of many invertebrates and fish. Many threats are known to weaken these habitats, such as invasive algae, eutrophication, the accumulation of trace metals, dredging, anchoring and an increase of turbidity (Francour et al., 1999). For these reasons, Posidonia oceanica is proposed by Pergent-Martini et al. (2005) as a proxy for monitoring the coastal environment because of its importance for many coastal species.

Benthic communities on rocky substrates are characterized by their dominance in terms of biomass of long-living species. These communities are among the most diverse in the Mediterranean Sea, and they are highly sensitive to perturbations because of their

long life cycles. On the rocky sub-littoral zone, benthic suspension feeders, such as tunicates, gorgonians and sponges, benefit from suspended particles, whereas grazers, such as sea urchins (Paracentrotus lividus and Arbacia lixula) or the limpet Patella caerulea, structure algal communities (Ruitton et al., 2000). Overgrazing can be observed in some areas of high herbivore population densities, but a low density also has consequences in the structure of the algal community and has an impact on the benthic assemblages.

Even for non-coastal fish, coastal zones, as highly productive areas, are often used as nurseries for juveniles or for spawning. Posidonia meadows are important for adults (Harmelin-Vivien, 1984) or fish larval assemblage. They show spatial and temporal variations (Francour, 1997; Deudero et al., 2008). Because they prey on herbivorous echinoderms, fish have a positive indirect effect on algal communities (Sala and Zabala, 1996). The structural complexity of rocky sub-littoral zones influences some fish species where they feed and shelter; in this area, herbivorous and omnivorous fishes seem to control algae in addition to invertebrates (Ruitton et al., 2000).

Off the coasts, most of the studies on demersal fishes on the continental shelf and slope were mainly conducted at the sub-regional scale, ranging approximately from 100 to 300 km of coast-line (e.g., Gaertner et al., 2005a, in the east cost of Corsica, Gristina et al., 2006, in the south part of Sicilia, and Kallianiotis et al. (2000), in the North Aegean Sea). All of these studies showed the dominant influence of depth on the spatial organization of demersal fishes (Kallianiotis et al., 2000; Colloca et al., 2003; Gaertner et al., 2005a; Garofalo et al., 2007), whereas some studies also showed the influence of substratum type and macrofauna composition (Gaertner et al., 1999) or fishing pressure (Gristina et al., 2006). In the Gulf of Lions, the observed patterns showed limited temporal variability at both seasonal (Gaertner, 2000) and annual scales (Gaertner et al., 2002). Contrary to what has been usually found regarding species composition, depth may have only a limited effect on the spatial distribution of diversity of demersal fishes within the continental shelf (Mérigot et al., 2007a). On a larger scale, knowledge of demersal fish patterns is very scarce and primarily based on the pooling of knowledge issued from disparate regional data sets (e.g., Garibaldi and Caddy, 1998; Bianchi and Morri, 2000; Quignard and Tomasini, 2000). Among the rare, large-scale studies based on the analysis of standardized data sets (MEDITS programme, Bertrand et al., 2002), Gaertner et al. (2005b) showed the influence of meso-scale permanent hydrographical structures on the distribution pattern of fish species composition and diversity. On the basis of similar data, Gaertner et al. (2007) also showed that the expected large-scale, longitudinal, decreasing trend in species richness did not occur at the scale of the entire northern Mediterranean Sea. Contrary to what is usually expected (e.g., Garibaldi and Caddy, 1998 and Quignard and Tomasini, 2000), this result strongly suggests that Atlantic inflow does not play a key role in the present spatial pattern of fish species richness within the northern Mediterranean Sea. However, all of the large-scale groundfish studies were focused on a limited number of diversity descriptors, such as species richness or evenness (Gaertner et al., 2005a; Gaertner et al., 2007), whereas diversity would be better characterized through a multi-component approach (Mérigot et al., 2007a,b).

8.1.2. Expected alterations

Benthic communities are among the most diverse in the Mediterranean Sea and are highly sensitive to perturbations because of their slow dynamic. Overfishing, invasive species and climatic changes are the main perturbations that significantly affect these communities. Mass mortality events were observed in 1999 and 2003 of marine invertebrates, such as sponges, cnidarians, bivalves, ascidians and bryozoans, in the upper 40 m layer of the NW

Mediterranean (Pérez et al., 2000; Cerrano et al., 2005; Romano et al., 2000; Garrabou et al., 2009). The authors assume that it was due to thermal anomalies, with high temperatures vertically homogeneous to 40 m for over 1 month. Changes of communities and species spatial distribution are some of the consequences of frequent thermal anomalies. Garrabou et al. (2003) have shown the increase of thermophile species in the north occidental Mediterranean, whereas the more cold-temperate species seem to decline. In total, these authors showed significant a change in distribution for 46 species.

Human activities significantly affect the diversity of coastal fish. Francour (1994) showed that there are significant differences in the diversity patterns of fish between no-take areas, where fishing is not allowed, and non-protected areas. The reserve effect contains higher proportions of large fish, and abundances are also higher. In a recent study, Dufour et al. (2007) showed that the age of marine-protected areas is more important, in term of diversity, than the size of the marine-protected areas, when they are more than 500 ha. However, new species are observed regularly in the Mediterranean regardless of whether they are due to lessepsian migrations, even for common groups (Francour, 2008; Francour and Mouine, 2008; Francour and Mangialajo, 2007; Francour and Javel, 2003; Francour and Mangialajo, 2007; Sartoretto et al., 1997). Climate change has also influenced fish communities. As noted by Francour et al. (1994) and Perez (UNEP-MAP-RAC/SPA, 2008), some species that were rare are now abundant in the north occidental Mediterranean even in the coldest regions, such as in the Gulf of Lion. Other species, such as *Epinephelus marginatus*, even reproduce in the north occidental basin, which was not previously the case (Bodilis et al., 2003a,b). More intriguing is that this change of temperature may favor some commercial species in the western basin (Sabates et al., 2006), such as *Sardinella aurita*, but it will not favor all of the species, as a decline was observed for *Sprattus sprattus* (Bombace, 2001), *Thunnus thynnus* and anchovies. Indirect positive effects are also observed for *Solea solea* in the Gulf of Lions, the abundance of which has increased due to higher flow from the Rhône river that favor polychaetes, preys of soles (Salen-Picard et al., 2002). No one knows what will be the impact of new top fish predators in the coastal zone of the north occidental basin.

No a priori benthic ecosystems can be described as indicators of climate and/or anthropic forcings because our knowledge is too sparse. The lack of a database on quantitative anthropic and environmental drivers limits an objective analysis to forecast possible changes of species composition and diversity of benthic or demersal assemblages on the continental shelf and slope. In this context, based on standardized data, there is an important need to provide multiple scales of information in the northern and southern Mediterranean Sea: (i) spatial and temporal patterns of species composition and diversity by means of a multi-component approach (e.g., species richness, evenness, and taxonomic and functional diversities), (ii) a database of anthropic and environmental drivers that generate these patterns (e.g., fishing pressure, productivity, habitat complexity, and temperature), (iii) an analysis of the role of the main complementary diversity components in demersal ecosystem functioning and (iv) an understanding of the possible consequences of diversity loss for ecosystem services.

8.2. Impact on pelagic realm ecosystems

8.2.1. Current knowledge

Despite its oligotrophic nature, the primary production rates reported for the Mediterranean (Estrada, 1996) are comparable to the values reported for the rest of the world (Morel and Andre, 1991). Mechanisms enhancing fertility at certain periods of the year in connection with hydrographic structures are important in creating regions with intense biological activity (Morel and Andre, 1991).

However, most of the existing results about Mediterranean plankton were obtained locally, and synoptic data are scarce. Several cruises in the 1970s and 1980s were performed, but the data analysis and interpretation were not performed at the regional level. Despite this low level of available information, large differences between East and West basin communities, between northern and southern communities, and between neritic and oceanic communities are obvious. From the observations on the physical structures and the information derived from satellite observations, we can propose the first regionalization. Because physical forcings are the main drivers for the spatial distribution of nutrients, marine production occurs at upwelling. Upwelling of nutrient-rich waters occurs in regions with winter convection (Ligurian sea and Gulf of Lions) or regions with high meso-scale variability (all along the AW and in south of the North Balearic front). Therefore, one can, at first, isolate three open ocean zones in the western basin (the area north of the Balearic front, the area south of the Balearic front and the Tyrrhenian sea), and the current and coastal zones.

Despite differences in the biogeochemical features, these regions remain interconnected by the flow of AW (0–200 m) and LIW (200–500 m). This circulation may favor the transport of planktonic organisms in such a way that identifying key species may be difficult. Thus, relevant differences may often refer to species diversity, relative abundances or life cycles rather than the presence of some particular taxa. Among copepods, for instance, some characteristic species alternatively dominate during the season in the neritic and oceanic areas (Pseudocalanus sp., Clausocalanus sp., Calanus helgolandicus, *Centropages typicus*, *Temora stylifera*, Acartia sp. and *Oithona similis*). Attention should also be given to the large-scale distribution of larger crustacean zooplankton, such as krill (Labat and Cuzin-Roudy, 1996). Species such as *Meganyctiphanes norgegica*, indeed, contribute largely to the diet of numerous high trophic-level organisms (squid Illex coindetti, red tunna Thunnus thynnus, fin whales, *Balaenoptera physalus*).

Larvae of small pelagic species comprise mainly anchovy (*Engraulis encrasicolus*) and gilt sardine (*Sardinella aurita*). Bakun (1998) defines the conditions for having the best reproductive and survival success for pelagic fish as the "ocean triad". The most suitable habitats correspond to areas where three conditions are encountered in a favorable sequence: enrichment by nutrients, concentration of recruits and retention. These areas can be located where upwellings are observed, in "productive planktonic hotspots" linked to cyclonic eddies or in convergent fronts all along the circulation of the AW flow. These meso-scale features have been shown to be zones of accumulation of marine snow particles, possibly due to physical accumulation and coagulation of marine production (Gorsky et al., 2002; Stemmann et al., 2008). Marine snow particles are hot spots for pelagic biology and probably zones where the prey of small pelagic fishes is increased.

8.2.2. Expected alterations

Few studies have addressed the potential impact of global climate change on marine phytoplankton diversity and distribution for the Mediterranean Sea (Duarte et al., 2000; Goffart et al., 2002; Gomez and Gorsky, 2003; Marty et al., 2002; Bosc et al., 2004; Ribera d'Alcala et al., 2004; Marty and Chiaverini, 2010). Over a decade, pigment analysis revealed a positive trend in phytoplankton biomass in response to the lengthening of the summer stratification, accompanied by an increase of small-sized phytoplankton (picoplankton and nanoflagellates) able to support regenerated production and a decline of diatoms, which are responsible for new production (Marty et al., 2002). Other studies based on nutrients, chlorophyll-a and pigment measurements also

suggested that warming favors picoplankton and flagellates, thus promoting a shift toward a non-siliceous, regenerative system (Goffart et al., 2002). Finally, from remote sensing, it was demonstrated that in recent years, the spring bloom occurred earlier, maybe in relation to earlier water warming and high irradiance, whereas the autumn bloom tended to disappear as a possible consequence of a lengthening of the stratification period (Bosc et al., 2004). A recent study on the central Ligurian Sea supports the hypothesis that the system has not shifted toward oligotrophy because of the strengthening of winter convection during low precipitation years. Convection as deep as 2000 m has been reported by Marty and Chiaverini (2010) to occur from winter 1999–2006 (except for 2001 and 2002). Deep convection brought a high load of nutrients to the surface that triggered intense phytoplankton blooms, mainly diatoms (Marty and Chiaverini, 2010). On an annual basis, the increase in phytoplankton biomass during the dry years has compensated for the summer's low phytoplankton biomass.

Regarding zooplankton evolution, the appearance of regime shifts has been recently highlighted, with turning points in 1987 in two northern Mediterranean coastal ecosystems (Adriatic and Ligurian Sea) and their synchrony with changes in the Atlantic ocean and the Baltic and Black seas (Conversi et al., 2010). The authors pointed to the positive trend of surface temperature in the northern hemisphere as the main forcing for the concomitant changes in such far and diverse locations. From a joint study of six zooplankton time-series in the Mediterranean Sea, a synchronous cooling and warming affecting the zooplankton community was observed between Trieste, Naples and Villefranche-sur-Mer, with, again, a main turning point in 1987 from high to low abundances of zooplankton (Berline et al., in press); however, no significant links with large-scale climate indicators, such as the NAO, were found.

In the Tyrrhenian Sea, Ribera d'Alcala et al. (2004) also revealed pronounced changes in the long-term patterns of rare copepod species, which have also been noted along other Italian coasts. These changes might represent a symptom of changes occurring at a much wider spatial scale rather than the response to local forcing (Ribera d'Alcala et al., 2004). In the Gulf of Lion, changes were observed in the copepod communities in the 1957–1964, 1986–1988 and 1993–1994 periods, with a decrease in the abundances of *Temora stylifera* and *Centropages typicus* and an increase of two Clausocalanus species. These changes were attributed to the increase of the sub-surface salinity and the winter temperature in that area (Kouwenberg, 1998).

In their analysis of the zooplankton time-series in the Ligurian Sea, Molinero et al. (2008) proposed a chain of events from the large-scale atmospheric perturbation over the North Atlantic to changes in local conditions forcing the phytoplankton productions in the NW Mediterranean Sea. According to the authors, large-scale climate forcing has altered the local environment and the pelagic food-web dynamics through changes in biological interactions, competition and predation. Environmental modifications reported regarding water column stability, nutrient availability and phytoplankton composition since the early 1990s may indicate a regime change to a more regeneration-dominated system in the Ligurian Sea. They suggest that the increased abundance in jellyfish between 1987 and 1993 was favored by greater stability of the water column in warmer conditions that permitted better survival and higher reproduction. The authors also suggest that the increasing trend in temperature, the dominance of small phytoplankton and predation pressure by jellyfish negatively affected copepod populations (recruitment, life-history traits and physiological thresholds) in the early 1990s, whereas chaetognaths were surpassed by jellyplankton as the most frequent copepod prey. In such a scenario, population growth of jellyfish would continue, whereas copepods and chaetognath populations would decrease. Licandro
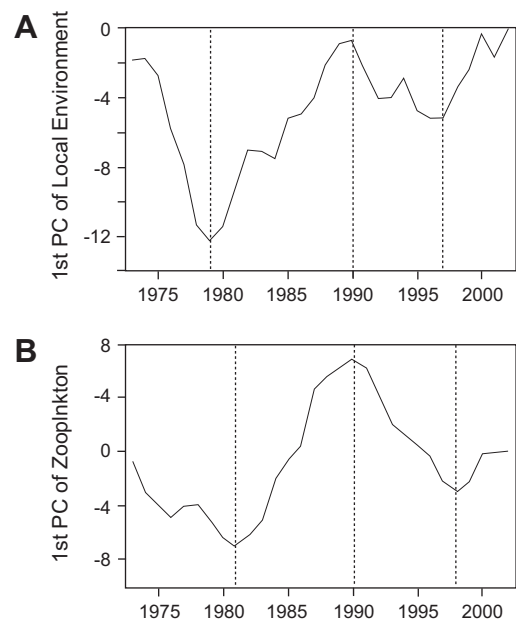

Fig. 18. Cumulative sum of annual normalized anomalies of the first principal components (PC) of (A) local environmental variables (water temperature and salinity, atmospheric pressure, rainfall, irradiance and Ekman depth) at point B in the Bay of Villefranche and (B) the abundances of zooplankton groups (copepods, decapod larvae, chaetognaths, siphonophores and jellyfish) at the same station. For (A), the first PC accounted for 33% of the general variability and was mainly driven by salinity and opposed by precipitation. The second PC (26%) reflected mainly the temperature signal. For (B), the first PC represented 44% of the total variance, and all zooplanktonic taxa contributed similar weightings in the same direction (redrawn from Coma et al., 2009).

et al. (2010) suggested that *Pelagia noctiluca* may be exploiting recent hydroclimatic changes in the northeast Atlantic to increase the extent and intensity of its outbreaks. Based on a monthly net sampling during 2 years at four locations, the authors proposed that in the western Mediterranean, the occurrence of *Pelagia noctiluca* swarms follows the progression of the Atlantic surface water stream, which flows eastwards from the Atlantic through the Strait of Gibraltar along the North African coast before circulating counter-clockwise around the western Mediterranean basin. The eastern Mediterranean and Black seas have also shown increases in jellyplankton, including ctenophores (Purcell et al., 2007). These proliferations of jellyplankton, possibly due to thermic anomalies or removal by over-fishing of their predators and competitors for mesozooplankton, are observed in many seas of the world. However, clear evidence of an increase in jellyfish in the Mediterranean Sea or globally has not been detected (Purcell et al., 2007).

A more recent study from the same Ligurian time-series updated with ten more years (up to 2003) revealed that the zooplankton, mainly copepods, recovered their initial concentrations after 2000, suggesting a quasi-decadal cycle (Coma et al., 2009; Fig. 18). In addition to the long-term warming trend, decadal climatic oscillations in the precipitation regime over the NW Mediterranean Sea has led to an increase in the upper salinity in the 1980s and in the late 1990s and early 2000s. Saline years are also years when the annual abundance of zooplankton is higher. The authors suggested that the upper seawater density increase led to intense winter convection events that brought high loads of nutrients in the surface and subsequent blooms. These blooms triggered zooplankton production, yielding the high-observed biomass of all groups during those years. Similar changes in the late 1990s were also observed in the Balearic Sea, although the hypothesis is different (Fernandez de Puelles and Molinero, 2007, studied period: 1994–2003). Low zooplankton abundances were observed

from 1995 to 1998, and a recovery of almost all groups was then observed from 2000. Such an inter-annual variability was linked to the NAO forcing. In its positive phase, the NAO drove colder temperatures during winter months, increasing the southward spread of rich northern Mediterranean waters in the Balearic Sea (Fernandez de Puelles and Molinero, 2007).

Therefore, the long-term changes of phytoplankton from large to small cells and low mesozooplankton concentrations are not straightforward, at least in the Ligurian and Catalan seas. These somewhat contradictory results on the current and future states of the pelagic ecosystem illustrate the difficulty in identifying long-term changes from decadal oscillation in short time-series of plankton. However, surface salinity appears to be a common physical indicator of changes in the pelagic ecosystem of the NW Mediterranean Sea for medusae (Morand et al., 1992; Buecher et al., 1997), dolioliids (Menard et al., 1997), crustacean (Kouwenberg, 1998; Garcia-Comas et al., in press) and phytoplankton (Marty and Chiaverini, 2010). Future investigations should examine the role of salinity in winter mixing and nutrient loading to the surface.

8.3. Impact on meso and deep-sea pelagic ecosystems

8.3.1. Current knowledge
In the meso and bathypelagic layers, the ecosystems depend on the vertical flux of resources from the surface in the open seas and from the continental slopes in the coastal regions. Temporally, the vertical flux varies seasonally, following the seasonal surface production regime (Miquel et al., 1994; Stemmann et al., 2002). However, during winter, short, intense bloom events can occur in specific physical situations. These blooms are followed by a large increase of vertical flux that may feed the mesopelagic organisms (Stemmann et al., 2002). Spatially, the lateral transport of particles from the coast is carried out in surface nepheloid layers that usually extend from the coast to the flow of the Modified Atlantic Water (Durrieu de Madron et al., 2000; Stemmann et al., 2008a). However, in the mesopelagic layer, the seaward extension of intermediate and deep nepheloid layers can be higher because the control by the current is different (Stemmann et al., 2008a).

Recent studies at the DYFAMED time-series station in the NW Mediterranean Sea have shown that the dominance of prokaryotes (Bacteria and Archaea) within the microbial community represented by biomass data increases with depth. The studies have also shown that the depth-integrated biomass of protists (heterotrophic flagellates and ciliates) in the mesopelagic layer is as large as that in the epipelagic layer and that the biomass of mesopelagic prokaryotes is controlled by both substrate availability (bottom-up control) and predation and viral infection (top-down control). Mesopelagic prokaryotes may not be simply remineralizers of organic carbon, but may also play an important role in supporting the production of organisms belonging to higher trophic levels (Tanaka, 2009).

We know from vertical nets, video profiling or acoustic observations that mesopelagic layers of organisms exist in different areas of the western basin (see Baussant et al., 1993, 1992; Stemmann et al., 2008b). Temperature profiles may explain the exclusion of organisms from some unfavorable layers, but vertical distribution also results from active migrations within a vertical temperature gradient, from hydrological structures like thermoclines, or from vertical water movements. The physical traits of the water column, which are temperature-driven, are of vital importance for planktonic organisms.

As Sardou et al. (1996) pointed out, the importance of vertical migration between the meso and epipelagic zone is crucial to estimating the vertical fluxes of particular organic matter and inorganic nitrogen (Angel, 1989; Longhurst and Harrison, 1989). Organic matter fluxes are largely higher if the vertical migrations are extensive and rapid, but data about migration processes are still required to improve vertical migration models. Among Euphausiids and fishes from the mesopelagic zone, Andersen and Sardou (1992) showed that only one euphausiid (*Stylocheiron longicorne*) and two fish species belonging to the Gonostomatidae (*Cyclothone braueri* and *Cyclothone pygmaea*) did not show migratory behavior in the Ligurian Sea. All the other species showed vertical migrations, with amplitudes ranging from 155 m to 630 m.

Gonostomatidae are the most abundant species, followed by Myctophidae (Andersen and Sardou, 1992). Palma (1990) studied their diet and found that they forage, as most mesopelagic species do, on zooplankton (mainly copepods) of wide vertical distribution. However, Myctophids are the most relevant in terms of biomass.

Among the few existing studies, Cuttitta et al. (2004) show that hydrographic features explained the distribution of mesopelagic larvae in the strait of Sicily and that larvae were found offshore more frequently than adults. Larvae found close to the coast might have been transported by an upwelling. Sabatés and Saiz (2000) showed the relationships among the prey size, prey selection and foraging abilities of six fish larvae species of the Myctophiformes. The niche differences between larvae may be an adaptation of the species such that larvae limit interspecific competition in an oligotrophic area. There are even fewer studies on the mechanisms by which mesopelagic fishes of the Mediterranean Sea accumulate reserves. Sabatés et al. (2003) studied the lipid content of some mesopelagic fish larvae. They showed that total lipid concentration values, as a proportion of dry mass, increased significantly from the larval to the juvenile stages, indicating that during their development, larvae accumulate energy reserves. These reserves are important to face the metamorphosis and habitat change associated with a change in behavior between the larval and the juvenile stage. Sabatés et al. (2003) assumed that "young fish convert energy into protein as they grow while older fish store more energy in the form of lipids."

8.3.2. Expected alterations
The availability of semi-labile DOC at depth represents an important input of energy for the deep-water microbial loop. The amount of DOC exported to depth will depend both on the DOC concentration at the surface and the amount of deep-water that forms at the surface in the NW Mediterranean Sea. The first is influenced by biological activity at the surface (both DOC production and consumption processes), and the second is influenced by climatic conditions. In general, the semi-labile DOC at depth is very quickly consumed, and this signal disappears in a few months (Santinelli et al., 2010). A consequence of this finding is that the export of DOC during Deep-Water formation plays an important role in the carbon cycle by linking Mediterranean atmospheric and surface water dynamics with deep-water microbial ecosystems, with possible consequences on larger organisms feeding on the microbial communities. Furthermore, changes in biological activity at the surface producing large settling particles may have an impact on the organisms that feed on the vertical flux.

Because of their relatively high abundance, mesopelagic fishes play an important role in the food web (Cuttitta et al., 2004; Olivar et al., 1998; Somarakis et al., 2002; Hare et al., 2001; Doyle et al., 2002). In addition, they are sensitive to environmental changes and are influenced by circulation patterns and hydrographic features. However, there are very few studies about them in the Mediterranean Sea, except in the Ligurian Sea. Because fish larvae concentrate in the epipelagic layer (Sabatés and Masó, 1990; Sabatés and Olivar, 1996) and are highly sensitive to changes in their environment, studying their assemblages can be a proxy for understanding the importance of climate change on the offshore and deep communities. In addition, the monitoring of larval diet and survival will indicate how mesopelagic fishes recruitment faces environmental changes that occur in the epipelagic zone.

9. Modeling as a tool for description and prediction of changes

Modeling is the integrative tool for investigating the question of how climate change and anthropic activities impact the cycle of biogenic elements and marine ecosystems. For this purpose, there are several steps. First, models should rely on a mechanistic description of processes to be adapted to a large range of forcing conditions. Second, models should be able to deal with the response of forcing on a key species or a trophic level and the consequences on another key species or trophic level. Third, the models should be realistic enough to reproduce the diversity of the Mediterranean ecosystem at the scale of the Mediterranean basin, namely, its contrasting patterns of nutrient availability, stratification, light and temperature between the south–north and the west–east gradients as well as between the deep basins and the coastal zones, especially along the northern coast enriched by riverine nutrient inputs. Fourth, the models should be able to simulate the past and current variabilities of the Mediterranean ecosystem, particularly the following:

– The inter-annual variations, to check if the models correctly respond to the wide variations of the mixed layer depth, especially during the winter mixing.
– The low-frequency changes of the ecosystem. This is clearly evidenced by various observations: changes in nutrient concentrations and ratios in the deep waters of the western Mediterranean (Béthoux et al., 2002a); changes of algal biomass and primary production between the 1980s and the 1998–2001 period, deduced from comparisons between CZCS and SEAWIFS time-series (Bosc et al., 2004); changes in the zooplankton population that are considered to be a regime shift linked to large-scale climate changes (Molinero et al., 2008); and the deep-sea ecosystem response to the eastern Mediterranean Transient (Danovaro et al., 2001).

Ecosystem models have to be governed by hydrodynamic and sediment transport models providing realistic conditions of temperature, vertical mixing, transport and light at the different time-scales as well as realistic boundary conditions for organic and inorganic compounds at the straits (Gibraltar and Dardanelles/Bosphorus), the river mouths and the air–sea interface.

In the following, we examine the different types of existing models and the questions that they allow us to address. Then, we analyze the need for new types of models or of coupling of models.

The first question concerns the need for budgets of biogenic elements and is generally addressed with biogeochemical models of primary production (referred to here as type I models) closed by a simplistic zooplankton compartment and by simple fluxes at the sediment-water interface. This approach, which oversimplifies the closure terms, is probably best adapted to determining the climatological functioning of the ecosystem but not to describing unsteady conditions marked by variations of the zooplankton pressure that often seems to be linked to climatic variations in the western basin (Molinero et al., 2008; Fernández et al., 2009).

A second question concerns the fate of species or communities in a complex environment. These models (referred to here as type II models) were developed with a focus on a species and may be restricted to a life stage crucial for the maintenance of the species, such as the larval stage. The behavior (nutrition, swimming) of individuals is described in relation to the forcing terms (temperature, dispersion by currents, preys and predator abundance.). The weakness of these models lies in their oversimplification of these forcings, especially in their representation of predators and prey, which are not explicitly simulated.

A third question concerns the capacity of a habitat to sustain biological production and is generally focused on commercial species. The ECOPATH models (Christensen and Walters, 2004), referred to here as type III models, represent the food chain according to functional groups interconnected by biomass fluxes that have to be balanced. This quasi steady-state approach requires fixed time-averaged biomass fluxes but does not allow for fully accounting for the variability in space and time of the ecosystem linked to external forcings (for example, climatic trends or extreme events that can have durable effects). This approach is often used for the management of fisheries or of marine-protected areas. Similar to type II models, a weakness of these models comes from the simplification of the processes regulating primary production, which may strongly impact the dynamics of the upper-levels of the food chain (Guénette et al., 2008).

A fourth question concerns the direct and indirect effects of chemical substances (organic contaminants and trace metals) on the ecosystem. There are different types of models that estimate distribution and the fate of contaminants into ecosystem compartments (water, suspended matter, sediment, and biomass). The high variability of external forces, inputs and biogeochemical processes is generally smoothed by long time periods and space scaling. Studying the impact of contaminants on biological production has lead to work on a smaller scale and to linking contaminant fate with sediment transport and plankton ecosystem models.

A fifth question arises from the Mediterranean Sea in particular, which, in spite of its relatively small size, is characterized by strong trophic gradients associated with strong gradients of meteorological and hydrological forcings (D'Ortenzio and d'Alcala, 2009). The diversity of the ecosystems potentially associated with these contrasted regions requires models that can reproduce sufficient complexity within their functional groups. Moreover, the small dimensions of the Mediterranean and the intensity of the cross-slope exchanges require models that are able to simultaneously represent coastal and deep regions.

Based on these constraints, we define below several sub-models addressing specific processes or specific parts of the ecosystem. Then, we discuss the need for coupling these different sub-models to answer the questions at the intersection of several objects.

9.1. Types of sub-models

Different sub-models have been defined to represent the cycle of biogenic elements and specific contaminants along the physical continuum, rivers, coastal and deep ocean, sediment, and along the food chain from the primary producers to the different levels of consumers and decomposers. These sub-models are as follows: (1) the planktonic models describing the main producers of organic matter and a source of food for the upper trophic levels; (2) the high trophic levels models generally used in connection with the upper trophic levels, especially the exploitable living resources, and also used for studies related to biodiversity; (3) the sediment biogeochemistry models dealing with the regeneration of marine- and river-borne organic matter providing nutrients for planktonic ecosystems; (4) the particulate/sediment transport models, which simulate the transport of terrigeneous matter through the coastal zone, and during energetic events, also simulate the transport of marine particulate matter from the coastal zone to deep areas; (5) the chemical contaminant models dealing with the transfer of contaminants in the food chain and the bioaccumulation in the organisms

9.1.1. Pelagic plankton ecosystems models

The development of biogeochemical models of pelagic plankton, first trophic levels of the food web, began at the end of the 1960s. These models, termed NPZD (nutrient–phytoplankton–zooplank-

ton–detritus) models, considered that the planktonic food web was dominated by large phytoplankton and mesozooplankton and that nitrogen was the main element limiting growth. In the last decade, it has become widely known that (i) the intracellular elemental composition may vary significantly even at short time-scales, and (ii) the phytoplankton diversity revealed by time series at one site or by onshore-offshore transects cannot be captured by simple models. A new generation of "multi-nutrient/multi-functional group models" has therefore been developed. The term multi-nutrient indicates the modeling of a cycle of several chemical elements (e.g., carbon, nitrogen, phosphorus, silicon, iron), the availability of which is liable to control the biological activity of plankton and/or to determine the structure of the planktonic food web (large vs. small plankton dominance). The expression "functional group" has no phylogenetic meaning here but rather refers to groups of organisms that mediate specific chemical reactions in the ocean. These developments appear fully justified for the Mediterranean, which presents limitations by nitrogen or phosphorus varying spatially and during the annual cycle, important trophic gradients linked to the decrease of nutrients and the increase of stratification from west-to-east.

Different authors have used and calibrated 1D models to the DY-FAMED site (Northwest Mediterranean). The applications of 3D models in the Mediterranean are still scarce. Lévy et al. (1998) showed, with an idealized model configuration of the Gulf of Lion convection zone, that meso-scale heterogeneity of the mixed-layer depth due to the baroclinic instabilities associated with deep-water formation is responsible for the meso-scale variability of primary production and that instantaneous primary production can be underestimated by a factor of four when meso-scale eddies are not explicitly solved. Tusseau-Vuillemin et al. (1998) showed that during winter, when phytoplankton growth is reduced and the cascading of dense waters is active along the Gulf of Lion shelf, the margin exports nitrate toward the open sea. Crise et al. (1999) assessed the respective roles of light and nutrients in limiting phytoplankton growth and suggested that the east–west trophic gradient is the result of the superposition of biological pump and estuarine inverse circulation. Recently, Petihakis et al. (2009) showed that their model, applied to the eastern Mediterranean in a climatological run, was able to reproduce the full range of scales of variability of chlorophyll, from the eutrophic in gulfs and shallow coastal waters to extremely oligotrophic in outer areas, and they emphasize the control of primary production by vertical mixing in the meso-scale eddies.

Even if the realism of models is rapidly increasing, partly thanks to the increase in computer efficiency, which allows for the representation of more state variables and processes, a large effort still needs to be made to ensure that the models are able to represent not only the primary production and deep-chlorophyll maximum gradients but also the different functional groups that are considered essential to understanding how the ecosystem can evolve in response to its forcing. This point requires a shared effort in modeling and field observations to gather the little available information at the different sites and to make it comparable with model results. In the future, observational strategies should be specially designed to calibrate and validate the models at different time-scales and at key sites marked by specific processes of the Mediterranean as strong meso-scale activity (northwestern, Algerian or Levantine basins), deep mixing (northwestern basin, southern Adriatic), permanent stratification, and river-dominated margins (northern Adriatic, Gulf of Lion shelf). Another point concerns specific processes that are still poorly represented by models, such as N_2 fixation by picoplankton, mixotrophic processes, autotroph and heterotroph calcification, and denitrification. The inclusion of mechanistic functions of grazing for the different heterotrophs' functional groups is a real challenge, as it requires continuity in the modeling of the trophic chain, which is probably crucial to cap-

turing the complexity of the ecosystem dynamics. In the same way, zooplankton mortality is a closure term that accounts for the unrepresented part of the ecosystem. It is used to calibrate the model rather than for its ecological meaning, but it should be kept in mind that it has a large influence on the model dynamics (Mitra, 2009). The only way to avoid this influential control is to replace the closure terms by adding a new ecosystem component and then close the ecosystem at a higher trophic level (see Section 8.2 for the coupling of sub-models).

9.1.2. Sediment biogeochemistry models

In marine biogeochemistry, especially in continental shelf waters, the water column biogeochemistry is tightly coupled with sediment biogeochemistry. Indeed, a large share of the recycling of terrestrial and marine particles occurs in sediments that sustain large primary productivity in these areas. Furthermore, sediments also act as a sink for marine compounds through burial (org-C and N, BSi), denitrification (NO^{3-}), and internal precipitation (FeS). Early diagenetic models aim at describing the dynamics of the organic matter mineralization and the recycling of biogenic silica and calcium carbonate after its deposition on the seabed by solving advection–diffusion–reaction equations in a porous medium (Boudreau, 1997). Most of the models in use are non-linear coupled models that are based on one-dimensional diagenetic equations. Solutes are transported by molecular diffusion and bio-irrigation, whereas solid phase compounds are transported by sedimentation and bioturbation. Concerning the Mediterranean Sea, the diagenetic model of Soetaert et al. (1996) has been validated on different environments of the Gulf of Lion by Denis (1999).

Few models were actually implemented to describe the unsteady coupling of the sediment with the water column, including the hydrodynamical forcings, although non-steady-state diagenetic models have the potential to reproduce the dynamics of sediment–water exchange fluxes (e.g., Rabouille and Gaillard, 1990; Boudreau, 1997; Soetaert et al., 1996). Moreover, some specificity of sediment models needs to be added if one wants to describe the Mediterranean system in its complexity. Mediterranean rivers are subject to flooding almost every year, and these floods promote a large input of material (70–80% of total annual input) in very short periods of time (days to a couple of weeks). These floods create large deposition events (10 cm to 1 m) in the vicinity of the river outlet (prodelta) that completely modify the physical and biogeochemical sedimentary environment. Such discontinuities in sedimentation can also arise near canyon lobes, where large amounts of material are deposited after the cascading of dense waters or turbidite deposition. Current models cannot treat discontinuities in deposition events because they are designed to only represent slowly varying processes.

Another specificity of the Mediterranean Sea coastal environments is the sediment transport on the continental shelf (e.g., Ulses et al., 2008b; Dufois, 2008 for the Gulf of Lion), which decomposes in alternate phases of short-term resuspension (enabling transport) during swell events and long-term deposition. Both phases may impact particle transformation. During resuspension, the succession of oxic and anoxic stages of degradation may promote certain diagenetic pathways and alter the nitrogen cycle. The representation of this process requires a coupling of sediment dynamics models with diagenetic models (see Section 8.2), at least on continental shelves. After deposition, organic matter will be used and reworked by benthic fauna, whose functional diversity along the sediment pathways should also be introduced in sediment biogeochemistry modeling.

9.1.3. High trophic level models

High trophic levels (HTL) in marine systems refer to nektonic or benthic metazoans that live longer than 1 year and are positioned

above the planktonic or benthic primary producers and their first micro-consumers (zooplankton and meiofauna). The sustainability of exploitable marine resources and the conservation of biodiversity in the Mediterranean Sea are two major issues for HTL models given the current demands of climatic change and anthropogenic pressure. Food webs of the Mediterranean Sea that contain high trophic levels have been mainly modeled by the box-structured model ECOPATH, which has been used for both pelagic fish communities (Coll et al., 2006) and benthic communities. However, in such "fisheries-oriented" models, the impact of climatic variations is not explicitly modeled, e.g., as an exogenous forcing on phytoplanktonic biomass or egg production. To assess the direct and indirect effects of climate and fishing on ecosystem dynamics, an adequate model should represent the key linkages among ecosystem components from the bottom to the top of the food web (Travers et al., 2007).

The second challenge is to understand how hydrodynamics influences populations and community structures, ultimately modifying marine habitats. Marine species live passively (as holoplankton) or actively (as nekton) in the water mass or rely on a dispersal phase to complete their life cycle (the meroplanktonic larval phases of benthic species, fish eggs and larvae). Understanding the connectivity of holoplanktonic populations or the invasion of new planktonic species requires numerical studies from the basin scale (e.g., exchange of plankton from the different regional seas in the Mediterranean) to regional scales; these studies should be based on Eulerian and Lagrangian flow models coupled with linear mortality estimates. The Lagrangian approach allows the incorporation of physiological changes during larval development that may affect organisms' swimming ability, physiology and sedimentation. In the Mediterranean Sea, dispersal studies have been limited to few case studies involving few species, such as annelid larvae (Verdier-Bonnet et al., 1997; Guillén et al., 2006).

A better understanding of both the bottom-up and top-down controls in marine food chains requires modeling efforts at the level of the whole ecosystem to couple low and high trophic levels (a point developed in Section 8.2) and at the level of species biology and biophysical coupling, including responses to temperature, salinity, light, turbulence, food quantity and quality. For instance, a species' response to temperature is key information for simulating and predicting seasonal succession. Biophysical couplings, including ontogenic or daily vertical migrational behavior, still need to be developed to identify structures favorable to population retention and production for the Mediterranean Sea.

9.1.4. Species distribution models

The modeling of species distributions is an increasingly important tool in conservation planning, resource management and understanding the effects of changing environmental conditions on biogeographical patterns. Models are constructed from estimates of species' responses to one or more environmental attributes (Koubbi et al., 2006; Loots et al., 2007). These attributes typically include habitat factors that affect the species either directly (e.g., the temperature, dissolved oxygen, trophic resources and bottom substrate for benthic organisms), or indirectly (e.g., the topography and latitude). In addition, some of the species' ecophases may take place in a restricted area coinciding with hydrographic frontal areas, transitions between water masses, upwelling, and freshwater inflow. These descriptions of the habitat may be generalized to the fundamental and realized niche concepts, which are respectively defined as the environmental range in which a species could exist in the absence of other species and that part of the fundamental niche to which a species is restricted due to interspecific interactions. As we observed, one threat to Mediterranean species comes from invasive species, particularly

northward colonizations by "warm" species whose ranges are shifting.

Many of the environmental attributes required for habitat modeling can be measured concurrently during scientific cruises or by satellites; they can also be provided by coupled physical/biogeochemical dynamic models of nutrients and the lower components of the trophic web (e.g., the size classes of phytoplankton and zooplankton) – see Chapter 7.

9.1.5. Organic contaminants and trace metals models

Contaminants introduced into marine waters by atmospheric fallout and river inputs are eventually transferred to all compartments of the ecosystem. Some of the contaminants have toxic effects on primary production and/or bioaccumulate in organisms. Long-term, multimedia and non-spatial models by Mackay et al. (1996) are able to evaluate the environmental fate of a variety of chemicals, including their tendency to accumulate in sediment or in fishes. For the most persistent contaminants, current scientific research emphasizes transfer at smaller scales, focusing on contaminant speciation and the vehicles of contamination to the trophic chain. Despite their obvious links, chemical contamination models are most often kept separate from ecological models. There are three types of models (described below) that require individually more study and application to improve our understanding of the fate of contaminants and their environmental toxicity.

9.1.6. Transport and distribution models for the water column and the sediment

The aim of these models is to study the transport of contaminants in marine waters and sediments and the contaminants' interaction with organic particles and plankton. The models' usefulness and the strength of their results are limited by the poor estimation of inputs (rivers and atmosphere) and by the simplified formulations of the biogeochemical processes and contaminant speciation. Parameters variability and multiple interactions demand new experimental studies of the processes involved, while the potential complexity of models (which should include multiple contaminants and multiple compartments) pleads for a step-by-step approach. An example of such a study in the Mediterranean continental shelf environment is given by Jurado et al. (2007), which showed the role of turbulence in determining the distribution of persistent organic pollutants (POP) in the water column.

9.1.7. Bioaccumulation models in living organisms

These models integrate nutrition, growth and the reproduction of biological organisms in a food chain. The models are usually specific to one type of contaminant and one population of fishes. Contaminant concentrations in the water or sediment derive from in situ measurements. For example, Bodiguel et al. (2009) and Casas and Bacher (2006) studied the accumulation of PCB in a Mediterranean population of European hake and trace metals in the Mediterranean mussel.

9.1.8. Models of intense or chronic toxicity

These models exist only at the population scale. Better knowledge of the effects of fish exposure to a mixture of contaminants is required from experimentations and measurements. Notably, current research focuses on the combined effects of contaminant exposure and climatic warming.

9.1.9. Sediment transport models

Because of their high contents in organic matter and microbial communities, suspended particulate matter and sediment play an important role in biogeochemical cycles and the transfer of pollutants. In addition, turbidity induced by resuspension and riverine solid fluxes is likely to influence primary production in shallow

waters. Consequently, scientific attention in the past few decades has focused on the development of sediment transport models to answer questions related to water quality and ecosystem functioning.

Sediment transport models typically (i) compute the suspended sediment concentration using the advection-diffusion equation, (ii) represent resuspension of sediment by wave-current combined forcing and (iii) deduce modifications of sea-floor characteristics, such as bed altimetry and characteristics using erosion/deposition formulations. Difficulties in modeling resuspension are, for example, inherent to the parameterization of turbulence in the wave and current boundary layers. Modeling challenges also arise in the complexity of the sediment's behavior, which depends on its nature (cohesive, non cohesive, mixed), its porosity, and the presence of biofilms or organisms reworking the sediment. In addition, the total amount and size distribution of inputs of particulate matter by rivers are often not periodically monitored. The consequences are especially pronounced considering the rapid variations that occur during flood events, which may sometimes constitute the majority of the annual solid fluxes flushed into the system. Particulate matter is submitted to flocculation processes, especially at the fresh/salt water interface. This process strongly affects sedimentation and is thus crucial to simulate the fate of the river-borne sediment.

Among studies of the Mediterranean, Ferré et al. (2008), Ulses et al. (2008b), Dufois (2008) modeled the fate of suspended matter brought by rivers and resuspended sediments on the Gulf of Lion shelf and their export towards the open sea during periods marked by intense cascades of dense water, strong onshore storms and high runoff from the Rhône River. Ulses et al. (2008b) and Dufois et al. (2008) showed that the major impact of marine storms on erosion was controlled by waves on the inner shelf and by energetic wind-induced bottom currents on the outer shelf. During the fall, particulate matter was mostly exported by storm-induced downwelling processes, which deposited significant amounts of shelf sediments in the canyon heads. In contrast, during the winter, downwelling currents interacted with dense water cascades and transported resuspended sediments toward the deeper reaches of the canyons. Ferré et al. (2008) compared resuspension and off-shelf export induced by trawls with those induced by waves and currents. Dufois (2008) investigated the contribution of the Rhône River input, the main source of particulate matter in the Gulf of Lions, and studied the transient deposition and erosion in the area of the prodelta.

Even if these models were able to incorporate extreme events over short time scales, several processes, such as the effects of flocculation on settling velocity and bed consolidation on erosion, still need to be better represented to accurately capture the transport of sediments from sources to sinks over larger time-scales. For example, Harris et al. (2008), modeling sediment dispersal in the Adriatic, obtained contrasting patterns of sedimentation for the Po and Apennine inputs due to the use of different settling velocities. Similarly, the effect of bioturbation on the availability of fine sediments is completely ignored by models, though Drexler and Nittrouer (2008) showed in a study of sediment cores in the Gulf of Lion that bioturbation generally erases the sediment stratification from floods.

9.2. The Need for coupled models

9.2.1. End-to-end modeling

To understand the combined impacts of climate forcing and over-fishing on marine ecosystems and to manage these marine ecosystems using an integrated, ecosystem-based approach, there is a growing need to link biogeochemical models with models that include high trophic levels. These end-to-end models should be able to efficiently represent any trophic level or functional group because they avoid the oversimplification of models that represent only subsets of the food web. The development of these end-to-end models, which represent ecosystem components from primary producers to top predators, is still a general objective of many on-going projects (the European project SESAME for the Mediterranean Sea and the European MEECE project: see for example Travers et al., 2009 for an application to the Benguela region).There are several challenges in coupling different models with different temporal and spatial scales (Travers et al., 2007): one must simultaneously balance the need for complexity in order to ensure generality and the desire to keep the model as simple as possible.

Models of low trophic levels are based on the representation of functional groups from phytoplankton to mesozooplankton in an Eulerian framework, whereas HTL models are mostly species-based to represent small pelagic fishes and/or large jellyplankton via individual-based models in a Lagrangian approach. Two main steps have to be implemented to unite these models. The first is to define adequate planktonic groups beyond the primary producers (i.e., to identify the key zooplanktonic functional groups). The second is to select the top predators of interest and identify the different prey species and their trophic levels down to the planktonic functional groups.

The two complementary modeling approaches will undoubtedly help to quantify the trophic web and the spatial distribution of organisms in the Mediterranean Sea, improving our understanding of the spatial dynamics of this food web. With this approach, it will be possible to reconcile the biodiversity and the functioning of the ecosystem.

The development of such an integrated model should be accompanied by adequate observations and laboratory investigations across trophic levels. In particular, there is a need to better study and parameterize (i) the responses of these functional groups and species to different environmental drivers and (ii) the interactions within planktonic functional groups, within the HTL species, and between the HTL planktivorous species and the planktonic prey. Due to the richness of marine food chains in the Mediterranean Sea, it would be important to select several marine food chains in targeted regions.

9.2.2. Coupling sediment biogeochemistry and sediment transport

Sediment biogeochemistry models widely ignore horizontal transport processes (Boudreau, 1997). Indeed, organic matter mineralization is expected to dominate in organic-rich fine sediment, the stability of which over time suggests that transport processes are limited (deep-sea environments). It was only recently acknowledged that apparently stable fine sediment deposit could be reworked during swell events from river mouths (Guillén et al., 2006) to the whole continental shelf and upper slope (Ulses et al., 2008b). This scheme pleads for a coupling of sediment biogeochemistry models with sediment transport models, starting from the input and dispersion of terrestrial organic matter by rivers to their final deposit in the deep-sea. Such a coupling should specifically include the impact of flood and swell events, during which impulsional releases to the water column of organic and inorganic compounds occur in particulate and dissolved forms. The conditions of bed sediment diagenesis are also modified in these events, affecting, e.g., sediment oxygenation, pore water drainage, and the vertical redistribution of the microbial community. However, including these short-term discontinuities in mid-to long-term models remains a challenge, requiring new developments in parameterization after time-averaging high-frequency processes, such as intra-wave and plume dynamics. It is likely that the coupling strategy will be different in coastal areas (continental shelf) and the deep-sea.

9.2.3. Coupling biogeochemistry and contaminant dynamics

Contaminant speciation depends often on suspended matter and on organic compounds (COP, COD), which also constitute food for the first trophic levels. Biological production is affected by the presence of several contaminants. These interactions lead to the need for coupling the dynamics of contaminant and organic matter. Further coupling with hydrodynamic and sediment transport is an important step in better simulating contaminant transfer and effects on ecosystem. However, this approach encounters several difficulties, including those noted above and below, and is difficult to validate because of the lack of measurements. It is nevertheless an enriching complement to simpler models that include zero or one spatial dimension and different levels of complexity.

9.2.4. Coupling biogeochemistry with hydrodynamics

The integration of biogeochemical/ecosystem models (from simple NPZD models to sophisticated multi-element, primary production models and models involving higher trophic levels) with a realistic hydrodynamic model for the Mediterranean has just begun. The next step is to conduct coupled simulations with state-of-the-art circulation and ecosystem models. This coupling should help address hypotheses related to the spatial distribution of primary production and the associated trophic gradients. For example, the relatively short residence time of the Levantine and western deep waters associated with their overturning cells, in contrast to what happens in the global ocean, may limit the supply of nutrients to the surface water and consequently the primary production. Another hypothesis to study involves the role of strong vertical movements to support production in specific regions where the meso-scale dominates. At smaller scales, which include filaments and sub-meso-scale coherent vortices, and with high-frequency processes, such as inertia-gravity waves, the enrichment associated with high vertical velocities and horizontal stirring are still debated, providing additional uncertainties on the control of production by meso-scale and sub-meso-scales (Lévy, 2008). Coupled modeling should allow understanding and quantification of the impact of intense events (e.g., strong winds, strong heat losses, precipitation, heat waves) on ecosystems. These impacts might include the rapid deepening of the mixed layer and upward nutrient fluxes, dense water cascades that flush coastal organic matter and contaminants toward deep areas, massive sediment resuspension and the associated release of organic and inorganic compounds, extreme temperatures, and last but not least, turbidity patterns.

Validation must be performed for both hydrodynamics and ecosystems as biases on physical structures such as the mixed layer depth and the intensity of meso-scale and sub-meso-scale activity will directly impact the ecosystem. Detailed knowledge of the performance of the coupled model, including the hydrodynamic and ecosystem sub-models and the impact of the hydrodynamic errors on the ecosystem, will be critical to improving the coupled model.

10. Summary, conclusions and research perspectives

10.1. The Mediterranean Sea, a changing ocean?

The Mediterranean Sea is unique and evolves rapidly, with large inter-annual to decadal variability and abrupt fluctuations. The semi-enclosed nature of the Mediterranean, together with its smaller inertia compared to large oceans, makes it more sensitive to natural variations in fluxes (between, e.g., the air and sea, freshwater and the sea) and water flows. These natural pressures interact with the trend of increasing human activities in the coastal regions, making the sea even more sensitive. Over the past century, the population along the Mediterranean coasts has expanded substan-

tially. Urbanization, industrialization and touristic exploitation (with associated impacts as land use change, increased demand for food and water, waste disposal, coastal erosion, etc.), intensive agriculture and aquaculture, riverine and atmospheric inputs and over-fishing are in fact only a few of numerous anthropogenic influences. These exogenous influences have exerted progressively growing pressure on the Mediterranean and Black Sea environment, putting their integrity at stake. In this review, the major exogenous forces influencing the ecosystems of the Mediterranean Sea have been itemized, and they are summarized below.

Previous descriptions of the large-scale Mediterranean thermohaline circulation were usually based on the assumption that the basin is a stationary system. This assumption has been disproven. During the past few decades, significant changes have been observed in the characteristics of the deep waters of the eastern and western basins, of the inflow and outflow waters at the Gibraltar Strait, and of the main atmospheric forcings. The impact of these shifts on the key biogeochemical processes in the basin and the consequences for associated ecosystems could be considerable. The Mediterranean Sea may be subjected to changes in the depth of the mixed layer and nutricline interfaces, in the vertical redistribution of nutrients in the water column related to dense water formation, and hence in the absolute and relative concentrations (i.e., Redfield ratios) of the deep nutrient reservoir. The trophic regimes of the basins could then be modified in both their spatial distribution and seasonality. For instance, changes in the basin's hydrodynamics could induce a more intense oligotrophy or a diffused augmentation of primary production. The first hypothesis would lead to an increased dominance of small algal cells with large consequences for the transfer of matter in food webs. The second would favor the growth of large opportunistic species.

The Mediterranean Basin is characterized by relatively high solar radiation levels due to its weak cloud covering, but its atmosphere is regularly modified by storm events from the Sahara Desert, biomass burning and anthropogenic aerosols from industrial activity. These factors can produce significant variability in the fluxes of direct irradiance at sea level. As a system low in nutrients and chlorophyll, the open sea allows strong penetration of solar radiation, which promotes photochemical reactions, affects the structure of the planktonic community and changes the chemistry of several organic compounds (e.g., lipids, organic acids, chlorophyll by-products). The warming of water and increased stratification will likely increase the exposure of organisms and organic compounds to solar radiation. These conditions will favor photochemical oxidation reactions, inducing the dominance of organisms adapted to intense light, such as *Synechococcus* and particular pico- and nano-eukaryotes. In contrast, an increase in wind events will lead to an occasional deepening of the mixed layer, which would isolate the more opportunistic species and also change planktonic community structure. Moreover, the high levels of solar radiation encountered in coastal regions, combined with high levels of photosensitizers, such as CDOM and NO_3^-, discharged by rivers, will enhance photochemical oxidation in coastal waters. Change in the oxidative capacity of Mediterranean waters may affect the chemistry of volatile organic compounds, including DMS, OCS and CO. DOM phototransformation may affect community structure and bacterial growth as well as primary productivity through in situ ammonium regeneration and nitrification.

Unlike the data for surface and deep-water temperatures, long-term time series of the carbonate properties of the Mediterranean Sea are scarce, and this situation precludes an accurate assessment of the degree and rate of acidification. However, acidification is expected to affect primary production rates and create a shift in planktonic size. These trends are likely to alter the capacity of the Mediterranean surface waters to yield organic matter at higher

trophic levels. The potential increase of primary production relative to the decrease of calcification rates will undoubtedly modify the carbon rain ratio (C_{org}/C_{inorg}) and the role of $CaCO_3$ as ballast material. Thus, these dynamics will modify the strength of the carbonate pump and the subsequent C:N:P:Si export ratios of POM and DOM.

The links between the specific stoichiometry of the Mediterranean Sea and the trophic interactions within the various ecosystems are still largely unknown (Krom et al., 2010), but the predicted changes in the environmental conditions will have important consequences for fluxes and the structure and organization of the ecosystem. At the large-scale, water warming and increased stratification will likely reduce the supply of nutrients to the photic layer through vertical transport and favor organisms with minimal nutrient requirements. Isolated changes in the input rates of nutrients or combined changes due to shifts in the planktonic population are expected to significantly modify the stoichiometry of Mediterranean nutrients. The DIN:DIP ratio in major Mediterranean rivers has dramatically increased during the past two decades, while the average Si:N ratio is currently decreasing. River discharges and atmospheric depositions have behaved similarly, strengthening P-limitation in the Mediterranean waters. The expected rise in the sea level and changes in rainfall regimes will certainly modify the fragile balance between seawater intrusion and sub-marine groundwater discharge, modifying the nutrient budget in a way that needs to be quantified. All of these changes have profound implications for the evolution of C:N:P:Si ratios. For example, one possible scenario is an increase in oligotrophic conditions and a consequent increase in the role of external inputs in controlling the nutritional status of the Mediterranean Sea. Finally, a change in ocean carbon chemistry will affect marine organisms directly by acting on their physiology (e.g., reduced calcification as pH decreases and pCO_2(aq) increases) or indirectly by altering the food web. Possible consequences include (i) enhanced new N to the Mediterranean waters (by stimulating N_2-fixing organisms, reinforcing the potential for P and/or Fe limitation), (ii) increased production of transparent exopolymer particles (TEP) by stimulating bacterial activity, leading to changes in the quality of exportable organic matter, and (iii) perturbed phytoplankton productivity.

Coastal areas are expected to face increasing inputs of emerging contaminants. Such pollutants, including organic contaminants (e.g., hormones, drugs, pesticides), organotin compounds and artificial radionuclides, are associated with new industrial processes and uses that are likely to increase along the Mediterranean coastal zone. Expected decreases of the freshwater supply will modify the input and dilution of these elements in the coastal zone, and their concentration will also be affected by ambient environmental conditions (e.g., oxygen concentrations, residence times in the euphotic zone, thermochemical and photochemical reactions) along their life cycles. All of these changes could also modify bioaccumulation and biomagnification processes that control the distribution and impact of these pollutants on ecosystems. The cycle of mercury is of specific concern for this environment, because Mediterranean species show higher concentrations than their Atlantic counterparts.

Alterations in the contrast between drought and wet seasons are expected for the Northern Mediterranean with a potential increase of floods.

Alterations in the distinction between dry and wet seasons, including a potential increase in floods in both seasons, are expected for the northern Mediterranean. This shift could result in more burial and mineralization, increasing the area of affected benthic habitat near the river outlets. In contrast, climate models predict that large swells linked to cyclone activity in the southern Mediterranean should decrease in the near future. This reduction

would help stabilize habitat for benthic fauna on the continental shelf. Similarly, climate projections indicate that dense water cascading should decrease in intensity and frequency, which would imply a severe reduction in the injection of organic matter into the deep ecosystems and limit the transport of particulate carbon, pollutants and nutrients to the shelf and open sea. The reduction of dense water cascading would also affect deep-sea biodiversity at the sub-basin-scale. The impact of atmospheric deposition on ecosystems, in particular from extreme events (e.g., dust events, fires, intense summer rain episode) could be more pronounced in the future. This influence would be pronounced in the stratification period due to changes in both the chemical composition of the atmosphere and meteorological conditions. In a scenario of increasing occurrence of extreme dust events, frequent, massive, and fast transfers of POC, mediated by organic-mineral aggregation, could occur. This transfer would permit less carbon remineralization, and the POC would sink fast to the deeper layer. Increasing reactive nitrogen from anthropogenic activities in the Mediterranean area mixing with Saharan dust could increase fertilization of biota by bringing bioavailable N and P to the surface waters, especially during the stratification period.

The benthic communities are among the most diverse communities in the Mediterranean Sea, and their slow dynamics make them very sensitive to perturbations. Overfishing, invasive species and climatic changes are the main perturbations that significantly affect these communities. Recently, mass mortality events of marine benthic invertebrates have been attributed to summer heat waves. In contrast, the pelagic ecosystem was relatively unaffected. Planktonic evolution seems to be more associated with decadal oscillations in dry conditions.

10.2. The future of the Mediterranean Sea: A need for international multi-disciplinary research coupling experiments, long-term observations, ecoregionalisation and modeling

There are still considerable uncertainties in our understanding of the complex interactions between the different forcings and their impacts on ecosystems. There is therefore a strong need to attain a mechanistic understanding of the relevant processes in order to predict changes in ecosystems. These changes clearly influence the cycles of major biogenic elements, biodiversity, fisheries, invasive species and ultimately have socio-economic impacts. There is a need to develop a comprehensive and holistic approach to address particular questions at the proper spatial and temporal scales.

10.2.1. Main questions to be addressed

We describe below what we believe to be the most relevant issues for the future of marine ecosystems in the Mediterranean:

- How would changes in stratification and destratification mechanisms and in the overall thermohaline circulation alter the spatio-temporal distribution of nutrients and their budgets? More specifically, what is the influence of dense water formation on the spatial and temporal variability of biogenic elements, the triggering of planktonic blooms, and the sequestration of biogenic elements, particularly carbon?
- How would likely changes in nutrient inputs from physical transport, rivers, atmosphere (including extreme events) and straits affect nutrient availability in the photic layer of the Mediterranean Sea, the relative abundance of primary producers, and higher trophic levels?
- What are the typical concentrations of chemical contaminants in the various water masses of the Mediterranean? What are their sources and sinks (e.g., atmosphere vs. rivers, especially for organic contaminants) and seasonal variations?

- Will changes in the frequency or magnitude of extreme events lead to the dispersion or dilution of carbon, nutrients, and pollutants or, in contrast, to their accumulation in specific compartments?
- What will be the impact of changes in light radiation on biogeochemical processes, including primary production, POC-degradation processes, and degradation of DOM and pollutants?
- What is the actual rate of change of both temperature and pH in the Mediterranean Sea? How will these variables evolve and impact the Mediterranean solubility pump? What impacts will they have on the functioning of pelagic and benthic Mediterranean ecosystems?
- Will the functioning of mesopelagic and deep-sea Mediterranean ecosystems be strongly affected by changes originating from surface ecosystem production and vertical fluxes or by changes in the hydrodynamics of the intermediate and deep waters?
- As the surface seawater warms, will the planktonic community of the pelagic ecosystem become dominated by nanophytoplankton and jellyfish, as suggested by several recent studies?

Such questions require international, multi-disciplinary, and large-scale research investigations at different temporal and spatial scales. Priority should be given to reassessments of the budgets of C, N, P, Si in their mineral, organic, dissolved, and/or particulate forms and on characterization of their primary fluxes; this information will permit understanding, via modeling, of the past and future evolution of these elements. The sensitivity and responses of key pelagic and benthic species to changing environmental factors, changes in the community structures of trophic food webs, the functioning and adaptation of marine ecosystems to changing environmental factors and their feedback on biogeochemical cycles should be explored. It is also crucial to study the transfer and transformation of biogenic material from rivers through the coastal zone to the open sea, including during extreme events. The fates of carbon, nutrients and contaminants in marine ecosystems should similarly be studied from end-to-end. The impact of submarine groundwater and urban areas on marine ecosystems should also be understood. Finally, assessments of the following key natural and anthropogenic air–sea interactions need to be completed: gas fluxes and acidification, atmospheric nutrient and particle inputs, and solar radiation. Improved knowledge of species' distributions over the entire Mediterranean is also necessary and such knowledge demands studying not only species' presence or abundance but also their chance of survival, conditions for growth and reproduction, and successful habitats in each ecosystem.

10.2.2. Proposed strategy

As previously stated, most of the questions that are still unresolved concerning Mediterranean biogeochemical dynamics deal with the temporal variability of the key processes that govern the functioning and budgets of the different physical, chemical and biological compartments. Observational limits are the principal causes of this uncertainty. Even though the Mediterranean basin is probably one of the most sampled oceans of the world, much remains to be understood. In this last section, we sketched the general lines of a new observational strategy to fill several major gaps in knowledge. The proposed strategy is based on a multi-disciplinary approach that combines modeling with multi-level, nested observations:

- *Multi-disciplinarity*. The complex interactions between atmospheric forcing, ocean dynamics and ecosystem responses require an observational effort to handle the high level of convolution of the interacting processes. On this point, the consensus is generally wide, but in practice, very few scientific collaborations involve atmospheric physicists, oceanographers, marine biogeochemists and biologists. Still rarer is the direct involvement of modelers in the design and implementation of field operations. Without multi-disciplinarity, most of the open questions on the Mediterranean functioning will remain unresolved.
- *Modeling*. Because in situ sampling remains difficult at key scales, modeling tools appear the only alternatives to represent the spectrum of variability at the basin scale and to quantify the impact of this variability in term of climatic change. In addition, numerical simulations are the only means to test hypothesis on the evolution of the Mediterranean over the next several decades and the impact of climate change. The main limitation of present-day Mediterranean models is the lack of data at the proper spatio-temporal scales for initializing, constraining and validating existing simulations. The principal reason for the mismatch between the availability of data and modelers' requirements is that the involvement of modelers in the preparation and development of observational systems remains rare. An observational strategy for the Mediterranean would thus sample the basin with an aim to efficiently constrain numerical models. Such sampling would focus on accurate representations of exchange processes, limiting errors with data from regular time-series.
- *Observational strategy*. The impacts of climate changes might be measured with "1D approach" time-series such as HOT or DYFAMED, but the relevance of this approach at the basin or sub-basin-scales has not been addressed. Understanding the evolution of the Mediterranean basin in the next few decades requires simultaneously analyzing long-term time-series, sub-basin assessments of budgets, and episodic biotic events (i.e., episodic blooms or regime shifts). For practical reasons, these simultaneous activities should be implemented at different spatial scales, although they should have a strong consistency in their parameters and sampling strategies. Here, we propose a three-level, nested system of observation. The final decisions about the sampling locations, the temporal resolution and the acquired key parameters should be made in conjunction with modelers. This approach implies the initial definition of reference models, which should be used to test sampling strategies and to integrate data in a wider context. For this reason, each observational level should be associated with a parallel modeling effort that is adapted to the unique scales and processes of that level. Simultaneously, an effort should be dedicated to refining existing models, initially on the basis of the existing data and later exploiting observations and results obtained from recent investigations.
  - *Long-term observation period (LOP) lasting approximately 10 years to gather and provide observations on the entire coupled system, including its atmosphere, hydrography, biogeochemistry, and biodiversity*. Networks of moorings, buoys, profilers, gliders, ships of opportunity and repeated R/V transects should be implemented for optimal coverage. The LOP level should acquire long-term time series, ensuring the coherence of the acquired observations. LOP observations should furnish the required observations to anchor modeling simulations to data over long temporal scales.
  - *Enhanced observation periods (EOP) for both the budget and process studies lasting one to 2 years*. These studies should provide information on the mass balances, processes and structuring of food webs in key areas of the basin. Supported by the LOP system, which will provide the observational basic "backbone", EOP should be mainly implemented by dedicated oceanographic cruises at the seasonal scale, although the use of autonomous platforms should be
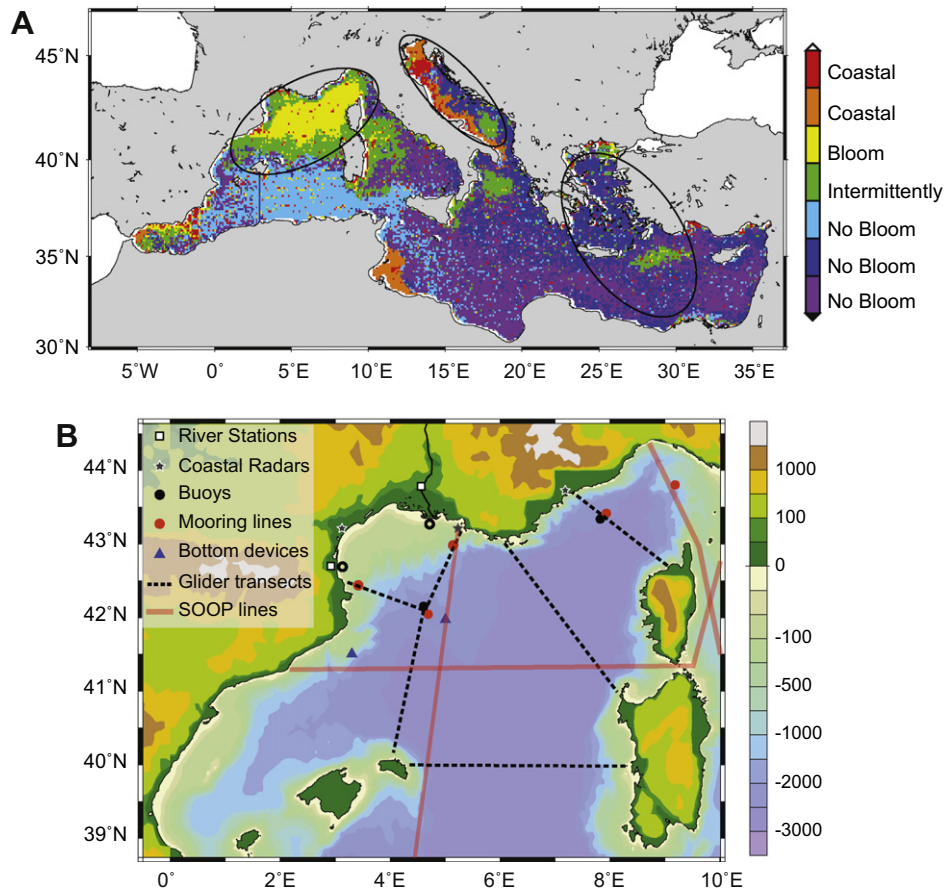
Fig. 19. (A) Mediterranean Sea eco-regions: the colors represent the trophic bioregions derived from 10 years of oceanic chlorophyll data from the SeaWiFS satellite. Regions showing the same color have similar biogeochemical dynamics [derived from D'Ortenzio and Ribera d'Alcalà, 2009]. Distinct sub-basin-scale regions with contrasted patterns are clearly delineated (e.g., NW Mediterranean, Adriatic Sea and Aegean Sea/Levantine Basin). (B) The long-term observational strategy, as implemented in the northwestern Mediterranean region including different and complementary observing platforms (moorings, buoy, gliders, lagrangian profilers float, ship of opportunity). This region presents very specific characteristics with a strongly urbanized coastline, large river inputs, and strong winds. It shows a well marked annual cycle, due to intense atmospheric events and dense water formation processes, and significant trophic gradients.

reinforced to dedicate ship-time to acquisition of parameters that cannot be automatically observed (i.e., nutrients and phytoplankton pigments). The meso- and sub-meso-scales should be resolved, at least for hydrographic and key biogeochemical parameters. EOP data would be heavily used in modeling, furnishing accurate estimates of water volume, heat, nutrients, carbon and contaminants at seasonal and at sub-basin-scales. These data would provide observations to initialize and constrain the reference simulations.

○ *Special observation periods (SOP) lasting several weeks*. These periods aim at providing detailed and specific observations to study key processes. In addition to the EOP observation framework, dedicated ground-based, shipborne and airborne means should be deployed during the SOPs. The SOP activities should be developed in close coordination with the LOP and EOP activities to maximize resources for studying processes. For example, during an EOP, a large vessel could acquire key basic parameters (e.g., hydrograph and nutrients) on a regular, meso-scale-resolved grid, while a smaller ship could focus on one or two stations of the EOP grid to perform improved (in terms of parameters and temporal resolution) sampling.

These ingredients (i.e., the multi-disciplinarity, the three-level observational system and the modeling) constitute, in our opinion, an innovative approach for Mediterranean ocean research. This approach can be considered as an integrated module that should be implemented in different Mediterranean key regions in a framework of nationally and internationally coordinated programs. The integrated module should be implemented on oceanic regions selected on the basis of existing understanding of the Mediterranean functioning, and, in particular, in light of the recent advances on the ecoregionalization of the basin. Ecoregionalization is one of the major approaches to defining appropriate spatial scales of biodiversity for the rational use of ecosystems. Eco-regions are "the assemblages of flora, fauna and the supporting biogeochemical and physical environment contained within distinct but dynamic spatial boundaries" (e.g Koubbi et al., 2010). They depend on classification methods based on spatial patterns of abiotic and geographic factors or surrogates of biological factors (e.g., D'Ortenzio and Ribera d'Alcalà, 2009). The French community, assembling scientists from the atmospheric and ocean sciences and combining modelers and observers, is proposing an ambitious research effort for the northwestern Mediterranean (Fig. 19), following the principles of the integrated module briefly presented here. This effort, together with philosophically similar initiatives developed by other Mediterranean countries, should lead to the emergence of a network of scientific modules. By encompassing all the Mediterranean eco-regions, these modules should make substantial progress in answering the scientific questions highlighted in this paper. Indeed, only international initiatives will be able to tackle such scientific questions at the scale of the whole Mediterranean Sea. Such effort requires long-term research and a significant effort in terms of funding (including R/V resources): these two components are

absolute prerequisites if we want to understand how global and anthropogenic changes are affecting and will affect the functioning of the Mediterranean Sea, their impact on biogeochemical cycles and the marine ecosystem, and the ensuing socio-economic consequences for Mediterranean populations.

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