

# Mediterranean Sea

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## 1 SUMMARY

The sources of anthropogenic radioactivity in the Mediterranean Sea are described and quantified, and the redistribution of the radionuclides in the different compartments of the marine environment is illustrated.

The time trend of the distribution of conservative ( $^{137}\text{Cs}$ ) and nonconservative ( $^{239,240}\text{Pu}$ ) radionuclides is analyzed for the coastal areas and the open sea, and the inventories in the water column and in sediments are calculated. Most anthropogenic radionuclides (90% of  $^{137}\text{Cs}$  and 50% of  $^{239,240}\text{Pu}$ ) still reside in the water column. For  $^{239,240}\text{Pu}$ , important reservoirs are the shelf and slope sediments, containing another 25% of its delivery. Concentrations in biota of  $^{137}\text{Cs}$  and  $^{210}\text{Po}$ , the main contributors to radioactive dose to the population, are also reported. The present radionuclide levels are of no concern from the radiological point of view.

The Mediterranean total inventories are going to decrease in the future, because

- there are no significant sources of anthropogenic radionuclides;
- there is a net outflow of  $^{239,240}\text{Pu}$  at Gibraltar, not balanced by the Black Sea input;

- $^{137}\text{Cs}$  concentrations are decreasing due to physical decay, not balanced by the input from the Black Sea (there is no net input at Gibraltar).

However, the Mediterranean Sea is considered as a “laboratory basin” for oceanography studies. So, in spite of the low concentrations, some radionuclides have been largely used as tracers to define the timescale of a variety of marine processes (water mass pathways, transit and renewal times, particle dynamics, sediment accumulation rates, etc.). The application of nuclear techniques to oceanography contributed and, thanks to innovative analytical techniques, will also, in the future, significantly contribute to a better understanding of the functioning of the whole Mediterranean marine ecosystem.

## 2 INTRODUCTION

Radioactivity monitoring in the Mediterranean started in the early 1960s, in relation with the fallout deriving from atmospheric nuclear weapon testing and with the beginning of national programs for the peaceful use of atomic energy (see *Anthropogenic Radioactivity*). National

programs for the survey of environmental radioactivity are active in most of the European Union Mediterranean countries and, thanks to technical cooperation programs of the International Atomic Energy Agency (IAEA) and initiatives of the Mediterranean Science Commission (CIESM), common protocols for radioactivity monitoring are being developed and adopted at basin scale and common data sets are being produced. These data mainly concern the coastal areas and are collected with the objective of defining baseline radioactivity levels in the main matrices and of estimating radioactive dose to the population from the marine pathway.

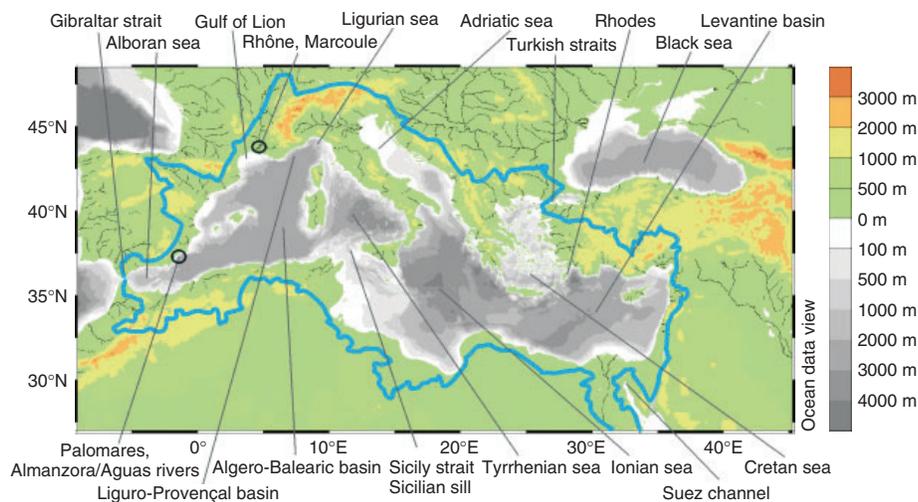
However, radionuclides, that have a known and well-characterized input function, are also an important tool for studying oceanic processes. The Mediterranean Sea is a regional sea, where all the main processes characterizing the oceans take place on smaller space and timescales. For this reason, in the past decades, it had largely been used as a “laboratory basin” for marine process studies. In the framework of these studies, the distribution of anthropogenic and natural radionuclides has been analyzed in detail, also in the open sea, contributing to the understanding of a variety of mechanisms and processes: water mass pathways, transit and renewal times, particle dynamics, sediment accumulation, etc.

In this article, we first describe the main physical and biogeochemical processes characterizing the Mediterranean Sea. We then analyze radionuclide distribution in the different compartments in relation to the oceanographic processes, draw a mass balance of  $^{137}\text{Cs}$  in the basin, and delineate future trends (*see Cesium; Global Trends in Cesium Distribution*). We finally identify future research needs, including the use of radionuclides as tracers for marine processes.

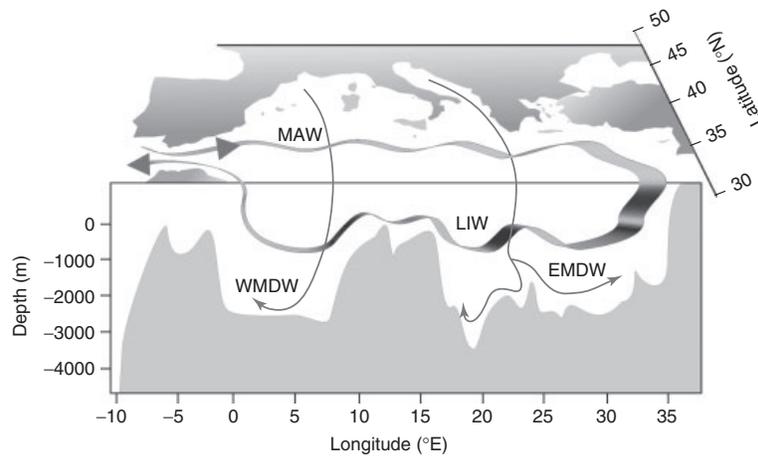
### 3 THE MEDITERRANEAN SEA

The Mediterranean Sea is a deep, semi-enclosed basin, communicating in the west with the Atlantic Ocean, through the narrow and shallow Gibraltar Strait, in the northeast with the Marmara and Black Seas, through the Turkish Straits System, and in the southeast with the Red Sea through the Suez Channel. Its mean depth is 1500 m and the continental shelf is generally very narrow, covering only some 10% of its surface. It is composed of two main basins, eastern and western, communicating through the Straits of Sicily. Only a few big rivers flow into the Mediterranean Sea, the most important being Rhône (France), Po (Italy), Ebro (Spain), and Nile (Egypt) (Figure 1).

The Mediterranean Sea is considered as a miniature ocean, where most of the processes characterizing the world’s oceans take place at smaller spatial scales.<sup>1</sup> It is a concentration basin, where evaporation exceeds precipitation and river runoff. At the Straits of Gibraltar, a surface flux of the Atlantic, low salinity water (36–36.5 ‰) enters the Mediterranean Sea, while a subsurface water mass, characterized by salinity higher than 37.5 ‰, leaves the basin. Circulating in the Mediterranean, the incoming surface Atlantic water increases its density due to evaporation and then forms new, denser water masses via convection events driven by intense local cooling from winter winds. The general circulation of the basin is complex and can be summarized as follows (Figure 2): after entering at Gibraltar, the Atlantic water proceeds eastward, forming small eddies, with its main path along the African coasts. After crossing the Sicily Straits it occupies the southern part of the Ionian Sea, heading to the Levantine Basin. Along its path eastward, due to evaporation, salinity increases to more than 39‰. In the area close to Rhodes, extensive winter cooling due to northerly winds gives rise to a saltier and



**Figure 1** The Mediterranean Sea: basins, bathymetry, and limits of the rivers’ catchment



**Figure 2** Schematic representation of the Mediterranean general circulation. (Modified from Tsimplis *et al.*,<sup>1</sup> with permission of John Wiley & Sons)

denser water mass, the Levantine Intermediate Water (LIW), that, being unstable at the surface, sinks and stabilizes in the depth interval 200–400 m moving westward. After following a rather complicated path, the LIW crosses the Sicilian Sill, circulates in the whole western basin, and finally flows out of the Mediterranean, crossing the Gibraltar Straits at an average depth of more than 150 m. This mechanism, the upper ocean conveyor belt, has a decadal timescale and constitutes the main engine of the Mediterranean circulation. The waters filling the deepest part of the Mediterranean are formed by the same mechanism in a few main areas: the Gulf of Lions (Western Mediterranean Deep Water, WMDW), the Adriatic (Eastern Mediterranean Deep Water, EMDW), and, to a lesser extent, the Cretan Sea (Cretan Deep Water, CDW). The renewal of these waters is relatively slow (multidecadal timescale), with their circulation being limited by the shallow sills at the Sicily and Gibraltar Straits. It has been shown that important changes can occur in the characteristics of the dense waters and in the formation areas; in the late 1980s, the strength of the Adriatic deep water source greatly decreased and the Cretan Sea started to produce very dense waters, which rapidly occupied the bottom layer of the whole eastern Mediterranean, replacing the old EMDW of Adriatic origin (the so-called Eastern Mediterranean Transient, EMT). In 2002, the “classical” circulation was reestablished, but the signal of the EMT is still visible and now producing effects in the western Mediterranean. The general circulation controls the distribution of the soluble fraction of the radionuclides. Because of the efficient deep water formation, global fallout radionuclides were detected in the deepest part of the Mediterranean already in the early 1970s, only 7 years after their main input into the atmosphere.

From a biological point of view, the Mediterranean is usually classified as an oligotrophic sea,<sup>2</sup> as the

primary production is weak (typical values in the western Mediterranean are around  $90 \text{ g C m}^{-2} \text{ year}^{-1}$ ), and chlorophyll concentration in the open sea rarely exceeds  $2\text{--}3 \text{ mg m}^{-3}$ . There are only few areas, geographically well defined, characterized by large spring blooms: the Liguro-Provençal basin, the S-Adriatic Sea, and the Alboran Sea. This implies that, in the open sea, radionuclides with high affinity for particulate matter (for example, transuranics) find very little particles to attach to, and their transport to depth and accumulation in sediments are relatively slow. An important role in the removal of these radionuclides from surface waters is played by the continental shelves, where high particle population, deriving from river inputs and coastal erosion, leads to effective scavenging and accumulation in fine-grained sediment deposits.

#### 4 SOURCES AND CONTAMINANT ELEMENTS

The main sources of anthropogenic radioactivity in the Mediterranean Sea are fallout from nuclear weapon testing in the early 1960s and the Chernobyl accident (April 1986) (see *Civilian Nuclear Accidents*).<sup>3,4</sup> Consequently, the main radionuclides still present are fission and activation products with relatively long half-lives, i.e.,  $^{137}\text{Cs}$ ,  $^{90}\text{Sr}$ ,  $^{238,239,240}\text{Pu}$ , and small amounts of  $^{241}\text{Am}$  deriving from the decay of the short-lived  $^{241}\text{Pu}$  (see *Cesium; Strontium; Plutonium; Americium and Curium*). The Chernobyl accident produced a significant fallout with a patchy deposition, depending on the air mass trajectories during the plant fire. The areas with the highest deposition were the northern and eastern basins. The elemental composition of the Chernobyl fallout was different from that of global fallout: among long-lived radionuclides,

only  $^{137}\text{Cs}$  was transported by the plume, whereas almost all strontium and plutonium isotopes were deposited close to the plant and never reached the Mediterranean area. As a result,  $^{137}\text{Cs}$  is the only radionuclide that contributed significantly to the Mediterranean inventory.

The following discussion is focused on two radionuclides: (i)  $^{137}\text{Cs}$ , conservative in the open sea, the most abundant anthropogenic radionuclide, and, among these, the main contributor to radioactive dose to the population, and (ii) the very long-lived  $^{239,240}\text{Pu}$ , nonconservative and the most abundant among the transuranics.

Time series data on deposition density starting in the early 1960s are mainly available for  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$ . At a few stations, Pu isotope deposition has been reported for relatively short time periods. Up to 2000, the integrated deposition density of  $^{137}\text{Cs}$  derived from the data collected at the Italian National Agency for New Technologies, Energy and Sustainable Economic Development (ENEA) station in La Spezia (NW Italy,  $40^\circ\text{N}$ ) and from the Italian national network for the survey of environmental radioactivity ( $4.4\text{ kBq m}^{-2}$ ) are in very good agreement with that reported by United Nations Scientific Committee on the Effects of Atomic Radiations (UNSCEAR)<sup>5</sup> for the latitude belt  $30\text{--}40^\circ\text{N}$  ( $3.8\text{ kBq m}^{-2}$ ). Deposition from the same source in the period 2000 to 2010 was relatively small, on average  $3\text{ Bq m}^{-2}$  per year. This corresponds to a cumulative deposition of  $1.6\text{ kBq m}^{-2}$  in 2010 from global fallout. In La Spezia, the contribution from the Chernobyl accident was  $1.8\text{ kBq m}^{-2}$ . However, deposition densities measured on land in the Mediterranean countries could be as high  $50\text{ kBq m}^{-2}$  (N. Greece and N. Italy), while the southern countries received only a minimum input from this source (Syria,  $0.2\text{ kBq m}^{-2}$ ).<sup>6</sup> The total deposition in the Mediterranean has been estimated to be  $2.5\text{ PBq}$  in 1986.<sup>3</sup> On the basis of these data, the total amount of  $^{137}\text{Cs}$  from global and Chernobyl fallout delivered to the Mediterranean Sea, decay corrected to 2010, has been estimated to be about  $6\text{ PBq}$ .

Part of the radionuclides deposited in the terrestrial environment is transported to the sea through river runoff and groundwater discharges, thus becoming, in some areas, secondary sources of radionuclides. As for the global oceans, the contribution from rivers is relatively small, if compared to the other sources. It is estimated that 2% of the Cs inventory on land will be removed by runoff.<sup>7</sup> With the conventional extension of the Mediterranean drainage basin being approximately  $1.86 \times 10^{12}\text{ m}^2$ , the total contribution of  $^{137}\text{Cs}$  from river runoff in 2010 will only be  $0.005\text{ PBq}$ .

With regard to effluents from the nuclear industry, spent fuel reprocessing plants represent the major source. The only installation of this type impacting the Mediterranean coastal area is the Marcoule reprocessing plant located along the Rhône river, exiting into the Mediterranean Sea in South France. The industry ceased its operation in 1997. The total liquid discharges of  $^{137}\text{Cs}$  were  $0.05\text{ PBq}$  in 1990,<sup>8</sup> corresponding to  $0.03\text{ PBq}$  in 2010.

**Table 1** Anthropogenic radionuclides delivered to the Mediterranean Sea from different sources (reference time: 2010). Mediterranean surface area:  $2.56 \times 10^{12}\text{ m}^2$

Source	$^{137}\text{Cs}$ (PBq)	$^{239,240}\text{Pu}$ (TBq)	References
Global fallout up to 2000	4.1	200	9, this work
Chernobyl fallout	1.4	0.02	3
Global fallout 2000–2010	0.03	1.2	11
Marcoule reprocessing plant	0.03	0.37	8, 10
Black Sea up to 1986	0.06	3	4
Black Sea 1986–2010	0.3	0.4	4, 12
Exchanges with Atlantic Ocean up to 1986	0.9	−40	4
Exchanges with Atlantic Ocean 1990–2010	=	−6.8	13
Input from rivers	0.005	—	this work
Total	6.8	158.2	

The mean integrated deposition density of  $^{239,240}\text{Pu}$  has been estimated, from the analysis of vertical profiles in soils,<sup>9</sup> to range between  $76$  and  $81\text{ Bq m}^{-2}$ , corresponding to a total input to the Mediterranean Sea of  $0.2\text{ PBq}$ . The output of Pu isotopes from the Marcoule reprocessing plant and that directly entering the Mediterranean sea through the Rhône river are estimated to be (1945–2000)  $365 \pm 95\text{ GBq}$  of  $^{239,240}\text{Pu}$  and  $67 \pm 18\text{ GBq}$  of  $^{238}\text{Pu}$ . These integrated activities represent 70% of the total activity discharged by the nuclear industry, the remaining fraction being retained in the river system.<sup>10</sup> It must be noted that the ratio  $^{238}\text{Pu}/^{239,240}\text{Pu}$  in the Marcoule discharge (0.2) is much higher than that in the global fallout (0.03) and is an important tool to trace this contribution in the river and coastal area. As the Marcoule plant is being dismantled, we expect, in the coming years, an increase in the amount of Pu isotopes that is discharged.

Additional sources of both  $^{137}\text{Cs}$  and  $^{239,240}\text{Pu}$  are the exchanges through the Strait of Gibraltar and the Turkish Straits, which are discussed in the following sections.

The total amounts of artificial radionuclides delivered to the Mediterranean Sea (reference time: 2010) from the different sources are summarized in Table 1.

## 5 RADIONUCLIDE DISTRIBUTION AND INVENTORIES IN THE WATER COLUMN

Anthropogenic radionuclides entered the Mediterranean Sea mainly through the atmosphere and through rivers. When in surface water, depending on their biogeochemical behavior, they can follow the water masses (soluble, “conservative” radionuclides like  $^3\text{H}$ ,  $^{137}\text{Cs}$ , and  $^{90}\text{Sr}$ ) or be scavenged by the particulate matter in suspension or taken in the biological cycle (“nonconservative” radionuclides like  $^{239,240}\text{Pu}$  and  $^{241}\text{Am}$ ).

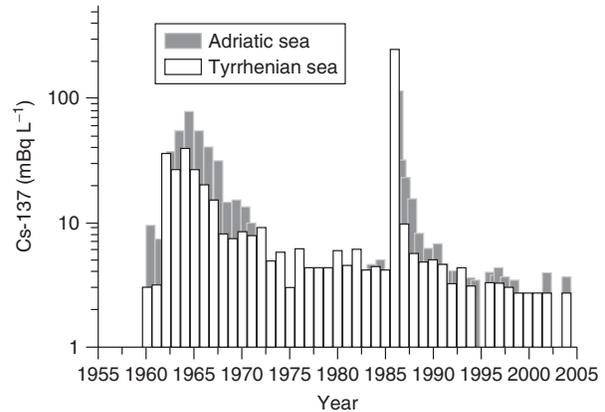
In the Mediterranean Sea,  $^{137}\text{Cs}$  is the most abundant anthropogenic radionuclide and also the main contributor to radioactive dose to the population from the marine pathway. Consequently, there is a very good definition of the time trend of its concentration in surface seawater, mainly deriving from institutional monitoring activities at the national level. In the last decade and following the Chernobyl accident, there also was a significant increase in the number of  $^{137}\text{Cs}$  measurements carried out in the water column of the open sea. Data are also available for  $^{90}\text{Sr}$ , monitored at the national level in surface water. Its vertical distribution is however less defined, with only sparse data available. The two radionuclides are present in seawater as positive ions and their distribution in the open ocean water column is mainly controlled by the water mass dynamics. A third ‘‘conservative’’ radionuclide extensively measured in the Mediterranean Sea is  $^3\text{H}$ . It is present in seawater as part of the water molecule and has largely been used as the tracer for water mass dynamics.

The data set on  $^{239,240}\text{Pu}$  and transuranics, in general, is much smaller, because of the low concentrations, absence of significant local sources, and cumbersome radiochemical procedures for their determination. Plutonium chemistry in seawater is complex: it can be present in any of the four oxidation states, III, IV, V, and VI. It is generally accepted that the reduced form is mainly Pu(IV), very likely as  $\text{Pu}(\text{OH})_4$ , adsorbed onto suspended particles, while the oxidized form is predominantly Pu(V), probably as  $\text{PuO}_2^{2+}$  and its complexes. In the Mediterranean Sea, the bulk of Pu inventory is in the oxidized form, particularly in open waters, while the quantities in particulate or colloidal form are comparatively small.<sup>14</sup> Only 5–10% of Pu is in the particulate form. However, it is this small fraction that makes its distribution different from that of the conservative radionuclides.

## 5.1 Conservative Radionuclides ( $^{137}\text{Cs}$ , $^{90}\text{Sr}$ , and $^3\text{H}$ )

### 5.1.1 Surface Seawater

The time trend of  $^{137}\text{Cs}$  concentration in surface seawater from 1960 to the early 2000s is shown in Figure 3, where we have reported the data collected for the Tyrrhenian Sea and the Adriatic Sea. Most data come from the Italian national network for the survey of environmental radioactivity, and they refer to the data for the Tyrrhenian Sea to the coastal stations of Naples and La Spezia and for the Adriatic Sea to the station in Venice.<sup>15</sup> The series has been completed for the 2000s with data collected by ENEA in the pelagic area of both seas. There is a clear decrease in concentrations after the Nuclear Test Ban Treaty (1963) and a leveling off in the 1970s. Maximum concentrations were reached in the second half of 1964:  $54\text{ Bq m}^{-3}$  in the Tyrrhenian Sea and  $100\text{ Bq m}^{-3}$  in the Adriatic Sea. Until 1970, concentrations were systematically higher in the Adriatic Sea, which was strongly influenced by river inputs carrying part of the radionuclides

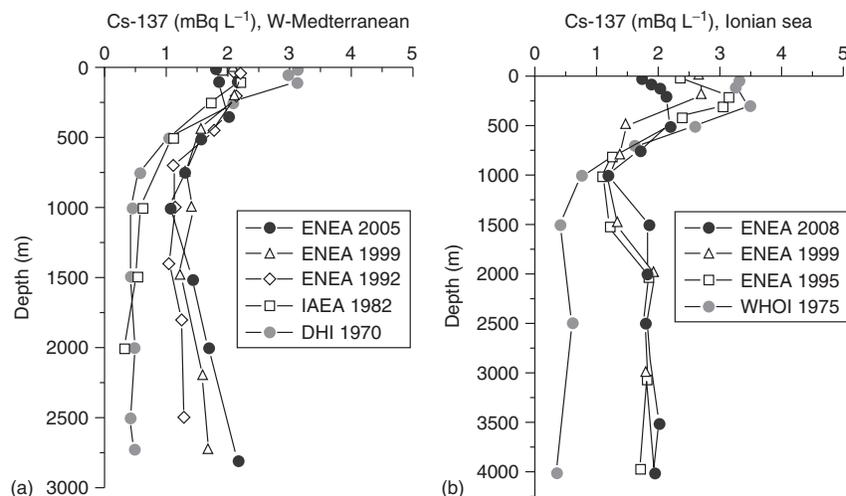


**Figure 3** Time trend of  $^{137}\text{Cs}$  concentration in surface seawater of the Adriatic Sea and Tyrrhenian Sea (1960–2005)

deposited on land to the sea. The Chernobyl fallout in 1986 produced a sharp increase in concentrations. In the Ligurian Sea, an increase of about 2 orders of magnitude (from 5 to almost  $500\text{ mBq L}^{-1}$ ) was observed in the first few days of May 1986. However, the intensity of the peak was very variable in the Mediterranean, and more intense in the northern and eastern basins. In 1990,  $^{137}\text{Cs}$  concentrations were back to the pre-Chernobyl value of about  $5\text{ mBq L}^{-1}$  all over the Mediterranean Sea, except in some areas of the Aegean Sea, which received the ‘‘contaminated’’ Black Sea input.<sup>16</sup> At present,  $^{137}\text{Cs}$  concentrations in surface seawater range between 2 and  $3\text{ mBq L}^{-1}$ . In the North Aegean Sea, the water of Black Sea origin still shows higher concentrations ( $5\text{--}10\text{ mBq L}^{-1}$ ). The decrease observed after 1963 is only partly related to the decrease in fallout deposition and to physical decay, being rather due to radionuclide vertical transport by diffusion and convection, as discussed above. The apparent half-life of  $^{137}\text{Cs}$  has been estimated to be 13 years, lower than the average value reported for the world’s oceans (28 years).<sup>7</sup> The decline in surface concentrations after the Chernobyl event was much faster than in the 1960s. This is in relation to the short input and to mixing with ‘‘noncontaminated’’ waters coming from the southern and western basins.

### 5.1.2 Water Column Profiles, Inventories, and Time Trend

Efficient convection processes, taking surface water and associated radionuclides to depth, occur in a few areas of the Mediterranean. Consequently, the vertical radionuclide profiles are different in different regions, depending on the distance from the dense water formation areas. It was between the late 1960s and the beginning of the 1970s that the water column measurements carried out by the Woods Hole Oceanographic Institution (WHOI:  $^{137}\text{Cs}$ ,  $^{90}\text{Sr}$ , and  $^{239,240}\text{Pu}$ ), by the Deutsche Hydrographisches Institut (DHI:  $^{137}\text{Cs}$ ,



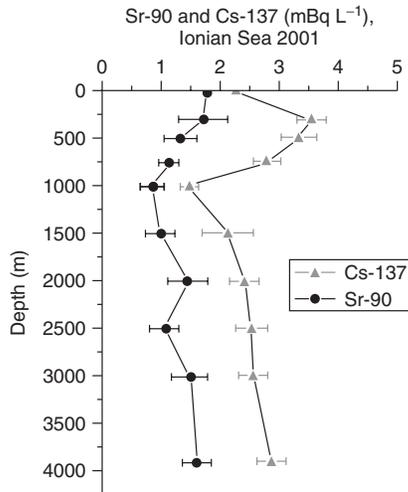
**Figure 4** Time trend of the vertical profiles of  $^{137}\text{Cs}$  in the water column of the Algero-Balearic Basin (a) and Ionian Sea (b)

$^{90}\text{Sr}$ ) and by the Miami University ( $^3\text{H}$ ) reported first these differences: both in the eastern and western Mediterranean  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  vertical profiles showed an almost exponential decrease from the surface to greater depths and a more or less pronounced subsurface maximum at intermediate depths (Figure 4(a) and (b)). Both radionuclides were detectable down to the bottom (3000–4000 m) as a result of deep convection. However, the concentrations in the deep layers of the western Mediterranean and western Ionian Sea were considerably higher than that in the deep Levantine Sea. This is because the first two basins are close to the formation areas of the WMDW and EMDW and their bottom layer contains “recent” waters, oxygenated and relatively rich in elements of atmospheric origin, like anthropogenic radionuclides. This is the basic mechanism making anthropogenic radionuclides important tools to trace water mass dynamics and define their timescales. Tritium (unlike  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$ ) could be determined with high precision also from small volumes of water, and it was then possible to define with a good resolution its distribution along ocean sections (see *Tritium*). In the Mediterranean Sea,  $^3\text{H}$  was analyzed along a section from Sicily to Cyprus in 1977 and in 1987.<sup>17,18</sup> In the deep layer, the recently formed EMDW coming from the Adriatic Sea was clearly visible as a bottom core with relatively elevated concentrations at the western end of the Ionian Sea, spreading eastward into the Levantine Basin. In the whole of Eastern Mediterranean there was a layer with minimum  $^3\text{H}$  concentrations, centered at 1500-m depth and with increasing thickness from west to east, which marked the oldest, least “ventilated” waters of the basin. We can assume that before the Chernobyl accident the distribution of  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  were similar to that of Tritium, having the same source and similar behavior.

These distributions have evolved with time, reflecting new inputs and changes in water circulation.<sup>19</sup> Let us consider

first  $^{137}\text{Cs}$  and, as an example, its vertical profiles in the Algero-Balearic Basin and in the Ionian Sea (Figure 4(a) and (b)). In the 1970s, the vertical profiles showed a clear subsurface maximum in the depth interval 200–400 m, corresponding to the LIW. This maximum was more pronounced in the Ionian Sea, relatively close to the LIW formation area, than in the western Mediterranean, where this water arrived after a few years and after traveling a long pathway, during which it was mixed with adjacent waters, both containing less  $^{137}\text{Cs}$ . Below the LIW, levels decreased almost exponentially and in both areas  $^{137}\text{Cs}$  was detectable down to the bottom, a few years after the maximum atmospheric input (1963). The profiles in the 1990s have been modified by two factors: the additional  $^{137}\text{Cs}$  input due to the Chernobyl accident, which temporarily increased surface levels in some areas, and the EMT that produced a massive input of Cretan Deep Water, having relatively high  $^{137}\text{Cs}$  concentration to the bottom layer of the eastern Mediterranean. The vertical profiles in this period in the Ionian Sea showed a pronounced  $^{137}\text{Cs}$  increase in the LIW and in the deep waters, below 1500 m. A tracer minimum still marked the “oldest” waters of the basin, confined to the depth interval 500–1500 m. In the western Mediterranean, the Chernobyl input was lower and the propagation of the EMT signal required some time. Consequently, the  $^{137}\text{Cs}$  vertical profile was smoother and the concentrations in surface water and LIW were only slightly higher than in the WMDW. In the 2000s, the thickness of the tracer minimum level in the eastern Mediterranean is further reduced, and the present profile in the western Mediterranean shows almost no differences in concentrations with depth. This tendency is expected also in the future.

From a quantitative point of view, in 2008, the inventory of  $^{137}\text{Cs}$  at the two stations has roughly doubled with respect to 1977, decay corrected (Ionian Sea, 4000 m: 3.4



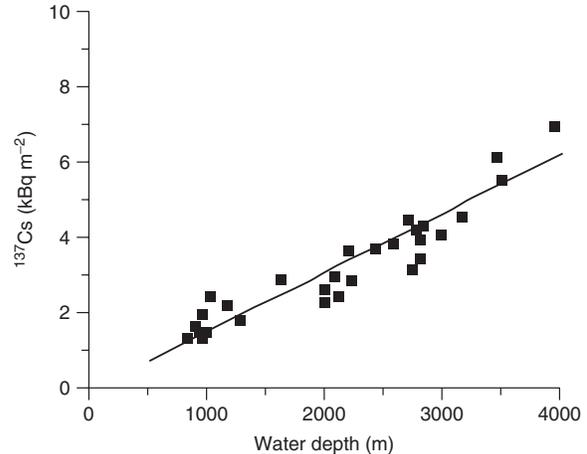
**Figure 5** Vertical profiles of  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  in the Ionian Sea (2001)

and  $7.4 \text{ kBq m}^{-2}$  in 1977 and 2008, respectively; Algero-Balearic Basin, 2800 m:  $2.1$  and  $4.5 \text{ kBq m}^{-2}$  in 1977 and 2008, respectively). It must be noted that already in 1975 the inventory in the two areas was higher than the cumulative fallout deposition (about  $3 \text{ kBq m}^{-2}$ ). The large inventories clearly reflect an efficient, continuous transfer of the radionuclide from surface and coastal areas to the deep sea. Besides, in 1986 there was the additional input due to the Chernobyl accident, which was partly responsible for the further increase in inventories. The contribution of the Chernobyl accident can be estimated by analyzing the distribution of  $^{90}\text{Sr}$ . As discussed before,  $^{90}\text{Sr}$  was not present in the Chernobyl fallout, and the ratio  $^{137}\text{Cs}/^{90}\text{Sr}$  in the Mediterranean before the accident was 1.5. Figure 5 shows its vertical profile at the station in the Ionian Sea: it is much smoother than that of  $^{137}\text{Cs}$ , which shows marked differences in LIW and in the deep water. From this profile and from the pre-Chernobyl  $^{90}\text{Sr}/^{137}\text{Cs}$  ratio, we have estimated a Chernobyl contribution of about 25% in 1999. Data from Lee (2003)<sup>11</sup> for the Ligurian Sea indicate that in 2001, in this area of the western Mediterranean, less than 10% of the inventory is related to the Chernobyl input.

In Figure 6, we report  $^{137}\text{Cs}$  inventories in the water column (decay corrected to 2010) as a function of depth. From these data we have derived a linear relationship between the two parameters:

$$^{137}\text{Cs Inv (Bq m}^{-2}) = 1.6 \times \text{Depth (m)}$$

Using the surface areas corresponding to various depth intervals, we have estimated the total  $^{137}\text{Cs}$  inventory in the Mediterranean water column to be  $6.1 \text{ PBq}$  (see Section 9, Table 2).



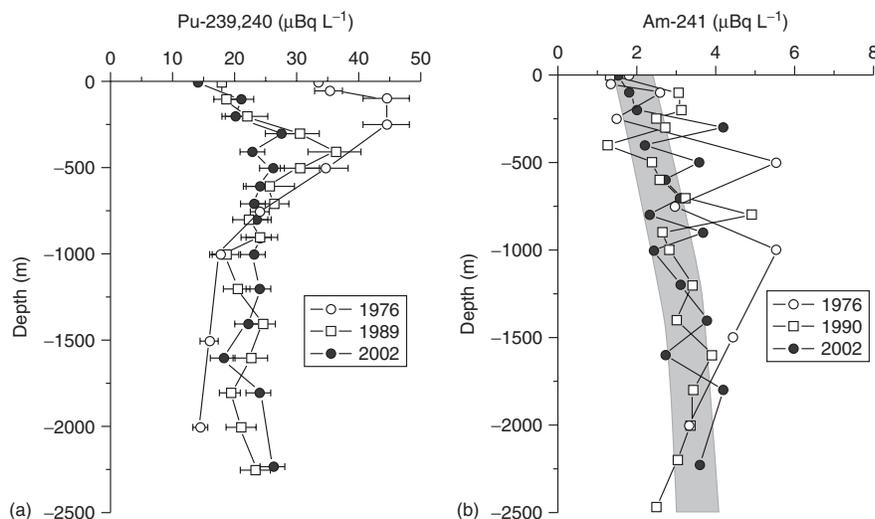
**Figure 6** Relationship between  $^{137}\text{Cs}$  inventory (decay corrected to 2010) and water column depth

## 5.2 Nonconservative Radionuclides

A recent analysis of the published  $^{239,240}\text{Pu}$  data for surface seawater<sup>3,20</sup> shows a relatively large variability in concentrations and a decrease from  $43 \mu\text{Bq L}^{-1}$  in 1975 to a range of  $8\text{--}14 \mu\text{Bq L}^{-1}$  in the period 1994–2001.<sup>11</sup> The decrease is exponential, with a decay constant of 13.6 years ( $t_{1/2}$ : 10.2 years), slightly shorter than that of  $^{137}\text{Cs}$ .

The removal of transuranics from surface waters is controlled not only by water dynamics (like conservative radionuclides) but also by association and sinking with particulate matter. In continental shelf waters, relatively rich in suspended particulate matter, about 10% of  $^{239,240}\text{Pu}$  and up to 45% of  $^{241}\text{Am}$  are found in the particulate fraction.<sup>21</sup> This percentage is smaller for open waters, characterized by low particle population, where typical values are about 5% for  $^{239,240}\text{Pu}$  and 10% for  $^{241}\text{Am}$ . However, the sinking and cycling of particles through the water column is the main mechanism controlling the shape of transuranics' vertical profiles, which, in the 1970s (Figure 7(a) and (b)), were characterized by pronounced subsurface maxima at intermediate depths (250–500 m). At these depths decomposition of organic matter takes place, releasing the associated radionuclides to the soluble phase. It was shown<sup>22</sup> that the depth and extent of the maximum can vary with time even at the same station, probably in relation with biological processes: a spring phytoplankton bloom may result in enhanced scavenging of plutonium and more pronounced maximum at depth.

Figure 7(a) shows the time trend of  $^{239,240}\text{Pu}$  in the water column of the northwestern Mediterranean from 1970 to 2002: there is a clear decrease in concentrations at surface and intermediate depths, the subsurface maximum fades, and levels increase at depth, below 1000 m. At this station, in the time interval considered, the inventory remains substantially



**Figure 7** Time trend of the vertical profiles of  $^{239,240}\text{Pu}$  (a) and  $^{241}\text{Am}$  (b) in the western Mediterranean (1976–2002).<sup>11,19</sup> The hatched area in (b) shows the trend of  $^{241}\text{Am}$  vertical profiles in 1990–2002

unchanged, around  $50 \text{ Bq m}^{-2}$ . However, it has been shown<sup>18,20</sup> that  $^{239,240}\text{Pu}$  inventory in the whole of western Mediterranean water column diminished exponentially from about 50 TBq in 1971 to about 25 TBq in 1994, indicating a loss of about 2% per year from the water column all over the basin. Part of this loss is due to  $^{239,240}\text{Pu}$  sinking in the open sea in association with particles. Particulate  $^{239,240}\text{Pu}$  flux in the northwestern Mediterranean at 2000 m was, in 1990,  $0.10\text{--}0.24 \text{ Bq m}^{-2} \text{ year}^{-1}$ , accounting for about 30–70% of the annual loss.<sup>22</sup> The remaining fraction should leave the water column through sedimentation processes in the coastal areas, where high particle population and enhanced scavenging processes are able to sequester relatively large quantities of transuranics in sediments (see Section 6). The water column inventory in this area, instead, remains constant, because the dense water formation process efficiently transfers  $^{239,240}\text{Pu}$  from surface and coastal areas to deeper regions, as it happens for  $^{137}\text{Cs}$ .

Little information is available for  $^{241}\text{Am}$  (Figure 7(b)) (see *Americium and Curium*). Its profiles show a general tendency of increasing levels with depth ( $1.5$  to  $4 \mu\text{Bq L}^{-1}$ ). More than one subsurface maximum is often present, usually not coincident with plutonium maximum, indicating different biogeochemical scavenging behavior of the two radionuclides. The vertical profiles obtained in 1976, 1990, and 2002 seem to differ more in the depth and intensity of the peaks than in the general trend.  $^{241}\text{Am}$  inventory in the depth interval 0–2000 m decreased by 24% from 1976 to 1990 ( $8 \text{ Bq m}^{-2}$  and  $6.1 \text{ Bq m}^{-2}$ , respectively) and remained substantially unchanged in the following 12 years ( $6.2 \text{ Bq m}^{-2}$ ).

A peculiar feature of the Mediterranean Sea is the increased  $^{241}\text{Am}/^{239,240}\text{Pu}$  activity ratio in bulk seawater at

depth, also reflected in deep-sea sediments. This feature was evidenced already in the 1970s, when Fukai *et al.*<sup>22</sup> calculated ratios of 0.05 at the surface and 0.2–0.3 below 1000 m. Recent (2002) ratios<sup>11</sup> are more homogeneous along the water column, with mean values of 0.10 in the upper 200 m and 0.14 below 1000 m. Fowler *et al.*<sup>23</sup> examined a large number of samples from the Mediterranean Sea and from an oligotrophic area of the Pacific Ocean, concluding that the  $^{241}\text{Am}/^{239,240}\text{Pu}$  ratio is much smaller in the Mediterranean than in the Pacific (on average, six times lower). They suggest that the reason for this peculiar behavior in the Mediterranean could be related to the frequent atmospheric inputs of massive amounts of aluminosilicate particles from the Sahara (Saharan dust), furnishing a particle type for which  $^{241}\text{Am}$  has a greater binding affinity than  $^{239,240}\text{Pu}$ . This, in turn, could lead to higher vertical transport rates of  $^{241}\text{Am}$  relative to  $^{239,240}\text{Pu}$  and higher  $^{241}\text{Am}$  transport, in general, compared with that in the open North Pacific where large-scale dust inputs are rare.

### 5.3 Natural Radionuclides ( $^{210}\text{Pb}$ , $^{210}\text{Po}$ , $^{238}\text{U}$ , $^{234}\text{Th}$ )

Uranium-238 ( $t_{1/2} = 4.7 \times 10^9$  years) is present in oxygenated ocean waters as the soluble uranyl carbonate species  $\text{UO}_2(\text{CO}_3)_3^{4-}$ . Its concentration is normally obtained from a standard relationship with salinity, which has been derived for the open ocean, assumed at steady state.<sup>24</sup> Small deviations from the linear relationship have been shown for low salinity (Baltic Sea) and anoxic (deep Black Sea) environments. Questions have also been raised for the Mediterranean, which is a semi-enclosed, high-salinity basin, characterized by the localized input from several

major rivers. A recent paper,<sup>25</sup> based on a large, trans-Mediterranean sampling, indicates a small enhancement of the concentrations with respect to the open ocean and suggests a new relationship, specific for the Mediterranean:  $^{238}\text{U}$  ( $\text{dpm L}^{-1}$ ) =  $(0.0713 \pm 0.0012) \times \text{salinity}$  (see *Natural Radioactivity; Uranium*).

Knowledge of uranium concentration is particularly important, because the  $^{238}\text{U}$ :  $^{234}\text{Th}$  disequilibrium has largely been used in recent times to derive particle fluxes in the upper ocean.<sup>26</sup>  $^{238}\text{U}$  decays to the particle-reactive nuclide  $^{234}\text{Th}$  ( $t_{1/2} = 24.1$  days), which is removed from solution in the presence of particulate material (see *Thorium*). The resulting disequilibrium is widely exploited to trace particle export from the euphotic zone and associated organic carbon cycling. It is through this method that a great part of the information on particulate organic carbon fluxes has been derived in recent years for the Mediterranean Sea, as for the global ocean.

Another group of natural radionuclides that recently received great attention, for their use as tracers for marine processes, is that composed of  $^{210}\text{Pb}$  ( $t_{1/2} = 22$  years) and its granddaughter  $^{210}\text{Po}$  ( $t_{1/2} = 138$  days) (see *Lead; Polonium*). Both radionuclides are particle reactive, but characterized by varying affinity in terms of efficiency and type of matter to which they associate. They are produced in the water column by the decay of  $^{226}\text{Ra}$  and, in addition, have an atmospheric source via the disintegration of  $^{222}\text{Rn}$  emanated by terrestrial rocks (see *Radium; Radon*). On land and in coastal areas,  $^{210}\text{Pb}$  gets rapidly associated to atmospheric particles and its residence time in the atmosphere is only a few days. So,  $^{210}\text{Po}$  (produced by the decay of  $^{210}\text{Pb}$ ) flux at the sea surface is only some 10–20% of that of  $^{210}\text{Pb}$ . In coastal areas the atmospheric flux dominates, while in the open sea the main source is  $^{226}\text{Ra}$  in situ decay. In coastal and surface waters,  $^{210}\text{Po}$  is efficiently taken up by marine organisms living in the photic zone, while  $^{210}\text{Pb}$  is transported to the seafloor in association with particles. In the Mediterranean, the reported concentrations of  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  in surface waters are highly variable, in relation to their biogeochemical behavior: the range is  $0.6\text{--}3.6\text{ mBq L}^{-1}$  for  $^{210}\text{Po}$  and  $0.6\text{--}2.4\text{ mBq L}^{-1}$  for  $^{210}\text{Pb}$ . The  $^{210}\text{Po}/^{210}\text{Pb}$  ratio in the particulate matter is usually  $>1$ . The estimated residence times in surface waters<sup>27</sup> are 0.8 years for  $^{210}\text{Pb}$  and 3 years for  $^{210}\text{Po}$  in the northwestern Mediterranean. Association of  $^{210}\text{Po}$  to biological particles and their recycling in the photic zone is the mechanism likely determining the long residence time of  $^{210}\text{Po}$ .

#### 5.4 Exchanges at the Gibraltar Strait

The narrow (15 km) and shallow (average depth 350 m) Gibraltar Strait, connecting the Mediterranean with the Atlantic Ocean, is characterized by a two-layer flow. The Atlantic Water (AW) flowing into the Mediterranean travels through the surface (0–200 m) to the Alboran Sea, to later become the Modified Atlantic Water (MAW) on its way eastwards along the North African shore. The Mediterranean

Outflowing Water (MOW) is a mixture of two denser waters: the LIW and the WMDW.

The fluxes of natural and anthropogenic radionuclides through the strait have been estimated by measurements carried out during several campaigns at the Strait, performed in different seasons, in the period 1997–1999.<sup>13</sup> The activity concentrations and fluxes of natural ( $^{210}\text{Pb}$  and  $^{210}\text{Po}$ ) and anthropogenic ( $^{239,240}\text{Pu}$  and  $^{137}\text{Cs}$ ) radionuclides have been determined in the different water masses crossing the Strait. Mean activity concentrations of  $^{210}\text{Po}$  ( $1.53 \pm 0.34\text{ Bq m}^{-3}$ ) and  $^{210}\text{Pb}$  ( $1.16 \pm 0.50\text{ Bq m}^{-3}$ ) in the AW entering the Mediterranean Basin are about double those measured in the Mediterranean outflow, namely  $0.84 \pm 0.34\text{ Bq m}^{-3}$  for  $^{210}\text{Po}$  and  $0.66 \pm 0.34\text{ Bq m}^{-3}$  for  $^{210}\text{Pb}$ . The opposite trend is observed for  $^{239,240}\text{Pu}$ , with average concentrations of  $9.9 \pm 3.0\text{ mBq m}^{-3}$  in the incoming Atlantic flow and  $22.0 \pm 3.0\text{ mBq m}^{-3}$  in the exiting Mediterranean water. In the case of  $^{137}\text{Cs}$ , the same concentrations were quantified in the waters moving inward ( $2.52 \pm 0.28\text{ Bq m}^{-3}$ ) and outward ( $2.14 \pm 0.52\text{ Bq m}^{-3}$ ) from the Mediterranean Sea. Assuming the flux of both AW and MOW at the strait<sup>1</sup> to be  $0.9 \times 10^6\text{ m}^3\text{ s}^{-1}$ , a net annual input flux of 14 TBq for  $^{210}\text{Pb}$  and 19 TBq for  $^{210}\text{Po}$ , and a net annual loss of 0.34 TBq for  $^{239,240}\text{Pu}$  were calculated, while  $^{137}\text{Cs}$  input and output fluxes appeared to be balanced.

Fluxes at the strait have changed with time, depending on the radionuclides' concentration in the surface AW and in the MOW. Before 1994, no direct measurements have been reported for the straits, but fluxes have been derived from the vertical profiles of  $^{137}\text{Cs}$  and  $^{239,240}\text{Pu}$  in 1970s and 1980s. Up to 1986, a total inflow of 1.5 PBq of  $^{137}\text{Cs}$  (corresponding to 0.9 PBq in 2010) and a total outflow of 40 TBq of  $^{239,240}\text{Pu}$  were estimated.<sup>4</sup>

#### 5.5 Exchanges at the Turkish Straits System

Also the Turkish Straits system is characterized by a two-layer flow: low-salinity surface water leaves the Black Sea through the very shallow and narrow Bosphorus and Dardanelles Straits and the Marmara Sea, balanced by a more saline, Mediterranean water flow at depth. A vigorous mixing takes place at the straits, deeply modifying the characteristics of the water masses. It is hence quite difficult to estimate the exchange of radionuclides between Black Sea and Mediterranean, based on the vertical profiles in the two seas. United Nations Environment Programme (UNEP),<sup>4</sup> based on vertical profiles of  $^{137}\text{Cs}$  and  $^{239,240}\text{Pu}$  in the Black Sea, reports a net input of 0.1 PBq of  $^{137}\text{Cs}$  from the Black Sea to the Mediterranean and an outflow of 0.25 TBq of  $^{239,240}\text{Pu}$  up to 1986. The Chernobyl accident produced a heavy input of  $^{137}\text{Cs}$  to the Black Sea. Taking the direct fallout and the delayed contribution from the rivers into account, Egorov *et al.*<sup>12</sup> estimated that, because of Chernobyl fallout, a total of 0.3 TBq will be exported to the Mediterranean Sea.

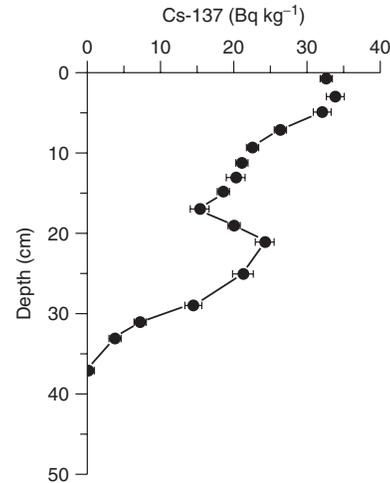
## 6 RADIONUCLIDES IN SEDIMENTS

Radionuclide concentrations and inventories in sediments are highly variable, being usually the highest on the continental shelf and near the river mouths and the lowest in the deep sea. In fact, the continental margins are areas where particles transported by rivers, with associated radionuclides, are deposited. Moreover, the high particle population also allows effective scavenging and transport of nonconservative radionuclides present in seawater to the seafloor.

The vertical profiles of anthropogenic radionuclides in the sediments of the coastal areas mainly reflect their input function: a peak at depth, corresponding to the maximum global fallout deposition, and a progressive decrease toward the surface. For  $^{137}\text{Cs}$ , a more or less pronounced subsurface maximum may also be observed near the surface, corresponding to the Chernobyl input. In Figure 8, we show a vertical profile of  $^{137}\text{Cs}$  in the sediments from the North Adriatic shelf, collected in 2001. The peak due to global fallout is visible at 22 cm, while the Chernobyl input produced a significant increase in concentrations in the upper 5-cm layer.  $^{137}\text{Cs}$  inventory here was  $6 \text{ kBq m}^{-2}$  in 2001. We can assume that this is a typical profile characterizing the Mediterranean shelf. However, Cesium-137 inventories in the sediments of the coastal areas show a wide range of values, also in relation to local sources and to the patchiness of the Chernobyl fallout. In the submerged deltas of major rivers inventories are as high as  $400 \text{ kBq m}^{-2}$  (Rhône prodelta), up to 2 orders of magnitude higher than in the surrounding areas ( $1\text{--}9 \text{ kBq m}^{-2}$ ). The studies show that a significant part of the sediments and associated radionuclides are only temporarily trapped in the prodelta. These deposits, usually located in very shallow areas (5–10 m water depth), can be effectively resuspended and particles can be transported elsewhere by the action of waves.<sup>8,28</sup>

A large data set has recently been published,<sup>29</sup> with inventories of  $^{137}\text{Cs}$ ,  $^{239,240}\text{Pu}$ , and  $^{210}\text{Pb}_{\text{ex}}$  in the Mediterranean deep-sea sediments from the Algero-Balearic Basin, the Ionian Sea, and the Levantine Basin at water depths between 2800 and 4000 m. With the sediment accumulation rate being in the order of a few centimeters per 1000 years, anthropogenic radionuclides reach in these sediments a maximum depth of 4 cm, and their concentrations generally decrease with depth and are mainly controlled by mixing processes.  $^{137}\text{Cs}$  inventories (decay corrected to 2000) range from  $74 \text{ Bq m}^{-2}$  in the Algero-Balearic Basin to  $100\text{--}140 \text{ Bq m}^{-2}$  in the Ionian Sea, and to  $97\text{--}127 \text{ Bq m}^{-2}$  in the Levantine Basin. In general, these inventories are only a small fraction, less than 2%, of the water column inventory. Also at shallower depths (270–1220 m, Algerian coasts)<sup>30</sup>  $^{137}\text{Cs}$  inventories are a small percentage (7%) of that in the water column, ranging from 180 to  $250 \text{ Bq m}^{-2}$ .

For  $^{239,240}\text{Pu}$ , the deep-sea sediment inventories are very similar all over the Mediterranean Sea,<sup>28</sup> with mean values of  $3 \text{ Bq m}^{-2}$  in the western basin and  $2.95 \text{ Bq m}^{-2}$  in



**Figure 8** Vertical profile of  $^{137}\text{Cs}$  in a sediment core from the North Adriatic Sea (2001)

the eastern basin. Although plutonium is a nonconservative radionuclide, these values are only a small fraction of the water column inventory (approximately 6%). As explained in the Introduction, the Mediterranean is an oligotrophic sea and in the pelagic areas particle concentration is usually very small, limiting the scavenging of particle-reactive radionuclides. Moreover, a significant part of the biogenic particles present in the surface photic zone, when sinking, is decomposed at intermediate depth, releasing the associated elements to the soluble phase. That is why the  $^{239,240}\text{Pu}$  inventories in sediments of the open sea are so small. In contrast, in the coastal areas, where particle population is much higher than in the open sea, they are generally higher than the cumulative fallout deposition: values 2–3 times higher than the cumulative fallout deposition have been reported for the Spanish and Italian continental shelf. Their vertical profiles in the sediments are similar to those of  $^{137}\text{Cs}$ , but do not show any Chernobyl signal. Along the continental slope, an important role is played by canyon systems: particles are preferentially transported down the canyon axis and deposited at the fan end. Hence, in these areas, relatively high sediment accumulation rates are found, associated with radionuclide inventories comparable to those on the shelf.<sup>3,31</sup>

## 7 HOT SPOTS

### 7.1 Rhône River Mouth

The area influenced by the Rhône river mouth has been studied in detail, because it receives the radioactive discharges from the Marcoule reprocessing plant. In this area,

a total inventory of  $^{137}\text{Cs}$  of 19.6 TBq in sediments was estimated in 1990.<sup>8</sup> At least 50% of the inventory was due to the liquid discharges of the reprocessing plant.

The distribution of  $^{238}\text{Pu}$  and  $^{239,240}\text{Pu}$  has been analyzed in surface sediments and in a long core collected in the Rhône prodelta. In this area, characterized by very high sediment accumulation rate, plutonium isotopes were present down to the bottom of the core at almost 5-m depth in the sediment. Present surface concentrations are below  $1\text{ Bq kg}^{-1}$  and the maximum activity is found down to 3 m ( $6\text{ Bq kg}^{-1}$ ). Relatively high  $^{238}\text{Pu}/^{239,240}\text{Pu}$  ratios (upper 50 cm: 0.14; at 170–190 cm: 0.27, maximum activity ratio; fallout: 0.04) indicated strong influence of the Marcoule discharges. Most Pu (almost 90%) is stored below a layer of 1.5 m of recent sediment and will be trapped here for a long time. The spatial distribution of Pu isotopes in the area shows a decrease in the  $^{238}\text{Pu}/^{239,240}\text{Pu}$  ratio with distance from the river mouth, reaching 0.06 at  $\sim 15\text{ km}$  off the river mouth, indicating the decreasing influence of the Marcoule discharges. The analysis of the time trend of concentrations and ratios from 1984 to 2001 indicates plutonium isotopes' decrease near the source, but no significant changes are found going offshore.<sup>32</sup> However, 30% of the total discharges from Marcoule are presently retained in the Rhône river system, mainly associated with sediments.<sup>10</sup> From a long-term perspective, depending on the hydraulic regime of the river and the frequency/intensity of the flood events, this “temporary deposit” might become a significant delayed source of transuranics in the marine environment.

## 7.2 Palomares

On January 17, 1966, a B-52 US bomber collided with a Kc-135 tanker while attempting to refuel. Three of the four unarmed B 28 hydrogen bombs carried by the B-52 crashed on the ground in the vicinity of Palomares, a village in Almeria, south of Spain, 10 km from the seashore of the Gulf of Vera. The high explosive of two of the bombs detonated, spreading transuranic elements to a vast area around the impact points. One bomb fell directly into the sea, and was recovered two months later, after a complex trial and rescue. During the accident, a significant amount of radioactive aerosol enriched in transuranics was transported to the nearby sea by the wind. Immediately after the accident, the top 10 cm of the soil was removed, but agricultural, underbrush, and urban areas remained partly contaminated by  $^{239,240}\text{Pu}$  and  $^{241}\text{Am}$  that reached the sea afterward, by ground weathering and the runoff of the Almanzora and Aguas rivers, flowing through the region.

As a result, the coastal area was contaminated by  $^{239,240}\text{Pu}$ ,  $^{241}\text{Am}$ , and  $^{235}\text{U}$ . Because of the physicochemical behavior of Pu and Am in the marine environment, the redistribution of the radioactivity deposited on land mainly affects the sediments of the shelf and of the complex canyon system of the Gulf of Vera.<sup>33</sup> The continental margin is in fact indented by canyons with pronounced slopes, which can act

as “conduits” for the sedimentary matter, flowing toward the deep sea through strong turbidity currents. The preferential area of contamination is found in the narrow continental shelf with estimated maximum inventories of 1.37 TBq of  $^{239,240}\text{Pu}$  and 0.3 TBq of  $^{241}\text{Am}$  (ingrowth from  $^{241}\text{Pu}$  is not considered).

## 8 RADIONUCLIDE CONCENTRATION IN ORGANISMS

Because of the low radioactivity levels and the almost complete absence of point sources in the Mediterranean area, very little information has recently been published in the open literature on radionuclide concentration in organisms.  $^{137}\text{Cs}$ , being the main anthropogenic contributor to radioactive dose to the population from the marine pathway, is the only radionuclide systematically measured by the different countries through their own national networks for monitoring environmental radioactivity. The time trend of its concentration in mussels and fish in the whole basin has been reviewed in the mid-1990s.<sup>3</sup> Before the Chernobyl accident, the levels were low ( $0.05\text{--}0.6\text{ Bq kg}^{-1}$  w.w. in mussels and  $0.1\text{--}0.9\text{ Bq kg}^{-1}$  w.w. in fish) and there was a large variability between basins, likely related to heterogeneity in species sampled (different food habits) and of the sampling area. The Chernobyl input increased the variability, in relation to the patchiness in deposition. The maximum concentrations reported after the accident were in general below  $10\text{ Bq kg}^{-1}$  in mussels and fish, although in a few cases levels up to  $30\text{--}60\text{ Bq kg}^{-1}$  were reported. The highest concentrations were measured in the North Adriatic and in the North Aegean Sea. Pre-Chernobyl levels were reached again by 1989–1990. The concentration factors were 100 in fish and 30 in mussels.

In 2002, the Mediterranean Science Commission (CIESM) launched the “Mediterranean Mussel Watch Program” with the main objective of documenting reliable baseline levels of radionuclides in the Mediterranean and Black Seas' coastal waters, using the mussel, *Mytilus galloprovincialis*, as a unique bioindicator. The samples were collected and analyzed according to a common protocol, and an intercalibration exercise has been performed, to assure comparability of the data.  $^{137}\text{Cs}$  levels in 2004–2006 (Figure 9) were found to be very low (usually  $<0.2\text{ Bq kg}^{-1}$ ) and decreasing from east to west.<sup>34</sup>

Among natural radionuclides,  $^{210}\text{Po}$  is effectively accumulated by marine organisms and is the main contributor of the radioactive dose to the population. Baseline data on  $^{210}\text{Po}$  concentrations in Mediterranean coastal areas are sparse. This is why the next phase, Phase II, of the CIESM Mediterranean mussel watch program will also include  $^{210}\text{Po}$  measurements. The first sampling campaign has been carried out in the Adriatic Sea in 2008. Preliminary results are already available,<sup>35</sup> showing levels ranging from  $90\text{ to }600\text{ Bq kg}^{-1}$  w.w.

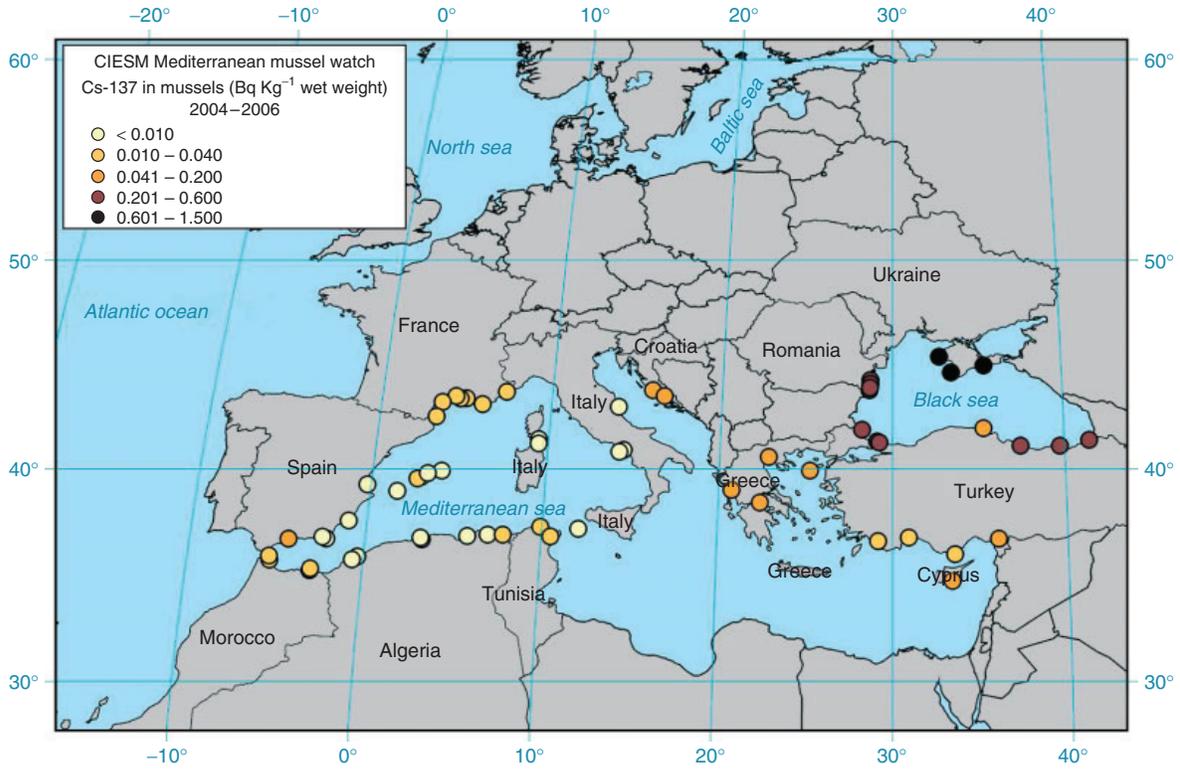


Figure 9 Concentration of <sup>137</sup>Cs in mussels (Bq kg<sup>-1</sup> w.w.) in the Mediterranean and Black Seas, 2004–2006

9 RADIONUCLIDE MASS BALANCE

On the basis of the distributions of <sup>137</sup>Cs and <sup>239,240</sup>Pu given above, we have estimated the total inventory of the two radionuclides in the Mediterranean Sea (Table 2).

<sup>137</sup>Cs, the most abundant anthropogenic radionuclide, has been efficiently redistributed in the water column. The

total inventory of <sup>137</sup>Cs in the water column of the whole Mediterranean is now (2010) 6 PBq, corresponding to 90% of the total input. Sediments only account for less than 10% of the water column inventory. The Mediterranean total inventory is going to decrease in the future, as the positive input from the Black Sea (Table 1) is too small to balance physical decay and there is no net input at Gibraltar. Nearly 2% of the total

Table 2 Inventory of <sup>137</sup>Cs and <sup>239,240</sup>Pu in the Mediterranean Sea (2010)

Compartment	<sup>137</sup> Cs (Bq m <sup>-2</sup> )	<sup>137</sup> Cs PBq	% of delivery	<sup>239,240</sup> Pu (Bq m <sup>-2</sup> )	<sup>239,240</sup> Pu TBq	% of delivery
Water column 0–100 m	80	0.2		1	2.3	
Water column 100–300 m	240	0.5		3	5.9	
Water column 300–1000 m	720	1.4		9	17	
Water column 1000–1500 m	960	1.4		12	18	
Water column 1500–2000 m	800	1.0		10	12	
Water column 2000–3000 m	1200	1.2		15	15	
Water column 3000–4000 m	1600	0.4		20	4.7	
<b>Water column 0–4000 m</b>		<b>6.1</b>	<b>90%</b>		<b>75</b>	<b>47%</b>
Sediment of shelf	1000	0.2	3 %	150	40	25%
Sediment of deep sea	100	0.2	3 %	3	6.9	4%
<b>Total Mediterranean</b>		<b>6.5</b>	<b>96%</b>		<b>122</b>	<b>76%</b>

inventory (0.13 PBq) is in fact lost due to physical decay, whereas the input from the Black Sea is estimated to be only 0.01 PBq per year.

More difficult is a mass balance for  $^{239,240}\text{Pu}$ , because of the lack of recent data and information on the eastern Mediterranean. The mass balance for this radionuclide is then affected by a very large uncertainty. The major fraction, like for  $^{137}\text{Cs}$ , still resides in the water column, although a significant amount is stored in shelf sediments.

## 10 CONCLUSIONS

From the radiological point of view, the Mediterranean Sea is a “clean environment”, as it only received fallout from nuclear weapon testing and the Chernobyl accident. Discharges from the nuclear industry are small and usually reach the sea through rivers, where they are retained for some time. On the shelf, they affect the sediments in relatively small areas, close to the river mouth. Concentrations in biota are presently undistinguishable from those in areas without point sources.

Actual knowledge on anthropogenic radionuclide distribution is sufficient to draw a picture of the present situation and delineate future trends. Most anthropogenic radionuclides (90% of  $^{137}\text{Cs}$  and 50% of  $^{239,240}\text{Pu}$ ) still reside in the water column. For  $^{239,240}\text{Pu}$ , important reservoirs are the shelf and slope sediments, containing another 25% of its delivery. The Mediterranean total inventories are going to decrease in the future, because

- there are no significant sources of anthropogenic radionuclides;
- there is a net outflow of  $^{239,240}\text{Pu}$  at Gibraltar, not balanced by the Black Sea input;
- $^{137}\text{Cs}$  concentrations are decreasing due to physical decay, not balanced by the input from the Black Sea (there is no net input at Gibraltar).

Concerning natural radionuclides, more detailed information is needed on sources and impact of industrial (phosphate) and extraction activities (oil, gas, and mines).

In the future, the existing valuable data set on radionuclide distribution in the Mediterranean should be better exploited in a multidisciplinary context, in connection to oceanographic and modeling studies: more information can be extracted on water and particle dynamics and on biogeochemical cycles.

Very sensitive analytical techniques are becoming more easily available and less expensive, allowing the determination of radionuclide tracers that, in the past, were not easily measured (e.g.  $^{129}\text{I}$ ,  $^{230}\text{Th}/^{231}\text{Pa}$ ) or required large samples and long shiptime ( $^{14}\text{C}$ ). Their distribution in seawater and sediments will contribute to a better understanding of the

functioning of the Mediterranean system and be an effective tool for the studies on the impact of climate change on the region and on the role of the Mediterranean in the global carbon cycle.

## 11 RELATED ARTICLES

Anthropogenic Radioactivity; Atlantic Ocean; Black Sea; Cesium; Global Trends in Cesium Distribution; Lead; Natural Radioactivity; Oceans and Seas; Plutonium; Polonium; Radium; Uranium.

## 12 ABBREVIATIONS AND ACRONYMS

AW = Atlantic Water; CDW = Cretan Deep Water; CIESM = Mediterranean Science Commission; DHI = Deutsche Hydrographisches Institut; EMDW = Eastern Mediterranean Deep Water; EMT = Eastern Mediterranean Transient; ENEA = Italian National Agency for New Technologies, Energy and Sustainable Economic Development; IAEA = International Atomic Energy Agency; LIW = Levantine Intermediate Water; MAW = Modified Atlantic Water; MOW = Mediterranean Outflowing Water; UNEP = United Nations Environment Programme; UNSCEAR = United Nations Scientific Committee on the Effects of Atomic Radiations; WHOI = Woods Hole Oceanographic Institution; WMDW = Western Mediterranean Deep Water.

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