9 Natural and Man-Made Radionuclides in the Black Sea

K.O. Buesseler and H.D. Livingston

A review is presented of current knowledge on natural and artificial radioactivity in the Black Sea. The unique features of this partially closed basin – an upper layer which is freshened by input from rivers overlying a major anoxic deep water mass – are shown to affect the levels and distributions of many radionuclides. Artificial radionuclides from atmospheric nuclear weapons tests and from the Chernobyl accident are major man-made sources. Both natural and artificial radionuclides are discussed in the context of their geochemical properties, *i.e.* as water or particle tracers. In particular the rapid transfer of uranium and plutonium to Black Sea sediments contrasts strongly with the behavior of these elements in most of the world ocean. The time-series evolution of both the bomb testing and Chernobyl-derived soluble tracers in the upper 500 m of the Black Sea are discussed in the context of upper water circulation and deep mixing. Finally, the radioecological situation in the Black Sea is contrasted with other ocean basins, and the very large dominance of natural radionuclides in terms of human radiation exposure is noted.

9.1. Introduction

As with any oceanic basin, a wide variety of natural and man-made radionuclides can be detected in the waters, sediments and biota of the Black Sea. In contrast to other oceanic settings however, the Black Sea is unusual in that it is the world's largest anoxic basin. As such, it has been extensively studied due to the unique geochemical processes that occur across the oxic/anoxic interface and in the sulfidic deep waters. Due to the stability of these anoxic conditions, the Black Sea can also be used as an analog to ancient anoxic seas. Anoxia is established due to restricted mixing between the brackish surface layers (salinities $\leq$ 18 ppt in upper 100-150 m) and the deeper waters ($\approx$ 22 ppt, max. depth = 2200 m). Riverine fluxes are dominated by inflow from the Danube and the rivers along the N boundary, and outflow is restricted to the narrow and shallow Bosphorus Straits in the

SW Black Sea. Mediterranean waters flow into the Black Sea as an undercurrent in the Bosphorus Straits. The general cyclonic circulation pattern leads to a doming of the isopycnal surfaces in the central basin, and a deepening of the depth of sulfide onset along the margins. The Black Sea is an ideal setting for mass balance studies since characterization of the inflows and outflows can be made. Radionuclides can be valuable tracers of both natural and anthropogenic processes in this basin, given their known sources and behavior.

For radiochemists, the low redox conditions in the Black Sea provide an interesting site to study redox transformations of radionuclides with multiple oxidation states. In addition, soluble tracers, such as ^{137}Cs, ^{90}Sr and ^{3}H introduced from weapons testing and the Chernobyl accident to Black Sea surface waters, can be used to estimate physical exchange rates between the surface and deeper layers. Finally, radionuclides can be used to date the deposition record that has been well preserved in the deep sediments. In this paper we will provide an overview of the sources and behavior of radionuclides in the Black Sea. An emphasis will be placed on those radionuclides whose behavior in the Black Sea contrasts most sharply with other oceanic settings, either due to the low salinities or changing redox environment which is characteristic of this basin.

9.2. Input of Radioisotopes to the Black Sea

The input of radioactivity to the Black Sea from natural and artificial sources is derived from atmospheric fallout and inflow of water from both rivers and Mediterranean inflow through the Bosphorus. However, the unique oceanographic characteristics of the Black Sea affect the behavior and relative activities of these radionuclides making their distributions very different from other seas and the open ocean.

9.2.1. Naturally Occurring Radionuclides

Perhaps the most important observation on Black Sea natural radioactivity derives from the effects of the huge freshwater inflow and relatively small saline inflow of water from the Mediterranean. As most Black Sea salinities lie in the range 18-22 ppt, the average salinity is almost one half that of the open ocean. Accordingly, the concentrations of many the naturally occurring radionuclides in seawater, ^{40}K, ^{87}Rb, ^{235}U, ^{238}U, etc., are correspondingly lower in proportion to open ocean levels. On the other hand, atmospheric input of natural radionuclides should not differ significantly from their input to the open ocean at the same latitude.

9.2.2. Atmospheric Nuclear Weapons Testing

Direct input of artificial radioisotopes from fallout of the products of the atmospheric nuclear weapons tests, in the 50's and 60's especially, would have had the same time history and deposition rate as found at other locations of similar latitude. As the 45° N latitude band of maximum fallout runs across the Black Sea, it must have received high levels of global fallout. By the end of 1985, fallout deposition at this latitude has been shown (Juzdan, 1988) to be 1.84 GBq km^{-2} for ^{90}Sr (which would be equivalent to 2.77 GBq km^{-2} for ^{137}Cs) and, from soil inventories (Hardy *et al.*, 1973), 81.4 MBq km^{-2} for $^{239,240}Pu$. According to Eremeev *et al.* (1993), average Black Sea surface ^{137}Cs activities in 1977 were about 17 Bq m^{-3}. Buesseler *et al.* (1991a) estimated the pre-Chernobyl level of ^{137}Cs in Black Sea surface water in 1986 to be 9 Bq m^{-3}. In a later paper, Buesseler and Livingston (1996) made a more accurate estimate using a salinity normalization technique and put the pre-Chernobyl ^{137}Cs at 18 ppt (a typical salinity in the mixed layer) to be about 14 Bq m^{-3}. From a few near surface ^{90}Sr measurement in ^{134}Cs free water, the corresponding pre-Chernobyl ^{90}Sr in surface water at 18 ppt would be about 18 Bq m^{-3}. From data on samples collected in 1988, Buesseler and Livingston (1996) estimate corresponding pre-Chernobyl ^{137}Cs and ^{90}Sr levels to be 14.8 and 19.0 Bq m^{-3} respectively. Surface levels of ^{137}Cs and ^{90}Sr in 1976 for open western Black Sea water reported by Eremeev *et al.* (1993) are in reasonable agreement, at 16.7 and 20.1 Bq m^{-3} respectively.

9.2.3. Chernobyl

The Black Sea received substantial amounts of fallout from the April 1986 Chernobyl accident. In fact, the levels of ^{137}Cs there are second only to the Baltic Sea in terms of marine areas affected by this source. In addition to the Cs isotopes, short lived reactive species such as ^{144}Ce and ^{106}Ru have been observed. The initial deposition pattern was quite patchy (Eremeev *et al.*, 1993; Vakvlovsky *et al.*, 1994) but subsequent mixing and circulation has both spread out and reduced this initial surface concentration pattern. Vakulovsky *et al.* (1994) report average levels of ^{137}Cs in surface waters declining from 159 Bq m^{-3} in summer 1986 to 26 Bq m^{-3} in 1991. Since they did not report their sampling positions nor actual data, it is impossible to know what this average means. Our data track higher than this, with average surface values in the open northwestern Black Sea in 1990 and 1992 of 64 and 52 Bq m^{-3} respectively (Buesseler *et al.*, 1991a; Buesseler and Livingston, 1996).

9.2.4. Rivers vs. Atmospheric Sources

The massive freshwater inflow to the Black Sea, primarily in the northwest, greatly modifies the initial composition of Black Sea artificial radionuclides derived from both global weapons fallout and from Chernobyl. Soluble radionuclides, especially ^{90}Sr and tritium, are preferentially transported in rivers to the Black Sea in higher concentrations than exist in the open Black Sea by direct fallout from these sources. Prior to the Chernobyl input, when the only source was global fallout, the freshwater input from the various large rivers reduced the ratio of ^{137}Cs to ^{90}Sr in the affected surface waters from the fallout ratio of about 1.5 to values of 1 or less. The reduction was inversely proportional to salinity, of course. Following the Chernobyl accident, the same process took place, but the influence of a ^{90}Sr rich signal from the Dnepr river, in particular, controlled the low salinity water ratios. A large amount of ^{90}Sr from intensely contaminated areas around the Chernobyl plant leads to the particularly high levels in the Dnepr, compared to other large rivers like the Danube (Polikarpov *et al.*, 1992). So, in recent years, Black Sea waters exhibit a range of ^{137}Cs to ^{90}Sr ratios. These range from high values in open Black Sea surface waters – up to 4-5 soon after the ^{137}Cs rich input arrived (Buesseler *et al.*, 1991a) – to values less than one in the low salinity waters fed by the Dnepr (Polikarpov *et al.*, 1991). Deep water values still show the fallout ratio closer to 1.5 derived from the effects of local fallout and inflowing Mediterranean water through the Bosphorus. In addition, the Chernobyl Cs isotope input was readily characterized by the presence of ^{134}Cs with a ^{134}Cs to ^{137}Cs ratio of 0.53 (Buesseler *et al.*, 1991a). Use of this ratio allowed the determination of the fraction of the observed ^{137}Cs levels in Black Sea waters which came from fresh Chernobyl input or from the older global fallout source (Buesseler *et al.*, 1991a; Buesseler and Livingston, 1996).

9.3. Geochemical Behavior of Radionuclides in the Black Sea

As discussed in the previous section, the Black Sea contains both naturally occurring and man-made radionuclides in measurable quantities. As summarized by Chesselet and Lalou (1988) at the first Cherbourg meeting (1-5 June, 1987), these radionuclides can broadly be broken down into the « swimming or diving » radionuclides. One radionuclide may fit both categories depending upon the time scales one is interested in and the geochemical setting. For example, ^{7}Be is a rather soluble tracer in off shore waters and the open ocean (*i.e.* a « swimmer »), but is quite rapidly scavenged in nearshore settings (a « diver »). The Black Sea is unusual as well in that a

single radionuclide may have widely differing geochemical properties depending upon whether one is interested in the surface oxic or deep anoxic waters. This is particularly important for elements with more than one redox state, such as U and Pu (see below).

9.3.1. Soluble Radionuclides

As in other ocean basins, the main anthropogenic radionuclides that have been used as water circulation tracers are ^{3}H, ^{14}C, ^{90}Sr and ^{137}Cs. In addition ^{134}Cs from Chernobyl has been studied.

9.3.2. Tritium

Although tritium has been widely used in ocean tracer studies, there have been relatively few Black Sea tritium studies reported in the Western literature. Early measurements in 1965 and 1975 were reported by Ostlund (1974) and Top and Clark (1983). Russian studies were summarized by Eremeev *et al.* (1993). All these sets of data point to some analytical problems. Both Ostlund (1974) and Top and Clark (1983) reported occasional non-zero tritium concentrations in deep waters. But much higher deep water values were reported in papers cited by Eremeev *et al.* (1993), *eg.* Vakulovsky *et al.* (1982). Newer data reported by Top *et al.* (1991) do not include any more high values. Neither in their data, the chlorofluorocarbon data reported by Bullister and Lee (1995), nor in deep ^{90}Sr measurements shown in this paper by Buesseler and Livingston (1996), is there any evidence of measurable signals below about 500 meters. The data shown in Figure 9.1. from Top *et al.* (1991) are likely to be the best Black Sea tritium depth distributions available at the present time. It can be seen that the tritium distribution is relatively similar to ^{90}Sr in deep waters but shows relative enrichment in waters at depths above the 21.5 salinity isohaline (Fig. 9.1.). Both tritium and ^{90}Sr from bomb fallout have entered the Black Sea from direct deposition and riverine input. However, additional input is possible for tritium alone through recycled tritium caught up in the hydrological cycle (evaporation and precipitation). In the ocean this has been recognized as a factor producing additional delayed tritium deposition relative to ^{90}Sr (Livingston *et al.*, 1985). This may be the most likely explanation for the Black Sea upper water tritium enrichment.

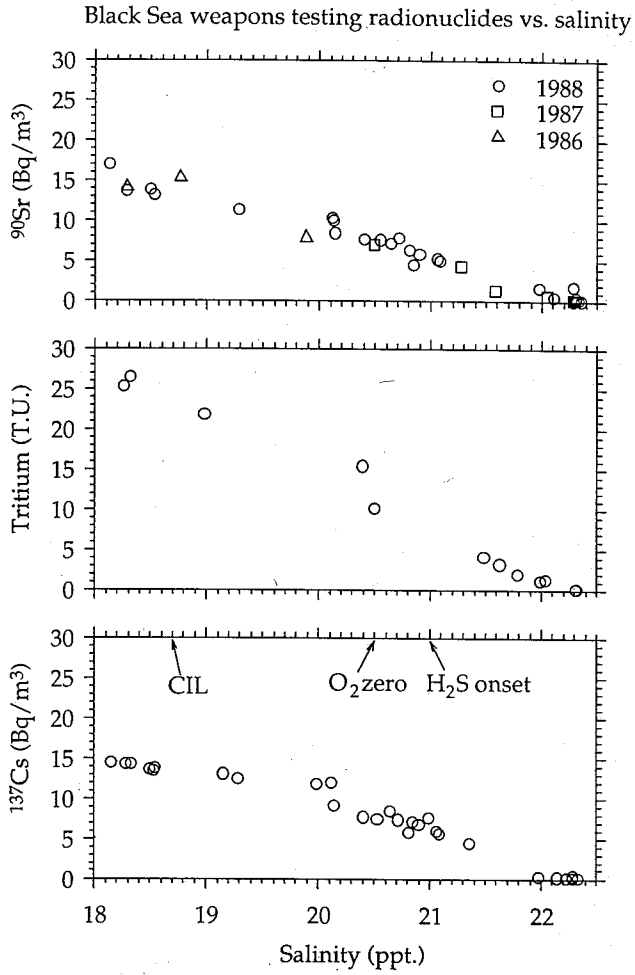

Fig. 9.1. Profiles of ^{90}Sr, ^{3}H and ^{137}Cs against salinity – Black Sea 1986-1988. Total ^{90}Sr data corrected for Chernobyl ^{90}Sr by subtracting Chernobyl ^{137}Cs multiplied by 8.6 (maximum 1986 surface value). Correction usually < 10%. Total ^{137}Cs corrected for Chernobyl ^{137}Cs (calculated by dividing the measured ^{137}Cs by the ^{134}Cs/^{137}Cs of 0.53). Approximate depths of the Cold Intermediate Layer (CIL), O_2 zero, H_2S onset and maximum depth of tracer penetration are around 40-70, 80-170, 100-250 and 500 meters, respectively.

9.3.3. Carbon-14

Carbon-14, produced by both natural processes in the atmosphere and in nuclear weapons fallout, has been used in the oceans in gas exchange, tracer and water mass dating studies. Results summarized by Eremeev *et al.* (1993) suggest that the Black Sea to sea to air flux of CO_2 is in the range 22-44 Mtons of CO_2 per year. Radiocarbon ages reported by Ostlund (1974) for Black Sea deep water suggest the bottom waters are 2000 ± 200 years old.

9.3.4. Pre- and Post-Chernobyl Evolution of Black Sea Depth Distributions of ^{90}Sr and Cs-Isotopes

Pre-Chernobyl profiles of ^{137}Cs and ^{90}Sr in the Black Sea have been reconstructed (Fig. 9.1.) using techniques mentioned earlier (Buesseler *et al.*, 1991a; Buesseler and Livingston, 1996). Basically, these profiles represent the evolution of mixing on the bomb fallout signal deposited on the Black Sea surface, plus the continued freshwater input of ^{90}Sr in river water. The influence of the freshwater input can be seen through comparison of the ratios $^{137}Cs/^{90}Sr$. They average 0.94 (range from 0.78 to 1.15, n =10) in near surface water (salinity 18.3 – 21 ppt) to ratios averaging 1.38 ± 0.15 in deep water (salinity > 21 ppt) – which is indistinguishable from the fallout input ratio of 1.5 – the lower ratios being a function of decreasing salinity in the near surface waters.

Buesseler and Livingston (1996) describe a set of time-series measurements of Chernobyl ^{137}Cs profiles in the western Black Sea. Presented normalized to salinity, they show the rapid mixing of the Chernobyl signal in the surface mixed layer, the Cold Intermediate Layer (CIL) and across the strong pycnocline into the upper anoxic water zone. Figure 9.2. shows the temporal evolution of total ^{137}Cs (from both Chernobyl and weapons testing sources) from 1987 to 1992 and one can see the contrast with the weapons testing profile estimated for 1986 (Fig. 9.1.). Presumably the gradient of the Chernobyl profile will approach that of the weapons testing profile after two decades of mixing.

9.3.5. Riverine Input of Chernobyl ^{90}Sr to NW Black Sea Shelf Waters

The large influx of ^{90}Sr in the Dnepr River from Chernobyl, mentioned earlier, has been noted in time-series measurements made at the mouth of the river (Polikarpov *et al.*, 1992). Concentrations of ^{90}Sr in river water rose from

pre-Chernobyl levels of around 10 Bq m^{-3} to a maximum of about 700 Bq m^{-3} in spring 1987. The pattern of concentrations showed maxima each spring and minima each winter. The annual input to the Black Sea declined from a maximum of 14.7 TBq in 1987 to 9.9 TBq in 1989. The unique source of ^{90}Sr represented by the Dnepr river was recognized through comparison of the concentrations and fluxes of ^{90}Sr between the Danube and Dnepr. Dnepr concentrations in 1988 were 1-2 orders of magnitude higher than found in the Danube, whereas Danube fluxes were 15% of those of the Dnepr. The magnitude of the Dnepr concentrations and fluxes, while not of radioecological significance, constitute an unique and substantial tracer of the circulation of this freshwater source in the western Black Sea basin.

The first indication that the Dnepr ^{90}Sr input to the northwest Black Sea could be detected away from the river mouth was reported by Polikarpov *et al.* (1991). They presented data for the western Black Sea and Aegean Sea on surface concentrations of Cs and Sr radionuclides in 1988. Sr-90 concentrations in the northwest Black Sea were in general twice as high as those in the central part. They noted that this was a consequence of the very high ^{90}Sr concentrations observed in the Dnepr river and estuary. In similar fashion, ratios $^{137}Cs/^{90}Sr$ were 2-3 times lower in the northwest relative to central regions.

A further refinement of these observations and the implications for water mass tracing has been described by Buesseler and Livingston (1996). Measurements at both shelf regions near the Danube and Dnepr inflow and in offshelf stations in the northwest Black Sea in 1990 were reported. The relationship of the river ^{90}Sr signal to the observed concentrations and ratios was examined by plotting the observed concentrations or ratios against salinity. When $^{137}Cs/^{90}Sr$ ratios were plotted against salinity, three distinct mixing process were revealed.

- Mixing of the high ^{90}Sr low salinity Dnepr river/estuary end member with Black Sea coastal water.
- Off shelf intrusions of this river derived high ^{90}Sr signal into sub-surface waters.
- Mixing of the high ratio (3-4) open Black Sea water with deeper water of bomb fallout origin and ratio (1.4).

Some of the same influence of the rivers on ^{137}Cs can be seen in 1990 and 1992 – shown here in Figure 9.2. at salinities < 18 ppt. Further work underway by Stokosov and Buesseler (1996), shows that it is possible to estimate the contributions of Danube, Dnepr and surface Black Sea water in this region using data such as these.

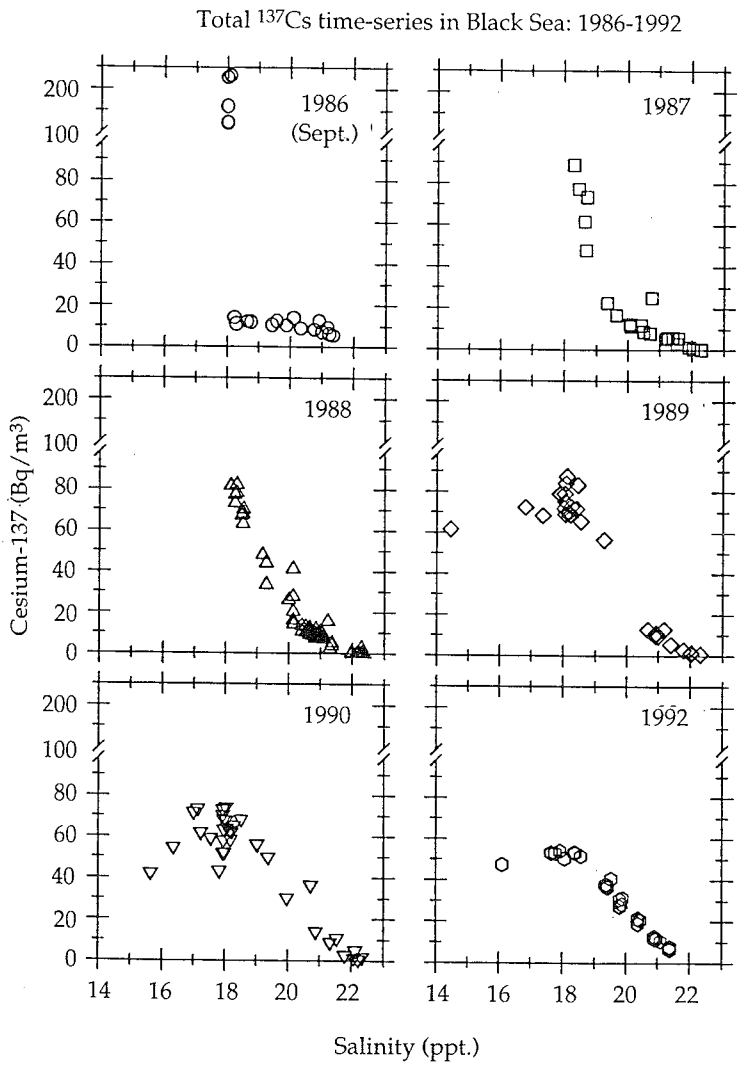

Fig. 9.2. Time-series of total ^{137}Cs for the Black Sea from 1986 (post-Chernobyl) through 1992. All data taken from this laboratory.

9.4. Particle-Reactive Radionuclides

In this section we focus on the behavior of the more particle-reactive isotopes with an emphasis on those radionuclides with a geochemistry that is strongly influenced by the unique low redox setting of the deep Black Sea. For the artificial radionuclides, this group includes the long-lived Pu isotopes, derived from both weapon's testing and Chernobyl fallout, as well as short-lived particle-reactive radionuclides such as ^{144}Ce, ^{141}Ce, ^{106}Ru, and ^{103}Ru studied most recently after the Chernobyl accident. For the natural radionuclides, U-series isotopes and their decay products (Th, Ra, and Pb isotopes) have also been used to study scavenging process in this basin.

Shortly after the early atmospheric weapons tests, Osterberg *et al.* (1963) detected short-lived fallout ^{141}Ce, ^{144}Ce and ^{95}Zr in deep Pacific sea-cucumbers. This finding led them to conclude that at least some fraction of fallout radionuclides were rapidly transported to the deep ocean, at rates far exceeding simple Stokes settling velocities. Immediately following the Chernobyl accident, sediment trap studies in the Black Sea were used to quantify these same sinking particle fluxes. These studies suggested that the residence times with respect to removal on sinking particles were on the order of 60, 70, and > 300 years for ^{106}Ru, ^{144}Ce and ^{137}Cs, respectively (Buesseler *et al.*, 1987; 1990). In confirmation of these rapid removal rates, one could detect a decrease in the relative ratio of ^{106}Ru and ^{144}Ce to ^{137}Cs in Black Sea surface waters (Livingston *et al.*, 1988). Such studies provide convenient time-scales of particle-removal and scavenging processes that can be used to model pollutant transport and sedimentation fluxes in general.

The cycling of redox sensitive elements across the shallow oxic/anoxic interface can strongly influence the residence time of a given radionuclide. This contrasts sharply to other marine basins, where most of the water column is oxygenated, and anoxic conditions are restricted to sediment pore waters and deeper layers after burial. Redox cycling can have an impact on those elements with their own redox sensitive geochemistries, such as Mn, Fe (Spencer *et al.* 1972; Lewis and Landing, 1991), and those radionuclides such as U, Pu whereby redox transformations produce a more or less soluble species. In addition, co-precipitation reactions that accompany the cycling of Mn and Fe across redox boundaries can influence the removal of radionuclides such as ^{106}Ru and ^{234}Th (Buesseler *et al.*, 1991b) as well as stable elements such as phosphorus (Shaffer, 1986 ; Buesseler *et al.*, 1994).

The cycling of U, in the Black Sea is thought to involve both oxidized and reduced forms. In oxidized seawater, U is thought to exist as a soluble uranyl carbonate species in the U(VI) oxidation state, and under these conditions, U is known to be conservatively distributed as a function of salinity (Ku *et al.*, 1977). Under reducing conditions such as exist in the sulfidic deep water of the Black Sea, U(IV) may predominate, and this form is much more particle-reactive in seawater. Studies by Anderson *et al.* (1989) suggest that U exists in an unstable U(VI) form in the deep Black Sea, with a relatively

short residence time for removal (200 years). In fact, a sharp break in the ^{238}U-salinity relationship is observed in the Black Sea at a salinity around 21.6 ppt, or at depths of elevated sulfide concentration (Wei and Murray, 1991). In these deep sulfidic waters, ^{238}U is 30-60% lower than one would find at a similar salinity in oxic marine basins. Sediment and pore water U were measured in the Black Sea by Barnes and Cochran (1991) in a study of U geochemistry. They used the depletion in pore water U with depth to calculate the diffusional flux of U into the deep sediments. This flux agreed within uncertainties with U removal determined from measurements of solid phase authigenic U accumulation. All of the evidence thus points to removal of U in the deep Black Sea, similar to that which has been observed in other anoxic inlets and fjords (Todd *et al.*, 1988). These data suggest that while the sediments underlying anoxic regions of the worlds oceans represent only a small fraction of the total area (0.4%), they can account for 20% of the oceanic U balance (Barnes and Cochran, 1991).

The aquatic chemistry of Pu in the Black Sea can be expected to be quite complex, due to the four possible oxidation states of Pu in natural waters (III, IV, V, VI) and the widely differing chemical properties expected for each form. In general, there is a clear relationship between the oxidation state of Pu and its affinity for particle surfaces, with the more reduced Pu species having a much higher particle reactivity than the more oxidized forms. In the Black Sea, one would expect therefore that the more reduced and highly particle reactive forms would dominate in the deep anoxic waters. This is indeed what Sanchez *et al.* (1991) found in two Pu oxidation state profiles collected in 1988. They determined that about 70% of the Pu was in the reduced oxidation states (III/IV) in the surface waters (total $^{239,240}Pu$ = 6-8 $\mu Bq\ l^{-1}$). Subsurface waters from the upper 100 m were dominated by oxidized forms (V/VI). Below the oxic/anoxic interface (approx. 150 m at the stations sampled) they found low activities of reduced Pu, but could not detect any oxidized Pu above errors (<1-2 $\mu Bq\ l^{-1}$). The total watercolumn inventory of Pu is 7-9 Bq m^{-2}, or only approx. 10% of the expected inventory of weapons testing fallout Pu in the 40-50° latitude band (Hardy *et al.*, 1973). This is in sharp contrast to the Atlantic or Mediterranean Seas, where 90% or more of the Pu inventory is found in the water column (Fukai *et al.*, 1987; Cochran *et al.*, 1987). In the Atlantic, > 85% of the Pu is found in the oxidized form using these same techniques (Cochran *et al.*, 1987). We can thus attribute the low watercolumn inventories in the Black Sea to the predominance of the reduced forms of Pu, and hence its faster rate of removal relative to other marine settings. Lower than expected watercolumn Pu implies a higher Pu sedimentary inventory, and this has now been confirmed in at least at one site (Buesseler and Benitez, 1994; and see below).

The Pu results presented by Sanchez *et al.* (1991) and those reported by Livingston *et al.* (1988) represent samples collected in the post-Chernobyl era, and one should ask the question to what extent the Chernobyl accident

contributed transuranics, such as Pu, to the Black Sea. The presence of short lived ^{242}Cm (half-life = 163 days) in dissolved and particulate samples collected in June and September of 1986 from the Black Sea (Livingston *et al.*, 1988), suggests that Chernobyl transuranics were indeed deposited in this basin (Tab. 9.I.). A clear indication of Chernobyl Pu is seen in the measured $^{238}Pu/^{239,240}Pu$ activity ratios. Global fallout is characterized by a $^{238}Pu/^{239,240}Pu$ ratio near 0.04 (post SNAP 9A releases in 1964; Perkins and Thomas, 1980), while Chernobyl debris has an elevated ratio near 0.47 (Aarkrog, 1988). The measured surface $^{238}Pu/^{239,240}Pu$ ratios in 1986 were near 0.25, suggesting that approximately half of the Pu activity found in surface waters is from the more recent Chernobyl source. This Chernobyl Pu was not detectable in any of the subsurface waters however. In « Chernobyl free » waters collected from 110 m in September 1986 (« Chernobyl free » based upon the lack of Chernobyl ^{134}Cs, see previous discussion), the $^{238}Pu/^{239,240}Pu$ ratio appears to be similar to global fallout, as expected (Tab. 9.I.). $^{240}Pu/^{239}Pu$ atomic ratios determined by mass spectrometry corroborate these ^{238}Pu data quite well. The same 110 m sample is characterized by a $^{240}Pu/^{239}Pu$ atom ratio near 0.18, which is the isotopic signature measured world-wide from global fallout Pu (Krey *et al.*, 1976; Perkins and Thomas, 1980). As with ^{238}Pu, elevated $^{240}Pu/^{239}Pu$ ratios (> 0.30) are found in surface waters. Assuming a mixing ratio of 50:50 for Chernobyl and weapons testing Pu (from ^{238}Pu), and a weapons testing $^{240}Pu/^{239}Pu$ ratio of 0.18, this suggests an end-member Chernobyl $^{240}Pu/^{239}Pu$ atomic ratio around 0.42. This highly elevated ratio is expected due to the build-up of the

Table 9.I. Plutonium and Curium Data.

Location	Sampling Dates*	Depth	Type	$^{239,240}Pu$ ($\mu Bq\ l^{-1}$)	$^{238}Pu/^{239,240}Pu$ (activity ratio)	$^{240}Pu/^{239}Pu$ (atom ratio)	^{242}Cm ($\mu Bq\ l^{-1}$)
offshore	June	surface	part	1.18 ± 0.13	0.25 ± 0.09	bd	22.50 ± 1.83
Black Sea			diss	15.67 ± 3.00	0.24 ± 0.04	0.22 ± 0.06	21.33 ± 2.50
	Sept.	surface	part	0.27 ± 0.07	bd	bd	5.75 ± 0.83
			diss	8.68 ± 0.92	0.26 ± 0.07	0.33 ± 0.05	20.67 ± 2.05
	Sept.	110 m	part	1.08 ± 0.35	bd	0.18 ± 0.04	bd
				8.78 ± 1.95	bd	0.15 ± 0.01	bd
nearshore	June	surface	part	0.60 ± 0.18	bd	0.19 ± 0.02	bd
Black Sea				6.08 ± 3.00	0.19 ± 0.05	0.32 ± 0.04	bd
	Sept.	surface	part	0.20 ± 0.12	bd	0.22 ± 0.04	0.90 ± 0.48
			diss	12.25 ± 1.35	0.23 ± 0.04	0.35 ± 0.04	33.40 ± 2.83
Atlantic	1978	surface	total	22.17 ± 4.50	0.04 ± 0.01	0.18 ± 0.01	bd
				$Bq\ kg^{-1}$			$Bq\ kg^{-1}$
Kefken Island	Sept.		total	0.40 ± 0.002	0.04 ± 0.01	0.17 ± 0.03	0.05 ± 0.02

bd = below detection

*All sampling dates were in 1986, unless otherwise noted.

higher masses of Pu in the core of the Chernobyl reactor. While most of the total Chernobyl releases were attributed to the loss of gases and volatiles during the accident, non-volatile components were also released. In fact, Chernobyl fallout in the Black Sea area is characterized by relatively high $^{106}Ru/^{137}Cs$ and $^{144}Ce/^{137}Cs$ ratios, compared to the Baltic Sea or more northerly sites (Livingston *et al.*, 1988).

While Chernobyl Pu can thus account for up to 50% of the Pu in the shallowest samples, total Chernobyl Pu inventories would be quite small with respect to global fallout Pu, which has been preferentially removed to the deeper watercolumn and sediments. In 1987, one soil sample was collected from Kefken Island in the southern Black Sea, and both ^{238}Pu and $^{240}Pu/^{239}Pu$ data are indistinguishable from global fallout (compare soil to Atlantic surface waters – Tab. 9.I.). While just above detection, the measured ^{242}Cm activity in this soil sample is too low to indicate measurable Chernobyl Pu.

9.4.1. Sediment Records

It has been long known that the lack of mixing and the seasonal nature of particle deposition leads to the formation of light and dark layers in deep Black Sea sediments (Ross and Degens, 1974; Müller and Stoffers, 1974). The light layers are composed primarily of shells from the coccolithophorid *E. Huxleyi*, while the dark layers are enriched in lithogenic matter (Hay *et al.*, 1990). The sediments represent a unique repository of the historical deposition records for a wide range of natural and man-made compounds. This is due to the complete lack of bioturbation effects, which in most other marine settings causes a partial or complete smearing of the input record over many cm depth, or over a time-scale of decades to > centuries. Resolution is thus limited only by sampling resolution (1-3 varves per mm) and sample size. Radionuclide data for ^{210}Pb and ^{14}C suggest that recognizable varves are not formed annually, hence sedimentation rates determined based upon varve counting may be overestimated (Buesseler and Benitez, 1994; Calvert *et al.*, 1991; Crusius and Anderson, 1992; Jones and Gagnon, 1994). Using fine-scale sampling in a deep Black Sea core (6-8 samples per cm depth), the peak in fallout Pu from the 1960's can be identified, as well as double peaks for ^{137}Cs from both weapons testing and Chernobyl sources (Buesseler and Benitez, 1994).

Overall, it appears that long term mass accumulation rates in the deep Black Sea have increased from approximately 35 to 65 g m^{-2} yr^{-1} (14 to 26 cm/1000 yr at a porosity of 90%) sometime between the last millennium (dated by ^{14}C) and the last century (dated by ^{210}Pb) (Buesseler and Benitez, 1994). In the shelf and margin regions, accumulation rates are much higher, and ^{210}Pb profiles suggest rates of 0.1-1 cm yr^{-1} (Anderson and Fleisher, 1991). One additional advantage in studying chronologies in Black Sea sediments, is that from east to west across the entire deep Black Sea basin, one

can visually identify strongly correlated varve couplet sequences (Ross *et al.*, 1970; Lyons, 1991). Thus from a single chronology at one site, it is possible to date major horizons in other cores over time scales of the past few thousand years, throughout the so-called Unit 1 sediments (*i.e.* past 1600-3200 years – Jones and Gagnon, 1994; Calvert *et al.*, 1991; Arthur *et al.*, 1994). In some cores, fine-grained turbidite layers interrupt this sequence, but they do not apparently erode the general layering or varve correlation between cores (Arthur *et al.*, 1994). The processes which trigger and deposit these turbidites layers are not well understood.

Sediment radionuclide inventories can used to examine the mass balance of a given radionuclide. In the central deep Black Sea, inventories of ^{210}Pb are in approximate balance with its source (from ^{226}Ra decay and removal in the watercolumn and atmospheric delivery- 50-100 dpm cm^{-2} Moore and O'Neill, 1991; Buesseler and Benitez, 1994). As stated above, for Pu, the low redox setting in the deep waters results in considerable enhancement of Pu removal. A sedimentary Pu inventory of 75 Bq m^{-2} was found in the central basin (Buesseler and Benitez, 1994). Together with the watercolumn inventory of 7-9 Bq m^{-2}, the total Pu inventory balances the expected weapons testing fallout at these latitudes (81 Bq m^{-2}) and one does not need to invoke any significant Chernobyl contribution to the total Pu balance for this basin.

9.5. Summary

9.5.1. Comparisons with Other Basins

The Black Sea has unique features compared to other ocean basins. It has a large freshwater inflow, a huge volume of anoxic deep water and has received significant fallout from the Chernobyl accident. As a result of the latter, a recent report (IAEA, 1995) shows that 1990 surface ^{137}Cs concentrations are only higher in the Baltic and Irish Sea when compared with other global ocean basins – see Table 9.II.

9.5.2. Comparison of Human Radiation Doses from Black Sea Radionuclides

The IAEA report (1995) mentioned above also provides a comparison between radiological doses to humans from natural as opposed to artificial radionuclides. This report was based on the conclusion that the highest dose to man from natural radionuclides in the ocean came from the consumption of ^{210}Po from seafood. The corresponding highest dose from artificial

radionuclides came from the consumption of ^{137}Cs in seafood, especially fish. The appropriate doses were calculated for the major FAO (Food and Agricultural Organization of the UN) fishing areas for both these nuclides. The Black Sea was included as part of FAO region 37 – which includes the Mediterranean. Because of this, the Black Sea ^{137}Cs doses can be higher than the average for region 37 (the ^{137}Cs water levels were about 7 times higher). But the low fish catches in the Black Sea offset this and hence the estimated values of 6 man Sieverts (^{137}Cs) may not be low by more than a factor of 2 or so. It is hardly relevant compared to the estimated doses of 700 man Sieverts for ^{210}Po. Also, doses from either or both radionuclides are considerably higher in other ocean areas such as the North Pacific and North Atlantic.

Table 9.II. Typical Surface Concentrations of ^{137}Cs in Surface Ocean Waters in 1990.

Basin	Average ^{137}Cs Bq m^{-3}
Baltic	125
Irish Sea	55
Black Sea	52
North/Barents Sea	10 – 12
Arctic	7.6
Mediterranean	5.4
North Pacific	4.0
North Atlantic	2.9
Indian Ocean	2.9
South Pacific	1.6
South Atlantic	1.4
Antarctic	0.4

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