

Table 53. Average concentrations of mercury in sea water for various regions of the sea.

Location	Year of Sampling	Depth (m)	Hg-concentration (ng/l) [*]		Reference
			Range	Average	
N. Adriatic		surface	37.5-40.3	39(2)	147
Mediterranean	1968	0-300	61-190	118(12)	129
Nova Scotia Coast		2-240	58-88	72(3)	148
N. Pacific	1970	0-4800	12-173	43(35)	149
Greenland Sea	1971	0-3169	16-364	125(21)	139
N.E. Atlantic	1971	0-4030	18-142	54(11)	112
E. Pacific		10-4080	29-270	73(9)	120
Long Island Sound	1972	surface	47-78	64(3)	19
World Ocean	1972	0.5	ND-127	47(28)	150
N.W. Atlantic	1972	0-4800	40-320	150(162)	122
Icelandic water	1972	0-1580	12-225	71(30)	151
E. China Sea	1972	surface	17-45	28(5)	152
S. China Sea	1972-73	"	6-37	16(9)	"
Indian Ocean	1972-73	"	6-35	16(14)	"
S.E. Atlantic	1973	"	6-25	14(5)	"
N.E. Atlantic	1973	"	7-34	18(5)	"
Tropical N. Atlantic	1973	"	10-54	34(10)	"
English Coast	1973	"	5-80	21(14)	"
Icelandic water	1973	0-800	4-142	25(36)	"
E. Pacific	1974	0-1233	3.6-5.6	5.0(52)	140
W. Mediterranean	1975	0-2000	8-78	31(64)	Present work

* = Numbers in parentheses are the number of data used in calculating averages

6.5 Measurements of transuranic elements in the Mediterranean

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In order to supplement the baseline data on the distribution of transuranic elements in the Mediterranean, which have already been reported⁵⁹, further measurements were carried out on sea water samples collected during 1974-75 cruises. In 1974 profile collections were conducted at a station approximately 50km south of Monaco in addition to surface sampling at a few stations, while surface waters were taken from several stations covering wider regions of the western Mediterranean during the 1975 cruises. The measurement of ²³⁸Pu as well as ²⁴¹Am were for the

first time successful on the 1975 samples. These data are considered valuable as the basis for understanding transuranic biogeochemistry in the Mediterranean environment.

At each station approximately 200ℓ of sea water were collected into several polyethylene barrels, acidified to pH ≈ 1 on board, transported ashore and processed. The analytical procedure for Pu measurements adopted for the 1974 samples was that described by Wong⁵⁷ with slight modifications. For the 1975 samples the procedure proposed by Hodge *et al.*¹⁵³ was used for co-precipitating Pu and Am with the mixed hydroxides and carbonates of Ca and Mg, which are present naturally in sea water. The volume of the first precipitates from a 200ℓ sample amounted to approximately 5ℓ. The precipitates were dissolved with concentrated HCl, and Pu and Am were again co-precipitated with ≈ 50mg Fe(III) by adding NH₄OH, leaving much of the Ca and Mg in the solution. The second precipitate was centrifuged and dried for 15 hours at 105°C. The residue was dissolved in ≈ 200 ml concentrated HCl and a few drops of 30% H₂O₂ was added. Thereafter, the modified procedure for Pu and Am analysis described in the present report (Section 4.1) was followed. The discs were counted for ≈ 10,000min. with a silicon surface barrier detector coupled to a 200-channel analyzer. The chemical yield, determined by the initial addition of ²⁴²Pu and ²⁴³Am prior to the precipitation steps were 50-60% for Pu and 40-50% for Am.

The results of these measurements are presented in Table 54. The locations of the sampling stations are illustrated in Figure 23. From the 1974 profile data given in Table 54, it can be seen that higher Pu concentration than that at mid-depth appears at 2000m. This tendency was already noted in a previous report⁵⁹. However, further detailed observations are required to relate the vertical distribution of Pu in the Mediterranean to some transport mechanisms.

Considering the counting statistics of the samples, the 1975 data indicate a rather homogeneous distribution of ²³⁹⁺²⁴⁰Pu, ²³⁸Pu, and ²⁴¹Am in the surface waters of the western Mediterranean. The average concentrations of ²³⁹⁺²⁴⁰Pu, ²³⁸Pu and ²⁴¹Am computed on the basis of these data are 0.99 ± 0.04 fCi/ℓ, 0.072 ± 0.009 fCi/ℓ and 0.05 ± 0.01 fCi/ℓ respectively. These average values give the following ratios:

$$\frac{^{238}\text{Pu}}{^{239+240}\text{Pu}} = 0.07 \pm 0.01$$

$$\frac{^{241}\text{Am}}{^{239+240}\text{Pu}} = 0.05 \pm 0.01$$

Miyake and Sugimura¹⁵⁴ gave the ratios ²³⁸Pu/²³⁹⁺²⁴⁰Pu of 0.25-0.47 (1968), 0.21-0.57 (1970-71), 0.58-0.75 (1972) and 0.10-0.20 (1973)

Table 54. Results of transuranic measurements on Mediterranean sea waters during 1974-75

Station No.	Date of Collection	Depth (m)	Chlorinity (%)	$^{239+240}\text{Pu}^*$ (fCi/l)	$^{238}\text{Pu}^*$ (fCi/l)	$^{241}\text{Am}^*$ (fCi/l)
74-M	12 June '74	200	-	1.13 ± 0.09	-	-
"	"	500	21.03	0.9 ± 0.01	-	-
"	"	1000	-	0.85 ± 0.06	-	-
"	"	2000	-	1.6 ± 0.2	-	-
74-R	26 June '74	surface	20.74	0.9 ± 0.1	-	-
75-M	2 July '75	surface	21.26	1.35 ± 0.06	0.06 ± 0.01	0.06 ± 0.01
75-CV	14 Sept. '75	5	-	0.91 ± 0.07**	0.10 ± 0.03**	0.03 ± 0.01**
75-0-5	17 " '75	"	20.56	0.77 ± 0.06	0.07 ± 0.02	0.08 ± 0.02
75-0-6	18 " '75	"	20.78	0.93 ± 0.07	0.06 ± 0.01	0.09 ± 0.02
75-0-8	20 " '75	"	20.12	1.04 ± 0.06	0.05 ± 0.01	0.05 ± 0.02
75-0-9	20 " '75	"	21.18	1.09 ± 0.09	0.05 ± 0.01	0.07 ± 0.02
75-0-12	21 " '75	"	21.11	0.95 ± 0.09	0.06 ± 0.02	0.05 ± 0.01
75-0-13	21 " '75	"	21.13	1.1 ± 0.1	0.06 ± 0.02	0.03 ± 0.01
75-0-14	22 " '75	"	21.17	1.10 ± 0.06	0.10 ± 0.02	0.05 ± 0.01

* Errors indicated are 1σ propagated errors

** The water sample was filtered through HA Millipore (0.45μm pore size)

for surface waters in the temperature zone of the North Pacific. The ratio obtained in the present work is lower than those cited above. The $^{238}\text{Pu}/^{239+240}\text{Pu}$ ratio in fallout deposition were studied by Hardy *et. al.*¹⁵⁵ and the ratios computed on their data are 0.024 and 0.036, respectively for pre-SNAP-9A period and post-SNAP-9A period, in the Northern Hemisphere latitudes between 40 and 50°N. The data obtained by Holm and Persson¹⁵⁶ give the ratios of 0.023 and 0.036 for respective periods at a station located in the Arctic area (62.3°N, 12.4°E). Although the ratio obtained in the present work is slightly higher compared with these post-SNAP-9A values the agreement is reasonable, when the counting statistics are taken into account.

As to the $^{241}\text{Am}/^{239+240}\text{Pu}$ ratio only one value, 0.033, obtained for Lake Michigan water is available to date⁷⁹. Our value is in reasonable agreement with this value. This fallout ratio can be compared with those obtained for samples taken near a fuel reprocessing plant, namely

Porphyra seaweed collected from the Irish Sea, where the $^{241}\text{Am}/^{239+240}\text{Pu}$ ratios range between 0.15 and 0.6¹⁵⁷. Their higher ratios are due both to the increased amount of ^{241}Am in the discharged waste and to its *in situ* build up from the decay of ^{241}Pu . Our value is believed to be representative, at least, for the surface waters of the Mediterranean.

6.6 Polychlorinated biphenyls in sea water, sediment and over-ocean air of the Mediterranean

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Because it has well defined limits and restricted mixing with the Atlantic ocean across the narrow Gibraltar strait, the Mediterranean sea should serve as a convenient system within which to study the distribution and dissemination of anthropogenic substances such as polychlorinated biphenyls (PCBs). Yet in spite of PCBs having been produced in kiloton quantities at least since 1957¹⁵⁸, and the evidence of their apparent ubiquity in the marine environment¹⁵⁹, there is a paucity of data concerning their concentration in the Mediterranean Sea. It has been estimated for North America that during 1970, of the 3.7×10^4 tons of PCBs produced, approximately 80% was eventually released into the environment¹⁶⁰. By comparison, in 1971 the combined PCB production for three Mediterranean countries was on the order of 10^4 tons¹⁶¹, so it is reasonable to assume that a considerable quantity of PCBs could have been deposited in the Mediterranean Sea. Evidence supporting this assumption has been presented by investigators who have analyzed mussels^{162,163}, shallow water sediments, plankton and coastal waters of the Mediterranean¹⁶⁴⁻¹⁶⁶. The data contained in these reports are for samples collected within the narrow coastal zone of a few scattered locations. PCB analysis of samples from the open Mediterranean has not been done. This situation led us to undertake a programme of open ocean sampling and analysis for PCBs in air, sea water and sediments. During this programme, we have maintained several objectives. First, we wanted to assess the present levels of PCBs in the open Mediterranean in order to provide a reference point for future work. Secondly, we hoped that by measuring sea water, sediments and over-ocean air we could begin to determine the inputs and reservoirs for PCBs and calculate their fluxes in the Mediterranean basin. Thirdly, we hoped that the information gathered on PCBs would be useful in predicting the environmental pathways of other related anthropogenic substances.

* G.R. Harvey, Woods Hole Oceanographic Institution, served as a Consultant in the Laboratory during September and October 1974 and July to Sept. 1975. His advice on the analysis of PCBs in water, sediments and air and in establishing the technique of measuring low molecular weight hydrocarbons in sea water has been invaluable.