Synthetic results in the radioactivity assessment of the Romanian Black Sea sector after 1992

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Introduction

A semi-enclosed tideless basin bordering six countries, the Black Sea is still considered a *"unicum hidrobiologicum"* because of its physical, chemical, and biological peculiarities; unlike any other sea, the Black Sea is permanently deficient in oxygen, or anoxic below a depth of 150-200 m (Bologa, 1994).

Major factors contributing to the deterioration of the Black Sea environment are pollution and improper use of natural resources (Osvath *et al.*, 1998). The Black Sea is an unique marine environment, one especially exposed to anthropogenic impact. Almost landlocked, besides the link with the shallow inland Azov Sea, its only exchange of water with the World Ocean is through the narrow Bosporus Strait.

The Black Sea encloses the largest body of permanently anoxic water in the world: some 90% of the sea's 5.37×10^5 km^3 total volume is deprived of oxygen and rich in hydrogen sulphide. Only the remaining 150 m thick surface water layer is capable of supporting marine life. The Black Sea drains a surface of land five time larger than its own area, shared by 17 countries and inhabited by over 160 milion people. Rivers, notably the Danube, Dnieper, Don, Kuban and Bug, bring in about 80% of the pollutants (50% from the Danube alone). They include agrochemicals, poorly treated industrial liquid effluents, and domestic wastewater. Atmospheric transport, predominantly from Europe, and coastal sources, such as direct industrial waste and sewage discharges or dump sites, account for the remaining 20%. Riverine input of nutrients, heavy metals, radionuclides, organic compounds and oil is a severe problem (Osvath *et al.*, 1998).

As to radioactive contamination, different IAEA programmes showed that concentration of anthropogenic radionuclides in the Black sea environment, although considerably higher than in other parts of the World Ocean, are such that no significant radiological consequences can be expected for the public (Osvath *et al.*, 1998).

Fallout from atmospheric weapon tests and from Chernobyl accident provided excellent radiotracers for the Black Sea, such as ^{90}Sr, ^{137}Cs and plutonium isotopes (Osvath *et al.*, 1998). The main input occurred through direct deposition on the sea surface. For strontium-90, the Dnieper river became a significant source after the nuclear accident.

Various radiotracers can be used to trace water mixing and circulation, as time markers to provide sediment deposition chronologies, to provide information on fluxes of particles and particle-reactive pollutants, and in planktonic primary production estimates by ^{14}C (relevant to eutrophication).

The Black Sea's radioactivity levels have been the subject of rigorous research in the riparian countries and among organisations participating in various international oceanographic cruises. After the Chernobyl accident interest in radiological research of the Black Sea increased. Studies have included both radioactivity surveys on abiotic and biotic compounds, and experiments on the biokinetics of radionuclides in the marine environment.

For the Romanian Black Sea sector such work has carried particular importance. The need for monitoring radioactivity level's is mainly explained by the continuing existence of fallout, by the Danube river's presence and by the use of nuclear energy in electricity generation (Bologa, 1994). The Danube continues to be the main collector of radioactive wastes from seven riparian countries before flowing into the Black Sea; this important river flow (80% of the total input of fresh water to the sea) contributes to radiocontamination of the marine ecosystem as well. The utilization of nuclear energy, following the completion of the CANDU nuclear power plant at Cernavoda/Romania will require environmental monitoring including the marine areas.

Studies of radioactivity in environmental components in the Romanian marine sector date back in 1962. Beginning in 1976, the Romanian Marine Research Institute (RMRI, later National Institute for Marine Research and Development *"Grigore Antipa"* – NIMRD) initiated the country's systematic study of marine radioactivity using a network of permanent stations located between the Danube mouths, the southern extremity of the Romanian littoral, and occasionally offshore up to 90 nautical miles (Bologa *et al.*, 1994; 1995). The monitoring programme has resulted in a fairly extensive database covering the last 20 years.

The monitoring is being done for a number of reasons. One objective was to define the levels of radioactivity in the marine environment as a baseline before the new NPP started operating. Another objective was the identification of bioindicators for studying radiocontamination of the marine ecosystem, and experimentally determining possible levels of accumulation of critical radionuclides in marine biota and biological systems having direct or indirect influences on the environment and human health.

The main research tasks have included completion of the database on marine radioactive levels. Data have been also used for studies of distribution coefficients (Kds) for marine sediments and seawater and of concentration factors (CFs) for relevant local species. Assessment of external and internal individual and collective doses from marine radioactivity due to immersion in seawater and/or sea food consumption is also being made (Patrascu and Bologa, 1990).

Several applications of use of radiotracers in marine research were promoted by RMRI/NIMRD, in co-operation, since 1970: determination of sediment transport in the nearshore area, determination of the turbulent diffusion coefficients, estimation of planktonic primary production.

Material and method

A network of stations including the whole area between the Danube mouths (Sulina) and the southern limit (Mangalia), from the shoreline to 90 n.m. offshore has been used for radioactivity monitoring in the Romanian Black Sea sector.

Samples of sediments, seawater, and biota (macrophytes, molluscs, benthic and pelagic fish have been continuously collected, at monthly, quarterly, and semi-annual intervals, using common methods on board (R/V "Steaua de mare"). The material has been prepared for measurement in the laboratory. The sediment samples were dry, the water samples were dried by evaporation under infrared lamp, and the organic samples were dried and then ashed, all those operations being followed by weighing.

Beta and gamma measurements have been used in accordance with international methodology. The method of radiochemical separation in the presence of carriers was used for ^{90}Sr measurements; the beta activity of its daughter ^{90}Y was measured after it had been kept at least for 21 days reaching ^{90}Sr – ^{90}Y equilibrium (Cuingioglu *et al.*, 1996; 1997). Total beta counts can be an indicator to select samples for radiochemical and gamma investigations.

Nuclear techniques used for beta measurements have been two instrument lines with plastic detectors: NE102A and ND304. Gamma spectrometry analyses were carried out on HPGe Pop Top ORTEC (12% eff, 1.85 keV resolution at 1332 keV), ORTEC-NORLAND 5500 multichannel analyzer and NIM associated electronics.

The standards used for calibration are volume sources (^{137}Cs, ^{152}Eu, KCl) produced at the Atomic Physics Institute in Bucharest. The measuring times are usually between 40,000-100,000 s for gamma and between 1,000-6,000 s for beta measurements.

The measuring geometry is cylindrical with F 80x35 mm – gamma and F 50x5 mm for beta (^{90}Sr is measured on cellulose filter)

Gamma spectrometry was used for analysing emerged and submerged sediments, seawater, macroalgae, invertebrates and fish of marine origin (Bologa *et al.*, 1991).

For all seawater samples, some physico-chemical parameters such as temperature, salinity, pH, and O_2 concentration were also measured. Gross beta activity, gamma radioactivity of sediments, seawater and biota have been determined.

Results and discussion

Previous studies revealed significant radionuclide CFs for the uranium-radium and thorium series in some seaweeds. They further found fission product concentration (originating from earlier atmospheric nuclear tests and post-Chernobyl environmental contamination) in different living and non-living marine components. Given their importance, special attention was paid to caesium-134 and 137, strontium-90 and plutonium isotopes, for which international organizations established maximum permissible limits for food products. Romanian studies thus particularly focused on computing the concentration of caesium-137 and strontium-90 for sediment and seawater in the pre-Danubian sector of the Black Sea.

The highest content of artificial gamma emitters was noticed in 1986, followed by its subsequent decrease in all components, excepting submerged sediments that are a sink for the isotopes. Environmental CFs for caesium-137 and strontium-90 in different Black Sea biota were also estimated (Figure 1). The radiometric investigations of the coastal marine ecosystem showed the presence of the long-lived anthropogenic radionuclides ^{90}Sr and ^{137}Cs (Table 1).

Significant ^{90}Sr activities (0.53-8.6 $Bq.kg^{-}$dry weight (d.w.)) were found in the submerged sediments collected from seven profiles between the northern and southern limits of the Romanian littoral (Table 1). The maximum values were recorded at the pre-Danubian zone, in good generally correlation with quality and origin of the sediments. For 1998 the ^{90}Sr level ranged from 2.1 to 7.8 $Bq.kg^{-1}$ d.w. in 1999 from 3.1 to 8.3 $Bq.kg^{-1}$ d.w. Emerged sediments were under lower limit of detection (<1.8 $Bq.kg^{-1}$ d.w.), emphasizing small influence of the aquatic environment and their processes.

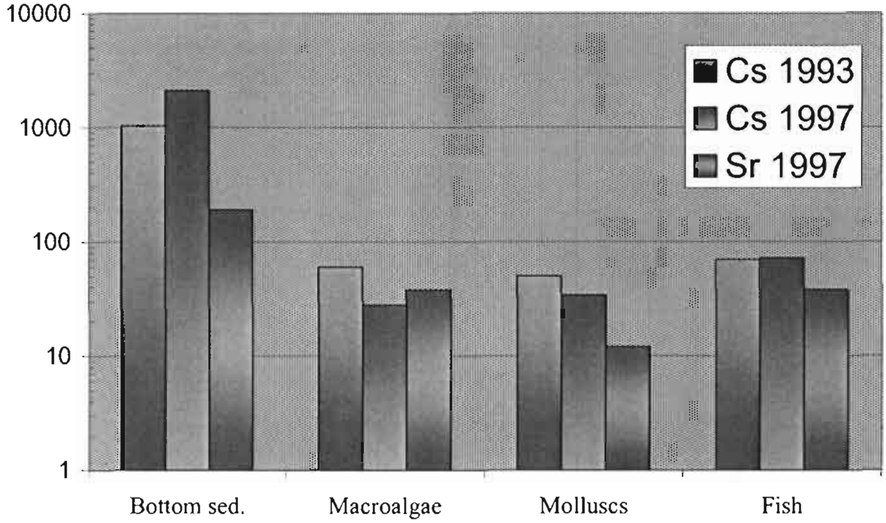

Figure 1
Concentration Factors for marine components.

Component	N	Gross beta	^{90}Sr	^{137}Cs
Sediment				
Emerged	141	30 -:- 1300	< 1.8	1.1 -:-11
Submerged	154	95 -:- 1470	0.53 -:-8.6	3.7 -:- 257
(Bq.kg^{-1}dryw.)				
Seawater	62	3300 -:- 7500	10.9 -:- 26	0.1 -:- 120
(Bq.m^{-3})				
Macroalgae (Bq.kg^{-1}f.w.)	52	39 -:- 683	< 0.16 -:- 12.3	0.2 -:- 81.4
Molluscs (Bq.kg^{-1}f.w.)	41	12 -:-192	< 0.13 -:- 0.7	0.4 -:- 2.6
Fish (Bq.kg^{-1}f.w.)	42	17 -:- 251	< 0.15 -:- 1.1	1.2 -:- 7.2

Table 1
Results on radioactivity level for marine components (1992-1997).

In surface seawater, ^{90}Sr recent content varied over a very narrow range, 19.2-21.8 $Bq.m^{-3}$ in 1997 and 18.6-21.6 $Bq.m^{-3}$ in 1998.

The green and red macrophytes had a ^{90}Sr content of 0.3-1.9 $Bq.kg^{-1}$ fresh weight (f.w.).

Molluscs low values had 0.17 ± 0.09 $Bq.kg^{-1}$ f.w in 1998 and 0.25 ± 0.12 $Bq.kg^{-1}$ f.w. in 1999. The recent measurement of ^{90}Sr in the most frequently collected benthic fish species resulted in significant values of 0.4-1 $Bq.kg^{-1}$ f.w. in 1998, and 0.5-1.1 $Bq.kg^{-1}$ f.w. in 1999.

In all samples caesium-137 persisted after 1986; thus it was possible to track the temporal changes in concentrations of caesium-137 (Patrascu, 1996; 1997).

The numerous investigations carried out on environmental pollution indicated ^{137}Cs concentrations of 3.7-257 $Bq.kg^{-1}$ d.w. in submerged sediments from the Romanian Black Sea sector until 1997. After this year, the range has been 21-139 $Bq.kg^{-1}$ d.w. for 1998 and 16-88 $Bq.kg^{-1}$ d.w. in 1999 (Figure 2). The maximum value was found off the Danube mouths. The local variations are remarkable and correlate with the hydrodynamic conditions and sediment quality, a fact which could explain the minimum value found in a nearshore area. The observations were extended along the entire coast in bottom sediments up to 70 m depth, resulting in radionuclide concentrations of up to 249 $Bq.kg^{-1}$ d.w.; the maximum value found at a depth of about 50 m indicated that other marine processes or phenomena may have been involved (e.g. sediment transport).

The most recent analyses carried out on the emerged sediments showed concentrations between 3.7-6 $Bq.kg^{-1}$ d.w. (in 1998).

The relatively slow decrease of caesium-137 concentrations in sediment compared to seawater confirmed the ability of sediments to concentrate radionuclides.

The determination of ^{137}Cs concentrations in a reference seawater samples (Constanta, offshore and Odessa offshore) showed a level between 18-36 $Bq.m^{-3}$ (Figure 2).

Marine biota had low caesium-137 concentrations of only a few $Bq.kg^{-1}$ f.w. The macrophytes had a radionuclide average content of 1.4 ± 0.8 $Bq.kg^{-1}$ f.w, the molluscs of 1.3 ± 0.3 and the fish of 2.4 ± 0.7 $Bq.kg^{-1}$ f.w. (in 1998). *Bryopsis plumosa, Ceramium rubrum, Mya*

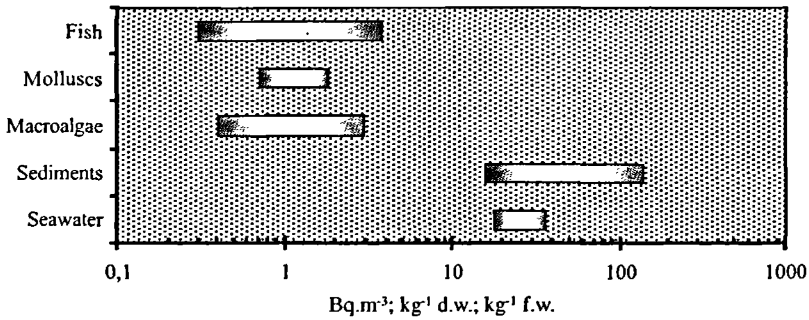

Figure 2
^{137}Cs level in marine components between 1998-1999.

arenaria, Mytilus galloprovincialis, Sprattus sprattus, Gobius melanostomus can be good bioindicators for radioactivity level in marine environment.

The highest caesium-137 and strontium-90 concentrations in edible marine biota (fish, molluscs) always ranged below the maximum permissible level allowed by FAO in 1987 and later.

The gross beta is a basic parameter in the routine control of environmental radioactivity. Gross beta measurements have been carried out in the Romanian Black sea sector for the main components of the coastal ecosystem (Table 1).

The results obtained for marine water in the reference point Mamaia have indicated values of 3,300-7,500 $Bq.m^{-3}$. The contribution of potassium is obvious. A comparative analysis effected on fresh water samples from the Danube-Black Sea Canal has shown this fact, as the values of gross beta were from 180-240 $Bq.m^{-3}$. In a sample collected from the neighbourhood of the nuclear power plant during the evacuation of the cooling agent has not indicated a significant increase of gross beta.

The emerged and interface sediments had gross beta values of 30-1300 $Bq.kg^{-1}$ d.w. (Table 1). The submerged sediments have values of 95-1470 $Bq.kg^{-1}$ d.w. The differences depend on the zone, depth, sediment quality.

The fish has a mean value of 100 $Bq.kg^{-1}$ f.w., an intermediate value between minimum for molluscs (25 $Bq.kg^{-1}$ f.w.) and maximum for algae (146 $Bq.kg^{-1}$ f.w.)

The continued monitoring of marine radioactivity is necessary either for avoiding of any nuclear risk and for comparative radiometric studies in the coastal zone (Patrascu and Bologa, 1990; Bolosa and Patrascu, 1998; Bologa *et al.,* 1998b).The knowledge and conservation of the environmental factor quality can be supported only by concrete results.

Romanian monitoring data of the annual concentrations of gamma emitting radionuclides were used in the IAEA and national data bases.

Conclusions

Several main conclusions resulted from this monitoring in the Romanian Black Sea Sector:

- the radioactivity monitoring in the Romanian marine sector has enabled the establishement of reference values for all categories of marine components;

- the Danube River mouths produce an additional impact zone owing to the Danube contribution;

- the abiotic and biotic components significantly concentrate artificial radionuclides in relation to the environmental concentrations;

- there is a remarkable concentration of caesium-137 in the submerged sediments, as a consequence of recent human activities dealing with nuclear material;

- the maximum concentration of ^{137}Cs and ^{90}Sr in edible marine biota (i.e. fish and molluscs) were always below "action level" or highest permissible limits enforced by FAO;

- background references on the present marine environmental contamination are required for the characterization of the impact of future nuclear activities near the Romanian coast (Cernavoda NPP, Danube-Black Sea Canal, Constanta-Agigea harbour).

Bibliography

BOLOGA A. S., 1994 — Radioecological research of the Black Sea: Report from Romania. *IAEA Bulletin.*, 2: 36-38.

BOLOGA A. S., OSVATH I., PATRASCU V., 1994 — "Monitoring of marine water, sediment and biota radioactivity in samples from the Romanian sector of the Black Sea by means of gamma spectrometry". *In* POVINEC P. P., (ed.): *Sources of Radioactivity in the Marine Environment and their Relative Contribution to Overall Dose Assessment from Marine Radioactivity (MARDOS).* IAEA-MEL-R2/94, June.

BOLOGA A. S., OSVATH I., DOVLETE C., 1995 — ^{137}Cs monitoring in the Romanian sector of the Black Sea. *Rapp. Comm. Int. Mer. Medit.*, 34: 224.

BOLOGA A. S., PATRASCU V., 1998 — "Radioactivity in the Romanian Black Sea sector one decade after Chernobyl". *In: One Decade after Chernobyl: Summing up the Consequences of the Accident,* IAEA-TECDOC-964., 2, Vienna, 469-475.

BOLOGA A. S., PATRASCU V., CUINGIOGLU E., 1998a — Distribution of total beta radioactivity, ^{90}Sr and ^{137}Cs content in the Romanian and NW Black Sea coast. *Rapp. Comm. Int. Mer. Medit.*, 35 (1): 234-235.

BOLOGA A. S., APAS M., COCIASU A., CUINGIOGLU E., PATRASCU V., PECHEANU I., PIESCU V., POPA L., 1998b — Present level of contaminants in the Romanian Black Sea Sector. IAEA-TECDOC-1094., Vienna, 58-63.

CUINGIOGLU E., BOLOGA A., BALABAN D., DOBRESCU E., PATRASCU V., *1996/1997* — Distribution of total beta radioactivity and ^{90}Sr in the Romanian Black Sea sector between 1994-1995. *Cercetari marine – Recherches marines.*, 29-30: 23-35.

OSVATH I., SAMIEI M., CARVALHO F., VILLENEUVE J. P., 1998 — Sustaining development in the Black sea region: A sea of changing fortunes. *IAEA Bulletin.*, 40 (3): 31-36.

PATRASCU V., 1996/1997 — Évolution post-Chernobyl de la concentration du ^{137}Cs dans le sédiments du littoral roumain de la mer Noire. *Cercetari marine Recherches marines.*, 29-30: 37-61.

PATRASCU V., BOLOGA A. S., 1990 — Evolution actuelle concernant l'irradiation humaine par certaines composantes marines. *Cercetari marine – Recherches marines.*, 23: 165-170