PRESENT LEVEL OF CONTAMINANTS IN THE ROMANIAN BLACK SEA SECTOR

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Abstract

The assessment of environmental quality in the Romanian Black Sea sector is being constantly made by the Romanian Marine Research Institute (RMRI) within the National Integrated Monitoring System. The contamination of the marine environment is expressed by considering four chemical and a biological parameter: nutrients ($N–NO_2$, $N–NO_3$, $N–NH_4$, $P–PO_4$, organic P, $Si–SiO_4$), heavy metals (Mn, Fe, Cu, Cd, Pb), artificial radionuclides (^{90}Sr, ^{137}Cs), total hydrocarbons, parasite and saprophyte fungi in sediments, sea water and/or biota. Present levels of contaminants are discussed as to their historical evolution during the last few years or decades. Inorganic N and P concentrations still exceed three to five times those before eutrophication started to intensify in the early '70s. Practical uses of results by national and regional authorities are discussed.

1. INTRODUCTION

The north–western sector of the Black Sea covers 63,900 km^2, with a depth less than 200 m, and it is directly influenced by the freshwater contribution from the Danube, Dniester and Dnieper (85% of the total); the hydrographic basin of those rivers amounts to about 1.4 million km^2, representing a catchment area by five times larger than the marine area they flow into. The Azov Sea mainly receives the waters of the Don and Kuban, as well as from three other smaller rivers.

The Romanian marine coast is 245 km long. Ten cities/towns and 100 rural localities amounting to about 650,000 inhabitants have developed along the littoral. They represent 8% of the population of the Danube basin (which is almost a half of the collectivity of the entire Pontic basin).

The climatic conditions depend on the season, and oscillate from the summer heat (25.5°C) to winter cold (down to –8°C). The wind force and direction are variable in time, the north winds are predominant during the cold season, and the south winds – during the warm season. The monthly averages of the severe winds in winter range from 4.7–7.1 m/s. The strong storms (with winds exceeding force 8) have a reduced frequency.

The development of the industrial and agricultural activities, the intensification of the river and maritime goods traffic in the Black Sea basin, as well as the population increase have caused an increase in pollution with dramatic effects on the coastal zone and marine ecosystem. It is well known that up to the beginning of the '90s, only the Danube contribution exceeded 34,000 t of mineral N, 60,000 t of total P, 6,000 t of Zn, 1,000 t of Cr, 280 t of Cd, 60 t of Hg and 50,000 t oil.

Besides erosion, the Romanian littoral as a whole has been affected by the high eutrophication of the coastal waters directly resulting in the alarming decrease of its biodiversity.

2. MATERIAL AND METHODS

The research regarding the evolution of environmental quality along the Romanian littoral is permanent within the framework of a general physico–chemical and biological monitoring programme.

More than 30 parameters are usually investigated as a consequence of the existing pollution sources (the influence of the Danube and other rivers, industrial and domestic sewage, port activities, intense tourism areas). Among these four chemical and a biological parameters have been analysed, namely: main nutrients ($N–NO_2$, $N–NO_3$, $N–NH_4$, $P–PO_4$, organic P, $Si–SiO_4$) in sea water, heavy metals (Mn, Fe, Cu, Cd, Pb) and artificial radionuclides (^{90}Sr, ^{137}Cs) in sediments, sea water and biota, total hydrocarbons in sea water, and parasite and saprophyte fungi.

The samples have been periodically collected from a network of stations off the Romanian coast, from various locations, depths and seasons, depending of the pollutant. The **nutrients** in the Danube water and coastal sea water have been analysed by using methods described by [1]. The **heavy metals** have been determined by atomic absorption using a spectrophotometer ATI–UNICAM, type SOLAR 9392, provided with a Zeeman correction cell and a system for automatic data recording and processing [2, 3]. Radiochemical separation of **^{90}Sr** and gamma spectrophotometry for **^{137}Cs** have been used for analysing the radioactivity of marine emerged and submerged sediments, water and biota: macrophytes, invertebrates, fish [4]. The UV spectrophotometric method (270–320 nm) for the liquid–liquid samples (sea water – 3 hexane7dichloromethane) has been used for **hydrocarbon** determination; the calibration has been carried out with Danube Reference Oil [5, 6, 7]. Several methods [8, 9, 10, 11, 12] have been used for quantitative and qualitative estimate of the **fungi** belonging to the phylum Mycophyta.

3. RESULTS AND DISCUSSION

3.1. Nutrients

The Black Sea receives a big volume of freshwater containing considerable amounts of inorganic nutrients. Owing to a strong thermohaline stratification and to a long residence time of water masses, the Black Sea ecosystem is highly sensitive to increased production of organic matter. The last thirty years represented a period of high intensification of the anthropogenic pressure on the coastal environment and high eutrophication, with negative effects on the whole ecosystem. Important nutrient and organic inputs from rivers and industrial and domestic drainage resulted in the increase of the magnitude and frequency of algal blooms followed by hypoxia and anoxia, benthic mortalities and a remarkable decrease of biodiversity. As the main current direction in the area is southward, the Romanian shelf representing 40% of the total shelf of the Black Sea is the most affected area. It receives water from the rivers Danube, Dnieper and Dniester, and the Danube contribution exceeds 70% of the total volume. The annual Danube water discharge between 1931 and 1995 indicates significant fluctuations and decadal trends, in addition to the expected seasonal variability. These fluctuations have therefore a major influence on the nutrient budgets of the western shelf water.

The annual nutrient loads, derived from the monthly averages of nutrient concentrations and water discharge, also displayed interannual changes. The data obtained at Sulina between 1988–1996 show that the Danube drained 4.1–8.1 x 10^5 t/year of dissolved inorganic nitrogen into the Black Sea, with a percentage of nitrates exceeding 90%. During 1980–1986, the annual phosphate and silicate loads in the Danube were of 0.06–0.33 x 10^5 t/year and 1.5–5.0 x 10^5 t/year, respectively.

A comparison with other data [13] shows that DIN discharge increased by a factor of 4 to 5, and phosphorus load increased more than 2 times. At the same time the silica discharge from the Danube was reduced very much. For the last 15 years, the annual average discharge of silica was less than a half of the estimated silica input before 1970. This fact has been related to the decrease of the solid river discharge, as a consequence of the damming works for energy production upstream the river and its tributaries, and of its intense consumption during the previous massive diatom blooms as well. A seasonal prevalence of the nutrient stocks followed the water discharge.

Considering the interannual changes of the nutrient stocks discharged by the Danube into the sea, a slight but continuous diminishing tendency should be noticed after 1990 (Fig. 1).

On the Romanian shelf, the highest nutrient stocks were reached in the '70s, they decreased considerably in the '80s and have slightly diminished during the '90s (Fig. 1). Even if a decrease tendency has been recorded during the last two years, the content of inorganic nitrogen salts is still high, exceeding by 3–5 times the levels before the eutrophication. The phosphorus values were similar to those before the eutrophication and it frequently reached the exhaustion stage. High N:P ratios (different from Redfield oceanic model) strongly suggest phosphorus as the nutrient with limiting role for the Romanian shelf waters [14]. The decrease of silica concentrations has been much more evident and is actually three times less than during the reference periods.

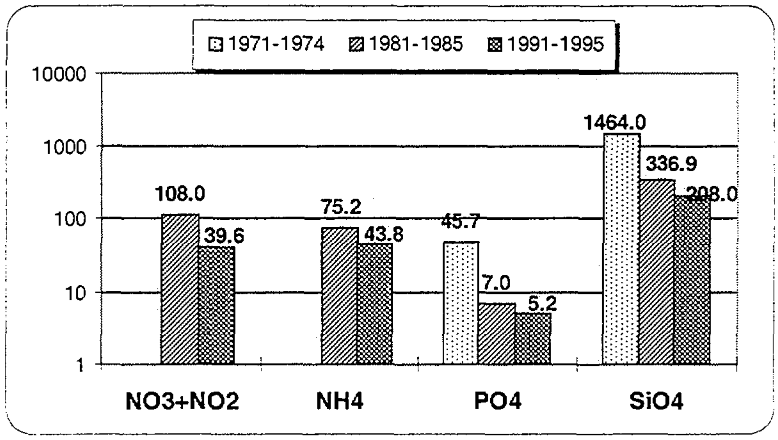

FIG.1 Time evolution of the nutrient stocks on the Romanian shelf (thousand tonnes)

3.2. Heavy metals

The control of environmental quality of the Romanian coast is achieved by a permanent monitoring of Mn, Fe, Cu, Cd and Pb.

In the northern sector, the content of heavy metals in sediments ranged between 2.43–4.24 µg/g Mn, 48.23–61.38 µg/g Fe, 14.71–17.89 µg/g Cu and 11.57–18.91 µg/g Pb. In the sea water, the heavy metal concentrations oscillated between 2.79–25.03 µg/g Mn, 30.36–193.8 µg/g Fe and 3.11–17.54 µg/g Cu. These values are rather high, the Danube influence being strong in the marine environment.

For the southern sector, the heavy metal content in sediments is higher than in the sea water: 18.6–284.88 µg/g Mn, 244.33–426.47 µg/g Fe, 21.52–360.56 µg/g Cu, 0.13–3.98 µg/g Cd and 3.93–131.3 µg/g Pb. Many of the maximum values have been found in Constanta port area and especially at berth 34 (Petromar), and most of the minimum values – offshore at a depth of 70 m. The maximum values were comparable with those found in front of the Danube mouths. For the coastal waters, the values were of 0.17–172.8 µg/L Mn, 0.41–417.8 µg/L Fe, 5.27–28.93 µg/L Cu, 5.82–17.67 µg/L Cd and 1.48–12.08 µg/L Pb. For depths of 10 m, the heavy metal contents were 0.35–13.20 µg/L Mn, 1.83–26.51 µg/L Fe, 0.39–20.37 µg/L Cu, 0.59–10.08 µg/L Cd and 2.15–4.79 µg/L Pb.

Among the marine biota, the mussels from Vama Veche (4.5–5.0, 5.0–5.5 and 5.5–6.0 cm) and several fish species from Mamaia Bay have been analysed. For mussels, the heavy metal contents were of 46.13–92.28 µg/g fresh weight Mn, 118.43–176.4 µg/g Fe, 16.66–22.45 µg/g Cu, 10.03–30.76 µg/g Cd and 4.44–9.36 µg/g Pb. The fish samples had heavy metal concentrations of 4.47–5.85 µg/g dry weight Mn, 52.86–66.18 µg/g Fe, 11.24–17.86 µg/g Cu, 13.62–16.77 µg/g Cd and 4.01–5.56 µg/g Pb.

As far as the heavy metal concentrations in sea water along the Romanian littoral are concerned, the concentrations of Fe, Cu and Pb either at the seashore (0 m) and at a depth of 10 m are lower when compared with other areas of the World Ocean. An exception is Cd, with values in shallow waters exceeding greatly those in other areas. The content of heavy metals is within the maximum limits of the Romanian standards for seawater: 300 µg/L for Cu, 30 µg/L for Cd and 50 µg/L for Pb [15].

3.3. Radionuclides

The radiometric investigation of the coastal marine ecosystem [16, 17, 18] was continued in 1997; the results showed the presence of the long-lived anthropogenic radionuclides ^{90}Sr and ^{137}Cs.

Significant ^{90}Sr activities (1.53–7.64 Bq/kg dry) were found in the emerged marine sediments collected from seven profiles between the northern and southern limits of the Romanian littoral. The maximum value was recorded at Chituc, station 2 (33.8 m depth).

In the surface seawater, ^{90}Sr content varied over a very narrow range, 19.18–21.83 Bq/m^3. During 1993–1997, this radioisotope varied between rather constant limits. The mean activity of ^{90}Sr was close to the mean value identified by other researchers studying the Black Sea waters [19] during 1975 and 1988–1991.

The green and red macrophytes had a ^{90}Sr content of 0.37–1.08 Bq/kg fresh weight, both maximum and minimum values measured in the green alga *Enteromorpha linza*. The molluscs samples represented by two bivalves and a gastropod had very low activities of ^{90}Sr, namely <0.13–0.28 Bq/kg f.w., of which 50% were below the detection limit. The maximum concentration of ^{90}Sr was determined for the bivalve *Mytilus galloprovincialis*. The measurement of ^{90}Sr in the most frequent benthic fish species collected resulted in significant values of 0.63–0.98 Bq/kg f.w. The maximum concentration was recorded for *Gobius melanostomus*, 24% higher than the values obtained for the same species in 1994 and 1995.

The numerous investigations carried out on environmental pollution up to 10 m depth in 1997 indicated ^{137}Cs concentrations of 6.6–86 Bq/kg dry in sediments collected from the southern coast. 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 dry; 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 low concentrations (at an average less than 5 Bq/kg f.w.). The fine beach sediments in the Constanta area did not exceed 10 Bq/kg f.w. The determination of ^{137}Cs concentration in a reference sea water sample (Constanta, offshore) showed a concentration of 0.036 Bq/L, close to the value of 52 Bq/m^3 recommended by [20]. Marine biota had low ^{137}Cs concentrations of only a few Bq/kg f.w. The macrophytes had a radionuclide content of 0.7–0.8 Bq/kg f.w. (maximum value for *Ceramium rubrum*). For molluscs, it varied between 0.4 and 1.9 Bq/kg f.w., with maximum values recorded in *Mya arenaria* and *Mytilus galloprovincialis*. Rather significant values were found for fish, where the ^{137}Cs concentrations ranged between 1.4 and 3.4 Bq/kg f.w., with the maximum value measured in *Sprattus sprattus phalericus*.

3.4. Hydrocarbons

Hydrocarbon monitoring was based on the analytical results of the total hydrocarbon content determined in sea water from the areas exposed to loading with oil polluting agents.

The spatial distributions of the concentrations in the river water and sea water demonstrate the impact of the river discharges estimated at 328.4 µg/L in 1997. The contributions of the river inputs located in the northwest Black Sea contaminated by oil exploitation activity and naval traffic cause the significant increases of the hydrocarbon loading at 20 m depth.

The pollution from oil decreased in 1995–1997, and the lowest values were recorded in 1997 [21], when that contamination was reduced by 4.2 times off the Sulina Channel and by 10.3 times off the Danube mouths marine area.

Between Navodari and Vama Veche, the results obtained in 1997 showed a pollution level of 91.4–1029 µg/L near the shore and 49.3–183.9 µg/L in offshore waters at 0–10 m depths; the spatial distribution of the hydrocarbon concentrations in that area of the coast illustrates the effect of the water treatment mainly along the depths of 0 m, where the mean pollutant loading is 67.3% higher than the mean value for the offshore area.

During 1995–1997, the temporal variability of hydrocarbon pollution was characterized by a reduction over time [21, 22].

3.5. Fungi

In time the mycological data from the shallow water area have shown the importance of this biological indicator of pollution. Certain groups of saprophyte and pathogenic micromycetes are indesirable as they endanger the sanitary condition of these waters including the bathing waters. The negative aspect of the excessive development of the mycoplankton resulting in "fungi blooms" concerns its quantitative and qualitative development.

The representatives of family Cryptococcaceae have been found permanently in the polluted water masses; they have become predominant and have generated ample "fungi blooms" caused by the genera *Candida, Rhodotorula, Cryptococcus* and *Trichophyton.* The strictly marine taxa belonging to the family Thraustochytriaceae were identified for the first time in Romanian sea waters [10] and then were found frequently in small quantities.

In comparison with the degree of fungus pollution in coastal waters for 1990–1997, and previous investigation periods, some slow but continuous changes have been noted concerning both the structure and dynamics of fungi by the exclusive proliferation of some pathogenic yeast fungi. For example, in 1997 an explosion of the reproduction elements (conidia, blastospores, arthrospores, bud cells) was noticed at Mamaia, Constanta South and Vama Veche in comparison with the previous years. During the same year, at the 10 nautical miles Tuzla reference station the fungi increased considerably and generated a *Geotrichum candidum* bloom.

4. CONCLUSIONS

1. The highest N and P stocks recorded in Romanian shelf waters in the '70s decreased considerably during the '80s but only slightly during the '90s; inorganic salt concentrations still exceed three to five times those existing before eutrophication began to intensify (1970).
2. Phosphorus values similar to those before eutrophication and the high N:P ratio suggest P as a limiting nutrient in the shelf waters.
3. Present silicon concentrations have apparently decreased as much as threefold compared to the afore mentioned reference period.
4. High concentrations of some heavy metals in Romanian littoral sediments including those in Constanta South area are mainly due to land based pollution sources (point sources, water treatment stations, port activities).
5. The ^{90}Sr content in marine biota is relatively low (maximum 1 Bq/kg fresh weight).
6. The highest values of ^{137}Cs are found in the submerged sediments (maximum about 200 Bq/kg dry).
7. Concentrations of ^{137}Cs in marine biota are a few Bq/kg f.w., and vary according to taxonomic group.
8. The temporal variation in hydrocarbon pollution demonstrates the anthropogenic input to the environment.
9. Off the Danube mouths, the mean concentration of oil of 170 μg/L is 42% higher than that determined for the southern part of the littoral at depths of 10 m.
10. Fungus pollution has increased with a predominance of the family Cryptococcaceae.
11. Many of the *Rhodotorula* species, found in 60% of the analysed samples, are pathogenic followed by the species belonging to the genera *Candida, Cladosporium* and *Penicillium.*
12. There are sensitive seasonal quantitative differences in the specific structure of the mycoplankton, among which the spring–summer species of the genera *Trichoderma* and *Epicoccum* are more important.
13. The potentially pathogenic yeast fungi have particularly proliferated reaching very high levels in all locations over the last few years.
14. The "fungi blooms" have been produced by the filamentous complex *Penicillium – Cladosporium* and pathogenic yeast complex *Rhodotorula – Candida – Geotrichum – Cryptococcus* off the localities most affected by waste overflows, namely Mamaia, Eforie North and Mangalia.
15. These results can be used as a support for environmental protection measures recommended by the Ministry of Waters, Forests and Environmental Protection and its subordinated organisms (Environment Protection Agency, "Romanian Waters"), requests of the Danube Delta Biosphere Reserve Authority through research projects, Black Sea Strategic Action Plan and fulfilment of Romanian obligations within the framework of the Convention on the Protection of the Black Sea Against Pollution (Bucharest Convention, 1992) and Odessa Ministerial Declaration (1993).

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