ENVIRONMENTAL ASSESSMENT OF THE RIVER DANUBE BETWEEN 1995 AND 1997

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Abstract. The European River-Ocean System, EROS - 2000 Danube Project (PHARE Contract No. 95-0339), aimed at assessing the environmental state of River Danube between 1995 – 1997. The studies were carried out along the entire Romanian Danube watershed. In time, the natural flow regime of the Dunube River was disturbed by anthropic intervention (damming and embankment). The existence of numerous industrial and agricultural objectives in the Danube's drainage basin altered the quality of the environment. In order to assess the anthropic impact on the Danube environmental quality, water and sediment samples were collected and analysed. The water samples analyses show the physical-chemical parameters and heavy metals, nutrients, organic pollutants contents. Grain size values, heavy minerals associations and heavy metals contents were performed on the collected bottom sediment samples. Studies were also made regarding the natural and artificial radionuclides contents in bottom sediments. Studies were made on diatoms associations, used as salinity and pollution markers. It can be remarked that the general environmental state along the Romanian Danube watershed improved from 1995 to 1997, unfurtunately due mainly to the economical recession.

Key words: EROS 2000, Danube River, environmental assessment, sediments, grain size, heavy metals, diatoms, radionuclides

INTRODUCTION

The European River-Ocean System, EROS - 2000 Danube Project, aimed at assessing the environmental state of River Danube between 1995 and 1997.

The studies were carried out in the framework of the PHARE Contract No. 95-0339 " Danube EROS - 2000 Research Programme - Romania" signed by the European Community Commission as "Contracting Party" and the National Institute for Marine Geology and Geoecology (GEOECOMAR) as "Contractor". The contract is placed under the co-ordination of the Danube Programme Co-ordination Unit.

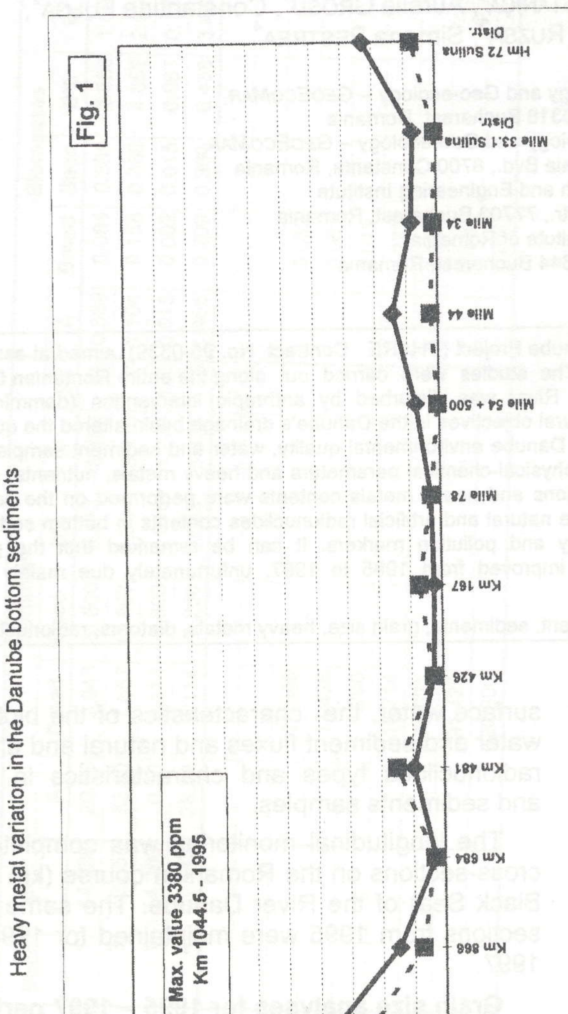
For the completion of the specific tasks of the project, the National Institute for Marine Geology and Geoecology worked in co-operation with several Romanian research institutes (National Research Institute for Environmentalal Protection – ICIM Bucharest, Geological Institute of Romania, "Lower Danube University" - Galati).

The present paper contains the comparison of the measured data and results for 1995, 1996 and 1997 cruises. The 1997 results are presented separately, as the samples collection and measurements cruise took place between November and December, while the cruises from the previous two years had been held between June and July. The main aspects are: the assessment of the quality of bottom sediments and surface water, the characteristics of the biotopes, water and sediment fluxes and natural and artificial radionuclides types and characteristics in water and sediments samples.

The longitudinal monitoring was completed on cross-sections on the Romanian course (km 1075-Black Sea) of the River Danube. The same study sections from 1995 were maintained for 1996 and 1997.

Grain size analyses for 1995 – 1997 period

In the Portile de Fier I reservoir two main depositional environments were observed: the upstream area (Km 1072.4 - Km. 1010), characterized by predominant sandy sediments and fine sediments (silts) in the lacustrine *"sensu stricto"* environment (Km. 1010 - Km. 943). Between Portile de Fier I (Km. 943) and Portile de Fier II (Km. 864) barrages, the sediments are constituted mainly of sands and gravel. Only close to the Portile de Fier II barrage there was found a thin layer (2 cm) of fine sediments. Between Portile de Fier II barrage (Km. 864) and Mile 44, the beginning of the Danube Delta, the bottom sediments are represented mainly by sands and seldom by gravel. The sediments collected from the four main distributaries of the Danube Delta (Chilia, Tulcea, Sulina and Sf. Gheorghe) are mainly sands. Finer sediments (from fine to medium grained silts) are present at the mouths of


Heavy metal variation in the Danube bottom sediments
Fig. 1
Cu (ppm) 1995
Cu (ppm) 1996
Max. value 3690ppm
Km 1044.5 1996
Max. value 3380 ppm
Km 1044.5 1995
500
450
400
350
300
250
200
150
100
50
0
Km 1072.4
Km 1044.5
Km 1040
Km 999
Km 947.2
Km 866
Km 684
Km 481
Km 426
Km 167
Mile 78
Mile 54 + 500
Mile 44
Mile 34
Mile 33.1 Sulina Distr.
Hm 72 Sulina Distr.

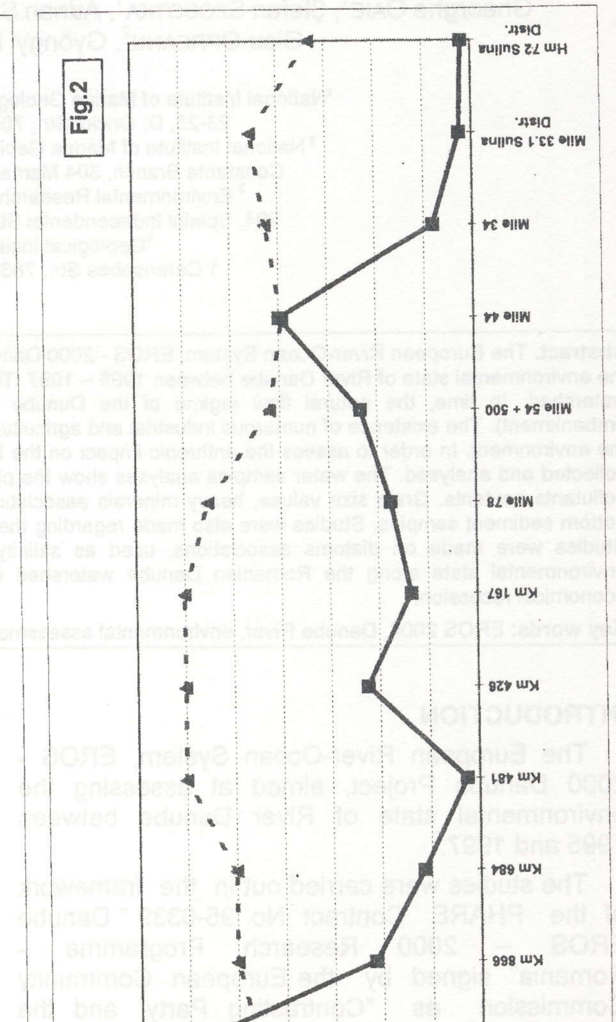


Fig.2
Cd (ppm) 1995
Cd (ppm) 1996
14
12
10
8
6
4
2
0
Km 1072.4
Km 1044.5
Km 1040
Km 999
Km 947.2
Km 866
Km 684
Km 481
Km 426
Km 167
Mile 78
Mile 54 + 500
Mile 44
Mile 34
Mile 33.1 Sulina Distr.
Hm 72 Sulina Distr.

the distributaries (Hm. 72 - Sulina; km 1.3 - Sf.Gheorghe). The samples collected from most Romanian tributaries, at the junctions with the Danube River, show distinct grain size features. The sediments are mainly sands in the following rivers: Topolnita, Jiu, Arges, Ialomita, Siret. Silts are predominant in Cerna, Olt, Vedea, Prut rivers.

Comparison of <u>heavy metals</u> contents from bottom sediments collected between 1995 and 1996 underlined the following main conclusions: **Cu** - insignificant changes in the Moldova Nouă area, (values of 3380 ppm in 1995, 3690 ppm in 1996), a slightly decreasing trend between Mile 78 and the Black Sea (Fig.1); **Zn** - the same maximal values in the Moldova Nouă section (1280 ppm in 1995, 1500 ppm in 1996); downstream Km 1040 section the values decreased in comparison with the previous year; **Pb** - the maximal values were measured in the Portile de Fier I dam lake in 1995 (Km 952 - 243 ppm, Km 947.2 - 195 ppm). These values suffered an important decrease, maintaining a relatively constant level till Mile 78; **Ni** - much lower contents in 1996 than in 1995, of the maximal values; approximately constant values between Km 866 - Black Sea; **Cd** - important decrease since 1995 between Km 1072.4 and Km 947 (Portile de Fier I lake); the values increased between Km 866 and the Black Sea (Fig.2); **Cr** - the same trends are maintained even by the maximal and minimal values for the two studied years; **Mn** - in comparison with 1995, the maximal values moved downstream the Portile de Fier II dam, reaching a peak of more than 1400 ppm at Km 866; between Km 684 and Mile 33 + 1000, the values remain relatively constant; **V** - relatively constant values in 1996 compared to 1995 were measured in the reservoirs; a peak of 60 ppm was measured in 1996 at Hm 72 - Sulina distributary.

In 1996, in comparison with 1995, the situation is generally improved, exception being the Cd contents (for the Portile de Fier II barrage - Mile 44 section). For the main Romanian tributaries, the measured values for 1996 generally have a decreasing trend in comparison with 1995 for the Cerna, Topolnita, Olt, Arges, Ialomita, Siret and Prut rivers. The situation became worse only for Jiu and Vedea tributaries, as most of the heavy metals contents increased very much as follows: Jiu River: Cu, Pb, Ni, Cd, Cr, Mn, As; Vedea River: Cu, Zn, Ni, Cd, Mn, V. Arges River maintains the same high pollution level for both years, even though there was observed a decrease for the following contents: Cu, Zn, Cd, Cr, Mn, As. Pb and Ni (Fig.3) were found here in the highest contents in comparison with all the other presented rivers.

The <u>water samples</u> from the Danube and its main Romanian tributaries were analyzed for: dissolved O_2 concentration and O_2 saturation,

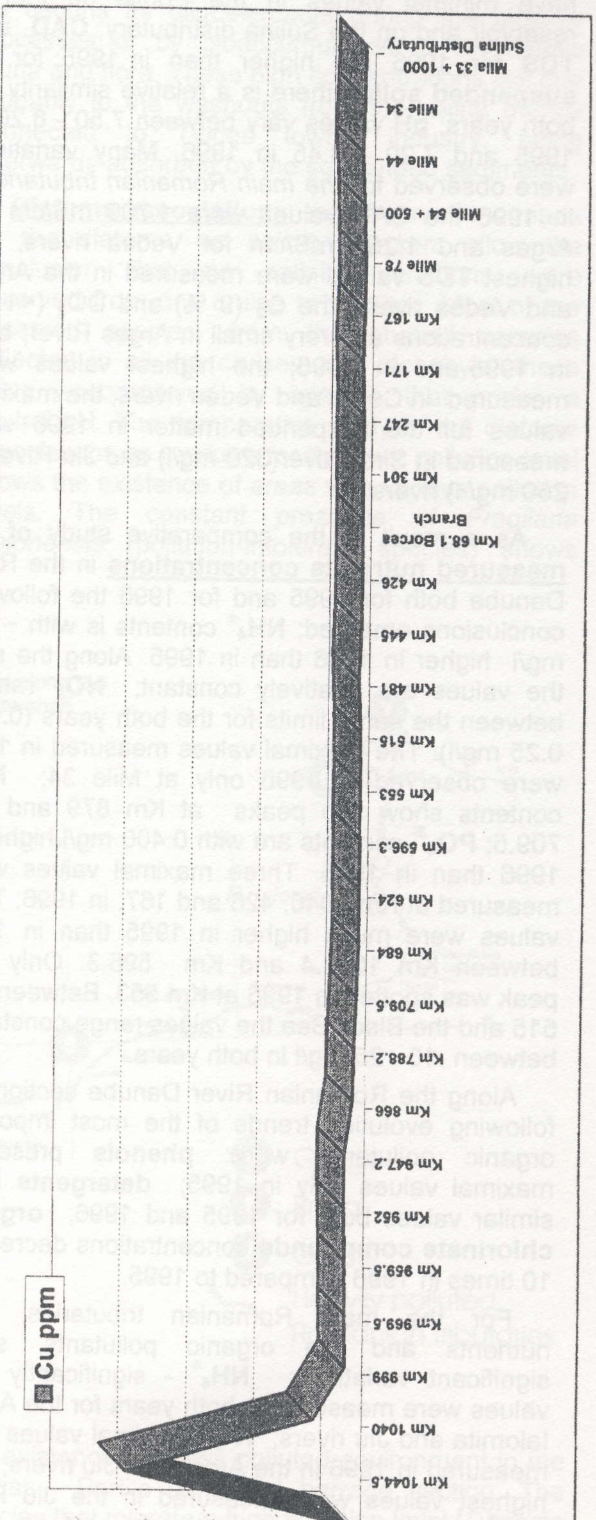


Fig. 3 Heavy metal variation in the Danube bottom sediments

CAD, TDS, pH, Eh, suspended solids and nutrients (NO^{3-}, NO^{2-}, PO_4^{3-}). Physical - chemical parameters show important variations: **DO_2** and **O_2** have minimal values in the Portile de Fier II reservoir and on the Sulina distributary; **CAD** and **TDS** for 1996 are higher than in 1995; for the **suspended solids** there is a relative similarity for both years; **pH** values vary between 7.50 - 8.20 in 1995 and 7.20 - 8.45 in 1996. Many variations were observed for *the main Romanian tributaries* : in 1996 the CAD values were 1.700 mS/cm for Arges and 1.250 mS/cm for Vedea rivers; the highest TDS values were measured in the Arges and Vedea rivers; the O_2 (9 %) and DO_2 (<1 %) concentrations are very small in Arges River, both in 1995 and in 1996; the highest values were measured in Cerna and Vedea rivers; the maximal values for the suspended matter in 1996 were measured in Siret River(320 mg/l) and Jiu River (> 250 mg/ l) rivers.

As a result of the comparative study of the **measured nutrients concentrations** in the River Danube both for 1995 and for 1996 the following conclusions emerged: **NH_4^+** contents is with ~ 0.2 mg/l higher in 1996 than in 1995. Along the river the values are relatively constant; **NO_2^-** ranges between the same limits for the both years (0.05 - 0.25 mg/l). The maximal values measured in 1995 were observed in 1996 only at Mile 34; **NO_3^-** contents show two peaks at Km 879 and Km 709.5; **PO_4^{3-}** contents are with 0.400 mg/l higher in 1996 than in 1995. Three maximal values were measured at Km 1040, 426 and 167, in 1996; **TOC** values were much higher in 1995 than in 1996 between Km 1072.4 and Km 596.3. Only one peak was spotted in 1996 at Km 553. Between Km 515 and the Black Sea the values range constantly between 10 - 25 mg/l in both years.

Along the Romanian River Danube section the following evolution trends of the most important organic pollutants were: **phenols** presented maximal values only in 1995; **detergents** have similar values both for 1995 and 1996; **organo-chlorinate compounds** concentrations decreased 10 times in 1996 compared to 1995.

For the main Romanian tributaries, both nutrients and the organic pollutants, suffer significant variations: **NH_4^+** - significantly high values were measured in both years for the Arges, Ialomita and Jiu rivers; **NO_2^-** maximal values were measured in 1996 in the Arges and Jiu rivers; **NO_3^-** highest values were measured in the Jiu River; **PO_4^{3-}** had an abnormally high value in Arges River in 1996.

The nutrients and the organic pollutants from the same main Romanian tributaries suffered significant alterings: **phenols**: the peaks observed in Cerna, Jiu, Olt and Arges rivers in 1995 disappeared; **detergents** - some of the high values maintained both for 1995 and 1996 in the Olt (> 0.1 mg/l) and Arges (0.14 mg/l) rivers. New high values were measured in 1996 on the Danube branches at Mile 44 (0.22 mg/l) and at Km 115.2 - Chilia distributary (0.14 mg/l); **organo-chlorinate compounds** - the high values measured in Cerna, Jiu, Olt, Vedea and Ialomita rivers in 1995 decreased to values less than 0.001 mg/l in 1996.

Heavy metals measured on filtered water samples show the following variations: **As** and **Se** contents overstepped the Romanian standards in all the water samples; **Cd** and **Zn** contents overstepped the standards in the upstream part of the Portile de Fier I reservoir; **Hg** contents are higher than the Romanian and E.U. standards. For the main Romanian tributaries: **Hg** contents were higher than the standards in Olt and Vedea rivers; **Cd** contents had the only abnormally high value in 1995 at the mouth of Arges River (3.4 ppb); **Se** and **As** contents exceeded both the Romanian and E.U. standards in the water samples collected in 1995, while in 1996 only in Jiu River (Se) and Cerna and Olt rivers (As); **Zn** contents in Arges, Siret and Prut rivers exceeded the Romanian standards in 1995. For 1996, these standards were overstepped in the samples from Cerna,Topolnita, Jiu, Olt, Vedea, Ialomita rivers.

The results obtained during the 1997 cruise are presented separately because the cruise was held between October and December.

Heavy metals contents in bottom sediments: the highest pollutants contents were found in the Portile de Fier I reservoir. The following heavy metals exceeded the standard values: Fe_2O_3, MnO, Pb, Mn, Zn, Ni, Cr, V, Hg, Cu, Cd. The most heavily polluted main Romanian tributaries in heavy metals were: Cerna (Fe_2O_3, TiO_2, Cd, Cr, V) and Vedea (MnO, Ni, Cu, Pb, Hg) rivers. The highest measured value for As was found in Ialomita River.

Heavy minerals in bottom sediments: the only issues that allowed the comparison of the results for the three years of study (1995 - 1997) are the heavy minerals. Their associations are not disturbed by the seasonal variations, as they depend only on the source areas. About 40 distinct heavy minerals have been identified in the fine bottom arenytes of the Danube River. In all the samples collected during the three cruises, the heavy minerals associations were dominated by garnet and occasionally by amphiboles and opacites.

Variation of physical - chemical parameters of water samples: Because the 1997 cruise was held in October - December, when the water temperature decreased from 16.7 °C in October to

5.7 °C in December, **dissolved oxygen** increased from upstream 5.54 mg/l (water temperature - 6.9 °C) to downstream (7.17 mg/l at a temperature of 16.7 °C), **pH** values increased from upstream to downstream, from 7.53 (Km. 999 profile) to 8.7 on the Km. 3 - Chilia distributary profile. The water alkalinity might be also due to the masses of polluted waters brought by the main Romanian tributaries. The **nutrients contents** (NH_4^+, NO_3^-, NO_2^-, PO_4^{3-}) respect the maximal values specified by the Romanian and E.U. standards. The measured **organic pollutants** (detergents, pesticides, phenols, CN^-, S^-, TOC) concentrations are well below the maximal standard values.

The main **heavy metals** measured on the water of the River Danube and its main Romanian tributaries water samples were: Cu, Pb, Zn, Fe, Mn, Hg, As, Se, Cr and Cd: Fe was found in concentrations higher than the standards in several profiles from the Portile de Fier I reservoir; Se and Hg were found in abnormal concentrations generally downstream the industrial towns.

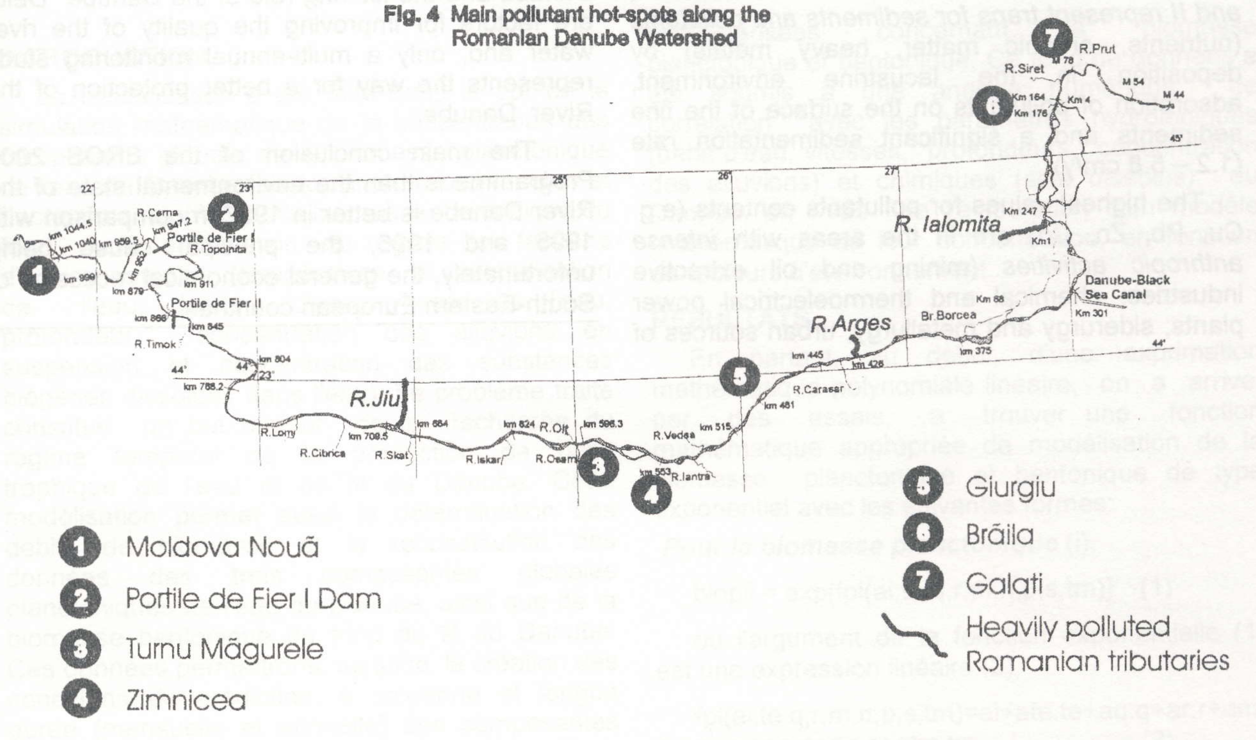


Fig. 4 Main pollutant hot-spots along the Romanian Danube Watershed

A special case is represented by the **Danube Delta**. The deltaic system acts like a buffer zone for the Danube water. The following conclusions can be presented: PO^{3-}_4, NH^+_4 and NO^-_3 ions are retentioned by the deltaic flora. PO^{3-}_4 accumulation is a cause for the lakes' eutrophication. The Danube water samples were analyzed also for the measurement of heavy metals concentrations (Hg, Cd, Pb, Zn, Cu, Cr, Fe, Mn, As, Se). It can be observed that the Danube Delta retains the Zn and Cu cations as oligoelements during the biologic processes or by bioaccumulation in the deltaic fauna and flora. These high concentrations are due probably to the washouts from the waste dumps connected to Tulcea town's industry, being afterwards adsorbed by the suspended sediments.

Diatoms associations: the observations made on the diatoms, as *salinity markers* allow the conclusion that no salinity variations were observed from one cruise to another. Most of the observed species, from the studied samples collected in all the cruises, are alcaphyle, these being accompanied by species that prefer a neutral pH. The comparative study of the diatoms associations as markers for the river pollution level shows the existence of areas with various pollution levels. The constant presence of *Fragilaria crotonensis* (pollution-intolerant species) shows the existence of a less polluted environment in the Bazias - Portile de Fier I barrage section. The species that tolerate a high pollution level (*Diatoma vulgare, Achnanthes minutissima, Nitzschia palea*) are constantly present in a high percentage in the samples collected during all the cruises in the following areas: Jiu and Ialomita rivers and Danube Delta area. This shows the constant presence in these areas of a highly polluted environment.

__Natural and artificial radionuclides__: the sediment samples were analyzed using the high resolution gamma spectrometry method for the natural and artificial radionuclides contents. Cs-137 has a major contribution in the studied samples. Cs-137 presence in the samples has as main causes the nuclear open air tests and the Chernobyl accident (May, 1986). The Chernobyl moment was used as marker for the computation of the sedimentation rates. The maximum contents in Cs-137 were considered as corresponding for 1986. By the use the Cs-134/Cs-137 isotopic fractions, considering a constant sedimentation rate, sedimentation rates of 1.6-2.3 cm/year were computed in the Portile de Fier I reservoir (results obtained in 1995).

CONCLUSIONS

In time, the natural flow regime of the River Danube was disturbed by anthropic interventions. The damming broke the bed load flux and introduce *disbalances in the Black Sea littoral sediment budget. The reservoirs Portile de Fier I and II represent traps for sediments and pollutants* (nutrients, organic matter, heavy metals) by deposition in the lacustrine environment, adsorption of pollutants on the surface of the fine sediments and a significant sedimentation rate (1.2 – 5.8 cm/y).

The highest values for pollutants contents (e.g. Cu, Pb, Zn, Cd) are in the areas with *intense anthropic activities* (mining and oil extractive industries; chemical and thermoelectrical power plants; siderurgy and metallurgy; urban sources of sewage waters), or affected by *accidents* (e.g. Chernobyl nuclear power plant) (Fig.4).

The *main polluted tributaries* (Jiu, Arges, Ialomita), represent important "hot spots" for the River Danube, but their effects are limited in space.

The annual monitoring of the pollution levels and distribution for River Danube and its tributaries brought to the conclusion that the main pollution sources could be divided in two categories:

1.natural: - geological source areas rich in ores; sedimentation conditions that allow the gravitational deposition (e.g. lakes, meanders); fine grained bottom sediments than adsorb the pollutants on their surfaces.

2.anthropic: untreated waste and sewage water spills; mining, drilling, oil extraction, agricultural and industrial activities; washout by meteoric waters of chemical elements and compounds from the waste dumps of ores, barren and ashes; regional or local accidents (e.g. Chernobyl accident from 1986).

The self regenerating capacity of the River Danube and the filtering role of the Danube Delta are factors for improving the quality of the river water and, only a multi-annual monitoring study represents the way for a better protection of the River Danube.

The main conclusion of the EROS 2000 Programme is than the environmental state of the River Danube is better in 1997 in comparison with 1995 and 1996, the principal cause being unfortunately, the general economical recession of South-Eastern European countries.