DANUBE POLLUTION CONTRIBUTING TO EUTROPHICATION OF THE ROMANIAN BLACK SEA COAST

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Abstract: *The trace metal concentrations in green algae Sea lettuce collected on the Romanian Black Sea coast near the Sulina channel (a branch of Danube river) mouth were determined. The concentrations of Cd, Co, Cr, Cu, Fe, Hg, Mn, Pb, V and Zn were determined through atomic absorption spectrometry and neutron activation analysis. The concentrations of trace metals in Sea lettuce samples were about 2.5 times higher compared to corresponding concentrations in the Eastern part of the Black Sea. The results obtained show that Sea lettuce may be used as a bioindicator for trace metal contamination of the coastal waters.*

It is well known that the macroalgae (as green algae *Chlorophyta*) can absorb and store nitrogen, phosphorus and heavy metal ions from water. Some green algae (Chlorophyta) species are potentially good biomonitors for water pollution. Earlier studies have determined that pollutant accumulation in macroalgae have gradually increased in Black Sea coastal waters.

Danube is the Europe's second biggest river and the world's 26th, with almost 2,900 km of length, a basin of over 800,000 sq.km, populated by some 80 million inhabitants in 8 countries. Pollutants poured into the rivers waters, including toxic metals, agrochemicals and radionuclides are released mainly via rivers draining out of Central and Eastern Europe. The factors of pollution are associated mainly with oil hydrocarbons, airborne pollutants (As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, V, Zn) released by different types of industries located in the Danube Basin and implicitly in Black Sea Basin, urban raw sewage, pesticide residues and other chemicals from farms.

Some algae species are potentially good biomonitors for water pollution monitoring studies. Earlier studies have determined that heavy metal accumulation in macroalgae have gradually increased in Black Sea coastal waters. Additionally, increased river supply of 'nutrients' such as phosphate, ammonium and nitrogen feed excessively algae communities that proliferate, causing an overproduction of the phytoplankton, which block the light reaching the sea grasses and algae. The bacteria quickly consume all the oxygen and the sea is virtually dead below a depth of about 180 m. Because the replenishment of the bottom waters with new seawater from the Mediterranean takes hundreds of years, the Black Sea remains the biggest natural anoxic basin in the word.

The present study was carried out in the framework of the project "The assessment of environmental pollution in the Southern part of Romania" (2000 - 2005) agreed between the Faculty of Physics of University in Bucharest and Frank Laboratory of Neutron Physics of the Joint Institute for Nuclear Research. This paper reports the heavy metal levels in the green algae *Sea lettuce* collected on the Romanian Black Sea coast.

MATERIAL AND METHODS

The *Sea lettuce* samples were collected on the Romanian Black Sea coast near the Sulina channel. The map comprising the algae sampling is shown in Fig. 1.

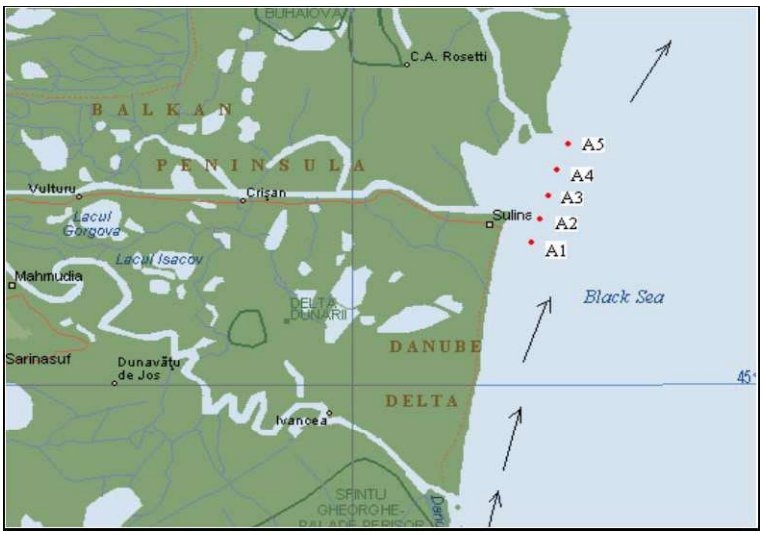

Fig. 1. – Map showing the sampling sites

At five sampling sites, samples were recorded in 1m^2 quadrates placed 20 m apart along belt transects for sampling. Prior to analysis the *Sea lettuce* samples:

- were carefully cleaned from all shells, dead material and attached litter;
- washed with distilled water ;
- were let to dry at room temperature on a filter paper;
- were kept at 40^{0}C for 48 hours in thermostat until constant weight;
- were finely powdered in an agate mortar.

The same material was subjected both to neutron activation analysis and flame atomic absorption spectrometry. By this combination of methods was determined an amount of 36 elements in the *Sea lettuce* samples analyzed.

The characteristics of irradiation channels for neutron activation analysis can be seen in Table 1.

The elements were measured as follows: Mn and V by their short half-lived radioisotopes, As by its medium half-lived isotope and Co, Cr, Fe, Ni, Zn by their long half-lived radioisotopes.

Table 1

The number of samples of different moss species collected

Irradiation channel	Neutron flux density 10^{12} x(n/cm^2 s)			T (°C)	ϕ channel (mm)	L channel (mm)
	E=0–0.55 eV	E=0.55–10^5 eV	E=10^5–25·10^6 eV			
Ch1 (Cd-screened)	0.023 ± 0.002	3.31 ± 0.3	4.23 ± 0.4	70	28	260
Ch2	1.23 ± 0.1	2.96 ± 0.3	4.1 ± 0.4	60	28	260

The elements Cd, Cu, Hg and Pb were determined by acroalga samples of 0.5 g (d.w.) were dissolved in 6 ml HNO_3 at 120^{0}C during 6 h. After cooling at room temperature, the samples were filtrated and distilled water was added up to 50 ml.

RESULTS AND DISCUSSIONS

The element concentrations are presented in Table 2.

Table 2

Elemental concentrations in algae samples, mg/kg (d.w.)

***Element*/Site**	**A1**	**A2**	**A3**	**A4**	**A5**	**EBS* (1995)**
As	12.3	29.0	27.5	17.6	15.8	
Cd	1.5	3.5	2.6	1.9	1.8	0.5
Co	3.4	11.1	9.0	8.0	7.7	0.05
Cr	0.8	8.4	3.2	1.4	1.1	<0.05
Cu	9.4	21.7	17.8	13.1	11.3	3.5
Fe	204	351	339	321	258	106
Hg	0.05	0.17	0.14	0.08	0.06	
Mn	16	83	26	21	18	23
Ni	0.48	1.03	1.05	0.61	0.58	2.3
Pb	1.1	18.3	13.7	3.1	2.9	<0.1
V	19.7	55.2	41.8	30.3	20.2	
Zn	15	22	21	19	19	59

*IAEA BULLETIN, 42/4/2000

The trace element concentrations for the samples A2 and A3 exceed considerably the values obtained for the last three samples. At the sample map it can be seen that these two samples are located in the middle of the transition zone between coastal and estuarine waters. From this follows that pollutants originate mainly in Danube River waters draining in the Black Sea. The general behavior of the values recorded shows a gradient along the marine current. This fact proves once more that the microelements are transported to Black Sea by Danube waters.

The concentrations of some trace metals exceed the corresponding values from 1995 recorded in the eastern part of the Black Sea by a factor of 7 to 15 times, excepting Pb concentration, that exceeds the 1995 value by 2 orders of magnitude, and also Ni and Zn, that present lower values compared with 1995 (Fig. 2).

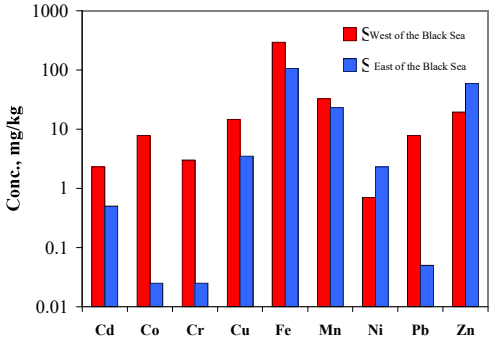

Fig. 2. – Comparison of the metal concentrations in western part of the Black Sea (Romanian coast) with corresponding values in the eastern part

CONCLUSIONS

The heavy metal content in green macroalgae samples from the Romanian Black Sea coast was studied for the first time. These results show that *Sea lettuce* is a reliable bioindicator for heavy metal pollution of the coastal waters. Data reported in this study suggest that a greater amount of pollution comes from Danube Basin. Also the results obtained proved once more that Europe is the dominant source of anthropogenic metals in the Black Sea environment.

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