

ASCOP is a multidisciplinary joint program which incorporates numerous physical, chemical, geological and biological parameters in monitoring of the Adriatic Sea. The aim of the program is to assess physical, chemical, sedimentological and biological characteristics of this marine environment as well the effects of pollution to the Adriatic Sea.

On the Croatian side three marine Institutes participate in the realization of this program, while on the Italian side several Institutes are involved. Sampling and the measurements within the ASCOP program refer until now to the international waters of the North and Middle Adriatic Sea.

Due to the fact that data on various parameters are collected at ASCOP cruises by different participating laboratories it is of primary importance to define how reliable these data are. In order to determine whether the results of the measurement are reliable or not, the performance of the individual laboratories should be evaluated by their participation in the intercalibration. Only analytically sound and reliable data can serve as the basis for comparison of the parameters as well as for drawing out the conclusions on certain processes occurring in the Adriatic Sea. Estimated accuracy and precision of measurement of the participating laboratories should be a fundamental part of the monitoring program and mandatory to the participating laboratories. Quality control of the measurement process should become a general practice for the participating laboratories being involved in the ASCOP.

In 1986 the program of intercalibration in the frame of ASCOP has been defined. It has been foreseen that the intercalibration activities should proceed in several steps with the purpose to identify possible sources of errors and to reduce the degree of non-reliability of the results of the same parameter measured by different laboratories as well within each individual laboratory.

Laboratory intercalibration in the frame of ASCOP, which is the subject of this presentation, proceeds in two steps:

- calibration of the measuring instrument(s) and/or the accuracy of the analyst. Calibration is performed with the standard reference material for which the amount of the measured component is known to the analyst;
- measuring the standard reference material for which the amount of the measured component in the sample is not known to the analyst. Methodology applied corresponds to the one usually applied for the monitoring purposes. Concentration level of the measured component(s) and the composition of the standard reference sample should mimic those of the samples from the marine environment (seawater, biota, sediments), which are collected during monitoring cruises.

Laboratory intercalibration exercise which took place during 1988 and 1989 for certain selected parameters proceeded in steps a) and b).

Calibration of the instrument and the accuracy of the analyst was tested on the parameters chlorofil *a* and nutrient salts with the standard reference material from Environmental Protection Agency (US EPA), Ohio, USA.

The reliability of the applied analytical method according to step b) was evaluated at two concentration levels with the Sagami standard reference material (SRM) for nutrients in seawater. Methodology for the determination of the content of trace heavy metals (Pb, Cu, Zn) in the sediment was evaluated with the SRM from US NIST (previous US NBS).

Achievements and problems appearing during laboratory intercalibration exercise will be discussed. Main problems are the following:

- Each parameter in the frame of the monitoring program should be documented with respect to sampling, sample storage, sample treatment and the analysis, which is applied by the participating laboratories for the realization of the monitoring program. The described protocol should be obeyed during the monitoring program as well as during the intercalibration. All possible changes of the protocol should be documented and verified with respect to the improvement achieved.

- It is further on necessary to elaborate in more extensive manner the SRM, which will be representative of the Mediterranean and additionally of the Adriatic marine environment. Representative SRM are crucial in obtaining reliable information on the consistency of the validated methodology.

- Beforehand, the overall policy of the monitoring program should include a defined attitude toward the laboratories avoiding to participate in the intercalibration activity.

#### REFERENCES

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#### Abstract

Bed-load sediments sampled on the both Danube river sides in front of the Nuclear Power Plant at Koslodui, by chemical and instrumental neutron activation analysis were investigated. The Cr ranged between (74 : 128) ppm, Zn(37 : 78)ppm, Ba (201 : 327) ppm, U (11 : 2.9) ppm.

From a radioecological point of view the study of stable elements in natural systems such rivers and seas is important since radioisotope introduced into the water follow similar pathways to the stable elements already present in nature. It is well known that the chemical composition of the river bed sediments has a great influence on the retention and the exchange of man-made radionuclides between crystalline lattice and the soluble form of the radionuclide in water (GEORGESCU *et al.*, 1973 and 1981).

The sampling was carried out with simultaneously hydraulic measurements on significant verticals according to the methodology applied by the National Institute of Meteorology and Hydrology in Bucharest. Each wet sample of about 1 kg was stored in plastic bags. The chemical analyses were effected as described by GEORGESCU and STROILA (1981). The instrumental neutron activation analyses were carried out at the VVRS nuclear reactor in Bucharest. The counting was made by means of HPGe crystal coupled to a multichannel analyzer.

In the Table 1 are listed contents of ten macroelements, in Table 2 of 24 macro- and microelements. The last column of Table 1 shows that the loss of weight at 1000°C in percent is low for organic matter. It must be outlined, an increasing of Fe, Ca, Ti, Mg, Mn, Na, K. The sediments of left river side have more As, Br, Cr, Th, U and Zn. Barium has a concentration of 327 ppm on the right and 201 ppm, on the left river side. Si and Al are about constant, while phosphorus is decreasing. These changes in the concentration of the microelements are correlated with the grain size diameter of the sediment, the velocity flow on the bed river, the surface and average velocity and turbidity.

It is a decrease of phosphorus and an increase of some toxic microelements in the investigated Danube sediments.

Cross-section and date of prelevation	Element										Loss of weight at 1000°C(%)
	Si	Fe	Al	Ti	Mn	Ca	Mg	P	Na	K	
Upstream Bechet right* 17.06.1991	38.4	2.2	1.5	0.1	0.1	3.2	1.3	0.03	0.8	1.0	2.5
Downstream Bechet right 18.06.1991	32.0	3.6	2.2	0.07	0.07	5.02	1.9	0.04	2.06	1.8	6.6
Turnu Magurele - left 19.06.1991	38.9	3.6	0.6	0.06	0.08	2.3	0.6	0.03	0.7	0.6	3.9

Table 1- Chemical composition of the sediments collected on the bottom of the Danube river, in percent dry weight.

Sample Elem.	River side		Sample Elem.	River side	
	left	right		left	right
As(ppm)	8.9 ± 0.3	6.2 ± 0.2	Lu(ppb)	84 ± 5	34 ± 3
Br(ppm)	3.7 ± 0.5	1.8 ± 0.5	Na(%)	1.38 ± 0.01	1.20 ± 0.01
Ba(ppm)	201 ± 40	327 ± 14	Nd(ppm)	26 ± 6	< 17
Ca(%)	0.40 ± 0.01	0.10 ± 0.01	Rb(ppm)	48 ± 22	27 ± 16
Ce(ppm)	60 ± 2	14 ± 1	Sb(ppm)	1.2 ± 0.1	0.60 ± 0.05
Co(ppm)	9.2 ± 0.8	7.0 ± 0.7	Sc(ppm)	8.2 ± 0.1	2.80 ± 0.06
Cr(ppm)	128 ± 4	74 ± 3	Sm(ppm)	4.9 ± 0.1	1.3 ± 0.1
Cs(ppm)	2.3 ± 0.4	0.6 ± 0.3	Tb(ppm)	0.50 ± 0.2	0.5 ± 0.2
Fe(%)	2.31 ± 0.07	1.10 ± 0.04	Th(ppm)	7.2 ± 0.4	1.5 ± 0.2
Hf(ppm)	6.2 ± 0.3	1.2 ± 0.1	U (ppm)	2.9 ± 0.3	1.1 ± 0.2
K (%)	1.09 ± 0.07	0.90 ± 0.07	W (ppm)	1.2 ± 0.4	0.7 ± 0.3
La(ppm)	26.5 ± 0.3	6.9 ± 0.1	Zn(ppm)	78 ± 19	37 ± 15

Table 2 - Microelements identified in the bed-load sediments of Danube river in front of Bechet site in June 1991 (long-lived radionuclides)

\* right - the right river side; left - the left river side.

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