## PRELIMINARY GEOCHEMICAL DATA FOR SEDIMENT SAMPLES FROM IAEA 1998 "RADEUX" CRUISE IN THE BLACK SEA

Dan SECRIERU and Adriana SECRIERU

National Institute of Marine Geology and Geo-ecology - GEOECOMAR Constanta Branch, 304 Mamaia Bvd., Constanta 8700, Romania Tel/Fax: +40-41- 69.03.66

Abstract. The paper presents some results of geochemical analyses made on sediment samples collected in 12 stations during the 1998 IAEA "Radeux" cruise in the Black Sea. The preliminary data indicate in some places strong heavy metal pollution and/or extremely high Ba concentrations, confirming previous GeoEcoMar researches during the 90<sup>th</sup>-s in the area.

Key words: Black Sea, IAEA, sediments, geochemical data

In the framework of the Technical Co-operation Project "Marine Environmental Assessement in the Black Sea Region" IAEA has organized between 9 and 23 September 1998 the international scientific cruise "Radeux". Several research institutes from Romania, Turkey, Bulgaria and Ukraine have participated at the cruise, GeoEcoMar being represented by a team of two.

Sediment samples for the assessment of anthropic contributions to the total heavy metals content of sediments have been collected from 11 sampling stations situated on the NW Black Sea continental shelf (Fig. 1) and 1 station off-shore Bosphorus (IAEA-18 – 41°29.97' N, 29°20.37' E). In each of these stations one multicorer tube was depth-serial sampled, at standard depths (0-1, 1-2, 2-4, 4-6, 9-11, 14-16, 19-21, 24-26 cm and so far), the local number of samples being a function of sediment penetrability.

As a results 123 sediment samples were collected and stored unfrozen in plastic boxes for subsequent geochemical analyses in GeoEcoMar central laboratory in Constantza including:

- determination of major and minor components exerting main controls on trace element concentrations or of possible help in interpreting trace element analytical data: CaCO<sub>3</sub>, TOC, Fe<sub>2</sub>O<sub>3</sub> (total), TiO<sub>2</sub>, MnO;
- determination of trace element concentrations: Rb, Co, Ni, Ba, Sr, Cu, Pb, Zn, Cd, Cr, V and Zr.

## **ANALYTICAL METHODS**

Prior to analysis all the samples were air-dried, grounded and sieved until the entire passed through a 0.063 mm mesh sieve.

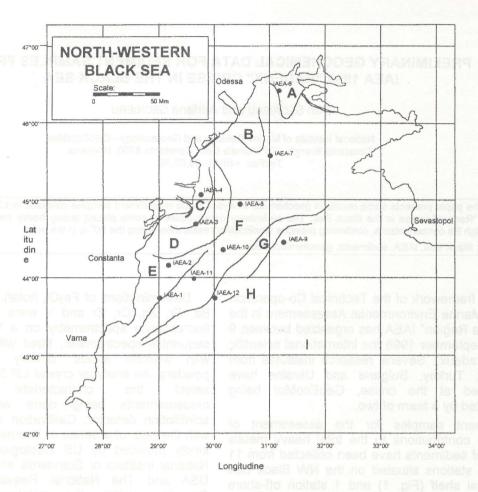
Titration methods were used for analysing CaCO<sub>3</sub> (Black, 1965) and total organic carbon (Gaudette et al., 1974).

Determinations of Fe<sub>2</sub>O<sub>3</sub> (total), TiO<sub>2</sub>, MnO, Ni, Ba, Sr, Zn, Cr, Zr and V were made by X-ray fluorescence spectrometry on a VRA - 30 XRF sequential spectrometer, fitted with a X-ray tube with wolfram anode, directly on compacted powders. An analyser crystal LiF 200 was used to the select characteristic wavelengths, measurements done with a Na(TI)J being scintillation detector. Calibration was carried out with the help of a series of international standards kindly provided by US Geological Survey, The National Institute of Standards and Technology -USA and The National Research Council the Canada. using relationship between concentration and the difference between the number of impulses recorded at the analytical line and the number of impulses at the background

Accuracy of analyses, checked with SDC - 1 standard reference sample, also provided by US Geological Survey, was better than 2% relative error for the major components and better than 5% for all the trace elements excepting Cr and V where the accuracy was approximately 10%. I results are reported on a dry-weight basis. Hygroscopic humidity was determined on a separate sample aliquot by drying in a electrical oven at 105° C until constant weight and the results were used to recalculate the primary analytical data. Major and minor components are reported as percentages; trace elements as µg/g.

## PRELIMINARY RESULTS

The preliminary data stress out the high sedimentary diversity typical for the NW Black Sea shelf, all components being characterized by large variation ranges and coefficients of variation (Table 1). The highest coefficients of variation are recorded for biologically controlled components (CaCO<sub>3</sub>, TOC, Sr), components highly sensible to redox conditions (MnO, V) and heavy metals



- -A Dniepr mouth zone
- -B Dniestr mouth zone
- C Danube Delta Front
- D Danube Prodelta
- E Area under Danube born sediment drift
- F Sediment starving continental shelf
- G Shelf break
- H Fan complexes
- | Abyssal plain

Figure 1. Research Cruise "RADEUX". GeoEcoMar sampling stations geochemical analyses on the NW Black Sea continental

suspected to be affected by anthropic infuences (Ba, Zn).

Table 1. Main statistical parameters for chemical analyses of sediment samples from the NW Black Sea

Component	X <sub>min</sub>	X <sub>max</sub>	X	M <sub>d</sub>	n	Cv
CaCO <sub>3</sub> %	6.55	80.41	35.97	35.85	84	63.73
TOC %	0.30	6.00	2.07	1.85	84	61.59
Fe <sub>2</sub> O <sub>3</sub> %	0.98	6.62	3.68	3.76	84	43.63
TiO2 %	ND	0.81	0.35	0.32	84	78.53
MnO %	0.028	1.604	0.124	0.094	84	82.40
Rb µg/g	20.16	140.26	82.16	76.08	84	41.79
Ni µg/g	ND	166.50	59.80	57.80	84	48.84
Ba µg/g	141.35	1292.58	431.02	334.02	84	52.99
Sr µg/g	200.56	1155.54	574.60	469.18	84	57.49
Zn µg/g	ND	149.73	53.28	36.08	84	90.31
Cr µg/g	18.17	124.06	68.56	63.31	84	42.17
V μg/g	ND	118.24	51.12	49.55	84	67.29
Zr µg/g	97.30	320.01	151.42	130.14	84	32.10

The significance of the notations used in Table 1 are:

- X<sub>min</sub> minimum recorded value for component concentration;
- X<sub>max</sub> maximum recorded value for component concentration;
- X average concentration of component;
  - M<sub>d</sub> median concentration of component;
  - n number of analyses;
  - C<sub>v</sub> coefficient of variation.

Strong manganese enrichments, up to 1.6% MnO, have been registered in stations 10, 11 and 12. All these stations are situated in the sediment starving continental shelf or at the limit continental shelf/shelf break, where the presence of high organic matter contents and numerous shells