ANTHROPIC INCREASES OF TRACE ELEMENT CONCENTRATIONS IN SEDIMENTS FROM THE BLACK SEA ROMANIAN SHELF

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Résumé: L'analyse statistique des données analitiques concernant les sédiments superficiels du plateau continental de la Mer Noire, dans le secteur roumain, a été utilisée pour mettre en évidence les augmentations des concentrations, dûes aux influences anthropogènes, pour une série des éléments en traces. Des augmentations relatives de 35% à 118% ont été ainsi identifiées pour les principales éléments technophiles.

Key words: Trace elements, superficial sediments, Black Sea shelf, statistical analysis, anthropic influences.

Because of an extreme compositional variability, the effects of technogen influences on the trace element concentrations in shelf sediments usually are difficult to trace out. This is especially true for superficial sediments from the Romanian sector of Black Sea internal and central shelf. Under the direct influence of Danube which gradually decreases towards south, with a bottom topography with a multitude of microrelief features interacting with the dynamic oceanographic factors and a very heterogeneous distribution of the benthic fauna, the Romanian internal and central shelf is characterised by frequent abrupt changes in the chemical composition of sediments, both spatial and temporal, superposed on the gradual change from north to south, due to the diminution of Danube influence. These changes determine very large regional variation ranges for the concentrations of chemical components and commonly mask the effects of anthropic influences.

In an attempt to trace out and evaluate the effects of anthropic influences on the chemical composition of superficial sediments the authors used a statistical approach based on the assumption that the sediments have two main fractions: a terrigenous, mainly silicated one and a biogenic carbonated one. The terrigenous fraction is considered as the main source of trace elements (with the notable exception of strontium, strongly associated with the carbonate fraction) while the calcium carbonate acts as a dilutant. If the two fractions are not subjected to significant quantitative and qualitative changes, in spite of local variations due to the relative mixing proportions of the two fractions imposed by local sedimentary conditions, the overall chemical composition of the sediments must not change significantly in time.

The presumption is simplifying because it does not take into account the effect of the third principal component of sediments - the organic matter, which can supply substantial quantities of some trace elements to the sediments. A study of the influence of organic material on the distribution of Co, Ni, Cu and V in deep water sediments of Black Sea (Volkov and Fomina, 1974) showed that about 21.5% of the total amount of V, an element characteristically enriched in organic matter, contained in the sapropelic muds is supplied by organic fractions. However, if we take into account the sapropelic mud content in organic carbon (≈10.5%; Volkov and Fomina, 1974) and the mean organic carbon content of the superficial shelf sediments (≈1.5%; Secrieru, unpublished data), the mean contribution of the organic matter to the total vanadium content of sediments must not exceed approximately 3%. For other trace elements the contribution of the organic matter to the total content of sediment is even smaller. In these conditions, for the purposes of this work, the effect of organic matter on the trace element concentrations can be ignored.

To test this hypothesis sediments from 60 sampling stations were chemically analysed. To achieve a good coverage of the area the stations were distributed on four transects: one approximately parallel with the shore, at water depths between 30 and 50 meters and three perpendicular on the shore at essential points for the Romanian littoral (E - St. George, E - Constanta and E - Mangalia). The sampling was done in 1994 as part of the geoecological

monitoring programme, in progress at the Romanian Centre for Marine Geology and Geoecology since 1990.

At each station a sediment pack was extracted from the sea bottom with a Van Veen type grab. The undisturbed part of the sediment pack was sampled for chemical analyses, from 0 - 1 cm and 10 - 12 cm depth in the pack, thus realising two sample selections (0-1 cm - selection 1 and 10-12 cm - selection 2). A third selection (selection 3), including samples from about 40 cm depth in the sediment pack has been realised in 33 from the previous 60 stations. The number of stations used in realising the selection 3 was limited by the grab penetration depth in the bottom sediments.

After subsequent preliminary treatment (drying, grinding and sieving to a grain-size less than 63μm), the three selections were XRF analysed for Fe_2O_3, TiO_2, MnO, Ni, Ba, Sr, Zn, Cr, Zr and V. Determinations of Co, Cu, Pb and Cd were made by FAAS after wet digestion of the sediment and $CaCO_3$ was volumetrically determined. The analytical data thus obtained were used to calculate the principal statistical parameters (mean and standard deviation) for each selection (Table 1). To avoid unrepresentative results, some obviously anomalous values (the so-called outliers) were neglected in calculating the statistical parameters. This made necessary the indication of the selection volume used in calculations (also Table 1).

Considering the sediments old enough to warrant the lack of, or very slight anthropic influences, the third selection was used as reference. In spite of the limited number of stations where sampling at 40 cm depth was possible, the coverage of the area was good and the selection statistical parameters may be considered as representative for the whole studied zone. $CaCO_3$, Fe_2O_3, TiO_2, MnO and the trace elements Sr and Zr, all of them less likely to be affected by anthropic influences, were used as indicators to appreciate the eventual changes in the sedimentary regimen.

After calculating the principal statistical parameters for all element distributions in each of the three selections, the selection means for most trace elements showed gradual increases toward the interface sediment - water. Some differences were also shown by the selection means of all the other analysed components.

To test the significance of mean changes in time, the selection means of each component were sequentially compared using the t and approximated t statistical tests (Möller, 1979). As a result of the testing the selection means of $CaCO_3$, TiO_2, MnO, Sr, Cr and Zr may be accepted as identical at a significance level $\alpha/2 \geq 0.025$, for all the three tested pairs of selections. Fe_2O_3 and V also showed a high coincidence degree of the means for the pairs of selections 1:3 and 2:3 but for selections 1 and 2 the coincidence of the means has a certain degree of uncertainty. In the case of V, this uncertainty is in perfect agreement with its geochemical behaviour particularities.

In iron case the uncertainty of means coincidence for selection 1 and 2 may be attributed either to iron concentration in the reducing part of the sedimentary column or to the insufficient area coverage of the sampling lattice. The reduced number of sampling stations making up the selection 3 may be responsible for the uncertainty of Ba means coincidence for selection 1 and 3.

In spite of these uncertainties, the recurrent high coincidence degree of the means of $CaCO_3$, Fe_2O_3, TiO_2, MnO, Sr and Zr, used as indicators of the relative mixing proportions of the terrigenous and carbonaceous fractions, suggested a high enough constancy of the sedimentary regimen in time. Consequently, the great disagreement between the mean concentrations of Co, Cu, Pb, Zn and Cd in selections 1 and 3 may be attributed to supplementary inputs, obviously of anthropic origin. The heavy metals Cr and V are unaffected by anthropic influences, although V is enriched in selection 2 (Table 2). Ni, still the subject of a greater enrichment in selection 2 than V leading to uncertainties in the means coincidence, also appears to be free of technogenic influences. The relative enrichments (Table 2) vary from 40% for Pb to 118% for Cu; for Cu, Cd and Zn are in good agreement with the indexes of relative pollution potential of these elements (Förstner and Müller, 1973). However, lead which has the highest index of relative pollution potential (35) is only the fourth in rank as relative enrichment.

The statistical testing of the means for selections 2 - 3 and 1 - 2 has underlined a constant increase of the anthropic copper input. Though the means of Cd, Co, Pb and Zn are higher in selection 1 (especially those of Pb and Cd) their inputs seem to become stabilised in the lapse of time between selections 1 and 2.

A special mention is necessary for barium. The mean Ba concentrations in selections 2 and 3 coincide at a very high significance level ($\alpha/2 > 0.3$). Although the coincidence or discordance of the means for selections 1 and 3 is uncertain (this uncertainty has been already explained), the disagreement between Ba mean concentrations in selections 1 and 2 significant at $\alpha/2 > 0.001$ demonstrate the recent appearance of a substantial supplementary Ba input, probably simultaneous with and because of the off-shore drilling activities. Due to its limited solubility, especially in marine conditions (Förstner and Wittmann, 1983) Ba is not in itself a very dangerous element for the

environment. However, the recent increase of the barium input, because of the natural association of barite with some readily available, highly toxic elements such as Cu, Zn and Cd, represents an alert signal of the drilling activity pollution potential.

Table 1. Statistical parameters

Selection	Parameter	$CaCO_3$ %	Fe_2O_3 %	TiO_2 %	MnO %	Ni ppm	Co ppm	Ba ppm
1	n	63	63	63	61	63	62	60
	Mean	32.47	3.36	0.333	0.0666	54.79	19.11	313.55
	St. dev	15.73	1.23	0.195	0.0263	23.73	6.35	164.4
2	n	63	63	63	63	63	63	63
	Mean	29.95	3.79	0.373	0.0593	63.34	19.02	232.94
	St. dev	12.53	1.19	0.183	0.0213	22.47	6.25	107.45
3	n	33	33	33	33	33	33	33
	Mean	35.47	3.22	0.350	0.059	47.55	14.24	241.52
	St. dev	16.73	1.81	0.270	0.0320	30.66	7.73	124.32

Selection	Parameter	Sr ppm	Cu ppm	Pb ppm	Zn ppm	Cd ppm	Cr ppm	Zr ppm	V ppm
1	n	63	63	63	63	63	63	63	63
	Mean	493.51	38.29	35.40	72.89	0.9335	60.99	144.10	43.28
	St. dev	207.29	19.03	10.24	35.59	0.3140	39.62	30.54	35.77
2	n	63	63	63	63	63	63	63	63
	Mean	447.48	29.34	30.73	67.34	0.8461	65.39	141.16	59.39
	St. dev	179.46	14.07	9.58	31.46	0.2458	35.09	24.91	38.32
3	n	33	33	33	33	33	33	33	33
	Mean	442.76	17.55	25.30	45.48	0.5300	69.52	141.42	46.86
	St. dev	183.89	9.43	13.61	32.70	0.1400	36.52	31.64	39.02

Table 2. Relative enrichments of chemical components

Selection	$CaCO_3$	Fe_2O_3	TiO_2	MnO	Ni	Co	Ba
1:3	-8.5 si	4.3 si	4.9 si	12.9 si	15.2 si	34.2 ss	29.8 su
1:2	8.4 si	-11.3 su	-10.7 si	12.3 si	-13.5 su	0.5 si	34.6 ss
2:3	-15.6 si	17.7 si	6.6 si	0.5 si	33.2 su	33.6 ss	-3.6 si

Selection	Sr	Cu	Pb	Zn	Cd	Cr	Zr	V
1:3	11.5 si	118.2 ss	39.9 ss	60.3 ss	76.1 ss	-12.3 si	1.9 si	-7.6 si
1:2	10.3 si	30.5 ss	15.2 si	8.2 si	10.3 si	-6.7 si	2.1 si	-27.1 su
2:3	1.1 si	67.2 ss	21.5 su	48.1 ss	59.6 ss	-5.9 si	-0.2 si	26.7 si

- ss - statistically significant at $\alpha/2 = 0.025$;
- su - statistically uncertain at $\alpha/2 = 0.025$;
- si - statistically insignificant at $\alpha/2 = 0.025$.

In conclusion the continental internal and central shelf of the Black Sea is characterised by a constant sedimentary regimen in the period represented by the sampled 40 cm sedimentary column. The small variations recorded for indicator elements are the result of the combined action of the reduced volume of selection 3 and errors in ship positioning, sampling and analysis. The higher mean variations recorded in some cases are due to the sensibility of the elements to the physico-chemical environmental parameters leading to post-depositional mobilisation and the consequent

enrichment of the elements in specific zones of the sedimentary column (e.g.: manganese enrichment at the water - sediment interface; iron, V and Ni enrichments in the reducing zone - selection 2).

As a result of anthropic influences Ba, Cd, Co, Cu, Pb and Zn are significantly enriched in the upper layers of sediment. For the superficial layer the relative enrichments of these elements vary from 35% for Ba to 118% for Cu.

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