GEOCHEMICAL DATA FOR SEDIMENT SAMPLES FROM THE INTERNATIONAL CRUISE "BLACK SEA SEDIMENT FLUXES"

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Abstract: Sediment samples, collected in 17 stations situated on Black Sea Bulgarian continental shelf during the international cruise "Black Sea sediment fluxes" were analyzed in GeoEcoMar laboratory. The results evidenced a dominantly terrigenous sedimentation, with significant contribution of coarser grain-size fractions, due to the high energy relief of the Bulgarian coast. The studied area is little affected by anthropic influences, only Cu, Pb and Cd being slightly enriched in sediments.

Key words: Black Sea, Bulgarian continental shelf, sediments, geochemistry.

1. INTRODUCTION

During the first leg of the international cruise "Black Sea sediment fluxes", performed between September, 23 and September, 27, 1998, in the framework of the Pilot Project N2 of the IOC Regional Program, with the Bulgarian hydrographic vessel "Admiral Branimir Ormanov", a GeoEcoMar representative has collected sediment samples for chemical analyses in 17 sampling stations (Table 1).

Table 1 GeoEcoMar sediment sampling stations for geochemical analyses

No	Station	Latitude, N	Longitude, E
1.	PP2-SSS	43°22.339'	28°25.584'
2.	PP2-201	43°19.384'	28°28.062'
3.	PP2-101	43°37.730'	28°40.080'
4.	PP2-102	43°37.457'	28°49.324'
5.	PP2-302	43°09.998'	28°10.423'
6.	PP2-301	43°09.902'	28°00.161'
7.	PP2-303	43°10.150'	28°19.623'
8.	PP2-304	43°09.578'	28°30.078'
9.	PP2-305	43°09.480'	28°39.530'
10.	PP2-402	42°48.200'	28°09.487'
11.	PP2-401	42°49.902'	28°00.426'
12.	PP2-501	42°29.546'	27°49.785'
13.	PP2-502	42°29.670'	27°59.588'
14.	PP2-503	42°29.498'	28°08.605'
15.	PP2-504	42°29.695'	28°19.837'
16.	PP2-902	43°02.540'	28°11.490'
17.	PP2-901	43°04.229'	28°03.189'

In each of these stations, the uppermost layer of sediments extracted with a Van Veen grab has been collected and stored unfrozen until subsequent analyses.

At the central laboratory in Constanza, after being air-dried and grounded until the entire quantity of material passed through a 0.032 mm mesh sieve, the sediment samples have been analysed for seventeen chemical components, including $CaCO_3$, TOC, Fe_2O_3 (total), TiO_2, MnO, Rb, Ni, Co, Ba, Sr, Cu, Pb, Cd, Zn, Cr, V and Zr.

The analyses have been performed using a complex of classical and instrumental methods.

Titration methods were used for analysing $CaCO_3$ (Black, 1965) and total organic carbon (Gaudette *et al.*, 1974).

Co, Cu and Pb were analysed by FAAS, using a slotted tube atom trap for Cu and Pb to enhance analytical sensitivity, and Cd by ETAAS on a Pye Unicam SOLAAR 939E double beam absorption spectrophotometer with deuterium lamp background correction. A wet digestion technique consisting in boiling with concentrated nitric acid (Jickells, Knapp, 1984) was used to solve the trace elements. After drying, the residue was solved in diluted hydrochloric acid and brought to 50 ml. Factory recommended parameters and optimising procedures were used for setting up the analytical system. The system was calibrated with a series of standard solutions prepared from spectral pure metals.

Fe_2O_3 (total), TiO_2, MnO, Rb, Ni, Ba, Sr, Zn, Cr, Zr and V were analysed by X-ray fluorescence spectroscopy on a VRA - 30 XRF sequential spectrometer, fitted with a X-ray tube with wolfram anode, directly on compacted powders. An analyser crystal LiF200 was used to select the characteristic wavelengths, measurements being done with a Na(Tl)J 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 – Canada, using the relationship between concentration and the difference between the number of impulses recorded at the analytical line and the number of impulses at the background line.

In spite of the relatively limited sampling area, the analytical results (Table 2) revealed a medium high sedimentary diversity, the sediments being characterised by large variation ranges of the chemical components, with coefficients of variation usually greater than 25% (Table 3).

The inshore sediments are mostly terrigenous, with $CaCO_3$ concentrations usually less than 15% and, probably as a result of the high energy relief of the

Bulgarian coast, a substantial participation of coarser grain-size fractions, demonstrated by the elevated Zr concentrations (>200 µg/g). The $CaCO_3$ concentrations increase steeply offshore, together with a corresponding decrease of the terrigenous material, reaching a maximum of 46.31% in station PP2/504. Zr, together with TiO_2 (Table 4), concentrates in heavy minerals, so the heavy minerals content of sediments should be significant.

Table 2 Results of geochemical analyses of superficial sediments samples from the International cruise "Black Sea sediment fluxes"

Station	$CaCO_3$ %	TOC %	Fe_2O_3 %	TiO_2 %	MnO %	Rb µg/g	Ni µg/g	Co µg/g	Ba µg/g	Sr µg/g	Cu µg/g	Pb µg/g	Zn µg/g	Cd µg/g	Cr µg/g	V µg/g	Zr µg/g
PP2/SSS	19.52	0.57	3.99	0.62	0.062	93	65	9.56	280	464	19.30	13.35	54	0.158	101	71	233
PP2/201	13.21	1.24	5.43	0.66	0.09	118	98	12.65	240	236	40.83	21.70	96	0.255	130	92	173
PP2/101	9.87	1.81	6.05	0.64	0.109	133	95	14.59	241	207	46.04	30.34	120	0.219	131	118	127
PP2/102	44.8	1.09	2.77	0.21	0.073	58	35	9.38	245	622	32.95	13.81	30	0.134	64	52	121
PP2/302	13.22	0.33	3.19	0.55	0.066	69	32	9.95	156	233	14.13	2.81	31	0.075	83	43	270
PP2/301	13.88	0.51	3.83	0.71	0.063	87	48	9.77	183	246	21.65	5.94	52	0.099	95	110	290
PP2/303	28.05	0.83	3.32	0.4	0.056	74	41	14.53	208	358	34.61	13.54	49	0.157	63	61	177
PP2/304	12.59	0.62	3.01	0.4	0.068	69	25	5.87	121	299	15.14	4.93	30	0.078	80	55	128
PP2/305	32.32	1.77	3.67	0.33	0.124	91	61	10.44	342	581	33.84	21.22	60	0.142	65	60	129
PP2/402	12.51	2	6.51	0.61	0.144	119	79	18.91	292	247	43.62	32.24	110	0.219	108	74	129
PP2/401	11.92	1.07	4.86	0.67	0.097	99	65	12.27	233	220	33.44	18.59	69	0.142	91	108	205
PP2/501	13.12	0.72	4.17	0.74	0.094	93	45	9.66	239	240	26.28	13.93	51	0.076	90	100	288
PP2/502	12.43	1.69	6.27	0.63	0.117	124	94	13.52	263	235	44.10	32.80	109	0.225	111	78	141
PP2/503	14.13	1.4	4.43	0.58	0.071	101	66	10.59	264	277	38.89	26.20	78	0.162	95	83	173
PP2/504	46.31	1.68	3.95	0.23	0.34	70	49	13.29	282	677	30.34	31.85	49	0.158	63	43	119
PP2/902	12	1.49	5.79	0.7	0.088	126	98	22.56	263	221	45.29	30.11	109	0.296	122	108	149
PP2/901	14.83	0.31	3.4	0.6	0.07	78	37	9.08	183	243	16.07	8.39	40	0.085	84	78	269

Table 3 Main statistical parameters

	Mean	Median	S_D	Range	X_{min}	X_{max}	Cv %	Count
Zr µg/g	183.6	173	63	171	119	290	34.32	17
V µg/g	78.5	78	24.31	75	43	118	30.98	17
Cr µg/g	92.7	91	22.45	68	63	131	24.21	17
Cd µg/g	0.1576	0.157	0.0663	0.221	0.075	0.296	42.05	17
Zn µg/g	66.9	54	30.88	90	30	120	46.18	17
Pb µg/g	18.93	18.592	10.323	29.997	2.806	32.803	54.54	17
Cu µg/g	31.56	33.436	11.046	31.917	14.126	46.043	35.00	17
Sr µg/g	329.8	246	155.56	470	207	677	47.17	17
Ba µg/g	237.4	241	54.08	221	121	342	22.79	17
Co µg/g	12.152	10.586	3.988	16.692	5.865	22.557	32.82	17
Ni µg/g	60.8	61	24.65	73	25	98	40.56	17
Rb µg/g	94.2	93	23.13	75	58	133	24.54	17
MnO %	0.1019	0.088	0.0662	0.284	0.056	0.34	64.97	17
TiO_2 %	0.546	0.61	0.1674	0.53	0.21	0.74	30.66	17
Fe_2O_3 %	4.391	3.99	1.2087	3.74	2.77	6.51	27.53	17
TOC %	1.125	1.09	0.5586	1.69	0.31	2	49.64	17
$CaCO_3$ %	19.101	13.22	11.5882	36.44	9.87	46.31	60.67	17

2. REZULTS

The offshore stations PP2/305, PP2/402 and especially PP2/504 are marked by intensive post-depositional mobilisation of manganese, probably associated with manganese nodules formation, materialising in abnormally high MnO concentrations (0.34% MnO in station PP2/504). As a result MnO is characterised by the highest C_v (≈65%).

TOC contents are slightly higher in the southern half of the area (x = 1.37% in the southern sector *versus* x = 0.96% in the northern one) and increase markedly offshore. An analysis of the Fe_2O_3 - TOC relationship (Table 4, Fig. 1) indicate the presence of excess TOC,

comparatively with the Fe_2O_3 contents, in the offshore stations PP2/102, PP2/303-304 and PP2/503-504. The excess could be attributed to the contribution of marine organic matter to the total TOC contents of sediments, in the near-shore stations the organic matter being mainly of terrestrial origin.

As a result of the terrigenous material dominance in the area, the heavy metal concentrations are relatively high. For Co, Ba, Cr and V the C_v are usually less than 32%.

Although Ba has the lowest C_v, due to the well known capacity of manganese hydrated oxides to concentrate Ba, the higher Ba concentrations are associated with the abnormally high manganese contents. However, the highest Ba concentration, recorded in station PP2/305 might be, at least partly, the result of some anthropic contribution due to offshore drilling activities. Some of the higher Co concentrations seem to be related to high manganese and/or TOC concentrations.

In the cases of the technophyllic heavy metals Ni, Cu, Pb, Zn and Cd, the higher C_v might be the result of some anthropic contributions. However, the extremely well defined linear correlations between Ni and Zn concentrations, on the one hand, and Fe_2O_3 or Rb (Table 4), both elements unaffected by anthropic influences and recommended for normalising heavy metal analytical data (Loring and Rantala, 1992), on the other, significant at confidence levels >99.9%, contradict this hypothesis.

On the contrary, for Cu and Pb the hypothesis is confirmed by their high linear correlation coefficients with TOC contens (Table 4). This means that a significant part of the total Cu and Pb is introduced into the sea in solution and scavenged from the water column by aquatic marine organisms.

Cd seems also to be affected by some anthropic contributions. Nevertheless, in all cases the anthropic contributions are probably small; the heavy metal pollution does not seem to be a major environment perturbing factor in the area.

Table 4 Linear correlation coefficients ($r_{17;0.5;95} = 0.482$)

	$CaCO_3$ %	TOC %	Fe_2O_3 %	TiO_2 %	MnO %	Rb µg/g	Ni µg/g	Co µg/g	Ba µg/g	Sr µg/g	Cu µg/g	Pb µg/g	Zn µg/g	Cd µg/g	Cr µg/g	V µg/g	Zr µg/g
$CaCO_3$ %	1																
TOC %	0.163	1															
Fe_2O_3 %	-0.490	0.689	1														
TiO_2 %	-0.882	-0.143	0.562	1													
MnO %	0.516	0.537	0.180	-0.406	1												
Rb µg/g	-0.593	0.602	0.948	0.659	-0.018	1											
Ni µg/g	-0.369	0.680	0.913	0.486	0.103	0.946	1										
Co µg/g	-0.128	0.618	0.726	0.250	0.244	0.646	0.687	1									
Ba µg/g	0.342	0.744	0.437	-0.111	0.429	0.420	0.547	0.438	1								
Sr µg/g	0.950	0.175	-0.479	-0.854	0.506	-0.546	-0.330	-0.215	0.432	1							
Cu µg/g	-0.041	0.863	0.782	0.127	0.208	0.748	0.819	0.746	0.615	-0.112	1						
Pb µg/g	0.059	0.929	0.793	0.042	0.560	0.698	0.780	0.712	0.730	0.057	0.875	1					
Zn µg/g	-0.445	0.737	0.969	0.498	0.111	0.968	0.953	0.745	0.475	-0.436	0.859	0.815	1				
Cd µg/g	-0.129	0.713	0.802	0.221	0.174	0.786	0.910	0.822	0.532	-0.142	0.861	0.802	0.868	1			
Cr µg/g	-0.720	0.286	0.817	0.764	-0.192	0.887	0.829	0.469	0.090	-0.672	0.498	0.422	0.818	0.668	1		
V µg/g	-0.629	0.119	0.577	0.799	-0.275	0.703	0.578	0.334	0.053	-0.644	0.400	0.233	0.593	0.357	0.711	1	
Zr µg/g	-0.380	-0.783	-0.310	0.545	-0.418	-0.219	-0.355	-0.368	-0.425	-0.395	-0.620	-0.650	-0.394	-0.557	-0.015	0.243	1

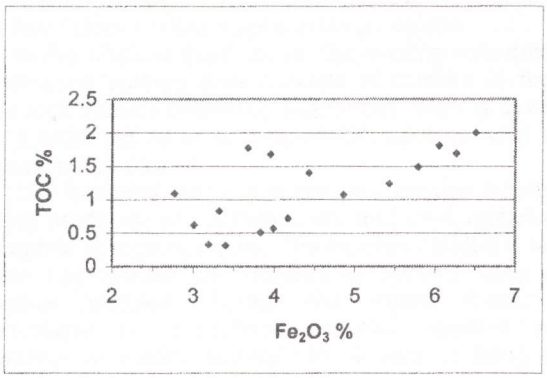

Fig.1 Scatter diagram Fe_2O_3 -TOC

Cd seems also to be affected by some anthropic contributions. Nevertheless, in all cases the anthropic contributions are probably small; the heavy metal pollution does not seem to be a major environment perturbing factor in the area.

3. CONCLUSIONS

The studied area is dominated by terrigenous material sedimentation, with a mean $CaCO_3$ content <20%. Due to the high energy relief of the Bulgarian coast, the coarser grain-size fractions play a significant part in the grain-size composition of the sediments. The area is little affected by anthropic heavy metal contributions of Cu, Pb and Cd. The other heavy metals are apparently not affected.

Acknowledgement: The authors are greatly indebted to the Black Sea Regional Committee of IOC, Varna, for providing the opportunity for one of our colleagues to participate in the cruise. We also thank our colleague, Silviu Rădan, who participated in the cruise and did the sampling for letting us use the samples.

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