METALS IN THE DANUBE RIVER SUSPENDED SEDIMENTS AT THE MOUTH OF THE SF. GHEORGHE DISTRIBUTARY

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Abstract. In order to establish the relationship between heavy metal contents in the Danube suspended sediments and various controlling factors, such as time (season), water temperature, Eh, pH, and others, sampling was performed near the Danube's Sf Gheorghe river mouth over a 9 month-long period. The identified and analyzed metals are Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Cd, Se, Sn, Sb, Pb, Bi, U. Most of the concentrations observed are normal for those usually met in this type of environment. It is interesting to mention that concentrations in suspended sediments of some metals such as Ti, V, Cr is variable and cannot be correlated to water temperature and Eh. Concentrations of most of the heavy metals associated to suspended sediments are strongly and directly correlated to the contents in clay minerals. No correlation between heavy metals and organic matter could be made. The major result of this study shows that organic matter has practically no role in heavy metal transport at the Danube River mouths and that clay minerals are a meaningful carrier instead. Therefore, the total amount of heavy metals delivered by the Danube to the Black Sea is depending on the quantity of clayey suspended sediments, which can be associated to the total discharge of the river.

Keywords: heavy metals, suspended matter, River Danube, Black Sea

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INTRODUCTION

Rivers represent one of the major sediment sources for the marine environment. Huge quantities of sediments and associated substances including nutrients, heavy metals and various other compounds are dispersed at river mouths and reach the coastal zones. Therefore, a great number of studies published worldwide deal with quantifying contents and loads of substances reaching the sea basins (e.g. Meybeck *et al*. 2003, Cave *et al*., 2005, Fox *et al*., 2004 and others). Numerous international research programs have been dedicated to this topic.

The Danube River is no exception. Although the last decades have shown a sharp decrease in sediment loads mainly due to the human intervention along the river basin (Panin, 1996, Popa, 1997, Ungureanu and Stănică, 2000), the Danube still carries the greatest amount of sediments to the sea in comparison with any other river around the Black Sea basin. Each year, about 35 millions tons of sediments (Ungureanu and Stănică, 2000) are discharged to the Danube Delta front. Despite the importance the Danube River has in respect of sediment and associated pollutants and nutrients transport, and although numerous studies were carried out (e.g. Panin *et al*., 1996, Oaie et al., 1997, Radan *et al*., 1997), up to now little is known about the intra-annual temporal variability of the quantity and especially of the quality of the sediments transported by the Danube.

During a long lasting national and international (FP4 EROS Project, financed by the European Commission and others) monitoring program of the Danube River-Danube Delta-Black Sea system carried out by GeoEcoMar, with the participation of the Faculty of Geology and Geophysics, the University of Bucharest, numerous samples of bed-load sediments were taken and many sedimentological data were obtained (technical reports GEOECOMAR). Other research institutes have managed their own sampling and analyzing programs of the Danube River, focused mainly on the Danube water quality. Most studies had yearly or, in best cases, seasonal sampling field campaigns (Radan *et al*., 1997, Oaie *et al*., 1997 and others). Thus, it was not possible to determine high frequency variability of the sediment discharge. Less studies were focused on the suspended matter. Up to now, only Bostan (1996) performed repeated centrifuge sampling in order to separate and analyze suspensions of the Danube River.

This study aims to contribute in closing the knowledge gap by sharing new data obtained during a year-long sampling program of Danube suspensions in Sf. Gheorghe.

METHODOLOGY

Two samples of suspended matter were taken every week (every Monday and Friday) using an Alfa-Laval continuous flux centrifuge in the time period between June 2001 and May 2002 in the Sf. Gheorghe area. No measurements were performed in January 2002 due to the freezing of the Danube. Water and sediment were pumped from a depth of 2 m below water surface at a distance of 10 m from the right riverbank for three hours each time. The sediment was separated on the bowl walls, then it was collected with a decontaminated Teflon spatula and immediately frozen at –4°C. The storage was done in laboratory at –12°C. The centrifuge itself was rinsed with distilled water and the bowl with hexane in order to prepare it for the next sampling. Each sampling recovered around 30 mg of suspended matter.

Additional measurements of physical-chemical parameters (pH, conductivity, dissolved oxygen, water temperature) of the river water were also performed.

In order to make ICP-MS investigations on the suspension samples, they were digested using two methods: partial attack with HNO_3 and total attack with HNO_3 and HF. All samples were treated using the first method and only seven using the latter method. The first method offers a better idea on which metals are available. The total attack dissolves all minerals, obtaining thus a total concentration of the analyzed metals. Available metals are those that can be removed under certain conditions from the sediment particles and are therefore potentially easy to be assimilated by organisms. The non-available metals are part of the mineral lattices.

The partial attack was done using 10 ml HNO_3 2 M for 1 g of sediment. The mixture has been kept for 16 hours at 100°C then centrifuged. The liquid was retained for analyses.

The total attack was done using 50-100 mg of samples and 7.5 ml HNO_3 and 2.5 ml HF for 1 hour in the microwave, adding 5 ml ultra pure HNO_3. At the end of the digestion another 2.5 ml of concentrated HNO_3 was added followed by 2.5 ml distilled water just before the ICP-MS analysis. The identified and analyzed metals are Ti, V, Cr, Ca, Mn, Co, Ni, Cu, Zn, Cd, Se, Sn, Sb, Pb, Bi and U.

Total organic matter was determined by pyrolisis of 50-100 mg of sediment at 550°C for 2 hours after dewatering the samples at 105°C. Several precision weightings were done till constant values were obtained. The method provides reliable results for organic matter content of the sediment.

Grain size of the suspended sediment was obtained using a Coulter® LS100 diffractometer. pH was measured using a field pH-meter.

RESULTS AND INTERPRETATION

Suspended sediment grain size is fairly constant for the entire sampling period. The fraction of 2-16 μm is dominating with about 50% (Fig. 1), followed by the fraction 16-32 μm. There are two samples with higher contents of coarser fraction, above 63 μm (22%).

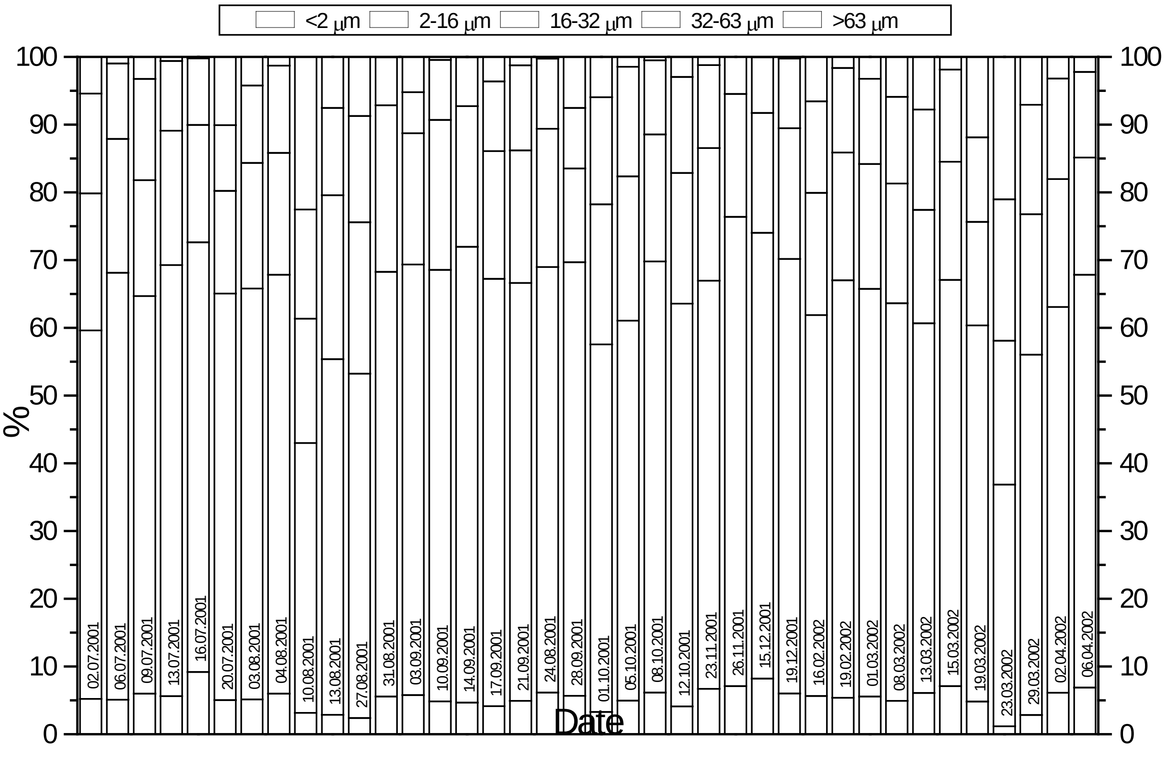

Fig. 1 Grain size of suspended sediments – Sf. Gheorghe

The water pH shows restrained variation within the range 7.59 - 8.52 (Fig. 2). After July, with relative small values, (average 7.7) August shows a sharp increase to values of 7.9-8.3. In September and October, the pH value decreases to about 7.75. Starting with November the pH starts to raise to a maximum reached in February. Spring is characterized by a gentle decrease in the pH value. A correlation between water temperature and pH has been observed. A slight negative correlation is valid for temperatures less than 15°C. At higher temperatures (up to 25°C) the correlation becomes positive. At even higher values, minor changes of temperature induce great variation of the pH.

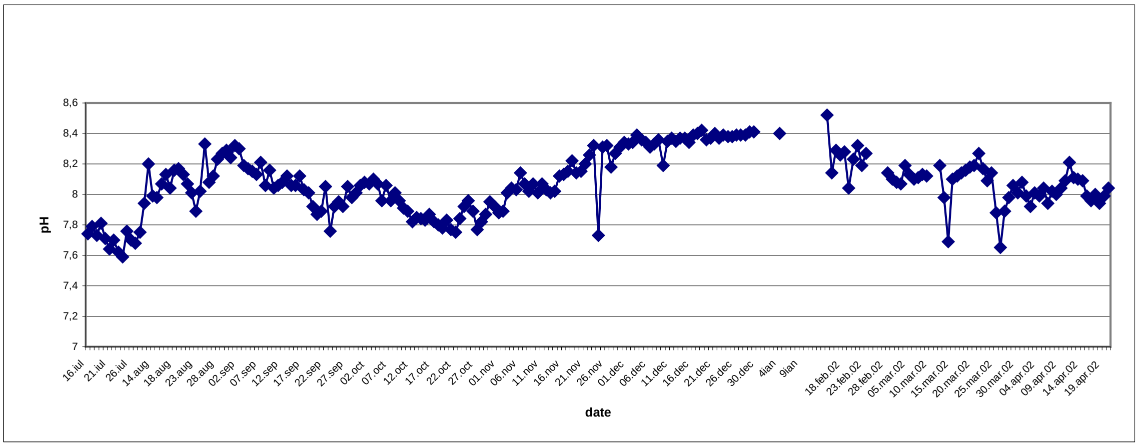

Fig. 2 pH variation of Danube water at Sf. Gheorghe

The organic matter content in suspended matter is highly variable in the whole period time (values 7-26%). Higher variations were noticed in the summer and till the middle of October. Small values are recorded in the cold season till April. Most of the organic matter is associated with the 2-16 μm grain size class (Fig. 3).

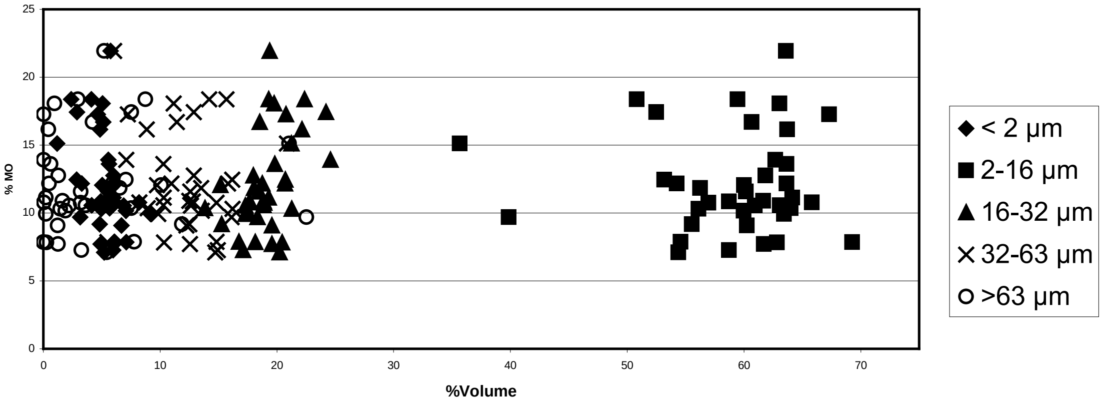

Fig. 3 Variation of organic matter content in respect with grain size

In Table 1 are presented: mean values for concentration in all metals measured, standard deviation and values from Martin and Meybeck (1979) that are typical for this type of setting. It can be observed that only Mn, Mg and Ca exceed the normal mean values. For the latter two elements, the available explanation is connected to the fact that at Mahmudia, upstream Sf. Gheorghe, a dolomite open cast is functioning and all the production is shipped away on barges. Loading the transport vessels creates a lot of fine dust that enriches the suspension with carbonates. For the Mn the explanation is not as quite forward, knowing the great affinity of this element for fine suspensions and colloids (Horowitz *et al*., 1989, Forstner and Whitmann, 1981).

We consider Al concentration as a proxy for the clay mineral content of the suspended sediment. High amplitudes (Fig. 4) characterize variation of Al and organic matter concentrations. Moreover, Al variation is very similar with the ones present for most metals (e.g. Cu, Zn, As, Be, V; Figs. 7 and 8). Values of metal concentration are shown in Figs. 5-8. They all present the same seasonal variability. In autumn the amplitude of metal concentration is not very high if compared with summer and winter seasons. This corresponds with the variation of sediment discharge in the same period of time. All these suggest that there is a close correlation between the content of clay minerals and metal concentrations in suspended sediments.

Correlation coefficients computed between metals on one hand and Al and organic matter on the other hand are shown in Table 2. The analyzed metals may be grouped in 4 main categories. Correlation plots between examples of each group and organic matter and Al are shown in Figures 9-12. One can notice that no metal has a good correlation with the content of organic matter, suggesting that the latter plays no role in their transport.

Concentrations of most heavy metals associated to suspended sediments are strongly and directly correlated to the contents in clay minerals. However, some analyzed metals do not show this behavior: Ti, Mn, Sn, Cs, Sb (Figs. 11 and 12). The probable reason for first three of them is their participation to the suspended matter with their own minerals. An argument is the presence of 4 “hieratic” points in the upper part of the correlation plot of Ti and Al in Figure 11, corresponding probably to samples with higher contents of Ti minerals.

Table 1 Mean concentrations of metals in suspended sediments of the Danube. Comparison with values from literature

	Average Martin & Maybeck, 1979	**mean**	**sd (yEr±)**	**se (yEr±)**
27 Al	94000	27873.954	7121.542	1186.924
9 Be		1.082	0.286	0.040
25 Mg	11800	12727.163	3174.035	440.159
43 Ca	21500	49402.162	12403.790	1720.096
47 Ti	5600	173.793	158.212	21.940
51 V	170	48.501	14.746	2.045
53 Cr	100	65.074	18.518	2.568
55 Mn	1050	2222.033	571.345	79.231
59 Co	20	16.768	4.261	0.591
60 Ni	90	71.309	20.302	2.815
63 Cu	100	86.737	33.573	4.656
66 Zn	350	161.714	52.266	7.248
75 As	5	13.186	3.293	0.457
82 Se		1.682	0.451	0.063
118 Sn		0.240	0.294	0.041
121 Sb	2.5	0.058	0.104	0.014
133 Cs	6	1.856	1.414	0.196
202 Hg		0.534	0.268	0.037
206-7-8 Pb	150	45.462	14.807	2.053
209 Bi		0.376	0.104	0.014
238 U	3	0.832	0.211	0.029
111-4 Cd		1.713	0.552	0.077

The strongest correlation to clay minerals contents is shown by Be, Mg, V, CR, Cu, Zn, As, Bi and U, all of them with correlation coefficients over 0.8 (Fig. 9). Computed correlation coefficients for Co, Se, Cd and Pb are in the range 0.7-0.8. It is worth mentioning that high contents of Zn were recorded in waters with suspensions of various clay minerals: illite (up to 3,200 ppm), caolinite (up to 3,300 ppm) and montmorillonite (up to 2%). This behavior leads to the idea that metals are associated with very fine clay particles, which have a greater retention capacity.

We notice also the strong correlation of Al with other elements such as Ca and Mg. These elements are important constituents of clay minerals. Hence, there is a very good correlation also between the latter two elements and other metals (e.g. Pb/Mg – 0.84, U/Mg – 0.966, Ni/Ca – 0.823, Bi/Ca – 0.805).

Another aspect is the good correlation between contents in Mn and elements such as Pb, Bi, U, Zn, Cd and others (e.g. Mn/Zn – 0.754, Mn/As – 0.909, Bi/Mn – 0.758). We consider that the main cause is the great affinity of these elements for Mn colloids present in water.

Elements with similar geochemical behavior show high correlation of measured contents. The best examples are Ni and Co (correlation coefficient of 0.912) and Zn and Cr (correlation coefficient of 0.936).

The lack of correlation with Al of other elements such as Sb is due to the medium ionic potential of these elements and to their higher hydrolize capacity. As a consequence, they are present in water with no correlation to suspension contents.

1. CONCLUSIONS

The first major finding is that the suspended Danube sediments at the river mouths are not heavily polluted with metals. Our high frequency sampling strategy helps to exclude a hypothesis of a “lucky” moment of sample collection. The recorded metal contents of Danube River suspensions are well within normal ranges for this setting. There are only three elements that show are somehow dissonant with this conclusion (Ca, Mg and Mn), but their high contents are easily explained.

Al is a very good proxy to estimate the role played by clay minerals in metal transport by riverine suspended sediments. Therefore, periods of time with high clay suspension quantities are also intervals of high transport of metals to the Black Sea. Seasons with high variability from the point of view of solid discharge correspond to period of times with high metal content variability.

The organic matter plays no role in the retention and transport of metals in the studied setting. This conclusion might seem odd, since organic matter is usually seen as a major player in these processes. We consider that the organic matter from the Danube River suspensions is not mature enough to play an important part in the metal transfer to the Black Sea in front of the Danube Delta.

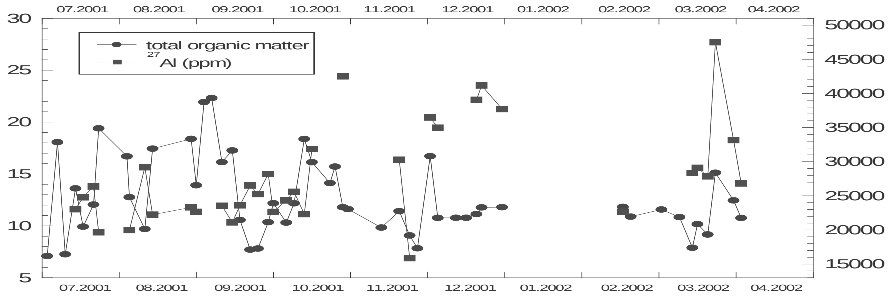

Fig. 4 Variation of ^{27}Al and total organic matter

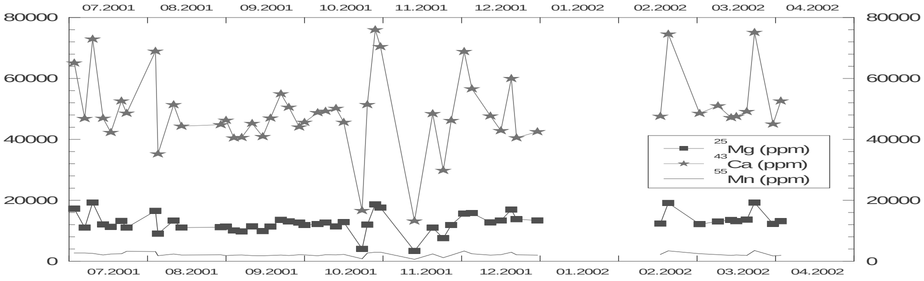

Fig. 5 Variation of ^{25}Mg, ^{43}Ca and ^{55}Mn

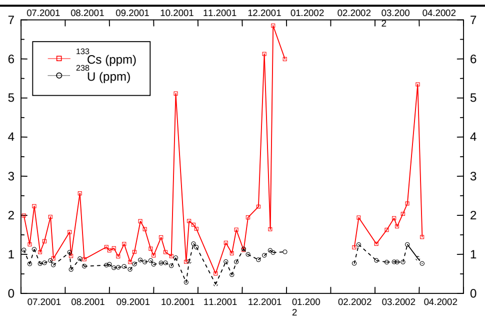

Fig. 6 Variation of ^{133}Cs and ^{238}U

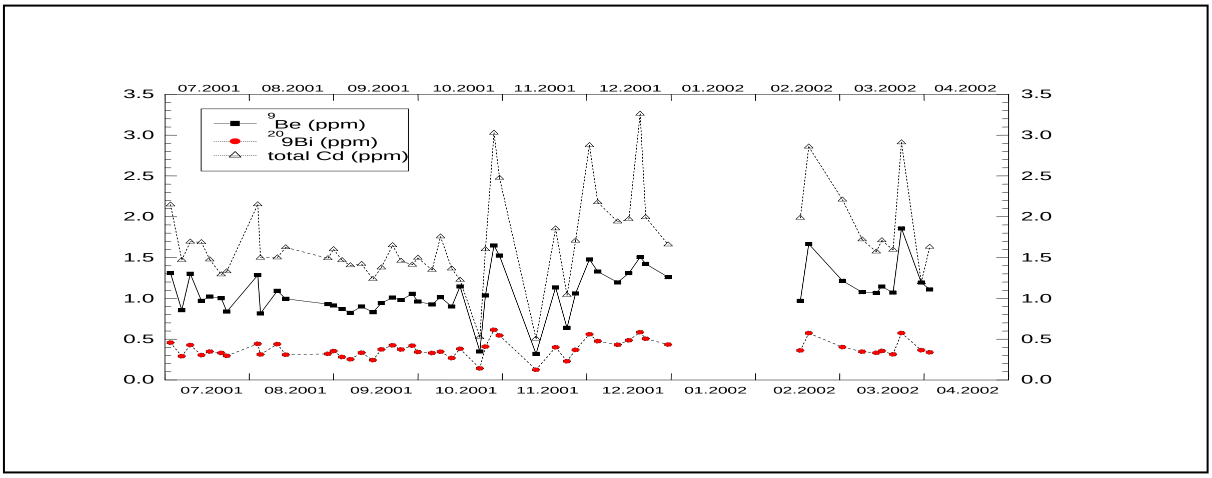

Fig. 7 Variation of ^{9}Be, ^{209}Bi and total Cd

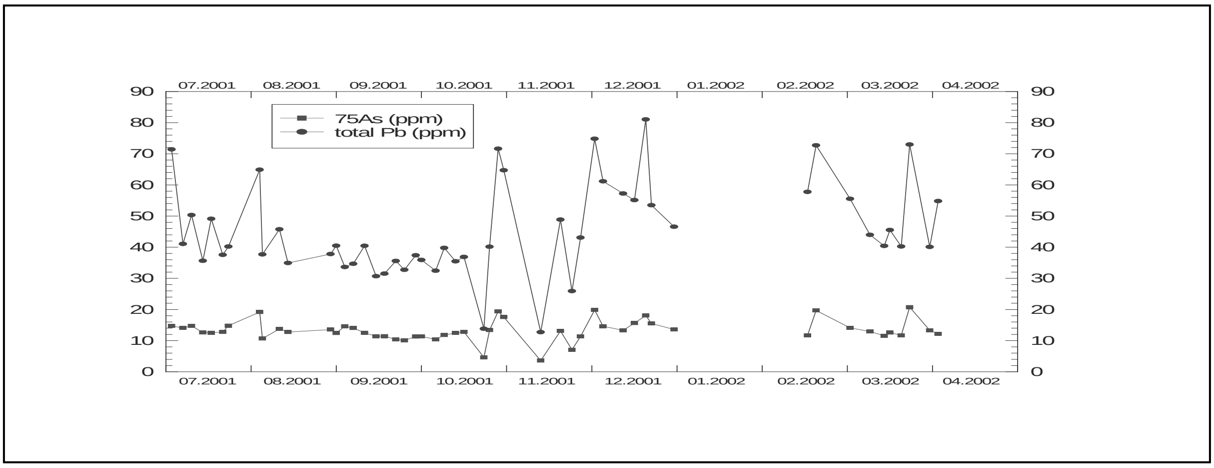

Fig. 8 Variation of ^{75}As and total Pb

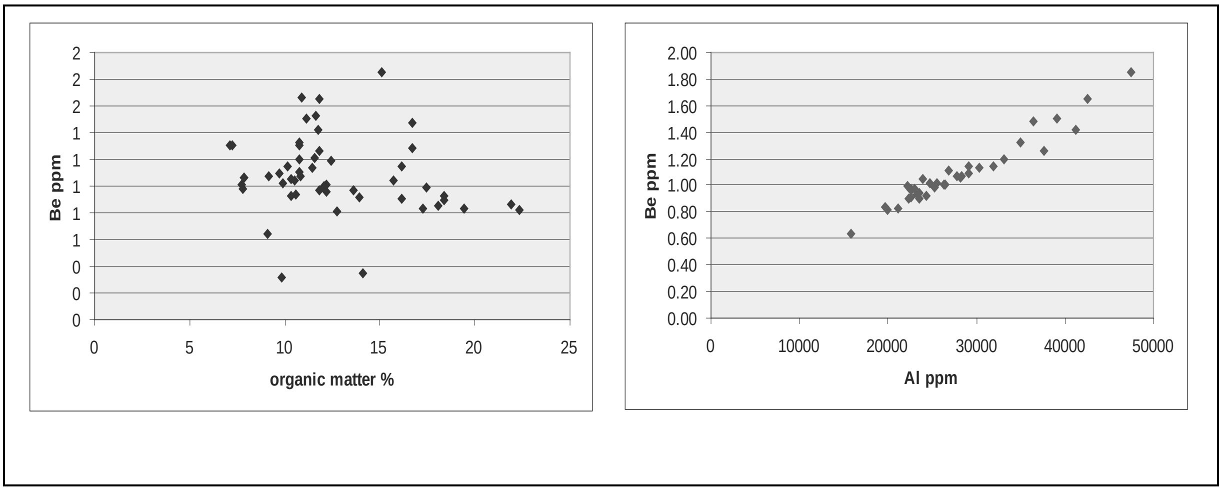

Fig. 9 Correlation plots ^{9}Be/organic matter and ^{9}Be/Al

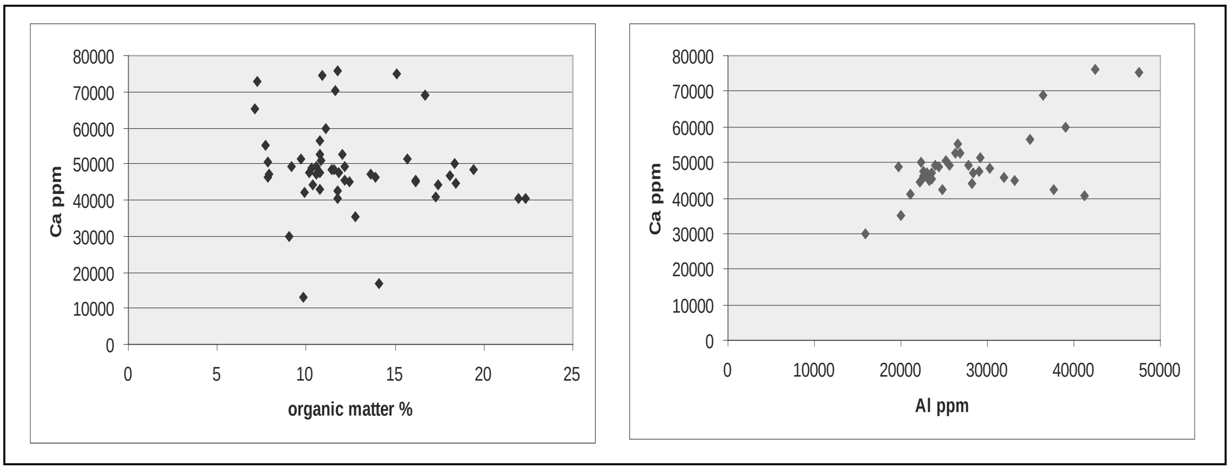

Fig. 10 Correlation plots ^{43}Ca/organic matter and ^{43}Ca/Al

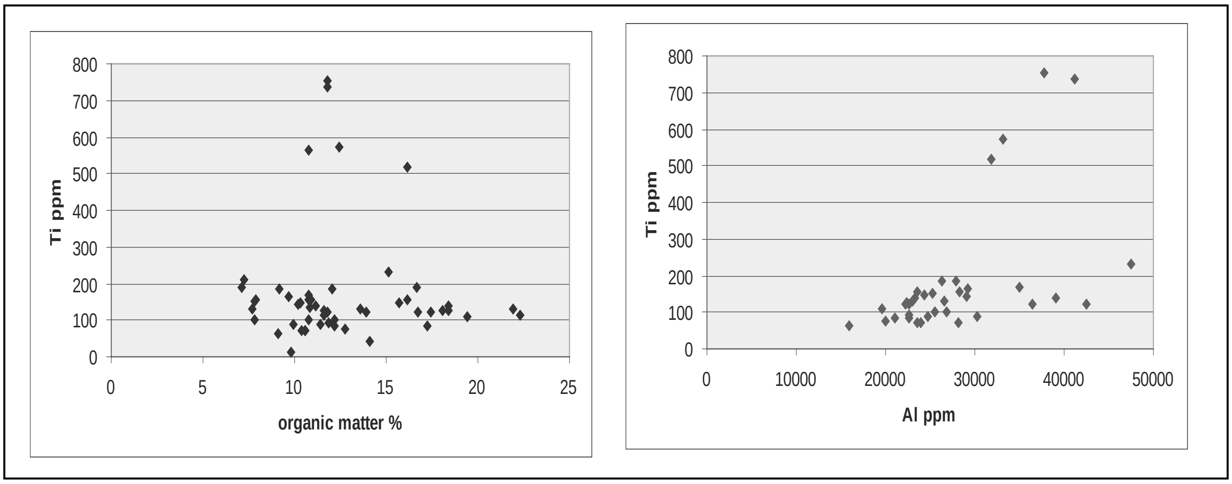

Fig. 11 Correlation plots ^{47}Ti/organic matter and ^{47}Ti/Al

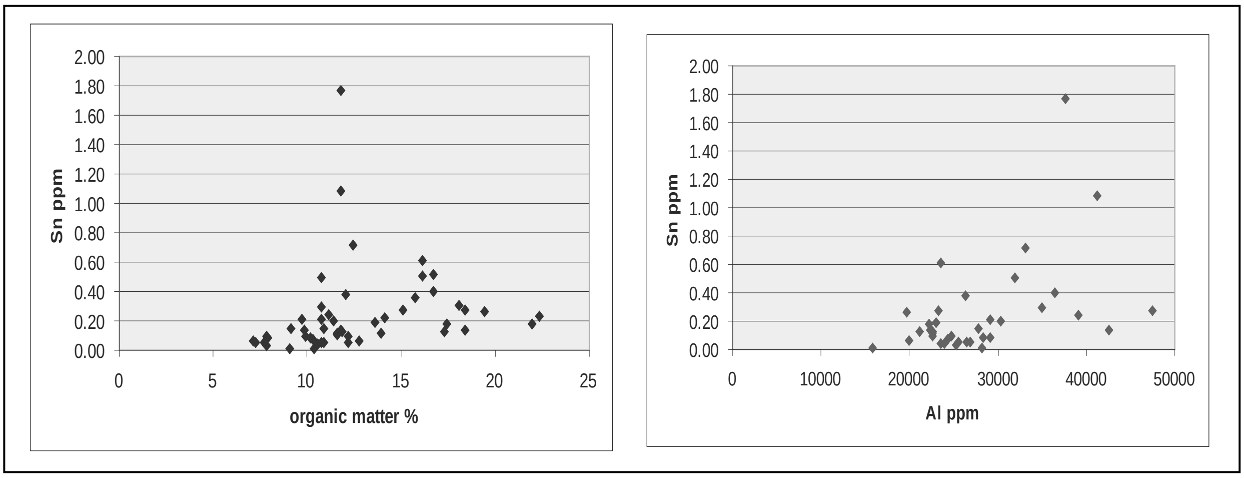

Fig. 12 Correlation plots ^{118}Sn/organic matter and ^{118}Sn/Al

ACKNOWLEDGEMENTS

The works presented in this paper were made possible by the Romanian National Universitary Research Council Grant no. 336. The authors wish to thank their colleagues from the National Institute for Marine Geology and Geoecology (*GeoEcoMar*) in Bucharest for their precious technical assistance both with know how and equipments. Many thanks also to all the 15 students who performed a month of field work each in the project.

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Table 2 Correlation coefficients between contents of metals, total organic carbon and Al – Danube River suspended sediments at Sf. Gheorghe

Be	**Mg**	**Ca**	**Ti**	**V**	**Cr**	**Mn**	**Co**	**Ni**	**Cu**	**Zn**	**As**	**Se**	**Sn**	**Sb**	**Cs**	**Hg**	**Pb**	**Bi**	**U**	**Cd**	
-0.177	-0.237	-0.100	-0.027	-0.173	-0.173	0.171	-0.160	-0.164	-0.129	-0.174	0.233	0.025	0.196	-0.002	-0.161	-0.044	-0.136	-0.236	-0.183	-0.087	**TOC**
0.971	**0.874**	0.674	0.524	**0.949**	**0.961**	0.596	**0.795**	0.689	**0.800**	**0.819**	**0.806**	0.733	0.471	0.447	0.573	0.695	**0.770**	**0.896**	**0.959**	**0.750**	**Al**
	0.925	**0.848**	0.368	**0.909**	**0.981**	**0.781**	**0.917**	**0.858**	**0.833**	**0.910**	**0.878**	**0.878**	0.219	0.265	0.411	0.696	**0.895**	**0.944**	**0.966**	**0.892**	**Be**
		0.947	0.234	**0.802**	**0.905**	**0.798**	**0.952**	**0.850**	0.734	**0.801**	**0.828**	**0.855**	0.075	0.094	0.269	0.588	**0.840**	**0.877**	**0.959**	**0.822**	**Mg**
			0.017	0.650	**0.827**	**0.801**	**0.951**	**0.823**	0.692	0.746	**0.837**	**0.890**	-0.070	-0.109	0.039	0.534	**0.806**	**0.805**	**0.889**	**0.806**	**Ca**
				0.705	0.369	0.052	0.079	0.103	0.166	0.188	0.254	0.117	**0.839**	**0.967**	**0.973**	0.324	0.163	0.318	0.396	0.080	**Ti**
					0.908	0.612	0.741	0.705	0.701	**0.767**	**0.767**	0.714	0.513	0.614	0.740	0.674	0.745	**0.871**	**0.910**	0.700	**V**
						0.783	**0.920**	**0.871**	**0.868**	**0.936**	**0.879**	**0.875**	0.252	0.271	0.418	0.741	**0.913**	**0.969**	**0.967**	**0.910**	**Cr**
							0.860	**0.810**	**0.670**	**0.754**	**0.909**	**0.866**	0.060	-0.042	0.053	0.557	**0.807**	**0.758**	**0.813**	**0.789**	**Mn**
								0.912	**0.786**	**0.860**	**0.866**	**0.914**	-0.020	-0.032	0.125	0.627	**0.871**	**0.917**	**0.940**	**0.884**	**Co**
									0.753	**0.874**	**0.815**	**0.845**	0.018	0.013	0.155	0.613	**0.846**	**0.855**	**0.867**	**0.825**	**Ni**
										0.868	**0.828**	**0.834**	0.193	0.102	0.202	**0.806**	**0.868**	**0.831**	**0.786**	**0.875**	**Cu**
											0.824	**0.817**	0.147	0.121	0.238	**0.757**	**0.928**	**0.905**	**0.858**	**0.935**	**Zn**
												0.745	0.227	0.159	0.246	0.656	**0.859**	**0.827**	**0.876**	**0.858**	**As**
													0.074	0.045	0.126	0.649	**0.855**	**0.852**	**0.883**	**0.880**	**Se**
														0.833	0.745	0.322	0.115	0.204	0.260	0.043	**Sn**
															0.939	0.265	0.087	0.229	0.281	0.002	**Sb**
																0.337	0.205	0.383	0.427	0.111	**Cs**
																	0.728	0.712	0.696	0.693	**Hg**
																		0.881	**0.867**	**0.937**	**Pb**
																			0.943	**0.896**	**Bi**
																				0.847	**U**