

Geochemical and Statistical Approach for Assessing Heavy Metal Accumulation in the Southern Black Sea Sediments

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Abstract

The assessment of heavy metal pollution in the sediment of the Southern Black Sea requires knowledge of pre-anthropogenic metal concentrations. The effects of anthropogenic activities on the accumulation of heavy metals, elements, and other compounds in the sediment were examined. The objective of this study is to investigate the levels of metals, organic carbon, carbonate, and chlorophyll degradation products in order to assess the extent of environmental pollution and to discuss the origin of these contaminants in the sediments of the Southern Black Sea. The heavy metals, metalloid, and elements were assessed by factor analysis. The results of the factor analysis have shown positive and/or negative correlations among Mo, Cu, Pb, Zn, Ni, Co, Mn, Fe, As, Sr, Cd, Sb, Bi, V, Ca, P, Cr, Mg, Ba, Ti, Zr, Sn, S, Y, Hg, organic carbon, carbonate, and chlorophyll degradation products and has indicated that heavy metals in the sediments of the Southern Black Sea have different anthropogenic and natural sources. Also, a sediment pollution assessment was carried out using the enrichment factor and geoaccumulation index. The Igeo accumulation index shows that the surface sediment of the Southern Black Sea is not contaminated with respect to Cu, Pb, Zn, Mn, Fe, As, Sr, Bi, V, Cr, Mg, Zr, Y, Sb, Sn, and Ni, but is moderately contaminated with respect to Hg and Cd, and moderately to strongly polluted with respect to S and Mo. Despite total sedimentary concentrations above their pre-industrial background levels, Igeo shows that the surface sediments are unpolluted with respect to P, Ba, and Ti. The ¹⁴C age determinations have shown that surface sediments in stations KD2A and KD5A belong to AD 130-350 and AD 1000 respectively, indicating undersea landslides and turbidity fluxes in the Southern Black Sea are not rare because of the sharp slope in the topography of this region and high bottom transportation in certain places. The requirement of age determination is of great importance to assess the extent of the anthropogenic contribution to pollution.

Keywords: Enrichment factor, factor analysis, geoaccumulation index, metal pollution, sediment.

Güney Karadeniz Sedimentlerinde Ağır Metal Birikiminin Jeokimyasal ve İstatistiksel Yönden Değerlendirilmesi

Özet

Güney Karadeniz sedimentlerinde ağır metal kirliliğinin değerlendirilmesinde endüstriyel öncesi ağır metal konsantrasyon değerlerinin bilinmesi önemlidir. Ağır metaller, elementler ve bileşiklerin sedimentte birikimi üzerine antropojenik faaliyetlerin etkileri araştırılmıştır. Çalışmanın amacı, çevre kirliliğinin derecesini değerlendirmek için metal seviyeleri, klorofil bozunma ürünleri, karbonat ve organik karbon seviyelerini araştırmak ve Güney Karadeniz sedimentlerinde bu kirlleticilerin orjinini tartışmaktır. Ağır metal, metaloid ve elementlerin sonuçları faktör analiz ile değerlendirilmiştir. Faktör analizi sonuçları Mo, Cu, Pb, Zn, Ni, Co, Mn, Fe, As, Sr, Cd, Sb, Bi, V, Ca, P, Cr, Mg, Ba, Ti, Zr, Sn, S, Y, Hg, organik karbon, karbonat, ve klorofil bozunma ürünleri arasında pozitif ve/veya negatif korelasyonlar olup, bu metallerin farklı antropojenik ve doğal kaynaklara sahip olduğunu göstermiştir. Ayrıca sediment kirliliği değerlendirilmesinde zenginleşme faktörü ve jeoakümülayon indeksi de kullanılmıştır. Jeoakümülayon indeksine göre, Güney Karadeniz'in yüzey sedimentleri Cu, Pb, Zn, Mn, Fe, As, Sr, Bi, V, Cr, Mg, Zr, Y, Sb, Sn and Ni açısından kirlenmemiş-kısmen kirlenmiş; Hg ve Cd açısından kısmen kirlenmiş ve S ve Mo açısından ise kuvvetlice kirlenmiştir. Sedimentteki toplam birikim konsantrasyonları endüstriyel öncesi background endüstriyel öncesi background (geçmiş) seviyelerinin üzerinde olmasına rağmen, jeoakümülayon indeksi yüzey sedimentlerinin P, Ba ve Ti açısından kirlenmediğini göstermektedir. Karbon 14 ile yapılan yaş tayininde KD2A ve KD5A istasyonlarında sırasıyla MS 1350-350 ve MS 1000 yılına ait olduğunu göstermiştir. Bu durum bu istasyonların belirli yerlerinde keskin eğim ve dip taşınımından dolayı Güney Karadeniz'de denizaltı heyalanlarının ve türbidite akışlarının ender olmadığını bize göstermektedir. Dolayısıyla denizeo ortamlarda kirliliğe antropojenik katkının derecesini net bir şekilde ortaya koymak için yaş tayini gereksinimi büyük öneme sahiptir.

Anahtar Kelimeler: Faktör analizi, jeoakümülayon indeksi, metal kirliliği, sediment, zenginleşme faktörü.

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INTRODUCTION

Sediments are an important repository for various pollutants such as pesticides and heavy metals and also play a significant role as sensitive indicators for monitoring contaminants in aquatic systems. Sediments which provide habitats for many aquatic organisms were polluted with various kinds of hazardous and toxic substances, including heavy metals. So, they are considered to be an important carrier as well as a sink of heavy metals in the hydrological cycle (Bat and Raffaelli 1998, Bakan and Buyukgungor 2000) and reflect the current quality of the system as well as provide information on the impact of pollution sources (Kruopiene 2007). Waste materials including organic and inorganic chemicals, terrestrial runoff, disposal of liquid effluents, and leachate carrying chemicals originating from numerous urban, industrial, and agricultural activities eventually accumulate in sediments. Anthropogenic and natural pollutants cause the accumulation of heavy metals in marine sediments. So, the majority of heavy metal emissions from anthropogenic sources accumulate in river and ocean sediments (Bat 2005, Bakan and Buyukgungor 2000).

All heavy metals exert toxic effects at some concentration, including mining, smelting, electroplating, and other industrial processes that have metal residues in their wastes and by non-point source surface runoff (Bakan and Ozkoc 2007). Some specific local sources such as discharge from smelters (Cu, Pb, Ni), metal based industries (Zn, Cr, Cd from electroplating), paint and dry formulators (Cd, Cr, Cu, Pb, Zn, Hg and Se), and petroleum refineries (As, Pb) may lead to metal accumulation in sediments (Bonnevie et al. 1994, Al-Masri et al. 2002, Harikumar et al. 2009, Yıldız and Yener 2010).

The pollution of the aquatic environment with heavy metals because of urbanization and industrial development has become a major problem during recent years. Metals may be present in the estuarine system as dissolved species, as free ions, or by forming organic complexes with humic and fulvic acids (Ustun 2011). Additionally, many metals associate readily with particulates and become adsorbed or co-precipitated with carbonates and oxyhydroxides, sulphides, and clay minerals (Spencer and MacLeod 2002).

Consequently, metals in sediments occur in

Table 1. Average concentrations of heavy metals in sediments of the Southern Black Sea.

station	metals (ppm)													
	Mo	Cu	Pb	Zn	Ni	Co	Mn	Fe	As	Sr	Cd	Sb	Hg	
west	KD01	2,76	72,46	37,76	97,9	56,9	12,9	416	33800	9,3	544	0,53	1,31	0,13
	KD2A	0,97	45,48	23,96	94,1	57,6	19,8	763	40100	12	230	0,23	0,87	0,05
	KD2B	11,8	59,97	38,82	183,9	93,3	21	654	45900	13,7	282	0,49	1,91	0,09
	KD2C	7,14	49,02	26,68	99	88,4	19,2	672	42500	12,5	258	0,25	1,15	0,07
	KD03	1,16	39,8	20,29	82,8	60	16,4	463	34800	9,4	309	0,18	0,95	0,03
east	KD04	0,82	57,83	30,59	105	140,6	23	567	43800	9	277	0,26	1,31	0,07
	KD5A	1,48	71,83	32,7	94,1	49,6	19,7	383	43900	8,4	192	0,24	1,38	0,05
	KD5B	16,1	59,61	23,98	83,9	120,5	24,7	755	46800	11,6	340	0,26	1,21	0,06
	KD5C	27,8	66,4	18,13	89,3	140	28,9	707	46100	18,4	373	0,45	1,52	0,05
	KD06	3,76	69,38	44,33	124,2	49,5	24,4	735	50100	10,2	237	0,27	1,2	0,04
station	Bi	V	Ca	P	Cr	Mg	Ba	Ti	Zr	Sn	S	Y		
west	KD01	0,38	88	1E+05	570	91	11000	309	3280	53,2	4	1800	20,7	
	KD2A	0,44	118	48400	690	89	14400	326	4260	84	2,6	900	19	
	KD2B	0,47	123	62900	640	117	18500	311	4020	69,3	3,3	12200	18,1	
	KD2C	0,36	115	61700	600	108	20400	303	3820	69,4	2,7	11100	16,9	
	KD03	0,28	111	72500	620	73	13600	317	3540	89,6	2,3	2300	18,9	
east	KD04	0,39	143	64500	760	147	22200	312	4250	84,5	2,5	900	18,9	
	KD5A	0,32	165	26900	660	54	17000	260	3810	107	1,9	1200	12,4	
	KD5B	0,26	146	62500	630	105	23000	273	3620	86,3	1,5	16800	15	
	KD5C	0,3	135	76700	610	129	24100	279	4200	80,4	1,8	18600	17	
	KD06	0,4	154	31100	710	68	21100	299	3870	80,9	2,6	8000	16,6	

different geochemical forms, which have distinct mobility, biological toxicity, and chemical behaviors. In the past years, tremendous efforts have been made to characterize to fate, loading and distribution of heavy metals in rivers, estuaries, and marine systems (Perin et al. 1997, Quyang et al. 2002, Bakan and Ozkoc 2007). Heavy metals are generally transported to the sea by rivers or by industrial discharge (Alp et al. 2011). Their concentrations are generally directly correlated to the organic matter content, so that problems are exacerbated in coastal sediments where heavy metals are known to accumulate especially near population centers, river outflows, and industrial outfalls (Danovaro 2003, Altas and Buyukgungor 2007).

Research shows, that there are many studies on the sedimentology and geochemistry of the sediments in the Black Sea (Murray et al. 1989, Bakan and Buyukgungor 2000, Secrieru et al. 2006, Altas and Buyukgungor 2007, Bakan and Ozkoc 2007, Bat et al. 2009, Boran and Altinok 2010). All of them have analyzed one or two details and have commented about those detailed results. Also, an evaluation with a geochemical approach using the deviations of organic carbon normalized the heavy metal values in the Southern Black Sea. The geochemical approach is an effective strategy for distinguishing anthropogenic from naturally occurring metal concentrations, particularly when it is used with the traditional quantitative statistical evaluations.

The aims of this study was (a) to evaluate the extent of heavy metal contamination and the degree to which heavy metals are influenced by other

Table 2. Pearson product moment correlations between each pair of variables normalized by Al p values below 0.005 indicate statistically significant non-zero correlations at the 95% confidence level (bold correlation coefficient).

	Mo	Cu	Pb	Zn	Ni	Co	Mn	Fe	As	Sr	Cd	Sb	Bi	V	Ca	P	Cr	Mg	Ba	Ti	Al	Zr	Sn	S	Y	Hg	CDP	CO ₃ ⁻²	Corg	
Mo		0,73	-0,06	0,17	0,6	0,73	0,31	0,48	0,68	0,52	0,87	0,64	0,17	0,68	0,44	0,53	0,16	0,39	-0,06	-0,11	0,1	0,03	-0,15	0,85	0,38	-0,01	0,07	-0,036	-0,08	
Cu			0,37	0,34	0,32	0,52	0,14	0,34	0,43	0,56	0,82	0,67	0,37	0,66	0,52	0,53	-0,01	0,11	0,18	-0,11	-0,09	-0,02	0,19	0,5	0,49	0,06	0,06	0,021	-0,03	
Pb				0,66	-0,51	-0,14	-0,24	-0,21	-0,07	0,29	0,17	0,32	0,77	-0,19	0,3	0,16	-0,38	-0,54	0,52	-0,15	-0,26	-0,51	0,73	-0,09	0,38	0,1	0	-0,047	-0,08	
Zn					-0,14	0,09	0,02	0,11	0,19	0,2	0,4	0,55	0,76	0,01	0,19	0,28	-0,06	-0,23	0,19	0,13	-0,27	-0,3	0,46	0,14	0,46	0,32	0	-0,096	-0,04	
Ni						0,6	0,4	0,45	0,44	0,23	0,47	0,34	-0,22	0,51	0,22	0,26	0,81	0,76	-0,3	0,14	0,07	0,12	-0,34	0,47	0,13	0,05	0,07	0,035	0,12	
Co							0,51	0,66	0,79	0,65	0,69	0,55	0,12	0,5	0,57	0,63	0,24	0,48	-0,05	-0,02	0,04	0,13	-0,24	0,6	0,44	0,04	0,21	0,065	0,06	
Mn								0,63	0,46	0,32	0,27	0,27	-0,06	0,08	0,28	0,35	0,29	0,64	0,01	0,24	0	-0,12	-0,24	0,6	0,25	0,08	0,16	0,038	0,17	
Fe									0,38	0,22	0,41	0,26	-0,14	0,54	0,1	0,32	0,13	0,68	-0,38	0,04	-0,03	0,19	-0,49	0,59	0,03	0,25	0,23	0,143	0,17	
As										0,69	0,69	0,68	0,27	0,23	0,67	0,67	0,18	0,26	0,22	0,16	0,11	0,02	0,05	0,66	0,63	0,04	0,1	-0,045	-0,02	
Sr											0,67	0,47	0,33	0,09	0,98	0,81	0,04	0,05	0,59	-0,2	-0	-0,23	0,33	0,5	0,73	-0,03	0,08	0,033	-0,03	
Cd												0,73	0,36	0,64	0,59	0,76	0,1	0,23	0,1	-0,01	0,04	0,02	0,06	0,68	0,62	0,03	0,06	-0,056	-0,07	
Sb													0,56	0,35	0,46	0,51	0,16	0,11	0,17	0,23	-0,04	-0,13	0,29	0,53	0,6	0,08	0,02	-0,158	-0,09	
Bi														-0,12	0,36	0,31	-0,1	-0,41	0,42	0,12	-0,17	-0,43	0,69	0,09	0,63	0,04	0,03	-0,099	-0,07	
V															-0,01	0,31	0,05	0,4	-0,43	-0,07	0,12	0,48	-0,46	0,4	-0,02	-0	0,08	0,07	0	
Ca																0,73	0,11	0,01	0,69	-0,17	-0,01	-0,31	0,45	0,41	0,77	-0,04	0,07	0,013	-0,02	
P																	0,03	0,16	0,31	0,1	0,06	0,11	0,09	0,47	0,67	-0,06	0,04	-0,015	-0,05	
Cr																		0,58	-0,15	0,32	-0,06	-0,14	-0,04	0,09	0,12	0,11	0,05	0,02	0,2	
Mg																			-0,41	0,15	0,01	0,05	-0,54	0,49	-0,11	0,11	0,2	0,161	0,27	
Ba																				-0,05	-0	-0,49	0,77	-0,06	0,59	-0,04	0,01	-0,001	-0,06	
Ti																						0,15	0,21	0,02	-0,15	0,23	0,03	-0,12	-0,183	-0,05
Al																							0,25	-0,14	0,02	-0,01	-0,68	-0,45	-0,605	-0,64
Zr																								-0,59	-0,13	-0,25	-0,12	-0,11	-0,02	-0,09
Sn																									-0,22	0,54	0,06	-0,05	-0,092	-0,07
S																									0,26	0,03	0,15	0,021	0,03	
Y																										0,04	0,02	-0,095	-0,04	
Hg																											0,38	0,544	0,59	
CDP																												0,644	0,84	
CO ₃ ⁻²																													0,79	
Corg																														

sedimentological parameters such as organic carbon, chlorophyll degradation products (CDP), and carbonate, (b) to provide information for the background levels of metals in the Black Sea sediments, (c) to identify different causes of enrichment by applying multivariate statistics on the studied elements, including correlation and factor analysis, and (d) compare the present results with similar studies undertaken elsewhere.

MATERIAL AND METHOD

Study Area

The Black Sea, which is a large semi-enclosed sea, is located between the latitudes of 40° 55' and 46° 42' and a longitude of 27° 27' and 41° 42'. It has historically been one of the most biologically and ecologically productive marine ecosystem in the world (Ivanov and Beverton 1985, Mee 1992, Bat et al. 2009). The Black Sea is surrounded by six countries from Europe and Asia: Bulgaria, Georgia, Romania, Russia, Turkey, and the Ukraine (Altas and Buyukgungor 2007). To the South, it is connected to the Mediterranean through the Bosphorus Strait, which is the world's narrowest strait, with an average width of 1.6 km, a depth of 36 m, and a total length of 31 km (Bakan and Buyukgungor 2000). To the North, The Black Sea is

connected with the Sea of Azov through the shallow Kerch Strait, which has a depth of less than 20m.

The most important property of the Black Sea is the permanent anoxic deepwater due to hydrogen sulfide which makes it the world's largest anoxic water mass. This H₂S provides the main condition for the accumulation of abyssal sediments rich in organic matter. The abyssal sediments of the Black Sea lack benthic fauna and consist of just plankton remains because of the H₂S contamination (Emelyanov et al. 2005).

Below the layer of oxygenated surface water, hydrogen sulfide is connected with the Exchange of the Mediterranean and Black Sea waters as a result of a very high fresh water runoff from the surrounding lands (Emelyanov et al. 2005). The hydrographic regime forms the low-salinity surface water of river origin and overlying high-salinity deep water of Mediterranean origin entering through the Bosphorus Strait. A steep pycnocline centered at about 50 m is the primary physical barrier to mixing and is the origin of the stability of the anoxic interface (Murray et al. 1989, Bakan and Buyukgungor 2000). Besides the major European rivers (Danube, Dniiper, and Don rivers) and Turkish rivers (Kızılırmak, Yeşilirmak, and Sakarya

ivers) discharge into the Black Sea and form the main source of pollution. Undamaged fishing, unrestricted shipping, mineral exploitation, dumping of toxic wastes, discharge of domestic wastes from the coastal cities, and pollutants carried by rivers mainly pollute the Black Sea (Tuncer et al. 1998, Altas and Buyukgungor 2007). On the other hand, the rivers provide an intensive supply of nutrients to the upper layer. There are a lot of large and little industries (food, fertilizer, cement, pesticide, textile, plastic, and cigarette manufacturing) in the vicinity of the Black Sea region of Turkey. Most of these factories have no treatment plants and have the potential to create local pollution (Altas and Buyukgungor 2007).

Especially from the hazelnut facilities, flour manufacturing, and fish-oil factories located in the eastern part of the Black Sea and then from the iron and steel factories located in the western part of the Black Sea, billions of tones of heavy metals and other pollutants are dumped into the Black Sea. Metal levels in the Black Sea have been augmented with the addition of oil pollution and airborne contaminants (Ozseker and Eruz 2011). Pollution from the land and coastal areas is carried to the sea through rivers and coastal erosion.

Analytical Procedure

In this study, 10 stations were selected to determine heavy metal concentrations in the sediments (Figure 1). Six stations were located in the periphery from the Bosphorus to Trabzon and four stations were located from the periphery to the west and east basin centers in the Black Sea. The surface sediments were sampled at 9 locations during the R/V Sürat-Araştırma-1 cruise in April 2008 (KD06), in May 2008 (KD03, KD04, KD5A, KD5B, KD5C), and the TCG-Çeşme cruise in September 2008 (KD01, KD2A, KD2B, KD2C).

Sediment samples were taken using the gravity corer and preserved in the vessels laboratory at 1-2°C before analysis. After transportation using cold chain, all of the cores were sliced at 2 cm intervals with the sediment extruding device. A part of the sediment slices were placed in acid cleaned polyethylene bottles and frozen at -20°C in a deep freeze until analyses for metals and chlorophyll degradation products. The other part of the sediment slices were dried in an oven at 50-60°C, homogenized and reduced to a fine powder for determination of organic carbon, carbonate, and

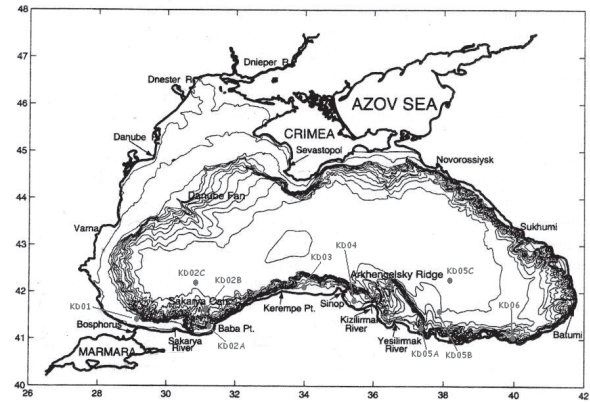


Fig. 1. Location map of the Black Sea and sampling stations (Modified from Besiktepe et al. 2001)

dating (^{14}C). Before the organic carbon analysis, homogenized sediments were moistened with distilled water and exposed to concentrated HCl flumes for 48 hour to remove carbonates.

The heavy metal analysis (except for Hg) in all subsamples was performed using the 4 acid digestion and ultra trace ICP-MS method by the ACME Analytical Laboratories Ltd. (Vancouver, Canada). Two stages of preparation, consisting of drying and screening, were performed on the sediment samples. Samples were dried at 60°C and were then 85% pulverized and passed through a 200 mesh sieve. Two 0.25 g subsamples were taken for digestion and were heated in $\text{HNO}_3\text{-HClO}_4\text{-HF}$ to dryness. The residues were then dissolved in HCl and the solutions were analyzed using the ICP-MS method. The ultra trace aqua-regia digestion method for Hg analysis was also used by Acme Labs. Subsamples of 0.5g were leached in hot (95°C) aqua-regia and the average values of the samples were used.

The amount of organic matter was measured by the Walkey Black Methods (Gaudette et al. 1974) which is based on the remaining dichromate with back titration ferrous ammonium sulfate using phenylamine as an indicator. The total carbonate content was determined by the gasometric method. This method is based on the measurements of the partial pressure of CO_2 released by acidification with 10% HCl (Martin 1972). Chlorophyll degradation products (CDP) were analyzed through acetone extraction and a spectrophotometer (Lorenzen 1971). Radio carbon dating of the bulk sedimentary organic carbon samples from selected depths, of the all cores, was performed using the

Standard AMS method with ^{13}C corrections by the Beta Analytic Inc. laboratory (Miami FL., USA).

Statistical Analysis

The data set has been subjected to correlation and factor analysis for elucidating the relationships between the heavy metals and geochemical characteristics such as Al, organic carbon (C_{org}), chlorophyll degradation products (CDP), and carbonate (CO_3^{2-}).

RESULTS AND DISCUSSION

Heavy metal levels in the sediment were determined for the east and west basin of the Southern Black Sea. The metal concentrations were measured at 10 stations, their average values are presented in Table 1. Generally, the highest amounts of heavy metals were found in the east basin of the Black Sea. The Cd, Bi, Y, and Hg metal concentrations have almost the same concentrations in both the eastern and western basins.

Organic Carbon and Carbonate

The total organic carbon in the sediments of the Southern Black Sea ranges from 11.77% - 0.22% in the east, to 8.99% - 0.36% in the west. The relatively high percentage of organic matter (11.77%) was recorded at station KD5C at a depth of 0-1 cm. Once the metals are released into the environment, they are transferred to the sediments through adsorption onto the suspended matter and subsequently the sedimentation (Hart 1982 and Seshan et al. 2010). The adsorption and sedimentation processes of metals mainly depend on the composition including grain size, carbonate content, level of organic matter, Fe-Mn oxyhydroxides etc. (Jonathan et al. 2003, Seshan et al. 2010). The relatively high content of organic matter in sediments of the Southern Black Sea is mainly related to anthropogenic and geological inputs such as weathering and runoff from the rivers and land-based sources. The co-precipitation with carbonate minerals is of importance for a number of metals such as cadmium and zinc (Forstner and Wittmann 1983, Alloway 1990, Ghrefat and Yusuf 2006). The carbonate content of the sediments of the Southern Black Sea ranges between 32.21% and 2.81%, with an average of 12.24%. The relatively high percentage of carbonate content (17.23%) was recorded at station KD5C at a depth of 10-11 cm.

As is known, heavy metals and organic carbon are attached to fine grain sediments at a clay-silt size. The effects of clay fraction are eliminated by

keeping the ingress of Al (clay minerals) into the marine environment. Therefore, to be better able to evaluate heavy metal levels, stemming from activities, in natural waters is achieved by dividing each metal concentration to Al.

The correlations of Al-normalized metals and other variables (CDP, CO_3^{2-} , C_{org} and P) are given in Table 2. Also, the correlations of C_{org} -normalized variables given in Table 3 are strikingly higher. It is remarkable that molybdenum (Mo) has only a correlation with CDP. Therefore, it was determined that the variable, which brings about a variation in the data to a large extent, is organic carbon (C_{org}). Metals and CDP, which is a component of autochthonous organic matter, not having a statically significant correlation proves the accuracy of the normalization operation. The linear correlations of variables, normalized by organic carbon with Al, their confidence limits, and estimation limits of 95% are given in Figure 2. Values outside of the estimation limits refer to anthropogenic contributions, except for diagenesis.

Surface sediment from in front of the city of Ordu (KD5A) seems to be enriched by anthropogenic contribution in terms of Cu, Pb, Cd, and Zn. However, sediment sample on the surface date to 1099 years before the present day or AD 851. The maximum Cu values date from 4000-5000 years before the present. Cd and Zn found at 40 cm are under the estimation limit at the same station; this explains the dilution effect with carbonate. As a matter of fact, the carbonate level in that layer is up to 22%. Anthropogenic contributions are evident at station KD01 for Hg at 2 cm (AD 1602), Hg and Pb at 4 cm (AD 1211), and 9 cm (AD 299). While it was expected that, organic carbon normalized metals, give an average fixed value with organic carbon, it is seen that it changes with organic carbon inversely (Figure 3). High Me_{org} (organic carbon -normalized metal) levels and low organic carbon are at the periphery while high organic carbon and low Me_{org} levels at the center of the basin are characteristic. This situation can be explained by the increasing contribution of autochthonous organic matter (Guo and Santschi 1997a-b) from the periphery towards the center of the basins via the sinking of Fe and the Al-enriched phase. Trace metals, bound to colloids participating dissolved fractions, explains the decrease of Me_{org} in the sediment. This is known as "colloidal pumping", (Honeyman and Santschi

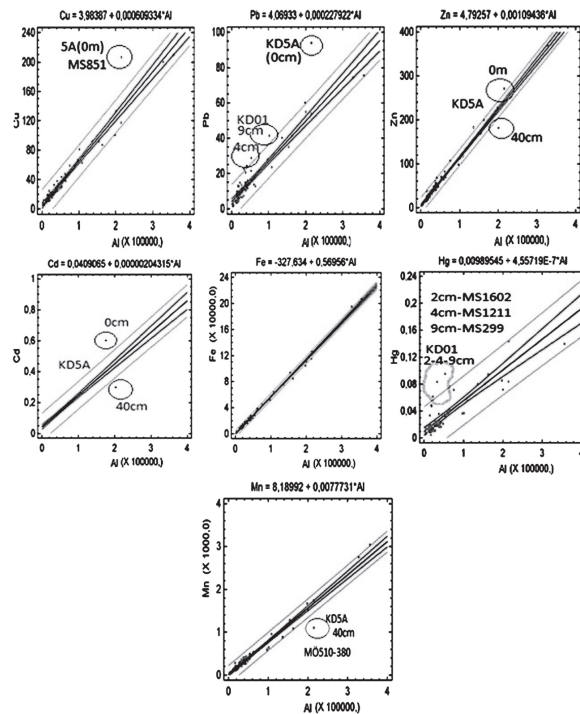


Fig. 2. The relationships of organic carbon-normalized metal values against Aluminum (red curves is the 95% confidence levels of population, orange curves is the prediction limits).

1989, Wen et al. 1997b). Another explanation of the decrease in Me_{org} concentrations is “the particle concentration effect”. The decrease of the partition coefficient between particle and dissolved phase of a metal with increasing concentrations of suspended solids (SS) at water column is denominated as “the particle concentration effect” (O’Connor and Connolly 1980, Honeyman and Santschi 1989, Santschi et al. 1997, Wen et al. 1997b). The correlations between Me_{org} and organic carbon of having an inverse relation with the change in metal-carrying phases are a result of sediment resuspension as seen in Galveston Bay in 1995 as reported by Wen et al. (2008) exhibits a similarity to the state of the Black Sea. It was stated that fresh NOM (natural organic matter), which is the source of organic carbon, changed from allochthonous to autochthonous at a specified date, could considerably affect the metal content of the suspended particles of Galveston Bay. It can be said that the phytoplankton export productivity in the Black Sea and the bacterial productivity joined in the redox processes in the suboxic zone and not only Mn (II) from the shallow coastal sediments around the suboxic zone (Kempe et al. 1992) but also

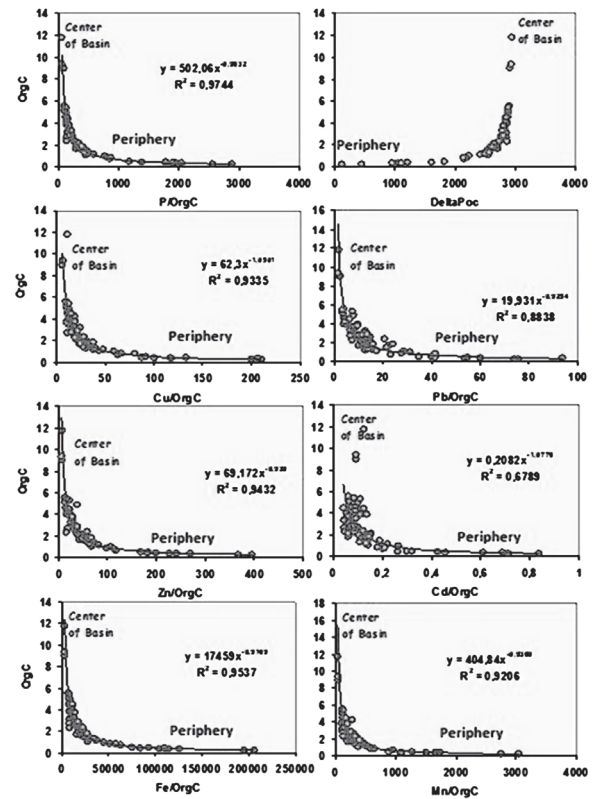


Fig. 3. The relationships between C_{org} -normalized elements and C_{org} .

sediments to a considerable degree in these steep sloped zones were resuspended. It is also known that villagers in the vicinity of Sinop collect from the beach charcoal fragments in great sizes which come from sea at certain periods. It should be taken into consideration that there can be a considerable degree of resuspension along the Inebolu-Sinop-Samsun line and turbidity currents could occur to a considerable extent via tectonic movements as in front of Ereğli and Ordu. It was reported that the estuary of the Kızılırmak withdrew 1 kilometer in 10 years related to the effect of the blocking of sedimentary material coming to sea by the Altinkaya and Derbent dams, coastal currents, and waves on the coasts (Yılmaz 2005). In Figure 3, a strong and inverse relationship obtained by metals between P_{org} and OC was attained as well. This curve with an inverse relationship approaches asymptotically the maximum P_{org} concentration (3000) in sediment. The difference is found when all the P_{org} values are subtracted from this maximum value which should be the remaining (non-precipitating) ΔP_{org} in the water column. ΔP_{org} values assumed very low at the periphery explain that productivity is strongly

Table 3. Pearson product moment correlations between each pair of variables normalized by organic carbon p values below 0.005 indicate statistically significant non-zero correlations at the 95% confidence level (bold numbers).

	Mo	Cu	Pb	Zn	Ni	Co	Mn	Fe	As	Sr	Cd	Sb	Bi	V	Ca	P	Cr	Ba	Ti	Al	Zr	Sn	S	Y	Hg	CO ₃ ⁻²	CDP
Mo		0,036	-0	0,016	0,048	0,053	0,056	0,044	0,057	0,05	0,096	0,038	0,001	0,04	0,006	0,037	0,024	0,009	0,019	0,037	0,033	-0,04	0,504	0,006	-0,03	0,068	0,446
Cu			0,971	0,972	0,846	0,951	0,924	0,974	0,922	0,914	0,947	0,97	0,96	0,98	0,85	0,965	0,857	0,945	0,958	0,971	0,982	0,911	0,603	0,93	0,895	0,842	0,084
Pb				0,949	0,753	0,893	0,874	0,932	0,898	0,886	0,925	0,96	0,96	0,93	0,82	0,947	0,777	0,943	0,929	0,937	0,957	0,924	0,569	0,906	0,893	0,766	0,057
Zn					0,898	0,977	0,969	0,991	0,976	0,942	0,968	0,97	0,99	0,98	0,92	0,988	0,918	0,984	0,994	0,993	0,988	0,959	0,628	0,984	0,897	0,9	0,111
Ni						0,959	0,952	0,924	0,897	0,881	0,861	0,83	0,86	0,91	0,91	0,878	0,996	0,855	0,914	0,911	0,856	0,821	0,575	0,904	0,805	0,959	0,2
Co							0,991	0,992	0,966	0,948	0,938	0,93	0,95	0,98	0,93	0,972	0,966	0,952	0,984	0,987	0,963	0,905	0,651	0,97	0,866	0,943	0,143
Mn								0,983	0,975	0,959	0,923	0,92	0,95	0,96	0,95	0,973	0,963	0,959	0,982	0,983	0,952	0,906	0,688	0,979	0,841	0,949	0,154
Fe									0,971	0,953	0,95	0,95	0,97	0,99	0,92	0,987	0,936	0,971	0,991	0,998	0,986	0,926	0,665	0,977	0,88	0,92	0,122
As										0,951	0,932	0,94	0,97	0,95	0,93	0,981	0,92	0,982	0,985	0,978	0,966	0,944	0,672	0,986	0,844	0,904	0,133
Sr											0,896	0,9	0,93	0,93	0,97	0,963	0,897	0,964	0,951	0,961	0,936	0,913	0,685	0,964	0,857	0,911	0,132
Cd												0,96	0,96	0,94	0,88	0,951	0,881	0,945	0,963	0,951	0,951	0,933	0,56	0,947	0,868	0,86	0,165
Sb													0,98	0,96	0,86	0,97	0,856	0,962	0,968	0,962	0,973	0,947	0,565	0,945	0,881	0,822	0,108
Bi														0,97	0,91	0,983	0,89	0,987	0,986	0,981	0,981	0,974	0,604	0,979	0,9	0,872	0,106
V															0,9	0,981	0,919	0,959	0,982	0,993	0,988	0,913	0,641	0,961	0,877	0,903	0,112
Ca																0,925	0,933	0,94	0,934	0,931	0,888	0,914	0,612	0,957	0,849	0,934	0,143
P																	0,898	0,99	0,991	0,993	0,99	0,941	0,662	0,984	0,865	0,892	0,108
Cr																		0,883	0,934	0,926	0,874	0,858	0,573	0,927	0,827	0,961	0,183
Ba																			0,985	0,982	0,978	0,97	0,651	0,989	0,879	0,88	0,085
Ti																				0,994	0,983	0,953	0,63	0,991	0,878	0,913	0,108
Al																					0,99	0,937	0,67	0,985	0,878	0,916	0,111
Zr																						0,933	0,65	0,968	0,866	0,867	0,075
Sn																							0,548	0,957	0,918	0,833	0,074
S																								0,652	0,5	0,636	0,26
Y																									0,869	0,92	0,108
Hg																										0,785	0,109
CO ₃ ⁻²																											0,179
CDP																											

limited in the water column by phosphorus and the ΔP_{org} values (remaining in the water column) approach the value 3000 while the C_{org} in the sediment (indicating the productivity) reach the maximum. ΔP_{org} values carry a proxy characteristic in the water column for organic productivity.

Factor Analysis

The geochemical data consist of the measurements of the 29 variables in the 70 sediment samples. The factor analysis was used to obtain simple patterns from this data set. It was actually performed on two groups with the correlation matrix between different parameters followed by the Varimax rotation. These are a normal data and C_{org} -normalized data set. The rotated loading, Eigen values, and percentage of variance of all six factors are given Table 4.

A set of normal data applied to the factor analysis results shows that 6 accesses with Eigen values greater than 1 were extracted in the analysis (Figure 4). The first six factors account for 85% of the total variance in the data set (Table 4). The first three of them explain with high communalities of the elements.

Factor 1 accounts for 30.8% of the total variance and contains very high positive factor loadings in Fe, V, Ti, Al, and Zr with statistically significant loadings

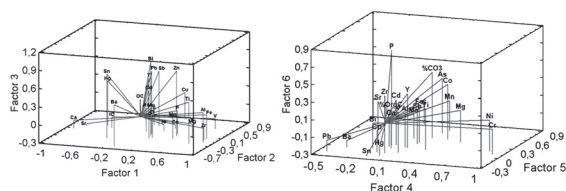
in Zn, Mn, P, and Mg with negatively correlated Sr, Ca, CO_3^{2-} , Hg, and Sn. This factor is considered as "aluminosilicates, carbonate, and iron oxyhydroxides": The most common constituent of siliciclastic carbonate (biogenic and detritus) marine sediments. Also, Fe and Mn association may be due to their common occurrence in basic rocks, since the concentration of these elements were lower than the background values ($I_{geo} = 0$).

Factor 2 accounts for 22.8% of the total variance and shows very high loadings in Mo, Cu, Cd, and C_{org} but also shows significant loadings in Co, Sb, V, Ba, S, and Hg. This factor is clearly considered as "the organic carbon carrier phase and anoxia": the enrichment of these metals which are most commonly associated with high total organic carbon in marine sediments (Aksu et al. 1998, Yasar et al. 2001). The Cd and Cu may be associated with the Na and Mg rich rocks found in the area.

Factor 3 accounts for 14.6% of the total variance and shows high factor loadings in Pb, Zn, Sb, Bi, Sn, Y, and Hg. This factor is considered as "the pseudo anthropogenic factor": mixed origins or retention phenomena of industrial and vehicular emissions or/and terrigenous influx from the upstream areas in runoff. As already known iron and steel factories as well as domestic waste water are probably the major

Table 4. Principle component analysis and factor loadings on elements in the Southern Black Sea sediments normal data.

Component	Eigen value	Variance (%)	Cumulative Variance (%)	Element	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6
1	8.62	30.80	30.80	Mo	-0.22	0.80	-0.13	0.08	0.39	-0.02
2	6.38	22.77	53.57	Cu	0.20	0.89	0.13	-0.04	-0.10	-0.05
3	4.10	14.64	68.21	Pb	0.12	0.07	0.74	-0.46	-0.20	-0.17
4	2.26	8.08	76.29	Zn	0.46	0.07	0.78	-0.01	0.10	0.07
5	1.41	5.05	81.34	Ni	0.20	0.27	-0.20	0.88	0.20	0.06
6	1.07	3.81	85.15	Co	0.28	0.42	-0.24	0.36	0.44	0.33
7	0.92	3.29	88.44	Mn	0.47	-0.07	0.06	0.28	0.70	0.04
8	0.63	2.24	90.68	Fe	0.88	0.05	0.10	0.18	0.29	0.12
9	0.54	1.93	92.61	As	0.00	0.17	0.10	0.25	0.62	0.32
10	0.41	1.48	94.09	Sr	-0.84	0.22	-0.26	-0.13	0.14	0.19
11	0.30	1.09	95.17	Cd	-0.28	0.85	0.13	0.03	0.16	0.22
12	0.26	0.91	96.09	Sb	0.04	0.47	0.61	0.19	0.23	0.09
13	0.21	0.74	96.83	Bi	0.14	0.00	0.93	-0.12	0.01	-0.01
14	0.17	0.60	97.43	V	0.78	0.52	-0.13	0.15	-0.06	0.17
15	0.14	0.52	97.95	Ca	-0.85	0.06	-0.17	0.03	0.05	0.06
16	0.12	0.42	98.36	P	0.43	0.16	0.09	0.00	0.13	0.79
17	0.10	0.35	98.71	Cr	0.20	-0.09	0.08	0.95	0.11	-0.01
18	0.08	0.30	99.01	Mg	0.69	0.05	-0.07	0.52	0.39	0.06
19	0.07	0.24	99.25	Ba	-0.08	-0.63	0.39	-0.35	-0.02	-0.23
20	0.05	0.18	99.43	Ti	0.77	-0.23	0.39	0.33	0.08	0.17
21	0.04	0.16	99.59	Al	0.91	-0.13	0.20	0.13	0.11	0.09
22	0.03	0.11	99.70	Zr	0.87	-0.02	-0.11	0.04	-0.11	0.35
23	0.03	0.09	99.79	Sn	-0.34	-0.27	0.75	-0.07	-0.24	-0.29
24	0.02	0.07	99.86	S	-0.04	0.49	-0.05	-0.02	0.83	-0.09
25	0.02	0.07	99.90	Y	0.17	-0.13	0.70	0.16	0.09	0.32
26	0.01	0.04	99.97	Hg	-0.69	0.31	0.43	0.04	-0.21	-0.19
27	0.01	0.02	99.99	Corg	-0.37	0.79	0.00	-0.10	0.34	0.04
28	0.00	0.01	100.00	CO ₃ ²⁻	-0.50	0.22	-0.12	0.23	0.45	0.45

**Fig. 4.** Plot of Factor 1, 2, 3, 4, 5 and 6 loadings by using normal data.

sources of these metals (Moore and Attar 2011).

The fourth, fifth, and sixth factors account for 8.1%, 5.1%, and 3.8% respectively of total variance. Factor 4 represents "chlorite": There is an association consisting of Ni, Cr, and Mg in factor 4. It is known that Cr substitutes with Mg as a chlorite mineral (aluminosilicates) (Petruk 1964, Muller and Staffer 1974, Sancar 2002). It is possible that Ni is being preserved within the chlorite mineral although it is a Chalcophile element.

Factor 5 constitutes an association among S, Mn, Co, As, and CO₃²⁻. This factor represents "Anoxia": The close association of S, Co, and As at the sulfide phases in the sapropel unit as reported by Sancar, (2002). Mn is precipitated in the form of Mn(II) carbonates in the anoxic zone in case the presence of inorganic carbon (carbonate) available is not enough. The dilution effect on the Mn carbonates with the input of the biogenic solid phase carbonates is more evident in Factor 1.

Factor 6 represents "the coccolith factor": This factor, which mainly consists of the association of P and CO₃²⁻, displays parallelism in all stations except KD5A, KD5B, and KD5C. It is known that

phosphorite deposits can be formed with the substitution of carbonate and phosphorus or siderite and vivianite can coexist. Troup et al. (1974) reported Siderite (FeCO₃) and vivianite (FePO₄)₂·8H₂O as being in balance in the anoxic sediments of the Chesapeake Bay.

A set of organic carbon-normalized data was applied to the factor analysis the results show that 2 accesses with Eigen values greater than 1 were extracted in the analysis (Table 5). The first two factors account for a total of 91.5% of the total variance in the data set (Figure 5). Factor 1 accounts for 85.5% of the total variance and contains very high positive factor loadings in Cu, Pb, Zn, Mn, Fe, Cd, P, Cr, Al, Hg, and CO₃²⁻ (Table 5). This factor is considered as "the anthropogenic factor": containing carrier phases of aluminosilicates, carbonate, and iron oxyhydroxides.

Factor 2 accounts for 6.07% of the total variance and contains very high loadings of Mo, S and CDP. This factor is considered as "the anoxic factor": It is understood that the close association of CDP (chlorophyll degradation products), which are part of the organic carbon phase, with Mo is more effective than C_{org}. In other words, Mo can be a proxy for pigment production in the water column.

Enrichment Factor (EF)

To better understand the quality of sediment in the Black Sea, the pollution levels of metal and various environmental assessment techniques were taken into consideration. One of them is the enrichment factor (EF), it is a powerful technique used extensively in distinguishing heavy metals coming from anthropogenic and natural sources. The EF technique was used to determine the degree of change in the composition of aerosols, sediment soil, and solid wastes (Pekey 2006). To identify anomalous metal concentration, geochemical normalization of the heavy metals data to a conservative element, such as Al, Fe, and Si was employed.

In this study, Al was used as a reference element to differentiate natural from anthropogenic components, the EF value of metal is defined as follows:

$$EF = \frac{(C_x / C_{Al})_{sample}}{(C_x / C_{Al})_{background}}$$

(C_x / C_{Al})_{sample} is the ratio of metal and Al concentrations of the sample and (C_x / C_{Al})_{background} is the

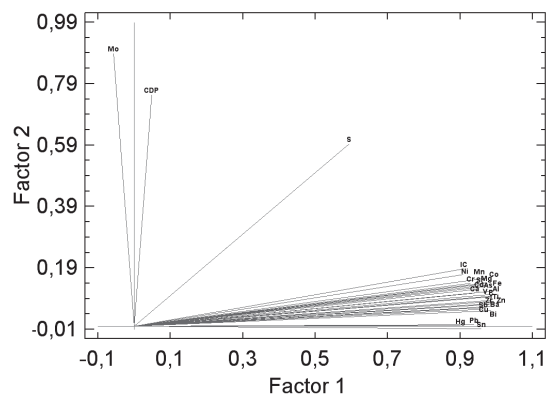


Fig. 5. Plot of Factor 1 and Factor 2 loadings by using C_{org} -normalized data.

Table 5. Principle component analysis and factor loadings on elements in the Southern Black Sea sediments with C_{org} -normalized data.

Component	Eigen value	Variance (%)	Cumulative Variance (%)	Element	Factor 1	Factor 2
1	23,93	85,45	85,45	Mo	-0,06	0,89
2	1,68	6,02	91,47	Cu	0,96	0,06
3	0,76	2,72	94,19	Pb	0,94	0,01
4	0,63	2,25	96,43	Zn	0,99	0,07
5	0,32	1,14	97,57	Ni	0,91	0,17
6	0,23	0,83	98,40	Co	0,98	0,14
7	0,19	0,67	99,07	Mn	0,97	0,16
8	0,10	0,34	99,41	Fe	0,99	0,11
9	0,05	0,19	99,61	As	0,97	0,13
10	0,03	0,11	99,72	Sr	0,96	0,14
11	0,02	0,08	99,80	Cd	0,95	0,12
12	0,02	0,06	99,86	Sb	0,96	0,06
13	0,01	0,05	99,91	Bi	0,99	0,05
14	0,01	0,03	99,94	V	0,98	0,10
15	0,01	0,02	99,96	Ca	0,94	0,11
16	0,00	0,01	99,97	P	0,99	0,10
17	0,00	0,01	99,98	Cr	0,93	0,14
18	0,00	0,01	99,98	Mg	0,97	0,14
19	0,00	0,00	99,99	Ba	0,98	0,06
20	0,00	0,00	99,99	Ti	0,99	0,08
21	0,00	0,00	99,99	Al	0,99	0,10
22	0,00	0,00	100,00	Zr	0,98	0,07
23	0,00	0,00	100,00	Sn	0,96	-0,01
24	0,00	0,00	100,00	S	0,59	0,59
25	0,00	0,00	100,00	Y	0,99	0,08
26	0,00	0,00	100,00	Hg	0,90	0,00
27	0,00	0,00	100,00	CO ₂ ⁻²	0,91	0,19
28	0,00	0,00	100,00	CDP	0,05	0,75

ratio of background metal and Al concentrations. Also, the average crust concentrations of elements (Goldschmidt 1937) were taken as background. The EF values were interpreted as suggested by Birch (2003) where $EF < 1$ indicates no enrichment, $EF < 3$ is minor; $3 \leq EF \leq 5$ is moderate; $5 \leq EF \leq 10$ is moderately severe; $10 \leq EF \leq 25$ is severe; $25 \leq EF \leq 50$ is very severe; and $EF > 50$ is extremely severe. Enrichment factors and classes for core samples of 10 stations are presented in Figure 6. Significant enrichments for S, Sb, and Mo belong to KD2A, KD2B, KD5A, and KD5C sediments from the populated areas of the Ereğli and Ordu. Samples having an EF greater than 5 are considered to be

contaminated with that particular element (Ameh et al. 2011).

Enrichment is higher in the center of the eastern basin than the western center of the basin. Taking into account the surface sediment samples, Mo was between minor enrichment and very severe enrichment in the Southern Black Sea. The $EF_{average} = 1.4$ at the coastal stations and it is considerably lower than the general average (5.2). It can be said that the overlying water in coastal waters contains H_2S from time to time. Cu, Pb, Zn, Ni, Co, Mn, As, Sr, Cd, Bi, V and Ca were either under minor or moderate enrichment in all stations. No enrichment was observed in the surface sediments for P, Ti, Sn, Cr, Na, K, Y, Mg, Ba, Zr and Hg. Sb exhibited moderately severe enrichment at all stations. Areas with EF.1 should be viewed with caution because of the potential for the release of metals, making them bio-available (Ameh et al. 2011). S (sulfur) showed either under severe and very severe enrichment towards the centre of the basin. Moderately severe enrichment for S was also observed in the other coastal stations. Also, S enrichment is more severe in the east than in the west. Even though the enrichment factor appears to be the first indicator for the potential anthropogenic contribution for an element, some natural sources can cause the observed enrichment (Atgin et al. 2000). Also, Ergul et al. (2008) attributed high Cu, Cd, Co, Zn, Fe, and Sb concentrations in sediment trap samples in the winter to the burning of fossil fuels and high degrees of terrestrial erosion. Anthropogenically, Mo comes from Cu metal processing, electrolytic Mn production, refinery of metal alloys, and coal burning processes (Anonymous 1979).

Geoaccumulation Index (Igeo)

The level of anthropogenic pollution in the Southern Black Sea was evaluated using the technique where the enrichment of an element above the background (geoaccumulation index) is calculated. This index is basically a single metal approach to quantify metal pollution in sediments when the concentration of toxic heavy metal is 1.5 times greater than their lithogenic background values (Gaur et al. 2005).

$$I_{geo} = \log_2 [C_n / 1.5 B_n]$$

Where C_n is the measured concentration of the element n and B_n is the geochemical background value element n in the average crust. The factor 1.5

is used to compensate for possible variations which may be attributed to the lithologic variations in sediment (Stoffers et al. 1986, Abraham and Parker 2008). In this study the background levels were calculated separately for each element. First of all, the quantity (C_m/C_x) is the concentration of some site related metal (e.g. Cr) C_m divided or normalized by the corresponding concentration of some non-site related metal (e.g. Al) C_x . Obtained from the quantile plots they may be generated using the logarithms of these ratios

$$\ln(Y) = \ln\{(C_m / C_x)\}$$

The quantile plot is evaluated for trends indicative of naturally occurring metal concentrations and deviations that indicate anthropogenic contamination. Because environmental data is frequently log-normal, it is usually convenient to construct normal probability plots for (C_m/C_x) (e.g. the values of (C_m/C_x) are related and plotted against the corresponding quantiles of a standard normal distribution or their associated probabilities). For normally distributed data "deviations" are "breaks" in a straight line.

Therefore, the values of 70 samples were normalized by aluminum and subsamples were distinguished from the probability plot by taking the $\ln$ values. Original values of the subsample data having the lowest value constitute the background sample. Median values of this obtained data set were employed as the background value. The sample sizes, the 95% confidence limits (it couldn't be given for those, which have small sample size), the median values obtained for each element, and chronological interval of the data in the background sample are given in Table 6. Background levels incorporate the current sediment and 6,965 years before the present day. The background values for each element were determined, benefiting from the probability plot method for the Southern Black Sea in this study and are given in Table 8.

Müller (1969) proposed the following descriptive classes for increasing values: >5 (class 6) extremely contaminated; 4-5 (class 5) strongly to extremely contaminated; 3-4 (class 4) strongly contaminated; 2-3 (class 3) moderately to strongly contaminated; 1-2 (class 2) moderately contaminated; 0-1 (class 1) uncontaminated to moderately contaminated, and <0 (class 0) uncontaminated.

According to this classification P, Ba, and Ti fall

into uncontaminated, Cu, Pb, Zn, Mn, Fe, As, Sr, Bi, V, Cr, Mg, Zr, Y, Sb, Sn, and Ni fall into uncontaminated to moderately contaminated, Hg and Cd moderately contaminated, and S and Mo fall into moderately to strongly polluted (Fig. 7).

Considering the surface sediment samples the average I_{geo} values of metals consisting of Cu, Co, N, Fe, Sb, V, Mg and Zr is -0.092 in the west and was found as 0.246 in the east and eastern basin as being contaminated with these metals. While the average I_{geo} values of metals consisting of Sr, Bi, Ca, Sn and Hg was 0.346 in the west and was -0.0044 in the east this demonstrates that the western basin is contaminated with these metals. Whilst the average I_{geo} value of the group formed by Mo, Pb, Cd, Cr and S is 0.753, there was no difference between the eastern and western basins. Whereas, the average I_{geo} value of the coastal stations is 0.21 this indicates that the centers of the basins are contaminated with these metals.

The average I_{geo} value of the group Zn, Mn, As, P, Ti and Y elements was -0.217 and the centers of the basins were not so different from this average (-0.146). There was no contamination with these elements, except for Zn. The I_{geo} value of 0.178 for Zn in the center of the western basin was class 1, higher than the east (-0.46) indicating the center of the western basin was contaminated with Zn.

CONCLUSION

The study of the distribution of heavy metals demonstrates that, the eastern and western areas of the Southern Black Sea are facing different contributions of heavy metals.

(1) Recorded Inorganic geochemical data shows a relatively high percentage of organic matter and carbonate in the eastern area of the Southern Black Sea. The high content of organic matter in the sediments was mainly related to anthropogenic and geological inputs such as weathering and runoff from the rivers and land-based sources. The increase of the CO_3^{2-} content was related to the sediment discharge from the rivers, leading to an increase in the relative proportion of the biogenous carbonate material in the sediment.

(2) The correlation of C_{org} -normalized variables was strikingly higher. The analysis of data showed positive correlations among Mo, C_{org} , and CDP indicating that these had complicated geochemical behaviors. It was remarkable to note that Mo (molybdenum) only had a correlation with CDP.

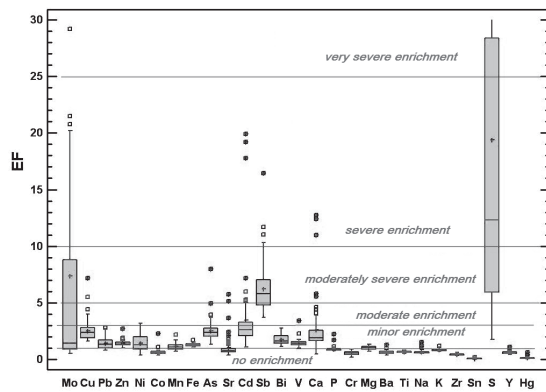


Fig. 6. Mean, median, 95% confidence levels, minimum, maximum values, and outliers of EF for 28 elements in the sediments of South Black Sea.

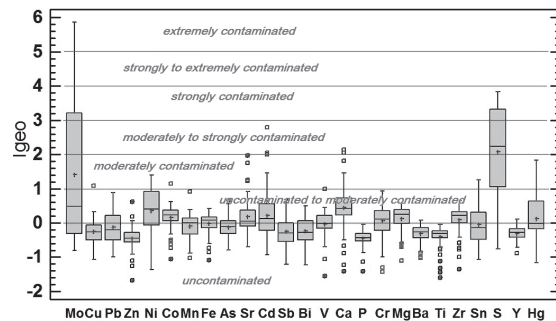


Fig. 7. Mean, median, 95% confidence levels, minimum, maximum values, and outliers of geoaccumulation index for 28 elements in the sediments of the Southern Black Sea.

Table 6. Calculated background concentrations of metals in the Black sea by using probability plot from $Y = \ln(\text{Me}/\text{Al})$ and chronological ranges of backgrounds.

Element	Sample size	Median	95% Lower Confidence Level	95% Upper Confidence Level	Before present (min)	Before present (max)
Mo	14	0,89	0,81	0,97	536	6208
Cu	12	41,94	37,12	44,01	975	6444
Pb	13	17,47	15,73	18,15	-59	5707
Zn	6	79,50			1718	2595
Ni	8	45,00			-58	4639
Co	4	12,55			-56	6444
Mn	4	416,50			149	6267
Fe	5	26900,00			149	6267
As	5	7,70			214	5707
Sr	5	192,00			234	6208
Cd	7	0,14			1418	4783
Sb	11	0,83	0,76	0,90	826	6444
Bi	6	0,24			1907	2595
V	10	84,50	48,84	107,84	-56	4639
Ca	8	33050,00			-58	3076
Cr	6	61,00			234	4783
Mg	7	11400,00			-58	2910
Ba	11	234,00	188,12	260,07	148	6965
Ti	4	3155,00			1567	4639
Zr	7	45,70			547	4639
Sn	18	1,40	1,33	1,50	-58	6965
S	5	900,00			245	1712
Y	4	13,60			1099	3076
Hg	3	0,03			1400	2297

BP= (Before Present)=AD1950

Metals and CDP, which is a component of autochthonous organic matter, not having a statistically significant correlation proves the accuracy of the normalization operation. It was seen that C_{org} -normalized metals change with organic carbon inverse relationally. High Me_{org} (organic carbon-normalized metal) levels and low organic carbon at the periphery while high organic carbon and low Me_{org} levels at the center of the basin are characteristic.

(3) A multivariate analysis, including the factor analysis, used in this study provides valuable information about the source of pollution. The factor analysis was divided into two different sets of data, normal data and C_{org} -normalized data. A factor analysis was applied to a set of normal data and was summarized into six main components which were associated with different potential sources of contribution. Six factors explain 85% of the total variance: First factor was the "alumi-nosilicates, carbonate and iron oxyhydroxides", second factor was the "organic carbon carrier phase", third factor was the "pseudo anthropogenic factor", fourth factor is "chlorite", fifth factor is "anoxia", and the sixth factor is the "coccolith factor". A set of C_{org} -normalized data was applied to the factor analysis and generated two sources of pollutants: (1) anthropogenic and (2) anoxic.

(4) Sediment pollution in the present study was assessed using the enrichment factor and geoaccumulation index values. The calculations of the enrichment factor showed that Cu, Pb, Zn, Ni, Co, Mn, As, Sr, Cd, Bi, V and Ca indicated minor or moderate enrichment in all stations, whereas, no enrichment was in the surface sediments for P, Ti, Sn, Cr, Na, K, Y, Mg, Ba, Zr and Hg although, the EF values of Mo, S and Sb were high. This possibly suggest that there is locally some point/nonpoint sources of input for these metals. The enrichment of these metals comes from anthropogenic activity due to agricultural activities and industrialization. The Southern Black Sea sediments serve as reservoirs for heavy metals and their concentrations are controlled by a variety of physical and chemical factors. It is important to determine the source of these metals and to manage their input into the Southern Black Sea. It can be said that P, Ti, Sn, Cr, Na, K, Y, Mg, Ba, Zr and Hg are directly related to geogenic sources. The Igeo accumulation index shows that the surface sediment of the Southern

Black Sea are uncontaminated to moderately contaminated with respect to Cu, Pb, Zn, Mn, Fe, As, Sr, Bi, V, Cr, Mg, Zr, Y, Sb, Sn and Ni, moderately contaminated with respect to Hg and Cd, and moderately to strongly polluted with respect to S and Mo. Despite total sedimentary concentrations above their pre-industrial background levels, Igeo showed that the surface sediments were unpolluted with respect to P, Ba, and Ti. The chemical partitioning data indicates that there are significant differences in the distribution of these two metals. S poses a high environmental risk whereas Cd poses a low environmental risk.

(5) ^{14}C age determinations have shown that surface sediments in KD2A and KD5A belong to AD130-350 and AD1000 respectively, indicating that undersea landslides and turbidity fluxes in the Southern Black Sea are not rare because of the sharp slope in the topography of this region and high bottom transportation in certain places. The requirements of age determinations are of great importance to assess the extent of the anthropogenic contribution to pollution.

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