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Trace metal composition of particulate matter of the Danube River and Turkish rivers draining into the Black Sea

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Abstract

We determined the composition of particles from several rivers entering the Black Sea as part of a broader study of the composition of suspended matter and sediments in the Black Sea. Suspended matter and surface sediment samples were collected from the Danube River draining from Europe and from four Turkish rivers (Sakarya, Yenice (Filyos), Kızılırmak and Yeşilırmak Rivers) in Anatolia. All samples were digested and analyzed by inductively coupled plasma-mass spectrometry and atomic absorption spectrometry (flame and graphite furnace) instruments. The elements analyzed included Al, Ti, V, Cr, Mn, Fe, Co, Cu, Zn, Mo, Ag, Cd, Ba, Pb and U. The concentrations were compared as solid phase concentrations (ppm) and as Metal to Al (Me/Al) ratios. The compositions of the particulate matter data from Turkish rivers and surface sediment from the Danube River were very similar to each other and the average for the world's rivers. Both had slightly higher concentrations than global average crust. A suspended matter sample from the Danube River had elevated concentrations for some elements (Ag, Pb, Zn, Cd, Cu and Mn) that were probably due to anthropogenic contamination suggesting that some hot spots may exist in the Danube that need to be studied more thoroughly. We recommend that the best choice for subtracting the terrigenous component from Black Sea particulate and sediment samples is the average of the Turkish rivers suspended matter and Danube River sediment samples.

Keywords: Black Sea; Riverine particulate matter; Trace elements; Heavy metals; Lithogenic end member

1. Introduction

River runoff is one of the main processes delivering solutes and particles to coastal and marginal seas. The major elements in riverine particulates have been well studied (e.g. Canfield, 1997). Particle chemistry appears to vary with average rates of runoff, with high runoff rivers transporting the most heavily altered particles. There have been fewer studies of trace elements in river particulates, but both natural and anthropogenic sources can be important. Many trace metals adsorb strongly on particles (Balistrieri et al., 1981; Balistrieri and Murray, 1981) and thus they are preferentially associated with particulate matter in rivers (e.g. Guieu et al., 1998; Guieu and Martin, 2002).

Particles from rivers are dominated by aluminosilicate material that is relatively unreactive. Al and Ti are

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normally considered to be conserved in the particulate phase during chemical weathering. In order to identify geochemical anomalies for trace elements arising from redox processes, researchers either normalize the composition to Al or Ti or else subtract the lithogenic component from the total concentration using Al or Ti as reference elements. It is usually assumed that lithogenic particles are the source of Al and Ti and have the composition of global average shale or crust. However, the best approach is to determine the composition of terrigenous particles with local samples because continental rocks can vary regionally (e.g. Klump et al., 2000).

The Black Sea is a large depositional basin for rivers discharging waters from Southeastern Europe, Caucasian Mountains and Northern Anatolia (Algan et al., 1999). The watershed includes 17 different countries. The total fresh water input to the Black Sea from rivers is 353 km^3y^{-1}. The five largest rivers are the Danube (203 km^3y^{-1}), Dneiper (54 km^3y^{-1}), Don (28 km^3y^{-1}), Kuban (13 km^3y^{-1}) and Dniesta (9.3 km^3y^{-1}) (Shimkus and Trimonis, 1974). There are also 28 km^3y^{-1} of fresh water contributions from a large number of smaller rivers and streams flowing along the Turkish and Bulgarian coasts (Balkas et al., 1990) and 17.7 km^3y^{-1} of river water discharged by the remaining small rivers and streams located around the basin.

The elemental composition of particles in the Black Sea is controlled by their origin. Spencer et al. (1972) suggested that particulate distributions in the surface waters of the Black Sea were dominated by the presence of particulate silicate detritus derived largely from rivers. We tested the hypothesis that global average crust is a suitable proxy for riverine particulate matter entering the Black Sea by analyzing the suspended particles from local rivers and comparing these compositions with global reference values. There have been very few previous studies of suspended matter in rivers entering the Black Sea. Most have focused on heavy metal pollution rather than geochemical processes. The goal of this paper is to present new analytical data for Al, Ti, Mn, Fe, V, Cr, Co, Cu, Zn, Mo, Ag, Cd, Ba, Pb and U in particulate matter and surface sediments from the Danube River and four Turkish rivers. Few, if any, previous studies have included such an extensive set of elements. The data will be compared with global average crust,

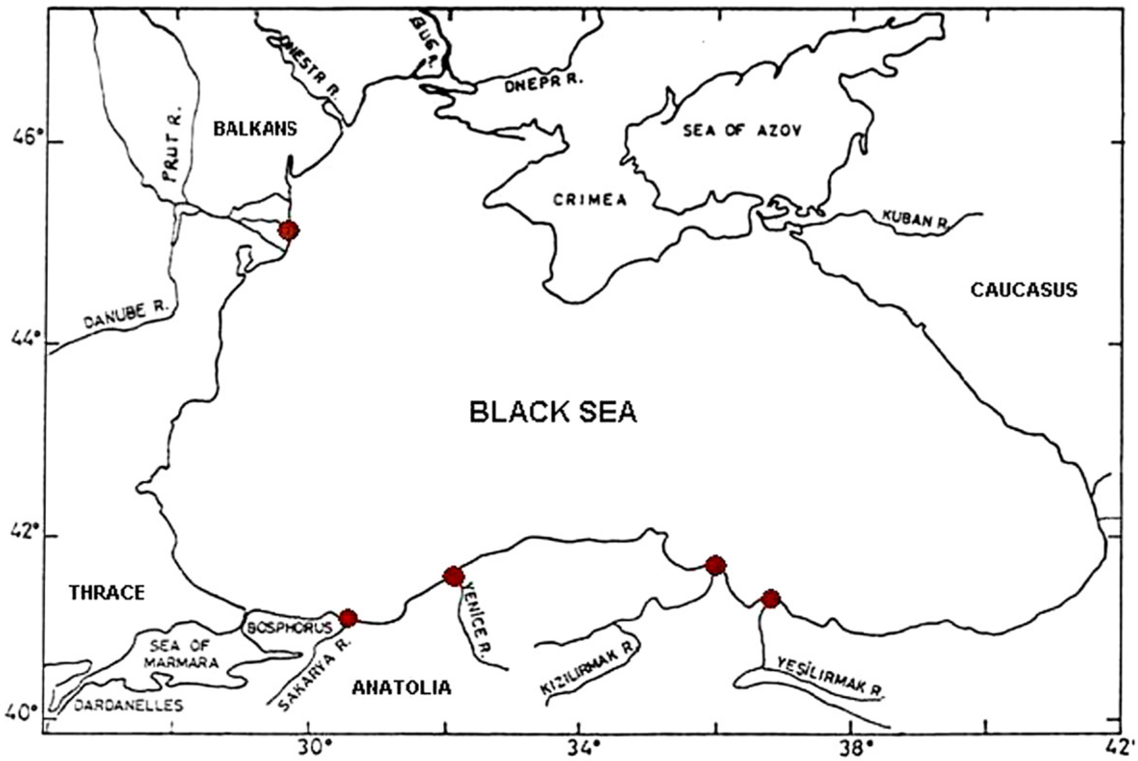

Fig. 1. Some of the major rivers (Danube, Sakarya, Yenice, Kızılırmak, Yeşilırmak) flowing into the Black Sea is given in the map. The solid circles are used to show river water sampling stations located at northwestern and southern Black Sea coasts.

Table 1
Results of certified reference sample analyses

Reference	Al	Fe	Ti	Mn	Ba	Zn	Cu
MESS-1 (measured; $n=3–4$)	57,200	28,100	5,300	546	338	208	24.4
±S.D.	±2,300	±200	±200	±15	±11	±9	±0.9
MESS-1 (certified)	58,400	30,500	5,400	513	NA	191	25.2
±S.D.	±2,000	±1,750	±170	±25	–	±17	±3.8
% difference	2.0	7.8	1.5	6.5	–	9.0	3.0
PACS-1 (measured; $n=5–10$)	65,600	46,100	4,100	469	704	863	419
±S.D.	±3,400	±3,260	±110	±13	±25	±32	±20
PACS-1 (certified)	64,700	48,700	4,200	470	NA	824	452
±S.D.	±1,160	±840	±66	±12	–	±22	±16
% difference	1.4	5.4	2.3	0.3	–	4.7	7.4

Reference	Cr	V	Pb	Co	Mo	U	Ag	Cd
MESS-1 (measured)	53.4	82.3	34.2	12.0	2.41	3.44	0.85	0.67
±S.D.	±2.7	±5.2	±2.2	±0.3	±0.8	±0.3	±0.10	±0.08
MESS-1 (certified)	71	72.4	34.0	10.8	NA	NA	NA	0.59
±S.D.	±11	±17	±6.1	±1.9	–	–	–	±0.10
% difference	24.8	13.7	0.6	11.1	–	–	–	13.6
PACS-1 (measured)	92.7	129	395	17.0	11.7	2.52	1.68	2.23
±S.D.	±4.6	±3.9	±23	±0.2	±0.3	±0.10	±0.10	±0.22
PACS-1 (certified)	113	127	404	17.5	12.9	NA	1.81	2.38
±S.D.	±8	±5	±20	±1.1	±0.9	–	±0.05	±0.20
% difference	18.0	1.7	2.2	2.9	9.3	–	–	6.3

NA signifies that no certified value was given. Concentrations are given in ppm. The Standard Deviation of the measured values gives precision. Comparison of the measured and certified values gives accuracy.

shale, and particulate matter from other world rivers. This study serves as the foundation for additional work (Yiğiterhan et al., submitted for publication) that assesses how the composition of particles and sediments in the Black Sea is influenced by redox processes.

2. Study sites

The Danube was sampled because it is the largest river in the region. The Turkish rivers were sampled because of their size and because there was no previous

Table 2
Comparison of solid phase suspended matter concentrations of Danube and four Turkish rivers and one sediment sample from the Danube River with previous work carried on Danube River (Guieu et al., 1998) and similar comparisons with the values for the average world rivers (Martin and Windom, 1991)

Source	Al	Fe	Ti	Mn	Ba	Zn	Cu	Cr	V	Pb	Co	Mo	U	Ag	Cd
Danube River (suspended)	13,900	13,300	898	1380	889	1934	328	103	34	236	7.04	–	0.47	9.44	3.20
(sediment)	83,500	42,800	4700	830	432	170	64	111	114	41.6	16.0	0.73	2.55	0.71	0.60
Sakarya River	21,400	38,600	4220	1070	313	128	51	142	126	20	21.2	0.45	1.85	0.26	0.20
Yenice River	28,700	35,200	3290	832	235	124	36	104	108	19	14.8	–	1.66	0.30	0.18
Kızılırmak River	81,500	58,300	4560	2880	300	149	72	179	160	31	28.7	–	2.16	0.60	0.27
Yeşilırmak River	84,500	56,500	3370	7780	458	182	103	117	182	35	26.5	7.91	2.02	0.88	0.86
Avg. Turkish Rivers (suspended)[a]	54,000	47,200	3860	3140	327	146	66	135	144	26	22.8	4.18	1.92	0.51	0.38
Avg. Danube River (suspended)[b]	60,100	36,000	–	1700	–	248	115	–	–	84	25.6	–	–	–	1.14
Avg. World River[c]	94,000	48,000	–	1050	–	250	100	–	–	35	20	–	3	–	1.2
Crust avg. values[d]	80,400	35,000	4560	600	550	71	25	35	60	20	10	1.50	2.8	0.05	0.10
Shale avg. values[e]	88,000	48,200	4600	850	580	95	45	90	130	20	19	2.6	3.7	0.07	0.8

The elemental concentrations are presented as ppm.
[a] Particle size ≥1.0 μM; measured in this study.
[b] Particle size >0.45 μM; Guieu et al. (1998).
[c] Martin and Windom (1991).
[d] Taylor and McLennan (1985), 95.
[e] Wedepohl, 1968.

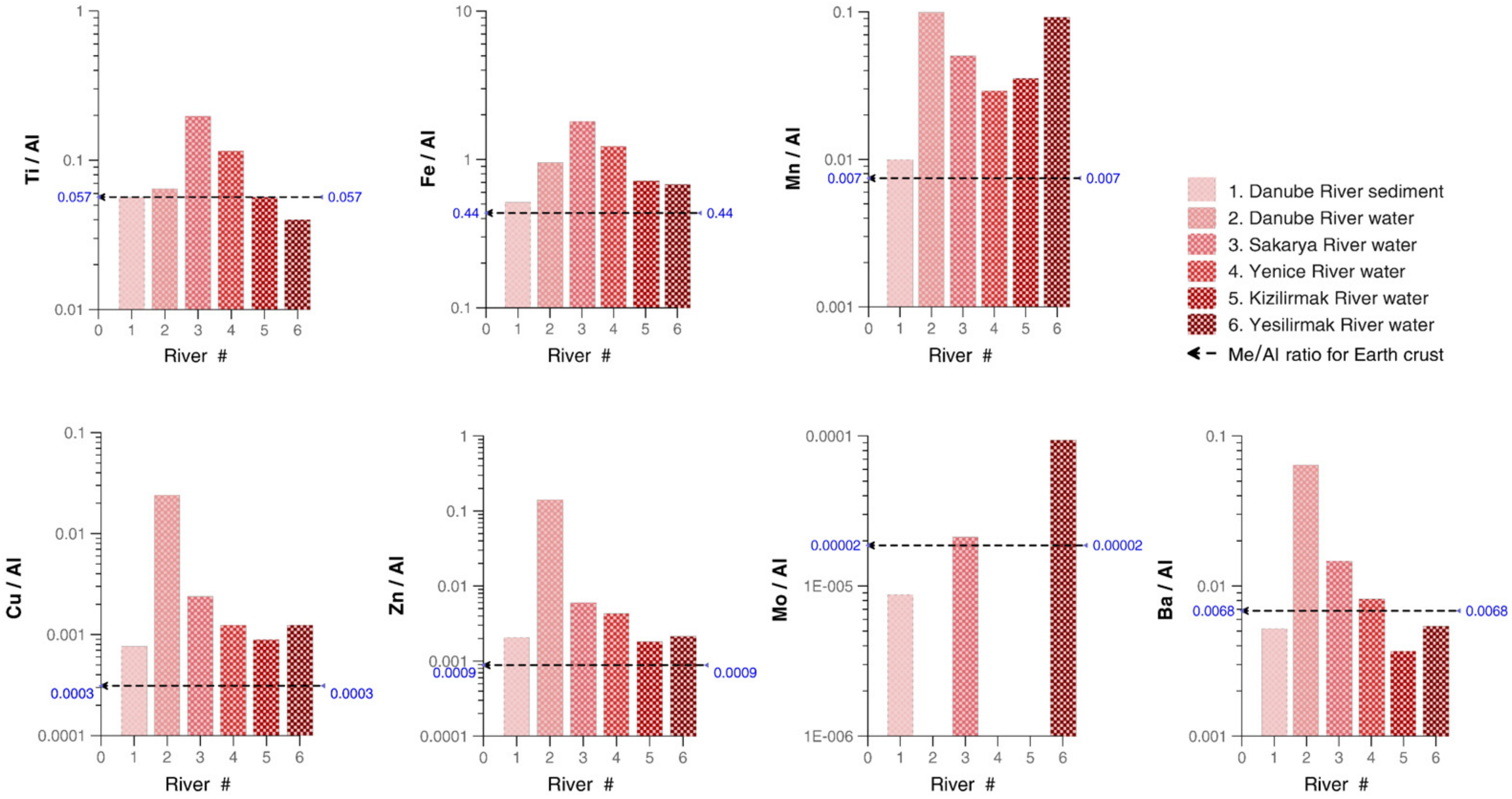

Fig. 2. Log Me/Al ratios in particulate matter samples from Turkish rivers and the Danube River. The dashed line is average crustal Me/Al ratio.

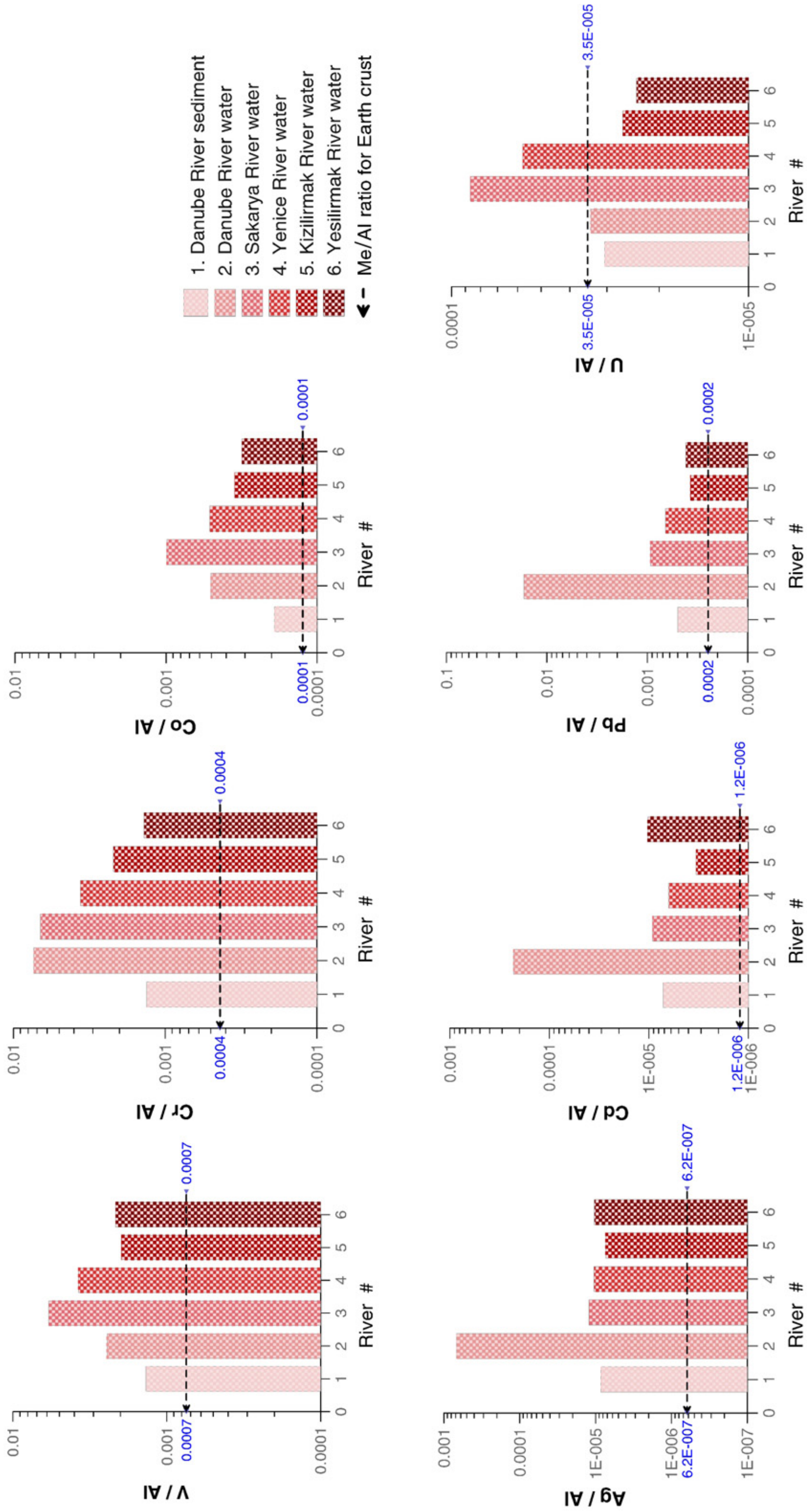

Fig. 2 (*continued*).

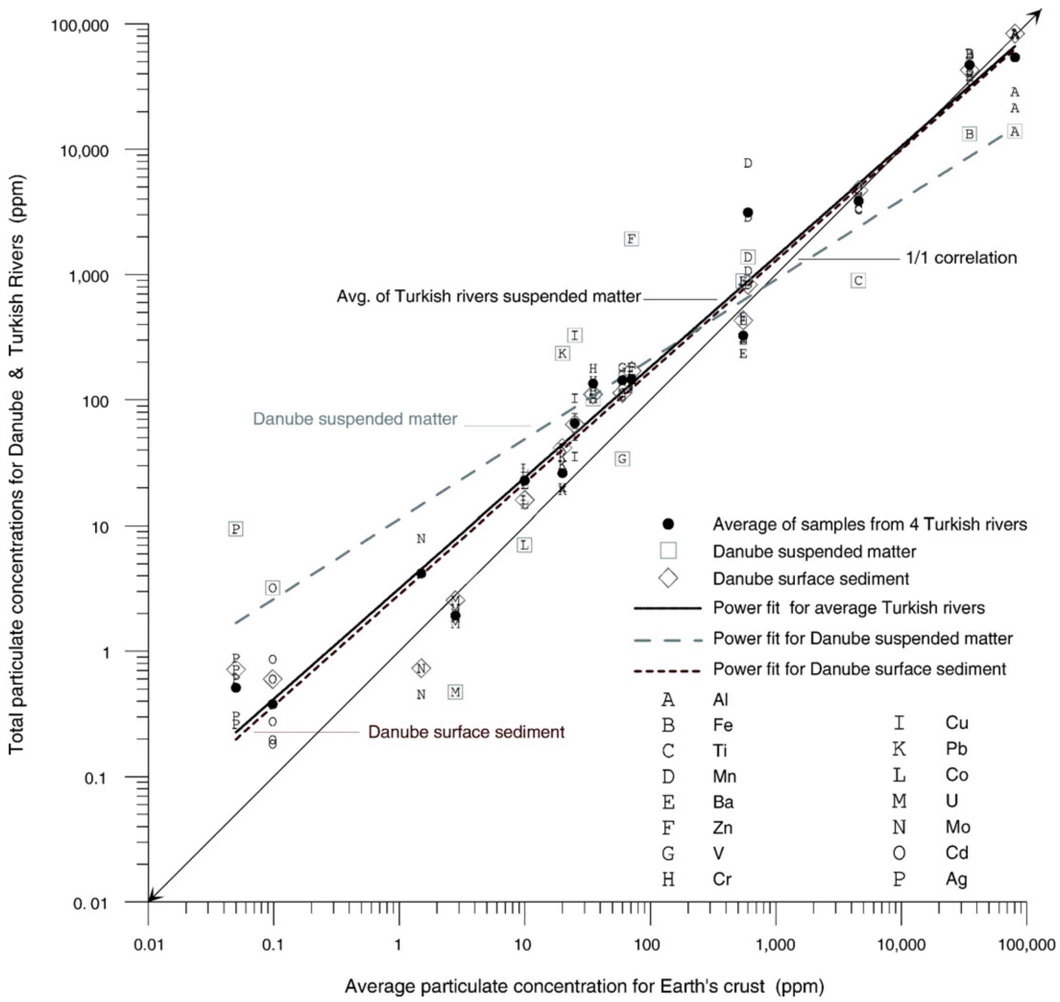

Fig. 3. The concentration of the Danube River and Turkish rivers versus the average Earth's crust (Taylor and McLennan, 1985, 1995) on log–log scales. The Turkish rivers are given individually and the solid dots are the average of the four rivers. Eq. for Avg. of Turkish river water vs. $\text{Crust}_{T\&M}$ line is: $\ln(Y)=0.88*\ln(X)+1.15$, $R^2=0.97$. Eq. for Danube suspended matter vs. $\text{Crust}_{T\&M}$ line is: $\ln(Y)=0.64*\ln(X)+2.42$, $R^2=0.73$. Eq. for Danube surface sediment vs. $\text{Crust}_{T\&M}$ line is: $\ln(Y)=0.89*\ln(X)+1.04$, $R^2=0.96$.

data for riverine particulate matter from this region (Fig. 1).

Danube River is the second longest river in Europe (after the Volga) with a length of 2800 km and a catchment area of 817,000 km^2. It represents 64% of the river runoff to the Black Sea and 80% of the runoff entering the northwestern Black Sea (Popa, 1993). It provides essential water resources for a population of over 70 million people living in the eight countries along it's course and six additional countries in the extended catchment area (Literathy and Laszlo, 1995). With such a large population and industrial activity there are many potential sources of pollution and thus the Danube represents the most significant source of river-borne pollution flowing into the Black Sea. Anthropogenic nutrients transported by the Danube are known to be the major reason for eutrophication and pollution on the northwestern shelf area (Mee, 1992; Windom et al., 1998; Lancelot et al., 2002).

There are two large dams on the lower Danube (Iron Gate I and II) that have provided the opportunity to study the environmental impacts of large dams on river discharge and coastal eutrophication (Cociasu et al., 1996; Humborg et al., 1997; Teodoru et al., 2006). These dams have reduced sediment discharge to 30–40% of it's historical value (Panin and Jipa, 2002; Teodoru et al., 2006).

The *Sakarya River* is the largest river of northwest Anatolia (length is 824 km) and the third longest river of Turkey with a drainage basin area of 53,800 km^2. Although, two of the largest hydroelectric power plants

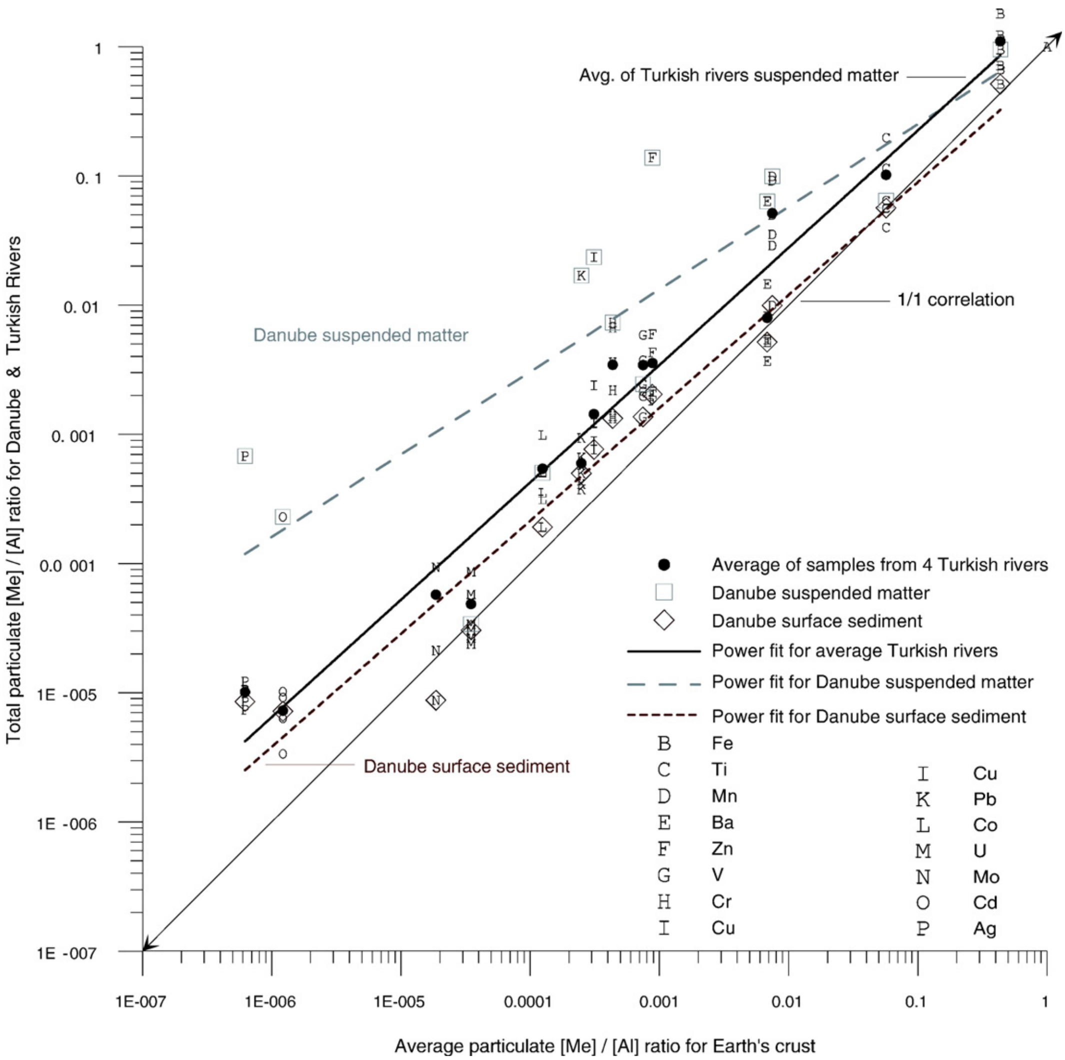

Fig. 4. The Me/Al ratios of the Danube River and Turkish rivers versus the ratios in the average Earth's crust from Taylor and McLennan (1985, 1995) on Log–Log scales. The Turkish rivers are given individually and the solid dot is the average of the four rivers. The legend lists the letter symbols that are used for the elements. The 1:1 relationship is given as a solid dark line. The lines represent the best power fits. Eq. for Avg. of Turkish river water vs. $\mathrm{Crust}_{T\&M}$ line is: $\ln(Y)=0.91*\ln(X)+0.60$, $R^2=0.97$. Eq. for Danube suspended matter vs. $\mathrm{Crust}_{T\&M}$ line is: $\ln(Y)=0.64*\ln(X)+0.09$, $R^2=0.67$. Eq. for Danube surface sediment vs. $\mathrm{Crust}_{T\&M}$ line is: $\ln(Y)=0.87*\ln(X)-0.40$, $R^2=0.95$.

in Turkey exist on this river, it's waters still have large particulate loads that are discharged into the surface waters of the southwestern Black Sea from the east of the Bosporus.

The *Yenice River* (288 km long) is called by many different names (Ulusu, Gerede Suyu, Soğanlı Çayı, Filyos Irmağı etc.) from it's starting point until it flows into the southwestern Black Sea. The Yenice River consists of several branches that combine in the Gökçebey–Zonguldak basin. From that point, the river flows 30 km to the north where it reaches the Black Sea with an enormous particulate load.

The Kızılırmak River originates from central Anatolia and is the longest river of Turkey (1355 km). There are several dams on the river and the suspended matter concentrations are low. The river enters the southern Black Sea near Cape Bafa.

The Yeşilırmak River is fairly long (519 km in length) with a drainage basin area of 2300 km^2. It also has low suspended matter concentrations and flows into the southern Black Sea east of Samsun.

Both the Danube River and the rivers flowing from the northern coast of Turkey, flow through very heterogeneous geological terrains. The mineralogical content of the Danube originates from 20–25 different types of igneous, sedimentary and metamorphic rock (Muller and Stoffers, 1974; Bogardi, 1978). The Danube sediments are mostly composed of quartz, limestone, and crystalline shale. In addition, the sediments contain considerable amounts of amphiboles, pyroxene and other minerals of granitic origin (Literathy et al., 1994). The rocks along the northern coast of Turkey are also a mixture of various kinds of crustal rock in the Pontic Mountains, which extend all along the southern coast of the Black Sea (Muller and Stoffers, 1974; Algan et al., 1999). The source rocks in Turkey contain less carbonates then those for the Danube. The western region of the coast between the Sakarya and Kızılırmak Rivers is mainly composed of flysch deposits of Cretaceous and Eocene ages (Algan et al., 1999). The Pontic Mountains, which extend along the northern coast of Turkey, rise sharply and do not allow development of large cities along the coast. The fairly small population lives in small settlements rather than large cities and the region is not heavily industrialized.

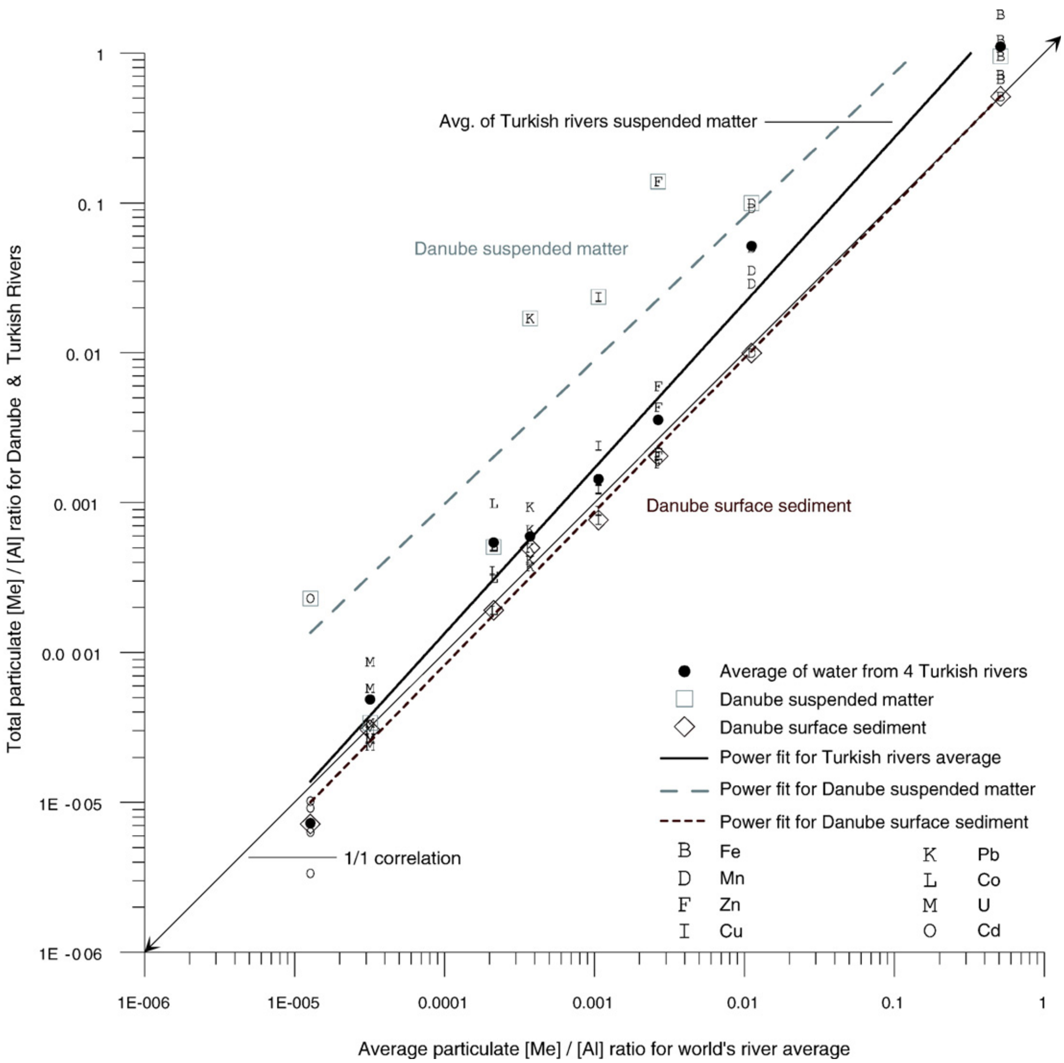

Fig. 5. The Me/Al ratios of suspended particulate metals in the Danube River and Turkish rivers versus the Me/Al ratios in the average world's rivers from Martin and Windom (1991). Log–Log scales. The Turkish rivers are given individually and the solid dot is the average of the four rivers. The legend lists the letter symbols that are used for the elements. The 1:1 relationship is given as a solid dark line through the origin. The other lines represent the best fit equations of: Eq. for Avg. Turkish river water vs. world's rivers water is: $\ln(Y)=1.10*\ln(X)+1.24$, $R^2=0.98$. Eq. for Danube suspended matter vs. world's rivers water is: $\ln(Y)=0.96*\ln(X)+1.90$, $R^2=0.82$. Eq. for Danube surface sediment vs. world's rivers water is: $\ln(Y)=1.02*\ln(X)-0.03$, $R^2=0.99$.

3. Sampling

Sampling location of the Danube River Delta in July, 2002 was on the Sulina branch in Romania (Fig. 1) at 45° 05′ N and 29 41′ E, about 8 km before entering the Black Sea. The Sulina branch is the smallest of the three main tributaries in the Danube Delta. The water at this site was totally fresh. Water samples were collected by hand as far from shore as possible in large acid-washed polyethylene carboys and transported quickly to the Institute of Marine Research in Constantza, Romania. Suspended matter samples were filtered on QMA filters (25 mm diameter, 1 μm pore size) using an acid rinsed plexiglass filter holder with low vacuum filtration. A total of 12 QMA filters were collected. The volumes filtered ranged from 0.5 to 2.1 L. A surface sediment sample (0–1 cm) was collected at the same location and stored in a clean zip-lock plastic bag.

Because of their remote location and limited access, sampling of the four Turkish rivers was done in mid-channel, either by hand from the side of a bridge or by foot when the water was shallow enough (after Canfield, 1997). We sampled from sites where significant local bank erosion was not evident. Samples were collected using an acid cleaned plastic bucket and transferred promptly to large acid-washed carboys. Samples were collected in April, 2002, when the water level was highest due to snow melt and spring rain. Priority was given to sampling as far as possible from point pollution sources. Well-mixed areas close to outflow points of river mouths were preferred. A mobile closed-system filtration system, based on vacuum filtration, was used to filter these samples in local hotels soon after collection. Samples were filtered through 142 mm diameter QMA filters (~1 μm pore size) in an acid-washed plexiglass filter holder. The volumes filtered ranged from 5 to 10 L for the Sakarya to 22 to 67 L for the Yeşilırmak. The filters were folded and stored in clean zip-lock plastic bags until analyses. A total of sixteen samples were collected and eight of these were analyzed in this study.

QMA (quartz) filters were cut from rectangular sheets using a stainless steel punch. Extensive studies of the filter blanks were conducted (Yigiterhan, 2005). These filters were used without pre-cleaning due to the large particulate load of river water and the large filtration capacity of QMA filters. These conditions resulted in sample to blank ratios much higher than three for all elements shown here.

We acknowledge that one time point is not representative of the variability in the annual flux for such rivers but because there is so little data available for this region and because our goal is to determine the composition of the particles, rather than the concentrations or fluxes, these data are a valuable addition. Previous studies (e.g., Kennedy, 1965; Martin and Meybeck, 1978; Thomas, 1988) have suggested that single sampling opportunities are representative of individual drainage basins because of the low variability of the composition of riverine suspended matter.

4. Materials and methods

The particulate matter and sediment samples were analyzed for a suite of trace metals after microwave digestion in a strong acid mixture. The acid mixture used for sample digestion was prepared from 4 ml reagent grade 23 M hydrofluoric acid (HF), 1 ml sub-boiled distilled 16 M nitric acid (HNO_3) and 1 ml sub-boiled 6 M hydrochloric acid (HCl). Ultrapure reagent grade hydrogen peroxide (J.T.Baker, Ultrex® Assay W/W 30%) was added at the end of digestion to ensure complete oxidation of organic matter. This method was modified from those of Murray and Leinen (1993) and Breckel et al. (2005). Total digestion was done using high pressure Teflon bombs (Savillex®). Digested samples were taken up to 20 or 40 g final weights to ensure the analytical criteria that the total amount of dissolved solids in the solutions analyzed would be less than 2%.

Three different types of standards were used to calculate concentrations. A multi-element standard was prepared in 1% HNO_3 (v/v) from 1 ppm single element standards to obtain concentration ranges typical of surface ocean marine particulate material. The standards were made at concentrations to obtain counts between 100,000 to 200,000 as required for best accuracy on the Inductively Coupled Plasma-Mass Spectrometry (ICP-MS).

A mixture of yield tracers was used for volumetric correction of the samples after digestion and to minimize volumetric errors caused by evaporation or loss of samples. The yield tracer was composed of 4 ppm Indium (In), Yttrium (Yt) and Terbium (Tb) and finalized to 50 ppb when the digested samples were diluted to 20 ml final volume using 1% HNO_3.

The digested filter solutions were analyzed using a *Perkin Elmer Sciex ELAN 5000* ICP-MS equipped with an *AS-90* Autosampler and/or *Perkin Elmer ELAN 5000* Atomic Absorption Spectrophotometry (AAS) or *Hitachi Z-9000* AAS. An external standard curve method was used for calculating concentrations. No sample matrix problem was observed for these samples.

Certified reference standards were analyzed multiple times over the course of this research to calculate precision and to determine accuracy (Yigiterhan, 2005). Two certified standards, produced by National Research Council of Canada (PACS-1 and MESS-1), were analyzed to evaluate the accuracy of our analyses. Both samples were chosen because they had trace metal compositions similar to our samples. In most cases the average measured values were within the 90–95% confidence limits of certified values of MESS-1 and PACS-1 (Table 1). The exception was Cr where our analyses were lower by about 20%. Because of this uncertainty we report our Cr data only to give some idea about the approximate particulate concentrations expected to be found in these river waters. A bulk Black Sea sediment sample (dried, ground and homogenized from 7–8 cm depth in a box core collected from the western basin of the Black Sea during R/V Knorr 2001) was run for precision and to ensure there was no drift in the analyses. One certified and one Black Sea reference standard were analyzed with each sample set. Precision was estimated by triplicate analyses of actual samples and these standard reference materials. Standard deviations (1σ) of the means were used to estimate precision. The precision of most analyses was about 5%. For Ag and Cd (which have much lower concentrations) the precision was about 10%.

5. Results

The Sakarya and Yenice Rivers had the highest metal concentrations (μg/l) for all elements because of their very high particulate matter concentrations. The Danube River had the lowest particulate concentrations for Al, Ti, V, Mn, Fe, Co, and U while the Kızılırmak and Yeşilırmak Rivers had the lowest particulate concentrations for Cr, Cu, Zn, Mo, Ag, Cd, Ba, and Pb. Volumetric concentrations (μg/l) are not presented here but can be found in Yigiterhan (2005). These values are a function of suspended load and water flow and thus are not a very useful way to compare samples from different times and different rivers.

The results were converted to solid phase concentrations (μg metal/g solid or ppm) (Table 2), which is required for comparison of these compositions with global average crust, shale or world rivers. Not all of the original samples were weighed, thus we weighed replicate undigested samples that had been collected at the same time and locations. We calculated the weight of solid per liter of water filtered using the recorded volumes. This ratio was multiplied times the volume filtered for the analyzed samples to estimate the weight of particulate matter in that sample. We were able to calculate the particulate matter concentration for 3–5 replicates for each river. The average values for the Danube, Kızılırmak and Yeşilırmak Rivers were low (1–3 mg l^{-1}) while the average values for the Yenice River (281 mg l^{-1}) and Sakarya River (429 mg l^{-1}) were high. The variability among the replicates was low and the resulting uncertainties on the particulate matter concentrations were ±10%.

To allow direct comparison with global reference data we examined the metal to Al ratios. Metal to Al ratios are a better way to compare results from different rivers (calculated using weight ratios in Fig. 2) because this ratio is less dependent of suspended matter concentration. These unitless ratios were all less than one (except for Fe in the Sakarya and Yenice Rivers). The Me/Al ratios decrease as the amount of total metal concentration decreases in the sample. The Mo/Al ratios are not shown for the Danube, Kızılırmak and Yenice Rivers due to low Mo concentrations in the samples.

Note that even though the Al and Ti concentrations were low in the Danube River suspended matter sample, the Ti/Al ratio was similar to the crustal value. The low concentrations of Al, Ti and Fe were probably because the sample was a combination of lithogenic and some additional biogenic material. The Me/Al ratios for Cu, Zn and Ba (biogenic elements) and Ag, Cd and Pb (pollution indicators) were especially high in the Danube River suspended matter sample.

6. Discussion

The rivers sampled in this study are representative of the total river flux to the Black Sea. Our goal was to define the lithogenic component entering the Black Sea so that we could identify the geochemical anomalies that exist under different redox conditions.

6.1. Comparison of metal concentrations

The solid phase compositions (ppm) for the Danube and Turkish rivers are compared with previous data from the Danube River (Guieu et al., 1998; Guieu and Martin, 2002), the world's average rivers (Martin and Windom, 1991) and global average crust and shale in Table 2. The comparison shows that the new data are generally in good agreement with historical data, though there was no previous Danube River data for Ti, Ba, Cr, V, Mo, U and Ag. Tuncer et al. (1998) analyzed Cd, Cu, Pb, and Zn in 24 different streams and rivers flowing into the Turkish Black Sea coast but they reported their values as fluxes rather than concentrations or ratios so it is not possible to compare their results with our data.

The individual and mean values for the Danube and Turkish rivers are plotted versus the average earth's crust (Taylor and McLennan, 1985, 1995) in Fig. 3. We used crust rather than shale because the regions where these rivers originate are geologically heterogeneous and are probably represented better by the crustal average than shale. The crust line is shown as a solid black line through the origin with a slope of 1. The data for the average Turkish rivers (individual values = black letters; average values = solid circles) tend to fall slightly higher than the crust line for elements with lower concentrations (e.g. Mn, Zn, V, Cr, Cu, Co, Mo, Cd and Ag). In many cases the differences from crust are negligibly small (e.g. Al, Fe, Ti, Ba, Pb, U). The regression fit to the average values for Turkish rivers has a slope less than one (0.88) reflecting the tendency for elements with low concentrations to be enriched relative to crust while those with high concentrations are equal to crust. The values for the Danube suspended matter (open squares), on the other hand, also have a slope less than one (0.64) but the enrichments for low concentrations are much higher and more variable. The elements with high concentrations (e.g. Al, Fe, Ti and U) are actually depleted relative to crust. Al, Fe, Ti, V and U were anomalously low and Zn, Cu, Pb, Ag and Cd were all anomalously high in the suspended matter sample but much more normal values in the surface sediment sample (open diamonds). The concentrations in the Danube River sediment sample were much more similar to the Turkish rivers and to average crust. We expect there would be exchange between suspended particles and surface sediment so either this does not occur or our suspended sample was contaminated or contained other material with low Al, Fe and Ti and high trace metal content.

Guieu and Martin (2002) reported that the Al, Ni, Cd, Co and Mn content of particulate matter in the Danube River and Danube River Plume was similar to uncontaminated world rivers. Evidence of contamination was seen for Cu and Pb. We observed low concentrations relative to crust for Al, U, Ti, Fe, V, Co (lowest to highest) in the suspended matter sample from the Danube River estuary (Fig. 3). The concentrations of Ba, Cu, Pb, Zn, Cd and Ag suggested contamination. Similar low values for Al, Fe and Co were seen by Guieu et al. (1998). They attributed these low concentrations to precipitation of dissolved metals as hydrated metal oxides as a consequence of relatively high pH (8.03–8.30) in the river water. The high pH values are due to the high values of alkalinity derived from weathering of carbonate rich source rocks (Guieu et al., 1998; Guieu and Martin, 2002).

6.2. Metal enrichments and depletions of river waters

Because the total sample can consist of materials from different origins, it is more convenient to compare the data using Me/Al ratios, rather than metal concentrations. These ratios are also a better way to compare results of different rivers because they are probably independent of suspended matter concentration. The Me/Al ratios for the Danube and Turkish river samples are shown as bar graphs with a log scale in Fig. 2. Horizontal dashed lines are drawn to indicate the ratio for average crust. The ratios for most elements for both the Turkish rivers and the Danube River were higher than the ratios in average crustal material. The values of Ba/Al and U/Al ratios were slightly lower than crust for the Kızılırmak and Yeşilırmak Rivers. These ratios suggest that suspended particles in these rivers are mostly enriched with respect to crust as can also be seen in Fig. 4. The enrichments are higher for the Danube suspended matter while the Danube sediments and the Turkish rivers were lower and in good agreement.

Among the Turkish rivers, the Sakarya and Yenice Rivers show the highest enrichments for Fe, Ti, V, Co, and U. Both the Sakarya and Yenice Rivers have very high amounts of particulate matter and they transport the products of erosion from the Anatolian highlands. Kızılırmak and Yeşilırmak Rivers have the lowest Me/Al ratios for all elements, except slightly higher values of Mn, Cu, Mo and Cd. On the other hand, the Danube River suspended matter has the highest Me/Al ratios relative to crust and the four Turkish rivers for Pb, Zn, Mn, Ba, Cu, Cr, Ag and Cd (from highest to lowest). The metal ratios in this sample were more than 100 times higher than those for crustal material for Ag, Pb, Cd, Zn; and more than 10 times higher than those for crustal material for Cu, Cr, Mn (Fig. 2).

Comparison of the Me/Al ratios for the Danube suspended matter and surface sediments and the four Turkish rivers with the ratios for the average world rivers (Martin and Windom, 1991) is shown in Fig. 5. The regressions for suspended matter from the Turkish rivers and Danube surface sediment were similar to that of the world average rivers. High ratios for Mn/Al, Fe/Al and Co/Al result in a regression with a slope slightly greater than one (1.10). The slope of the regression for the Danube suspended matter was about the same as for the average world rivers but is offset to higher concentrations by about an order of magnitude.

6.3. Anthropogenic effects

It is usually assumed that rivers entering the Black Sea should be polluted with heavy metals because countries in this region have few pollution control measures (Windom et al., 1998). Most of the available data are for the Danube and have resulted from the GEF Black Sea Environmental Program (Mee and Topping, 1998) and the European Union EROS project (Lancelot et al., 2002). These studies generally found that trace metal concentrations (especially dissolved) in the Danube River were lower than expected.

Literathy and Laszlo (1995) suggested that the mean concentrations of Cr, Cu, and Pb in Danube River bottom sediments were significantly higher at some locations because of natural processes. The metal enriched sediments had a higher percentage of the clay–silt size fraction, which has a higher surface area and metal sorbing capacity. Some indications of contamination were observed by Ricking and Tertyze (1999) for Danube River surface sediments. In some cases the sources of contamination could be identified. For example, shipyard activity was a source of Pb and metal processing factories were a source for Cd. Literathy and Laszlo (1999) found that some elements like Pb, Zn, Cu, Ag and Cd were especially high in samples from the three main branches of the Danube River delta and tributaries. This result is consistent with anthropogenic contamination (Gruiz et al., 1998). Guieu and Martin (2002), however, found that particulate concentrations of most trace metals were low and did not show evidence of contamination. The concentrations of Pb and Cu were higher than average 'world rivers' by factors of 3 and 14 respectively, suggesting contamination for those two elements from mining activity upstream and in the delta region. Woitke et al. (2003) suggested that suspended solids and sediments of the Danube River were unpolluted for Cr, Cu and only slightly polluted for Pb and Zn. However, contamination was significant for Cd, especially in the lower stretch of the river, below the Iron Gate Dam. Relatively constant or slightly decreasing levels of pollution were found in the lower part of the river in the Danube Delta. Unfortunately similar comparison with previous data for the Turkish rivers is not possible because there have been no previous studies.

Comparisons of individual concentrations (ppm) in our data set (Table 2) suggested that the concentrations of Zn, Cu, Pb, Ag and Cd were high in our Danube suspended matter sample. The data points for these elements also stand out as being anomalously high when the concentrations are compared with average crust (Fig. 3). While our single Danube sample is probably not representative of the river as a whole, it does suggest that hot spots may exist and thus the river merits more thorough study. Most of the average values for the Turkish rivers and our Danube sediment sample fall closer to the average crustal line, but the elements with the lowest concentrations (Ag, Cd, Mo Co, Cu and Cr) fall above the crustal line.

An indication of anthropogenic effects can be seen a little more clearly in the plots of Me/Al ratios in river particles versus the ratios in the crust (Fig. 4) and average world rivers (Fig. 5). The slope through the ratios for average Turkish rivers and Danube sediments are similar to crust but shifted to higher values. The ratios for the Danube suspended sample are significantly higher for all elements (except U), especially those with low concentrations. Our Danube River suspended matter sample was especially enriched in Ag, Pb, Zn, Cd, Cu, Cr and Mn. The first five elements in particular are well known indicators of pollution. These high Me/Al ratios in our Danube suspended matter sample suggests that this sample was more contaminated than the samples from the Turkish rivers. Otherwise the Danube sediment and Turkish river suspended matter are in quite good agreement with the average world's rivers (Martin and Windom, 1991) (Fig. 5).

7. Conclusions

The assumption of using the average crust or shale values as a lithogenic reference in the Black Sea was tested. The crust composition, rather than shale, was used as the reference for most of the data analysis because the Black Sea catchment area is geologically heterogeneous and is better represented by a more diverse set of source rocks which crust represents.

The original question that initiated this study was what would be the best way to characterize the lithogenic component of particulate matter in the Black Sea? Should we use average crust, average world's rivers particulate matter or the composition of particulate matter from local rivers entering the Black Sea? The composition of crust and world's rivers is actually quite similar and could be used interchangeably for most elements. The solid phase concentrations for Danube River sediments and Turkish rivers suspended matter agree with each other quite well and both have elevated compositions relative to crust, especially for trace elements. These elevated concentrations could be due to either natural variability in the source rocks or to contamination. When viewed as Me/Al ratios the Danube sediments and the Turkish rivers suspended matter are very similar to both crust and world rivers. The largest anomalies are for the Danube suspended matter and may be of anthropogenic origin. Being as we only had one sample of suspended matter from the Danube, and because the surface sediment sample did not contain the same anomalous values, we conclude that until we know more about the composition of particulate matter from the Danube River, we should consider the average of the Danube sediment and Turkish suspended matter as the best reference for terrigenous lithogenic material added to the Black Sea.

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