



Potentially toxic element levels in the Eocene sandstones from Gümüşhane area (NE Turkey)

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Abstract

The aim of this study, the level of potentially toxic elements (Zn, Cu, Sc, Co, Pb, Ni, As, Hg) was determined in Eocene sandstone samples in Gümüşhane area (NE Turkey). The potentially toxicity of studied elements was defined by evaluating enrichment factor (EF) and geo-accumulation index (*I_{geo}*). On average, the potentially toxic elements follow a decreasing concentration order, that is, Zn>Cu>Sc>Co>Pb>Ni>As>Hg in the Eski Gümüşhane section and Zn>Ni>As>Pb>Cu>Sc>Co>Hg in the Kelkit section in Gümüşhane area. A positive correlation exists between total organic carbon (TOC) and Ni, Hg in study area. The As, Ni and Hg are particularly enriched in sandstone samples. The sandstone samples were unpolluted to moderately polluted by Cu, Pb, Zn, Co, Ni, Sc, Hg and moderately polluted by As. The high As levels in the Eocene sandstone samples from Gümüşhane area probably originated from agricultural activities. Proper measures should be taken by authorities to ensure appropriate use of fertilizer and insecticides.

Keywords: Plastic injection parameters, genetic algorithm, response surface methodology, finite element analysis.

1. Introduction

Geochemical study of siliciclastic rock has been performed broadly to comprehend the perspectives of weathering, provenance, tectonic setting, paleoclimate, erosion and fluvial processes, the evolution of the lithological and anthropogenic impact on the environment [1-11]. The chemical composition of siliciclastic sedimentary rocks is controlled by some factors, such as nature and extent of weathering of the source rocks, source rock composition, recycling and sedimentary sorting, and post-depositional changes during metamorphism and diagenesis [1, 12-14] and anthropogenic activities, such as agricultural activities, industrial wastes. Therefore, the level of potentially toxic element in siliciclastic sedimentary rocks depends on geological sources and anthropogenic activities. Potential toxic element levels arising from anthropogenic activities and natural geological sources may increase in

sediments over time. Anthropogenic activities exchange the biogeochemical cycle of many elements, significantly potentially hazardous elements. Their concentrations in the environment modify particularly, in part in relation to geologic settings and partly due to anthropogenic activities [15-17]. Potentially hazardous elements in sediments can be connected to atmospheric deposition, geological weathering and erosion, and chemicals originating from different agricultural.

The aim of this study, the level and distribution of potentially toxic elements (Sc, Zn, Pb, Cu, Co, Ni, As, Hg) were determined in Eocene sandstone samples in Gümüşhane area (NE Turkey), and if the samples are enriched with potentially toxic elements, it is to reveal the possible source of these elements.

2. Geological setting

The basement rocks of the Gümüşhane area consist of metamorphic rocks, including both low and high-grade lithologies such as gneiss, migmatite, schist, amphibolite, marble and phyllite and granitoids [18-23]. Early- Middle Jurassic volcanics, volcanoclastic, and clastic deposits, including conglomerate, red

limestones, sandstones, siltstones, marl, lie disconformable on this basement rocks and called as Şenköy Formation [24]. This unit is overlain by Malm-Lower Cretaceous aged Berdiga Formation [25] characterized as pelagic and neritic carbonates. The Upper Cretaceous, known as the Kermodere

Formation [26], consists of micritic limestone, sandy limestones and turbiditic facies in Gümüşhane area [9]. Eocene age rocks [27, 28] in Gümüşhane region are composed of volcanic, volcano-sedimentary and siliciclastic rocks, including sandstones, limestones,

marls, and called as Alibaba Formation [26], units that contain coal [29] in various places. This sequence is widespread in the region and discordantly overlies the older rocks (Figure 1).

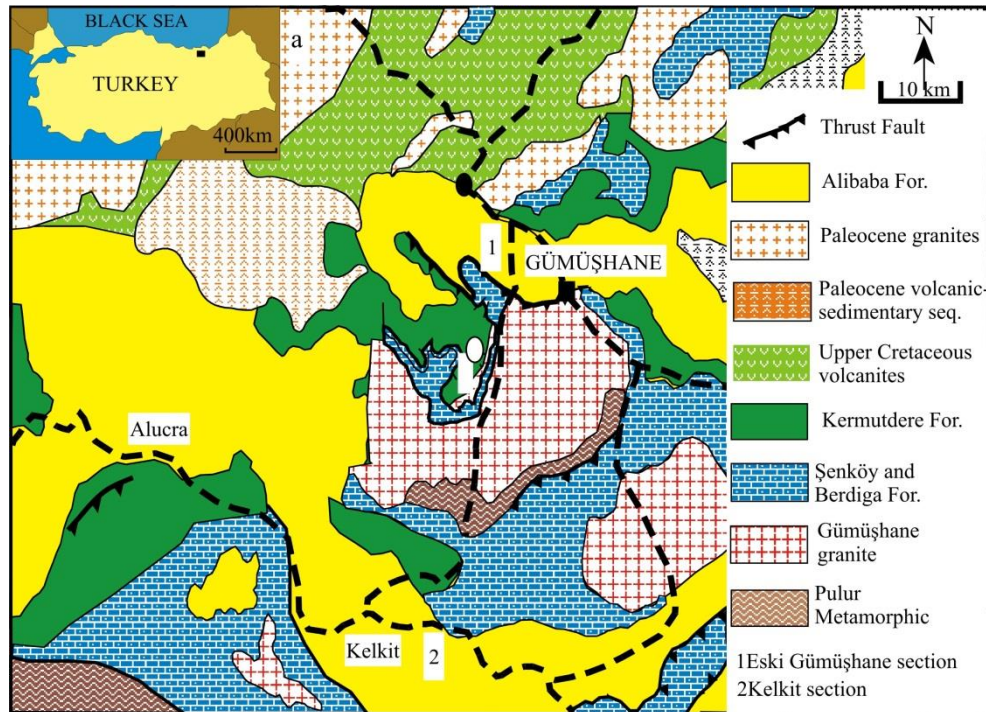


Figure 1. Simplified geological map of the Gümüşhane and its surroundings (after [30]), and location map of the study areas.

3. Materials and methods

3.1. Lithology and sedimentology features

Eocene age volcanoclastic deposit lies over Upper Cretaceous units with turbiditic characteristics in Gümüşhane region with discordance. Stratigraphic section of Eski Gümüşhane (Gümüşhane) was measured around Venk Yayla. Based on data obtained from field surveys, deposit starts with grey colored thick layered limestone at the base and is sequenced upward with thin-thick layered, dark grey, brown colored sandstones, thin-thick layered grey, green, yellowish brown colored marl-claystone and tuff (Figure 2a). Eocene age sedimentary rocks in Kelkit (Gümüşhane) region are composed of siliciclastic turbidities. Deposit comes over Cretaceous age turbiditic characteristic rocks of this

region with discordance. Kelkit (Gümüşhane) measured stratigraphic section was taken around north of Kelkit town. Field surveys indicate that the unit in the region starts with grey colored, coarse grained, medium layered sandstone and similar characteristics continue up to top. Later comes a very thin-medium layered yellowish brown colored sandstone over it. It is then sequenced upward with thin-thick layered, light grey, brown colored sandstone, and thin, medium layered, green, greenish grey, yellowish brown marl (Figure 2b). The thickness of the Eocene deposits is measured as 195 m in Eski Gümüşhane and 280 m in Kelkit [31].

3.2. Analytical techniques

Trace elements were determined at the commercial Acme Analytical Laboratories Ltd. in Vancouver, Canada. The trace element compositions were measured by inductively coupled plasma optical emission spectrometry and inductively coupled plasma mass spectrometry (ICP-MS) using 0.2 g of

rock powder fused with 1.5 g of LiBO_2 dissolved in 100 mL of 5% HNO_3 . Ignition loss was determined using dried samples heated to a temperature of 1,000 °C for 15 min. The detection limits were in the range of 0.1 ppm to 10 ppm for trace elements. Calibration and verification standards together with reagent

blanks were added to the sample sequences. STD SO-18 was certified in-house against 38 certified reference materials, including CANMET SY-4 and USGS AGV-1, G-2, GSP-2, and W-2 as known external standards. The analytical accuracy is better

than 4%. Trace element analyses were separately applied to 16 sandstone samples (i.e., Eski Gümüşhane section =6, Kelkit section = 10) in this study.

3.3. Statistical analysis

Relationship analyses were directed according to the non-normal distribution of the data. The Spearman’s relation matrix is used with a statistical software

SPSS 15.0. Data detail was used through Microsoft Office Excel 2013.

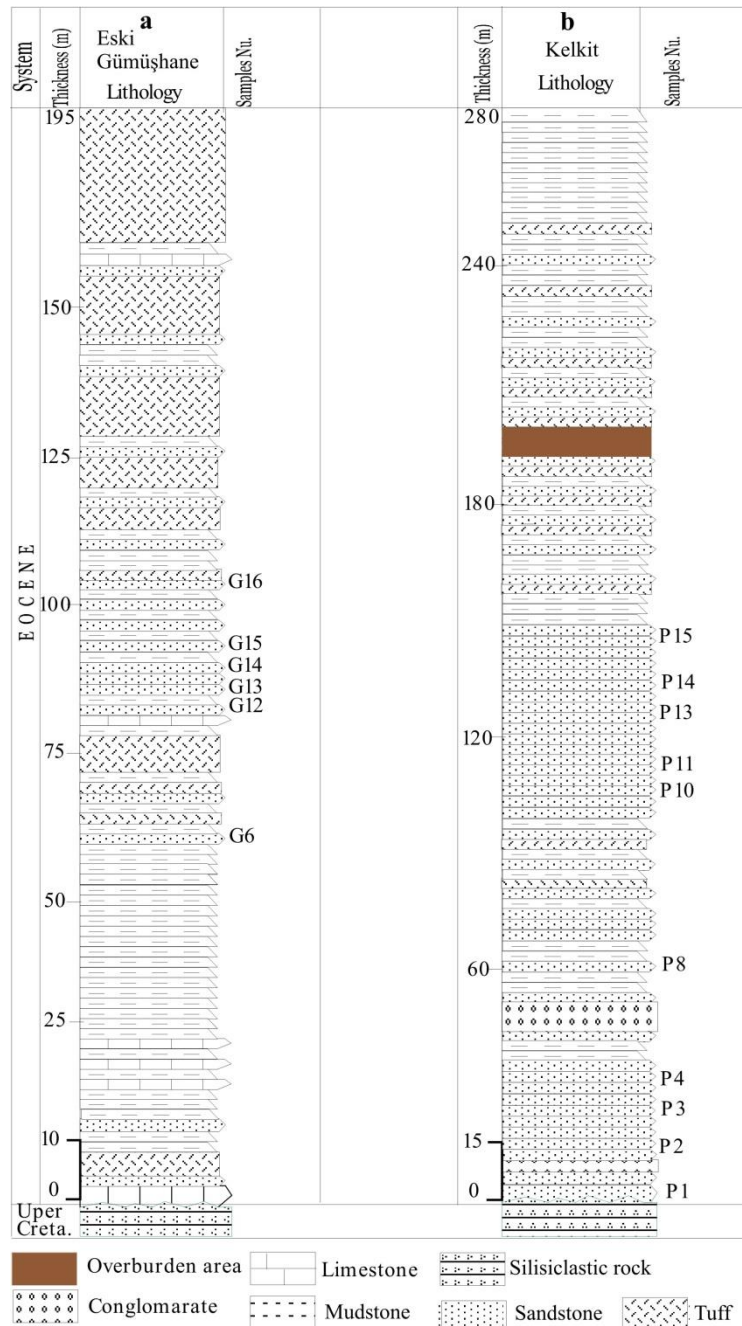


Figure 2. Stratigraphic section of Eocene deposits.

4. Results and discussion

4.1. Geochemistry

4.1.1. Existence and distribution of potentially toxic elements Eocene-aged sandstones from Gümüşhane area

The values and spatial distribution patterns of the studied potentially toxic elements are given in Table 1. On mean, the toxic elements follow a decreasing concentration order, that is, Zn>Cu>Sc>Co>Pb>Ni>As>Hg in the Eski

Gümüşhane section and Zn>Ni>As>Pb>Cu>Sc>Co>Hg in the Kelkit section in Gümüşhane area.

Table 1. Potential toxic element levels, Al/Si ratios and TOC values of Eocene sandstones in the Gümüşhane area.

Sample	SiO ₂ *	Al ₂ O ₃ *	Al/Si	TOC*	Cu	Pb	Zn	Co	As	Ni	Sc	Hg
Eski Gümüşhane section												
G6	51	16	0.3	1.2	22	5.6	34	12	1.2	5.4	15	.01
G12	53	16	0.3	0.6	36	7.4	54	20	10	9.2	18	.02
G13	53	16	0.3	1.1	24	6.5	38	13	2.3	5.8	14	.01
G14	50	16	0.3	1.4	22	5.7	38	12	2.5	3.9	15	.02
G15	50	16	0.3	0.9	33	11	59	22	19.1	7.8	20	.03
G16	58	18	0.3	0.2	46	7.9	45	14	3.3	4.1	16	.01
Mean	52	16	0.3	1.0	29	7.0	42	13	2.9	5.6	16	.02
Kelkit section												
P1	61	12	0.18	2.2	8.1	8.4	38	6.9	8.2	13.7	7	.13
P2	53	8	0.16	3.9	7.7	6.5	30	6	7.9	13.8	6	.08
P3	59	10	0.17	2.7	7.5	7.7	33	4.7	11	12.5	7	.10
P4	59	10	0.17	2.7	7.2	7.6	32	7.5	8.1	16.4	7	.04
P8	59	9	0.16	2.6	6.4	8.3	30	6.2	7.4	12.2	6	.04
P10	65	9	0.14	2.1	6.3	7.2	23	4.1	12	10.4	6	.10
P11	60	9	0.16	2.7	7	8.8	34	9.2	8.6	14.7	6	.06
P13	64	9	0.14	2.1	7	6.5	25	4.5	15	10.3	6	.12
P14	60	8	0.14	2.8	5.9	6.5	23	4	7.2	13.3	6	.05
P15	66	8	0.13	2.1	6.6	8.4	24	5.2	11	12.3	6	.08
Mean	60	9	0.16	2.7	7.0	7.7	30	5.6	8.4	12.9	6	.08

* [31]

Zinc

Zinc in the sediment derives from natural rock composition of surrounding areas and originates from human activities, such as pesticides, phosphate fertilizers, air-conditioning, swage, wood combustion, ducts and sludge [32].

Natural background levels of Zn are generally detected up to 100 ppm in sediments [33-35]. In this study, Zn values range from 34 mg/kg to 59 in the Eski Gümüşhane section and from 23 mg/kg to 38 mg/kg in the Kelkit section in Gümüşhane area (Table 1). The highest mean Zn value is observed in the Eski Gümüşhane section (Figure 3a). Zn exhibits a positive correlation with Al₂O₃, Cu, Pb, Co, Sc, Al/Si and a negative correlation with SiO₂, TOC, Ni, Hg in the samples. This indicates that the presences of Zn in the studied area are controlled by geological sources and clay minerals. In addition to, grain size

controlled for the presence of Zn in the investigated sandstones because it was found a general increase in Zn content with Al/Si, as sediments become finer [36].

Nickel

Nickel is originated from natural rocks and anthropogenic activities, such as metal plating, lubricating oil, diesel fuel, brushing wear, phosphate fertilizers and brake lining wear [32].

Nickel values change between 3.9 and 9.2 mg/kg in the Eski Gümüşhane section and 10.3 16.4 mg/kg in the Kelkit section in Gümüşhane area (Table 1). The highest mean Ni value is observed in the Kelkit section (Figure 3b). Ni shows a positive correlation with SiO₂, TOC, Hg, and a negative correlation with Al₂O₃, Cu, Zn, Co, Sc, Al/Si in Gümüşhane area (Table 2). The presences of Ni are probably

controlled by organic matter, geological sources in Gümüşhane area.

Arsenic

Sources of As in the sediment are natural rock composition and human activities, such as industrial emission, coal burning, waste materials, and use of As-rich phosphate fertilizers [37].

Arsenic is defined in Gümüşhane area in the range of 1.2 mg/kg to 19.1 mg/kg in the Eski Gümüşhane

section, 7.2 mg/kg to 15.2 mg/kg in the Kelkit section (Table 1). The highest mean As value is followed in the Kelkit section (Figure 3c). The As shows a positive correlation with SiO₂, Pb, Hg and a negative correlation with Al₂O₃, Al/Si in Gümüşhane area. The enrichment of As was mainly related to anthropogenic factor and partly geological sources in the studied area. The anthropogenic sources of As are waste materials, coal burning, industrial emission, and use of As-rich phosphate fertilizers [37].

Table 2. Correlation coefficients (r) from the correlation matrix obtained using geochemical data from the Gümüşhane area (n=16 for studied sandstones) **Correlation is significant at the 0.01 level, * is significant at the level 0.05).

	SiO ₂	Al ₂ O ₃	Al/Si	Cu	Pb	Zn	Co	As	Ni	Sc	Hg	TOC
SiO ₂	1											
Al ₂ O ₃	-.59**	1										
Al/Si	-.85**	.88**	1									
Cu	-0.72**	.81**	.85**	1								
Pb	.27	-.09	-.14	-.02	1							
Zn	-.67**	.82**	.87**	.92**	.23	1						
Co	-.74**	.79**	.84**	.88**	.17	.93**	1					
As	.44	-.44	-.42	-.24	.52*	-.16	-.26	1				
Ni	.47	-.68**	-.59*	-.57*	.35	-.46	-.51*	.29	1			
Sc	-.71**	.88**	.91**	.90**	-.01	.89**	.85**	-.17	-.63**	1		
Hg	.73**	-.72**	-.69**	-.61*	.26	-.56*	-.75	.65**	.64**	-	1	
TOC	.36	-.76**	-.60*	-.72**	.03	-.69**	-.66**	.03	.87**	-	.56*	1

Copper

Sources of Cu in the sediment are natural rock composition of surrounding areas and human activities, such as phosphate fertilizers, fungicides and insecticides, antifoulants and metal plating [32]. Copper ranges from 21.5 mg/kg to 46.2 mg/kg in the Eski Gümüşhane section, from 5.9 mg/kg to 8.1 mg/kg in the Kelkit section (Table 1). The Cu shows a high variation and heterogeneous distribution in the Eski Gümüşhane section and the highest average Cu value is observed in this section (Figure 3d). A positive correlation exists between Cu and Al₂O₃, Zn, Co, Sc, Al/Si and a negative correlation exists between Cu and SiO₂, TOC, Ni, Hg in study area (Table 2). The presences of Cu are probably controlled by geological sources and clay minerals in study area. The Al/Si ratio values of the examined samples exhibit a positive correlation with Cu in the Gümüşhane area (Table 2). This indicated that grain size controlled for the presence of Cu in the studied samples.

Lead

Lead is a toxic element, and is released from natural and anthropogenic activities, such as automobile

exhaust, phosphate fertilizers, insecticides, and sewage sludges [32].

Lead values were measured between 5.6 mg/kg and 10.9 mg/kg in the Eski Gümüşhane section, between 6.5 mg/kg and 8.8 mg/kg in the Kelkit section (Table 1). The Pb shows a low variation in the investigated samples. The highest mean Pb value is observed in the Kelkit section (Figure 3e). Pb exhibits a positive correlation with As, Ni in the samples (Table 2).

Cobalt

Cobalt is released from geological composition of surrounding areas and potential anthropogenic sources of Co are vehicular emission, plastic manufacturing, gasoline combustion and industrial emission.

Cobalt values change between 11.8 mg/kg and 22.1 mg/kg in the Eski Gümüşhane section, between 4.0 mg/kg and 9.2 mg/kg in the Kelkit section (Table 1). The highest mean Co value is observed in the Eski Gümüşhane section (Figure 3f). The Co shows a positive correlation with Al₂O₃, Cu, Zn, Sc, Al/Si and a negative correlation with SiO₂, TOC, Ni, Hg in sandstone samples (Table 2). The presences of Co are probably controlled by geological sources, clay

minerals and grain size in the sandstone samples.

Scandium

Scandium in the sediments come from commonly the natural rock composition of surrounding areas.

Scandium values range from 14 mg/kg to 20 in the Eski Gümüşhane section from 6 mg/kg to 7 mg/kg in the Kelkit section (Table 1). The Sc shows a low variation and homogeneous distribution at the samples belonging to each section, and the highest mean Sc value is followed at the Eski Gümüşhane section (Figure 3g). Sc exhibits a positive correlation with Al₂O₃, Cu, Zn, Co, Al/Si and a negative correlation with SiO₂, TOC, Ni, Hg in study area (Table 2). This indicates that the presences of Sc in the studied area are controlled by geological sources, clay minerals and grain size.

Mercury

Mercury is released from natural rock composition and widely in agricultural activities, such as phosphate fertilizers, insecticides.

Mercury values were measured between 0.01 mg/kg and 0.03 mg/kg in the Eski Gümüşhane sections, between 0.04 mg/kg and 0.13 mg/kg in the Kelkit section (Table 1). The Hg exhibits a low variation and homogeneous distribution at the studied samples belonging to each section and the lowest mean Hg value is observed in the Eski Gümüşhane section (Figure 3i). The Hg exhibits a positive correlation with SiO₂, TOC, As, Ni and a negative correlation with Al₂O₃, Cu, Zn, Co, Sc, Al/Si in study area. This indicates that the presences of Hg in Gümüşhane area are controlled by geological sources and organic matter (Table 2).

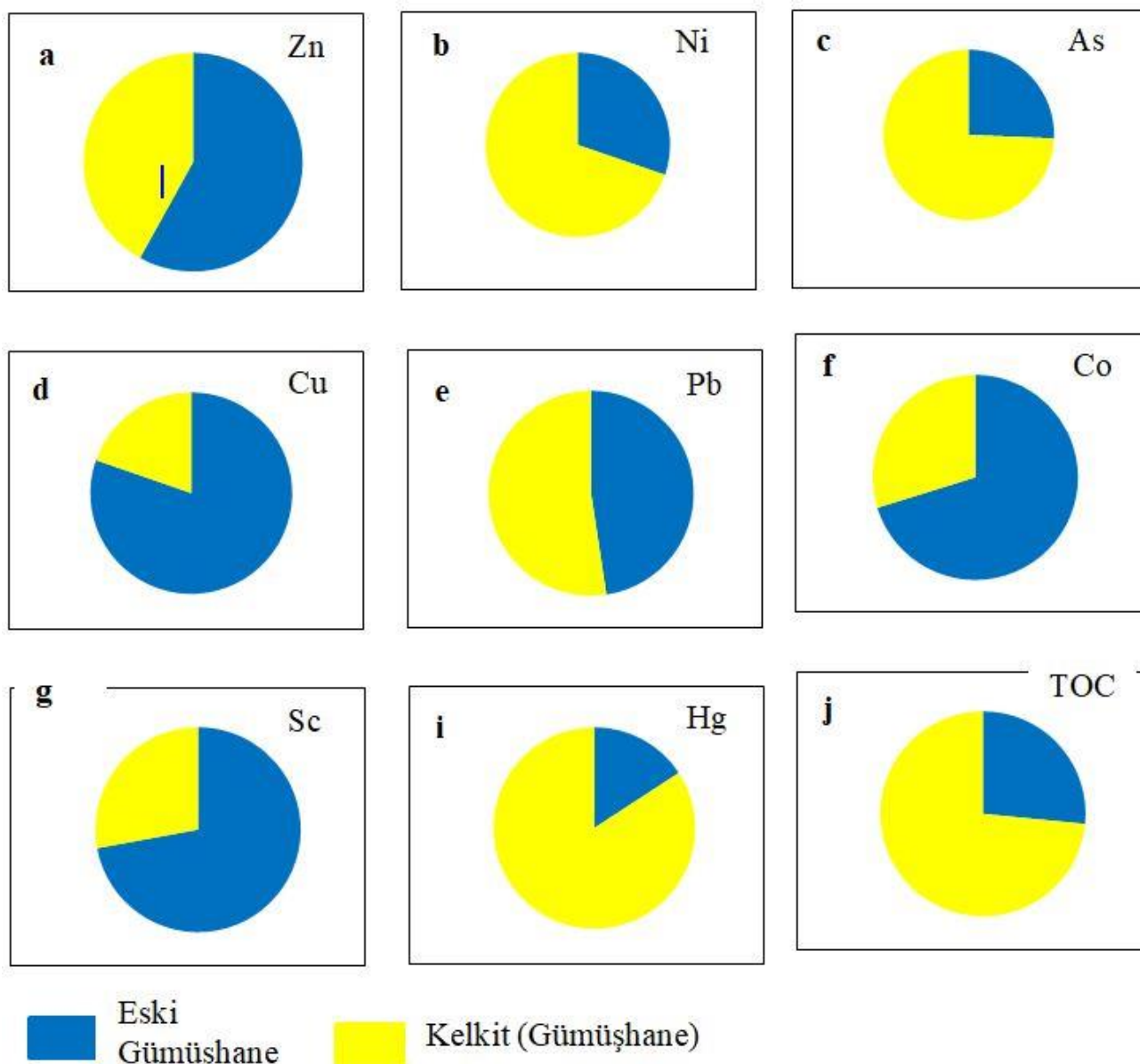


Figure 3. Potentially toxic elements distribution in the Eski Gümüşhane and Kelkit sandstones samples of Eocene sequence.

4.2. Estimation of pollutant indicators

4.2.1. Enrichment factor

The enrichment factor (EF) is generally used as a suitable approach to effective tool to evaluate the magnitude of contaminations in the environment based on the use of a normalization element to lighten the variations produced by heterogeneous sediments [34- 35, 38-39]. Toxic element concentrations were normalized to the textural property of sediments with respect to Sc, which is used as reference material. The EF is utilized to identify the changes in sediment composition and is calculated as follows:

$$EF = \frac{\left(\frac{C_{Element}}{C_{Scandium}}\right)_{Sediment\ sample}}{\left(\frac{C_{Element}}{C_{Scandium}}\right)_{UCC}}, \quad (1)$$

where $\left(\frac{C_{Element}}{C_{Scandium}}\right)_{Sediment\ sample}$ is the ratio of the content of the analyzed element to that of Sc as a reference element in the studied sample and $\left[\left(\frac{C_{Element}}{C_{Scandium}}\right)_{UCC}\right]$ is the ratio of the content of the analyzed element to that of Sc as a reference element

in the UCC [1].

The EF values of potentially toxic elements in the studied samples are given in Table 3. The results show that the EF for As, Co are between 1 and 3 (minor enrichment), Cu, Pb, Zn, Ni and Hg <1 (no enrichment) in the Eski Gümüşhane section, for As are between 10 and 25 (severe enrichment), Hg are between 3 and 5 (moderate enrichment), Co, Ni 1 and 3 (minor enrichment), Cu, Pb, Zn <1 (no enrichment) in the Kelkit section (Table 3). The high EF values for the potentially toxic elements demonstrate that this element input was due to anthropogenic activities, which can release certain amounts of As and Hg in the sandstones in Kelkit section (Figure 4). Insecticides and weed killers are identified as sources of As contamination in agricultural areas and in the vicinity of Kelkit, intensive agricultural activities are being carried out. In the examined samples, Hg correlates with both organic matter and arsenic, so Hg probably originated from organic matter.

Table 3. Enrichment factor (EF) for potential toxic elements in the studied sandstones and average upper continental crust.

	Zn	Ni	As	Cu	Pb	Co	Hg	EF	Enrichment level ^b	
EF average values										
Eski	0.42	0.20	2.60	0.81	0.24	1.03	0.27	EF<1	No enrichment	
Gümüşhane									EF=1-3 EF=3-5	Minor enrichment Moderate enrichment
Kelkit	0.72	1.13	11.26	0.49	0.66	1.02	3.49	EF=5-10 EF=10- EF=25-	Moderately severe Severe enrichment Very severe	
UCC ^a values	71	20	1.5	25	20	10	0.04	EF>50	Extremely severe	
^a [1] ^b [40]										

4.2.2. Geo-accumulation index

The geo-accumulation index (I_{geo}) for the toxic element concentrations was calculated by utilizing the following formula defined by Müller [41-42] and subsequently modified by Aiman et al. [43]. with respect to the log base:

$$I_{geo} = \log_2 \left[\frac{(C_n)}{(1.5)(B_n)} \right] \quad (2)$$

where C_n is the measured concentration of toxic Table 4. The I_{geo} classes for the eight analysed potentially toxic elements for each sample location are listed in Table 4. The I_{geo} values for Pb, Ni, Hg were < 0 for Eski Gümüşhane section and for Cu, Pb, Zn, Sc < 0 for Kelkit, which show that the sandstones

element n (mg/kg) in the studied sample, B_n is the geochemical background value (mg/kg) of the element in the background sample, and factor 1.5 is utilized to minimize the influence of possible variations in the background values that may be connected to lithogenic effects. The crustal abundance data of Turekian and Wedepohl [44] were used as background data. The I_{geo} values were commented using the classification of Abraham and Parker [45], which is supplied in

were unpolluted these elements. The I_{geo} values for Cu, Zn, Sc were between 0 and 1 for Eski Gümüşhane section, which indicate that the sandstones were unpolluted to moderately polluted by these elements. The I_{geo} values for Co were

between 1 and 2 for Eski Gümüşhane, which show that the investigated sediments were moderately polluted by Co. The I_{geo} values for As were between 2 and 3 for Eski Gümüşhane and Kelkit section,

which indicate that the sandstones were moderately to strongly polluted by As in the Gümüşhane area (Figure 5).

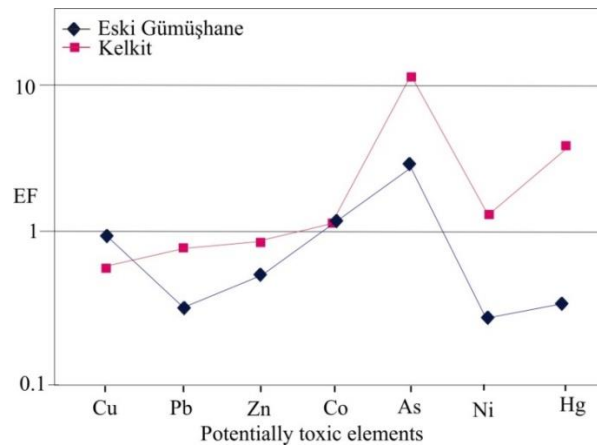


Figure 4. Comparison of EF for potentially toxic elements in the Eski Gümüşhane and Kelkit sections.

Table 4. Index of geo-accumulation (I_{geo}) for potential toxic elements in the studied sandstones and average background values.

Studied sections	Zn	Ni	As	Cu	Pb	Co	Sc	Hg	I_{geo} value ^b	I_{geo} class ^b	Pollution level ^b
Eski Gümüşhane	0.1	-	2.	0.61	-	1.73	0.89	-	≤ 0	0	Unpolluted
	6	0.73	33		0.45			4.97	0-1	1	Unpolluted to moderately polluted
Kelkit	-	0.37	2.	-	-	0.32	-	0.59	1-2	2	Moderately polluted
	0.4		97	1.52	0.40		0.57		2-3	3	Moderately to strongly polluted
	5								3-4	4	Strongly polluted
									4-5	5	Strongly to very strongly polluted
									>5	6	Very strongly polluted
Background values ^a	60	15	1.9	30	15	7	14	0.08			

^a [44], ^b [41]

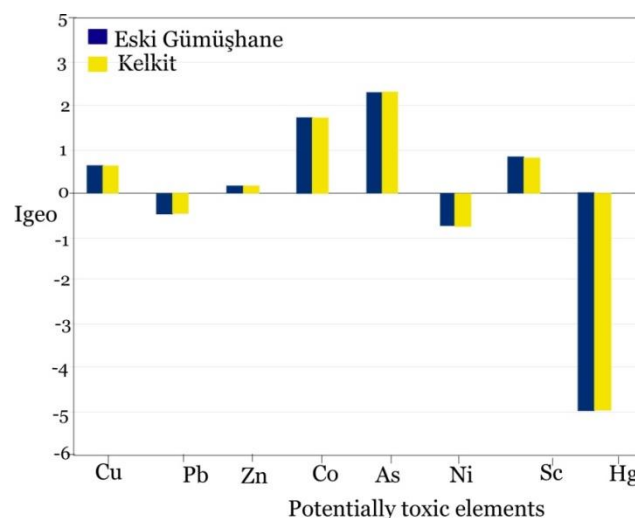


Figure 5. Comparison of I_{geo} for potentially toxic elements in the Eski Gümüşhane and Kelkit sections.

4.3. Spatial distribution of potentially toxic elements in Eocene sandstones from Gümüşhane area

The pollution levels of Gümüşhane area are exhibit in Figure 6. The average EF value for As of the Eski Gümüşhane section is 2.60 and the I_{geo} value is 2.33. The average EF value for As of the Kelkit section is 11.26 and the I_{geo} value is 2.97, which reflect the

moderate levels of anthropogenic pollution (agricultural activities). The investigated sandstones were unpolluted by Zn, Cu, Pb, Co, Sc and Hg elements in Gümüşhane Eocene sandstones.

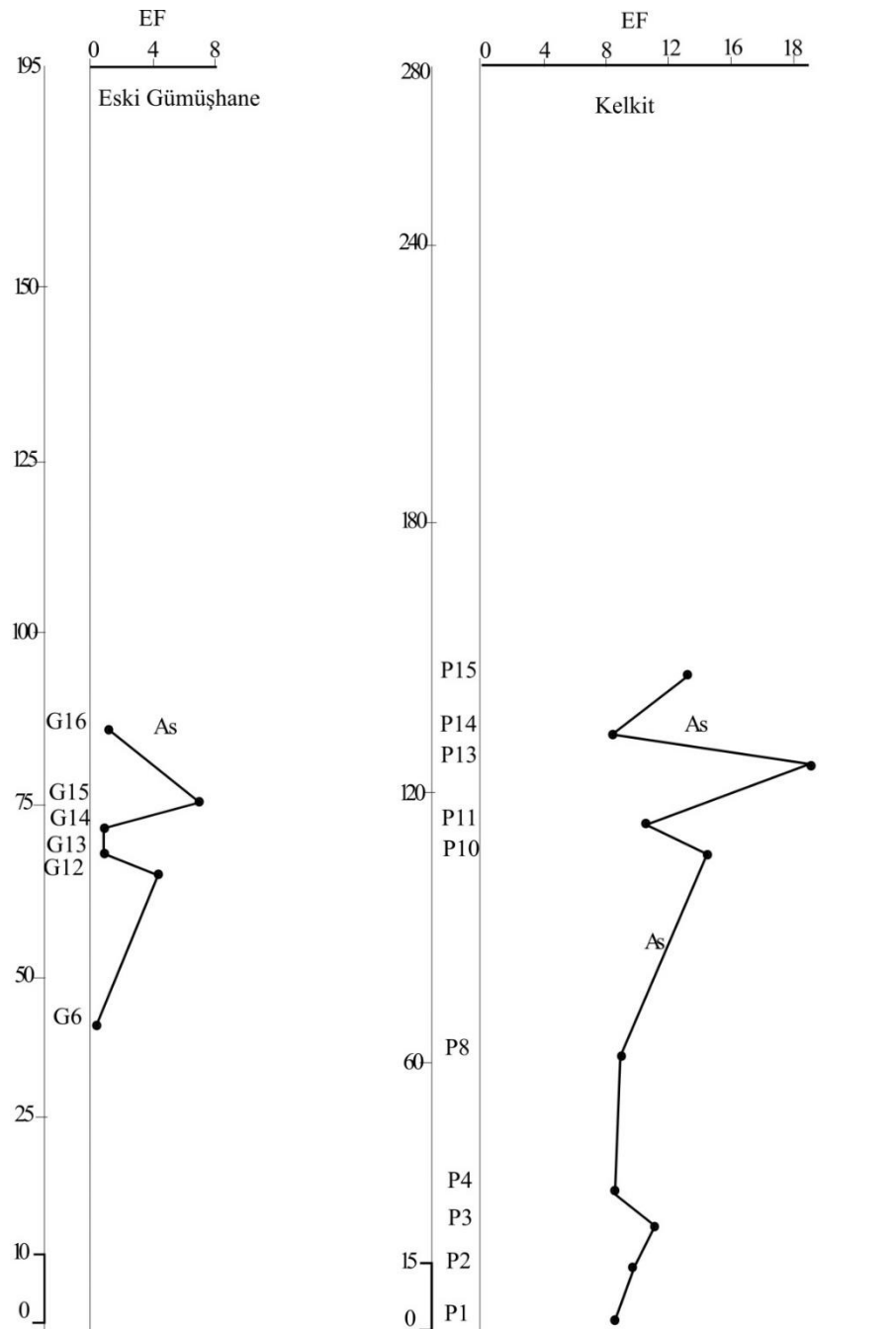


Figure 6. Polluting element (As) distribution in the Eski Gümüşhane and Kelkit sandstones samples of Eocene sequence.

5. Conclusions

The main goal of this study was to assess the levels of potentially toxic elements and possible sources of

Eocene age sandstones in Gümüşhane area.

The highest mean Zn, Cu, Sc, Co values are observed in the Eski Gümüşhane section and the highest mean Ni, As, Pb, Hg value is observed in the Kelkit section (Gümüşhane).

The EF for As is minor – severe enrichment in the sandstone samples in Gümüşhane area. According to *Igeo* values, the sandstone samples of Gümüşhane area were moderately polluted by As.

The high levels of the As in Gümüşhane area are due to anthropogenic pressure; indeed, human influence related to agricultural activities, such as fertilization and insecticides, and might create and adverse effect on the ecosystem. To avoid this, the use of chemicals for agricultural purposes should be strictly controlled. The fertilizer type and amount required by the soil should be determined and applied at the appropriate time.

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