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Research Article

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Determination of Metal Concentrations in Değirmendere Stream Drainage Area of Southeastern Black Sea Coast of Turkey

Değirmendere Deresi'nin (Güneydoğu Karadeniz-Türkiye) Drenaj Alanında Metal Derişimlerinin Belirlenmesi

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ABSTRACT

This study aims to determine the metal concentrations and enrichment levels in the drainage area of the Değirmendere Stream located Southeastern Black Sea coast of Turkey. Sediment samples were collected with Ekman grab from five stations in three periods. Aluminum (Al), Vanadium (V), Chrome (Cr), Manganese (Mn), Iron (Fe), Cobalt (Co), Nickel (Ni), Copper (Cu), Zinc (Zn), Arsenic (As), Cadmium (Cd) and Lead (Pb) concentrations in the sediment samples were measured with ICP-MS after digestion with a microwave system. Differences in metal concentrations between the stations were not statistically significant (p>0.05). However, the concentration of many metals (Fe, Mn, Co, Ni, Cu, Zn, V) in station 1 at the river mouth was relatively higher than the others. The enrichment factor (EF) by normalized with aluminium were 1.5-2.1 for V; 0.6-1.0 for Cr; 0.8-1.7 for Mn; 1.1-1.7 for Fe; 1.1-2.0 for Co; 0.4-0.9 for Ni; 1.3-2,3 for Cu; 1.4-3.9 for Zn; 0.8-1.4 for As; 0.5-4.1 for Cd and 0.9-4.2 for Pb. Moderate enrichments were observed for Cu Zn, Pb in the some stations.

Key Words

Değirmendere stream, drainage area, sediment, metal enrichment.

ÖZ

Bu çalışmanın amacı Güneydoğu Karadeniz'in Türkiye kıyılarında denize boşalan Değirmendere deresinin drenaj alanında sedimentteki metal derişimlerinin ve zenginleşme düzeylerinin belirlenmesidir. Çalışmada 5 ayrı istasyondan üç arklı mevsimde yüzey sediment örnekleri Ekman Grap kullanılarak alınmıştır. Sedimentteki V, Cr, Mn, Co, Ni, Cu, Zn, As, Cd, Pb, Al ve Fe derişimleri mikrodalga sistemde çözünürleştirildikten sonra ICP-MS ile ölçülmüştür. Metal derişimleri açısından istasyonlar arasındaki farklılık istatistiksel olarak anlamlı düzeyde değildir (p>0.05). Ancak nehir ağzına yakın konumda bulunan 1 nolu istasyonda bazı metallerin (Fe, Mn, Co, Ni, Cu, Zn, V) derişimleri diğer istasyonlardan nispeten daha yüksek bulunmuştur. Aluminyum normlizasyonu sonucunda tespit edilen zenginleşme düzeyleri V için 1.5-2.1; Cr için 0.6-1.0; Mn için 0.8-1.7; Fe için 1.1-1.7; Co için 1.1-2.0; Ni için 0.4-0.9; Cu için 1.3-2.3; Zn için 1.4-3.9; As için 0.8-1.4; Cd için 0.5-4.1 ve Pb için 0.9-4.2 aralığında bulunmuştur. Bazı istasyonlarda Cu, Zn ve Pb elementlerinin orta derecede zenginleşme gösterdiği tespit edilmiştir.

Anahtar Kelimeler

Değirmendere Deresi, Drenaj alanı, sediman, metal zenginleşmesi.

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INTRODUCTION

The Black Sea ecosystem is rapidly varying due to anthropogenic activities and climatic change. The pressures on coastal ecosystems through excessive nutrient release, chemical pollution, alteration of river regimes, dams and land reclamation are increasing day by day. Chemical pollution in coastal areas is one of the biggest problems for the ecological sustainability of coastal ecosystems and negatively affects the biotic and abiotic environment.

The determination of the current state of the ecosystem is vital to reveal the level of chemical pollution. Heavy metals are regarded as one of the leading environmental pollutants affecting environmental quality [1]. As widespread, persistent contaminants, heavy metals are hazardous and possess potential ecological risks to living organisms due to their toxicity, non-degradable, and bioaccumulation characteristics [2, 3]

Heavy metal pollution is of widespread concern for the ecological management of aquatic ecosystems. Both anthropogenic pressures (e.g. industrial activities, mining, and urban runoff) and natural processes (such as weathering) account for heavy metals in aquatic ecosystems [4, 5].

Heavy metals like chromium (Cr), lead (Pb), zinc (Zn), copper (Cu), nickel (Ni), arsenic (As), cadmium (Cd) are the most critical elements among the frequently observed contaminants in sediments. Both industrial activities and the level of urbanization are greatly responsible for the heavy metal increase in the environment [6].

Sediment has an accumulation area of heavy metals in marine environments. For this reason, sediment provides an indicator function in the determination of heavy metal pollution in aquatic environments. The material input from terrestrial area to aquatic environments through rivers makes a generous contribution to the sediment layer [7].

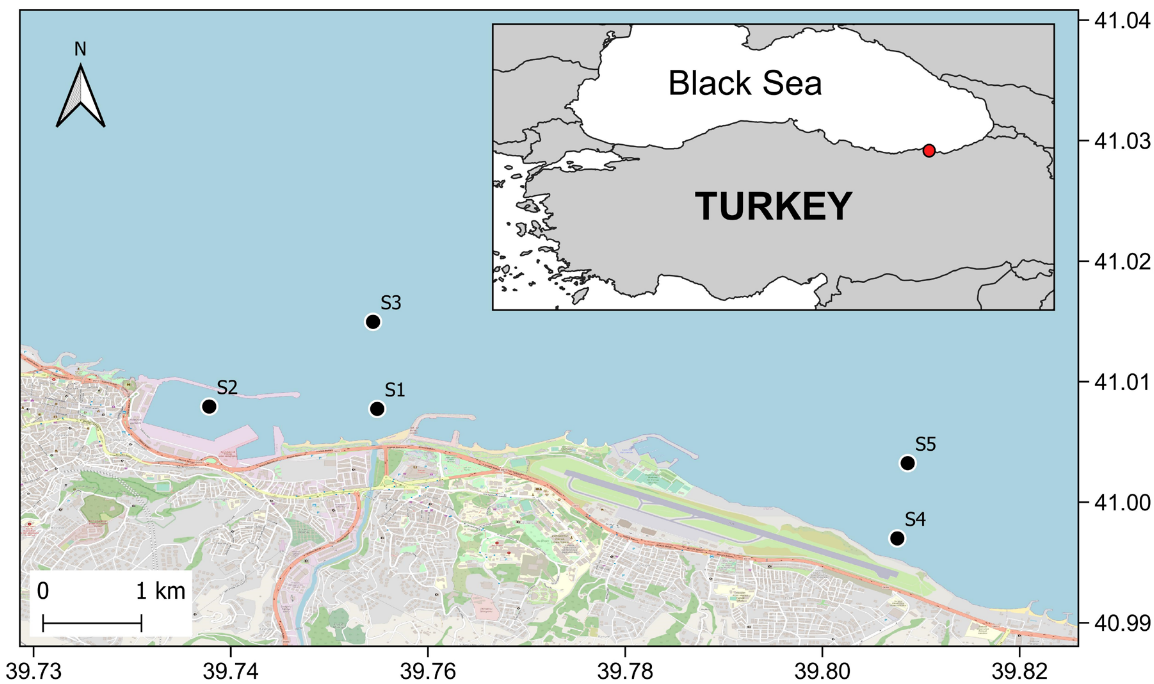

Figure 1. The study area and sampling stations.

Table 1. Coordinates of sampling stations.

Station Code	S1	S2	S3	S4	S5
Latitute	41° 00.331' N	41° 00.344' N	41° 00.808' N	40° 59.622' N	41° 00.034' N
Longitute	39° 45.442' E	39° 44.522' E	39° 45.419' E	39° 48.290' E	39° 48.347' E

Değirmendere stream, which has an average annual flow of 11.36 m^3/s and has a total length of 60 km within the borders of Trabzon, is one of the most important streams of the Eastern Black Sea Region. It is the major terrestrial input source of the region [8]. There are also some important industrial facilities such as a large number of coal storage, stone crushing and screening, ready-mixed concrete, asphalt casting, metal casting industry, fuel stations, marble processing, auto industry. The region also hosts an international busy transportation network in the north-south direction. Due to the region's topographic structure of the region and the high rainfall rate, the Değirmendere stream carries an erosion-induced load.

Sediment Enrichment Factor (SEF) is an effective tool for evaluating the magnitude of contaminants in the environment. The SEF is an indicators used to assess the presence and intensity of anthropogenic contaminant deposition on surface sediment [9]. This study aims to determine to determine the current state of natural and anthropogenic metal pollution in the coastal sediments under the effect of the Değirmendere basin.

MATERIALS and METHODS

This study was carried out five stations located in which are located in the coastal ecosystem of the Southeastern Black Sea region (Figure 1). Coordinates relating to the stations are presented in Table 1. The surface sediment samples layer (0-5 cm) were taken with Ekman grab bottom sampler seasonally in 2018.

Sediment samples were placed in polyethylene bags using a clean plastic spatula to prevent contamination. Samples were placed in a cooler with ice, and transported to the laboratory where they were stored at -18°C until being analyzed [10]. Prior to analysis, samples were dried at 45°C. For grain size distribution, sediment samples were sieved using distilled water in an AS 200 vibratory sieve shaker. For metal analysis, sediment samples were sieved to pass < 63 µm because metals are generally related to small grains. Aluminum (Al), Vanadium (V), Chrome (Cr), Manganese (Mn), Iron (Fe), Cobalt (Co), Nickel (Ni), Copper (Cu), Zinc (Zn), Arsenic (As), Cadmium (Cd) and Lead (Pb) concentrations were measured with ICP-MS after digestion with microwave system.

Sediment Enrichment Factor is one of the most preferred approaches to predict anthropogenic effect in sediment quality. In applications known as normalization, generally, Al is used as a reference metal in many studies. Enrichment Factors (EF) were calculated as $(Metal/Al)_{sample}/(Metal/Al)_{background}$ [11]. In this study, Turekian and Wedepohl (1961) recommended average crustal values are used as the background values [12].

The following table (Table 2) was used to assess the enrichment level of sediment.

RESULTS and DISCUSSION

The distribution of the average metal concentrations according to the stations were given in Table 3. The highest average concentrations were determined for V, Mn, Fe, Ni, Cu and As at station 1, for Zn, Cd and Pb at station 2, for Co and Cr at station 3 and for Al at station 4. Differences between stations in terms of metal concentrations were not statistically significant ($p>0.05$). Although the concentration of many metals containing abundant elements in the Earth's crust was relatively higher at station 1 near the river input, it is interesting to note that anthropogenic/industrial origin metals such as Cd, Pb and Zn were higher in station 2, which is located in the harbor.

Table 2. SEF categories.

SEF	Level of Sediment Quality
< 2	Deficiency to minimal enrichment
2-5	Moderate enrichment
5-20	Significant enrichment
20-40	Very high enrichment
> 40	Extremely high enrichment

Table 3. Metal concentrations by stations (mean ± standard deviation)

Metal	S 1	S 2	S 3	S 4	S 5
Al (%)	5.4±2.3	4.9±1.0	5.4±1.3	5.8±1.2	4.5±0.8
V (mg/kg)	158.0±41.7	140.0±26.0	152.4±22.9	155.3±21.3	130.0±39.6
Cr (mg/kg)	51.8±15.6	41.0±4.0	54.6±10.3	51.3±10.9	44.3±20.1
Mn (mg/kg)	736.3±82.8	690.5±115.0	603.2±132.2	691.4±64.7	540.8±74.1
Fe (%)	4.4±1.0	3.8±0.5	4.0±0.7	4.1±0.4	3.4±1.0
Co (mg/kg)	17.6±3.5	15.9±1.6	18.4±0.9	16.4±1.5	14.9±3.3
Ni (mg/kg)	36.3±12.5	24.4±3.1	35.2±5.6	30.0±5.4	26.5±15.2
Cu (mg/kg)	61.9±17.3	49.8±4.6	53.2±11.0	51.2±6.5	42.5±18.1
Zn (mg/kg)	128.6±14.2	148.3±50.9	109.0±9.4	142.8±26.0	85.6±20.7
As (mg/kg)	10.3±2.3	8.5±1.0	9.2±1.7	9.4±1.4	8.3±3.3
Cd (mg/kg)	0.2±0.0	0.4±0.3	0.3±0.1	0.3±0.1	0.3±0.1
Pb (mg/kg)	18.3±2.6	25.4±18.4	15.7±1.5	16.8±2.3	13.6±2.9

Table 4. Distribution of sediment grain size by stations (%).

Grade	S1	S2	S3	S4	S5
Granule	1	-	-	3	-
Fine gravel	3	-	-	2	-
Very coarse sand	5	1	3	7	2
Coarse sand	15	2	4	14	7
Medium sand	28	10	10	22	13
Fine sand	32	23	20	33	20
Very fine sand	5	26	23	9	24
Clay	11	38	40	10	34

Table 5. Varimax normalized factor loadings of metal concentration in the sediment.

	Factor 1	Factor 2	Factor 3
Al	0.733399	0.031496	0.553668
V	0.757160	-0.104949	0.593113
Cr	0.966824	-0.083452	0.146119
Mn	0.141519	0.032592	0.963253
Fe	0.676641	-0.017304	0.731612
Co	0.927926	-0.028969	0.047164
Ni	0.966912	-0.067174	0.183772
Cu	0.753719	0.295412	0.501034
Zn	0.046072	0.893717	0.323062
As	0.730234	-0.079531	0.630557
Cd	-0.126799	0.828934	-0.399497
Pb	-0.022082	0.961626	0.005187
Expl.Var	5.439772	2.529863	3.091422
Prp.Totl	0.453314	0.210822	0.257619

Overall mean (mg/kg) ± std. dev. and (min-max) values of the metal concentrations were determined as 146.4±27.3 (100.1-187.5), 48.4±12.1 (25.9-65.7), 646.4±109.1 (473.2-818.3), 16.6±2.2 (11.2-20.1), 30.0±9.0 (11.845.1), 51.0±11.8 (26.0-74.1), 122.4±34.8 (68.2-206.2), 9.0±1.8 (6.0-12.1), 0.32±0.14 (0.12-0.70), and 17.9±8.5 (11.4-46.6) for V, Cr, Mn, Co, Ni, Cu, Zn, As, Cd and Pb respectively. Al and Fe concentrations were also measured as % 5.17±1.3 (3.4-7.0) and % 3.9±0.7 (2.7-5.1).

In this study, average metal concentrations were found as Mn> V> Zn> Cu> Cr> Ni> Pb> Co> As and Cd. This order was found by Alkan et al. (2015) on the Eastern Black Sea coastal sediments as Mn> Zn> Cu> Pb> Cr> Ni> Co> As> Cd. Although the results obtained are similar, the average Ni, Cr, Cu and Zn values determined in this study are relatively higher than the background values determined by Alkan et al. 2015 [13].

It was reported that the Değirmendere stream has the highest suspended solid amounts among the rivers of high flow rates in the Eastern Black Sea Region. [14]. In a study conducted by Özşeker et al., 2014, it was stated that the spatial and temporal distributions of the metal concentrations of the region were caused by the increase in the clay content in the sediment layer carried and deposited by rivers [15]. Although the Southeastern Black Sea is not a region containing large amounts of industrial waste, the presence of natural ore beds and abundance of river resources and the discharge of untreated urban effluents contribute to pollution [13]. Erosion due to river transport in the region can also be considered to be the most important source of natural and anthropogenic metal input [15].

In another study conducted by Özşeker et al., 2016 Değirmendere drainage nearby and Trabzon harbor. The average metal concentrations were reported as mg/kg, to be Cr 40.12 ± 24.00, Cu 104.17 ± 80.13, Pb 70.58 ± 27.41, Zn 145.24 ± 67.20, Ni 42.23 ± 29.98 and As 24.19 ± 17.32 [16]. Pb and As concentrations measured in the stated research are higher than the values determined in this study.

When the metal results obtained in this study were compared with the avarege shale values (Wedepohl, 1968), it was found that the Cr, Mn, Co, Ni, Pb and Cd concentrations measured in this study were lower than the shale values and the Cu and Zn concentrations were higher.

Table 6. Correlation values within the metals.

	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Cd	Pb
Al	1.00											
V	0.97	1.00										
Cr	0.84	0.86	1.00									
Mn	0.61	0.67	0.26	1.00								
Fe	0.89	0.94	0.75	0.80	1.00							
Co	0.62	0.70	0.86	0.24	0.67	1.00						
Ni	0.76	0.82	0.96	0.30	0.80	0.91	1.00					
Cu	0.75	0.77	0.73	0.60	0.89	0.74	0.83	1.00				
Zn	0.21	0.13	0.04	0.34	0.24	0.06	0.06	0.43	1.00			
As	0.86	0.90	0.81	0.68	0.96	0.66	0.84	0.87	0.14	1.00		
Cd	-0.20	-0.37	-0.24	-0.34	-0.40	-0.17	-0.30	-0.10	0.56	-0.42	1.00	
Pb	-0.01	-0.13	-0.11	0.00	-0.02	-0.07	-0.07	0.31	0.82	-0.07	0.74	1.00

Regarding the sediment grain size distribution, it was seen that the clay ratio was substantially higher in stations 2, 3, and 5 than in other stations. This means that smaller particles can be transported more efficiently to shore except station 2, which is less affected by water movements since it is located in the harbor (Table 4).

Factor analysis was also applied for the metal concentrations belonging to the stations. As a result of this analysis, it was determined that the concentrations of metals were controlled by three main factors which can explained 92 % of the total variance. Factor 1 explaining 61 % of the total variance (in relation to the elements Al, V, Cr, Co, Ni, Cu and As) is the sign of stream-derived inputs. Factor 2, which is related to Zn, Cd and Pb is an indicator of harbor anthropogenic effects. Factor 3 can be interpreted as a reflection of the toxic environment's presence, especially concerning the redox-active metals Fe and Mn (Table 5).

Correlation values within the metal were indicated in Table 6. It is noticeable that strong positive correlations (over 90 %) occur within the elements of Al-V, Fe-As, V-Fe, V-As and Cr-Ni.

The enrichment factors (EF) related to the metal concentrations calculated using Turekin (1961) data as the background value were given in Figure 2. The enrichment factors normalized with aluminum were 1.5-2.1 for Vanadium; 0.6-1.0 for Cr; 0.8-1.7 for Mn; 1.1-1.7 for Fe; 1.1-2.0 for Co; 0.4-0.9 for Ni; 1.3-2.3 for Cu; 1.4-3.9 for Zn; 0.8-1.4 for As; 0.5-4.1 for Cd and 0.9-4.2 for Pb. Moderate enrichments were observed for Cu at station 1, for Zn, Pb and Cd at station 2 and for Zn at station 4.

It is important to take the necessary measures to protect the Black Sea's natural ecosystem, which is a fascinating semi-enclosed inland sea due to its unique characteristics by determining the levels of pressures applied by rivers and industrial activities.

Acknowledgments

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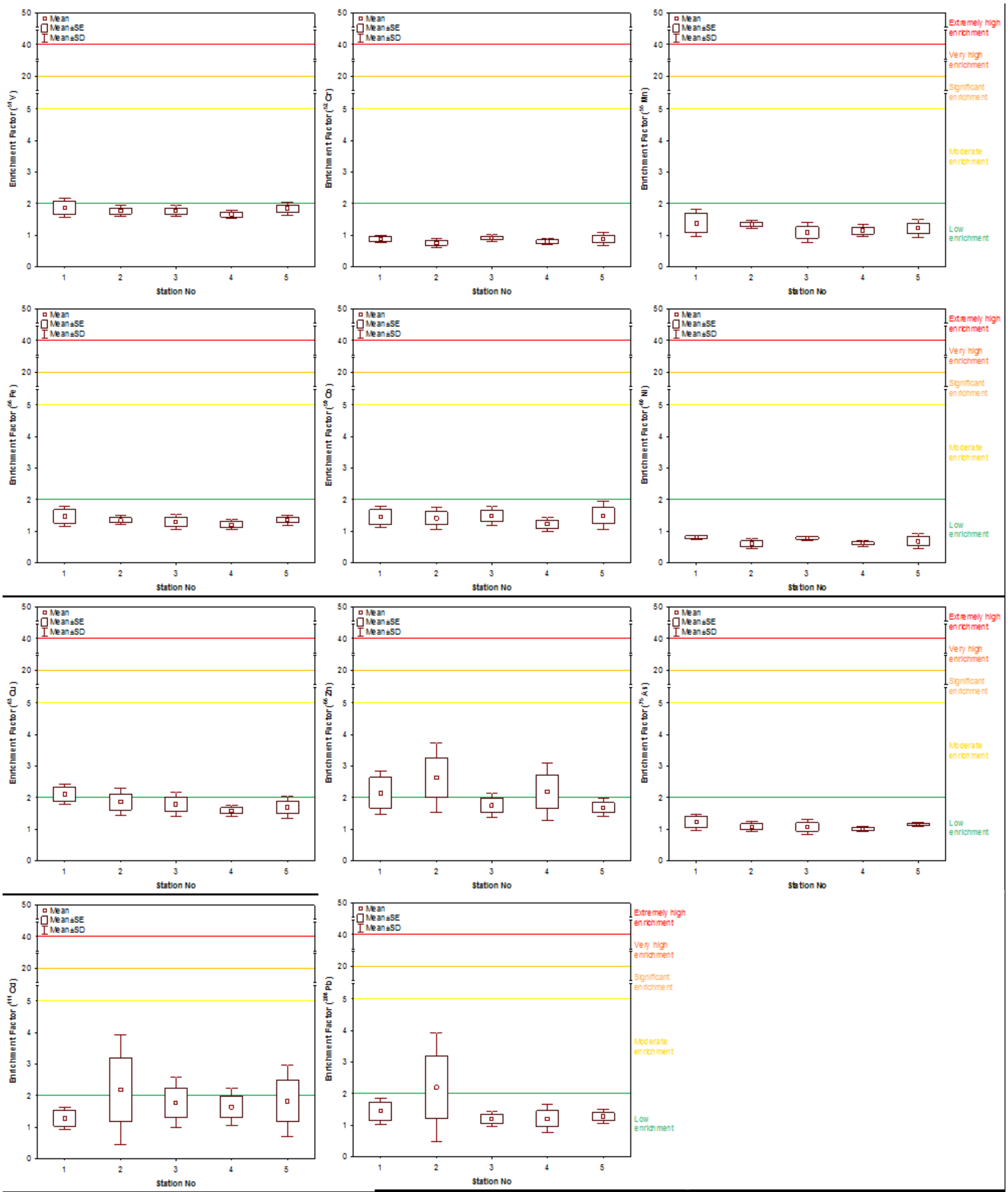

Figure 2. Enrichment factors for V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Cd and Pb.

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