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Heavy metal levels in sea water and sediments of Zonguldak, Turkey

Zonguldak deniz suyunda ve sedimentlerinde ağır metal seviyeleri

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Abstract

Heavy metal levels were measured in seawater and sediment in Zonguldak which is on the Black sea shore of Turkey. The samples were collected near the industrial areas and city beaches. Maximum concentrations of metals dissolved in seawater were found (nM) Cd 15.0±0.98 around Çatalağzı Power Station, Cr 112±8.6 in Alaplı Creek delta, Mn 715±8.3 in Filyos creek delta, Cu 122±1.5, Ni 142±10.6, Pb 39±9.0 and Zn 834±4.1in Zonguldak city beaches. Heavy metal levels in sediment were found as (µg/g) Cd 0.47±0.34, Cr 67.95±27.6, Cu 30.21±9.27, Mn 274.4±74.8, Ni 37.03±13.25, Pb 39.14±11.22, and Zn 84.6±18.5. Heavy metal concentrations were compared with the US EPA limitations and the other localities and seawater found to be highly polluted than the other Black Sea shores and similar to Rize and Hopa waters. According to recommendations of US EPA under the priority toxic pollutants list Cd, Cu, Ni, Pb and Zn levels are above the limits in Zonguldak seawater. Metal levels in sediment samples were found as polluted as the estuarine areas of other countries in the region.

Key words: Heavy metal, sea water, sediment, Black Sea

Introduction

The presence of heavy metals in the aquatic systems is increasing at an alarming rate due to the increased human activities. US_EPA strongly recommends limiting the heavy metal concentrations for Estuarine /coastal aquatic life in the United States.

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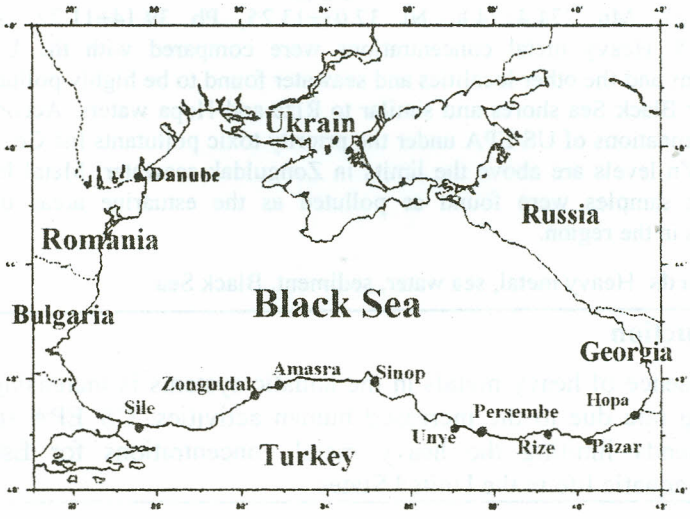
Heavy metal pollution in the coastal area of Zonguldak is important, while it is a coal production area. The local coal was used for power and domestic heating and the pollution is caused by solid wastes and fly ash from surrounding industry Ereğli Steel Works (ESW), Çatalağzı Power Station (ÇPS). Fishing is a very important activity in this area. It is affected by marine pollution and may create additional human health problems. Coal combustion is considered an important possible source of heavy metals pollution. Heavy metals contained by fly ashes derived from bituminous coal combusting in Çatalağzı power plant were reported as (ppm) Cd: 4.0, Pb: 118.5, Zn:138.3, Cu:98.8, Cr:138.3, Ni:118.5, Mn:790.0 (Bayat 1998). These results correlate closely with atmospheric heavy metal contamination of Zonguldak, which has recently been reported (Uyar et al. 2009). Metal pollution in Black Sea coasts has been investigated by various authors in water (Haraldsson and Westerlund 1988, Zeri et al. 2000, Guieu et al. 1998, Tankere et al. 2000, Jordanova et al. 1999, Lewis and Landing 1991, 1992), in algae (Strezov and Nonova 2005, Güven et al. 1992, Jordanova et al. 1999, Topçuoglu et al. 2001, 2003 a,b 2004), in sediments, mussels and fish (Bologa et al. 1998, Topçuoglu et al. 1998, 2002, 2003b, 2004, Güven and Topçuoglu 1991, Secrieru and Secrieru 2002, Balkıs et al. 2007, Çevik et al. 2008, Wilson et al. 2008, Slaveykova et al. 2009). But there is no information on seawater heavy metal concentrations from Zonguldak coasts.

Figure 1. Black Sea stations investigated in present work and other authors.



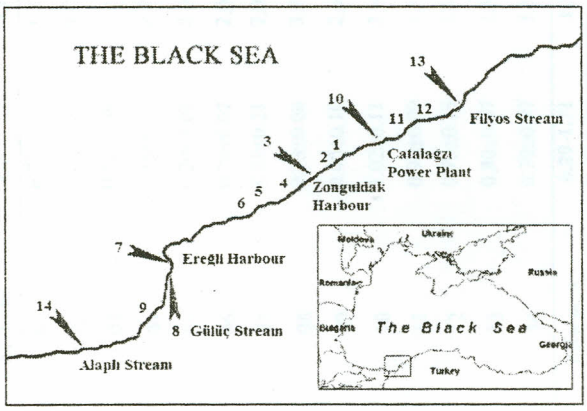
In this study, heavy metal contents of seawater and sediment were investigated in marine environment of Zonguldak.

Materials and method

Seawater samples

Seawater samples were taken from 14 stations covering whole coastline: the bays, ports, deltas and near the industrialized areas as surface water (Figure 2). They were collected with 2.5 l high-density polyethylene bottles (acid-cleaned) and filtered directly using Teflon filter holders, through acid cleaned membrane filters (mixed cellulose esters) (0.45 mm pore size; 47 mm in diameter (Millipore). The filtered samples were acidified at pH 2 with conc. HNO_3 of supra pure grade (Merck, Germany); they were stored, in acid-cleaned high-density polyethylene bottles. Dissolved trace metals in the samples were separated and preconcentrated from seawater using ammonium 1-pyrrolidinedithiocarbamate (PDTC) (Fluka) as fallows. 500 ml seawater sample was taken, filtered and pH value was adjusted to 7 by using HNO_3 (Merck) and 35% ammonia solution (Merck). 10 ml of PDTC added and the pH of the solution was adjusted to 5.8-6.1 for optimum complexation. Metal complexes were extracted with 30 ml of chloroform in a separating funnel and organic phase was transferred into a glass beaker. 1 ml of conc. HNO_3 was added, chloroform was evaporated at 50°C and organic material was oxidized for 12 hours. To the residue 1 ml HCl was added and transferred into a 10 mL volumetric flask by dilution with 1 M HCl (Bruland et al. 1985).

Figure 2. The sampling stations



Sediment samples

4 cm of the top sediment samples taken with by divers into plastic bags, rocks were removed and the sediment stored in plastic boxes. About 50 g of samples were dried at 85 °C for 24 h. The samples were kept away from metallic materials and dusty conditions to avoid contamination.

One gram of dry sediment sample was put into a glass beaker, 10 ml conc. HNO_3 added and heated on the hot plate at 120°C for 30 min then 5 ml of conc. $HClO_4$ was added and continued to heat until dry. 5 ml conc. HF was added for the digestion of silicates and digestion took place in Teflon beakers. The samples were dissolved in 1 M HCl and diluted to 50ml in volumetric flasks.

The samples were transferred into acid washed plastic bottles for the analysis.

Standard curves of metals were plotted by reference compound purchased from Merck. The measurement of heavy metal concentrations was made using atomic absorption spectrophotometer Shimadzu 6701F. The values were expressed as the mean of three analyses for each sample. The accuracy of the analysis was verified by analyzing the IAEA's certified reference material.

Results and Discussion

Heavy Metal concentrations of seawater in Zonguldak were shown (Table 1) and the values were compared with the other parts of the Black sea coastline (Table 2).

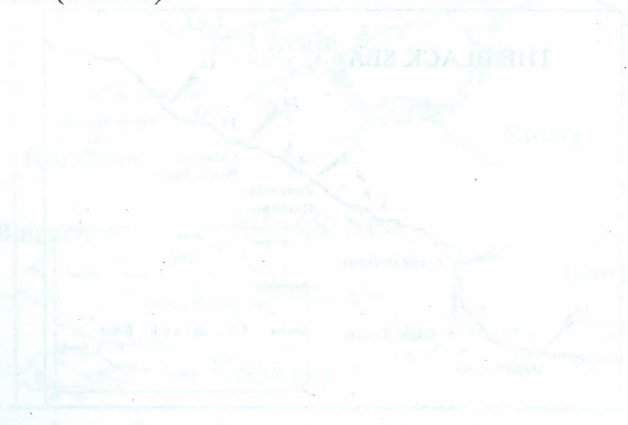


Table 1. Heavy metal concentrations of sea water from 14 stations in Zonguldak (ppb).

Stations	Cd	Cr	Cu	Mn	Ni	Pb	Zn
01	0.29±0.05	1.33±0.37	3,23±0,37	2,88±0,79	4,95±0,99	8.02±1.87	14,30±0,13
02	0.40±0.04	4.09±0.23	3,72±0,15	2,75±0,47	5,41±1,28	5.19±0.18	13,08±0,09
03	0.33±0.06	1,55±0,20	4,57±0,06	2,03±0,18	3,17±0,53	6.47±1.11	26,17±0,12
04	0.40±0.10	2.95±0,25	6,06±0,17	1,12±0,72	5,16±0,41	<0.02	16,15±0,06
05	0.20±0.07	2.50±0.26	3,62±0,90	2,56±0,37	2,79±0,71	<0.02	54,22±0,27
06	0.20±0.07	2,06±0,22	7,73±0,01	4,25±0,34	8,39±0,61	<0.02	43,78±2,08
07	1.71±0.21	2,08±0,78	3,78±0,25	12,92±0,04	4,66±0,57	<0.02	28,85±0,31
08	0.33±0.06	3,37±0,48	4,36±0,14	9,19±0,16	4,89±1.16	<0.02	19,36±0,10
09	0.40±0.10	2,66±0,47	4,60±0,12	3,94±0,27	4,71±0,57	<0.02	13,54±0,13
10	1.02±0.11	2,66±0,21	4,12±0,40	22,56±0,42	5,14±0,55	<0.02	21.42±0.05
11	0.90±0.09	1,55±0,20	3,75±0,27	4,31±0,21	3,04±0,59	<0.02	12,51±1,34
12	0.79±0.13	3,06±0,58	4,09±0,22	4,93±0,10	3,43±0,46	<0.02	13,52±0.06
13	0.80±0.07	2,50±0,24	3,86±0,13	39,34±0,46	3,91±0,97	<0.02	19,47±0,19
14	0.70±0.07	5,83±0,45	2,84±0,29	3,74±0,16	5,83±0,65	<0.02	11,35±0,10
Min-max	**0.29-1.71**	**1.33-5,83**	**2,84-7,73**	**1,12-39,34**	**2,79-8,39**	**5.19-8.02**	**11,35-54,22**

Table 2. Comparison of the seawater analysis with the literature (nM) and US EPA standards.

Place	Cd	Cr	Cu	Mn	Ni	Pb	Zn
Zonguldak 2004 (Present study) min and max values given	2.5-15.0	25-112	45-122	20-715	47-142	25-39	174-834
Black sea (off shore) (Lewis and Landing, 1992)	0.05-2.58	-	0.16-2.83	0.55-25.5	7.67-10.9	-	-
Çamburnu, Rize (Çevik et al. 2007)	26.7	-	118-323	-	-	140	100-180
Hopa (Çevik et al. 2007)	-	-	307	-	-	188	1200
Romanian coasts (Haraldsson and Westerlund, 1988)	0.08	-	9.4	5.6	9.4	-	-
Romania (Tankere et al. 2001)	0.07-0.09	-	1-8	0.7-9.6	8-12	0.1-0.2	0.9-2.0
Danube delta (Guieu et al. 1998)	0.1	-	36	19	15	0.08	6
Danube delta (Zeri et al. 2000)	0.4-13.7	-	4.7-36.2	0.01.-29.1	-	-	-
Bulgaria (Slaveykova et al. 2009)	2.58	-	2.83	-	10.9	-	-
US EPA.1999	71	-	45	-	120	28	1180

Table 3. Comparison of heavy metal concentrations of the **sediment** samples collected from Zonguldak Harbor and around and literature (ppm-dry weight).

Locality, year (reference)	Cd	Cr	Cu	Mn	Ni	Pb	Zn
Zonguldak 2004 Present study	0.47±0.34	67.95±27.6	30.21±9.27	274.4±74.8	37.03±13.25	39.14±11.22	84.6±18.5
Amasra (Topcuoglu et al. 2002)	0.73	58.5	37.3	338.2	33.5	21.4	92.6
Sakarya (Balkıs et al. 2007)	<0.02	2,496	39.1	3,696	134.3	<0.01	456.6
Sinop (Topcuoglu et al. 2002)	0.89	115.5	69.9	424.3	65.2	15.1	91.5
Perşembe (Topcuoglu et al. 2002)	0.93	21.8	95.5	514.1	18.5	31.1	82.9
Ünye (Topcuoglu et al. 2004)	<0.02	245.0	111	2803	79.2	52.9	148.0
Samsun (Balkıs et al. 2007)	<0.02	1,276	59.9	2,915	128.1	<0.01	325.3
Samsun (Bakan and Özkoç, 2007)	<0.02	99.3	64.85	668.7	49.25	223.7	261.65
Rize (Topcuoglu et al. 2003)	<0.02	-	67.8	649.8	-	67.8	483.1
Rize, Çamburnu (Çevik et al. 2007)	34	1,000	69,000	17,900	362	652	28,000
Hopa (Çevik et al 2007)	53	1,760	100,000	30,472	273	1,700	35,000
Romania (Secrieru and Secrieru, 2002)	0.75	61.9	32.2	1000	66.4	15.0	64.6
Ukraine (Wilson et al. 2008)	2.1	107	117	-	-	614	114
Georgia (Wilson et al. 2008)	2.7	7.0	-	-	-	-	3.35

- not measured or mentioned, for seawater analysis results min and max values are given in the Table 2.

In general, Zonguldak and Ereğli city beaches (stations 1-6, 8 and 9) are less polluted than places like the industrialized areas like Filyos Creek, Çatalağzı Power Plant and Ereğli Steel Works (stations 7, 11-14).

Minimum and maximum concentrations of the metals were used and metal concentrations of ppb scale were converted to nM scale for comparison with the literature in Table 2.

Cadmium level in industrialised Danube delta and intense mining city of Turkey, Rize is as high as 13.5 and 26.7 nM respectively in comparison to the 2.5 nM in Zonguldak city beach waters but 8.9 and 15.0 for Çatalağzı power station and Ereğli Steel Works coasts respectively (Zeri et al. 2000; Çevik et al. 2007). The cadmium levels in the other areas of the Black sea are 10 to 100 times lower than it is in Zonguldak (Lewis and Landing 1992, Haraldsson and Westerlund 1988, Tankere et al. 2001, Guieu et al. 1998, Slaveykova et al. 2009).

Chromium concentration is very high in Zonguldak. We could not find a about Cr content of the Black sea water.

Copper levels in Zonguldak coasts are higher than the other countries' coasts in Black sea area (Lewis and Landing 1992, Haraldsson and Westerlund 1988, Tankere et al. 2001, Guieu et al. 1998, Slaveykova et al. 2009, Zeri et al. 2000). The copper levels in the intense copper mining areas of Turkey, Rize and Hopa are 3 times higher than Zonguldak (Çevik et al. 2007).

Nickel levels are very similar in the Black sea countries. Manganese levels in Zonguldak on the other hand slightly higher than Bulgarian, Romanian and Ukrainian coasts (Lewis and Landing 1992, Haraldsson and Westerlund 1988, Tankere et al. 2001, Guieu et al. 1998, Slaveykova et al. 2009).

The other toxic metals Zn and Pb are also very high in Zonguldak coasts compare to the other countries in the region while Rize and Hopa waters are much more polluted with these metals (Lewis and Landing 1992, Haraldsson and Westerlund 1988, Tankere et al. 2001, Guieu et al. 1998, Slaveykova et al. 2009, Zeri et al. 2000, Çevik et al. 2007).

The limitations of the metals of concern are listed according to US EPA and compared with our results in Table 2. According to the priority toxic pollutants list of US EPA National recommended water quality criteria, metal levels in Zonguldak coasts are just under for Cd levels in the Ereğli Harbour and Çatalağzı power station coasts or well above the limits for Cu, Ni, Pb and Zn levels.

Solubility of heavy metals in seawater is not constant in fact varies depending on the elements. Because of this, sampling must cover whole year and the mean values should be used.

In sediment samples taken from Zonguldak coasts, heavy metal pollution especially cadmium, chromium and lead levels were very high like the other Black sea countries shown in Table 3. However recent values from Rize, Hopa and Samsun coasts (Figure 1) have very high level pollution regarding all heavy metals because of the intense mining activities. Hopa and Rize sediments are the most polluted ones among the other Turkish Black Sea coasts while sediment samples from Zonguldak have the second highest Zn and Pb levels.

The results clearly indicate that, in the Zonguldak coastal area heavy metal pollution is continuing along. Heavy metal concentrations especially Cd, Cu, Zn and Pb in sea water and Cd, Cu, Cr and Pb in sediments are high. High levels of metals found in the environment possibly caused by fly ash from coal combustion and wastes from cement and lime plants in the area.

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Özet

Bu çalışmada Karadeniz kıyısındaki illerden olan Zonguldak deniz suyunda ve dip çamurunda ağır metal seviyeleri ölçüldü. Örnekler endüstriyel alanlardan ve şehir plajlarından toplanmıştır. Deniz suyunda çözünmüş metal konsantrasyonları Çatalağzı termik santralı kıyısında (nM) Cd 15.0±0.98, Alaplı deresinde Cr 112±8.6, Filyos çayında Mn 715±8.3, Zonguldak plajlarında Cu 122±1.5, Ni 142±10.6, Pb 39±9.0 ve Zn 834±4.1 maksimum değerler olarak bulunmuştur. Dip çamurunda bulunan ortalama konsantrasyonlar ise (□g/g) Cd=0.47±0.34, Cr=67.95±27,6, Cu=30.21±9.27, Mn=274.4±74.8, Ni=37.03±13.25, Pb=39.14±11.22, Zn=84.6±18.5 şeklindedir. Kirlilik seviyeleri diğer US EPA limitleriyle ve diğer Karadeniz şehirleri ve devletlerine ait değerler ile karşılaştırılmış ve Zonguldak diğer Karadeniz devletleri kıyılarından daha kadar kirli bulunmuştur. Bu arada Rize ve Hopa kıyılarının benzer kirliliğe sahip olduğu bulunmuştur. Bu çalışmada deniz suyundaki öncelikli toksik metallerin (Cd, Cu, Ni, Pb ve Zn) seviyeleri tavsiye edilen değerlerin üzerinde olduğu saptanmıştır. Sedimentteki metal seviyeleri ise diğer ülkelerin örnekleri kadar kirli bulunmuştur.

References

Bakan, G. and Özkoç, H.B. (2007). An ecological risk assessment of the impact of heavy metals in surface sediments on biota from the mid-Black Sea coast of Turkey. *Int. J. Environ. Studies* 64: 45–57.

Balkıs, N., Topcuoğlu, S., Güven, K.C., Öztürk, B., Topaloğlu, B., Kırbaşoğlu, Ç. and Aksu, A. (2007). Heavy metals in shallow sediments from the Black sea, Marmara sea and Aegean sea regions of Turkey. *J. Black Sea/Mediterranean Environ.* 13: 147-153.

Bayat, O. (1998). Characterisation of Turkish fly ashes. *Fuel* 77: 1059-1066.

Bologa, A. S., Apas, M., Cociasu, A., Cuingioglu, E., Patrascu, V., Piescu, I. and Popa, L. (1998). Present level of contaminants in Romanian Black Sea Sector Marine pollution. In: Intl. Workshop on Marine Pollution, AIEA, IOC, UNEP, Monaco, 5-9 Oct. 1998. Proceeding SM-354/26: 58–63.

Bruland, K. W., Coale, K. H. and Mart, L. (1985). Analysis of seawater for dissolved cadmium, copper, and lead: An intercomparison of voltametric and atomic absorption methods. *Mar. Chem.* 17: 285-300.

Cevik, U., Damla, N. Kobya, A.I. Bulut, V.N. Duran, C. Dalgıc, G. Bozacı, R. (2008). Assessment of metal element concentrations in mussel (M. Galloprovincialis) in Eastern Black Sea, Turkey. *J. Hazardous Materials* 160: 396–401.

Guieu, C., Martin, J-M., Tankere, S. P. C., Mousty, F., Trincherini, P., Bazot, M. and Dai, M. H. (1998). On trace metal geochemistry in the Danube River and Western Black Sea. *Estuar. Coast Shelf S.* 47: 471-485.

Güven, K. C., Okus, E., Topcuoğlu, S., Esen N., Kücükcezzar, R., Seddigh, E. and Kut, D. (1998). Heavy metal accumulation in algae and sediments of the Black Sea Coast of Turkey. *Toxicol. Environ. Chem.* 67: 435-440.

Haraldsson, C. and Westerlund, S. (1988). Trace metals in the water columns of the Black Sea and Framvaren Fjord. *Mar. Chem.* 23: 417-424.

Jordanova, A., Strezov, A., Ayranov, M., Petkov, N. and Stoilova, T., (1999). Heavy metal assessment in algae, sediments and water from the Bulgarian Black sea coast. *Water Sci. Tech.* 39: 207-212.

Lewis, B. L. and Landing, W. M. (1991). The biogeochemistry of Mn and Fe in the Black Sea. *Deep-Sea Res.* 38 (Suppl. 2), S773.

Lewis, B. L. and Landing, W. M. (1992). The investigation of dissolved and suspended particulate trace metal fractionation in the Black Sea. *Mar. Chem.* 40: 105-141.

Slaveykova, V.I., Karadjova, I.B., Karadjov, M. and Tsalev, D.L. (2009). Trace Metal Speciation and Bioavailability in Surface Waters of the Black Sea Coastal

Area Evaluated by HF-PLM and DGT *Environ. Sci. Technol.* Articles ASAP (30.03.2009).

Secrieru, D. and Secrieru, A. (2002). Heavy Metal Enrichment of Man-made Origin of Superficial Sediment on the Continental Shelf of the North-western Black Sea. *Estuarine, Coastal Shelf Sci.* 54: 513–526.

Tankere, S. P. C., Muller, F. L. L., Burton, J. D., Statham, P. J., Guieu, C. and Martin, J. M. (2001). Trace metal distributions in shelf waters of the northwestern Black Sea *Cont. Shelf Res.* 21: 1501-1532.

Topcuoglu, S., Kırbasoglu, Ç. and Gungor, N. (2002). Heavy metals in organisms and sediments from Turkish coast of Black Sea, 1997-1998. *Environ. Int.* 27: 521-526.

Topcuoglu, S., Ergul, H. A., Baysal, A., Olmez, E. and Kut, D. (2003). Determination of radionuclide and heavy metal concentrations in biota and sediment samples from Pazar and Rize stations in the eastern Black Sea. *Fresenius Environ. Bull.* 12: 695-699.

Topcuoglu, S., Olmez, E., Kırbasoglu, Ç., Yılmaz, Y. Z. and Saygin, N. (2004). Heavy metal and radioactivity in biota and sediment samples collected from Ünye in the eastern Black Sea. 37th CIESM Congress, 7-11 June 2004, Barcelona, Spain, Poster.

Uyar, G., Avcil, E., Oren, M., Karaca, F. and Oncel, S. (2009). Determination of Heavy Metal Pollution in Zonguldak (Turkey) by Moss Analysis (*Hypnum cupressiforme*). *Environ. Eng. Sci.* 26: 183-184.

US EPA (1999). National Recommended Water Quality Criteria correction office of paper, EPA 822-Z-99,001, pp 25.

Wilson, J.G., Komakhidze, A., Osadchaya, T., Alyomov, S., Romanov, A., Tediashvili, M. (2008). Evaluating ecological quality in the north-eastern Black Sea coastal zone. *Mar. Poll. Bull.* 57: 202–207.

Zeri C. and Voutsinou-Taliadouri F. (2003). Processes affecting the distribution of dissolved trace metals in the North Aegean Sea (Eastern Mediterranean). *Cont. Shelf Res.* 23: 919-934.

Zeri, C., Voutsinou-Taliadouri, F., Romanov, A. S., Ovsjany, E. I. and Moriki, A. (2000). A comparative approach of dissolved trace element exchange in two interconnected basins: Black Sea and Aegean Sea. *Mar. Poll. Bull.* 40: 666-673.

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