E.Ü. Su Ürünleri Dergisi 2006
E.U. Journal of Fisheries & Aquatic Sciences 2006
Cilt/Volume 23, Sayı/Issue (3-4): 445–448

ISSN 1300 - 1590
http://jfas.ege.edu.tr/

Research Note / Araştırma Notu

Heavy Metal Deposition in Sediments from the Delta of the Gediz River (Western Turkey): A Preliminary Study

*Hatice Parlak, Ayşe Çakır, Meltem Boyacıoğlu, Özlem Çakal Arslan

Ege University, Faculty of Fisheries, Dept. of Hydrobiology, Bornova, Izmir Turkey
**E mail: hatice.parlak@ege.edu.tr*

Özet: ***Gediz Nehri Deltası (Batı Türkiye) sedimentlerinde ağır metal birikimi.*** Bir Ön Çalışma: Gediz Nehri bölgede tarımsal açıdan önemli olduğu kadar deltası da Dünya Doğal Yaşamı Koruma Federasyonu tarafından Önemli Kuş sahası olarak değerlendirilmiştir. Bunun yanı sıra, Gediz Deltası 1998 yılından beri Ramsar alanı olarak koruma altındadır. Öte yandan Gediz Nehri'nin tarımsal, evsel ve endüstriyel atıklar ile yoğun bir şekilde kirlendiği rapor edilmektedir. Bu ön araştırmada Gediz Deltasından toplanmış sediment örneklerinde bazı ağır metaller (As, Pb, Cd, Ni, Cu, Co ve Cr) analiz edilerek kirliliğin etkisi tayin edilmeye çalışılmıştır. Elde edilen sonuçlara göre, As, Cu, Cd, Co, Ni ve Pb için bir kirlilik riski olmadığı sonucuna varılabilir. Bununla beraber, arıtma tesisi olmasına rağmen özellikle deri sanayinin atık sularının döküldüğü kanalın birleştiği yer olan istasyon 2 ve 3'de yüksek Cr içeriği saptanmıştır (2565.5 ppm maksimum).

Anahtar Kelimeler: Gediz Deltası, Sediment, Ağır metaller, Kirlilik.

Abstract: The Gediz River is of great importance for agriculture in the region as well as its delta being an extensive wetland, qualified as an Important Bird Area by the WWF. Besides this, the delta has been protected as a Ramsar site since 1998. On the other hand it has been reported that the river is heavily polluted by agricultural, domestic and industrial discharges. In this preliminary investigation the deposition of some heavy metals (As, Pb, Cd, Ni, Cu, Co and Cr) in sediments of the delta was analyzed to estimate the effect of pollution. According to the results, it can be concluded that there is no pollution risk for As, Cu, Cd, Co, Ni and Pb. However, a high Cr content (2565.5 ppm maximum) was detected especially at station 2 and 3, where the wastewater of the leather industry was discharged into the channel connected to station 2, even though the plant has a treatment system.

Key Words: Gediz Delta, sediments, heavy metals, pollution.

Introduction

The Gediz River with its 401 km length is the second largest river flowing into the Aegean Sea from Anatolia. The Gediz Delta is located on the coast of the Aegean Sea, just south of the mouth of the Gediz River, 25 km northwest of Izmir (Figure 1). The Gediz Delta is an extensive wetland consisting of bays, salt marshes, freshwater marshes, large saltpans and four lagoons at the former mouth of the Gediz River. The WWF-Turkey office had declared that the site qualified as an IBA (Important Bird Area) for its breeding populations of many bird species. Gediz Delta is one of Turkey's nine Ramsar site (site No.945) protected by the Ramsar with the agreement number 7TR009 since 1998 and the Bern Convention (Ermert 2003).

The Gediz River is heavily polluted due to agricultural drainage water, industrial wastewater and virtually all domestic wastewater from the entire area (Usak, Manisa and Izmir) (Elmaci et al. 2002). The effects of pollution on the Gediz Delta are so far unknown. Anaerobic water from the salines is thought to cause sea pollution. An international dockyard and harbour were planned for construction near the site, but after an unfavourable environmental impact assessment construction was cancelled. Organized dumping of sludge from Izmir Bay into the delta was also prohibited.

Although there have been many attempts to improve the enforcement of water quality and protect the natural environment, the most recent one was established in early 1998 as a coordinating committee named "Environmental Protection Service Association of Gediz Basin Provinces" with association of three provincial offices of the Ministry of Environment. However, since its establishment this service has achieved little due to lack of resources and inefficiency in the enforcement of existing standards and regulations. It also includes a reduction in support for utilisation of fertilizers and agricultural chemicals as non-point source pollution problems.

Under these circumstances, it has been concluded that the Gediz River and its delta must be protected as natural resources and a heritage for future generations. This investigation also aimed to consider the pollution problems of the delta and to obtain some data about the heavy metals loads of sediments which have the role of a depository compartment in ecosystems.

Material and Methods

Sediment samples were collected in the months February, April, May, July and September 1998. The sampling was done from 8 stations which cover different sites in the Gediz Delta

(St.1, 2, 3) and several sites on the adjacent coastal area (St.4, 5, 6, 7, and 8). The locations of sampling points are depicted in Fig.1. The stations were selected considering their water usage and drainage of the effluents from several industrial and domestic sites. The samples were collected with a Van-ween grab from the top 15 cm of the sediment layers which are defined as the "surface sediments. The samples were removed from the sampler and the outer parts separated to prevent contamination from the metallic body of the sampler. Teflon spatulas were used for the same purpose. The samples were placed in pre-cleaned plastic bags and kept in ice-box for a few hours until arriving at the laboratory.

Samples were then dried in an oven at 60°C for approximately 3 – 4 days. Dried samples were homogenized and sieved to a fine powder. Samples were solubilized using the wet-digestion system. Approximately 0.5 g dried and homogenized sediment was weighed and placed into an acid-washed container to which 5 ml of a mixture of perchloric and nitric acid (1:5 v:v) were added.

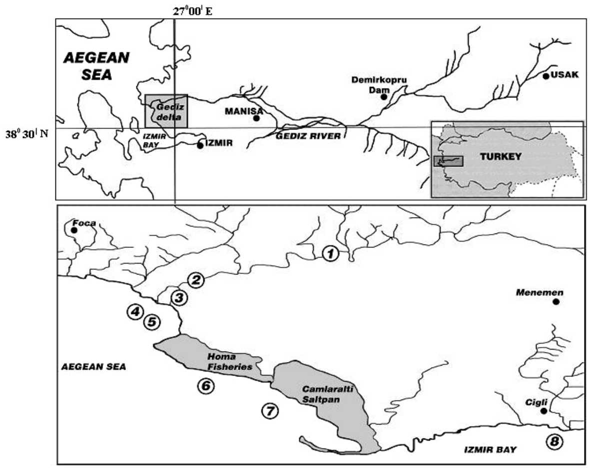

Figure 1. Sampling sites for sediments on the delta of the Gediz River.

The containers were connected to a water condenser to prevent the escape of acid fumes. The containers were placed in the water bath and heated at 140 °C for 12 hours keeping a continuous flow of cooling water through the condenser. The digested samples were transferred into a 50 ml polyethylene flask, diluted to 50 ml with bidistilled water and the flask transferred into polyethylene bottles which had been pre-cleaned with acid wash for storage. Special attention was paid to ensuring that the reagent was supra pure grade for the digestion process. Triplicate samples were prepared from each sediment sample and the same procedure was applied for blank samples (Anonymous 1991). The samples were analysed by ICP-MS (HP Model 4500) to determine chromium, cobalt, nickel, copper, arsenic, cadmium and lead concentrations. The certified reference materials were used to check the accuracy and reliability of the method. The results were given in mg/kg dry weight. One-way ANOVA and Multiple Range Test were applied to asses the statistically important differences in temporal and spatial variations.

Results and Discussion

The data can be considered in two main groups as freshwater (sampling site no 1, 2 and 3) and marine stations (sampling site no 4, 5, 6,7and 8). Therefore, the results of heavy metal concentrations of the sediment of the Gediz River delta and adjacent marine stations are presented in Table 1, Table 2.

Heavy metal concentrations in sediments from the delta varied according to the sampling period and the difference was statistically significant ($p< 0.05$) except Cu at station 2 and Cd in station 3. The difference in heavy metal contents of the sediments according to the stations was also significant ($p<0.05$) except As and Cd. The maximum and minimum amounts of heavy metal concentrations in the delta were Cr: 2565.5-5.97, Co: 14.51-2.95, Cu: 25.28-0.23, As: 21.47-3.54, Ni: 66.78-12.08, Pb: 79.30-1.04, Cd 0.54-0.04 mg/kg dry weight.

The highest As, Cu, Cd, Co, Ni and Pb amounts determined at the stations in the Gediz River delta were quite low according to the sediment quality criteria (Long et al 1995, Anonymous 2003). Also, Akcay et al (2003) had found Cu concentrations between 108 –152 ppm for the Gediz River but also declared that there is no pollution risk considering speciation data. These results are also in correlation with other data from several rivers sediments (Facetti et al 1998, Phuong et al 1998, Rozales-Hoz and Carranza-Edwards 1998, Molisani et al 1999, Akcay et al 2003, Liua et.al 2003).

The Cr amount of the samples was of importance ranging between 2565.4-5.97 ppm in the sampling period. The sediments from station 2 and station 3 have considerably high Cr concentrations ($p<0.0000$) according to the sediments quality criteria accepted by many countries (Long et al 1995, Anonymous 2003). These criteria varied according to the purpose of usage but the concentration never exceeded the level which we found from this investigation. For example, according to NOAA's National Status and Trends Program, Sediment Quality Guidelines as effect range low (ERL) and effects range median (ERM) levels for Cr is 81 ppm and 370 ppm respectively (Long et al. 1995). 270 ppm was accepted as the sediment clean up level by Washington State Dept. of Ecology (Anonymous 2003).

This level of chromium is also higher than Paraguay River sediments (Facetti et al.1998). According to Akcay et al (2003) chromium analyses indicated the presence of pollution in the Gediz River and especially high Cr (VI) values show that the pollution originated from industrial activities. Izmir Bay as the basin which collects the effluents of the city and drainage water via the rivers around such as the Gediz River does not have such a level of chromium in its sediments (Küçüksezgin et al 1999, Türkoğlu and Parlak 1999, Küçüksezgin 2001). It is thought that this high level of chromium resulted from the leather industry located near to station 2 and connected to station 3 by a channel.

Heavy metal concentrations at marine stations also varied according to the sampling period ($p<0.005$) except Cd at station 7. The difference in heavy metal concentrations between the stations was statistically significant ($p<0.005$) as well, except Pb and Cd. The maximum and minimum concentrations varied as follows: Cr: 488.73 – 5.87, Co: 15.22 – 2.21, Cu: 30.97 – 0.39, As: 22.08 – 1.18, Ni: 57.4 – 8.68, Pb: 23.94 – 1.82, Cd: 0.44 – 0.01 mg/kg dry weight.

These results are not higher in comparison with the data of studies from other basins of the Mediterranean Sea. But Izmir Bay (Egemen et al. 1998) and Bilbao estuary (Ruiz and Saiz-Salinas 2000) seem to be more polluted than our sampling sites with higher Cd (4-112 ppm), Cu(118-1785 ppm) and Pb(126-1112 ppm) amounts. On the other hand a high Cr level at station 3 in some periods was recognized, but the fluctuation of values in the study period showed that the contamination was not regular.

It is well known by researchers and governors that the Gediz River receives domestic effluents and industrial discharges of three big cities located along the river. Some problems such as cumulative fish death or contaminated vegetables often arise due to the polluted river water. This has become a serious problem for the health of the public and wildlife over many years. This preliminary investigation aimed to determine the level of heavy metal pollution on the delta of the river which is an important area for birds. Therefore, it is necessary to continue such research to control the trend of pollution. The results show that the most important areas for birds namely stations 2 and 3, were seriously contaminated with Cr and have a substantial amount of Pb which may potentially be harmful in the future.

Further studies should be aimed at preserving and maintaining the succession of wild life to be left to future human generations.

Table 1. Heavy metal concentrations of the sediment samples collected from freshwater stations of the Gediz Delta (mg/kg dry weight).

Metal	Station No	February	April	May	July	September	Mean±SD
Chromium	1	50,95	9,89	5,97	33,22	21,75	24,36±17,21
	2	1801,38	657,44	540,60	200,47	879,84	815,94±595,11
	3	2565,49	665,70	1264,98	663,27	802,48	1192,39±768,04
Cobalt	1	10,80	3,48	2,96	5,29	5,46	5,60±2,89
	2	14,51	7,81	6,32	6,04	8,02	8,54±3,47
	3	9,10	4,90	4,92	6,36	5,61	6,18±1,673
Copper	1	16,02	0,23	0,65	21,19	5,62	8,743±8,91
	2	25,29	11,33	7,79	13,90	11,90	19,982±23,11
	3	13,92	4,78	5,41	8,74	10,69	8,708±3,91
Arsenic	1	13,16	3,54	3,57	6,78	5,22	6,46±4,10
	2	21,47	7,22	5,84	8,19	6,19	9,78±6,19
	3	3,93	7,05	6,41	8,18	7,18	6,55±1,65
Nickel	1	34,88	14,50	12,09	24,38	23,81	21,93±8,89
	2	66,78	42,04	34,04	29,15	42,69	42,94±14,47
	3	44,24	26,40	24,78	27,51	31,16	35,45±17,42
Lead	1	8,31	1,38	1,04	8,50	3,68	4,58±3,58
	2	79,30	29,50	24,36	24,31	46,958	40,89±22,23
	3	54,59	29,35	57,85	25,76	29,00	39,31±16,66
Cadmium	1	0,07	0,04	0,04	0,54	0,20	0,18±0,23
	2	0,13	0,09	0,08	0,42	0,08	0,16±0,17
	3	0,12	0,03	0,07	0,14	0,10	0,10±0,04

Table 2. Heavy metal concentrations of the sediment samples collected from marine stations adjacent to the Gediz Delta (mg/kg dry weight).

Metal	Station No	February	April	May	July	September	Mean±SD
Chromium	4	75,28	86,40	24,69	53,66	15,10	51,03±29,80
	5	46,91	19,47	5,87	8,90	11,59	18,55±15,62
	6	60,07	23,87	27,97	38,15	39,28	37,87±13,27
	7	57,96	76,69	15,84	26,76	61,27	47,70±24,30
	8	366,58	47,10	19,51	66,91	488,74	189,76±186,95
Cobalt	4	12,99	7,88	3,71	15,22	5,32	9,03±4,93
	5	10,33	4,34	2,57	2,21	2,63	4,42±3,22
	6	10,63	4,69	5,88	7,61	7,68	7,27±2,12
	7	10,28	14,30	4,11	6,25	10,48	9,09±3,70
	8	10,01	4,90	4,55	5,69	6,50	6,33±2,12
Copper	4	25,00	19,97	4,11	30,98	3,34	16,68±11,56
	5	14,12	4,11	0,68	0,39	2,34	4,33±5,28
	6	17,41	3,39	5,14	8,91	8,844	8,74±5,02
	7	14,94	29,15	2,70	5,48	19,67	14,38±9,96
	8	28,22	4,31	3,45	8,87	21,32	13,23±10,22
Arsenic	4	22,09	10,37	3,15	15,93	4,19	11,15±7,57
	5	9,56	3,54	1,19	1,346	2,18	3,56±3,25
	6	11,84	3,84	5,76	7,705	7,01	7,23±2,77
	7	9,17	5,55	4,44	0,028	6,34	5,11±3,12
	8	3,96	3,59	2,55	2,626	4,63	3,47±0,84

Nickel	4	57,43	35,44	14,32	46,01	17,38	34,12±17,23
	5	41,59	20,38	8,68	9,83	11,70	18,44±12,76
	6	53,02	24,97	23,73	35,81	37,76	35,06±11,04
	7	43,85	36,28	17,26	28,14	38,09	32,73±9,63
	8	30,03	24,15	15,82	23,28	25,19	23,69±4,86
Lead	4	11,50	8,54	2,47	27,72	2,67	10,58±9,58
	5	14,94	3,18	3,70	2,52	1,83	5,24±5,08
	6	37,55	8,06	4,47	9,58	7,18	13,37±12,80
	7	11,03	13,81	1,83	3,55	17,63	9,59±6,25
	8	15,83	4,01	3,06	4,77	23,94	10,32±8,54
Cadmium	4	0,06	0,05	0,05	0,22	0,04	0,08±0,08
	5	0,18	0,04	0,05	0,28	0,01	0,11±0,11
	6	0,02	0,05	0,02	0,39	0,06	0,11±0,51
	7	0,06	0,07	0,04	0,04	0,05	0,05±0,02
	8	0,05	0,06	0,05	0,44	0,13	0,14±0,16

References

Akcay H., A. Oguz., C. Karapire. 2003. Study of heavy metal pollution and speciation in Buyuk Menderes and Gediz River sediments. Water Research 37: 813-822.

Anonymous 1998. The Ramsar Convention on Wetlands. The Annotated Ramsar List: Turkey. http: //www .wetlands. org/ RDB/ Ramsar_Dir /Turkey/ tr009D02.pdf 8.02.2003 and http :// www. ramsar. org/ profiles_ turkey.htm

Anonymous 1991. Analytical Techniques in Environmental Chemistry. Pergamon Series on Environmental Science, 3:615-618.

Anonymous 2003. Sediment quality chemical criteria. Washington State Dept of Ecology, Toxic Cleanup programme. 9.01.2003. http:// www. ecy.wa .gov/ programs/tcp/smu/sed_chem.htm

Dauvalter V., S.Rognerud. 2001. Heavy metal pollution in Sediments of the Pasvik River drainage. Chemosphere 42:9-18.

Elmaci O.L., S. Delibacak, M.Secer, A. Bodur.2002. Fertility status, trace elements and heavy metal pollution of agricultural land irrigated from the Gediz River. Int.J.Wat. 2, 2/3:184-194.

Ermert A. 2003. Turkey goes to court to protect Gediz Delta. http:/ /www. panda. org/ about_ wwf/ what_we _do/freshwater /news /news. cfm? uNews ID=5322 9.Jan.2003.

Facetti, J., V.M. Dekov, R. Van Grieken. 1998. Heavy metals in sediments from the Paraguay River: a preliminary study. The Sci. of the Tot. Environ.209: 79-86.

Kucuksezgin, F., B.Caglar, O.Uslu, 1999. Polycyclic aromatic hydrocarbons in red mullet (*Mullus barbatus*) and sediments from the Eastern Aegean Sea. Toxicol.Environ. Chem. 73:247-256

Kucuksezgin, F.2001. Distribution of heavy metals in the surficial sediments of Izmir Bay (Turkey). Toxicol.Environ.Chem. 80:203-207.

Liua, W.X., X.D. Lia, Z.G. Shena., D.C. Wanga., O.W.H. Waia., Y.S. Lia. 2003. Multivariate statistical study of heavy metal enrichment in sediments of the Pearl River Estuary. Environmental Pollution 121:377–388.

Long, E. R. , D. D. Macdonald, S. L. Smith , F. D. Calder. 1995. Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. Environm. Management 19(1), pp 81-97.

Molisani, M. M., M. S. M. B. Salomão., A. R. C. Ovalle., C. E. Rezende., L. D. Lacerda., C. E. V. Carvalho.1999. Heavy Metals in Sediments of the Lower Paraíba do Sul River and Estuary, R.J., Brazil. Bull. Environ. Contam. Toxicol. 63:682-690.

Egemen, E., U.Sunlu, A.Kaymakçı. 1998. Heavy metal concentrations in some molluscs and in surficial sediments from Izmir Bay/Turkey. 35th CİESM Congress Proceedings, Dubrovnik (Croatie), 35(1), 250-251.

Phuong P. K., C. P. N. Son., J.-J. Sauvain, J.Tarradellas. 1998.Contamination by PCB's, DDT's, and Heavy Metals in Sediments of Ho Chi Minh City's Canals, Viet Nam. Bull. Environ. Contam. Toxicol 60:347-354.

Rosales-Hoz, L., A.Carranza-Edwards, 1998. Heavy Metals in Sediments from Coatzacoalcos River Mexico. Bull. Environ. Contam. Toxicol 60: 553-561.

Ruiz, J.M., J.I. Saiz-Salinas. 2000. Extreme variation in the concentration of trace metals in sediments and bivalves from the Bilbao estuary (Spain) caused by the 1989-1990 droughts. Mar. Environ. Res. 49, 307-317.

Svendson M., D.H..Murray-Rust, N. Harmancıoğlı.,N.Alpaslan.2000. Governing Closing Basins: The Case of The Gediz River in Turkey. Intersectoral Management of River Basins. Section D: Case studies of national river basins. Proceedings of an Int. Workshop "Integrated Water Management in water stresses River basins in developing countries: strategies for poverty alleviation and Agricultural growth" Loskop Dam, South Africa, 16-21 Oct.2000.

Türkoğlu, M., H. Parlak, 1999. Accumulation and distribution of total chromium in seawater, sediment and some organisms and its behaviour processes in Izmir Bay (Aegean Sea). EgeUniversity Journal of Fisheries and Aquatic Sciences. 16(1-2): 47-58.