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ANALYSIS OF HEAVY METALS IN SEAWATER SAMPLES COLLECTED FROM BEACHES OF ASIAN SIDE OF ISTANBUL

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ABSTRACT

This study proposed to investigate the quality of seawater to protect health of people which do recreational activities such as swimming. Ni and Pb concentrations in seawater samples taken from Kucuksu, Fenerbahce and Suadiye beaches in Asian side of Istanbul between Feburary 9 and May 4, 2009 were investigated. Agilent 7500 A inductively coupled plasma mass spectrometry (ICP-MS) instrument was used to perform water samples analysis. The nickel concentrations were mostly below the recommended marine recreational water quality criteria for water pollution. But the lead concentrations in seawater were above the limit.

Keywords: Heavy metal concentrations, sea water, beach

İSTANBUL ANADOLU YAKASINDAKİ PLAJLARDAN TOPLANAN DENİZ SUYU ÖRNEKLERİNDE AĞIR METALLERİN ANALİZİ

ÖZET

Bu çalışmada, yüzme gibi rekreasyon amacıyla kullanılan deniz sularının insan sağlığı açısından kalitesi araştırılmıştır. 9 Şubat ve 4 Mayıs 2009 tarihleri arasında İstanbul Anadolu yakasındaki Küçüksu, Fenerbahçe ve Suadiye plajlarından alınan deniz suyu örneklerinde nikel ve kurşun konsantrasyonları ölçülmüştür. Su örnekleri analizinde Agilent 7500 A ICP-MS cihazı kullanılmıştır. Nikel konsantrasyonları genel olarak Su kirliliği Kontrol Yönetmeliği'ndeki deniz suyu rekreasyon kriterlerindeki sınır değerin altındadır. Fakat deniz suyundaki kurşun konsantrasyonları limitin üstündedir.

Anahtar kelimeler: Ağır metal konsantrasyonları, deniz suyu, plaj

1. Introduction

Seawater is under the risk of high pollution because of domestic wastewater, industrial wastewater, sea traffic, accident potential, port services and wastewater, bilge and ballast water disposals related to port services. Marine waters are identified as having the following beneficial uses: a habitat for marine organisms generally, recreational bathing beach. Heavy metals such as lead and nickel are toxic priority pollutants, that commonly interfere with the beneficial usage of wastewater for irrigation and industrial applications. In recent years, contamination of sea water by heavy metals is becoming major problem for aquatic life and human health.

The well known long term toxic effects of heavy metals lead (Pb) and nickel (Ni) are of both scientific and environmental concerns. The presence of these heavy metals in water, create a societal health risk that, which is useful for fisheries. Fish play an important role in human nutrition and therefore need to be carefully and routinely screened to ensure that there are no high levels of heavy metals being transferred to man through their consumption (Muiruri et al., 2013, p.891). In aquatic environment, larger animals such as fish have been exposed to heavy metals as a direct consequence of biomagnifications (Ekwanyanwu et al., 2011, p.; Javed and Usmani, 2011, p.660).

The current literature includes some investigation on concentration of heavy metals in sea water in several different coastal areas of the world. One of them was studied in Indonesian by Lestari, 2004, p.52. His observation on heavy metals (Hg, Pb, Cd, Cu, Zn and Ni) content in sea water in beaches, were carried out in Jakarta Bay waters in May 2004. His observation was conducted with fish total quantity of death.

Another example is that, a survey on the metal concentrations (As, Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sr, V, Zn) in beach water and sediments was reported from the tourist destination of Acapulco city on the Pacific coast of Mexico by Jonathan et al., 2011, p.845. Their comparison results suggested that the beach water quality had deteriorated more than the sediments and special care needed to be taken to restore the beach quality.

Additionally, heavy metal levels were measured in seawater and sediment in Zonguldak, which is on the Black sea shore of Turkey by Coban et al., 2009, p.23. Their samples were collected near the industrial areas and city beaches. 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 were above the limits in Zonguldak seawater in their study.

There are literatures about pollution of Marmara and heavy metals in aquatic life (Bradl, 2005; Cunningham and Cunningham, 2004; Erturk and Yonsel, 2002; Oguzulgen, 1995, p.108-126; Okay *et al.*, 2011, p.55-65; Okus *et al.*, 2007, p.35-38; Tan and Otay, 1999, p.871-892; Taub, 2004; Ulengin, 1994, p.771-785; Wright and Welbourn, 2002; Yaşar et al., 2001,p.299-313).

Table1. The legislation of Water Pollution Control (Water Pollution Control Regulation, 1988).

Parameter	Unit (parts per million)	Maximum Allowable Limits
Lead	ppm	0.1
Nickel	ppm	0.1

There are some regulations in Turkey about marine heavy metal standards to protect aquatic life and human health. It is principle to obey the criteria of general quality sea waters for the conservation of all coast and sea waters in a healthy environment state, whether it is taken for classification in terms of usage for any aim or not (Table 1).

The legislation of Water Pollution Control last issued ambient water quality criteria recommendations for recreational waters in 1986. Criteria are designed to protect the public while participating in water-contact activities such as swimming, wading, and surfing in all waters designed for such recreational uses. Typical surface waters have pH ranging from 6 to 9 (Water Pollution Control Regulation, 1988).

Marmara coasts have suffered from pollution as a result of a rapid and uncontrolled industrial development and intensive urbanization. There is an extensive water pollution problem especially caused by the discharge of domestic and industrial discharge loads, occured in Marmara coasts. Beaches are used as a recreation area for local people. Main purpose of this study, to measure element concentrations, pH and temperature values in coastal seawater to compare with water quality criteria for marine recreational waters.

2. Study Area

The Marmara Sea, connected to the Black and Aegean seas by the Strait of Istanbul and Dardanelles straits, is an inland sea forming a transition zone between the Black Sea and Mediterranean Sea (Besiktepe et al., 1994, p.285-334). Seawater samples were collected once in every week during February 2009 to May 2009 from three beaches as Kucuksu beach, Fenerbahce beach, and Suadiye beach (Figure1).

Figure1. The location of sampling points;
(1)Kucuksu Beach, (2) Fenerbahce Beach, (3) Suadiye Beach.

3. Materials and Methods

The samples were taken from a depth of 50 cm below the surface using polythene bottles(500 mL) attached to the top of 3-4 m long telescopic bar (Figure2a) (Graeme, 1991).

Figure2.(a) Equipment for sampling seawater (Mart, 1979). **(b)** TFA LT-101 Digital Thermometer. **(c)** TPP (Filtermax) Vacuum Systems. **(d)** WTW inoLab pH 720 Benchtop Meter.

After sample bottles were rinsed three times with seawater, bottles were filled fully. The temperature of seawater was determined using digital thermometer dipped below sea. Then, samples were stored on ice for transfer to the laboratory of Marmara University for analysis, according to the methods of Strickland & Parsons, 1968, p.. In Laboratory, samples were firstly filtered by using TPP (Filtermax) Vacuum Systems (Large 49 cm^2 square PES (polyethersulfone) 0.2 µm membrane) which were connected to a vacuum pump. Secondly, the pH of the samples was determined using pH-meter with electronic glass electrode (Figure2(b),(c),(d)) and values show in Table2.

Sample volume was reduced by using automatic pipette until 98 mL and transferred to an empty TPP bottle, with the addition of 2 mL concentrated HNO_3 , in order to preserve the metals and also to avoid precipitation. The prepared samples were stored in frozen room till ICP-MS analysis starts. Before the analysis in ICP-MS, prepared seawater samples were respectively diluted to the 1:10 ratio and 1:100 ratio.

Firstly, samples were diluted to 1:10 ratio. 88 mL distilled water was measured by using graduated cylinder for each polypropylene bottle (50mL or 100 mL). After distilled water poured to each bottle, 2 mL nitric acid (HNO3) and 10 mL seawater sample added to each bottle by using automatic pipette.

Then, samples were diluted to 1:100 ratio. 88 mL distilled water was measured by using graduated cylinder for each bottle. After distilled water poured to each bottle, 2 mL nitric acid (HNO_3) and 10 mL diluted (1:10) seawater sample added each bottle by using automatic pipette. Each bottle was named and dated with respect to the value of ratio, name of beach, and date of sampling.

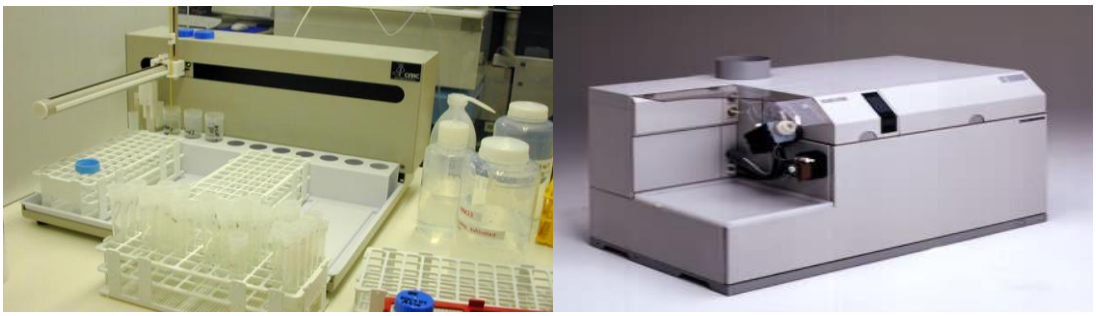

Figure3.(a) Autosampler (CETAC ASX-51).**(b)** ICP-MS (Agilent 7500a).

Determination of concentrations of metals by using Inductively Coupled Plasma Mass Spectrometry (ICP-MS): Original, diluted to 1:10, and diluted to 1:100 samples, which were prepared for Kucuksu Beach, Fenerbahce Beach, and Suadiye Beach, located CETAC ASX-510 autosampler respectively. Then they were analyzed by using ICP-MS. After all samples were located in sampler, samples which are diluted to 1:100 ratio have been analyzed by using ICP-MS. The number of elements which analyzed in each sample were thirteen (Figure3(a) and (b)). Although thirteen elements were analyzed, we have focused on two elements. Because Ni, and Pb elements were fluctuated in a wide range, according to the results of analyses.

4. Results and Discussions

Ni and Pb concentrations in seawater samples taken from Kucuksu, Fenerbahce and Suadiye beaches located in Anatolian side of Istanbul between February 9 and May 4, 2009 are investigated. For most of samples taken from one of three beaches located in Anatolian side, measured concentrations are relatively close to each other beaches and concentrations of Nickel are generally below the limits imposed by regulations. Ni concentration in Kucuksu beach is generally below the allowable limit value of 0.1 ppm (Table2, Figure4).

Table2. Nickel and Lead concentrations as ppm for three beaches.

Date	Kucuksu Beach		Fenerbahce Beach		Suadiye Beach	
	Ni	Pb	Ni	Pb	Ni	Pb
09.02.2009 (1st week)	-------	-------	0.100	0.100	0.163	0.163
16.02.2009 (2nd week)	0.084	0.084	0.158	0.158	0.085	0.085
23.02.2009 (3rd week)	0.083	0.083	0.078	0.078	0.105	0.105
02.03.2009 (4th week)	0.087	0.087	0.080	0.080	0.086	0.086
09.03.2009 (5th week)	0.077	0.077	0.083	0.083	0.103	0.103
16.03.2009 (6th week)	0.184	0.184	0.137	0.137	0.127	0.127
23.03.2009 (7th week)	0.107	0.107	0.105	0.105	0.145	0.145
30.03.2009 (8th week)	0.083	0.083	0.088	0.088	0.101	0.101
06.04.2009 (9th week)	0.108	0.108	0.082	0.082	0.078	0.078
13.04.2009 (10th week)	0.100	0.100	0.144	0.144	0.119	0.119
20.04.2009 (11th week)	0.087	0.087	0.081	0.081	0.169	0.169
27.04.2009 (12th week)	0.104	0.104	0.112	0.112	0.098	0.098
04.05.2009 (13th week)	0.081	0.081	0.083	0.083	0.174	0.174

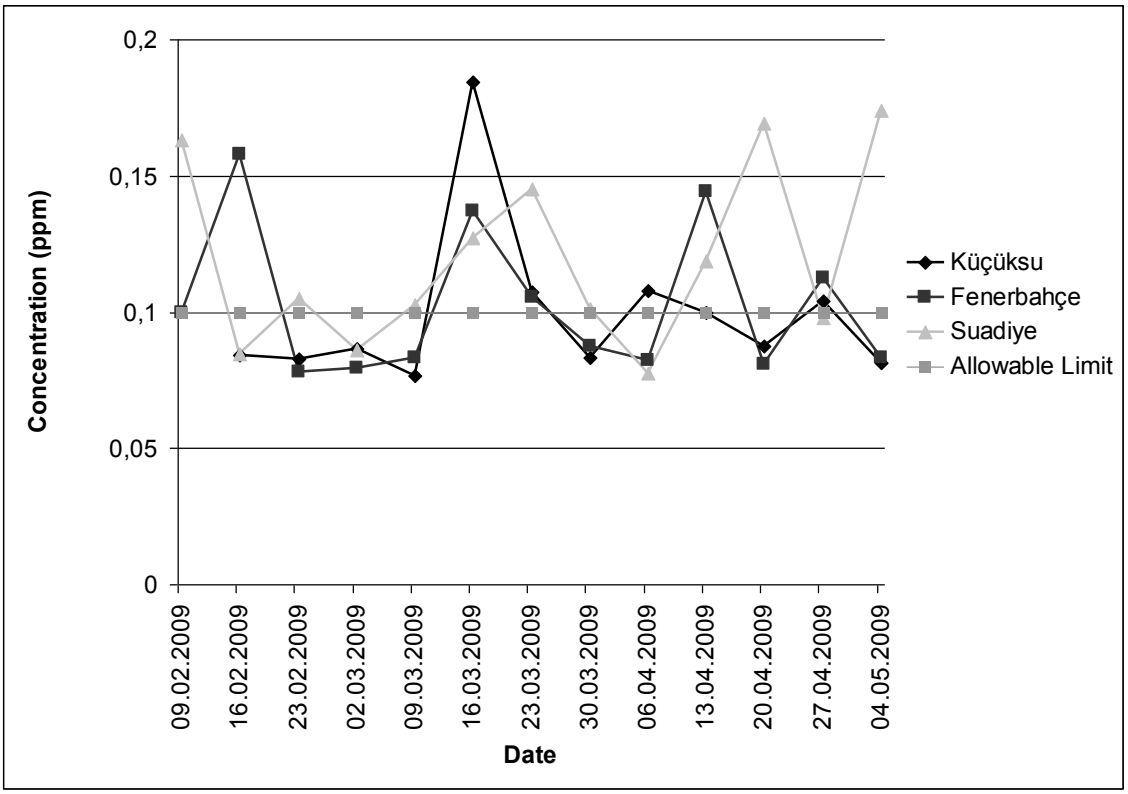

Figure4. Nickel concentrations for three beaches.

The concentrations of Pb in seawater were detected were found to be higher than WHO recommended limit (Table2, Figure5).

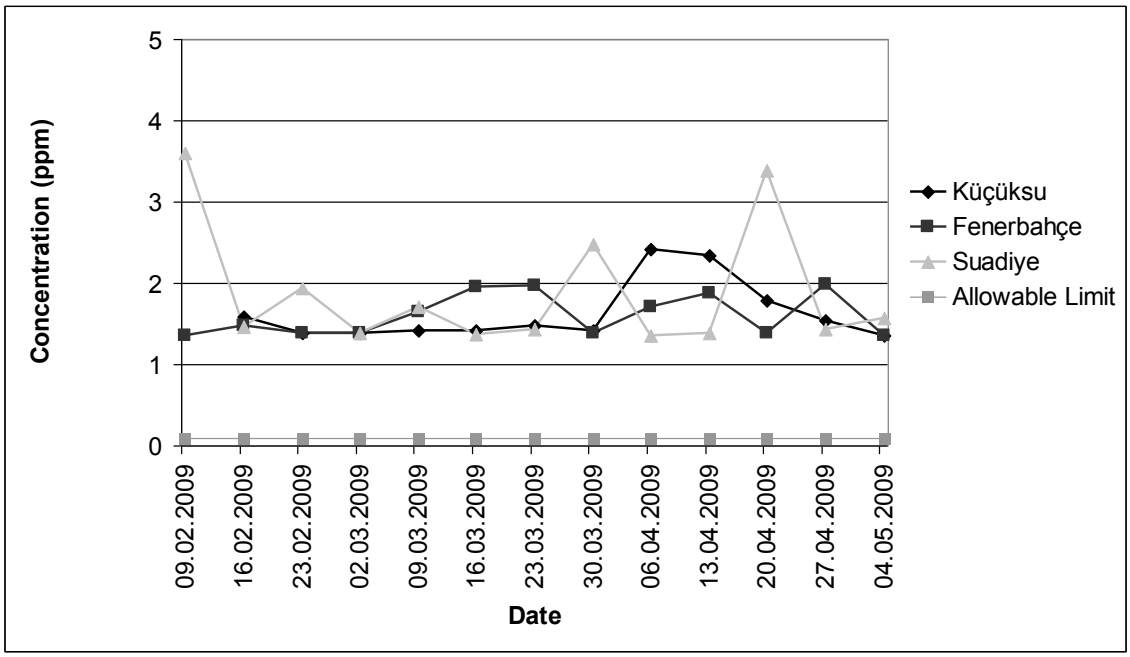

Figure5. Pb concentrations for three beaches.

Marine waters within the Marmara Sea are identified as having the following beneficial uses: a habitat for marine organisms generally, recreational bathing beach. Human activity should not cause the natural pH range to be extended by more than 0.2 units. Waste discharges shall not cause the natural daily temperature range to change by more than 2.0^{o}C. The pH of the water should be within the range 6 – 9 units (Yüzme Suyu Kalitesi Yönetmeliği, 2006). Table3 presents the pH and temperature values. Based on the analyzed data, the pH of seawater ranged from 8.15 to 8.42. The pH values of seawater samples were alkaline. The pH and temperature levels were within the allowable limits.

Table3. Water pH and temperature values of three beaches.

	Kucuksu Beach		Fenerbahce Beach		Suadiye Beach	
Date	Temperature(^{o}C)	pH	Temperature(^{o}C)	pH	Temperature(^{o}C)	pH
09.02.2009	-----	---	8.5	8.21	9.2	8.22
16.02.2009	7.1	8.25	8.7	8.28	9.4	8.36
23.02.2009	7.2	8.26	9.1	8.24	9.6	8.25
02.03.2009	7.4	8.19	9.4	8.17	9.7	8.18
09.03.2009	7.9	8.19	9.8	8.15	10.4	8.24
16.03.2009	7.9	8.25	9.3	8.32	9.6	8.42
23.03.2009	8.1	8.20	9.7	8.35	9.8	8.28
30.03.2009	8.9	8.24	10.4	8.26	10.6	8.18
06.04.2009	9.3	8.27	12.1	8.24	14.3	8.28
13.04.2009	12.3	8.32	15.3	8.34	17.4	8.22
20.04.2009	18.1	8.29	22.9	8.32	24.4	8.37
27.04.2009	21.6	8.38	22.9	8.31	24.6	8.35
04.05.2009	24.1	8.32	23.6	8.35	27.6	8.42

5. Conclusions

Seawater samples taken from three beaches were characterized, because coastal seawater may have been contaminated. Heavy metal concentrations were quantitatively determined by ICP-MS in 0.05-5ppm. Measurements made on samples taken from Kucuksu, Fenerbahce and Suadiye beaches located in Anatolian side of Istanbul per week between Feburary 9 and May 4, 2009.

Based on this study, concentrations of Ni contained in 0.08-0.18 ppm were generally below the allowable limit value of 0.1 ppm with the exception of a few days where related concentration was slightly higher than limits. Ni concentration in Kucuksu beach was considerably lower than other two beaches, due to effect of Black Sea and flow in Bosphorus.

This study provided also the Pb data on the contamination status of heavy metals in seawater samples collected from beaches of Asian side of Istanbul. Pb concentrations in Kucuksu beach were relatively lower than the other beaches in February and March, whereas they were higher in April. Observation of relatively higher concentrations in comparison to the other beaches in the samples taken in the first week of April from Kucuksu beach, which was generally low in concentration, shows that there was pollution effect in the region. The fact that concentrations in Kucuksu beach decrease again in the other weeks of April indicates that, sea streams clean the area.

As a result, constant monitoring of heavy metals concentration in Marmara Sea is recommended, since sea serves as a source

of swimming and fisheries for the local inhabitants. The results of our research also could contribute to comparison with further experimental and theoretical investigations in same beaches for quantifying concentration changes with time.

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