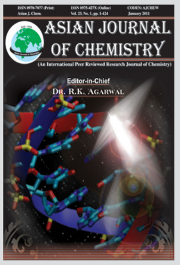
Asian Journal of Chemistry; *Vol. 23, No. 8 (2011), 3320-3324*

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in



Metal Pollution in Surface Sediments of the Golden Horn Estuary (Marmara Sea, Turkey) after the Remedial Actions

M.S. ERSAN[1,*], N. BALKIS[1], E. MÜFTÜOGLU[1], A. AKSU[1] and S. BURAK[2,3]

[1]Department of Chemical Oceanography, Istanbul University, Institute of Marine Science and Management, Vefa 34134, Istanbul, Turkey
[2]Marine Biology and Physical Oceanography, Istanbul University, Institute of Marine Science and Management, Vefa 34134, Istanbul, Turkey
[3]Department of Marine Environment, Istanbul University, Institute of Marine Sciences and Management, Vefa 34134, Istanbul, Turkey

*Corresponding author: Fax: +90 212 526 84 33; Tel: +90 212 4400000; E-mail: mselim@istanbul.edu.tr

(*Received*: 7 September 2010; *Accepted*: 11 April 2011) AJC-9793

The present study investigated the metal pollution of the surface sediment samples from the Golden Horn Estuary in Istanbul. It has connection with the Marmara Sea directly and with the Black Sea *via* Bosphorus and was polluted by different kinds of industrial plants until 1999. In addition to this, municipal wastewater of around one million people has been discharged into this receiving media. Greater part of the estuary was almost blocked off by sediment islands. Extensive effort was spent to dredge out sediment in 1999. This created quite a convenient condition for aquatic medium in the estuary. In this study, metal pollution of sediment was investigated to get clue about water quality of the estuary after the remedial actions. For this purpose, surface sediment samples were collected for a single time at six stations along the estuary in 2007. Contents of Hg, Al, Fe, Cr, Mn, Pb, Cu, Cd, $CaCO_3$, Corg were measured in surface sediments of the estuary. The metal values were also evaluated according to the enrichment factors (EF's).

Key Words: Golden Horn, Metal pollution, Sediment, Enrichment factors.

INTRODUCTION

Estuaries are among the most heavily environmentally impacted coastal ecosystems[1]. Sediment and water quality in estuaries have been found to be greatly influenced by urbanization and industrialization[2-5].

Because of the ever increasing human activities in coastal areas there is a continued need for a better understanding of pollution in these estuaries. The sediment compartment represents the most concentrated physical pool of metals in aquatic environments[6]. More than 90 % of the heavy metal load in aquatic systems is bound to suspended particulate matter and sediments[7].

More than 90 % of the heavy metal load in aquatic systems is bound to suspended particulate matter and sediments[7]. Therefore, sediments serve as a pool of metals that could be released to the overlying water from natural and anthropogenic processes such as bioturbation and dredging, resulting in potential adverse health effects[6,8,9]. Since estuaries are among the most productive marine ecosystems in the world, serving as feeding, migration routes and nursery grounds of many organisms, it is important that sediment contamination by trace metals be evaluated and that natural *versus* anthropogenic contribution be distinguished for effective remedial actions against metal pollution[10-12].

The Golden Horn was a heavily polluted estuary in Istanbul, the largest metropolitan centre of Turkey with a population of approximately 15 millions. Industrial and domestic discharges, solid small churn and straw and erosion from land-based sources constitute the main sources of the pollution in the Golden Horn[13]. Ergin *et al.*[14] showed that most of the bottom sediments in the Golden Horn are derived from land erosions and carried into the estuary by the aforementioned two major (Alibeyköy and Kagithane) creeks. In 1994, Istanbul Municipality initiated the Golden Horn Environmental Restoration Project[14]. Approximately 5 millions cubic meters of mud were dredged to allow boats entrance through the Golden Horn[15]. A new operational collector system was constructed surrounding the estuary to reduce the discharges of domestic and industrial wastewater. Forestation reduced the erosion in drainage areas of the Alibeyköy and Kagithane Creeks. The aim of this study is to investigate the metal pollution of the Golden Horn surface sediments after the remedial actions.

EXPERIMENTAL

Study area: The Golden Horn is a 7 km long and 250-700 m wide (average 370 m) estuary with a surface area[16] of about 2.5 × 10^6 m^2. The water depths decrease from about 40 m at the mouth to 5 m in the innermost estuary. Alibeyköy and

Kagithane Creeks discharged 3×10^5 m^3/day freshwater in the past[16,17]. However, their discharges were much lower (3×10^5 m^3/year) in the late 1990s[15]. Therefore, the only main freshwater source of the Golden Horn is rainfall and to a lesser extent uncontrolled anthropogenic discharges[18,19].

Sampling and analysis: Sediment samples were taken during August-2008 cruise of R.V ARAR I using Van Veen-Type Grab from surface sediments in the Golden Horn at six locations which are depicted in Fig. 1. Samples were placed on a glass tray and homogenized with a stainless steel spatula. Any foreign objects such as leaves, snail or shells were discarded. Samples were transferred to plastic bags and placed in a cool box at 4 ºC until transporting to the laboratory and stored at -20 ºC, until further analysis. Samples were digested with an acid mixture involving $HNO_3 + HClO_4 + HF$ for metal analyses. Total metal contents were performed by flame (Fe, Mn, Pb, Al, Cd, Cr, Cu), cold vapour and hydride generator unit (HVG-1 Hydride vapour generator) (Hg) with AAS (Shimadzu-6701F), using the manufacturer's conditions and with background corrections.

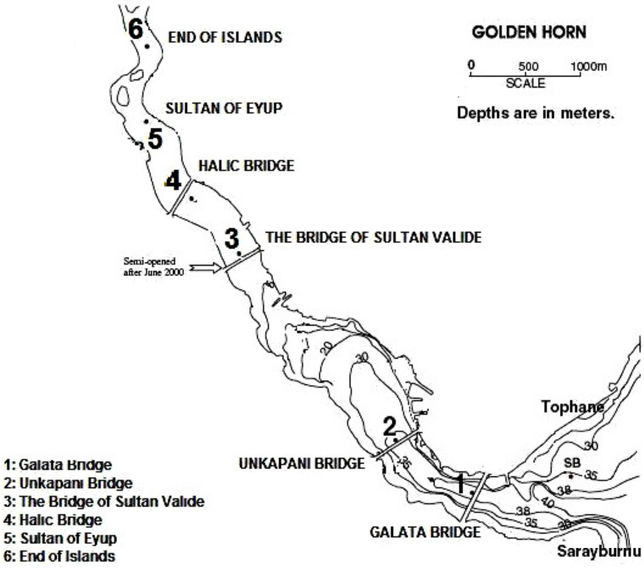


Fig. 1. Location of six sampling stations in the Golden Horn

The total carbonate level of surface sediments was determined with a gasometric-volumetric method[11]. Total organic carbon (C_{org}) was analyzed by the Walkey-Blake method, which involves titration after a wet combustion of the sample[8,12].

The accuracy of the 'total' analyses was checked by analyzing the IAEA433, 405 and 407, QTM080MS (open sea sediment) and QTM081MS (harbour sediment) reference materials (Table-1). The metal values of sediment samples were normalized to eliminate the grain-size effects using metal/Al ratios[20].

Enrichment factors (EF): The main component of elements in sediments is the alumino silicate material. If there were no anthropogenic sources, concentrations of elements should be explained by this source. However, composition of sediment is changed by contributions from various man-made sources. The degree of the change chemical composition of sediments may be different at each sampling point because of different extent of source contributions at each station[21]. If enrichment factors's values equal to 1.0 or < 1.0, enrichment of metals belong to crust. If enrichment factors's values are higher than 1.0, source of metal pollution belong to anthropogenic sources.

TABLE-1
ACCURACY OF AAS ANALYSES USED IN THIS STUDY, AS DETERMINED BY ANALYSIS OF REFERENCE MATERIALS (THE RSD OF MEASURED VALUES WERE ≤ 7 %)

Reference material	Element	Measured value (this study) ppm (µg/g)	Certified value or range ppm (µg/g)
IAEA433	Fe	42800	40300-41300
IAEA433	Al	78200	76800-79600
IAEA405	Cr	81.8	80-88
IAEA433	Mn	316	312-320
IAEA405	Cu	47.3	46.5-48.9
QTM080MS	Zn	126	148
QTM081MS	Ni	24.1	27.5
IAEA405	Pb	76.9	72.6-77
IAEA407	Hg	0.209	0.222
IAEA433	Cd	0.153	0.145-0.161

Elemental concentrations can be compared with reported natural abundance of the metals in soils and/or crustal rocks, by normalizing against geochemical markers (for example Al, Fe, Cs, Rb, Li, Si, total organic carbon, grain size) of the main natural mineralogical phases[6,11,22-24]. These markers can also compensate for constituent variability in sediments resulting from granulometric variations. Aluminum is a conservative element and a major constituent of clay minerals and has been used successfully by several researchers[10,18,21,25].

The enrichment factors's can be calculated by the equation:

$$(\text{Enrichment factors's}) = (C_x/C_{Al})\ \text{sample} \,/\, (C_x/C_{Al})\ \text{crust}$$

where (C_x/C_{Al}) sample is the ratio of concentration of the element being tested (C_x) to that of Al (C_{Al}) in the sediment sample and (C_x/C_{Al})crust is the same ratio in unpolluted reference baseline. In previous studies they have been commonly used values to provide reference concentrations[26-28]. In this study, Mason's soil composition was used as the reference and Al was used as normalizing element.

RESULTS AND DISCUSSION

The means of Fe, Mn, Pb, Cu, Cd, Cr, Hg, Al concentrations at different stations are presented in Fig. 2. Average crustal abundance values of the trace metals are often used as elemental background concentrations for comparison.

Total carbonate content of surface sediments ranged between 2.2-9.4 % (Fig. 2). The values were generally lower than the average shale of 6.0 % except for Galata Bridge and Unkapani Bridge stations. The high carbonate content was mainly of biogenic origin, composed of gastropod and bivalve shells.

The C_{org} content of the samples varied between 5.1 and 6.3 % (Fig. 2). The values were generally higher than the average shale of 0.6 %[29]. The highest values occurred among the Golden Horn. This distribution pattern indicates that the organic matter is originated not only terrestrially but also anthropogenically (domestic + industrial). The estuary sediment

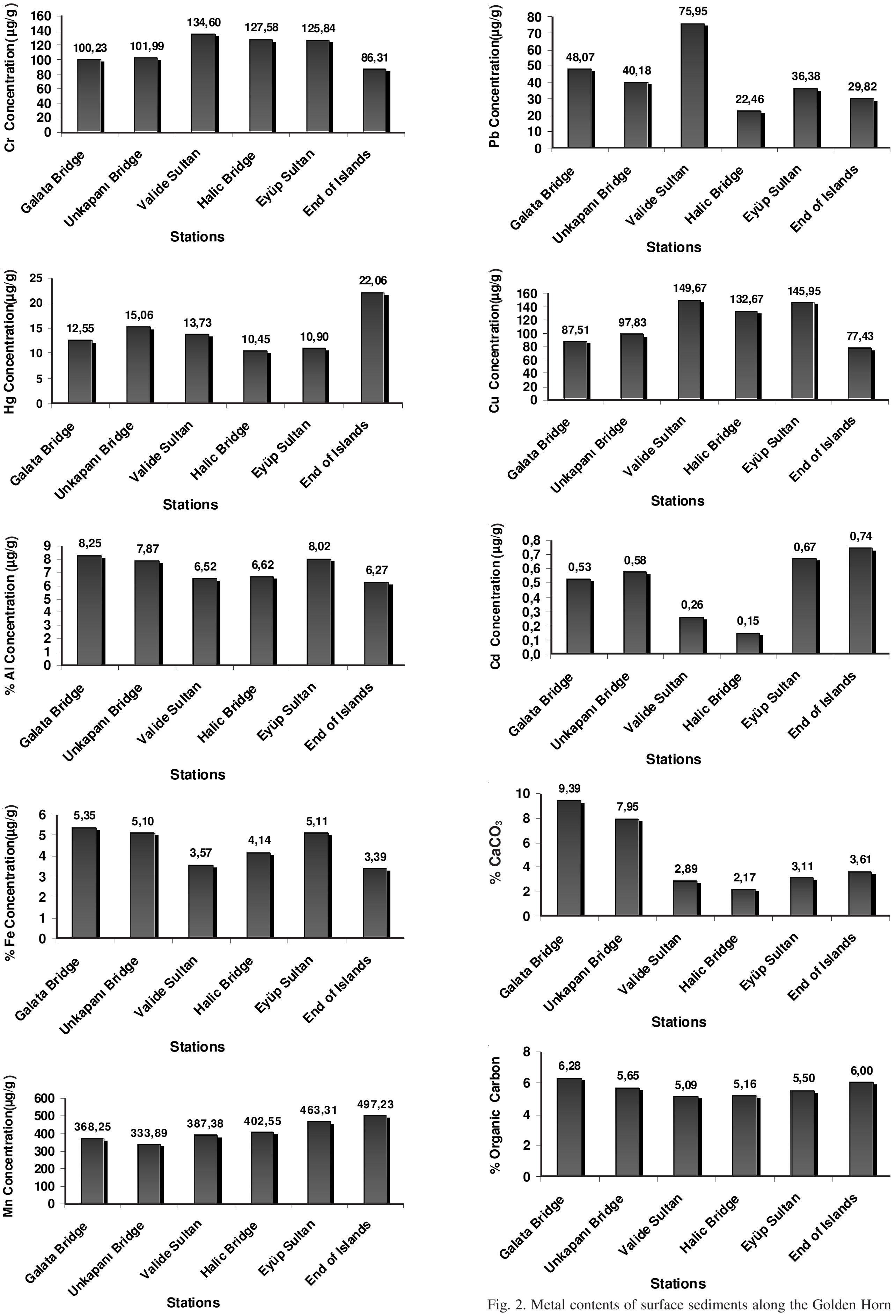


Fig. 2. Metal contents of surface sediments along the Golden Horn

TABLE-2
CORRELATION COEFFICIENTS AND ENRICHMENT FACTORS OF SEDIMENTS MATRIX

	Cr	Hg	Al	Fe	Mn	Pb	Cu	Cd	C_{org}	$CaCO_3$	Enrichment factor
Cr	1.00	**0.75**	0.10	0.07	0.15	0.36	**0.98**	**0.70**	**0.86**	0.49	1.2-1.54
Hg		1.00	0.46	0.54	0.43	0.08	**0.67**	0.57	0.43	0.03	38.3-102.1
Al			1.00	**0.98**	0.42	0.07	0.10	0.35	**0.90**	0.54	*
Fe				1.00	0.47	0.13	0.09	0.25	**0.84**	0.51	1.05-1.27
Mn					1.00	0.37	0.01	0.43	0.09	0.46	0.5-0.8
Pb						1.00	0.33	0.23	0.21	0.12	1.2-4.3
Cu							1.00	0.56	**0.86**	0.61	2.1-3.4
Cd								1.00	**0.70**	0.14	0.5-3.4
C_{org}									1.00	0.72	*
$CaCO_3$										1.00	*

includes lots of gastropod and bivalve shells. Because of undiscardable gastropod and bivalve shells, the high correlation was observed between C_{org} and $CaCO_3$ ($r = 0.72$) (Table-2).

Aluminium concentrations ranged between 6.3-8.3 % and were generally lower than the shale average value of 9.2 % (Fig. 2). The highest values were observed at Galata Bridge station. The high Al contents suggested both terrestrial natural and anthropogenic (domestic + industrial) inputs into the estuary. Al contents of the Golden Horn sediment show a great correlation with C_{org} ($r = 0.90$) and Fe ($r = 0.98$) (Table-2). Due to this relation Al can be accumulated on C_{org} and use the same pathway with Fe.

Iron concentrations were found between 3.4-5.3 %, generally above the shale average value of 4.7 % (Fig. 2). The highest values were measured, similar to Al, at Galata Bridge stations. The Fe distribution in the Golden Horn sediments is controlled mainly by the anthropogenic inputs such as ship traffic. Fe evidenced a high correlation with the C_{org} ($r = 0.84$) (Table-2).

Mercury concentrations ranged between 10.5-22.1 µg/g and were extremely higher than the shale average value of 0.3 µg/g (Fig. 2). The highest values were observed at end of Islands station. This means that industrial wastewater reaches to the estuary by means of uncontrolled discharges and creeks. Hg values show the highest correlation factor with Cu contents ($r = + 0.67$) (Table-2).

Lead concentrations varied between 22-76 µg/g being above the shale average value of 20 µg/g. The high values of Pb seemed to have been controlled mainly by the anthropogenic (domestic and industrial) inputs *via* the creeks and rainfalls and originating from ship traffic different from the other elements. Pb contents show not only weak correlation with C_{org} ($r = + 0.21$) but also great enrichment factors value (1.2-4.3) (Table-2). These High enrichment factors's indicate that Pb reach the sediment by anthropogenic pathway.

Manganese concentrations were generally lower than the average abundance of this element's shale value (< 800 µg/g) (Fig. 2). The low values can be related with Mn which gets through the water column in reductive conditions. The correlation factor between Mn and C_{org} contents is found as $r = +0.09$ (Table-2). In addition to this, when the manganese concentration are normalized according to aluminum, enrichment factors's value vary between 0.5-0.8. Mn concentrations are increased at the end of the estuary which is affected from Alibeyköy and Kagithane creeks' inputs.

Chromium concentrations varied between 86-134 µg/g being above the shale average value of 100 µg/g except for End of Islands station (Fig. 2). This element evidenced a high correlation with the C_{org} and Cu contents ($r = 0.86$ and 0.98, respectively) (Table-2). The high enrichment factors's (1.2-1.54) suggested that chromium supplied by anthropogenic (domestic and industrial) inputs.

Copper concentrations varied between 77-149 µg/g along the Golden Horn surface sediments. The mean value of Cu is 115.17 µg/g (Fig. 2). The highest value was observed at Valide Sultan Bridge station. The contents of Cu are considerably higher than the shale average (< 50 µg/g). The high Cu contents suggested anthropogenic (domestic + industrial) inputs *via* creeks and rainfalls into the estuary. Cu contents is show a great correlation with C_{org} ($r = 0.86$) and Cd ($r = 0.61$) (Table-2). The high results show that Cu can be accumulated on organic matter. The high enrichment factors's (2.1-3.4) indicate that Cu enriched *via* anthropogenic pathway.

Cadmium concentrations were found between 0.15-0.74 µg/g, generally above the shale average value of 0.3 µg/g (Fig. 2). The highest values were measured at end of Islands stations. enrichment factors's varied between 0.5-3.4 along the Golden Horn surface sediments (Table-2). The high values suggested the anthropogenic (domestic and industrial) inputs *via* Alibetköy and Kagithane creeks. Cd contents show a high correlation with C_{org} contents ($r = 0.70$) (Table-2). This result show that Cd accumulates on organic matter.

Conclusion

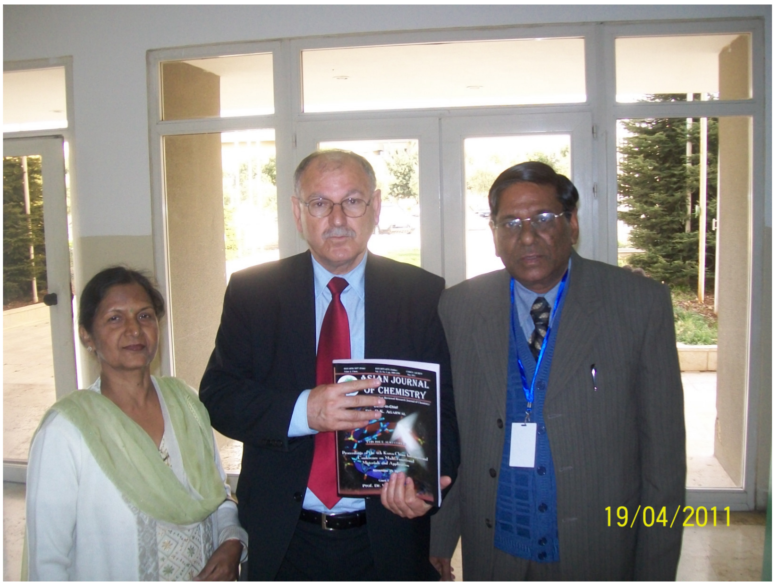
In this study, metal contents of the estuary surface sediments were generally found higher than the previous years' results despite the implementation of remedial actions. As the circulation is very limited at the inner part of the estuary, the sedimentation is faster; therefore the metal concentrations are higher in the region around end of Islands station. These results indicated the continuous uncontrolled inputs to the estuary. For this reason, lateral inputs must be stopped completely and chemical treatment projects must be handled at industries around the Golden Horn. In this way, concentrated pollution is expected to decrease gradually over the years and that water quality improves.

ACKNOWLEDGEMENTS

The captain, crew, scientists and technicians on boat RV Arar-1/ of the Institute of Marine Sciences and Management of Istanbul University are acknowledged for their help with heart and soul during the collection of water samples. Financial support by Research Foundation of the Istanbul University to M.S. Ersan, for this work (T1831) is gratefully appreciated.

REFERENCES

1. M.A. Lewis, J.C. Moore, L.R. Goodman, J.M. Patrick, R.S. Stanley, T.H. Roush and R.L. Quarles, *Water, Air Soil Pollut.*, **127**, 65 (2001).
2. R.R. Cave, J.E. Andrews, T. Jickells and E.G. Coombes, *Estuarine, Coastal, Shelf Sci.*, **62**, 547 (2005).
3. H. Feng, X. Han, W. Zhang and L. Yu, *Mar. Pollut. Bull.*, **49**, 910 (2004).
4. R.T. Ramessur, *Environ. Int.*, **30**, 1039 (2004).
5. S.K. Sarkar, S. Franciskovic-Bilinski, A. Bhattacharya, M. Saha and H. Bilionski, *Environ. Int.*, **30**, 1089 (2004).
6. K.D. Daskalakis and T.P. O'Connor, *Environ. Sci. Technol.*, **29**, 470 (1995).
7. W. Calmano, J. Hong and U. Förstner, *Water Sci. Technol.*, **28**, 223 (1993).
8. E. Argese, E. Ramieri, C. Bettiol, B. Pavoni, E. Chiozzotto and A. Sfriso, *Water Air Soil Pollut.*, **99**, 255 (1997).
9. E.R. Long, D.D. MacDonald, S.L. Smith and F.D. Calder, *Environ. Manag.*, **19**, 18 (1995).
10. P.W. Balls, S. Hull, B.S. Miller, J.M. Pirie and W. Proctor, *Mar. Pollut. Bull.*, **34**, 42 (1997).
11. P.M. Chapman and F. Wang, *Environ. Toxicol. Chem.*, **20**, 3 (2001).
12. Z.B. Din, *Mar. Pollut. Bull.,* **24**, 484 (1992).
13. M. Karpuzcu, *Mar. Pollut. Bull.*, **5**, 27 (1974).
14. M. Ergin, *Boll Oceanol Teorica Applicata*, **8**, 135 (1990)
15. M. Öztürk, A. Bastürk, I. Öztürk, C. Kinaci, D. Topacik and M.F. Sevimli, Haliç Islah Projesi Uygulama Çalismalari. Büyüksehirde Atiksu Yönetimi ve Deniz Kirlenmesi Kontrölü Sempozyumu, Istanbul-Turkey. (pp. 233-242). Istanbul: General Directorate of Istanbul Water and Sewerage Administration (1998).
16. DAMOC Consortium, Master Plan and Feasibility Report for Water Supply and Seawage for the Istanbul Region. (Vol. III, Part II) (1971).
17. N. Kor, Ph.D. Thesis, Istanbul Technical University, Istanbul, Turkey (1963) (in Turkish).
18. E. Müftüoglu, M.Sc. Thesis, Istanbul University, Institute of Marine Science and Management (2002).
19. H.I. Sur, E. Okus, H.Z. Sarikaya, H. Altiok, V. Eroglu and I. Öztürk, *Water Sci. Technol.*, **46**, 29 (2002).
20. D.H. Loring and R.T.T. Rantala, *Earth Sci. Rev.*, **32**, 235 (1992).
21. R.S. Atgin, M.Sc. Thesis, Department of Environmental Engineering, METU, Ankara, Turkey (2000).
22. F. Ackerman, *Environ. Technol. Lett.*, **1**, 518 (1980).
23. D.H. Loring, K. Naes, S. Dahle, G.G. Matishow and G. Illin, *Mar. Geol.*, **128**, 153 (1995).
24. D.H. Loring, *Mar. Chem.*, **29**, 155 (1990).
25. B. Rubio, M.A. Nombela and F. Vilas, *Mar. Pollut. Bull.*, **40**, 968 (2000).
26. B.J. Mason, Introduction to Geochemistry, John Wiley, New York, edn. 3 (1966).
27. A.P. Vinogradov, The Geochemistry of Rare and Dispersed Chemical Elements in Soils, Consultants Bur., New York, edn. 2 (1959).
28. K.H. Wedepohl, in ed.: L.H. Ahrens, Origin and Distribution of the Elements, Pergamon Press, London, pp. 999-1016 (1968).
29. S.K. Sarkar, S. Franciskovic-Bilinski, A. Bhattacharya, M. Saha and H. Bilionski, *Environ. Int.*, **30**, 1089 (2004).



Mrs. Pushpa Agarwal, Managing Editor and Prof. (Dr.) Ram K. Agarwal, Editor-in-Chief, Asian Journal of Chemistry presenting a copy of Asian Journal of Chemistry to Prof. (Dr.) Sultan T. Abu-Orabi, President of Yarmook Yarmook University, Irbid, Jordan on 19th April 2011.