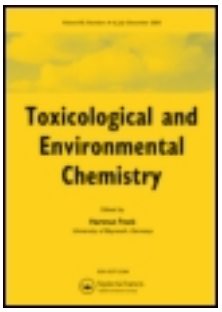

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ELEMENTAL POLLUTION OF THE GOLDEN HORN SURFACE SEDIMENTS

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The total and acid leachable composition of Golden Horn surface sediments have been investigated for Pb, Zn, Cu, Cr, Ni, Co, Mn and Fe. Quantitatively, the majority of the Pb, Zn and Cu defined to be from anthropogenic origin and the sediments classified as contaminated with respect to these elements. The natural change in the depth of halocline, results in the remobilization of loosely held metals from sediments. Mediterranean water is more effective in remobilization of the loosely held metals than the brackish Black Sea water.

INTRODUCTION

The historically famous, unpolluted state of the Golden Horn is now shown to represent the unique example of an end product of industrial and domestic pollution. A major scheme to rechannel sewage from Istanbul into the layer of salty water moving northwards from the Sea of Marmara towards the Bosphorus which is submerged beneath a layer of fresh water flowing down from the Black Sea has been started. This study has been carried out to determine the present trace elemental composition within the sediments of the Golden Horn prior to the proposed channeling of the surface layer through a marine outfall.

The Golden Horn is an estuary of the Bosphorus, approximately 7 km long and with a maximum depth at the entrance of 40 m. The bottom shallows rapidly after the first few kilometres from the entrance, and the depth decreases to about 2 m at a distanced approximately 3 km from the mouth. The hydrographic stations shown in Figure 1 are confined within this area due to the navigational problems.

EXPERIMENTAL

Twenty-six stations were sampled by Vaan–Wien type grab sampler in April 1966, Fig. 1. Samples were stored in pre-cleaned plastic bags at −20 °C. Thawed sediment samples were sieved by using 50 μ meshes dried at 55 °C for 72 h, grounded in agate mortar. Homogenization is done by using WAB Turbula System Schatz homogenizer for 24 h. The total dissolution of the sample is done by $HNO_3 + HF$ mixture in teflon-lined pressure digestion unit at about 130 °C.[1] For the acid extraction procedure a method described by Chester and Voutsinou[2] is applied. Blank samples were routinely run throughout the analysis to check for contamination. The elemental composition is determined by Varian Techtron model 1250 and AA-6 atomic absorption spectrophotometer equipped with background corrector. To control the data quality, metal analyses of the sub

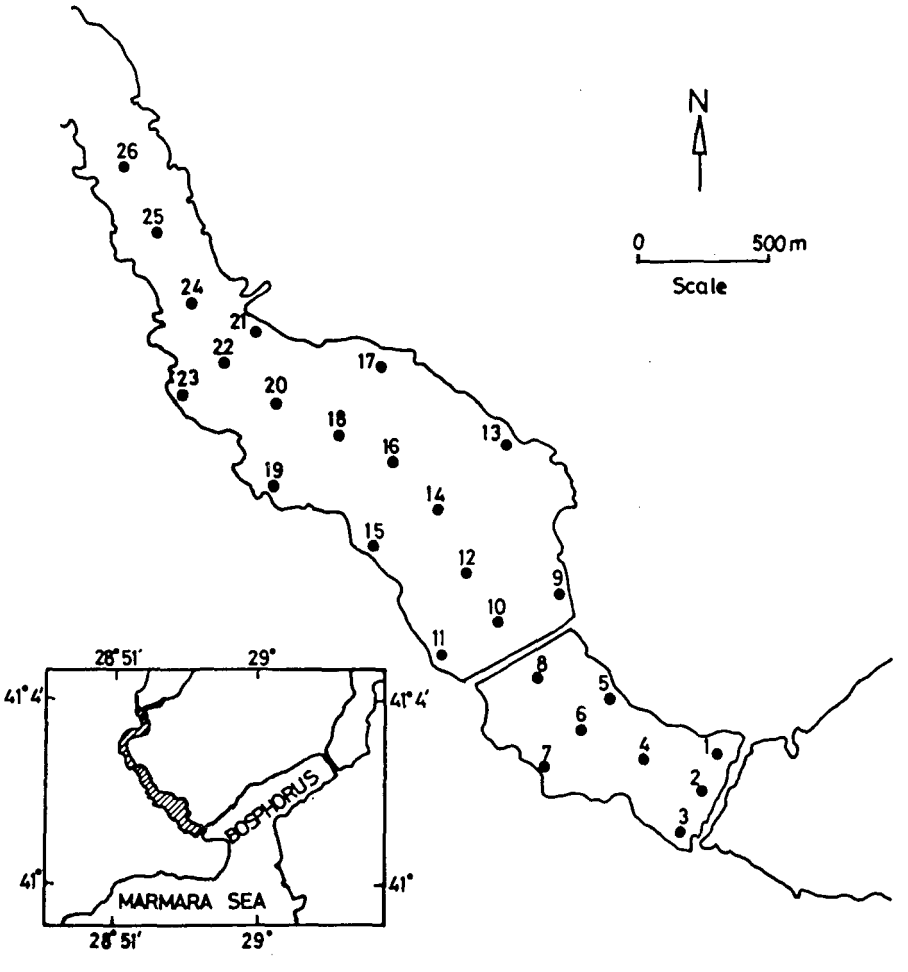

Figure 1 The sampling stations in Golden Horn.

samples have also been analyzed by the Plasma Induce Emission Spectroscopy at the Geology Department of Imperial College, London.

A method described by Walkley and Black,[9] as modified by Gaudette *et al.*[3] is used for the determination of organic carbon in each sediment. The sediments from sta. 13–19 (Figure 1) were shaken up by pre-cleaned 15.9 ppt Black Sea water and 38.4 ppt Mediterranean Sea water up to 7 days. The trace elements were recovered from sea water by a column packed with 10% 8-hydroxyquinoline coated on 80–100 mesh Porapak T and mixture of 10 ml of 0.1 N HCl and 0.1 N HNO_3 used to elute the samples. During recovery 8-hydroxyquinoline was also removed from the packing material therefore, for each elution a new set was prepared from same stock. The absorption efficiency of the column was 76% for Pb, 75% for Zn, 73% for Cu and 55% for Mn.

RESULTS AND DISCUSSIONS

The results of the monthly hydrographical studies carried out between August 1985–September 1987 have shown that, the properties of the water column in the Golden Horn corresponds closely to the properties of the water column in the Bosphorus. The two layer flow, Figure 3, a brackish Black Sea water which forms the surface layer and the Mediterranean origin deep layer maintains their characteristic temperature, salinity and dissolved oxygen (DO) content with the exception of the top 2–3 m whose properties are greatly changed due to various surface discharges of sewerage from industrial and municipal sources.

The properties of the surface layer is greatly modified by the obstruction of the surface currents by the 4 m deep pontoons of "Galata Bridge" at the entrance and the "Unkapani Bridge" further up in the estuary. The inputs of the domestic and industrial effluents is the main reason of the local modification of the Black Sea water.

The upper layer, located on the average between 3–25 m has properties characteristic of the Black Sea upper layer with temperatures of 4 °C to 23 °C, salinities of 18–20 ppt and with high DO content corresponds to a 70–100% saturation on an annual basis. The bottom layer, originating from below the halocline in the Sea of Marmara, has relatively constant temperature (13–14 °C), salinity 38–39 ppt and dissolved oxygen 1.2 mg/l.

The average total concentration of Pb, Zn and Cu are 294, 1256 and 971 μg/g (dry wt) respectively (Table 1). The distribution of total elemental composition of Pb, Zn and Cu exhibits some common properties along the Golden Horn. Their average concentrations are in order of magnitude greater than the adjacent seas such as Black Sea, Marmara Sea and Northern Aegean Sea. The level of Pb, Zn and Cu within the Golden Horn sediments are much more pronounced than the sediments of the Izmit Bay where severe industrial pollution problems exist.[8] The latest work on the total sediments of the Izmit Bay sediments reported Pb, Zn and Cu concentrations as 36, 73 and 25 μg/g, for the unsieved dry sediments.[8] Therefore, these concentrations should be accepted as the lowest limit of concentrations for these elements. Within these limitations it can be concluded that the sediments of the Golden Horn can be classified as severely contaminated with respect to Pb, Zn and Cu.

The average concentrations of Cr (326 ± 63 μg/g), Ni (125 ± 21 μg/g), Co (23 ± 5 μg/g), Mn (397 ± 62 μg/g) and Fe (3.2 ± 0.26%) within the sediments of Golden Horn do not differ much from the average concentrations of sediments classified as unpolluted (Table 2). When compared with the sediments of adjacent seas it can be seen that the level of Cr, Ni, Co, Mn and Fe within the Golden Horn sediments are at the same order of magnitude as the adjacent seas.

In Table 1 the organic carbon (OC) content of the sediments are shown together with the elemental composition of the total sediments. The average OC content of the sediments is 4.8 ± 1.2% with a range of 2.8 to 7.3%. Such amounts of OC content of the sediments reflects the importance of industrial and municipal waste discharged into the Golden Horn.

For the quick assessment of the pathways of trace element incorporation into

Table 1 Total metal and organic carbon contents of the Golden Horn surface sediments (μg/g dry sediment except Fe and OC which is as % wt.)

Stations	*Pb*	*Zn*	*Cu*	*Cr*	*Co*	*Ni*	*Mn*	*Fe*	*OC*
H-1	241	806	595	299	17	98	375	3.3	3.8
H-2	230	600	535	271	17	100	358	3.1	3.8
H-3	354	819	1368	285	14	120	400	2.9	6.1
H-4	339	1908	1160	328	23	126	376	3.2	5.0
H-5	702	8750	3900	313	20	167	380	3.1	5.4
H-6	215	731	595	242	17	98	358	2.9	4.4
H-7	343	906	1011	299	23	117	375	3.1	7.0
H-8	256	800	565	271	20	106	333	3.1	4.1
H-9	336	1675	1030	328	20	117	338	2.9	6.5
H-10	253	900	704	285	20	109	346	3.0	4.9
H-11	392	931	711	299	17	148	403	2.6	7.3
H-12	238	850	714	328	23	123	378	2.9	2.8
H-13	241	862	516	256	29	120	398	3.4	2.8
H-14	124	481	546	256	26	103	371	3.3	4.1
H-15	354	498	297	285	23	84	427	3.6	4.7
H-16	279	1094	971	385	26	114	376	3.1	4.0
H-17	324	1212	1100	427	23	134	360	3.3	3.5
H-18	321	1506	1268	442	29	140	380	3.3	4.6
H-19	324	1375	1279	399	23	154	358	3.4	5.8
H-20	219	787	952	328	20	112	363	3.3	5.3
H-21	264	950	565	370	23	137	340	3.6	3.8
H-22	124	450	803	328	29	131	565	3.0	4.9
H-23	509	1243	902	399	29	156	456	3.8	6.3
H-24	264	1081	1100	413	26	156	462	3.6	5.7
H-25	252	881	1092	485	29	151	496	3.5	5.1
H-26	126	637	981	370	31	134	565	3.2	4.2

the sediments, the loosely held fraction of the sediments is of prime interest since this fraction of the sediments is more susceptible to any changes in the ambient conditions. For this purpose the partitioning chemistry of the Golden Horn sediments carried out by using 0.5 N HCl. The acid leached fraction of the elements is accepted as to represent the anthropogenic fraction.[2]

The acid leachable fractions of Pb, Zn and Cu constitutes nearly 80% of the total sediments (Figure 2). This fraction is 45% for Cr, Co and Ni and only 35% for Mn and Fe. Thus on the basis of this partitioning scheme the abundance of the loosely trace elements within the sediments of the Gold Horn can be ranked as

$$\text{Pb, Zn, Cu} > \text{Cr, Co, Ni} > \text{Mn, Fe.}$$

Similar studies carried out at some other regions suffered from severe pollution problems such as Los Angeles harbour[4] and in Lower Rhine River[6] reported similar trace metal fractioning within the sediments (Figure 2). From the percent-

Table 2 The distribution of trace elements in some estuarine and shelf sediments

	Thermaikos Gulf[a]	*Rhode Island Sound*[b]	*Saanic Inlet*[c]	*Solway Firth*[d]	*Pagassitikos Gulf*[e]
Unpolluted sediments μg/g dry wt.					
Pb	45	15	20	37	28
Zn	105	40	88	63	30
Cu	28	10	38	10	16
Cr	130	10	86	35	43
Ni	120	—	33	38	—
Co	20	—	9	16	—
Mn	950	—	370	360	—

	Severn Estuary[f]	*Rhine-Meuseand Estuary*[g]	*Branford Harbour*[h]	*Clyde Estuary*[i]	*Sorfjord Norway*[j]
Polluted sediments μg/g dry wt.					
Pb	119	231	265	528	11000
Zn	280	870	55	1680	20000
Cu	38	99	35	225	2424
Ct	—	—	—	624	—
Ni	36	31	—	69	—
Co	—	—	—	60	—
Mn	417	—	331	1600	—

	Eastern Aegean Sea[k]	*Eastern Marmara Basin*[l]	*Southwestern Black Sea*[m]	*Izmit Bay*[n]
Polluted sediments μg/g dry wt.				
Pb	17	55	22	23–52
Zn	39	108	129	45–114
Cu	18	48	24	13–49
Cr	92	127	193	6–81
Ni	143	89	79	34–98
Co	16	25	21	43–105
Mn	925	125–550	832	112–678

[a]Voitsinou *et al.*, 1983.
[b]Kester *et al.*, 1983.
[c]Gross, 1967.
[d]Perkins *et al.*, 1973.
[e]Chester and Voitsinou, 1981.
[f]Chester and Stoner, 1975.
[g]Salamons and Mook, 1977.
[h]Lyons and Fitzgerald, 1980.
[i]Skei *et al.*, 1972.
[j]Chester and Stoner, 1975.
[k]Taliadoury *et al.*, 1982.
[l]Ergin and Evans, 1988.
[m]Hirst, 1974.
[n]Yoruk, 1988.

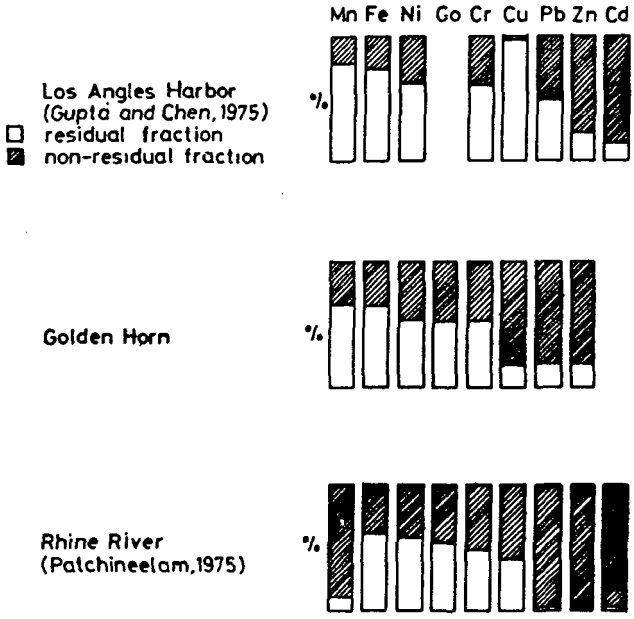

Figure 2 The residual and non-residual fractions of heavy metals.

age categories displayed in Figure 2 it can be seen that anthropogenic elements falls into same percentage categories irrespective of the geological positions.

The annual cycle of salinity and temperature profiles for station H2 is given in Figure 3. It can be inferred from the figure that the depth of halocline varies between 15–30 m and the area between these contour lines is estimated as 185 000 m^2.[5] Therefore an area of 185 000 m^2 is exposed to different ionic strength water mass for certain time periods of the year. This natural change in the ambient conditions has forced us to investigate the possibility of the remobilization of trace elements from the sediments. The elements studied are Mn, Pb, Zn and Cu.

In Figure 4 the rate of mobilization of Pb as a function of time is given. After initial high rate of mobilization the steady state levels have been reached within couple of days. It can also be seen that high ionic strength Mediterranean originated water is more effective in the remobilization processes than the brackish Black Sea water. The reported flushing time for the Golden Horn estimated as 3 days.[7] Therefore in natural processes the sediments cannot be in contact with the overlying waters more than the flushing time of the estuary which is estimated to be $\sim$70 h.

Laboratory experiments have shown that the equilibrium is reached within c. 40 h for Mn, 60 h for Pb and 100 h for Zn and Cu. Therefore the elements can be ranked with respect to their rate of remobilization as

$$Mn > Pb > Zn\ Cu.$$

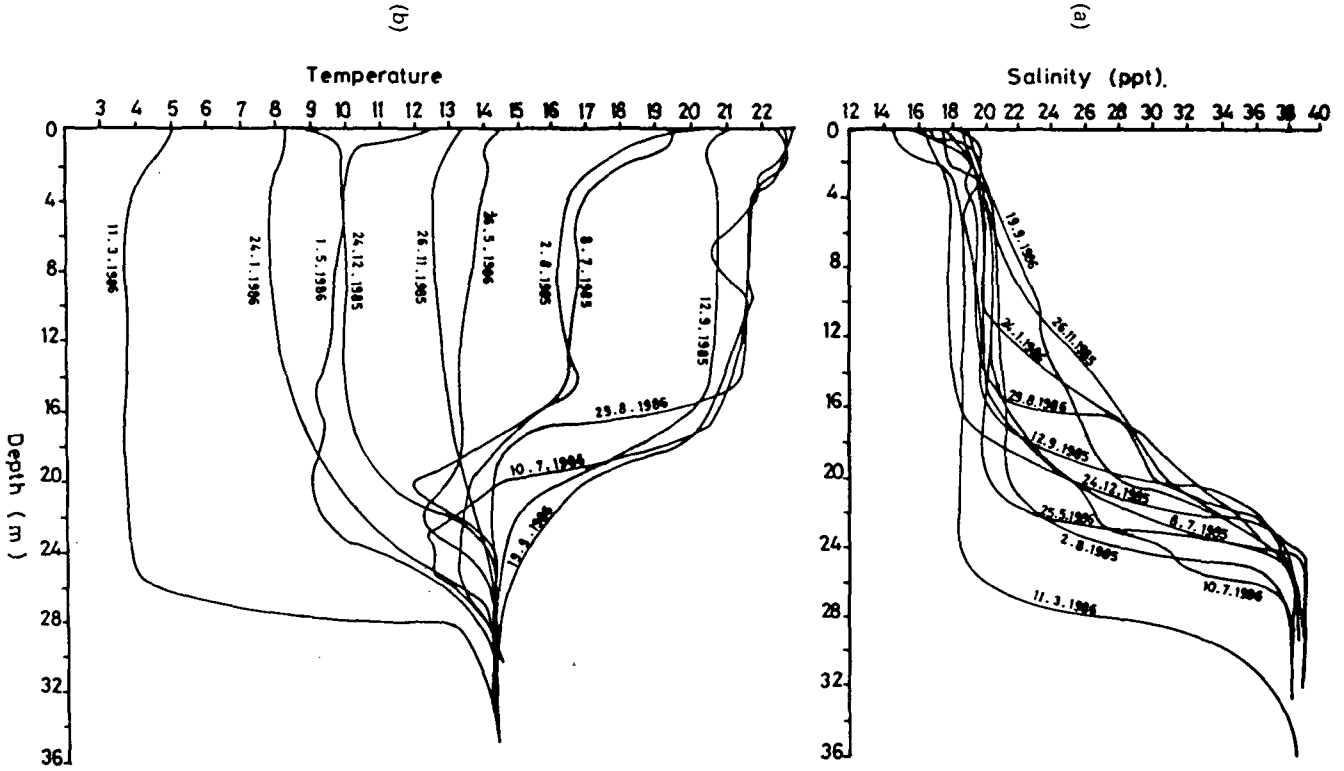

Figure 3 (a) Temperature profiles for station H-2, July 1985–September 1986;7 (b) Salinity profiles for station H-2, July 1985–September 1986.7

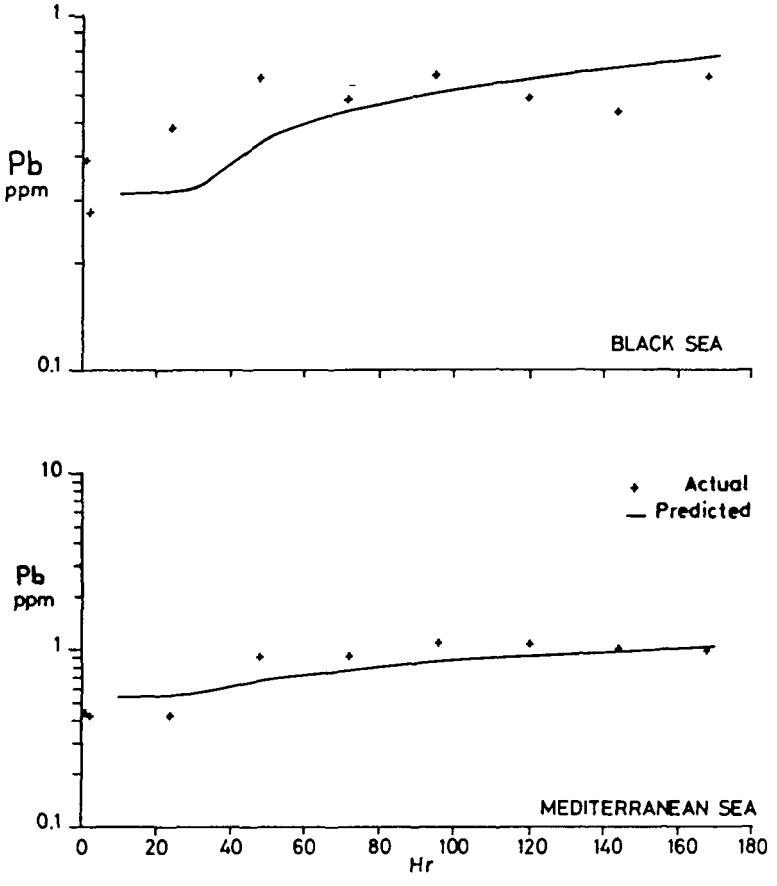

Figure 4 The rate of mobilization of lead by Black Sea and Mediterranean.

In other words the contact time of the overlying waters with the sediments is sufficient enough to allow each element to reach their relative equilibrium concentrations.

CONCLUSIONS

The extent of metal contamination of the surface sediments is clearly seen from the distribution of metals along the Golden Horn. Same kind of study should be carried out with sufficient time period after major rechanneling of the sewerage system and the reconstruction of Galata Bridge which will increase the circulation within the surface layer of Golden Horn. This will eventually result in change in the composition of waste residues or relative amounts of soluble to insoluble residues, hence the composition of trace elements discharged into the Golden Horn.

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