Fresenius Envir. Bull. 7: 269-276 (1998)
© Editors, Freising-Weihenstephan/FRG
1018-4619/98/5-6/269-08 DM 2.50 + 030/8

EVALUATION OF HEAVY METAL CONTENTS, POLYAROMATIC PETROLEUM HYDROCARBONS AND SOME INORGANIC POLLUTANTS IN THE SOUTH MARMARA RIVERS, TURKEY

A. Yılmaz[1], U. Özer[2], S. Yemenicioğlu[1], S. Aksoy[2] and T. Torunoğlu[3]

1 Middle East Technical University, Institute of Marine Sciences, P.O.Box 28, 33731, İçel-TURKEY
2 Uludağ University, Arts & Science Faculty, Chemistry Department, Görükle, 16059, Bursa-TURKEY
3 D.S.İ. (State Hydraulic Works) Laboratory, Bursa-TURKEY

Summary: Nilüfer River is the main receiving body of water for the industrial and domestic wastes of 1.000.000 populated Bursa metropolitan area and it combines with Kocasu River before entering the sea at the south Marmara region, Turkey. Variations in concentrations of Na, K, Ca, Mg, Fe, Cl, SO_4, PO_4, NH_4, NO_3, NO_2, BOD_5, COD, polyaromatic petroleum hydrocarbons (PAH), pH and some heavy metals (Hg, Cd, Cr, Zn, Pb) were seasonally determined in 1991-94 period. The results showed that these rivers are included in the heavily polluted class of waters.

Key Words: Heavy metals, polyaromatic hydrocarbons, water quality, Marmara region (Turkey)

Introduction: Bursa is a metropolitan which is located in the southern Marmara region, Turkey (Fig. 1). Metal, machinery, textile, automotive industries are concentrated in Bursa; Turkey's two big car factories are located here. Due to the high increase in population -mainly by migration- and industrialisation, either domestic or industrial discharges cause high level of environmental pollution. Dense agricultural activities in this area make also contribution. The inland waters which are polluted by the above mentioned factors, are used for watering in the wide spread agricultural areas, that causes further pollution of plants and soil. Essentially no significant treatment is given to any effluent apart from septic tank or land treatment in the area and the wastes are directly discharged into Nilüfer River. The environmental problems of Bursa district were defined during "Bursa Pollution Inventory Study, 1989-1991". Even the domestic and industrial flows are approximately the same, the inputs are quite different for different pollutants: BOD_5 is $28x10^3$ and $18x10^3$ kg/d, COD is $0.3x10^3$ and $38x10^3$ kg/d, total-N is 16 and 77 kg/d and total-P is 5441 and 3 kg/d for respectively for domestic and industrial inputs[1].

Material and Methods: Study area and sampling stations are shown in Fig.1. The water samples were collected on a seasonal base at four stations namely Geçit(1), Göbelye (2), Hayırlar(3) and Ekmekçi(4) in Nilüfer and Kocasu rivers. Standard wet methods[2] were used for the determination of inorganic constituents (Na^+ K^+ Ca^{2+} Mg^{2+} Fe^{2+} Cl^- SO_4^{2-} PO_4^{3-} NH_4^+ NO_3^- NO_2^-) and in general spectrophotometric measurements were performed. BOD_5 was determined using incubation technique (at 20 °C); before and after incubation dissolved oxygen was measured by Winkler titration[2]. COD measurements were performed using standard oxidation (with $K_2Cr_2O_7$) technique in acidic medium[2]. The amount of Cr (+6) which was not used during oxidation was determined by back titration with standard Fe^{2+} solution. Water samples were extracted n-hexane for the fluorometric determination of polyaromatic petroleum hydrocarbons (PAH)[2]. The concentration of PAH was measured as its Chrysene equivalent. Water samples were preserved using conc. H_2SO_4 and %5 $KMnO_4$ solution until mercury analysis. Cold vapour Atomic Absorption technique was used for determination of mercury[3,4]. The method used for the analysis of Hg is developed recently and eliminates the contamination problems during the analysis, thus the values are lower than expected. Concentrated HNO_3 was used for the preservation of water samples for Cd analysis and all constituents of Cd were digested in aqua regia ($HCl+HNO_3$) and the concentration of total cadmium was determined by Atomic Absorption Spectrophotometry[5]. Total Cr, Zn and Pb were determined by Atomic Absorption technique using flame[6]. It is necessary to mention here that all metal concentrations given, include both particulate and dissolved fractions as well as inorganic & organic compounds and all valances(*e.g.* $M^{+n,m,..}$).

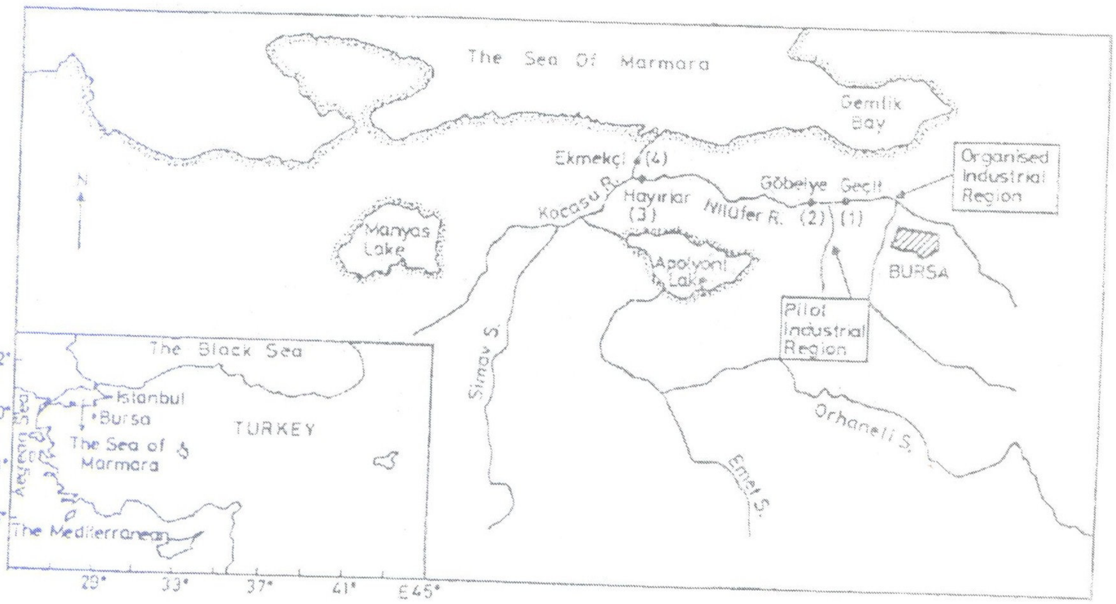

Fig. 1. Bursa metropolitan area and the sampling stations in the Nilufer and Kocasu rivers

Results and Discussion: The seasonal variability of pH and inorganic parameters are presented in Fig. 2. As is clearly seen, the overall trend is being an increase with time such as observed very significantly for Na, K, Cl and NH_4. The concentration of some of the inorganic parameters, such as Ca, Mg, Fe, SO_4 fluctuates within certain limits. The concentration of especially PO_4, NO_3,

NO_2 showed a decreasing trend with time, most probably because of adsorption on Cr(III) and Pb(II) colloidal particles and consequent export from the aquatic medium to the sediment[7]. Since the concentrations of these metals are considerably high in Nilufer River and they showed an increasing trend within the same period. The pH of these waters was slightly basic at the beginning of the monitoring but the water has come to slightly acidic conditions at the end. As an indicator of biodegradable organic pollution, BOD_5 has shown a fluctuating increase with time while COD increased with more acceleration after 1992 (Fig.3). PAH showed an increasing trend most probably parallel to the increase in fuel consumption in houses and industry and its production as by-products in some chemical industries (Fig.3). The observation of oil slicks was very common in these rivers during the study period. The seasonal + interannual changes in the concentrations of heavy metals exhibited increasing trends in general and they were significant for especially Zn, Cr and Hg (Fig.4).

All parameters were correlated with the standard limits of the water quality criteria (of WHO) and classification of waters were performed according to the Turkish governmental regulations (Tab. 1). The results showed that the waters of the monitored rivers are included in the **"Heavily Polluted"** class of waters in terms of most of the inorganic constituents, organic pollutants and heavy metals. The most polluted station was determined as Geçit which is the first station after the main industrial and the domestic effluent are introduced (Fig. 1). Sewage, industrial effluent, and especially use of sodium compounds for corrosion control and water-softening processes all contribute to high concentration of Na. Na concentration is given in the range of 1-300 mgL^{-1} for surface waters[8] and Na concentration was close to upper limit in the monitored rivers (Tab. 1). The presence of Fe in natural waters is due to the dissolution of rocks and minerals, acid mine drainage, sewage, iron-related industry. Fe in surface water is generally present in the ferric (Fe^{3+}) state and if the conditions are reducing and in the absence of sulfide and carbonate constituents high concentration of soluble ferrous iron (Fe^{2+}) is found. Particulate Fe is more abundant in river waters *e.g.* the particulate Fe concentration is about 48000 $\mu g\,g^{-1}$ in the worlds rivers[9] and the dissolved iron concentration is recorded as only 40 μgL^{-1}. 5120 μgL^{-1} of average Fe concentration was measured in Carnon river in Great Britain[10]. Nilüfer and Kocasu rivers have comparatively high concentration of Fe (Tab.1). The presence of Cl in natural waters can be attributed to dissolution of salt deposits, of effluent from chemical industries, sewage discharges and irrigation drainage. Cl is generally low in natural waters[11] *e.g.* level in unpolluted water is often less than 10 mgL^{-1} but the mean Cl concentration is considerably high for the monitored rivers (Tab.1). The concentration of SO_4 in most freshwater is very low; levels of 20-50 mgL^{-1} are common[12]. $Al_2(SO_4)_3$, which is extensively used as a flocculant for water treatment increases the SO_4 concentration which indeed exceeds the above range and closes to the limit given for the IV Class of waters. PO_4, NH_4 and NO_2 concentrations and also the BOD_5 exceed the standard limits of heavily polluted class of water. These two groups reflect the high quantity of domestic input. Inorganic nutrient salts are used in fertilisers and because of the area being one of the active

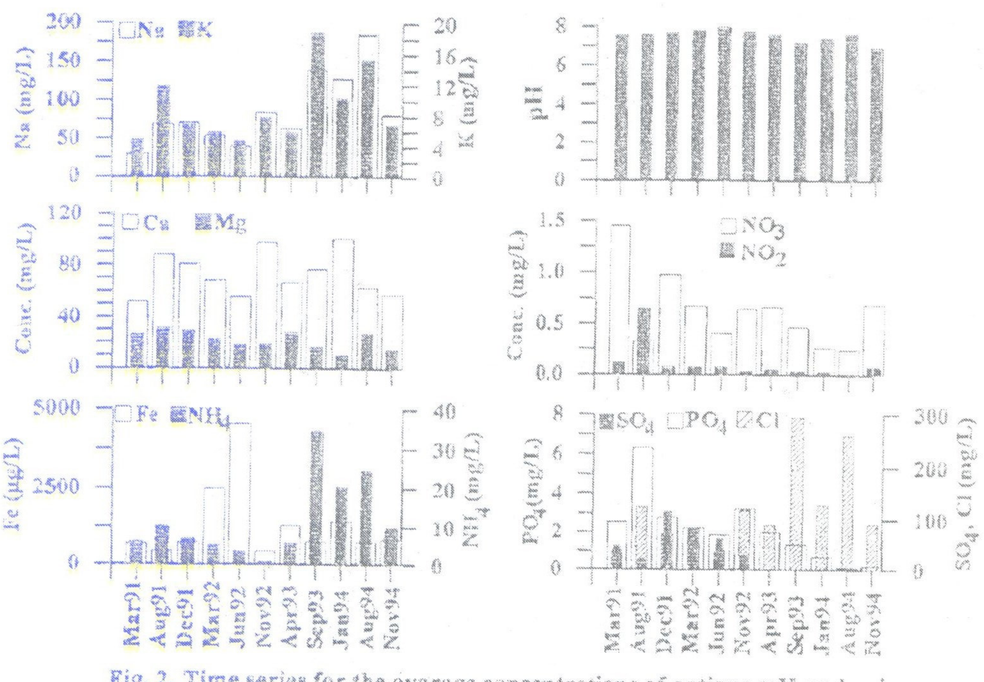

Fig. 2. Time series for the average concentrations of cations, pH and anions in Nilüfer&Kocasu Rivers

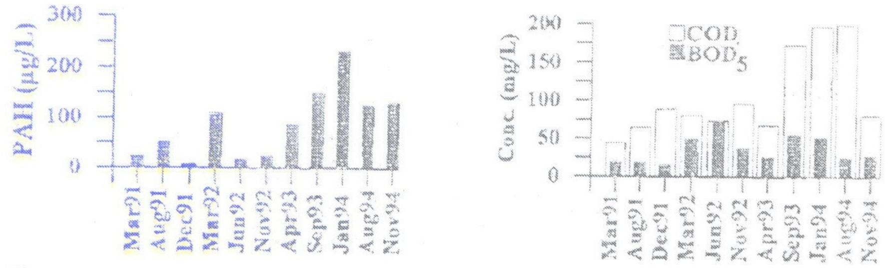

Fig. 3. Time series for the average concentrations of Polyaromatic Haydrocarbons and Biological/Chemical Oxygen Demands(BOD/COD) in Nilüfer&Kocasu Rivers

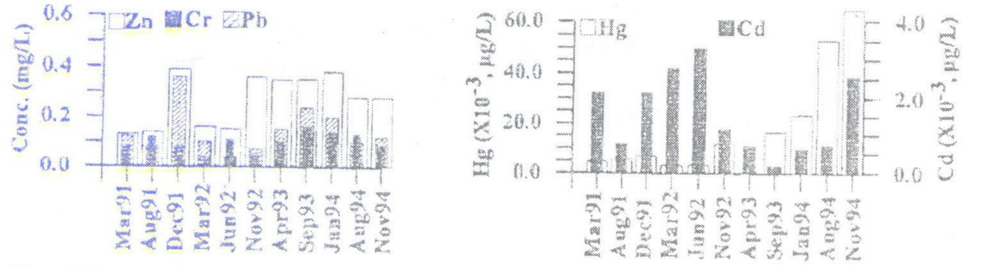

Fig. 4. Time series for the average heavy metal concentrations in Nilüfer&Kocasu Rivers

agricultural areas in Turkey, the artificial input of P- and N- compounds should also be considered. A number of studies have revealed levels of NO_3 in the range of 5-10 mgL^{-1} in the river waters and the concentration is always much higher than the NO_2 concentration in polluted waters[13]. NO_2 is especially harmful since it can oxidise haemoglobin to methaemoglobin, pigment that is incapable of a carrier for oxygen. Under certain conditions, nitrites may react with amines and amides to form nitrosamines, some of which are considered to be carcinogenic and these constituents can be transported via food chain including human[14]. Therefore the use of Nilüfer river waters for watering purposes in agricultural areas has to affect human health. Almost all of the industries located in the region discharge their effluent without any treatment. As a consequence chemical oxygen demand values exceed the standard limits given for the clean inland waters. Cr and Pb concentrations are above the standard limits given for the heavily polluted Class (IV) of waters as one consider the heavy metal pollution. In nature, Cr is present as trivalent form in chromite ore but the presence of hexavalent Cr shows both natural occurrence as well as the industrial contamination. The major uses of Cr are for Cr-alloys, Cr-plating, oxidising agent, corrosion inhibitors, pigment manufacturing in the textile, ceramic, glass and photographic industries which are mostly concentrated in Bursa metropolitan area. Total Cr in unpolluted world rivers is given as 1 μgL^{-1} (dissolved) and 100 $\mu g\, g^{-1}$ (particulate) respectively[9].

Table 1. Classification of surface waters according to general quality criteria (Turkish Ministry of Environment) and comparison with the present data

Parameter	Unpolluted[I]	Less Polluted[II]	Polluted[III]	Heavily Polluted[IV]	Nilüfer& Kocasu R
pH	6.5-8.5	6.5-8.5	6-9	<6->9	6.5-8.7
Na(mgL^{-1})	125	125	250	>250	12.3-274
K(mgL^{-1})	-	-	-	-	3.4-20.8
Ca(mgL^{-1})	-	-	-	-	5.8-112.5
Mg(mgL^{-1})	-	-	-	-	6.2-45.7
Fe(μgL^{-1})	300	1000	5000	>5000	120-7400
Cl(mgL^{-1})	25	200	400	>400	15.9-358.7
SO_4(mgL^{-1})	200	200	400	>400	4.4-131.0
NH_4(mgL^{-1})	0.2	1	2	>2	0.04-35
NO_3(mgL^{-1})	5	10	20	>20	0.16-3.1
NO_2(mgL^{-1})	0.002	0.01	0.05	>0.05	0.009-0.8
PO_4(mgL^{-1})	0.02	0.16	0.65	>0.65	0.01-6.77
BOD(mgL^{-1})	4	8	20	>20	3.2-85.6
COD(mgL^{-1})	25	50	70	>70	20.0-378.4
Hg(μgL^{-1})	0.1	0.5	2	>2	$(1.4\text{-}159)\times10^{-3}$
Cd(μgL^{-1})	3	5	10	>10	$(0.04\text{-}4.6)\times10^{-3}$
Cr(mgL^{-1})	0.02	0.05	0.2	>0.2	BDL-0.3
Pb(mgL^{-1})	0.01	0.02	0.05	>0.05	BDL-0.6
Zn(mgL^{-1})	0.2	0.5	2	>2	0.03-0.8

(BDL: Below Detection Limit)

The maximum total Cr concentration recorded in Nilüfer river is almost 2.5 times higher than this showing heavy industrial input. Pb in the environment exists almost entirely in the inorganic form but small amount of organic Pb results from the use of leaded gasoline and from natural alkylation processes. Pb is used in acid accumulators' manufacturing, alkyl lead compounds for gasoline, solder, pigments, ammunition, caulking and cable sheathing. The Pb content of river waters has been estimated to be 0.1 μgL^{-1} and 100 μg g^{-1} for respectively dissolved and particulate fractions[9]. 0-10 μgL^{-1} and 0.7-17.6 μgL^{-1} (filtered samples) of Pb concentrations are reported for German rivers *e.g.*, Rhine, Elbe, Danube[15] and Welsh rivers, Great Britain[16] respectively. Zn levels show some input of this metal into Nilüfer and Kocasu rivers and the waters are included in polluted class of waters (Class III). Zinc is an abundant element in the earth and the carbonates, oxides, and sulphides of Zn are sparingly soluble in water, while the highly soluble chloride and sulfate salts tend to hydrolyse to form zinc hydroxide and carbonates. As a result, concentration of Zn in natural waters is low. Adsorption onto sediments further depletes the levels of dissolved Zn. On average, 30 μgL^{-1} of dissolved Zn and 250 μg g^{-1} of particulate Zn are given for the worldwide river waters[9] but much higher Zn concentrations (1520-10000 μgL^{-1}) for Carnon river (Great Britain) which receives effluent from working metalliferous mines was also reported[10]. 0-200 μgL^{-1} of Zn concentration was reported for German rivers[15].

The major source of mercury is the natural degassing of the earth's crust. Burning of fossil fuels, smelting of various metals, cement manufacturing, chloralkali plants, dye industry, battery industry, agricultural chemical industry release also Hg into the surrounding environment. The level of total Hg is less than 1 μgL^{-1}, average being in the range of 10-50 ngL^{-1} in natural waters[17]. Total Hg concentration ranges in between 8-36 ngL^{-1} for the Turkish rivers flowing to Mediterranean[18]. In polluted rivers and lakes levels up to 30 μgL^{-1} Hg have been reported[19]. Cd is uniformly distributed in trace amounts in the earth's crust. Practically all Zn-ores contain Cd. In the last 30 years, the use of this element is steadily increasing. The principal uses of Cd are in the fabrication of alloys and solders, metal plating, as pigments, as stabiliser in plastic materials and in batteries. Unpolluted waters generally contain less than 1 μgL^{-1} of Cd[20]. 0.5 μgL^{-1} and 0.27 μgL^{-1} of Cd are reported for respectively German rivers[15] and St. Lawrence river which drains one of the most heavily populated and industrialised region of North America[21]. Cd is also associated with particulate matter in aquatic environments, 0.02 μgL^{-1} for dissolved fraction and 1 μg g^{-1} for particulate fraction are reported for the worldwide rivers[9]. As is seen from Tab. 1 and is compared with the reported values, the mercury and cadmium pollution are not significant but present in the monitored rivers. This may be attributed either to the absence or less input from the natural sources in this region or the related industries such as chlor-alkali, petrochemical, explosives, pesticide, cement industries for mercury pollution and iron and steel, ceramic and coal industries for cadmium pollution.

When the total loads are considered in Nilüfer river, one can easily notice a significant amount of inputs of inorganic and organic pollutants in Bursa region (Tab. 2). The striking figure is the high increase in domestic inputs such as the high levels of fluxes calculated for nitrogen and phosphorus constituents as well as BOD load which is almost the double of the 1989-1991 value[1]. COD input seems to increse almost six times when compared with the same period. When the total loads are compared with the ones estimated for some other big rivers in Turkey such as Seyhan, Sakarya (polluted rivers) and Göksu (unpolluted river), most of the pollutants have the same order of magnitude inputs in spite the flow rate of Nilüfer River is almost seven times smaller than their flow rates. The most highest input for NH_4, BOD_5, PAH, PO_4 were observed in Nilüfer River while the total input of metals were at the same order of magnitude with the other big and generally polluted rivers. If one compares, for example, BOD and COD loads with the corresponding loads from Turkey Mediterranean coast ($80x10^6$ kg/y and $645x10^6$ kg/y respectively[22]) and from the whole Mediterranean countries ($3300x10^6$ kg/y and $8600x10^6$ kg/y respectively[23]), there are significant amount of input from domestic and industrial discharges in Bursa metropolitan area. These results show that although the Nilüfer River is a very small river, it is overloaded with the most harmful and toxic pollutants. The pollution level is at the alarming state thus the action for the stop or at least the reduction for further pollution should be immediately considered.

Table 2. Annual loads of some water constituents of Nilüfer River and some other Turkish Rivers

Parameters	Nilüfer River	Sakarya R.[24]	Seyhan R.[24]	K.MenderesR.[24]	Göksu R.[22]
Q (Flow Rate, km^3/y)	0.85	6.0	6.2	0.73	4.3
pH	7.6	8.0	8.1	7.8	7.9
Na ($x10^7$ kg/y)	6.31	19.91	7.95	-	-
K ($x10^7$ kg/y)	0.73	2.73	-	-	-
Ca ($x10^8$ kg/y)	0.60	3.72	-	-	-
Mg ($x10^8$ kg/y)	0.19	1.82	-	-	-
Fe ($x10^6$ kg/y)	0.92	10.45	1.48	-	-
Cl ($x10^8$ kg/y)	0.89	1.31	1.21	0.56	-
SO_4 ($x10^7$ kg/y)	5.15	19.91	20.7	-	-
NH_4 ($x10^6$ kg/y)	8.75	2.58	1.92	0	-
NO_3 ($x10^6$ kg/y)	0.58	6.84	3.65	1.01	3.1
NO_2 ($x10^5$ kg/y)	0.93	1.26	0.6	1.02	-
PO_4 ($x10^5$ kg/y)	14.79	10.21	2.4	4.23	0.2
BOD_5 ($x10^6$ kg/y)	22.71	11.41	7.44	-	6.25
COD ($x10^8$ kg/y)	0.84	1.2	-	-	0.95
PAH ($x10^4$ kg/y)	5.18	-	-	-	0.58
Hg (kg/y)	14.02	-	-	-	13.8
Cd (kg/y)	1.31	3.0x104	-	-	7.3
Cr ($x10^6$ kg/y)	0.08	3.0	-	-	-
Pb ($x10^6$ kg/y)	0.11	3.0	-	-	-
Zn($x10^5$ kg/y)	2.04	-	-	-	-

Acknowledgements: This work was supported by the Turkish Scientific and Technical Research Council (TÜBİTAK) . The special thanks are also for the administration and technical staff of the State Hydraulic Works, Bursa I[st] Directory, for the field studies. Particular and deep gratitude are due to the academic and technical staff of the Institute of Marine Sciences of METU and Chemistry Department of Uludağ University for their encouragement and analytical skill.

References:

1 Bursa Environment Project Report, 1992, Water Supply and Sewerage, Volume 4, Industrial Wastewater, GAST Bursa Water and Wastewater Joint Venture.

2 APHA, AWWA,WPCF, 1985, Standard Methods for the Examination of Water and Wastewater, 16th edition, Greenberg, A.E., R.R. Trussel and L.S. Clesceri (Eds.)

3 Yemennicioğlu, S.,1990, Basin scale fate of mercury in the Sea of Marmara, Ph.D. Thesis, METU-IMS, Erdemli-İçel/Turkey.

4 Tuncel, G., G.J.Ramelow and T.I. Balkaş, 1980, Mercury in water, organisms and sediments from a section of the Turkish Mediterranean coast, Marine Pollution Bulletin, 11,18-22.

5 Ediger, R.D. *et al.*, 1974, AA Newsletter, 13,3,61.

6 Ramelow G.J. and T.I. Balkaş, 1976, A survey of the trace elements concentration of lake Eymir water, METU, Journal of Pure and Applied Sciences, Vol.9, No.12, pp.249-260.

7 Manahan, S.E., 1991, Environmental Chemistry, Lewis Pub., (Fifth edition), Mishigan.

8 WHO, 1979, Sodium, chlorides and conductivity in drinking water. Report on a WHO working group, Copenhagen, WHO Regional Office for Europe, 1979,(EURO Reports and Studies, No.2).

9 Martin, J.M. and M. Meybeck, 1979, Elemental massbalance of material carried by world major rivers, Marine Chemistry, 7:173-206.

10 Aston et al., 1974, Cited in: Metal Pollution in the Aquatic Environment, Forstner and Wittmann (eds.), Berlin, Springer Verlag, 1979. C:Metal Concentrations in River, Lake and Ocean Waters, Goldberg& Forstner (eds).

11 Bond, R.G. and C.P Straub, 1973, Handbook of environmental control, Vol.3, Cleveland, Chemical Rubber Co.

12 Katz, M., 1977, The Canadian sulphur problem. In:Sulphur and its inorganic derivatives in the Canadian environment. Ottawa, National Research Council of Canada, pp. 21-67.

13 NRC, 1977, National Research Council. Drinking water and health. Washington DC, National Academy of Sciences.

14 EHC, 1978, Nitrates,nitrites and N-nitroso compounds. Geneva, WHO, 1978, Environmental Health Criteria 5.

15 Anon, 1974, Cited in: Metal Pollution in the Aquatic Environment, Forstner and Wittmann (eds.), Berlin, Springer Verlag, 1979. C: Metal Concentrations in River, Lake and ocean Waters, Goldberg&Forstner (eds).

16 Abdullah and Royle, 1974, Cited in: Metal Pollution in the Aquatic Environment, Forstner&Wittmann (eds.), Berlin, Springer Verlag, 1979. Chapter C: Metal Concentrations in River, Lake and Ocean Waters, Goldberg and Forstner (eds).

17 Fitzgerald, W.F., 1979, Distribution of mercury in natural waters. In: The biogeochemistry of mercury in the environment, Nriagu, J.O. (Ed.), Elsevier, North Holland, Biomedical Press.

18 Salihoğlu, İ., C. Saydam and S. Yemenicioğlu, 1989, Biogeochemical cycle of mercury in the NE Mediterranean, Southern coast of Turkey, MAP Technical Reports Series No.32, FAO. UNEP Athens, 1989.

19 FWQA,1970, Investigations of mercury in the St. Clair River-Lake Erie systems. Washington DC, US Department of the Interior, 1970, (Report of the Federal Water Quality Administration),p.108.

20 Hiatt, V. and Juff J.E., 1975, The environmental impact of cadmium: an overview. International J.Environ. Studies, 7:277.

21 Yeats, P.A., J.M. Bewers and A. Walton, 1978, Sensitivity of coastal waters to anthropogenic trace metal emissions, Marine Pollution Bulletin, Volume 9, pp.264-268.

22 Yılmaz A., S. Yemenicioğlu, C.Saydam, S. Tuğrul, Ö. Baştürk and İ. Salihoğlu,1995, State of pollution of the Turkish coast of the Mediterranean by land-based sources. *Presented at XXXIIIe Congres-Assemblee pleniere de la C.I.E.S.M., Trieste, Octobre2-17, 1992.* In: Rapp. Comm. int. Mer. Medit., 33, 1992, p. 189.

23 UNEP, 1984, UNEP/ECE/UNIDO/FAO/UNESCO/WHO/IAEA: Pollutants from land-based sources in the Mediterranean. UNEP Regional Seas Report and Studies No.32.

24 Annual Reports of State Hydraulic Work, Turkey.

Received 02 November 1997
Revised 09 January 1998
Accepted 14 January 1998