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# Transportation of Pollutants of the Danube River into the (Western) Black Sea

A.E. MUFTUOGLU

Istanbul University, Institute of Marine Sciences and Management, BERKARDA Remote Sensing and GIS Laboratory, 34134 VEFA, Istanbul, Turkey

Corresponding author: Fax: +90 212 5268433; Tel: +90 212 4400000; E-mail: edip@istanbul.edu.tr

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At 14 stations on the Western Black Sea shelf, water and sediment samples were collected from the water column and the sea-bed during August 2003 and June 2004. The metals content (Al, Fe, Mn, Pb, Cu, Zn, Ni, Cd, Cr and Hg) of these samples was investigated to determine the influence and transportation of metal pollutants in the Danube River on the Western Black Sea. Pb, Cd, Hg and Cr concentration in the sediment was above the shale average (20, 0.2, 300 and 100 μg $g^{-1}$ respectively) while Fe, Cu, Zn including Ni concentration was determined to be below the shale average (4.7 %, 50, 90 and 80 μg $g^{-1}$ respectively). High total organic carbon (TOC, 2.5-4.11 %) and dissolved hydrogen sulfur (DHS, 249-419 μg $g^{-1}$) observed, suggested widespread pollution, cause by carry-over water and suspended solids in the Danube River. Additionally, the high concentration of Pb, Cd and Hg, in the surface sediment indicated that anthropogenic input is a major contributor of pollution *via* the Danube River.

**Key Words: Danube River, Dissolved hydrogen sulphide, Dissolved oxygen, Pollution, Total metals.**

## INTRODUCTION

The Danube river originates in the black forest and its tributaries, Brigach and Breg Rivers; converge at Donaueschingen (German) as it flows southeastward for a distance of 2850 km, emptying into the Black Sea *via* the Danube Delta (Romania and Ukraine). It passes several central and Eastern European capitals and it carries surface run-off water and discharge (even if some part is treated) of a large area into the black sea. The Black Sea is an inland marine basin located North of Turkey. Of all the inland seas, such as the Baltic or the Mediterranean Sea, it is the most isolated comparison to others. It is connected to the Mediterranean Sea through the Bosporus, the Marmara Sea and the Dardanelles Strait. Most of the river inflow into the Black Sea comes from the northern and north-western shelf area which comprises a 35 % of the total catchment of the basin. The Danube River alone contributes *ca*. 200 $km^3$/yr of discharged water, which corresponds to 3/4 of the north-western river runoff and 2/3 of the total riverine input (370 $km^3$/yr) into the basin. Particulate organic matter loading into the Black Sea from the Danube River was estimated as $0.913 \times 10^3$ tons/yr[1,2]. Presently the influence of the Danube River on the Black Sea is predominantly associated with the sedimentation of particulate matter on the Northwestern Black Sea shelf area. This influence extends far southward to the Bosporus region[3]. The Black Sea's chemical composition was attributed to its particular hydrography and eutrophication[4]. Beyond the effect of naturally occurring change, the chemistry and biology of the Black Sea have been severely impacted by anthropogenic activity.

Although several studies have been conducted on the western Black Sea, information on both water and bottom chemistry is limited. In this study, dissolved oxygen, total suspended solids, dissolved hydrogen sulphure (DHS), total organic carbon and total metals content (Al, Fe, Mn, Pb, Cu, Zn, Ni, Cd, Cr and Hg ) were examined in the water column and the surface sediments in order to determine the influence of the Danube River on the Western Black Sea. Additionally, flux patterns were determined using satellite images. A large quantity of the Black Sea surface water which carry the Danube water and have been polluted *via* the Danube River, thus enter the Bosporus. This study, which present information on the contribution of the Danube River's pollutants on the Black Sea, will provide information which can be used for further studies.

## EXPERIMENTAL

At the seven stations located on the continental shelf of the Western Black Sea (TBK 1, 2, 13, 14, 16, 51, 52) and Bosporus (K0, B7, B2) sampling was carried out from the water column and the sea-bed sediment during; August 2003 and June 2004 (Fig. 1). Dissolved oxygen measurements at the identified stations were carried out using the Winkler method[5] whereby water samples were drawn to prevent

biological activity and atmospheric exposure. The variation in dissolved oxygen concentration was determined to be ±1.9 %.

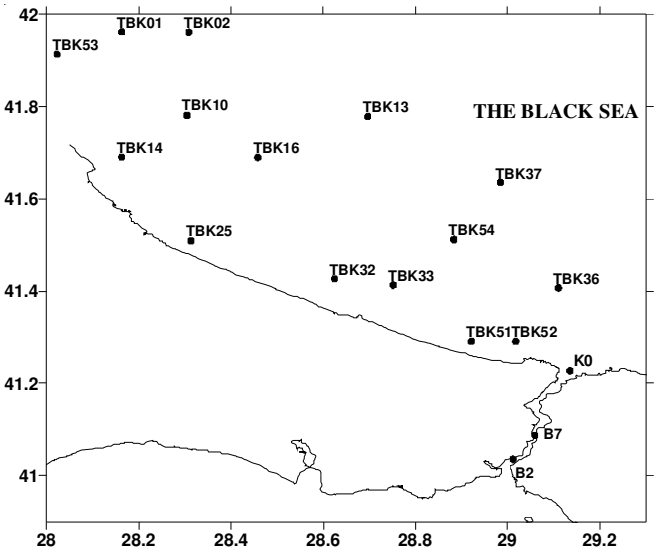


Fig. 1. Station map (Western black sea, coast of Turkey)

Dissolved hydrogen sulfide was measured only at stations where dissolved oxygen concentrations was lower than the detection limit of (0.03 mg $L^{-1}$) (Fig. 1), using an iodometric titration method[6].

Water samples were transferred to plastic bottles for the analysis of total suspended sediments whereby the water was filtered through pre-weighed GF/C filters that were dried at 105 ºC for 3 h and let to cool in a desiccator. After the filtration step was completed, the filter papers were kept at -20 ºC until the analysis in the laboratory[5].

The water samples for metal analysis were transferred to plastic bottles which were pre-washed with 30 % nitric acid and then rinsed with Milli-Q water. All samples water samples were filtered using, 0.45 µm membrane filters (Whatman), cleaned in 1 M HCl bath, then washed with Milli-Q water, dried and weighed)[7]. The filtration volume was approximately 1 L. The filtrates were transferred to the sampling bottles, acidified to < pH 2 and kept in the dark in a cool place. In the laboratory, 500 mL filtered seawater was first adjusted to pH = 2 with concentrated $HNO_3$ and 10 mL of 4.0 M APDC (ammonium pyrrolidine dithiocarbamate) solution was added[8]. Metals were extracted into 25 mL of chloroform in a separatory funnel. The chloroform phase bearing the metal complexes was stripped with concentrated nitric acid and the acidic aqueous phase (after evapouration and dilution) was analyzed by flame atomic absorption spectrophotometer[5]. Blank values have been observed for Fe, Mn, Cu, Cd and Pb as 0.10 ± 0.05 µg $L^{-1}$; 0.10 ± 0.02 µg $L^{-1}$; 0.15 ± 0.08 µg $L^{-1}$; 0.05 ± 0.03 µg $L^{-1}$; and 0.20 ± 0.30 µg $L^{-1}$, respectively.

For mercury analysis, 300 mL of sample was transferred to a dark bottle, to which 5 mL of 5 % $KMnO_4$ and 5 mL of $H_2SO_4$ were previously added for preservation purposes and kept in a cool (+4 ºC) and dark place[9]. To prevent the sample 5 mL of 0.5 % hydroxylamine hydrochloride was added and excess amount was reduced by permanganate just before analysis. Mercury was analyzed by using hydride vapour generation (HVG) unit. The absorbance due to elemental mercury vapour was measured by the atomic absorption spectrometer (Shimadzu AAS-6701).

The 0.45 µm membrane filter papers were preserved at -20 ºC after filtration for the TSS-metal analyses. Metal contents of total suspended solids were determined by atomic absorption spectrophotometer after a 'total' digestion, involving $HNO_3$ + $HClO_4$ + HF acid mixture[10,11].

The surface sediment samples were collected from 7 stations (TBK 1, 2, 13, 14, 16, 51 and 52) with sediment layer having thicknesses varying between 2 and 4 m using a Van Veen type grab sampler during June-July 2005; April-May 2006 and June-July 2006 (Fig. 1). The sediment samples were kept in a refrigerator (2 ºC) immediately after collection before drying and grinding. Total metal contents were determined by atomic absorption spectrophotometer after a total digestion, involving $HNO_3$ + $HClO_4$ + HF acid mixture. Mercury was analyzed by a flameless-atomic absorption spectrophotometer method following hot $HNO_3$ decomposition.

The accuracy of the total analyses was checked by analyzing the IAEA433, 405 and 407, QTM080MS (open sea sediment) and QTM081MS (harbor sediment) reference materials (Table-1). The metal values of sediment samples were normalized to eliminate the grain-size effects using metal/Al ratios[12].

TABLE-1
VALIDITY OF THE METAL ANALYSIS FOR THIS STUDY

| Reference material | Element | Measured values (in this study) ppm (µg $g^{-1}$) | Certificate values ppm (µg $g^{-1}$) |
|---|---|---|---|
| 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 |

The CTD data was collected by a CTD system SBE 9/11. The satellite images are processed from the NOAA images in the Berkarda Remote Sensing Lab. of the Institute of Marine Sciences and Management.

## RESULTS AND DISCUSSION

The satellite images showed the general pattern of the surface water in the Western Black Sea where the Danube fresh water was mostly carried along the Turkish northwestern coasts toward the Bosporus (Fig. 2) and reaches the Bosporus approximately within a month while most of the Danube water enters into the Marmara Sea *via* the Bosporus[13]. The brackish water measured in June 2004 at the Black Sea-Bosporus junction has slightly less saline water which also showed inflows of the Danube water into the Bosporus (Fig. 3). These findings also support the phenomenon that the metal contents originated from the Danube River were carried towards the northwestern coasts of Turkey.

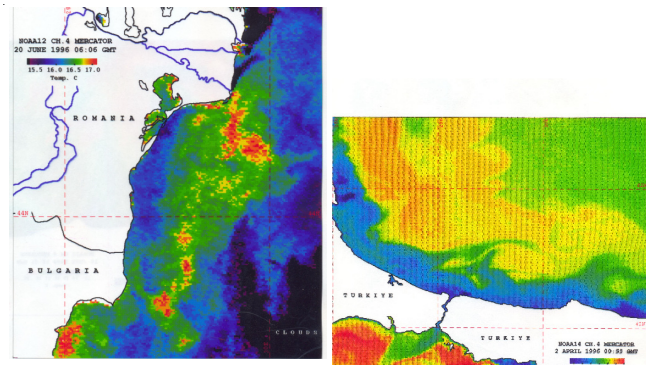


Fig. 2. Satellite images (NOAA12 & NOAA14; channel 4) that showed the Danube water path

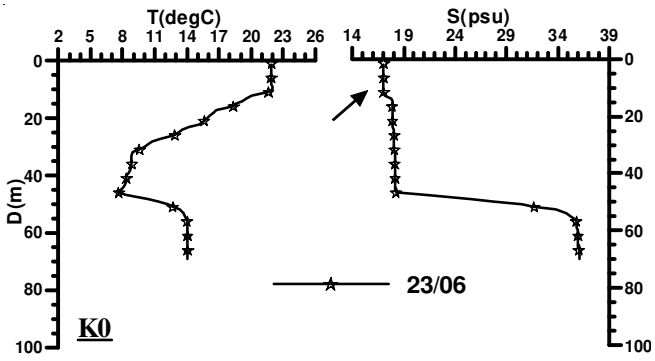


Fig. 3. Temperature and salinity profiles of the water column at the Black Sea-Bosporus junction

Dissolved oxygen concentration and total suspended solids of the western black sea waters are given in Figs. 4 and 5 and metals content of water column, suspended matter and surface sediments are listed in Tables 2-5.

The concentration of dissolved oxygen varied between 4.63 and 9.29 mg $L^{-1}$ in August 2003, whilst the range was between 7.92 and 11.34 mg $L^{-1}$ in June 2004. Dissolved oxygen levels were measured below the detection limit (< 0.03 mg $L^{-1}$) in the lower water layer of the TBK37 station for both periods. Dissolved hydrogen sulphide content was observed in the lower water layer of TBK13 and TBK37 stations for which the range was between 1.81 and 12 mg $L^{-1}$. The highest dissolved hydrogen sulphure values observed was determined in June 2004. Total suspended solid was found to be high in the surface water of TBK2 and the lower water layer water of TBK13 and TBK37 (Figs. 4 and 5).

Furthermore, dissolved oxygen was higher at interface/mixing layer and bottom water at the Western Black Sea, as the water column is subjected to enough sunlight for photosynthesis, thus the generation of oxygen, at the Black Sea[14]. Although, the Interface/mixing layer (suboxic), in which dissolved oxygen was measured at a minimum, at a depth of 125 to 145 m, depths changed with vertical mixture[14] with oxic conditions disappearing a depth of 150 m depth. In addition the concentration of the total suspended solid was the highest in the bottom water. These results indicate the heavily organic material production.

The dissolved metals concentrations in the water column and metal contents (Al, Fe, Mn, Pb, Cu, Cd, Zn and Hg) in the

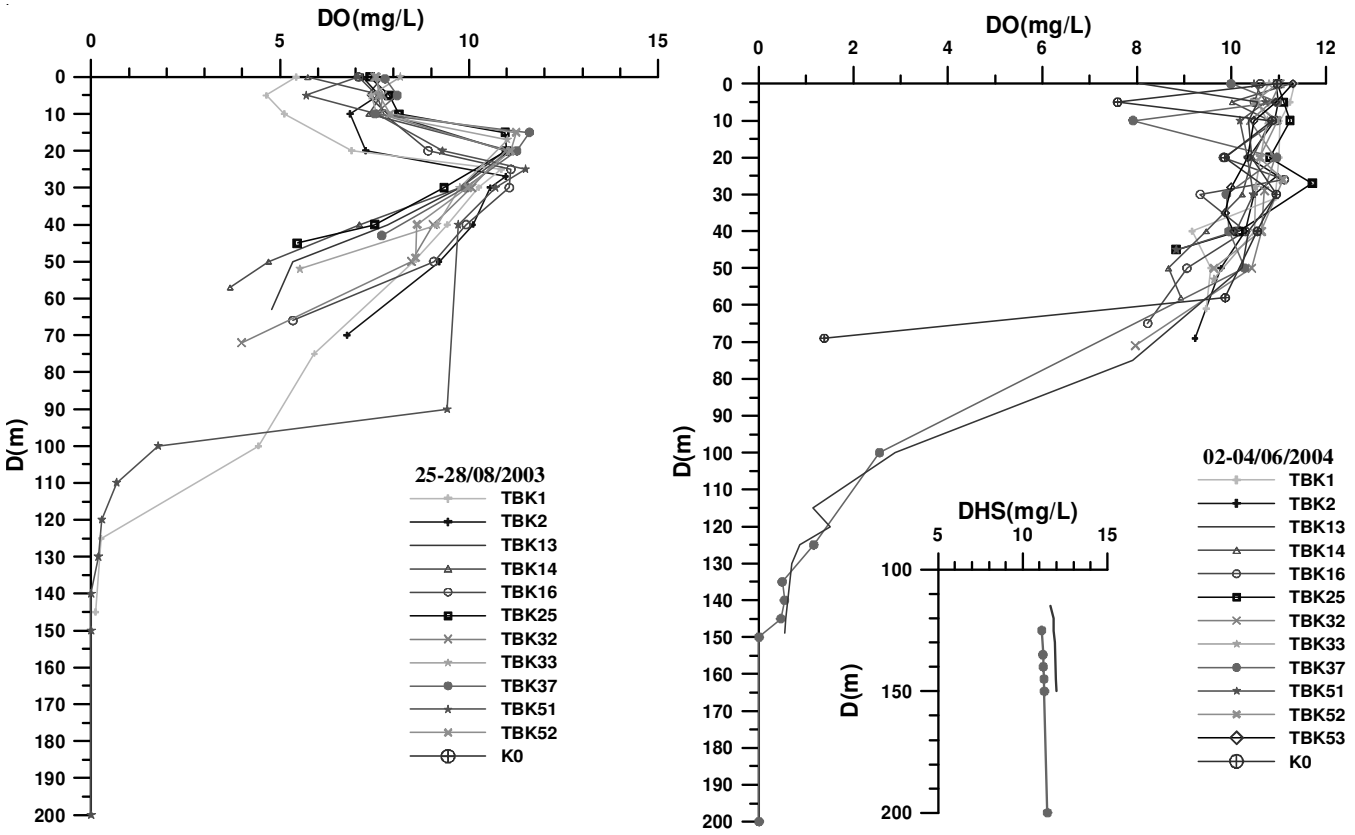


Fig. 4. Dissolved oxygen and hydrogen sulphide profiles of the water column at the Western Black Sea, Turkey

TABLE-2
DISSOLVED METAL CONCENTRATIONS IN THE WATER COLUMN (μg $L^{-1}$) (08/2003)

| Metal species | Sampling stations | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Western black sea | | K0 | | B7 | | B2 | |
| | Upper water | Lower water | Upper water | Lower water | Upper water | Lower water | Upper water | Lower water |
| Mn | 0.8-56 | 1-348 | 6-13 | 2-6 | 2-3 | 1.6-2.1 | 1.0-6.0 | 0.2-1.3 |
| Fe | 5.7-16.3 | 7.3-37 | 11-14 | 11-22 | 13-15 | 9-11 | 7.5-15 | 6.2-6.3 |
| Pb | 0.4-2.9 | 0.08-2.4 | 0.7-2.1 | 0.7-2.2 | 0.5-0.6 | 0.18-0.4 | 1.5-1.9 | 0.5 |
| Cu | 0.4-2.2 | 0.2-2.7 | 0.8-1.3 | 0.6-6.0 | 0.5-0.64 | 0.28-0.34 | 0.8-1 | 0.2-0.4 |
| Cd | <0.02-0.36 | <0.02-0.08 | 0.04-0.3 | 0.04-0.08 | 0.02-0.04 | <0.02-0.02 | <0.02-0.04 | <0.02-0.02 |

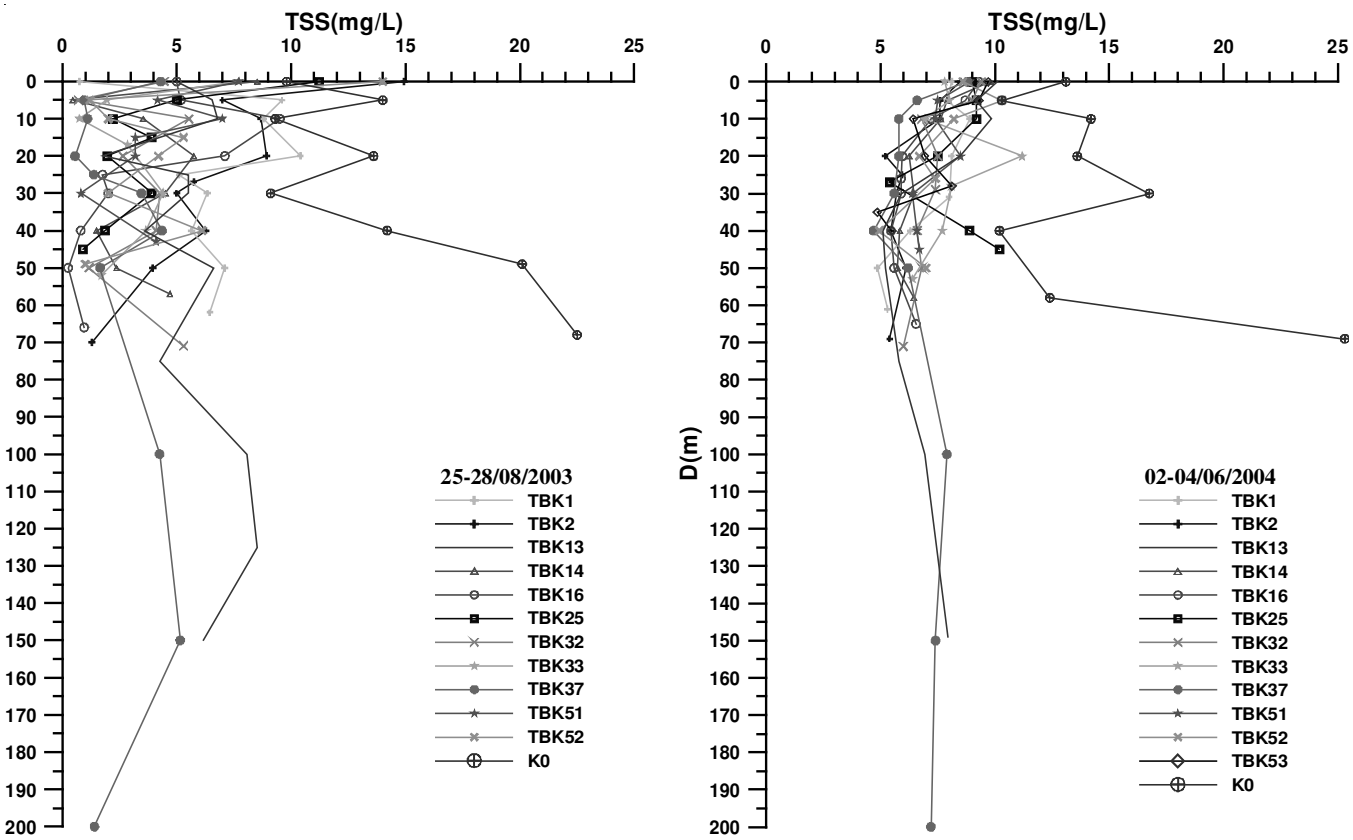


Fig. 5. Total suspended solid material profiles of the water column at the Western Black Sea, Turkey

TABLE-3
DISSOLVED Mn, Fe, Pb, Cu AND Zn CONCENTRATIONS IN THE WATER COLUMN (μg $L^{-1}$) AND Mn, Fe, Pb, Cu AND Zn CONTENTS IN THE SUSPENDED SOLID MATERIAL (μg $g^{-1}$) IN THE NORTH ADRIATIC SEA, THE NORTHWEST BLACK SEA AND THE WEST BLACK SEA

| Metal species | Northern Adriatic Sea (Ref. 16) | Northwestern Black sea (Ref. 17) | Western Black sea (Present study) |
|---|---|---|---|
| In the water column | | | |
| Mn | 6.7-192 | 1.2-1350 | 0.7-56 |
| Fe | 0.05-25 | 0.4-181 | 3.3-30 |
| Pb | 0.039-0.75 | 0.03-0.61 | 0.4-3 |
| Cu | 3.14-24.4 | 2.9-28.8 | 0.3-2.7 |
| Cd | 0.071-0.22 | 0.03-0.161 | <0.02-0.52 |
| In the suspended solid material | | | |
| Mn | 56-5460 | 80-62700 | 818-13867 |
| Fe | 800-78700 | 16-13000 | 500-17000 |
| Pb | 9.7-496 | 2.4-121 | 19-305 |
| Cu | 21-1560 | 5-225 | 13-89 |
| Zn | 166-2020 | 12-359 | 125-1330 |

suspended solid material are found to be high according to the international acceptable limits (Tables 2-4). However, some part of these metals are originated from crust and that's why Pb content is higher than the Cd and Hg contents as they are having the same amount ratio in the crust. Ayas *et al.*[15] also mentioned the order of the amounts of the metals Pb and Cd in another area (Mersin Gulf) as observed in our study. The main features that rule the metal distribution are the transportations from the mine lode zone near the shelf and the anthropogenic (domestic + industrial) inputs from the Danube River. The similar studies performed along the South Black Sea Shelf indicate the Danube River contributions to distributions in the west of the shelf.

Pb, Cd and Mn contents are higher than the shale average in total suspended solids and surface sediments[18] (Tables 3-5). The high total carbon and dissolved hydrogen sulphur contents of surface sediments are supported these distributions (Table-5). The high values are pointed that the anthropogenic (domestic

TABLE-4
VARIATIONS OF THE METAL CONTENTS IN THE SUSPENDED SOLID MATERIAL (μg $g^{-1}$) (08/2003 AND 06/2004)

| (08/2003) | Sampling stations | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Western black sea | | K0 | | B7 | | B2 | |
| Metal species | Upper water | Lower water | Upper water | Lower water | Upper water | Lower water | Upper water | Lower water |
| Mn | 2-1064 | 55-2461 | 3-37 | 9-88 | 7-247 | 20-91 | 39-44 | 117-142 |
| Fe (%) | 0.01-4.4 | 0.16-4.7 | 0.05-0.08 | 0.03-0.4 | 0.1-9 | 0.1-0.3 | 0.14-0.17 | 0.2-0.3 |
| Pb | 0.9-492 | 57-339 | 3-51 | 6.-43 | 7-127 | 8-14 | 21-39 | 21-49 |
| Al (%) | 0.15-85 | 0.14-4.8 | 0.01-0.06 | 0.04-10 | 0.4-2.7 | 0.2-1.1 | 0.15-0.18 | 0.28-0.31 |
| Cu | 0.5-416 | 21-188 | 3-16 | 8-9 | 13-52 | 6-19 | 19-43 | 36-39 |
| Zn | 10-17000 | 600-29000 | 200-300 | 100-200 | 100-2000 | 100-400 | 300-400 | 500-1000 |
| (06/2004) | | | | | | | | |
| Mn | 818-13867 | 960-5600 | 9-27 | 4949 | 1512-1642 | 2655-3446 | 3-17 | 43 |
| Fe (%) | 0.05-1.7 | 00.1-1 | 0.01-0.12 | 0.62 | 0.19-0.21 | 0.34-0.43 | 0.15-0.31 | 0.53 |
| Pb | 19-305 | 20-197 | 6-35 | 15 | 7-14 | 4-5 | 3-44 | 35 |
| Al (%) | 0.1-4 | 0.1-1.4 | 0.02-0.8 | 0.3 | 0.31-0.35 | 0.44-0.53 | 0.45-0.69 | 0.98 |
| Cu | 15-84 | 13-89 | 6-57 | 16 | 3 | 22-23 | 5-21 | 37 |
| Zn | 125-1206 | 260-1330 | 40-1131 | 39 | 115-143 | 130-152 | 189-740 | 452 |

TABLE-5
TOTAL METAL, TOC AND DHS CONTENTS IN THE SURFACE SEDIMENTS

| (08/2003) | Sampling stations | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Metal species | TBK1 | TBK2 | TBK13 | TBK14 | TBK16 | TBK51 | TBK52 | Shale average (Ref. 18) |
| Al (%) | 9.76 | 9.66 | 9.25 | 8.19 | 8.07 | 7.49 | 6.74 | 9.2 |
| Fe (%) | 1.99 | 2.1 | 2.23 | 2.19 | 2.42 | 2.2 | 2.03 | 4.7 |
| Mn (μg $g^{-1}$) | 465 | 468 | 656 | 391 | 402 | 423 | 419 | 850 |
| Pb (μg $g^{-1}$) | 34 | 43 | 43 | 56 | 34 | 27 | 29 | 20 |
| Cu (μg $g^{-1}$) | 16 | 21 | 22 | 17 | 16 | 18 | 19 | 50 |
| Zn (μg $g^{-1}$) | 62 | 83 | 78 | 56 | 66 | 57 | 65 | 90 |
| Ni (μg $g^{-1}$) | 24 | 28 | 28 | 17 | 25 | 37 | 38 | 80 |
| Cd (μg $g^{-1}$) | 0.9 | 1.3 | 2.4 | 2.4 | 2,4 | 2.5 | 2.7 | 0.2 |
| TOC (%) | 1.86 | 2,5 | 4.11 | 2.13 | 2.32 | 1.66 | 1.11 | 0.8* |
| DHS (μg $g^{-1}$) | 86.1 | 40.8 | 249 | 29.5 | 31.7 | - | - | |
| (06/2004) | | | | | | | | |
| Mn (μg $g^{-1}$) | 254 | 428 | 604 | 333 | 355 | 336 | 244 | 850 |
| Pb (μg $g^{-1}$) | 10 | 31 | 48 | 30 | 36 | 22 | 26 | 20 |
| Cu (μg $g^{-1}$) | 22 | 36 | 64 | 42 | 43 | 46 | 47 | 50 |
| Zn (μg $g^{-1}$) | 31 | 91 | 18 | 97 | 94 | 78 | 90 | 90 |
| Ni (μg $g^{-1}$) | 20 | 58 | 62 | 55 | 47 | 71 | 69 | 80 |
| Cd (μg $g^{-1}$) | 0.91 | 1.00 | 1.3 | 1.37 | 1.31 | 1.05 | 1.12 | 0.2 |
| Hg (ng $g^{-1}$) | 362 | - | 350 | 260 | 270 | - | - | 300 |
| Cr (μg $g^{-1}$) | 94 | 98 | 100 | 140 | 69 | 102 | 101 | 100 |
| TOC (%) | 1.96 | 1.42 | 2.6 | 1.53 | 1.64 | 1.63 | 1.66 | 0.8[a] |
| DHS (μg $g^{-1}$) | 406 | 407 | 419 | 397 | 401 | - | - | - |

– = Not analyzed; * = Ref. 24

and industrial) transports *via* Danube River. The metals content ranged between; Pb 10-56 μg $g^{-1}$, Cd 0.91-2.7 μg $g^{-1}$, Hg 260-362 ng $g^{-1}$ and Cr ranged between 69-140 μg $g^{-1}$. TOC values ranged between 1.11-4.11 % and dissolved hydrogen sulphure content changed between 29.5-419 μg $g^{-1}$ (Table-5).

Nevertheless indicating high Mn values are showed that terrestrial inputs from the Binkiliç manganese mineralized zone by small streams and its corrosion to the marine system. Besides especially the surface sediments Fe, Cu, Zn, Hg and Ni contents are lower than the shale average[18]. These results are harmonious the previous studies including the Black Sea sediments of Cu, Ni, Co, Mn, Ba and V contents[19-22] (Table-3). In addition, Pb and Cd contents which are above the shale average in station TRK51 are harmonious with the results of the study handled around Igneada by Topçuoglu *et al.*[23].

## Conclusion

The results presented above clearly demonstrated that the western black sea coast of Turkey is facing pollution *via* the Danube River. Also Bosporus acts like a collector system that carries most of the load into the Sea of Marmara. The physical parameters (salinity and temperature values of the surface water) and the processed satellite images support this phenomenon. However, Gaye *et al.*[25] claim that the domestic and industrial discharges, which are shown to be important sources of marine pollution in major cities along the Black Sea coast of Turkey, are important in terms of annual pollutant loads to the Black Sea. The other international rivers are also crucial in the pollution of the Black Sea, although the Danube river is the dominant pollutant source[26]. Therefore, further monitoring studies should be held in a particular period and the

regulations must be revized by the stakeholders (the related countries) for preventing the Western Black Sea.

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