TRANSPORT OF HEAVY METALS WITHIN A TWO LAYERED SYSTEM: THE MARMARA-MEDITERRANEAN-BLACK SEAS SYSTEM

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Abstract

The Marmara Sea is a passage between the Mediterranean and Black Sea. The hydrography of the Marmara Sea is dominated by the Mediterranean and Black Sea water. The great difference between the salinity of the two water masses results in a well stratified water column with a marked halocline separating a superficial layer salinity 22-25‰ from underlying saline 38.5‰ water mass. It is connected to Aegean Sea and Mediterranean Sea via Dardanelles Strait and to Black Sea via Bosphorus Strait. Within the strait system two major currents are prevailing. The under current is generated by the Mediterranean water flowing in to the Marmara Sea through the Dardanelles Strait and out to the Black Sea through the Bosphorus Strait. The surface current is generated by Black Sea waters flowing in to the Marmara Sea through the Bosphorus Strait and out to the Aegean Sea through the Dardanelles Strait.

The concentration of some heavy metals (Zn, Cu, Ni, Cr, Cd, and Hg) in the water column was determined along the Dardanelles Strait and Bosphorus Strait and in the Marmara Sea. The metal concentrations are ranging between 13.26-144.9 µg/L for Zn, 0.23-0.77 µg/L for Cu, 0.41-5.42 µg/L for Ni, 0.26-2.56 µg/L for Cr, 0.67-12.67 ng/L for Cd and 2.0-5.3 ng/L for Hg.

By utilising the average metal concentrations within the straits and annual average water fluxes between Aegean Sea-Marmara Sea-Black Sea, the metal fluxes in the region were determined.

1. INTRODUCTION

The hydrography and the water circulation of the system is extensively studied and published by Ünlüata et al.[1], and Beşiktepe et al.[2] and can be summarised as follows:

The Marmara Sea is a small inter-continental basin. It connected to Aegean Sea and Mediterranean Sea via Dardanelles Strait and to Black Sea via Bosphorus Strait. Turkish Straits system are shown in Figure 1. The hydrography of the Marmara Sea is dominated by the Mediterranean and Black Seas water. Within the strait system two major currents are prevailing. The under current is generated by the Mediterranean waters flowing in through the Dardanelles and out through the Bosphorus. The surface current is generated by Black Sea waters flowing in through the Bosphorus and out through the Dardanelles (Ünlüata et al[1]., Beşiktepe et al[2]., Özsoy et al[3]). The current systems and the water fluxes in the studied region are shown in Figure 2. The great difference between the salinity of the two water masses results in a well stratified water column with a marked halocline separating a superficial layer salinity 22-25o/oo from underlying saline 38.5o/oo water mass. The strong stratification of the water masses coupled with the topographic restrictions inhibits the efficient ventilation of deep waters.

The Dardanelles Strait is 60 km long and 1.3-7 km wide. Its average depth is 55 m with a maximum depth of 105 m. The Bosphorus Strait is 30 km long and 0.7-3.5 km wide. The average depth is 36 m and its maximum depth is 110 m.

The biochemical properties of the Marmara Sea are dominated by the inflowing waters of the Aegean and Black Seas and their vertical mixing at the halocline. The algal production is always limited to the upper 20 m. Because of the presence of a permanent halocline between 20-25 m, the subhalocline waters have oxygen concentrations as little as 1-2 ppm throughout the year. With the above mentioned physicochemical characteristics, the Turkish Straits and the Marmara Sea constitute a unique system for the modeling of fluxes.

2. MATERIAL AND METHODS

The sea water samples were collected during the monthly cruises of R/V BİLİM belonging to METU-Institute of Marine Sciences in the Marmara Sea between 1987 and 1989. Sampling locations are shown in Figure 1.

2.1 METHODOLOGY

Mercury content of the sea water was measured by cold vapour AAS technique. The concentration step was achieved by $NaBH_4$ reduction and amalgamation on silver packed microcolumn. Mercury free nitrogen gas was used to strip reduced mercury from the reaction bottle. Desorption of amalgamated mercury was done by heating the microcolumn at about 500 ^{o}C and send to the absorption cell by nitrogen gas and the absorbance was measured (Yemenicioğlu & Salihoğlu[4], Yemenicioğlu[5]). The other metals Zn, Cu, Ni, Cr, and Cd was analysed with flameless AAS. The metals are extracted from 100 ml of sea water in to freon and DDDC+APDC mixture and then back extracted into HNO_3.

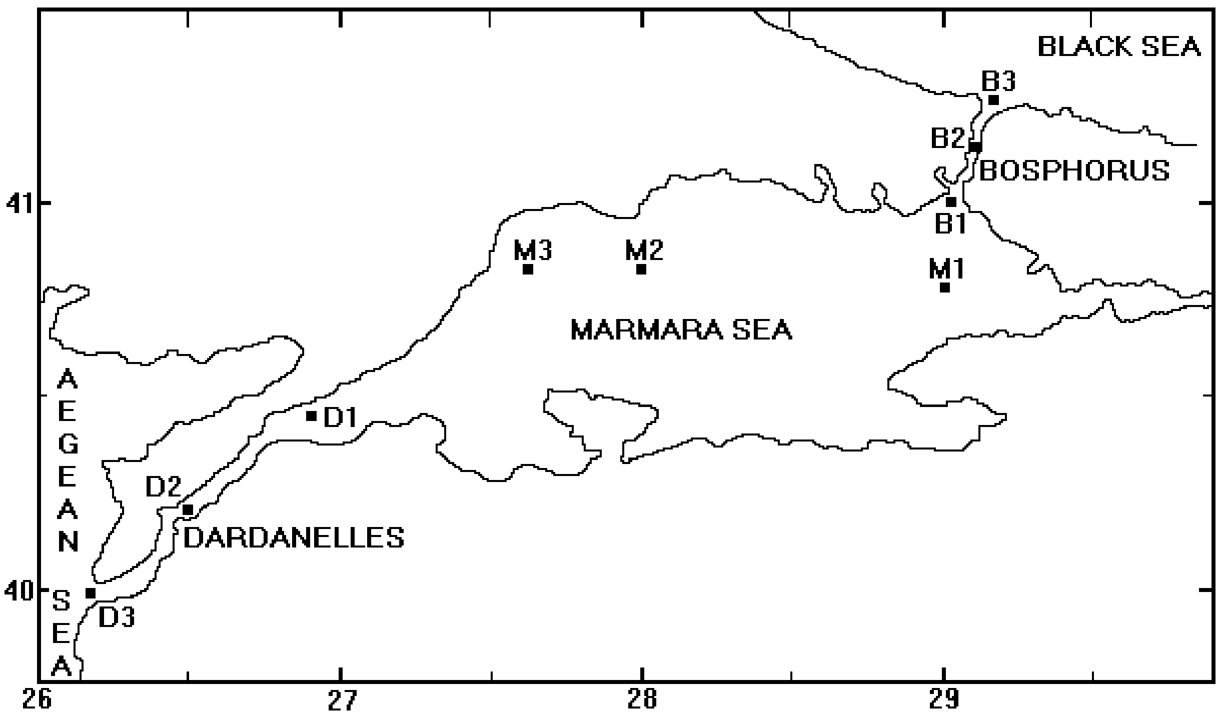

FIGURE 1. Sampling locations.

3. FLUXES OF HEAVY METALS WITHIN THE TURKISH STRAITS SYSTEM

The fluxes of metals between the Black Sea-Marmara Sea-Mediterranean Sea through the Turkish Straits are calculated by substituting the average metal concentrations and water volume fluxes proposed by Beşiktepe et al.[2] into the equations 1, 2, 3, 4, 5 and 6. For this purpose the whole system is divided into two vertical layers and three boxes, Bosphorus Strait, Marmara Sea and Dardanelles Strait. Vertical exchange between the two layers within each boxes were allowed to take place. The abbreviations used in the formulas are summarised in Figure 2.

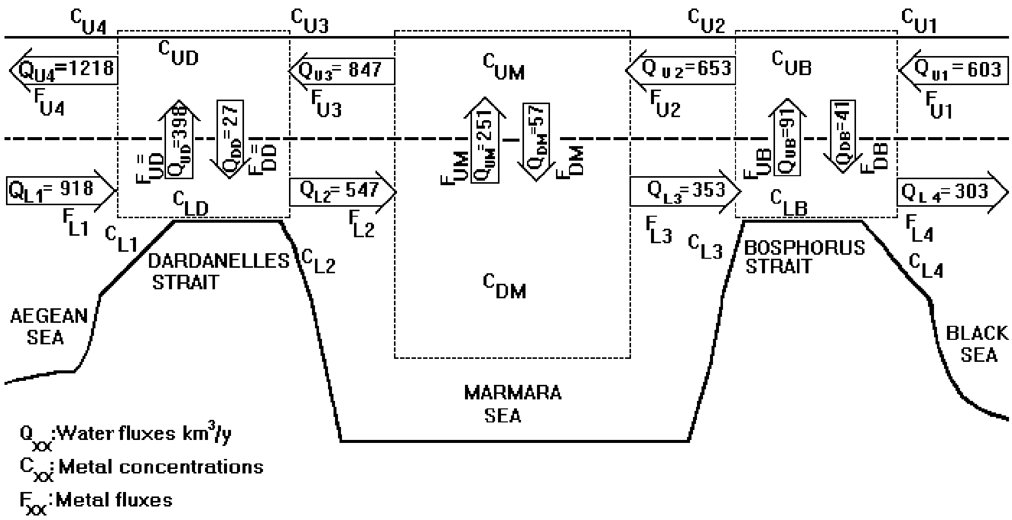

FIGURE 2. Water fluxes in the Turkish strait system and symbol description used in flux calculations.

3.1 BOSPHORUS LOWER LAYER FLUXES

Under the steady state conditions the amount of a substance entering in a system must be balanced by an out-flow. By considering this concept, for the metal fluxes through the Bosphorus lower layer we can write equation (1).

$$Q_{L3}\, C_{L3} + Q_{DB}\, C_{UB} = Q_{L4}\, C_{L4} + Q_{UB}\, C_{LB} \qquad \textbf{(1)}$$

The fluxes of metals in and out of the Bosphorus lower are calculated and given in Table 1 and Table 2.

Calculations done by using the fluxes in Tables 1, 2, 3 and 4 shows that inputs of Hg, Cr, Cu and Zn are almost balanced by the outflow from the Bosphorus lower layer. The Cd and Ni outflow exceeded the input from the Marmara Sea and upper layer. Both metals are used for industrial purposes and as a result industrial effluent draining directly into the Bosphorus are the probable sources of excess of these metals.

TABLE 1. Metal fluxes in to the Bosphorus lower layer.

Metal	From Marmara Sea (F_{L3})	From the upper layer (F_{DB})
Mercury	$1.34x10^{6}$ g/y	$0.16x10^{6}$ g/y
Cadmium	$1.62x10^{6}$ g/y	$0.45x10^{6}$ g/y
Chromium	$338.88x10^{6}$ g/y	$45.1x10^{6}$ g/y
Nickel	$95.31x10^{6}$ g/y	$51.66x10^{6}$ g/y
Copper	$109.43x10^{6}$ g/y	$28.29x10^{6}$ g/y
Zinc	$2.93x10^{10}$ g/y	$0.39x10^{10}$ g/y

TABLE 2. Metal fluxes out of the Bosphorus lower layer.

Metal	To the Black Sea (F_{L4})	To the upper layer(F_{UB})
Mercury	$1.09x10^{6}$ g/y	$0.34x10^{6}$ g/y
Cadmium	$2.12x10^{6}$ g/y	$0.52x10^{6}$ g/y
Chromium	$290.88x10^{6}$ g/y	$99.19x10^{6}$ g/y
Nickel	$139.38x10^{6}$ g/y	$33.67x10^{6}$ g/y
Copper	$81.81x10^{6}$ g/y	$27.3x10^{6}$ g/y
Zinc	$2.5x10^{10}$ g/y	$0.76x10^{10}$ g/y

4.2 BOSPHORUS UPPER LAYER FLUXES

In this section of the Turkish Straits System the fluxes are given by equation (2).

$$Q_{U1}\,C_{U1} + Q_{UB}\,C_{LB} = Q_{U2}\,C_{U2} + Q_{DB}\,C_{UB} \qquad \textbf{(2)}$$

The metal fluxes obtained from equation 2 are summarised in Table 3 and 4.

TABLE 3. Metal fluxes in to the upper layer of Bosphorus.

Metal	From Black Sea (F_{L1})	From lower layer(F_{UB})
Mercury	2.23 $x10^{6}$ g/y	$0.34x10^{6}$ g/y
Cadmium	$6.33x10^{6}$ g/y	$0.52x10^{6}$ g/y
Chromium	$633.15x10^{6}$ g/y	$99.19x10^{6}$ g/y
Nickel	$723.6x10^{6}$ g/y	$33.67x10^{6}$ g/y
Copper	$259.29x10^{6}$ g/y	$27.3x10^{6}$ g/y
Zinc	$4.57x10^{10}$ g/y	$0.76x10^{10}$ g/y

TABLE 4. Metal fluxes out of the Bosphorus upper layer.

Metal	To the Marmara Sea (F_{U2})	To the lower layer(F_{DB})
Mercury	$2.74x10^{6}$ g/y	$0.16x10^{6}$ g/y
Cadmium	$7.31x10^{6}$ g/y	$0.45x10^{6}$ g/y
Chromium	$718.3x10^{6}$ g/y	$45.1x10^{6}$ g/y
Nickel	$750.95x10^{6}$ g/y	$51.66x10^{6}$ g/y
Copper	$300.38x10^{6}$ g/y	$28.29x10^{6}$ g/y
Zinc	$5.22x10^{10}$ g/y	$0.39x10^{10}$ g/y

4.3 DARDANELLES UPPER LAYER FLUXES

The metal fluxes in to the upper layer of the Dardanelles is given by equation (3) and the results obtained are summarised in Table 5 and 6

$$Q_{U3}\,C_{U3} + Q_{UD}\,C_{LD} = Q_{U4}\,C_{U4} + Q_{DD}\,C_{UD} \qquad \textbf{(3)}$$

TABLE 5. Metal fluxes in to the upper layer of Dardanelles Strait.

Metal	From Marmara Sea (F_{U3})	From lower layer (F_{UD})
Mercury	$3.30x10^{6}$ g/y	$1.67x10^{6}$ g/y
Cadmium	$2.96x10^{6}$ g/y	$1.53x10^{6}$ g/y
Chromium	$612.38x10^{6}$ g/y	$298.9x10^{6}$ g/y
Nickel	$296.45x10^{6}$ g/y	$103.48x10^{6}$ g/y
Copper	$330.33x10^{6}$ g/y	$191.04x10^{6}$ g/y
Zinc	$5.55x10^{10}$ g/y	$1.73x10^{10}$ g/y

TABLE 6. Metal fluxes out of the Dardanelles upper layer.

Metal	To the Mediterranean Sea (F_{U4})	To the lower layer(F_{DD})
Mercury	$4.75x10^{6}$ g/y	$0.1x10^{6}$ g/y
Cadmium	$4.26x10^{6}$ g/y	$0.1x10^{6}$ g/y
Chromium	$915.94x10^{6}$ g/y	$20.14x10^{6}$ g/y
Nickel	$415.34x10^{6}$ g/y	$9.77x10^{6}$ g/y
Copper	$533.48x10^{6}$ g/y	$11.61x10^{6}$ g/y
Zinc	$7.05x10^{10}$ g/y	$0.16x10^{10}$ g/y

4.4 DARDANELLES LOWER LAYER FLUXES

The Dardanelles lower layer metal fluxes is given by equation (4). The results are summarised in Tables 7 and 8. From Tables 5-8 it is found that the metals input in to the Dardanelles is balanced by the out fluxes.

$$Q_{L1}.C_{L1} + Q_{DD}.C_{UD} = Q_{L2}.C_{L2} + Q_{UD}.C_{LD} \qquad \textbf{(4)}$$

Table 7. Metal fluxes in to the lower layer of Dardanelles.

Metal	From Mediterranean Sea (F_{L1})	From upper layer (F_{DD})
Mercury	$3.95x10^{6}$ g/y	$0.1x10^{6}$ g/y
Cadmium	$3.58x10^{6}$ g/y	$0.1x10^{6}$ g/y
Chromium	$697.68x10^{6}$ g/y	$20.14x10^{6}$ g/y
Nickel	$293.76x10^{6}$ g/y	$9.77x10^{6}$ g/y
Copper	$459x10^{6}$ g/y	$11.61x10^{6}$ g/y
Zinc	$3.86x10^{10}$ g/y	$0.16x10^{10}$ g/y

TABLE 8. Metal fluxes out of the Dardanelles lower layer.

Metal	To the Marmara Sea (F_{L2})	To the upper layer(F_{UD})
Mercury	$2.3x10^{6}$ g/y	$1.67x10^{6}$ g/y
Cadmium	$2.2x10^{6}$ g/y	$1.53x10^{6}$ g/y
Chromium	$371.41x10^{6}$ g/y	$298.9x10^{6}$ g/y
Nickel	$207.86x10^{6}$ g/y	$103.48x10^{6}$ g/y
Copper	$301.94x10^{6}$ g/y	$191.04x10^{6}$ g/y
Zinc	$2.79x10^{10}$ g/y	$1.73x10^{10}$ g/y

4.5 THE LOWER LAYER FLUXES OF MARMARA

The metal fluxes in the Marmara Sea lower layer is given by equation 5. In calculations input from sediment and removal by sedimentation are neglected. The metal fluxes obtained from equation 5 are given in Tables 9 and 10.

$$Q_{L2}.C_{L2} + Q_{DM}.C_{UM} = Q_{L3}.C_{L3} + Q_{UM}.C_{LM} \quad \textbf{(5)}$$

TABLE 9. Metal fluxes in to the lower layer of Marmara Sea.

Metal	From Mediterranean Sea (F_{L2})	From upper layer (F_{DM})
Mercury	$2.3 x 10^{6}$ g/y	$0.22 x 10^{6}$ g/y
Cadmium	$2.2 x 10^{6}$ g/y	$0.28 x 10^{6}$ g/y
Chromium	$371.41 x 10^{6}$ g/y	$57 x 10^{6}$ g/y
Nickel	$207.86 x 10^{6}$ g/y	$17.67 x 10^{6}$ g/y
Copper	$301.94 x 10^{6}$ g/y	$18.24 x 10^{6}$ g/y
Zinc	$2.79 x 10^{10}$ g/y	$0.35 x 10^{10}$ g/y

TABLE 10. Metal fluxes out of the lower layer of Marmara Sea.

Metal	To the Bosphorus (F_{L3})	To the upper layer(F_{UM})
Mercury	$1.34 x 10^{6}$ g/y	$0.85 x 10^{6}$ g/y
Cadmium	$1.62 x 10^{6}$ g/y	$1.28 x 10^{6}$ g/y
Chromium	$338.88 x 10^{6}$ g/y	$251 x 10^{6}$ g/y
Nickel	$95.31 x 10^{6}$ g/y	$85.34 x 10^{6}$ g/y
Copper	$109.43 x 10^{6}$ g/y	$42.67 x 10^{6}$ g/y
Zinc	$2.93 x 10^{10}$ g/y	$1.56 x 10^{10}$ g/y

4.6 THE UPPER LAYER FLUXES OF MARMARA

The upper layer fluxes in the Marmara Sea is given by equation 6.

$$Q_{U2}.C_{U2} + Q_{UM}.C_{LM} + F_A + F_D = Q_{U3}.C_{U3} + Q_{DM}.C_{UM} + F_E \quad \textbf{(6)}$$

Since the surface area of the Marmara Sea is small the atmospheric deposition (F_D) and emission to the atmosphere (F_E) is omitted. The anthropogenic input (F_A) also omitted since the anthropogenic input are included in the straits fluxes. The metal fluxes obtained from equation 6 are summarised in Table 11 and 12.

TABLE 11. Metal fluxes in to the upper layer of Marmara Sea.

Metal	From Black Sea	From lower layer
Mercury	$2.74 x 10^{6}$ g/y	$0.85 x 10^{6}$ g/y
Cadmium	$7.31 x 10^{6}$ g/y	$1.28 x 10^{6}$ g/y
Chromium	$718.3 x 10^{6}$ g/y	$251 x 10^{6}$ g/y
Nickel	$750.95 x 10^{6}$ g/y	$85.34 x 10^{6}$ g/y
Copper	$300.38 x 10^{6}$ g/y	$42.67 x 10^{6}$ g/y
Zinc	$5.22 x 10^{10}$ g/y	$1.56 x 10^{10}$ g/y

TABLE 12. Metal fluxes out of the upper layer of Marmara Sea.

Metal	To the Mediterranean Sea (F_{U3})	To the lower layer (F_{DM})
Mercury	$3.30x10^6$ g/y	$0.22x10^6$ g/y
Cadmium	$2.96x10^6$ g/y	$0.28x10^6$ g/y
Chromium	$612.38x10^6$ g/y	$57x10^6$ g/y
Nickel	$296.45x10^6$ g/y	$17.67x10^6$ g/y
Copper	$330.33x10^6$ g/y	$18.24x10^6$ g/y
Zinc	$5.55x10^{10}$ g/y	$0.35x10^{10}$ g/y

The metal fluxes for the Marmara Sea as a whole is summarised in Table 13:

TABLE 13. Metal Fluxes in the Marmara Sea.

Metal	From the Bosphorus	From the Dardanelles	Total input
Hg	$2.7x10^6$ g/y	$2.3x10^6$ g/y	$5.0x10^6$ g/y
Cd	$7.3x10^6$ g/y	$2.2x10^6$ g/y	$9.5x10^6$ g/y
Cr	$718x10^6$ g/y	$372x10^6$ g/y	$1090x10^6$ g/y
Ni	$751x10^6$ g/y	$208x10^6$ g/y	$959x10^6$ g/y
Cu	$300x10^6$ g/y	$302x10^6$ g/y	$602x10^6$ g/y
Zn	$5.2x10^{10}$ g/y	$2.8x10^{10}$ g/y	$8.0x10^{10}$ g/y
Metal	to the Bosphorus	to the Dardanelles	Total output
Hg	$1.34x10^6$ g/y	$3.30x10^6$ g/y	$4.64x10^6$ g/y
Cd	$1.62x10^6$ g/y	$2.96x10^6$ g/y	$4.58x10^6$ g/y
Cr	$339x10^6$ g/y	$612x10^6$ g/y	$951x10^6$ g/y
Ni	$95x10^6$ g/y	$297x10^6$ g/y	$392x10^6$ g/y
Cu	$110x10^6$ g/y	$330x10^6$ g/y	$440x10^6$ g/y
Zn	$2.9x10^{10}$ g/y	$5.4x10^{10}$ g/y	$8.3x10^{10}$ g/y

From the results summarised in Table 13 it can be seen that the input fluxes exceeded the output fluxes. These excess input must be balanced by output. This can be balanced by removal to the sediment site, ie. the F_S term in the right hand side of equation 5 must be equal to the difference between the input and output fluxes.

Since the atmospheric and river inputs in to the region are not included in the calculations the given fluxes must be taken as under estimated.

5 CONCLUSION

The results obtained from the flux calculations indicate that, within the inherent error limits of the fluxes and the method used, heavy metal input into the Marmara Sea is balanced by the output. This could be the result of the high primary productivity (Ünlüata et al[6]) within the basin which removes metals from the water column. This idea is further supported by the relatively high metal concentrations in the underlying sediments (Yemenicioğlu unpublished data).

Since the atmospheric and river input in to the region are not included in the calculations the above values are under estimated.

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