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Transport of heavy metals within a two-layered system: the Marmara-Mediterranean-Black Seas system

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Abstract

The concentration of heavy metals (Zn, Cu, Ni, Cr, Cd, and Hg) in sea water was determined along the Turkish Straits (Dardanelles and Bosphorus) and in the Marmara Sea. The 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 utilizing the average metal concentrations and annual average water fluxes between Aegean-Marmara-Black Seas the metal fluxes in the region were determined.

1. INTRODUCTION

Turkish Straits system are shown in Figure 1. The hydrography and the water circulation of the system is extensively studied and published by Ünlüata et al.[1], and Beşiktepe et al.[2] Özsoy[3] and can be summarized as follows:

The Marmara Sea is a small inter-continental basin. It connected to Aegean and Mediterranean Seas via Dardanelles Strait and to Black Sea via Bosphorus Strait. 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[4]). 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 body 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.

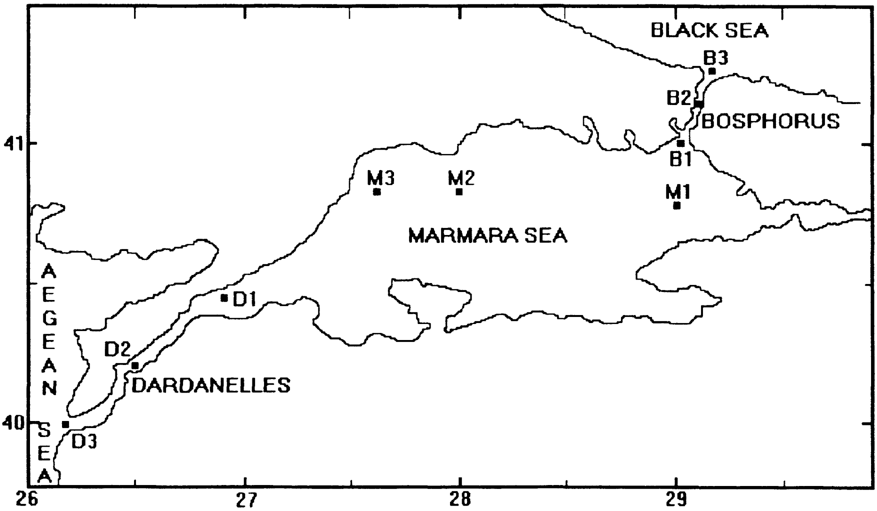

FIGURE 1. Sampling locations.

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 concentration was measured by cold vapor AAS technique. The reduction step was achieved by $NaBH_4$ and reduced mercury was collected on silver packed microcolumn as described by Yemenicioğlu & Salihoğlu[5]. Mercury free nitrogen gas was used to strip reduced mercury from the reaction bottle. By heating the microcolumn at about 500 ^oC mercury was desorpted and swept in to the absorption cell by nitrogen gas and the absorbance was recorded on a strip chart recorder (Yemenicioğlu & Salihoğlu[5], Yemenicioğlu[6]). The metals

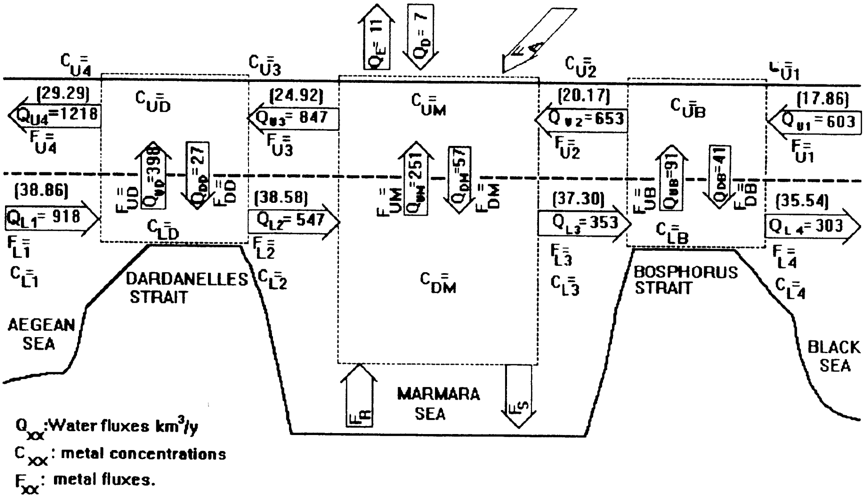

FIGURE 2. Volume fluxes across the Turkish Straits system using 4 yr (1986-89) average salinities. Number in paranthesis are average salinity values used in the computations.

other than mercury were extracted from 100 mL of sea water at pH 8 in to freon and DDDC+APDC mixture and then back extracted into HNO_3. The extraction was done as follows; 100 ml of sea water was transferred to 250 ml pyrex separating funnel. 5 ml of complexant and 10 ml of freon (5% APDC +5% DDDC) was added and the funnel was shaked for 10 minutes. When the organic and aqueous phases had fully separated the freon was drawn off into a 20 ml screw-capped polyethylene vial. Another 5 ml of clean freon was added to the funnel and shaked for a further 10 minutes. Again the freon was drawn off and added to the previous 10 ml freon. For the back extraction 35 µl of concentrated HNO_3 was added to the combined freon in the vial and shaked for 6 minutes. Then 875 µl of distilled deionized water was added and the vial were shaked for a further 6 minutes. The aqueous phase was then carefully drawn off by using a micropipette and transferred to 3 ml vial. The whole back extraction was repeated and the second aliquot was added to the first. The samples were then analysed using a GF 3000 GBC Graphite Furnace AAS.

The volume fluxes through the straits were calculated by using long term averages (1986-1989) salinity values and published by Beşiktepe et al.[2] The flux computations are based on the Knudsen relations expressing the steady-state mass budgets. Sea Bird Electronics SBE 9 CTD profiler was used for the hydrographic measurements. More information about the station grids, annual and interannual variations of the fluxes can be found in Beşiktepe et al.[2].

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 long term average metal concentrations and water volume fluxes (calculated and published 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. To determine the boundaries of the upper and lower limits, the salinity values $S_1^*=S_S+0.2(S_B-S_S)$ and $S_2^*=S_B-0.2(S_B-S_S)$ were assigned as the salinity limits characterising the upper and lower layer waters respectively. Here S_S is the average salinity for the first 5 m and S_B is the average salinity within 5 m from the maximum depth of each cast. The abbreviations used in the formulas and the volume fluxes are summarized in Figure 2.

3.1 FLUXES WITHIN THE BOSPHORUS STRAIT

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 we can write equation (1) for the Bosphorus lower layer and equation (2) for the upper layer.

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

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

The fluxes of metals in and out of the Bosphorus are given in Table 1 and Table 2. The metal fluxes in Tables 1 and 2 show that inputs of Hg, Cr, Cu and Zn are almost balanced by the outflow from the Bosphorus. The Cd and Ni outflow for the lower layer exceeded the input from the Marmara Sea and upper layer. Both metals are used for industrial activities which discharge their effluents directly into the sea. These industrial effluents draining directly into the Bosphorus are the probable sources of excess of these metals.

3.2 FLUXES WITHIN DARDANELLES STRAIT

The metal fluxes for the upper layer of the Dardanelles is given by equation (3) and for the lower layer by equation (4). Results obtained are summarized in Table 3 and 4. From Tables 3and 4 it is found that the metals input in to the Dardanelles Strait is balanced by the out fluxes.

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

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

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TABLE 1. Metal fluxes in 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
	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

TABLE 2. Metal fluxes in 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
	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

TABLE 3. Metal fluxes in 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
	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

Table 4. Metal fluxes in 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
	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

3.3 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 processes are are not known and for simplicity of calculations are neglected in the equation. The metal fluxes obtained from equation 5 by ommiting F_S and F_R terms are given in Table 5.

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

TABLE 5. Metal fluxes in the lower layer of Marmara Sea.

Metal	From Mediterranean Sea (F_{L2})	From upper layer (F_{DM})
Mercury	2.3×10^6 g/y	0.22×10^6 g/y
Cadmium	2.2×10^6 g/y	0.28×10^6 g/y
Chromium	371.41×10^6 g/y	57×10^6 g/y
Nickel	207.86×10^6 g/y	17.67×10^6 g/y
Copper	301.94×10^6 g/y	18.24×10^6 g/y
Zinc	2.79×10^{10} g/y	0.35×10^{10} g/y
	To the Bosphorus (F_{L3})	To the upper layer(F_{UM})
Mercury	1.34×10^6 g/y	0.85×10^6 g/y
Cadmium	1.62×10^6 g/y	1.28×10^6 g/y
Chromium	338.88×10^6 g/y	251×10^6 g/y
Nickel	95.31×10^6 g/y	85.34×10^6 g/y
Copper	109.43×10^6 g/y	42.67×10^6 g/y
Zinc	2.93×10^{10} g/y	1.56×10^{10} g/y

3.4 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 supposed to be small and balance each other, thus cancelled from both side of the equation (6). 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 summarized in Table 6.

TABLE 6. Metal fluxes in the upper layer of Marmara Sea.

Metal	From Black Sea	From lower layer
Mercury	$2.74x10^6$ g/y	$0.85x10^6$ g/y
Cadmium	$7.31x10^6$ g/y	$1.28x10^6$ g/y
Chromium	$718.3x10^6$ g/y	$251x10^6$ g/y
Nickel	$750.95x10^6$ g/y	$85.34x10^6$ g/y
Copper	$300.38x10^6$ g/y	$42.67x10^6$ g/y
Zinc	$5.22x10^{10}$ g/y	$1.56x10^{10}$ g/y
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

TABLE 7. 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
	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

The metal fluxes for the whole Marmara Sea (lower layer and upper layer together) is summarized in Table 7. From the results in Table 7 it can be seen that the input in to the Marmara Sea exceeded the output fluxes. This excess input must be balanced by output. In section 3.3 the F_S term (removal to sediment) in equation 5 was omitted for simplicity of calculations but here we see that the most probable mechanism to balance the excess input is removal to the sediment site, i.e. 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 resuspension from sediment, atmospheric and river inputs in to the region are not included in the calculations the given fluxes must be taken as under estimated.

4 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[7]) 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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