Distribution of mercury: its sources and dispersal in the Marmara Sea, Black Sea and Mediterranean Sea

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Abstract- Long-term vertical and spatial distribution of total mercury (Hg_T) in seawater was determined in the Marmara Sea, Black Sea and Mediterranean Sea. Within the Turkish Straits, (Dardanelles and Bosphorus), Marmara Sea, Black Sea system two permanent layers are separated by a sharp halocline. The upper layer of the Marmara Sea has a thickness of about 20 m. The spatial variation of total mercury (Hg_T) concentration in the Marmara Sea was small. The concentration of Hg_T in the Marmara Sea lies between 2.70 ng/L and 5.30 ng/L. Mediterranean Sea water contains Hg_T in the range of 2.50-7.5 ng/L while Aegean concentrations lies between 4.0 ng/L and 16.6 ng/L. Hg_T concentration in the Black Sea was in the range of below detection limit (0.15 ng/L) and 11.0 ng/L.

Keywords- Total mercury (Hg_T), Black Sea, Mediterranean Sea, Aegean Sea, Marmara Sea.

Introduction

The mercury (Hg) concentration of sea water is generally low. Mercury (Hg) and many of its compounds enters and cycles in the environment as a result of natural and anthropogenic activities. The amount of mercury (Hg) released and cycling in the biosphere has increased since the beginning of the industrial age. Most of the Hg in the atmosphere is elemental Hg vapour (Fitzgerald, 1986) and can circulate in the atmosphere for up to approximately 6 years (Matsunaga and Goto, 1976), and hence can be reach to remote sites from the sources of emission. Most of the Hg in water, soil, sediments, or plants and animals is in the form of inorganic Hg salts and organic forms of Hg (e.g., methyl-Hg) (Salihoğlu and Yemenicioğlu, 1986, Fitzgerald, 1979). The inorganic form of Hg, when either bounded to airborne particles or in a gaseous form, is readily removable from the atmosphere both by precipitation and dry deposition. Wet deposition is the primary mechanism for transporting Hg from the atmosphere to surface waters and land. As it cycles between the atmosphere-land-water, Hg undergoes a series of chemical and physical transformations, many of which are not completely understood. Hg itself and its compounds are very toxic to the living organisms. It is biomagnified through the food chain and it can be transformed into the more toxic methylmercury by biotic and abiotic pathways, thus it is one of the metals which receive great concern. Predatory organisms at the top of the food web generally have higher Hg concentrations. Nearly all of the Hg that accumulates in fish tissue is methyl mercury (Salihoğlu and Yemenicioğlu, 1986; Salihoğlu et al, 1987).

Inorganic Hg, which is less efficiently absorbed and more readily eliminated from the body than methyl mercury, does not tend to bioaccumulate. Effects of Hg on fish, birds and mammals include death, reduced reproductive success, impaired growth and development and behavioural abnormalities. Sublethal effects of Hg on birds and mammals include liver damage, kidney damage, and neurobehavioral effects. Effects of Hg on plants include death and sublethal effects. Sublethal effects on aquatic plants can include plant senescence, growth inhibition and decreased chlorophyll content. Sublethal effects on terrestrial plants can include decreased growth, leaf injury, root damage, and inhibited root growth and function.

Description of the region

The Black Sea is a land-lock basin having limited interaction with the Mediterranean Sea through the Turkish Strait System. Its strong density stratification inhibits vertical mixing. The supply of oxygen to the deep waters by lateral influxes is very poor. As a result, permanent anoxia exists and make Black Sea worlds largest anoxic basin. One of the most important futures of the basin that make it different from the other basins is the existence of a transitional layer so called sub-oxic layer at the oxic-anoxic interface. The redox potential in this layer changes sharply from +150 mV to –150 mV due to the lack of oxygen and presence of H_2S. The environmental crisis and subsequent dramatic changes in the Black Sea's ecosystem and resources were a direct consequence of anthropogenic pollution due to enormous increase in the nutrient and pollutant load from rivers discharging into the north-western region of the sea; industrial and municipal wastewater pollution along the coast; and dumping on the open sea. As a result, the major part of the Black Sea, particularly its northwestern region, has become critically eutrophic, and hypoxic (Zaitsev and Mamaev, 1997). A more detailed description of the mass budget, current systems and circulations can be found in Oğuz et al., (1993); Oğuz and Beşiktepe, (1999), Özsoy and Ünlüata, (1997).

The Marmara Sea is a small inter-continental basin. It is a passage between Black Sea and Mediterranean Sea. It is connected to the Aegean Sea via Dardanelles Strait and to the Black Sea via Bosphorus Strait. The hydrography of the Marmara Sea is dominated by the Mediterranean Sea 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. 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 (Beşiktepe et al., 1994). The strong stratification of the water masses coupled with the topographic restrictions inhibits the efficient ventilation of deep waters. This cause the sub halocline waters to have DO concentrations as little as 1-2 ppm throughout the year. The algal production is always limited to the upper 20 m.

Northeastern Mediterranean is bordered to the north by Turkey, to the east by Syria and Lebanon and to the west by the strait of Crete. The southern border extent up to 34° N. The general water circulation in the region is from south to north along Syria and Lebanon coasts and from east to west along Turkish coast. Two main water masses are dominating the hydrographic characteristics of the region. The Levantine Intermediate Water which is formed in the region of Rhodes gyre and sinks down to about 300 m depth (Özsoy *et al.*, 1989) and the Atlantic water coming in through the Gibraltar Strait, follows the path to the east along the African coast and on reaching Northeastern Mediterranean it split into two branches. One of them turns to the north by following an anticlockwise path and the other continues to the eastward direction and on reaching Lebanon coast turns to the north. On reaching to the Turkish coast it changes its direction once again and flows to the west following the southern coast of Turkey. The continental shelf between Marmaris and Mersin is relatively narrow (average width 4.5 km) and deep. In the area between Mersin and Iskenderun a 70 km wide continental shelf has been built by the action of several rivers draining to this region.

Material and Methods

The sea water samples were collected during the cruises of R/V Bilim in the Marmara Sea, Black Sea Mediterranean Sea and Aegean Sea between 1985 - 1990. Sampling locations are shown in Fig. 1.

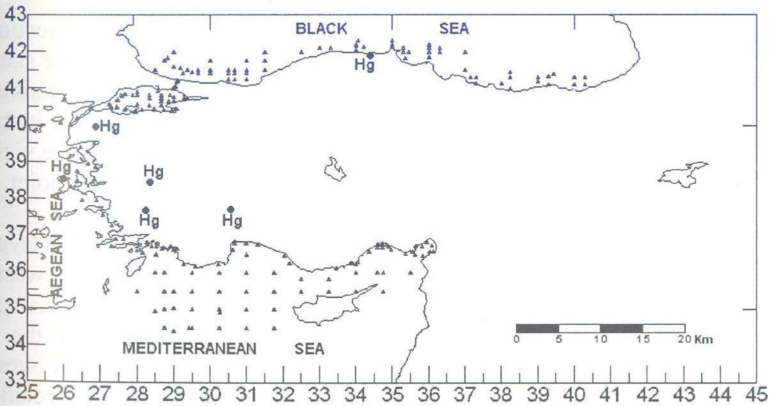

Fig. 1. Sampling positions and natural mercury ore deposits of Turkey

The samples were collected either with a plastic centrifugal pump 1.5 meter below the surface or from a rubber boat just below the surface directly in to the storage bottle as described by Yemenicioğlu and Salihoğlu 1994. In this study Hg concentration were measured in unfiltered samples by employing cold vapor AAS technique, first developed by Hatch and Ott, (1968). The Hg was reduced by

$NaBH_4$ and concentrated by amalgamation on silver packed micro column. Hg free nitrogen gas was used to sweep reduced Hg from the reaction bottle. Desorption of amalgamated Hg was achieved by heating the micro column at about 500 ^oC. The desorpted Hg was carried to the quartz-window absorption cell by nitrogen gas at which the absorbance was measured (Yemenicioğlu and Salihoğlu 1994).

Results and Discussion

The concentrations of total mercury (Hg_T) in seawater were measured along the coasts of Turkey. The maximum, minimum and average (Hg_T) concentrations measured in different seas around Turkey are given in Table 1. The findings indicate that the highest (Hg_T) concentration was measured in the Aegean Sea. Excluding the hot point stations, the highest (Hg_T) measured in the Aegean Sea was 16.0 ng/L (Fig. 2). This amount is comparable with the one measured in the Black Sea (11.0 ng/L), but it is almost twice the amount measured in the Mediterranean Sea and three fold of the Marmara Sea concentrations. The somewhat high concentration of mercury in the Aegean Sea is thought to have resulted from the natural Hg deposits on the hinterland (Fig. 1). Comparison of the (Hg_T) concentrations measured in all seas showed that Black Sea rank in the second order with a concentration of 11.0 ng/L. This relatively high amount of (Hg_T) was measured at stations 43-48 (Fig. 3). These stations are taking place just in the vicinity of the Hg ore deposit. Thus the source of high mercury concentrations measured at these stations is the mercury deposit at inland area.

Fig. 3 summarises the trend of (Hg_T) concentration in west to east direction in the Black Sea. It is possible to see the effects of the Danube River at the stations located in the western site of the Black Sea (stations 11, 9). The Hg_T concentration at these stations is relatively high and in going towards eastern Black Sea it shows an decreasing trend, but upon reaching to the stations that are located in the vicinity of Hg ore deposit (stations 43 and 48) it increase again. After this point Hg_T concentrations continue to decrease towards eastern Black Sea.

Trend of Hg_T distribution in seawater in the Mediterranean Sea is displayed in Fig. 4. The stations shown on the graph are arranged from east towards west i.e. station 20 is at eastern part in the Golf of Iskenderun and station 55 is at the western part off the Marmaris peninsula. It is easily concluded that the Hg_T concentration shows a decreasing trend in going from east towards western Levantine, an opposite trend of the one met in the Black Sea (Fig. 3). The relatively high Hg_T concentration in the eastern part of the Mediterranean Sea is thought to have resulted from intensive agricultural activities in the Çukurova region. In the Çukurova region which is the catchment area of the rivers (Seyhan, Ceyhan and Berdan rivers) draining into the eastern part of the studied area, cotton is cultivated and mercury based fungicides are used extensively. The rivers draining in this region contains more mercury than the worlds average (Yemenicioğlu et al., 1996).

Table 1. Total mercury concentrations measured in this study.

Hg-W ng/L	BLACK SEA	MARMARA SEA	AEGEAN SEA	MEDITERRANEAN SEA
MIN	<0.15	2.7	4.0	2.5
MAX	11.0	5.3	16.0	7.5
AVERAGE	5.66	3.8	6.9	5.94

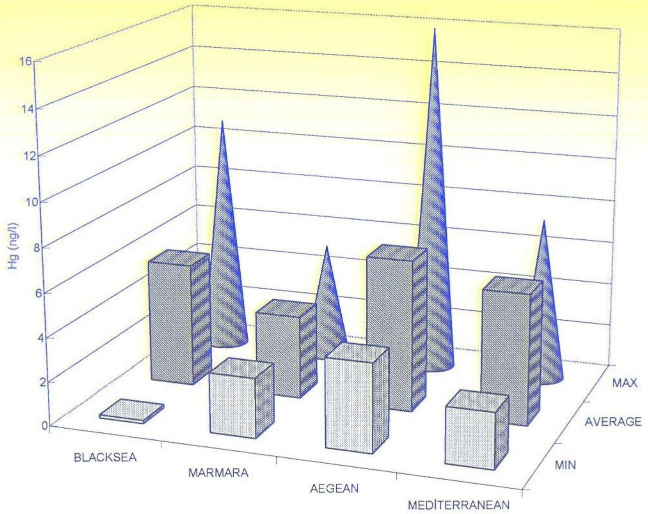

Fig. 2. Concentrations of mercury in seawater samples taken from the seas around Turkey.

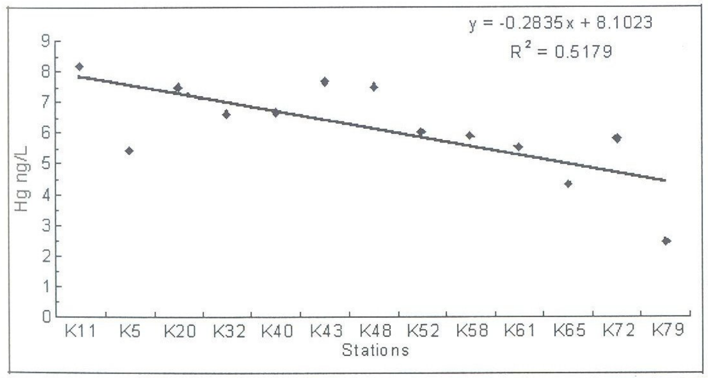

Fig. 3. Mercury trend in the Black Sea from west to east direction.

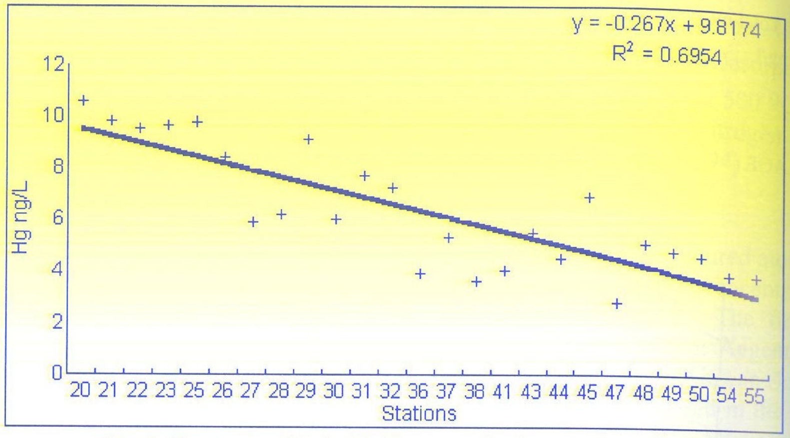

Fig. 4. Mercury trend in the Mediterranean Sea in east to west direction.

Furthermore this region is intensively industrialized and hence population intensity is high. The sewage and most of the industries discard their effluents directly into the region. The Hg_T concentrations measured along Mediterranean coasts surface and subsurface water ranges between 2.5 to 7.5 ng/L with an average of 5.94 ng/L.. More then half of the Hg introduced in to the region by rivers is in the particulate form (about 64%) (Yemenicioğlu et al., 1996). Thus, at the estuaries or coastal zone great portion of the introduced Hg is expected to settle down by precipitation of the particulate materials and incorporated in to the sediment. Contribution of these to the open sea is expected to be very small. Thus those high Hg_T concentrations that are measured at the coastel stations situated at the eastern part of the studied area where intense industrial activities and farming taking place (the stations in the vicinity of hot spots) are not included in this study.

The Hg_T concentration measured in the Marmara Sea was almost uniform within the basin. Since there is no main rivers draining in to the region the source of Hg introduced in the Marmara Sea is the Black Sea. The renewal time of the surface water which originate from the Black Sea is very short. Thus Hg carried from Black Sea are either transported to the Aegean Sea by currents or removed from solution by primary producers (Yemenicioğlu and Salihoğlu, 1995).

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