



QUANTITATIVE COMPARISON OF THE INFLUXES OF NUTRIENTS AND ORGANIC CARBON INTO THE SEA OF MARMARA BOTH FROM ANTHROPOGENIC SOURCES AND FROM THE BLACK SEA

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ABSTRACT

The Sea of Marmara, an intercontinental basin with two narrow and shallow straits permitting the exchange of the Mediterranean and Black Sea waters, receives 2.8×10^4 tons TP (total phosphorus), 2.7×10^5 tons TN (total nitrogen) and 1.9×10^6 tons TOC (total organic carbon) per year from the Black Sea inflow, from the lower layer by vertical mixing and from anthropogenic inputs of various origins including riverine discharges. The Black Sea input through the Bosphorus constitutes about 35, 64 and 77 %, respectively, of the total annual loads of TP, TN and TOC entering the Marmara surface waters. Pollution loadings from Istanbul make up a major fraction (40–65%) of the total anthropogenic discharges. The biochemical properties of the productive Marmara upper layer appear to be dominated by the inputs both from its lower layer by vertical mixing and from the Black Sea throughout the year. Pollution discharges from Istanbul have secondary importance for the nutrient and organic carbon pools of the Marmara Sea; however, the land-based chemical pollution has drastically modified the ecosystem of coastal margins and semi-enclosed bays (e.g. Golden Horn, Izmit and Gemlik) where water exchanges with the open sea are limited. Biologically labile nutrients increasingly exported from the Black Sea in the spring–early summer, are compensated by importation from the Marmara Sea through the Bosphorus underflow. The less labile dissolved organic nitrogen and carbon input from the Black Sea appears to reach as far as the Aegean basin of the Northeastern Mediterranean in 4–5 months without contributing to the net production in the Marmara Sea.

KEYWORDS

Marmara Sea; Black Sea; Bosphorus; pollution; nutrients; organic carbon; anthropogenic inputs; exchange fluxes.

INTRODUCTION

The Sea of Marmara, a semi-enclosed basin which has been subject to considerable human use and influence, connects the Black Sea to the Aegean Sea through narrow and shallow straits (Fig.1). Therefore, the basin is occupied by two distinctly different water masses throughout the year; brackish waters (22–26 ppt salinity) of Black Sea origin forming a relatively thin surface layer (10–15 m thick) with a mean

residence time of about 4–5 months, separated from the subhalocline waters of Mediterranean origin (38.5–38.6 ppt salinity) by a sharp interface (pycnocline) about 10–20 m thick (Ünlüata *et al.*, 1990; Besiktepe, 1991). Because of the large volume of water inflow from the adjacent sea (about 600 km³, see Fig. 1) into the relatively small upper layer volume (≈225 km³) of the Marmara Sea, its upper layer ecosystem has been influenced to a large extent by the Black Sea inflow. The biochemically modified surface water of the southwestern Black Sea in the Bosphorus region evolves from alongshore currents from the northwestern coastal margin (Sur *et al.*, 1994; Polat and Tugrul, 1995) which, in recent decades, have become polluted by river (mainly the Danube) and wastewater discharges (Bologa *et al.*, 1981; Mee, 1992). Unlike the inflow from the Black Sea, the Aegean salty waters entering the Marmara basin are relatively poor in both nutrients and organic carbon. However, during their stay of about 6–7 years in the basin, the inflowing, saline waters become enriched 10-fold with inorganic nutrients whilst their dissolved oxygen content drops from saturated to suboxic levels, 30–50 μM (Bastürk *et al.*, 1990) and consequently they leave the Marmara basin with markedly modified chemical properties (Polat and Tugrul, 1995).

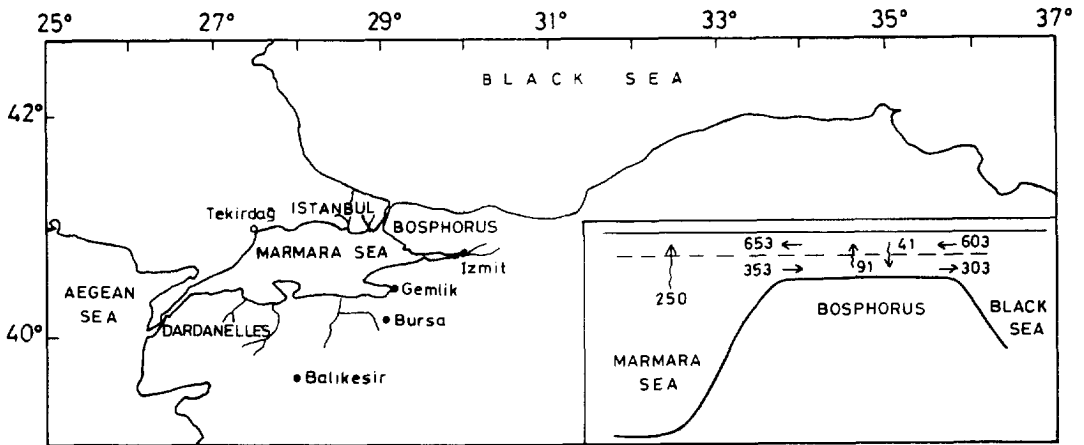


Figure 1. The study area (as a catchment basin) and the volume fluxes of water (km³·y⁻¹; after Besiktepe, 1991) in the Bosphorus region.

The Marmara basin acts as a receiving water not only for pollutants from the adjacent seas but also for land-based chemical pollutants of various origins. According to the estimates of Orhon *et al.* (1994), the Istanbul Metropolitan Area (hereafter called Istanbul) which houses about 15% of the population of Turkey and about 40% of the industrial activity, is the major pollution source for the Sea of Marmara. Comparison of natural and anthropogenic (land-based) inputs of nutrient and organic carbon into the Marmara Basin and of their export through the straits, should encourage policy makers to develop a technically and financially sound masterplan for wastewater treatment and discharge so as to restore the changed ecosystem of the Marmara Sea. However, the implementation of such a management programme necessitates a thorough understanding of the principal hydrodynamical and biochemical properties of the Marmara Sea, including the two straits.

In this context, the systematic chemical data collected by the IMS-METU (Institute of Marine Sciences, Middle East Technical University) during cruises of the R.V. BILIM in the Bosphorus region between 1986 and 1992 have been examined extensively by Polat and Tugrul (1995) so as to estimate the annual fluxes of nutrients and organic carbon exchanged between the Black and Marmara Seas through the Bosphorus. Orhon *et al.* (1994) have discussed the waste discharged from Istanbul into the Bosphorus and the Marmara coastal margin and compared these land-based loads with the estimated fluxes of inorganic nutrients exchanged between the adjacent seas through the Bosphorus, disregarding the organic components of nutrients existing in the seawater. In this paper, we first summarize the seasonal variability of the various forms of nutrients and organic carbon in the exchanging waters of the Black and Marmara Seas, based on

systematic data obtained during the 1986–1994 period and including more recent data than in Polat and Tugrul (1995). We then define the relative significance of natural and land-based inputs of nutrient and organic carbon into the upper layer of the Marmara Sea, based on comparison of the annual estimates of the chemical influxes from its lower layer by vertical mixing, from the Black Sea through the Bosphorus and from the anthropogenic sources including riverine inputs.

CHEMICAL PROPERTIES OF THE OUTFLOW FROM THE BLACK SEA

The biologically labile nutrient and organic carbon contents of the Black Sea surface waters outflowing through the Bosphorus exhibit remarkable variations with season, as recently discussed by Polat and Tugrul (1995). Specifically, the nitrate concentrations, as high as 4.5–7.5 μM in winter, diminish to trace levels (< 0.1 – $0.2 \mu\text{M}$) in the summer–autumn period. Very high winter concentrations observed in both the Bosphorus (Polat and Tugrul, 1995) and Romanian surface coastal waters (Bologa *et al.*, 1981) imply that southerly along-shore surface flow, drastically polluted with nutrients of riverine and wastewater origin, may reach as far as the Bosphorus region without, under severe winter conditions, being consumed by photosynthesis. The reactive phosphate concentration of the outflow exhibited a similar variation with season, ranging from $< 0.05 \mu\text{M}$ in the July–October period to values of 0.3–0.6 μM in winter. The estimated annual averages of nitrate and phosphate concentrations are 1.5 and 0.16 μM , respectively, in good agreement with the means given by Orhon *et al.* (1994) for 1987–1989 and by Polat and Tugrul (1995) for the period of 1987–1992. The annual average of ammonia concentration, estimated as 0.5 μM for the outflow by Polat and Tugrul (1995), is about one-third the annual mean nitrate concentration, 1.3 μM .

Between 1991 and 1994 particulate organic nitrogen concentrations of the outflowing waters varied from 0.5 μM in summer to 5.5 μM during late winter–early spring, yielding an annual mean of nearly 2.0 μM . The particulate phosphorus data displayed a similar seasonality, remaining in the range 0.07–0.23 μM with an annual average of 0.15 μM . The average concentrations of dissolved organic nitrogen (DON which is primarily of terrestrial origin and resistant to bacterial decay) and dissolved organic phosphorus (DOP) have been estimated as 0.20 μM and 18 μM , respectively. The dissolved organic carbon (DOC) in the outflow, primarily composed of less labile compounds, varied seasonally from 158 μM to 250 μM , yielding an annual average of 195 μM for the 1987–1994 period. More labile particulate organic carbon, ranging from 7 μM to 40 μM with an annual mean of 17 μM , constitutes nearly 10% of the mean TOC concentration, 212 μM in the outflow. The estimated ratios of particulate forms of organic carbon and organic nutrient concentrations (POC:PON:PP) are nearly 112:13:1, consistent with the classical Redfield ratio of phytoplankton for the oceans (106:16:1; Redfield *et al.*, 1963).

The concentrations of total phosphorus (TP), estimated from the sum of the reactive phosphate, dissolved organic phosphorus plus particulate phosphorus (DIP+PP+DOP) concentrations, have ranged seasonally between 0.30 and 0.80 μM in the Black Sea outflow (Fig. 2a), with an annual mean of nearly 0.50 μM for 1991–1994. Even though the TP in the outflow is composed primarily of DIP in winter and PP during the bloom, the annual mean of TP comprises comparable levels of DIP, PP and DOP. Biologically labile nitrogen, mainly composed of dissolved inorganic and particulate organic nitrogen (DIN+PON), makes up merely 20% of the annual average of total nitrogen estimated for the outflow (see Table 1). However, about 10% of DON in the outflow may be assumed to be degradable on a monthly time scale since large quantities of inorganic and organic nutrients are introduced by the riverine and waste discharges into the northwestern Black Sea shelf waters. Such waters thus contribute to the labile DON pool of the coastal surface waters flowing toward the southwestern Black Sea by the alongshore currents. The concentrations of dissolved inorganic nitrogen + particulate organic nitrogen (DIN+PON) in the outflow increased to 8.8–10.3 μM (mean: 6.7 μM) in the winter–early spring months of December–March (the low data from March 1993 were excluded) but then decreased steadily to 1.2–3.0 μM (mean: 2.0 μM) during the late spring–late autumn period. Thus, it appears that the outflux of biologically labile nitrogen (DIN+PON) and TP from the Black Sea may increase during the winter–spring period if variation in the water outflow is assumed insignificant throughout the year. In fact, the water outflow decreases from summer to early spring during which the labile nutrient concentrations of the outflow generally increase; the water outflow then rises markedly in the late spring–early summer months when the labile nutrients in the outflow decrease due to the

consumption and sedimentation of the particulate fraction in the Black Sea. Similarly, the seasonal means of particulate organic carbon concentrations were 22.7 μM for the winter–spring period and 13.0 μM for the summer–autumn period, with an annual mean of 17 μM . On a total concentration basis, the annual variation of the total organic carbon (TOC=POC+DOC) and probably the total nitrogen (TN) concentrations in the outflow, is, however, of the order of 10% of their seasonal values because the TOC and TN in the Black Sea outflow are primarily dominated by bacterially resistant dissolved organic compounds of terrestrial origin.

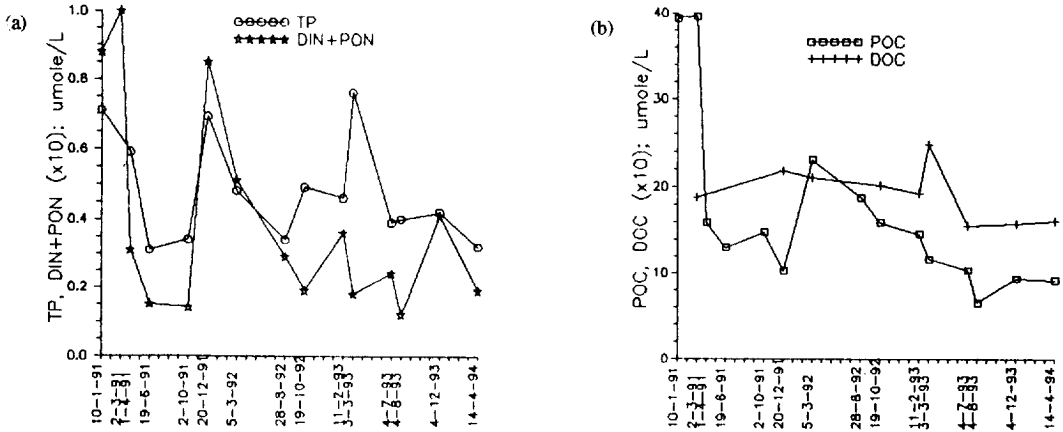


Figure 2. The seasonal variations of the depth-averaged concentrations (μM) of nutrients and organic carbon in the Black Sea outflow. (a) Total phosphorus (TP) and dissolved inorganic nitrogen + particulate organic nitrogen (DIN+PON); (b) dissolved and particulate organic carbon (DOC, POC) versus time.

Table 1. The annual average concentrations (μM) of nutrients and organic carbon in the exchanging waters of the Black and Marmara Seas for the 1986–1994 period

Parameter	Brackish Outflow from the Black Sea	Saline Outflow from the Marmara Sea
Total Phosphorus (TP=IP+PP+DOP) *	0.56 (0.11+0.15+0.30) *	1.09 (0.99+0.05+ 0.05) *
Total Nitrogen (TN=DIN+PON+DON) (DIN=NH ₄ +NO ₃) *	21.8 (1.8+2.0+18.0) * (0.5+1.3) *	13.2 (9.8+0.4+3.0) * (9.6+0.2) *
Total Org-Carbon (TOC=DOC+POC) *	212.0 (195.0+17.0) *	77.3 (72.6+4.7) *

(*) The numbers in parenthesis represent the annual average values of dissolved inorganic, particulate and dissolved organic nutrients or dissolved and particulate organic carbon concentrations (μM) of the outflow.

NUTRIENT AND ORGANIC CARBON IN THE OUTFLOW FROM THE MARMARA SEA

In the Sea of Marmara where photosynthesis is limited to the upper layer, including the interface between 15 and 30 m, nutrient and organic carbon concentrations of the subhalocline waters show much less seasonal variation than in the outflow from the Black Sea (Basturk *et al.*, 1990). Between 1986 and 1994, nitrate and reactive phosphate concentrations monthly ranged from 9 to 11 μM (annual mean: 9.6 \pm 0.5 μM) and from 0.9 to 1.2 μM (annual mean: 0.99 \pm 0.07 μM). The molar ratio of nitrate to phosphate is about 10 for the outflow. The ammonia content of the outflow, as low as 0.2 μM , is certainly much less than the mean nitrate value (9.8 μM) as clearly seen from Table 1. The outflow is also poor in particulate nutrients, varying between 0.17 and 0.60 μM for PON and between 0.04 and 0.07 μM for PP, with respective annual averages of 0.38 and 0.05 μM . The mean DOP, nearly 0.05 μM (Polat and Tugrul, 1995), is much less than the reactive phosphate content of the outflow whilst the estimated DON value (3.0 μM ; Polat and Tugrul, 1995) constitutes about 23% of TN (13.2 μM). The DOC data from the salty water outflowing from the Marmara lower layer exhibited small seasonal variations (Tugrul, 1993; Polat and Tugrul, 1995); the concentrations ranged between 58 and 83 μM with an annual average of 73 μM , whilst the annual mean of POC, derived from the seasonal data varying between 2.1 and 9.3 μM , was 4.7 μM , which is only 6% of TOC in the outflow (Table 1).

COMPARISON OF THE CHEMICAL INPUTS INTO THE MARMARA SURFACE LAYER FROM THE BLACK SEA, LAND-BASED SOURCES AND SUBHALOCLINE WATERS

The total nutrients and the organic carbon exchanged annually between the Black and Marmara Seas through the Bosphorus two-layer flows have been calculated from the average chemical concentrations and the recent volume fluxes given in Table 1 and Fig. 1 respectively, assuming these values to be constant on a yearly time scale. The chemical inputs from the subhalocline waters of the Marmara Sea mixed vertically into the surface layer, especially in the Bosphorus region and in winter throughout the basin, have been estimated from the vertical volume fluxes displayed in Fig. 1 together with the average chemical concentrations of the upper subhalocline as 69 μM for TOC, 11.5 μM for TN and 0.92 μM for TP (Polat, 1995). The pollution loadings from Istanbul, 8.0×10^4 tons of TOC (estimated from the $\text{BOD}_5/\text{TOC}=1.5$ relationship given for municipal wastes by Benefield and Randall, 1980), 2.0×10^4 tons of TN and 3.3×10^3 tons of TP per year, are based on the data given in Orhon *et al.* (1994). The total waste inputs from the other sites of the Marmara region, derived from a project report prepared for ISKI by DHI (1994), are 5×10^4 tons of TOC, 2.0×10^4 tons of TN and 4.4×10^3 tons of TP per year, which include the riverine inputs especially those from the Susurluk drainage area. The estimated annual loads of chemicals entering the Marmara surface layer from the Black Sea, from land-based sources and from the subhalocline waters of the sea by vertical mixing are compiled in Table 2.

The surface layer of the Marmara Sea receives a total of about 2.8×10^4 tons of TP annually, with comparable contributions from the three major sources as clearly appearing from Table 2. Nevertheless, the input from the basin lower layer, estimated as 1.02×10^4 tons y^{-1} (37% of the total input), is larger than the annual loads of the other two sources. The TP input from the Black Sea (0.98×10^4 tons y^{-1}), comparable with the total input of anthropogenic origin (0.77×10^4 tons y^{-1}), is about 3 times the loading from Istanbul region but 4.5 times that discharged only into the Bosphorus region when the pollution data given in Orhon *et al.* (1994) is considered. However, the TN input from the Black Sea (1.72×10^5 tons y^{-1}) is the major source for the Marmara surface layer because it is at least 3 and 4 times the influx, respectively, from the lower layer and from the land-based sources including riverine discharges (Table 2). It should be noted that these comparisons have been made disregarding the biodegradability of the DON which makes up a major fraction of the TN imported from the Black Sea. The Black Sea input is at least 9 times the total loading from Istanbul. If only 10% of the DON in the Black Sea inflow is assumed to be utilized by biological processes in the Marmara Sea, the TN inputs from different sources become consistent with the relative importance of the TP inputs from the major sources; the Black Sea input is at least 2.5 times the total discharge from Istanbul and 4.5 times the pollution load given only to the Bosphorus region. Similar ratios can be obtained

when TOC influxes into the Marmara surface waters are compared (Table 2). The input from the Black Sea (about 1.4×10^6 ton y^{-1}) is nearly 5 times the inputs mixed from the lower layer (0.3×10^6 ton y^{-1}) and 10 times the total anthropogenic inputs (0.13×10^6 ton y^{-1}). Briefly, the majority of the total TOC input ($\approx 1.9 \times 10^6$ ton y^{-1}) into the Marmara Sea is provided by the Black Sea inflow which generally consists of less labile organic compounds. If only about 10% of the DOC in the Black Sea inflow is assumed to be degraded in the Marmara basin, then the labile TOC input from the Black Sea (0.24×10^6 ton y^{-1}) becomes 3 times the total TOC loading from Istanbul, but 1.2 times the total anthropogenic input.

In this context, the chemicals exported from the Marmara lower layer by the Bosphorus underflow can be compared with the land-based pollution loads, using the annual estimates of chemical fluxes given in Table 2 for the Marmara basin and for Bosphorus exchanges. The TP export from the Marmara Sea (0.9×10^4 ton y^{-1}) is nearly three times the total input from Istanbul. A similar conclusion can be drawn for the TN which, in the Marmara outflow, is mainly composed of nitrate. The annual loads of TP and labile nitrogen compounds (DIN+PON+10% of DON) exported from the from the Black Sea through the Bosphorus are comparable with the loads carried from the lower layer of the Marmara Sea in the form of ortho-phosphate and nitrate. However, one should note again that the DOC exported from the lower layer of the Marmara Sea to its surface layer and to the Black Sea through the Bosphorus underflow is principally in a refractory form and only a minor fraction (of the order of 10%) is in labile form on a monthly time-scale. Thus, one can derive a ratio of about 0.5 from the annual loads of the natural TOC exported from the Marmara Sea to the Black Sea and the TOC loading from Istanbul to the Marmara Sea. Therefore, the deep outfalls of wastewaters from Istanbul, with their present TOC loads, are expected to cause critical oxygen depletions in the Marmara lower layer waters (which are, indeed, currently poor in dissolved oxygen), especially in the regions of the discharges where the general circulation is relatively weak during the stratified seasons.

Table 2. Annual rates (in tonnes per year) of total nutrient and organic carbon inputs to the Marmara upper layer and the export form the Marmara to the Black Sea

Parameter	Chemical inputs from					Total Input to Marm.	Export from Marmara to B.S.
	<u>Black Sea</u>	<u>Lower Layer</u>	<u>Anthrop. Sources</u>	<u>Istan. Disc.</u>	<u>Other land-based sourc.</u>		
TP ($\times 10^4$)	0.98 (35%)	1.02 (37%)	0.77 (28)	0.33 (12%)	0.44 (16%)#	2.77	0.89 (32%)
TN ($\times 10^5$)	1.72 (64%)	0.57 (21%)	0.40 (15)	0.20 (7.5%)	0.20 (7.5%)	2.69	0.48 (18%)
TOC ($\times 10^6$)	1.43 (77%)	0.29 (16%)	0.13 (7%)	0.08 (4%)	0.05 (3%)	1.85	0.24 (13%)

(#) The percentages in paranthesis represent the relative importance of the influx to the total.

CONCLUDING REMARKS

The total chemical loads from anthropogenic sources are comparable with the TP and labile chemical fractions of TN and TOC from the Black Sea but much less than the total natural inputs (see Table 2). On the annual basis, the labile nutrient input from the Black Sea nearly compensated by the nitrate and reactive phosphate export from the Marmara lower layer through the Bosphorus underflow. The nitrate to phosphate molar ratio (about 10) for the Marmara subhalocline waters is markedly less than the Redfield ratio; the nitrogen-rich waste discharges are, therefore, expected to facilitate primary production in the surface layer of

the Marmara Sea. However, systematic bio-assay data and specific process studies are needed to define the environmental factors controlling the algal growth in space and time. On the other hand, less labile organic matter entering the Marmara Sea from the Black Sea and other sources reaches as far as the Aegean basin of the Mediterranean Sea through the Dardanelles without contributing to the net production in the Marmara surface water.

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