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Nutrient and organic carbon exchanges between the Black and Marmara Seas through the Bosphorus Strait

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Abstract—Recent systematic chemical data, together with a new estimate of the water fluxes, permit the calculation of the total phosphorus (TP), nitrogen (TN) and organic carbon (TOC) exchanged between the Black and the Marmara Seas through the Bosphorus. Assuming the chemical concentrations of the exchanging waters to be constant on a yearly time scale, the estimated total annual fluxes are as follows.

	TP	TN	TOC
Influx into the Marmara Sea	1.2×10^4	1.9×10^5	1.52×10^6 tons
Influx into the Black Sea	1.0×10^4	0.6×10^5	0.35×10^6 tons

The mainly river-borne annual flows of TN and TOC into the Sea of Marmara from the Black Sea are about three times those from the Marmara Sea into the Black Sea whereas the TP exchanges are comparable. The large TN export by Black Sea waters relative to the TP outflux is the result of the high N:P ratio of nutrients [primarily in the forms of nitrate, less labile dissolved organic nitrogen (DON) and ortho-phosphate] introduced by the polluted rivers to the northwestern Black Sea. The DON comprises about 75% of the TN inflow into the Marmara Sea whereas nearly 50% of the TP inflow is composed of dissolved inorganic phosphorus. Biologically labile nutrients exported from the Black Sea, corresponding to a new production of (3.5–4.9) $\times 10^5$ tons C y^{-1} in the Marmara Sea, are almost compensated by the Bosphorus underflow as nitrate and phosphate primarily of biogenic origin.

INTRODUCTION

The Black Sea, an inland sea having sulphide-bearing waters below a depth of 100–200 m (Grasshoff, 1975; Sorokin, 1983; Codispoti *et al.*, 1991), is connected to the world ocean system via the Turkish Straits and the Mediterranean Sea (Fig. 1). Accordingly, its brackish waters (S = 17–18 ppt) flowing out through the narrow and shallow Bosphorus Strait first enter the Sea of Marmara remaining for several months (Ünlüata *et al.*, 1990; Beşiktepe, 1991) before eventually reaching the Dardanelles and passing through to the Mediterranean. A counterflow through the Turkish Straits permits the salty Mediterranean waters to flow into the intermediate layer of the Black Sea via the Marmara Sea bearing various chemical fluxes with them (Sorokin, 1983; Baştürk *et al.*, 1990; Latif *et al.*,

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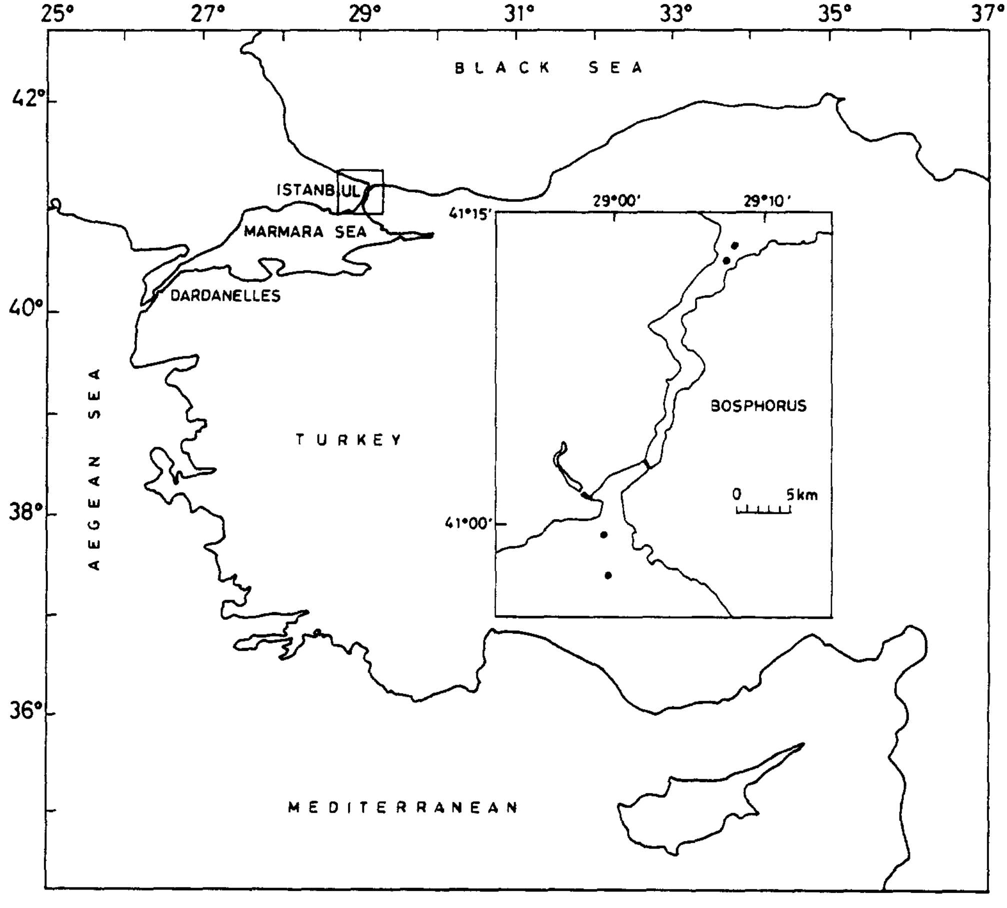

Fig. 1. Map showing the Turkish Strait System connecting the Black Sea to the Mediterranean.

1991; Oğuz *et al.*, 1992). The consequent two-layer flow regimes in the straits generate a permanent and stable pynocline and thus furnish two distinctly different ecosystems in both the Black and Marmara Seas (Gunnerson and Özturgut, 1974; Grasshoff, 1975; Sorokin, 1983; Ünlüata *et al.*, 1990; Murray *et al.*, 1991; Codispoti *et al.*, 1991; Tuğrul, 1993).

Although, in recent years, the two-layer regime of the Bosphorus has been investigated extensively, no data based on long term measurements have yet been published on the chemical exchanges. Deuser (1971) and Fonselius (1974) obtained total phosphorus and organic carbon balances for the Black Sea, basing their calculations on a very old water balance and on limited chemical analyses. However, scientific evidence clearly indicates that profound changes have occurred in the Black Sea ecosystem during the last two decades (Bologa, 1985; Murray *et al.*, 1989; Tuğrul *et al.*, 1992; Mee, 1992), the most dramatic, observed on the northwestern shelf, being primarily the result of chemical discharge by rivers (Bologa, 1985; Mee, 1992), even though fresh water inflow by the major rivers has been reduced by 25–50% during the same period (Tolmazin, 1985). Such long-term changes in both the hydrochemical and biological regimes of the Black Sea are

Table 1. Cruise dates of the R.V. Bilim *in the Bosphorus region between* 1986 *and* 1992

1986	1987	1988	1989	1990	1991	1992
8 May	1 Feb.	25 Jan.	10 Jan.	8 Mar.	10 Jan.	5 Mar.
18 Jul.	2 May	19 Mar.	13 Feb.	4 May	2 Mar.	14 May
27 Aug.	30 Jul.	27 May	24 Mar.	28 Jul.	19 Jun.	28 Aug.
24 Sep.	17 Aug.	3 Jul.	31 Aug.	25 Oct.	1 Apr.	19 Oct.
21 Nov.	2 Sep.	13 Aug.	21 Sep.		2 Oct.	
	11 Oct.	24 Sep.			20 Dec.	
		15 Dec.				

very likely to have modified the Marmara Sea ecosystem since the Black Sea outflow through the Bosphorus evolves principally from alongshore currents from the north-western shelf (Grasshoff, 1975; Sorokin, 1983; Oğuz and Rozman, 1991) whose waters, being seriously polluted with man-made chemical discharges, possess modified biochemical properties (Bologa, 1985; Mee, 1992).

The exports of nutrients and of organic carbon by the Bosphorus surface outflow are possibly too small to influence the budgets for the whole Black Sea system (Deuser, 1971; Fonselius, 1974; Karl and Knauer, 1991). However, such exports may be critical to budget estimates for the Marmara Sea, whose upper-layer water is renewed at least twice a year by the Black Sea inflow (Ünlüata and Özsoy, 1986; Ünlüata *et al.*, 1990; Beşiktepe, 1991).

On the other hand, during their 6–7 years in the Marmara Sea (Ünlüata and Özsoy, 1986; Ünlüata *et al.*, 1990; Beşiktepe, 1991), the saline Mediterranean waters entering through the Dardanelles, initially poor in nutrients and almost saturated with oxygen, become enriched 10-fold with dissolved inorganic nutrients though also becoming impoverished in dissolved oxygen to the levels of 30–50 μM (Baştürk *et al.*, 1990; Tuğrul, 1993), thereby generating a loss of nitrate from the subhalocline waters by denitrification. The Mediterranean waters with their modified chemical properties eventually leave the Marmara basin through the Bosphorus.

The concentrations of the different forms of nutrients and of organic carbon in the exchanging waters of the Bosphorus are also likely to show temporal variations, depending on plant production and the decay of biogenic organic matter by biochemical processes in the Black and Marmara Seas. Reliable estimates of these exchanges can be made only from data collected systematically in the region itself. Such data are of great importance, not only for calculation of the nutrient and organic carbon budgets in the adjacent seas but also to ensure the success of management programmes for the recovery of the damaged marine ecosystems.

With these goals, the Institute of Marine Sciences of the Middle East Technical University (IMS-METU), Turkey, has undertaken an ongoing national monitoring and research study in the Marmara Sea including the Bosphorus and Dardanelles Straits. In the present paper we first discuss the principal hydrochemical properties of the brackish and saline waters exchanging through the Bosphorus and then discuss the annual fluxes of nutrients and organic carbon based on a new estimate of the water fluxes.

NUTRIENT AND ORGANIC CARBON DATA

During the cruises of the R.V. *Bilim* in the Marmara Sea between 1986 and 1992 (Table 1), nutrient and organic carbon samples were collected at the southern and northern entrances of the Bosphorus (see Fig. 1). Phosphate and nitrate + nitrite concentrations were determined by a Technicon model multichannel auto-analyzer, slightly modified from the operating manual, the methods being very similar to those given in Strickland and Parsons (1972). Water samples for particulate organic carbon (POC), nitrogen (PON) and phosphorus (PP) determinations were filtered through pre-ignited GF/F filters under low vacuum. The PON and POC contents of the filters pretreated with HCl fumes were determined quantitatively by a Carlo Erba Model 1108 CHN analyzer. Particulate phosphorus collected on filters was measured by the method described in the Hawaii Ocean Time-Series Programme: Field and Laboratory Protocols (September, 1990). Briefly, filters were combusted at 450–500°C for 3 h in order to oxidize organic phosphorus compounds to the inorganic form. The filters were then extracted with 0.5N HCl at 90°C for 1.5 h. After adjusting the pH to 8.0 and the final volume to 20 ml, the concentrations were determined colorimetrically by the ortho-phosphate method. Dissolved organic carbon (DOC) concentrations in the water samples were determined either by the persulphate–UV oxidation (WET) method using a Technicon model colorimeter or by the high-temperature catalytic oxidation (HTCO) technique using a Shimadzu model TOC-500 (or TOC-5000) instrument. Details of the methods have been described by Polat (1989) and Tuğrul (1993). The instrument blank (IBLANK), of crucial importance in obtaining reliable DOC data from various WET and HTCO methods as strongly emphasized during the Seattle DOC Workshop (see special issue of *Marine Chemistry*, Vol. 41, 1–3, 1993) as well as by other recent papers (Sharp, 1993; Sharp *et al.*, 1993), was low for the Shimadzu HTCO system. The linear regression of the data obtained when various volumes (50–400 μl) of synthetic seawater (SSW) or distilled-deionized water (DDW) were injected indicated that the IBLANK is negligible (about 1.0–2.0 μM) for the Shimadzu instrument in the absence of the injection of water but is most probably dependent upon the injection volume. Participation in a world-wide interlaboratory exercise (Broad Community DOC Methods Comparison) initiated by J. H. Sharp (from the University of Delaware, U.S.A.) in 1993 to address the reliability of DOC data, has permitted us to determine the IBLANK using a very low-carbon deionized water (LCW) which contained about 1–4 μM DOC (J. H. Sharp, unpublished data). The total (instrumental + water) blank values from replicate injections of 200 μL LCW on different days varied between less than 10 and 24 μM, the average being about 16.5 μM. Thus, the Shimadzu HTCO technique yields an instrument blank of the order of 15 μM for an injection of 200 μl of water, which is not far from the precision of the method (2–10 μM). In the Technicon WET method, sample values were calculated from peak heights measured relative to wash-water (SSW). This procedure would underestimate the apparent carbon content of samples if, due to difficulties in obtaining carbon-free DDW, the SSW contained some DOC. Analysis of DDW and SSW by the Shimadzu instrument suggested that the SSW appeared to have an apparent DOC content of 8–30 μM after the appropriate instrument blank (10 μM) was subtracted. The Technicon data have therefore been corrected by adding a value of 20 μM throughout this paper.

The outflowing water from the Black Sea

The depth of the brackish waters flowing from the Black Sea through the Bosphorus can be deduced from typical salinity profiles and velocity vectors (Fig. 2). At the northern entrance of the Bosphorus Strait, the outflow has almost uniform salinity (isohaline

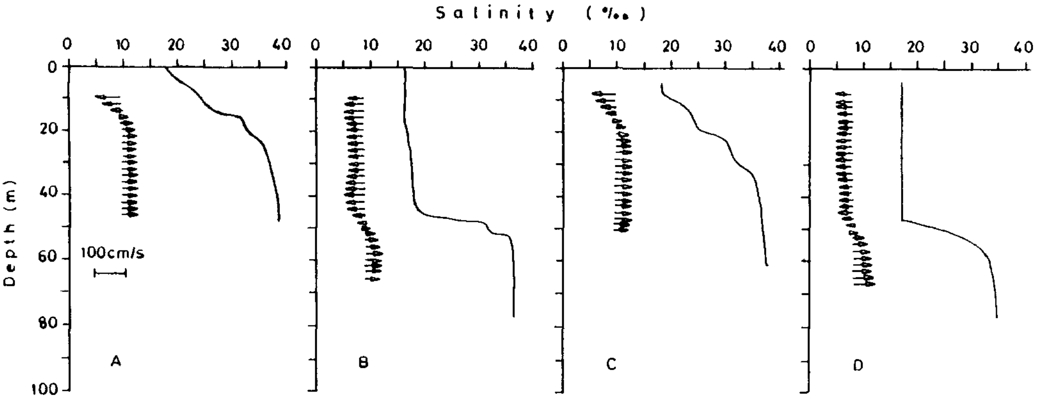

Fig. 2. Salinity profiles and velocity vectors (adapted from the recent acoustic doppler current profiler data, after Latif *et al.*, 1992) at the northern and southern entrances of the Bosphorus. (A) South and (B) North, August 1991; (C) South and (D) North, December 1991.

waters) with depth down to 45–50 m, below which a thin layer of diluted Mediterranean water flows toward the Black Sea. The thickness of the upper flow decreases to 10–15 m at the southern exit of the Bosphorus where the saline Marmara Sea waters ($S > 30$ ppt) of Mediterranean origin flow toward the Black Sea through the Strait. Water flow in the relatively narrow interface between the isohaline surfaces of 25 and 30 ppt at the southern entrance to the Strait is small. Because of the vertical mixing of the counterflows through the halocline in the strait, the Black Sea water has a higher salinity when it reaches the Marmara Sea compared to its value at the northern entrance (Ünlüata *et al.*, 1990; Oğuz and Rozman, 1991; Latif *et al.*, 1991). Similarly, the salinity of the Marmara Sea water decreases as it flows toward the northern exit of the Strait.

Systematic measurements made at the northern entrance of the Bosphorus between 1986 and 1992 indicate that nutrient concentrations of the Black Sea outflow vary significantly with season but little with depth (Fig. 3). The concentrations increase sharply in the halocline (salinity gradient layer that flows in the opposite direction) due to the dilution of the nutrient-rich, saline Mediterranean waters by the brackish Black Sea waters which have low inorganic nutrient concentrations, especially during biologically productive seasons. As the depth-averaged chemical data (Fig. 4) show, the inorganic nutrient content of the outflowing waters increases at least 10-fold from autumn to winter and then decreases again to trace levels in summer. The nitrate (actually nitrate + nitrite) concentration, for example, reached peak values of 4.5 μM in February 1987 and 7.6 μM in December 1991 and diminished to less than 0.1–0.2 μM in the August–October periods between 1986 and 1992 [Fig. 4(a)]. The high concentration in December 1991 implies that a significant fraction of the nutrients (primarily of anthropogenic origin) introduced both by the major rivers and by the wastewater outfalls to the northwestern coastal margin of the Black Sea may have reached as far as the Bosphorus without, because of the severe winter conditions, being consumed by photosynthesis. The data of Bologa *et al.* (1981) indicate that the nitrate content of Romanian surface coastal waters, which have salinities greater than 15 ppt, exhibit a similar seasonality, increasing to concentrations of 4.5–5.5 μM during the December–February period. In the Bosphorus upperflow similar seasonal changes are displayed by reactive phosphate (termed here dissolved inorganic phos-

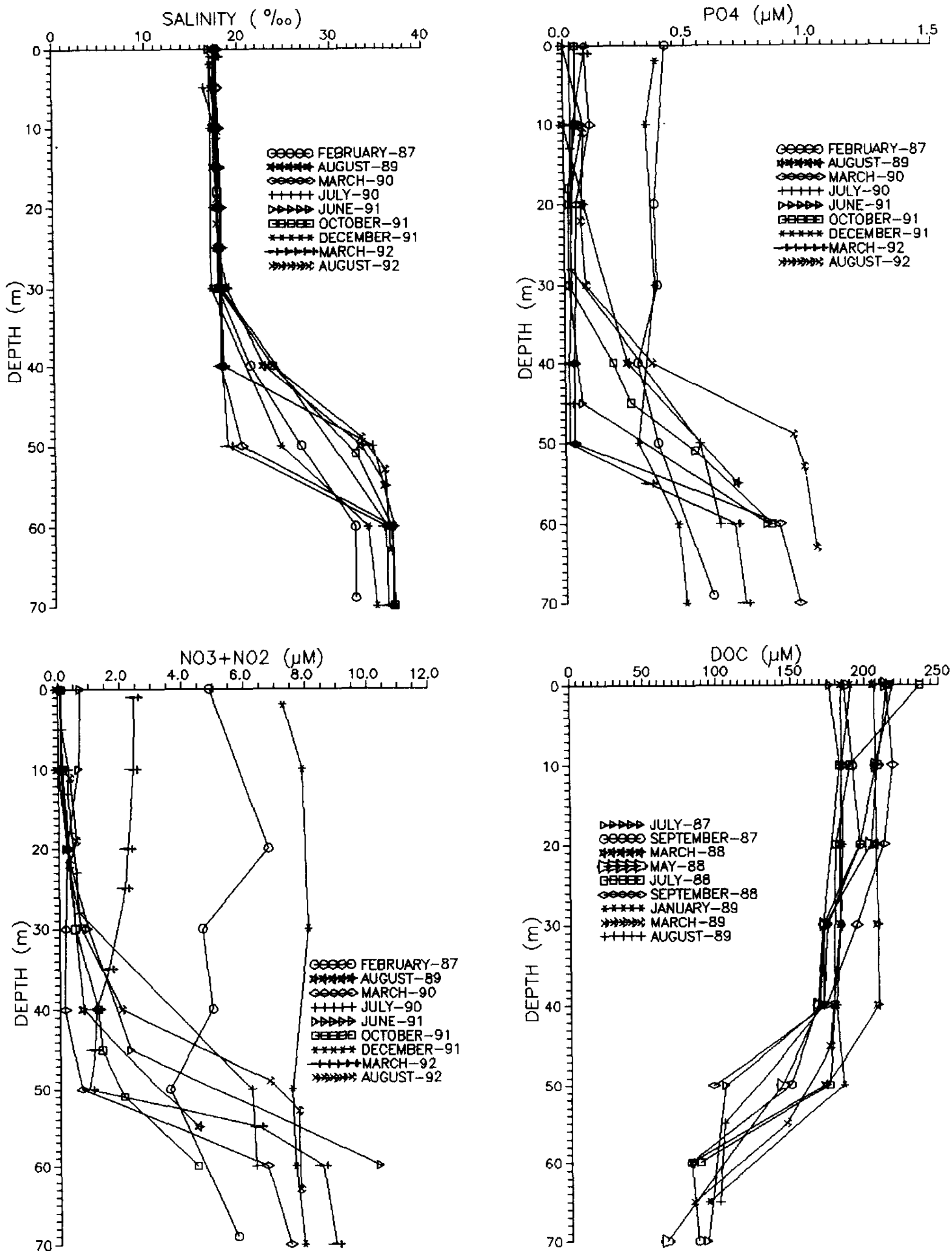

Fig. 3. Typical seasonal profiles of salinity, nutrients and dissolved organic carbon at the northern entrance of the Bosphorus.

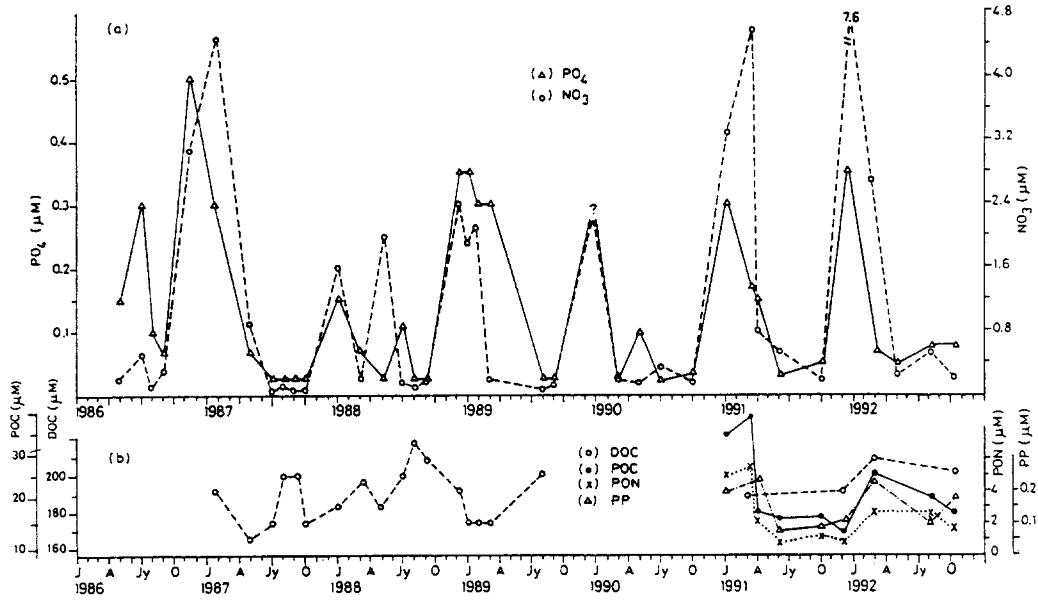

Fig. 4. Seasonal variations of the depth-averaged concentrations of inorganic nutrients (a), and particulate nutrients, dissolved and particulate organic carbon (b) in the mixed layer of the Black Sea at the northern entrance of the Bosphorus.

phorus, DIP). Concentrations of DIP, as low as 0.05 μM in the July–October period, have been observed to reach 0.3–0.6 μM during the winter [Fig. 4(a)]. Because of the difficulty in assessing the annual averages of concentrations from seasonally fluctuating data, we first determined the averages for each month of the year by taking the arithmetic means of the data obtained between 1986 and 1992. The annual means estimated from the monthly averages are 1.6 ± 1.6 μM for nitrate and 0.18 ± 0.18 μM for DIP.

Although ammonia has yet to be measured systematically in the region, the limited data reported by Sen Gupta (1971), Kirikova (1986), Sapozhnikov (1990) and Codispoti *et al.* (1991) and collected during the R.V. *D. Mendelyev* cruise 44 in July–September 1989 (unpublished data) indicate that, in the surface waters of the southwestern Black Sea, concentrations vary seasonally between 0.1–0.3 μM in summer to about 0.7 μM in March. No new data are available for the late autumn–early winter period when uptake of nitrate and subsequent regeneration of ammonium by biological processes was limited in the surface water. Nevertheless, one expects the winter concentrations of ammonium always to be less than the nitrate content of the outflowing water because the nitrogen input to the surface waters of the western Black Sea by the rivers and from the oxic aphotic layer of the sea occurred mainly as nitrate and possessed large nitrate to ammonia ratios (Chirea and Gomoiu, 1986; Codispoti *et al.*, 1991; Tuğrul *et al.*, 1992). These findings suggest an average annual ammonia concentration of 0.5 μM in the Bosphorus upperflow.

The concentrations of particulate organic nitrogen, PON, in the Bosphorus outflow were observed to be as low as 1.0 μM during the nutrient-poor summer period but to have reached their maximum values of 4.8–5.0 μM during the late winter–early spring [Fig. 4(b)]. The particulate phosphorus (PP) concentrations showed a similar seasonal variation, remaining always in the range of 0.1 to 0.2 μM [Fig. 4(b)]. The annual means were 2.4 μM for PON and 0.17 μM for PP, yielding a PON:PP ratio of nearly 14.

Dissolved organic phosphorus (DOP) concentrations: the difference between the total phosphorus (TP) and the (DIP + PP) concentrations, ranged seasonally from 0.10 to 0.18 μM with an annual mean of 0.15 μM for 1992. Dissolved organic nitrogen (DON) has yet to be measured in the Bosphorus outflow and only very limited data are available for the western Black Sea. Nevertheless, a close relationship between the DON and the inorganic nitrogen (IN) contents of rivers, yielding a DON:IN ratio of 0.5–1.0 for polluted rivers (Meybeck, 1982), together with the observation of significant increases in the IN input by rivers to the northwestern Black Sea in recent years (Mee, 1992), strongly suggests that large quantities of biologically less-labile DON (of both man-made and natural origins) are discharged to the northwestern shelf waters flowing toward the Bosphorus. The DON content of the Bosphorus outflow is therefore expected to be larger than in the pelagic waters of the Black Sea. This, together with the average concentrations of about 17–18 μM reported by Sorokin (1983) for the surface waters of the Black Sea, suggests that a mean DON concentration of 18.0 μM may be presumed for the Bosphorus outflow. This is larger than the concentrations measured by Karl and Knauer (1991) in the central Black Sea in the summer of 1988. However, it is consistent with a mean value of 15.6 μM for the subsurface waters of the Baltic Sea (Sen Gupta, 1973) and with the DON data from the estuarine and coastal waters of other seas (Gardner and Stephen, 1978; Sharp, 1983).

In 1991–1992, concentrations of particulate organic carbon (POC) ranged from 10 to 40 μM [Fig. 4(b)], the annual average in the outflow being 21 μM. The dissolved organic carbon (DOC) contents of the Bosphorus outflow show only small seasonal changes relative to the concentrations of nutrients and POC (Fig. 3). The depth-averaged DOC concentrations (obtained with the WET method till 1989 and then by the HTCO technique) varied seasonally from 167 μM to 217 μM [Fig. 4(b)], yielding an annual average of 191 μM for the 1987–1992 period. Observed increases in the DOC concentrations following the early spring bloom in the southwestern Black Sea were probably generated by biological processes as reported for other seas (Wafar *et al.*, 1984). Recent developments and the known difficulties in accurately measuring trace levels of DOC residing in seawater (Sugimura and Suzuki, 1988; Hedges *et al.*, 1993; Sharp, 1993; Wangersky, 1993; Williams, 1993) naturally lead one to question the reliability of the DOC data and the similarity of the results given by the HTCO and WET methods in this study. Previously, Tuğrul (1993) compared the blank-uncorrected TOC data measured by these two methods in deep waters of the Marmara and Black Seas; the Shimadzu TOC values were consistently higher than the Technicon data by 10–30 μM. Such differences would diminish when the blank corrections applied to the raw sample values as discussed previously. Furthermore, two different and independent interlaboratory exercises arranged by J. I. Hedges (University of Washington, Seattle, U.S.A.) before the Seattle DOC Workshop in 1992 and by J. H. Sharp in 1993 have allowed us to assess the reliability of the Shimadzu and Technicon DOC data. The DOC concentrations of aged water samples determined by the authors by the Shimadzu HTCO technique were very similar both to the average values of 34 participants (Hedges *et al.*, 1993) and to the concentrations previously determined by J. H. Sharp (unpublished data). The Technicon WET method was used only in the Seattle DOC exercise; blank uncorrected concentrations were lower than the averages of the 34 participants (Hedges *et al.*, 1993). Our present blank correction would not reduce the difference completely, partly due to the poorer quality of the SSW

Table 2. Estimates of the annual average concentrations (μM) of inorganic, particulate and dissolved organic nutrients, particulate and dissolved organic carbon for the brackish waters of the Black Sea and saline water of the Marmara Sea exchanging through the Bosphorus two-layer flows

Parameter	Outflow from Black Sea C_1	Outflow from Marmara Sea C_2
DIP ($PO_4 - P$)	0.18	1.01
PP	0.17	0.05
DOP	0.15	0.05
TP	0.50	1.11
$NH_4 - N$	0.5	0.2
$NO_3 + NO_2 - N$	1.6	9.5
DIN ($NH_4 + NO_3 + NO_2 - N$)	2.1	9.7
PON	2.4	0.4
DON	18.0	3.0
TN	22.5	13.1
DOC	191.0	73.0
POC	21.0	5.2
TOC	212.0	78.2

used in 1992 and partly due to incomplete oxidation by the prescribed WET technique. Recent papers (Hedges *et al.*, 1993; Sharp, 1993; Wangersky, 1993; Williams, 1993) have suggested that the WET method generally underestimates the concentration of DOC in seawater by a few 10%, though some intercomparison experiments have produced similar results by both WET and HTCO techniques (Sharp, 1993; Sharp *et al.*, 1993). The Bosphorus DOC concentrations determined by the WET method are thus very similar to the HTCO data obtained in the region since 1990. Even if the WET technique underestimated the DOC contents of the productive outflow waters by 10–20 μM, this small difference is negligible compared both to seasonal changes and to the magnitude of the annual average DOC concentrations used to estimate fluxes. The DOC concentrations reported here are lower than previous concentrations determined by throughout the entire Black Sea by the dry combustion method (Deuser, 1971; Sorokin, 1983) but higher than recent values from the central Black Sea (Karl and Knauer, 1991).

Table 2 shows the estimated annual averages of the nutrient and organic carbon concentrations for the Black Sea outflow. The total phosphorus (TP) concentration calculated from the sum of the DIP, PP and DOP concentrations is 0.50 μM, in agreement with the annual mean of the TP data measured seasonally in the outflowing waters from December 1991 to October 1992 (0.45 μM). The TN computed from the mean DON, PON and DIN data is 22.5 μM. The biologically labile fraction (DIN + PON) constitutes about 20% of the TN and the rest consists of less labile DON. Nevertheless, during periods of high primary productivity, because of large and continuous nutrient inputs by the major rivers to the Black Sea, the outflowing water may contain concentrations of biochemically labile dissolved and colloidal DON of photosynthetic origin amounting to at least 5–20% of the total DON (Gardner and Stephens, 1978; Chen and Wangersky, 1993; Koike *et al.*, 1990; Agatova, 1992) and contributing to the new production in the Marmara Sea, whilst the less labile DON reaches the Mediterranean several months later through the Dardanelles Strait. The TOC:TN:TP and POC:PON:PP ratios estimated from the annual average values in Table 2 are 425:45:1 and 124:14:1, respectively, indicating the TN:TP ratio to be much larger than either the ratio of biogenic PON to PP in the outflow or the Redfield ratio of 16 for the ocean. This is due principally to the high TN:TP input ratio of the major rivers (especially the Danube) discharging into the Black Sea (Meybeck, 1982; Chirea and Gomoiu, 1986; Mee, 1992) and is consistent with the similar high ratios of nutrients observed in polluted rivers flowing into the North (Skjoldal, 1993), Baltic (Kullenberg, 1981) and Adriatic Seas (Bethoux *et al.*, 1992).

The outflowing water from the Sea of Marmara

Simply put, the Sea of Marmara is a two-layer system separated by a sharp interface, generally formed between 15 and 25 m depths, in which the surface layer is occupied by brackish waters from the Black Sea whilst the lower layer below the interface contains saline waters of Mediterranean origin. As clearly shown by the salinity and velocity profiles illustrated in Fig. 2, the waters below the 30 ppt isohaline surface leave the Marmara by flowing over a 35 m sill at the entrance to the Bosphorus (Sorokin, 1983; Ünlüata *et al.*, 1990; Oğuz and Rozman, 1991; Latif *et al.*, 1991). These waters eventually spread horizontally into the intermediate layer of the southwestern Black Sea after successive dilutions along the Bosphorus Strait (Latif *et al.*, 1991; Oğuz and Rozman, 1991; Codispoti *et al.*, 1991; Murray *et al.*, 1991). Photosynthesis being limited to the surface waters of the Marmara Sea (including the interface between 15 and 25 m) (Baştürk *et al.*, 1990; Tuğrul, 1993), seasonal changes in nutrient and organic carbon concentrations in the chemically modified Mediterranean water flowing out through the Bosphorus are much less than those in the waters leaving the Black Sea. Nutrient concentrations in the upper subhalocline waters of the Marmara Sea change little with depth in the region of the Bosphorus (Fig. 5), permitting one to compute depth-averaged values of the Marmara outflow. The chemocline coincides closely with the sharp and thin halocline formed by the mixing of brackish and saline waters in the Bosphorus. Data collected between 1986 and 1992 show that, throughout each year, nutrient concentrations in the saline Marmara Sea waters entering the Bosphorus have ranged from 7 to 12 μM for nitrate and from 0.7 to 1.2 μM for phosphate. These concentrations are similar to those found in the deep basin waters of the eastern Marmara Sea (Sen Gupta, 1971; Baştürk *et al.*, 1990; Friederich *et al.*, 1990). The annual averages calculated from the 6-year data are 1.0 ± 0.10 μM for phosphate and 9.5 ± 0.86 μM for nitrate. Although ammonia has yet to be measured in the Bosphorus underflow, the limited data reported by Friederich *et al.* (1990) for the eastern Marmara Sea strongly suggest that the ammonia concentration may be as low as 0.2 μM in the outflowing saline waters and certainly much less than the corresponding nitrate concentration.

Depth-averaged PP and PON concentrations in the Marmara outflow have been computed from the measurements made in the Bosphorus region at 30 and 50 m between 1991 and 1992. These concentrations varied seasonally between 0.27 and 0.60 μM for PON and between 0.04 and 0.06 μM for PP, with annual averages of 0.41 and 0.05 μM, respectively. The concentrations of DOP estimated from the differences between TP and (DIP + PP) for 1992 are rather uncertain due to the large content of DIP in the samples,

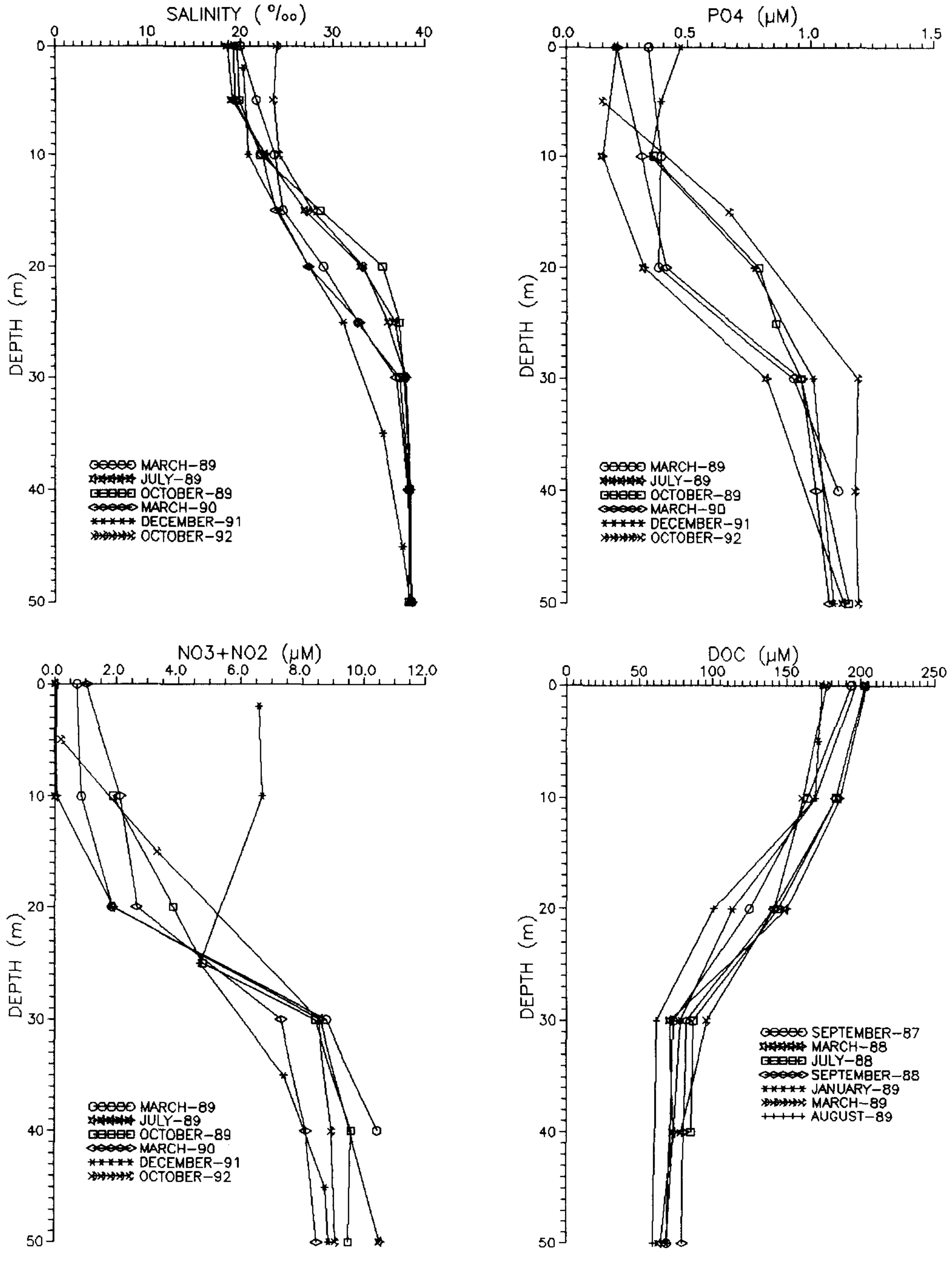

Fig. 5. Typical seasonal profiles of salinity, nutrients and dissolved organic carbon at the southern entrance of the Bosphorus.

but were, nevertheless, always less than 0.1 μM, suggesting an annual mean of 0.05 μM for the outflow. The low DOP and PP concentrations in the Marmara outflow are very similar to those reported by Coste *et al.* (1988) for the Mediterranean waters flowing out through the Gibraltar Strait. Though DON has yet to be measured in the Marmara Sea, a mean value of 3.0 μM may be proposed for the saline water of Mediterranean origin flowing out through the Bosphorus, based on those DON concentrations given by Coste *et al.* (1988) for the western Mediterranean water flowing through the Straits of Gibraltar. A similar DON concentration can be computed from the DOC:DON ratio for the aphotic layer of the western Mediterranean [from the relevant data of Coste *et al.* (1988); Cauwet *et al.* (1990) and Copin-Montégut and Arvil (1993)] together with the DOC concentrations measured in the lower layer of the Marmara Sea by Tuğrul (1993).

In 1991–1992, very low POC concentrations were observed in the Marmara outflow, varying seasonally between only 2.5 and 9.1 μM with an annual average of 5.2 μM. The blank-corrected DOC concentrations measured by the Technicon WET method between 1986 and 1989 ranged from 65 to 80 μM (see typical DOC profiles in Fig. 5). These DOC values are very similar to the concentrations measured by Tuğrul (1993) in the subhalocline waters (Mediterranean origin) of the Marmara Sea and in the deep waters of the western Mediterranean by Cauwet *et al.* (1990) and Copin-Montégut and Arvil (1993) using the Shimadzu HTCO method. The estimated annual average DOC for the Marmara outflow is 73 μM, much larger than the POC concentrations.

The annual means of the various forms of nutrients and of organic carbon estimated for the Marmara outflow are compiled in Table 2. DIP, DIN and DOC constitute the major fractions of the total nutrients and organic carbon in these saline waters. The computed TOC:TN:TP molar ratios are 70:12:1, whereas the IN:IP ratio is about 9.6, suggesting denitrification in the oxygen-depleted aphotic waters of the Marmara Sea. The TP content of the Marmara outflow is twice that of the inflow from the Black Sea. A similar feature is encountered when labile constituents of TN are compared by excluding DON.

WATER FLOWS THROUGH THE BOSPHORUS

Earlier current measurements (Gunnerson and Özturgut, 1974) and very recent Acoustic Doppler Current Profiler (ADCP) surveys (Latif *et al.*, 1992; Özsoy *et al.*, 1992) in the Bosphorus demonstrate that the two-layer flow regime in this narrow Strait shows both short- and long-term changes, depending on the meteorological and hydrological conditions in the adjacent seas and the total fresh water input to the Black Sea. The upper flow carrying the Black Sea waters into the Marmara increases during the spring–early summer period and decreases during the autumn–winter period (Ünlüata *et al.*, 1990; Latif *et al.*, 1991). According to the limited ADCP data of Latif *et al.* (1992) and Özsoy *et al.* (1992), the upper flow ranges between 15,000 and 20,000 $m^3 s^{-1}$ during the spring period. However, diurnal changes in the upper flow may be significant and on rare occasions this flow can be blocked for several hours at the southern end of the Bosphorus by a strong northeasterly winter wind (Latif *et al.*, 1992; Özsoy *et al.*, 1992). Similarly, the blockage of the counter flow at the northern end of the Bosphorus has been observed following the development of unsteady conditions during which the upper layer flux may reach an extreme value of about 50,000 $m^3 s^{-1}$ (Özsoy *et al.*, 1992). The recent long-term salinity and current measurements carried out by the IMS-METU at the northern entrance of the Bosphorus show that, under normal conditions, the saline waters of Mediterranean origin

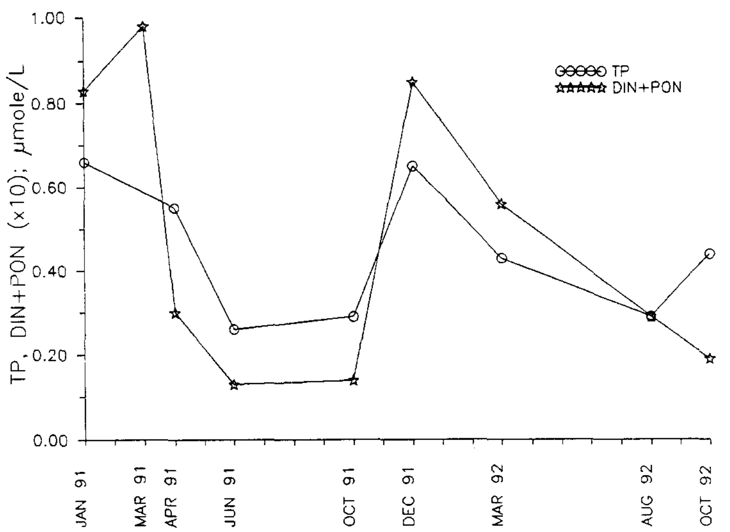

Fig. 6. Seasonal variations of (inorganic + particulate organic) nitrogen (DIN + PON) and total phosphorus (TP) in the Black Sea outflow between 1991 and 1992.

flow from the Marmara to the Black Sea throughout the year (Latif *et al.*, 1992; Özsoy *et al.*, 1992).

Ünlüata and Özsoy (1986), using recent data for the net fresh water input to the Black Sea surface layer, together with salinity data measured monthly or seasonally in the Turkish Strait System between 1985 and 1986, estimated the water balance in the Sea of Marmara from the equations of conservation of water and salinity. Subsequently, Ünlüata *et al.* (1990) and Beşiktepe (1991) refined the calculation of the water balance of the Marmara Sea and thus the volume fluxes through the Bosphorus, using more recent salinity data. According to Beşiktepe's estimates [see Fig. 7(a)], of the approximately 600 $km^3 y^{-1}$ of the brackish waters of the Black Sea that flow into the Marmara Sea through the Bosphorus, about 40 $km^3 y^{-1}$ are entrained by the counterflow in the lower layer. In contrast, about 300 $km^3 y^{-1}$ of saline Mediterranean waters are carried into the intermediate depths of the Black Sea by the Bosphorus underflow, including the entrainment of sea water from the upper flow in the strait. These water fluxes are larger than those that were used by Deuser (1971) and Fonselius (1974) to estimate organic carbon and phosphorus fluxes through the Bosphorus.

NUTRIENT AND ORGANIC CARBON FLUXES THROUGH THE BOSPHORUS

Because of temporal variability in both the Bosphorus two-layer flows and in the chemical concentrations of the exchanging waters, the quantities of the various forms of nutrients as well as the organic carbon exchanged between the Black Sea and Marmara Sea vary with season. Such changes are more pronounced for biologically labile chemicals exported from the Black Sea by the Bosphorus surface flow. For example, the concentration of biologically labile nitrogen (DIN + PON) in the Black Sea outflow was as high as 8.2–9.8 μM (mean = 8.2) in the winter–early spring (December–March) period of 1991–1992 but then decreased steadily to levels of 1.3–3.0 μM (mean = 2.2) during the late spring–late autumn period (Fig. 6). On the other hand, the TP concentrations of the

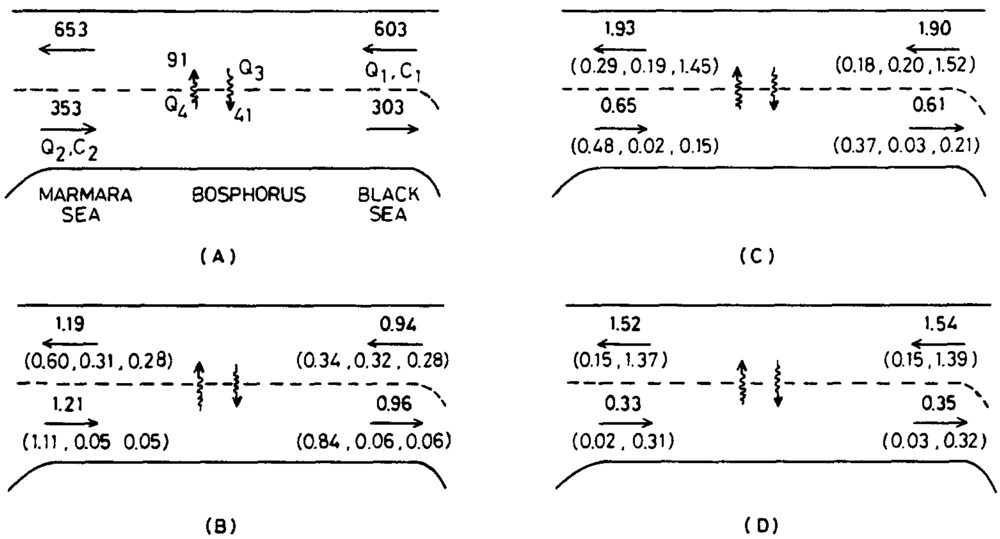

Fig. 7. Schematic presentation of water and chemical fluxes through the Bosphorus: (A) volume fluxes ($km^3\ y^{-1}$; after Beşiktepe, 1991); (B) phosphorus fluxes ($\times 10^4$ ton P y^{-1}); (C) nitrogen fluxes ($\times 10^5$ ton N y^{-1}); (D) Total Organic carbon fluxes ($\times 10^6$ ton C y^{-1}). The values above the arrows represent TP, TN or TOC whereas the ones in parantesis indicate (DIP, PP, DOP), (DIN, PON, DON) or (DOC, POC), respectively.

outflow ranged seasonally between 0.29 and 0.65 μM. Thus, the quantities of the biologically labile nutrients (DIN + PON, TP) exported from the Black Sea during the winter–spring period (5–6 months) were at least 2–3 times the total outflows for the summer–autumn period, assuming that the water fluxes for these two periods were comparable. The water outflow, in fact, is relatively high during the spring and early summer months, resulting in greater export of (DIN + PON) and TP as compared to the outfluxes in the summer–autumn period when both the chemical concentrations and the water flow are relatively low. For the winter–spring and summer–autumn periods, the mean POC concentrations were 25.8 μM and 15.8 μM, respectively, these concentrations deviating by about 25% from the estimated annual mean (21 μM). On a total concentration basis, the annual variation of the TOC (possibly TN) concentrations in the outflow, however, is of the order of 10% because these total values are dominated by the biologically less labile DOC (and possibly DON). Unfortunately, there are no long-term measurements of water flows to permit the estimation of the seasonal export rates of nutrients and organic carbon carried by the Black Sea outflow through the Bosphorus.

As we stated previously, the nutrient and the TOC concentrations of the Marmara Sea outflow also vary seasonally but by as little as a few tenths of the annual means (Table 2). Their export by the Bosphorus undercurrent, on a seasonal time scale, is principally determined by the fluctuating water flow. Nevertheless, the mean chemical concentrations of the Marmara outflow (Table 2) can be used to estimate the annual quantities carried by the Bosphorus underflow.

The average concentrations of chemicals (Table 2), together with the fluxes of water [Fig. 7(a)], assuming these are constant on a yearly time scale, permit one to estimate the annual quantities of the total nutrients and organic carbon exchanged between the Black and Marmara Seas. The annual chemical fluxes leaving the surface layer of the Black Sea and those leaving the lower layer of the Marmara Sea by the Bosphorus counter flow have been calculated simply from their respective volume fluxes, 603 and 353 $km^3\,y^{-1}$ [Fig. 7(a)] and the annual average concentrations of the chemicals the waters contain (Table 2). The total inputs from the flows into the Marmara and Black Seas are, however, slightly modified by upward and downward entrainment of the exchanging waters through the halocline in the strait. The magnititude of this modification is proportional to the chemical concentrations and to the volume of the waters entrained by the counter flows in the Strait. Allowing for the physical mixing of the flows in the Strait, the total inputs into the Marmara and the Black Seas of each chemical parameter have been calculated by the following equations:

$$\text{Influx into the Marmara Sea} = [(Q_1 - Q_3) \times C_1] + [Q_4 \times C_2] \quad (1)$$

$$\text{Influx into the Black Sea} = [(Q_2 - Q_4) \times C_2] + [Q_3 \times C_1] \quad (2)$$

where Q_i is the volume flux [Fig.7(a)] and C_1, C_2, respectively, are the chemical concentrations of the Black and Marmara Sea outflows (Table 2).

The flux estimates above, given in Fig. 7(b)–(d), represent the order of magnitude of the annual exchanges between the Black and Marmara Seas. These values should be used cautiously in examining short-term exchanges due to the seasonal variation in both the volume fluxes and the chemical properties of the flows.

Figure 7(b) shows that about 9000 tons of TP are exported annually from the productive layer of the Black Sea through the Bosphorus upper flow. The entrainment of the IP-rich water originating in the saline waters of the Marmara Sea, by the interface in the Bosphorus Strait, increases the TP input into the upper layer of the Marmara Sea to about 12,000 tons y^{-1}. Hence the IP constitutes about 50% of the TP input by the Bosphorus upper flow. The TP exported from the surface layer of the Black Sea through the Bosphorus is nearly equal to the total input (9600 tons y^{-1}) by the Bosphorus underflow. Since the Marmara outflow is diluted by the DIP-poor counter flow in the strait, the IP accounts for about 88% of the TP input (9600 tons) to the Black Sea. These estimated fluxes are larger than those suggested by Fonselius (1974), who used an underestimated TP concentration of 0.32 μM and a volume flux of 2300 tons y^{-1} for the Bosphorus underflow towards the Black Sea.

Estimated nitrogen fluxes [Fig. 7(c)] indicate the TN outflowing from the Black Sea (approximately 190,000 tons y^{-1}) to be three times the input (61,000 tons y^{-1}) by the Bosphorus underflow. A similar conclusion can be reached for the Marmara Sea, though the fluxes are in the opposite direction, due to the large DON input from the Black Sea. Biologically labile nitrogen (DIN + PON) constitutes approximately 25% of the TN fed into the Marmara surface layer and 66% (primarily nitrate) of that fed into the Black Sea by the Bosphorus; the remainder of the TN consists of less labile DON. Comparison of the (DIN + PON) exchange fluxes suggests that biochemically labile nitrogen exported from the Black Sea is compensated by the Bosphorus counterflow principally as nitrate. Such an (DIN + PON) influx into the surface waters of the Marmara Sea by the Bosphorus upper flow corresponds to a new production of 2.7×10^5 tons y^{-1} in terms of carbon. However, the DON input from the productive Black Sea, assuming about 10% of the DON to be of biogenic origin and oxidized in the Marmara Sea by bacteria, contributes about 0.8×10^5

tons y^{-1} of carbon to the new production. The new production estimated from the sum of (DIN + PON) and the biologically labile fraction of DON (3.5×10^5 tons C y^{-1}) is in harmony with the estimate (4.9×10^5 tons C y^{-1}) derived from the TP input, assuming all phosphorus to be utilized by plant production with a C:P atomic ratio of 106:1.

The remarkable differences in both the volumes and the organic carbon contents of the waters exchanged between the Black and the Marmara Seas through the Bosphorus cause the DOC and the POC exchange in the strait to exhibit different behaviour; there exists a net input of organic carbon into the Marmara Sea (difference between the influx and outflux) through the Bosphorus. As Fig. 7(d) shows, the annual amount of the TOC introduced to the surface waters of the Marmara Sea is about 1.5×10^6 tons, which is about four times larger than the TOC input (0.35×10^6 tons) into the Black Sea by the Bosphorus undercurrent. A similar ratio can be obtained from the POC fluxes through the Bosphorus; the Black Sea outflow introduces about 0.15×10^6 tons of POC y^{-1} to the Marmara Sea, whereas the input by the Bosphorus undercurrent is only 0.03×10^6 tons. The POC amounts to only 10% of the TOC flowing into the Marmara and Black Seas through the two layers of the Bosphorus.

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