



PERGAMON

Deep-Sea Research II 49 (2002) 2303–2318

DEEP-SEA RESEARCH
PART II

www.elsevier.com/locate/dsr2

Iodine chemistry reflects productivity and denitrification in the Arabian Sea: evidence for flux of dissolved species from sediments of western India into the OMZ

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Received 30 January 2001; received in revised form 8 September 2001; accepted 15 December 2001

Abstract

Dissolved iodine species and total iodine concentrations were measured in the Arabian Sea during the Spring Intermonsoon of 1995. Two separate regimes of iodine chemistry are highlighted in this study: (1) the well-oxygenated surface layer (WOSL) where iodide concentrations were in the range of 158–558 nM, and (2) the oxygen minimum zone (OMZ) where total iodine concentrations [primarily as iodide and in excess to the oceanic iodine/salinity ratio of ~ 13] varied from ~ 200 to 950 nM. Iodine data in the WOSL of the Arabian Sea are contrasted with data from the Bermuda Atlantic Time-series Station (BATS), the Hawaii Ocean Time-series Station ALOHA (HOT), VERTEX in the Pacific and the Black Sea. Total iodine concentrations in excess of 400 nM were observed in eastern portions of the OMZ. The eastern portion of the basin has a permanent denitrification zone as well as high concentrations of dissolved Mn^{2+} (d-Mn^{2+}) and iodide. While there is precedent for high values of iodide and total iodine in several other isolated basins, this is the first report of such values in open-ocean waters. Potential sources of excess total iodine to the OMZ include advection along isopycnals, from hydrothermal vents or margin sediments; atmospheric deposition; and remineralization of sinking particulate organic iodine (POI) associated with elevated productivity in surface waters. We estimate that only 3.6% of the excess total iodine can result from remineralization of sinking POI from the WOSL to the OMZ. Advection from margin sediments off of India is the most plausible source of iodine to the OMZ and contributes $\sim 96\%$ of the total excess iodine to the OMZ. I^- is maintained as the dominant form of iodine via in situ reduction of iodate by bacteria. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

Iodate (IO_3^-) is the thermodynamically favored form of iodine in the oxic ocean (Wong, 1991). Iodide (I^-) is kinetically stable (Luther et al., 1995)

and concentrations of 50–250 nM have been reported in surface waters as a product of biological cycling (Tsunogai and Sase, 1969; Jickells et al., 1988; Nakayama et al., 1985; Luther and Campbell, 1991; Campos et al., 1996). Tsunogai and Henmi (1971) were the first to provide direct evidence of I^- formation by in situ reduction of IO_3^- , whereas several workers (Tsunogai and Sase, 1969; Moisan et al., 1994;

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Udomkit, 1994; Brandão et al., 1994) showed that phytoplankton, grown in culture, reduce IO_3^- to I^- . Higher I^- concentrations (200–800 nM) are present as a product of chemical reduction in anoxic or sulfidic zones such as brines or isolated basins (Wong and Brewer, 1977; Wong et al., 1985; Ullman et al., 1990; Luther and Campbell, 1991; Luther et al., 1991). However, I^- is not generally found at concentrations greater than 10 nM below the euphotic zone (Luther et al., 1995).

In an earlier study of the Arabian Sea, iodine speciation was determined in samples collected during the Netherlands Indian Ocean Programme (NIOP) Fall Inter-monsoon cruises (September–November 1992). During that sampling period, in western portions of the basin, the waters of the Arabian Sea below 100 m were suboxic (O_2 concentrations $< 12.5 \mu\text{M}$) but non-sulfidic (Theberge et al., 1997). Nitrate concentrations were high ($> 30 \mu\text{M}$) within this oxygen minimum zone (OMZ). At five stations located north of the Carlsberg Ridge in the Arabian Basin, modestly elevated total iodine values ($\sim 650 \text{ nM}$) were observed and subsurface I^- maxima occurred at depths between 250 and 800 m (Farrenkopf et al., 1997a).

An aim of the US Joint Global Ocean Flux Study (JGOFS) program was to determine the processes controlling the flux of carbon and other nutrient elements in the ocean (Smith et al., 1991). Iodine speciation has been suggested for use as a proxy for both primary production and carbon flux based on work at the time-series stations in the Atlantic and Pacific Oceans (Jickells et al., 1988; Jickells et al., 1990; Campos et al., 1996) and in the Black Sea (Luther et al., 1991). Using annual averages, Campos et al. (1996) reported that integrated concentrations of I^- are directly proportional to primary productivity measured in surface waters of the Atlantic and Pacific Oceans. In addition, iodate and nitrate have similar electron acceptor properties for organic matter decomposition (Farrenkopf et al., 1997b; Luther et al., 1998), and dissolved I^- in porewaters indicates the zone of denitrification in sediments (Luther et al., 1998). In this study, the objective was to evaluate iodine as a proxy for carbon and nitrogen processes in the Arabian Sea.

An extensive OMZ exists throughout the Arabian Sea with distinct areas that encompass upwelling zones and a permanent secondary nitrite maximum (Naqvi et al., 1990; Naqvi, 1991; Jochem et al., 1993; Mantoura et al., 1993; Olson et al., 1993; Morrison et al., 1998; Codispoti et al., 2001). The US JGOFS cruise track (Fig. 1) was specifically designed to obtain samples from different regions of varying oxygen and nitrite concentrations and to contrast those regions to a reference station at 10°N (S15). Iodine data presented here are from the Spring Intermonsoon cruise US JGOFS (TN045) in March–April 1995.

Iodine data in this study are shown from four distinct geographical regions of the Arabian Basin. These are the western stations of the north section (N2 through N7), the eastern portions of the north section (stations N8 through N11), the 10°N reference stations (S14 and S15) and the southern stations (S2 through S11) (Fig. 2(a)–(e)). Iodine data are reported along with nutrient and density data in the US JGOFS Arabian Sea database (<http://usjgofs.whoi.edu/arabian.html>) and in Farrenkopf (2000). Two distinct patterns emerged

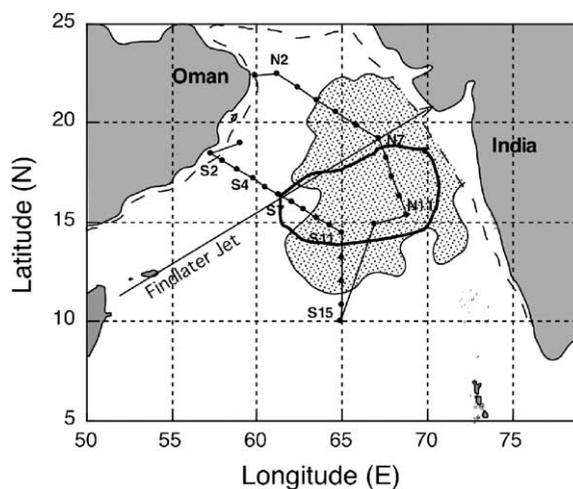


Fig. 1. Stations (filled circles) shown from R/V *Thomas G. Thompson* US JGOFS Spring Intermonsoon cruise TN045, March–April 1995 (adapted from Smith et al., 1998). The dotted area indicates the zone where the maximum nitrite concentration (the secondary nitrite maximum) exceeds $1 \mu\text{M}$ in the OMZ (Naqvi, 1991). The irregular oval indicates the extent of excess total iodine measured in this study.

from the iodine data set and are discussed separately for I^- and for total iodine. The first set of data is from the well-oxygenated surface layer (WOSL), and the second set of data is from within the OMZ. In addition, carbon accumulation, particle flux, and flux of dissolved material from sediments are investigated with respect to potential sources of the high values of total iodine (in excess to that predicted by salinity) measured in the OMZ.

2. Methods

During the Spring Intermonsoon cruise, samples were collected from Niskin bottles on routine hydrocasts and filtered through 0.45- μm (Gelman Supor) membranes prior to analyses. To avoid contamination during sampling, samples were drawn after the dissolved oxygen reagents that contain iodine were removed from the sampling area.

Electrochemical measurements were made in 10-ml glass polarographic cells using EG&G Princeton Applied Research model 384B polarographic analyzers equipped with 303A hanging drop mercury electrode (HDME) stands or an Analytical Instrument Systems Inc. model DLK-100 potentiostat equipped with a 303A (HDME). In all instances, the reference electrode was a saturated calomel electrode (SCE) and the counter electrode was a platinum wire. Concentrations were determined on samples in triplicate by the method of standard additions.

Iodide was measured using cathodic stripping square wave voltammetry (CSSWV) (Luther et al., 1988). Iodide gives a peak at a potential of -0.306 V . Total iodine ($\sum I$) was measured using CSSWV and a modification of the ascorbic acid reduction method (Campos, 1997; Farrenkopf, 2000). The instrument minimum detection limits in seawater for I^- and $\sum I$ using polarography were 2 and 20 nM, respectively. Based upon triplicate measurements of individual samples, precision for I^- is within 5–10% in samples greater than 200 nM and within 1–2% for concentrations less than 200 nM. Method precisions for iodide standards in 3.5% NaCl were +1% (1 rsd; $n > 3$). Deep-sea-

water from either 2000 or 4000 m was consistently run as a blank between samples to verify instrument stability and lack of carry over. Likewise, all $\sum I$ measurements were begun with an analysis of the borate buffer to ensure the absence of cross-contamination of reagents and glassware.

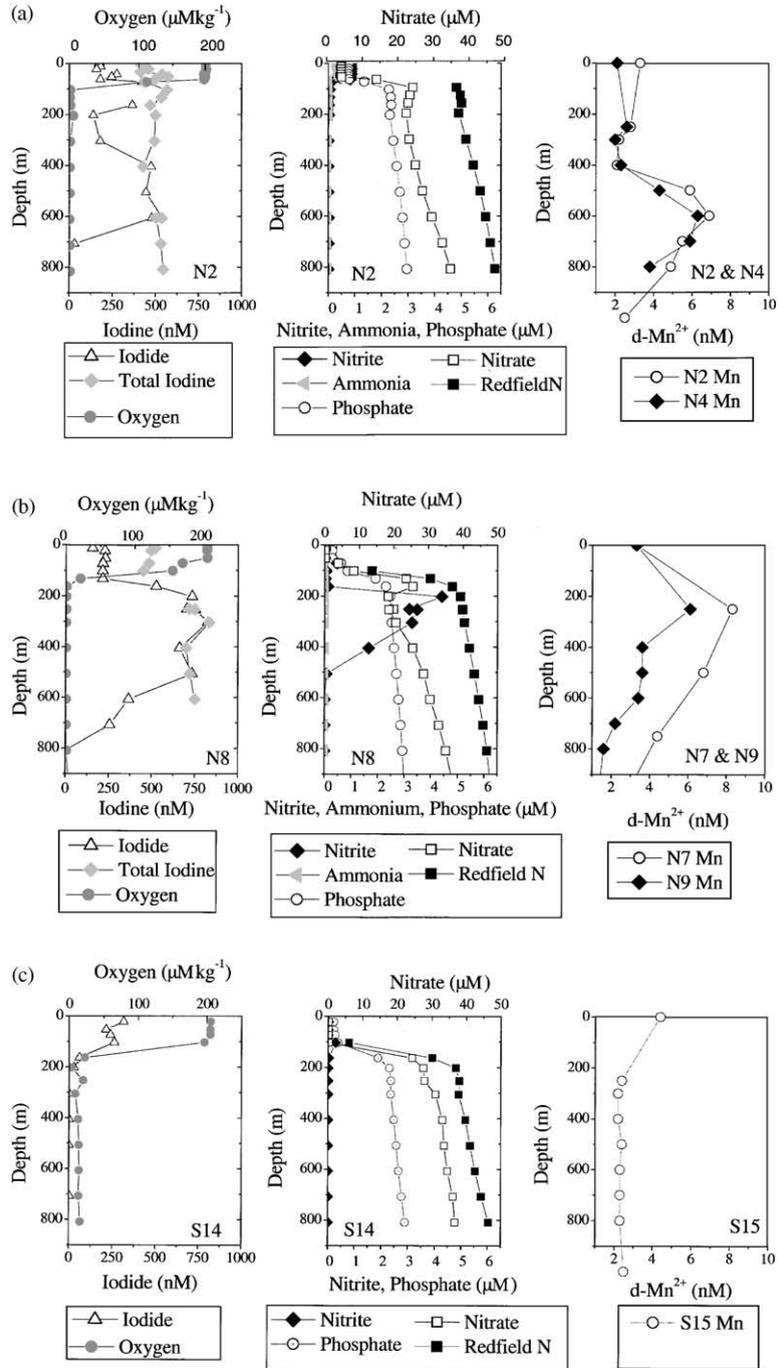
Also measured aboard ship by voltammetry were sulfide (via CSSWV), oxygen and peroxide (via linear sweep voltammetry). Sulfide samples were drawn anaerobically via syringe from bottles not previously sampled for Winkler oxygen. Syringe samples were analyzed by voltammetry within ten minutes of collection (Luther et al., 1991; Farrenkopf et al., 1997a; Theberge et al., 1997) and were taken at depths of 200, 300, 400, 500, 600 and 800 m at stations N3, N5, N7, N9 and S1. Depths chosen at each station coincided with levels of high iodide or high nitrite. The minimum detection limit for sulfide in seawater samples is 0.1 nM [100 Hz, pulse height 25 mV] (Luther and Tsamakis, 1989).

Ancillary data, which are reported in the tables (depth, sigma theta and nutrient concentrations), were taken from the US JGOFS Arabian Sea database (<http://usjgofs.whoi.edu/arabian.html>).

3. Results

3.1. Study area—spring intermonsoon

During the US JGOFS cruises, the oxygen minimum zone was ubiquitous and most pronounced in the eastern portion of the basin (Morrison et al., 1998, 1999; Codispoti et al., 2001). The secondary nitrite maximum zones persisted only in the central and eastern portions of the basin and were frequently characterized by an intermediate nepheloid layer between 130 and 300 m (Naqvi et al., 1993; Gundersen et al., 1998). The nepheloid layer did not appear to be an advective feature as it was tightly coupled with the presence of denitrifying bacteria (Gundersen et al., 1998; Morrison et al., 1999). During the Spring Intermonsoon cruise, a subsurface Chl *a* and a particulate organic carbon (POC) maximum tracked the top of the nutricline. The nutricline was considerably deeper than the bottom of the



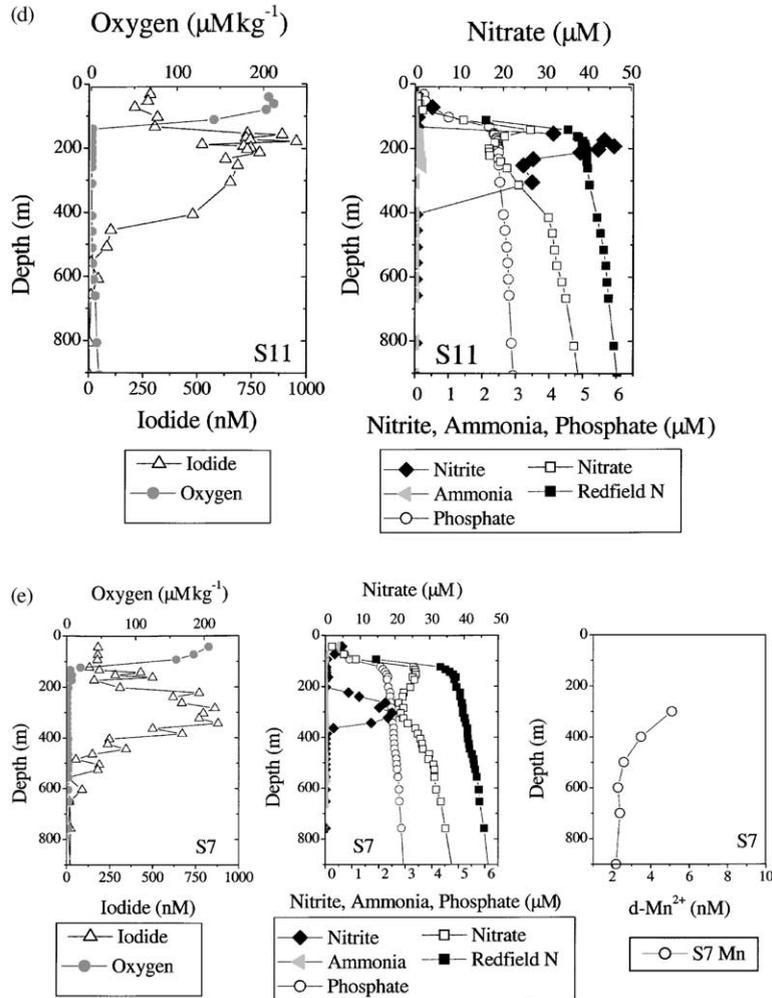


Fig. 2 (continued).

mixed layer in the eastern portion of the northern section (Stations N2 through N11) and throughout the southern section, which limited the entrain-

ment of nutrient-rich waters into the mixed layer during the Spring Intermonsoon. In the center basin, primary productivity varied by less than a

Fig. 2. (a) Station N2 iodide, total iodine, and oxygen concentrations are plotted vs. depth in the left panel and nutrient species are plotted in the center panel. For this figure and (b) to (e), the Redfield N was calculated by multiplying the measured phosphate concentration by 16 and is shown here only for comparison. It is well known that $N/P < 16$ in many areas of the Arabian Sea (Morrison et al., 1998; Naqvi et al., 1990; Mantoura et al., 1993). Symbols as indicated in each graph legend. Dissolved Mn^{2+} data from US JGOFS database, with permission of B. Lewis and G. Luther. (b) Station N8 iodide, total iodine, and oxygen concentrations plotted vs. depth in the left panel, nutrient species in the center panel, and dissolved Mn^{2+} in the right panel. (c) Station S14 iodide, total iodine, and oxygen concentrations plotted vs. depth in the left panel, nutrient species in the center panel, and dissolved Mn^{2+} in the right panel. (d) Station S11 iodide, total iodine, and oxygen concentrations plotted vs. depth in the left panel, nutrient species in the center panel, and dissolved Mn^{2+} in the right panel. (e) Station S7 iodide, total iodine, and oxygen concentrations are plotted vs. depth in the left panel nutrient species in the center panel, and dissolved Mn^{2+} in the right panel.

factor of 2, with the lowest values at station S15 and the highest at station S7 (Table 1). Primary productivity generally decreased from S2 to S15, and the fraction of surface derived organic carbon preserved in the sediments decreased with increasing distance from the Oman coast (Lee et al., 1998). A program overview is detailed in Smith et al. (1998).

3.2. Iodide

Representative iodide, nutrient and oxygen profiles from each of the regions [western stations of the north section (N2 through N7), eastern portions of the north section (stations N8 through N11), 10°N reference stations (S14 and S15), and southern section (stations S7 and S11)] are shown in Fig. 2(a)–(e). Iodide values in the well-oxygenated surface layer (WOSL) ranged from 158 to 558 nM, with an integrated average concentration over the upper 105 m of $2.44 \times 10^{-2} \text{ mol I m}^{-2}$ for all stations. Integrated I^- concentrations in the WOSL did vary from station to station, but were about 20% higher than surface values observed at the Hawaii Ocean Times (HOT) series station ALOHA (Table 1).

Iodide was less than 0.2 nM in the OMZ at station S14. Such a low concentration was expected since this station had no subsurface nitrite maximum, and O_2 ($\sim 12.5 \mu\text{M}$) was depleted. There was a slight maximum in the discrepancy between the calculated Redfield NO_3^- and the measured NO_3^- at 250 m, which corresponded with the pre-existing O_2 depleted signature of Indian Central Water and Arabian Sea Intermediate Water (Morrison, 1997; Farrenkopf, 2000).

Stations N2, N8, N11, S7, and S11 showed considerable variability as I^- values ranged from 32 to 953 nM in the OMZ. These stations were all characterized by subsurface I^- maxima. The highest values of I^- were observed at stations S7, S11 and N8 (Fig. 3). Station N2 had an upper (150 m) and a lower (500 m) maximum, and no I^- was detected at a depth of 700 m at N2. Station N8 had a broad I^- maximum centered at 350 m that extended into the deeper portions of the OMZ, but dissolved I^- concentrations below 800 m were low to non-detectable. Even considering different

sampling resolution, the subsurface maximum at S7 was less broadly distributed than the other stations, but was centered at 300 m and decreased sharply at 400 m (Fig. 3). Iodide was not detectable at depths greater than 650 m at S7. The subsurface I^- maximum at station S11 was similar in structure to S7 but was centered at 200 m depth.

At stations N2, N8, S7 and S11, the I^- subsurface maxima were near or ~ 20 m below the base of the oxycline. Stations N8, S7 and S11 had corresponding subsurface nitrite maxima and dissolved manganese (d-Mn^{2+}) maxima (Fig. 2(a)–(e); Lewis and Luther, 2000). These subsurface maxima corresponded to the maximum discrepancy between the calculated Redfield NO_3^- and NO_3^- measured (Fig. 2(a)–(e)). The upper part of the subsurface I^- maximum corresponded to the secondary fluorescence maximum and, in some instances, to increased abundance of picoplankton and heterotrophic bacteria (Campbell et al., 1998). Relative to the other stations, a deeper subsurface I^- maximum appeared in the N2 profile. This deeper feature broadened, then disappeared from N2 to N8 and again sharpened between S7 and S11. The disappearance of this broad feature may be due to dilution or oxidation, and similar features appeared in the dissolved Mn^{2+} profiles (Lewis and Luther, 2000).

For depths sampled within the OMZ at station N8, I^- accounted for more than 95% of the total iodine. This was in contrast with station N2 where I^- accounted for 70–80% of the total iodine in the upper I^- maximum and more than 95% in the deeper I^- maximum.

3.3. Total iodine

Total iodine concentrations in the WOSL were consistent with previous oceanographic measurements. During March 1995, total iodine values were consistently 500 ± 45 nM for all depths measured (0–4000 m) on the northern section (stations N2 to N7). At station N8, in the eastern-most portion of the northern section, elevated total iodine concentrations (800 nM) were observed at depths from 250 to 600 m. Samples were not analyzed for total iodine below 600 m so the elevated total may also extend below this

depth. Total iodine concentrations in the OMZ were elevated at N11 and along the southern section (S7 to S11), when considering I^- to be the predominant form of total iodine. I^- values as high as 953 nM were observed at station S11. The highest I^- concentrations for the southern section were observed near the top of the OMZ (150–300 m), in contrast to station N8 where the values of total iodine were uniformly high and persisted to at least 600 m. An average total iodine profile, from stations N2 through N7 is presented and contrasted with station N8 in the east and stations S7 and S11 in the south (Fig. 4).

3.4. Sampling resolution

In order to distinguish local, temporal and mesoscale variability from possible seasonal variability, two stations were sampled at high resolution (depth intervals of 5–10 m) through the OMZ. These stations were sampled over several days from sequential bottle casts (24 depths per cast). Variability was observed in both iodide and nitrite profiles from the same stations, but no evidence of internal waves or vertical instabilities was observed as is seen in the overlapping down cast plots of

sigma theta. Thus, the fine structures in the iodide and nitrite profiles are likely in situ cycling features and not the consequence of advection from a specific water mass with a unique density signature (Farrenkopf, 2000).

3.5. Sulfide

Free sulfide was not measurable (<0.1 nM) at any of the stations or depths sampled during March or April 1995, but detectable (~ 2 nM) sulfide was observed in October 1992 (Theberge et al., 1997).

4. Discussion

We divide the discussion into two parts: (i) the interconversion between iodine species within compartments and (ii) the significance of excess total iodine in the OMZ.

Processes that interconvert iodine species are well known (e.g., Wong, 1991) and are shown in Fig. 5. These processes include (a) phytoplankton uptake/remineralization (in the WOSL, iodine converts between dissolved and particulate pools

Table 1
Euphotic zone primary productivity is presented to compare stations during March–April 1995

Arabian sea station	Range of primary productivity for the year (mmole C m ⁻² d ⁻¹)	Spring intermonsoon (mmole C m ⁻² d ⁻¹)	Nearest station	Depth integral for integrated Iodide		
				0–100 m	100–200 m (nmol m ⁻² d ⁻¹)	200–300 m
N2	83–125			274	380	160
N7	52–108	108	N8	207	422	754
S15	51–130	64	S14	256	116	26
S7	80–147	80		180	272	686
S11	70–129	71		270	669	705
N2	83–125	(3 month average)		179	182	317
HOT	48	(6 month average)		215	129	<10
BATS	27	(8 month average)		129	49	<10

Productivity ranges are reported for the six-process cruises. Data for station N2 are from Marra and Knudson (pers. comm.) based upon in situ incubations. All other Arabian Sea primary productivity data are from Barber et al. (2001) and the US JGOFS database. Integrated iodide concentrations are based on integrations to the nearest 5-m of the depth interval. Iodide values for N2 at the bottom of the table include integrated concentrations from October 1992 and August 1995 (Farrenkopf et al., 1997a, 2000, respectively) and are shown to compare with data from HOT and BATS (Campos et al., 1996). Productivity data from HOT and BATS were provided by Karl (pers. comm.) and Michaels et al. (1994), respectively.

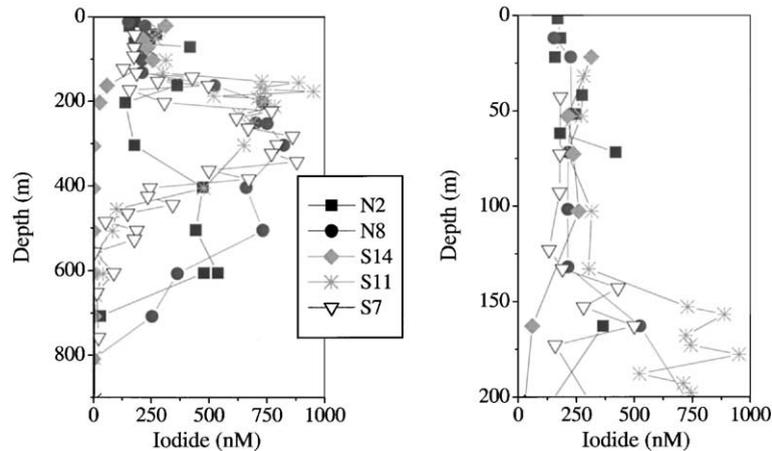


Fig. 3. Dissolve iodide from representative stations during the Spring Intermonsoon N2, from the East of the northern section N8, the 10°N station S14, and southern section stations S7 and S11. Note depth axis change. The right-hand plot is shown to a depth of 200 m to show that iodide is uniform in concentration throughout the mixed layer and below to a depth of ~100 m.

resulting in iodide production), (b) iodide oxidation (can be microbially mediated, dominates in WOSL and deep water but may also contribute to cycling in OMZ), (c) bacterial dissimilatory iodate reduction (in OMZ, converts iodate to iodide in the dissolved pool), (d) remineralization of organic matter (converts POI to dissolved iodide), and (e) the reaction of IO_3^- and I^- with organic matter in sediments to produce POI and DOI (dissolved organic iodine; Francois, 1987).

We model the Arabian Sea as four compartments as shown in Fig. 6 to assess the source of excess total iodine to the OMZ. These compartments are the WOSL, the OMZ, deep water and sediments. Hydrothermal vents, which release high I^- concentrations (e.g., Guaymas Basin; Muramatsu and Wedepohl, 1998), are not considered as sources because the only known vents are in the Southern Indian Ocean (van Dover et al., 2001) well south of the Arabian Sea. Riverine sources for iodine to other ocean systems (e.g., Wong, 1991) are small whereas atmospheric sources for iodine are unknown; thus, these sources are considered to be minor in the Arabian Sea. The model addresses two aspects of iodine cycling, the flux of (total) iodine between model compartments and the transformations of iodine within a single compartment (between iodate and iodide and between particulate and dissolved iodine).

Processes contributing to the flux of iodine between compartments include (1) sinking of POC/POI, (2) up/downwelling, and (3) diffusive flux from sediments and advection to the intermediate water column.

4.1. Primary productivity—iodine relationships in the WOSL

Using six phytoplankton species, Udomkit (1994) showed that the I^- production rate in surface waters is typically lower than the IO_3^- uptake rate because some iodine is incorporated into the organism and some into dissolved organic iodine (DOI). Because of phytoplankton processing of IO_3^- to DOI, POI and I^- , Campos et al. (1996) developed a model that showed integrated concentrations of I^- are directly proportional to the primary productivity measured in surface waters of the Atlantic and Pacific Oceans. Table 1 shows that integrated surface layer I^- concentrations vary from station to station in the Arabian Sea during March and April 1995, but not in a uniform way with primary production. For example, primary productivity at S7 was 14% higher than that at S11, but I^- production was 50% higher at S11 than at S7.

In addition, primary productivity at S7 was 66% greater than that at HOT in the Pacific

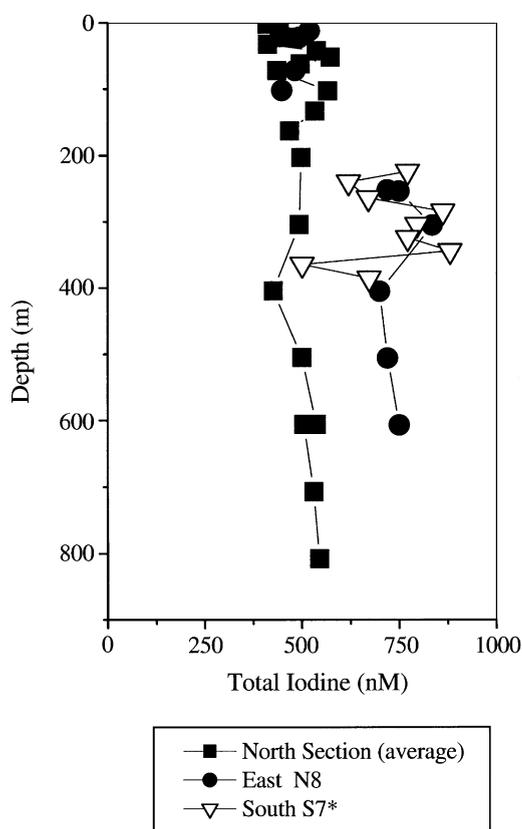


Fig. 4. Total iodine concentrations presented as an averaged value for stations N2 through N7, and N8. These stations are compared with iodide values from station S7. The averaged data presented for N2 through N7 are not statistically different from either the Atlantic or Pacific data presented in Campos et al. (1996). Error bars for the total iodine and iodide measurements shown are for 1 relative standard deviation (rsd) $n \geq 3$.

Ocean, which in turn is 77% greater than the productivity at the Bermuda Atlantic Time Series (BATS) in the Atlantic Ocean [$80 \text{ (mmol C m}^{-2} \text{ d}^{-1}$; Arabian Sea) $> 48 \text{ (HOT)} > 27 \text{ (BATS)}$]. Integrated I^- concentration at S7 in the Arabian Sea was 17% higher than at HOT and 40% greater than at BATS. These data show that the primary production/iodide proportionality does not directly apply to the Arabian Sea and may be due to rapid re-oxidation of I^- . Campos et al. (1996) estimated a half-life of 70 days for oligotrophic surface waters and iodide-iodate transformations may occur at this scale or shorter (compare station N2 this work and in Farrenkopf

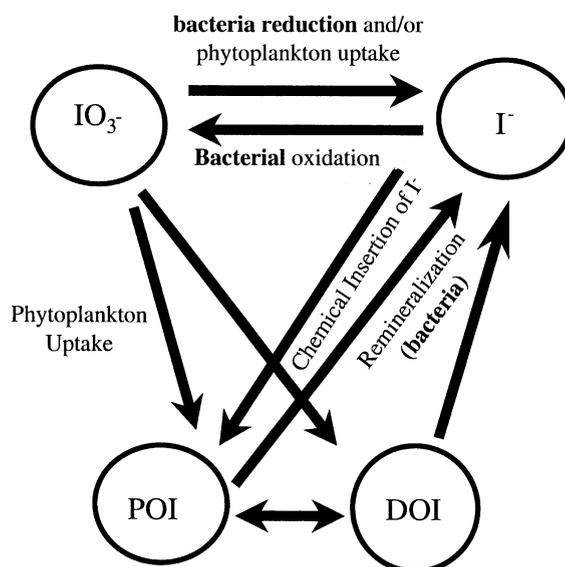


Fig. 5. Iodine Cycling. This cartoon is different from previous representations of the cycling of iodine in marine waters because of the emphasis on bacterial processes. Dissolved iodate is reduced to iodide and dissolved organic iodine (DOI). Iodide may be subsequently incorporated into particulate organic matter (POI) or oxidized. Iodide also may be formed as a result of remineralization of dissolved or particulate organic iodine. Calculations suggest that a maximum of 15 nM of iodide could be produced by the flux of carbon observed in the Arabian Sea. Recent work by Wong and Cheng (1998) suggests that DOI could account for up to 40 nM in surface waters. There does not appear to be a significant pool of DOI in the present study.

et al., 1997a). I^- oxidation may occur on the order of hours to days based on data from repeat hydrocasts in the WOSL and OMZ (Farrenkopf, 2000).

4.2. Dissimilatory reduction of iodate by bacteria in the OMZ

Bacterial dissimilatory reduction of IO_3^- in the OMZ of the Arabian Sea may play a significant role in maintaining I^- as the major iodine species. Culture experiments have shown dissimilatory microbial reduction of IO_3^- to I^- during the growth of *Shewanella putrefaciens* strain MR-4 (Farrenkopf et al., 1997b), which is closely related to *Pseudomonas/Alteromonas* group I, cultured from the Arabian Sea by Nair et al. (1994). Other

evidence to support the importance of bacterial redox processes within the OMZ include the presence of a nepheloid layer (Naqvi et al., 1993; Ramaiah et al., 1996; Gundersen et al., 1998), of a subsurface nitrite maximum (Morrison et al., 1998, 1999), and of a d-Mn²⁺ subsurface maximum (Fig. 2(a)–(e); Lewis and Luther, 2000). Other possible IO₃⁻ reductants include sulfide and organic matter. Significant sulfide levels were not observed in the OMZ during the Spring Intermonsoon; thus, sulfide does not contribute to IO₃⁻ reduction in the Arabian Sea. Reduction of IO₃⁻ by lactate (as a surrogate for natural organic matter) has been demonstrated but is very slow compared to that observed during shipboard incubations and in laboratory cultures (Farrenkopf et al., 1997b). Dissimilatory reduction of IO₃⁻ by bacteria accounts for maintaining iodine as I⁻ in the OMZ; however, it does not account for increases in total iodine. Therefore, sources of iodine external to the OMZ must be considered.

4.3. Oxygenated deep waters

Iodate predominates (90% to >99%) in waters below 1100 m to at least 100 m above the sediment water interface. Very little I⁻ was observed below the OMZ; in fact, the dissolved I⁻ concentrations in the deep waters were frequently below our detection limit (<0.2 nM). Lee et al. (1998) showed that little organic carbon was remineralized in waters below the OMZ, which indicates that POC (and POI) remineralization should be very small. Particulate organic iodine is found in surficial sediments of the Arabian Sea (Pedersen et al., 1992), so some sinking POC and POI does reach the bottom (Lee et al., 1998) and can be an important fraction of the carbon budget. Our dissolved iodine data indicate that there is negligible release of I⁻ from sediments or sinking POC to oxygenated deep water. No other information about iodine is available for deep waters.

4.4. Dissolved flux between OMZ and surface/deep waters

Excesses in total iodine concentration and high I⁻ concentrations occurred in the OMZ of the

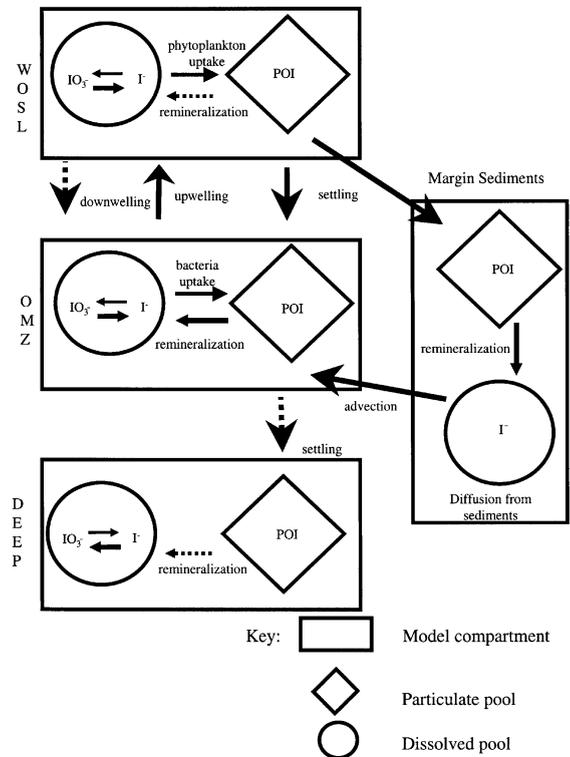


Fig. 6. The four components include: (1) well-oxygenated surface layer (WOSL), (2) oxygen minimum zone (OMZ), (3) deep water, and (4) margin sediments. Size of arrows indicates relative importance of processes in a particular model compartment with heavy arrows indicating the most important processes and dashed arrows indicating the least important process (or one of unknown importance). Iodine is transferred among model compartments and inter-converted among different forms within a single compartment.

eastern Arabian Sea during the spring intermonsoon period (Fig. 4). The area of enhanced iodine chemistry is shown with the irregular oval in Fig. 1. Excess total iodine concentrations were not observed at northwestern stations (N2 to N7) and western stations (S1 to S6) during the spring intermonsoon period. Upwelling from deep water and downwelling from the WOSL are not significant sources for I⁻ to the OMZ. Both surface and deep waters are depleted in I⁻ and total iodine relative to the OMZ so iodine flux is expected to be out of the OMZ. Although we cannot quantify the upwelling and downwelling contribution to

iodine flux, iodine flux to the OMZ is considered to be minor by these pathways.

4.5. Total iodine is not conservative with respect to salinity in the OMZ

Normalizing total iodine to salinity (also called specific iodine) permits an understanding of processes that occur in different water masses. Specific iodine values from several oceanic regimes are tabulated in Table 2. Lower values of specific iodine (10.7) in surface waters of the Black Sea have been related to carbon (and iodine) uptake followed by particle export from the euphotic zone to deeper and more saline waters of the OMZ with subsequent release of I^- on remineralization (Luther et al., 1991). In a study conducted at BATS and HOT, constant specific iodine values of ~ 13.2 were found at BATS whereas at HOT they were 6% lower in the upper 100 m (Campos et al., 1996). These decreased values in the upper 100 m were consistent with a loss of iodine associated with sinking particulate matter over the residence time (~ 10 yr) of the surface layer (Campos et al., 1996).

In surface waters at all stations along the northern section of the Arabian Sea (averaged over the upper 100 m), the values of specific iodine (13.2 to 13.4) were similar to values measured in both the Atlantic and Pacific Oceans (Campos et al., 1996). Total iodine data at station N2 during the Spring Intermonsoon showed small increases in specific iodine as a function of depth, and are similar to values obtained at a Pacific Ocean Vertex station by Rue et al. (1997). These data indicate that there is some POC/POI export flux from surface waters to the OMZ. In the Arabian Sea, specific iodine data from surface samples indicate that there was no large surface depletion of iodine, which is supported by POC export data from the WOSL to the OMZ (see below).

Total iodine concentrations and specific iodine values in the OMZ were almost twice the values found at BATS, HOT and the Vertex station (Table 2). Specific iodine increases with depth were also much higher than those observed in the Black Sea (Luther et al., 1991; Luther and Campbell, 1991). There is also precedent for elevated total

iodine concentrations in brines such as the Orca Basin (~ 750 nM, Wong et al., 1985) and the Mediterranean Sea (~ 1500 nM, Ullman et al., 1990). These basins accumulate total iodine because they are isolated and have long water residence times (e.g., Wong and Brewer, 1977; Ullman et al., 1990). Because these areas serve as a repository for the settling of POI, the remineralization of carbon and iodine produces high total iodine concentrations. The Arabian Sea OMZ residence time (on the order of 11 years; Swallow, 1984; Olson et al., 1993) is shorter than these basins, which indicates that carbon and iodine flux from the WOSL to the OMZ should not be important for producing elevated total iodine concentrations as shown below. In addition, excess total iodine in the Arabian Sea is not affiliated with a salinity-maximum; therefore, brines may be discounted.

4.6. POI flux from surface waters to the OMZ

Flux of particulate organic iodine from the WOSL to the OMZ in the Arabian Sea followed by remineralization may be calculated from the POC export and by assuming that the phytoplankton I/C molar ratio is 10^{-4} . POC flux in the Arabian Sea was variable and ranged from -0.3 to 25.8 $\text{mmol C m}^{-2} \text{d}^{-1}$ (Buesseler et al., 1998). Negative fluxes indicate net flux into the WOSL and positive values indicate net flux into the OMZ. The higher value was observed close to shore in the western portion of the basin. Values from eastern portions of the basin, where total iodine was enriched, had smaller POC fluxes ranging from -0.2 to 8.0 $\text{mmol C m}^{-2} \text{d}^{-1}$. Assuming $I/C = 10^{-4}$, POI flux from the WOSL to the OMZ could range from -0.020 to 0.80 $\mu\text{mol I m}^{-2} \text{d}^{-1}$. These POI fluxes based upon POC export would necessarily be upper limits since the other bioavailable, nutrient-like elements are observed in ratios less than Redfield stoichiometry (Redfield, 1958; Redfield et al., 1963; Morrison et al., 1998, 1999).

Using the phytoplankton I/C ratio of 10^{-4} , we calculate that a POC flux of at least 220 $\text{mmol C m}^{-2} \text{d}^{-1}$ (equal to 22 $\mu\text{mol I m}^{-2} \text{d}^{-1}$) would be needed to account for a 400 nM increase

in total iodine in the OMZ. This calculated POC flux is more than twice the primary productivity measured in the US JGOFS sampling area (Barber et al., 2001; Table 1). Moreover, the largest flux of POC recorded for the Spring Intermonsoon was only $8 \text{ mmol C m}^{-2} \text{ d}^{-1}$ (Buesseler et al., 1998). The POC flux calculation shows that POC export from the WOSL to the OMZ can account for only 3.6% of the excess in total iodine. Although, POI may be enriched in iodine relative to phytoplankton, this is unlikely because a larger remineralization signal in the phosphate or total nitrogen profiles is not observed (Fig. 7). Therefore, these data at the eastern Arabian Sea stations (like N8) do not reflect sinking particulate matter, but instead reflect another source of iodine at depth. Our observations agree with those of Naqvi and Shailaja (1993), who demonstrated that respiration in the OMZ could not be supported by sinking particles.

4.7. Sedimentary source of excess total iodine to the OMZ

Accumulation of I^- also has been attributed to release of dissolved I^- from sediments (Chapman, 1983) or advection of other water masses (Wong et al., 1985). But no distinct water masses are readily identifiable as advective sources in the Arabian Sea (Morrison, 1997; Hansell and Peltzer, 1998). Release of diagenetic Mn^{2+} from margin sediments to the OMZ has been proposed as the source for the deep Mn maxima observed by Lewis and Luther (2000) along both the northern and southern sections of the Arabian Sea. However,

excess total iodine was not observed in the western portion of the northern section (N2 to N7 in Figs. 1 and 4). Thus, the increased total iodine cannot come from the margin sediments of Oman and Pakistan. “Focussing” of particulate organic matter followed by offset remineralization (i.e. geographical displacement between carbon production and particle flux to the OMZ) has been hypothesized to explain the absence of a nearshore nitrite maximum in the northwestern portions of the basin (Naqvi et al., 1993; Gundersen et al., 1998). However, the amount of primary productivity produced in the WOSL cannot provide the elevated total iodine levels as shown above.

Sediments from the western margin of India are the likely source of I^- to the OMZ. Sedimentary organic material has an order of magnitude higher I/C molar ratio than that found for phytoplankton. I/C values from 10^{-3} to 3×10^{-3} have been reported in pelagic sediments (e.g., Kennedy and Elderfield, 1987). Although we do not have sedimentary iodine data from the sediments off western India, surface sediments of the Oman Margin are enriched in iodine with a molar I/C as high as 2.48×10^{-3} (Pedersen et al., 1992). This iodine enrichment in surface sediments is over one order of magnitude higher than that found in phytoplankton and should support dissolved I^- flux to the OMZ.

Although data supporting iodine flux to the Arabian Sea from the western margin sediments of India are not available, other areas are well characterized and we estimate iodine flux based on comparisons to these areas. Estuarine, hemipelagic and pelagic sediments provide a range of

Table 2
Total iodine normalized to salinity (specific iodine)

Pelagic integral	Atlantic	Pacific	Pacific*	Arabian sea		Black sea	Black sea integral
	BATS	HOT	Vertex III	N2	N8		
\int_0^{100}	13.2 ± 0.6	12.0 ± 0.6	13.4 ± 0.7	13.2 ± 1.8	13.4 ± 0.7	10.7 ± 3.0	\int_0^{65}
\int_{100}^{500}	13.2 ± 0.6	13.0 ± 0.9	14.3 ± 0.5	14.1 ± 1.1	20.9 ± 1.2	13.9 ± 0.6	\int_{65}^{95}
\int_{500}^{800}	na	14.4 ± 1.2	14.6 ± 0.2	14.8 ± 0.4	22.1 ± 0.6	15.3 ± 1.4	\int_{95}^{250}

BATS data and HOT Pacific data from Campos et al. (1996); Vertex III Pacific* data from Rue et al. (1997); Black Sea data from Luther (1991); Arabian Sea data from this study (March–April 1995 Spring Intermonsoon). Confidence intervals are based on one relative standard deviation for all the values used to calculate the average specific iodine for each depth interval.

dissolved I^- flux (e.g., Pedersen and Price, 1980; Francois, 1987; Kennedy and Elderfield, 1987; Ullman et al., 1988; Shimmield et al., 1990; Calvert and Pedersen, 1993). For example, Ullman and Aller (1980) and Ullman et al. (1988) reported a flux of I^- from estuarine sediments ranging from 5 to $41 \mu\text{mol m}^{-2} \text{d}^{-1}$, which is within the range of I^- flux ($22 \mu\text{mol I m}^{-2} \text{d}^{-1}$) needed to support the excess total iodine found in the OMZ. If the flux of I^- from porewaters to the OMZ is similar to or greater than the fluxes measured by Ullman and Aller (1980), then the flux of iodine from sediments can be responsible for the excess total iodine in the OMZ. Passier et al. (1997) measured porewater I^- concentrations from the sediments in the OMZ of the western Arabian Sea and found up to 6 times more dissolved I^- in these surface porewaters than those from the estuary investigated by Ullman and Aller (1980). Assuming similar chemical properties for eastern and western margin sediments of the Arabian Sea, we estimate that $\sim 96\%$ of the excess total iodine is derived from flux of dissolved I^- from western Indian margin sediments.

Excess total iodine as I^- was observed nearly 400 km off the coast. Thus, limited oxidative loss during transport across the basin is required, and the eastern OMZ of the Arabian Sea provides significant reducing conditions including IO_3^- reduction in the water column as discussed above. Sediment release of dissolved iodine was also

proposed for the Benguela Current upwelling system (Chapman, 1983). Flux of dissolved material to the OMZ of the Arabian Sea also was used to explain some aspects of denitrification and decreased oxygen concentrations (Naqvi, 1987) and of dissolved Mn^{2+} increases (Yadav, 1996; Lewis and Luther, 2000). In this study we were able to estimate the extent of dissolved I^- and total iodine flux from Indian margin sediments because total iodine exhibited non-conservative behavior only in the OMZ.

5. Conclusions

Dissimilatory reduction of iodate to iodide by bacteria does not account for increases in total iodine as iodide in the OMZ; i.e. total iodine is not conservative with salinity. Therefore deep external sources of iodine from lateral transport at sedimentary margins are needed. For both the well-oxygenated surface layer (WOSL) and the deep waters, total dissolved iodine is conservative with salinity. In the WOSL, IO_3^- uptake is dominated by phytoplankton physiology. In the oxygen minimum zone, IO_3^- uptake/turnover is dominated by bacterial reduction. In deep oxygenated waters, reduction of IO_3^- is not a quantifiable feature, although iodide does persist above the detection limit in some very deep waters.

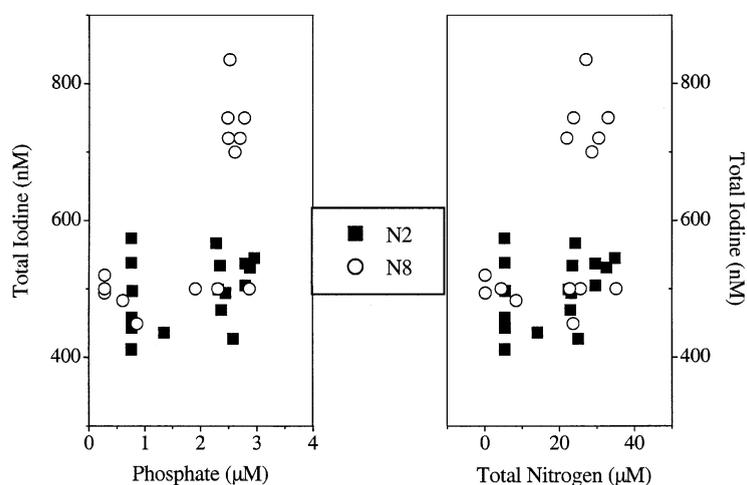


Fig. 7. (left panel) Total iodine vs. total inorganic phosphate; (right panel) total iodine vs. nitrogen.

The iodide profiles shown here from the 1995 Spring Intermonsoon period were significantly different from the subsurface iodide maxima observed during the 1992 Fall Intermonsoon (Farrenkopf et al., 1997a). The highest observed concentrations of dissolved iodide and total dissolved iodine in the open ocean are from the Arabian Sea as reported here. This observation is different from the previously existing paradigm of oceanic iodine cycling in which phytoplankton pathways were perceived as dominant regulators of speciation. The increase in total iodine concentration in the OMZ is one of the most convincing pieces of evidence to support the importance of sediment and associated porewater flux of dissolved species into the OMZ of the eastern Arabian Sea. Our data suggest that the source for denitrification in the OMZ of the eastern Arabian Sea may also have a strong sedimentary signature.

Acknowledgements

We are grateful for assistance from Captain Glen Gomes, the crew of the R/V *Thomas G. Thompson*, the nutrient technicians from the University of Washington, and the US JGOFS Office for logistical and cruise support. Revisiting the work of Hilary Kennedy and invaluable discussions with Tim Jickells, Vic Truesdale, Piers Chapman, and Lucia Campos helped with the interpretation of the data set. Special thanks to Chief Scientist John Marra, Lou Codispoti, Hugh Ducklow, John Morrison, Karen Wishner and Ken Brink for continued discussions. We also thank Janet Hering and the anonymous reviewers for comments and suggestions on earlier versions of this manuscript. This study was supported by National Science Foundation grants OCE-9217245 and OCE-9310792. This is US JGOFS contribution number 702.

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