



Processes controlling the distribution and cycling of manganese in the oxygen minimum zone of the Arabian Sea

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Abstract

Vertical and horizontal distributions of dissolved and particulate manganese were investigated in the Arabian Sea (Northwestern Indian Ocean) during the 1995 Spring Intermonsoon period (March–April; US JGOFS Process Cruise 2; TN045). The region is characterized by an intense, basin-wide oxygen minimum zone (OMZ) that strongly influences the manganese distribution. In the OMZ, two distinct dissolved Mn (d-Mn) maxima were observed, at depths of 200–300 m and 600 m, respectively. The latter peak displayed concentration maxima of approximately 6 nanomolar and was largely confined to stations north of 19°N latitude (Stations N2–N7). This mid-depth maximum was associated with the low oxygen core of the OMZ ($[O_2] < \sim 2 \mu\text{M}$), and appears to be maintained by a southward horizontal advective–diffusive flux of dissolved manganese from highly reducing Pakistan margin sediments, rather than input from the Oman Margin as previously suggested by Saager et al. (1989, *Geochimica et Cosmochimica Acta*, 53, 2259–2267). This signal was largely absent at stations along the southern transect, likely due to oxidative scavenging of d-Mn to the suspended particulate phase. Mid-depth particulate Mn maxima at some southern stations (Stations S4–S11) appear to be remnants of this feature. The upper d-Mn maximum (200–300 m depth) was more widely distributed than the 600 m peak, with d-Mn concentrations of ~ 3 to as high as 8 nm at most stations east of about 62°E longitude. The signal was everywhere correlated with the secondary nitrite maximum, at stations within the main denitrification zone delineated by Naqvi (1991). Nepheloid layers, presumably bacterial, also were associated with this depth interval. Particulate Mn profiles displayed corresponding concentration minima and low Mn/Al and reactive/refractory Mn ratios for this same depth interval, suggesting reductive

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dissolution of Mn-oxyhydroxides. These observations imply that in situ microbially mediated processes may be the predominant source of d-Mn in the upper OMZ, while horizontal advection is more important deeper in the water column. © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

Manganese was one of the first trace elements in the oceans for which reliable data were obtained. Studies of manganese cycling in the world's oceans span nearly 25 years, with most investigations focused upon the Pacific (Jones and Murray, 1985; Klinkhammer and Bender, 1980; Landing and Bruland, 1980,1987; Martin and Knauer, 1980,1982,1984,1985; Martin et al., 1985; Murray et al., 1983) and northern Atlantic Oceans (Bruland and Franks, 1983; Jickells and Burton, 1988; Kremling, 1985; Statham and Burton, 1986; Yeats and Bowers, 1985). More recent studies have added to the data base for manganese in the North Atlantic (Saager et al., 1997; Yeats et al., 1992), as well as extending that data base into the South Atlantic (Statham et al., 1998) and Indian Oceans (Morley et al., 1993; Saager et al., 1989).

From these investigations, a well-documented coherent picture of Mn cycling in the oceans has emerged. Representative profiles of dissolved manganese in the Atlantic and Pacific Oceans are shown in Fig. 1. The salient features of the marine manganese cycle are as follows:

- (1) Elevated surface layer concentrations of dissolved Mn (d-Mn), generally 1 to 2 nM in the central gyres, supported primarily by aeolian inputs and photo-reductive dissolution of Mn (Guieu et al., 1994; Shiller, 1997; Sunda and Huntsman, 1988), and increasing to several nM in coastal regions, where inputs via continental runoff and remobilization from reducing shelf and slope sediments predominate (e.g., Heggie et al., 1987; Jones and Murray, 1985; Trefry and Presley, 1982).
- (2) A rapid decrease in the d-Mn concentration with depth from surface values to near the top of the thermocline, to reach relatively uniform and constant values (< 0.5 nM) below 500–1000 m (e.g., Landing and Bruland, 1987; Morley et al., 1993; Statham et al., 1998), typical of elements with relatively short residence times and removal via particle scavenging. For manganese, the mechanisms for scavenging onto suspended particles appear to be microbial Mn oxidation (Cowen and Silver, 1984; Cowen and Bruland, 1985; Moffett, 1997; Sunda and Huntsman, 1987; Tebo et al., 1984) and/or passive scavenging onto the surface of biogenic and organically coated particles (Balistrieri et al., 1981; Martin and Knauer, 1980,1983,1984). Scavenging of manganese from dissolved to particulate phases is reflected in particulate Mn/Al ratios above average crustal values and high “reactive” (acetic acid leachable) to refractory particulate Mn ratios in oxygenated deep waters (e.g., Landing and Bruland, 1987; Martin and Knauer, 1982,1984; Statham et al., 1998).

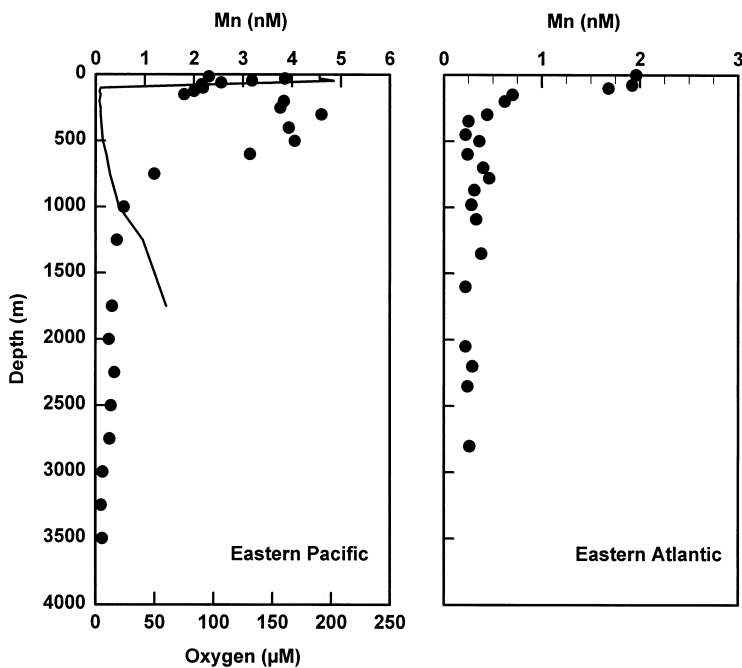


Fig. 1. Representative profiles of dissolved manganese (closed circles) versus depth in the eastern Pacific (after Landing and Bruland, 1987) and eastern Atlantic (after Statham et al., 1998). The eastern Pacific station illustrates the behavior of manganese in an oxygen minimum zone. The solid line shows the dissolved oxygen concentration versus depth.

- (3) Dissolved manganese maxima at intermediate depths in suboxic “oxygen minimum” zones (e.g., Klinkhammer and Bender, 1980; Landing and Bruland, 1980, 1987; Martin et al., 1985; Saager et al., 1989) or resulting from hydrothermal inputs (Jones and Murray, 1985; Klinkhammer et al., 1985; Massoth et al., 1999; Weiss, 1977). Corresponding minima in p-Mn and in p-Mn/Al and HAc/REF manganese ratios also have been observed (e.g., Landing and Bruland, 1987; Martin and Knauer, 1984). For the Pacific, Klinkhammer and Bender (1980) reported increased d-Mn levels where oxygen in the upper water column dropped below $100 \mu\text{mol/kg}$, with especially high d-Mn concentrations at stations where nitrate reduction occurred. Dissolved Mn maxima in suboxic zones are supported in part by in situ recycling of particulate organic matter and reductive dissolution of Mn oxyhydroxide phases exported from the surface layer and by horizontal advective inputs from margin sediments (e.g., Landing and Bruland, 1980, 1987; Martin and Knauer, 1984). The relative importance of each will vary depending upon distance from shore, local hydrodynamics, and the source strength of inputs to the surface layer.

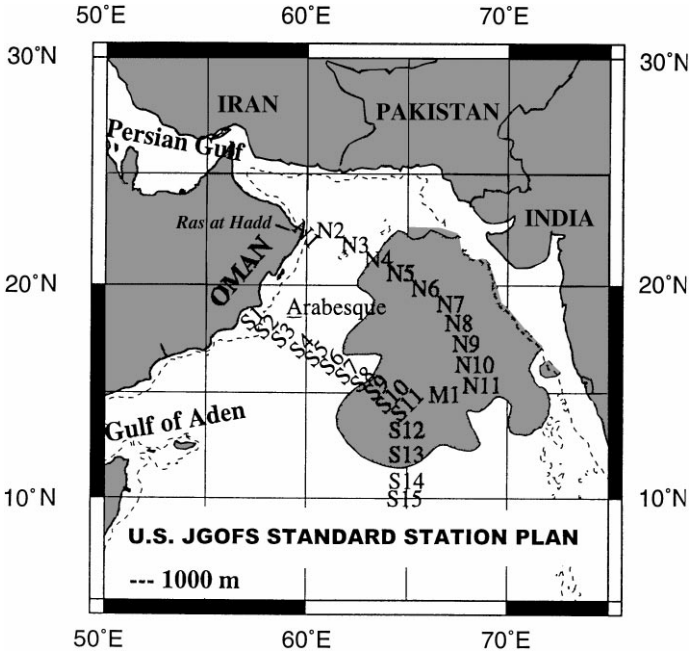


Fig. 2. Standard station positions for the US JGOFS Arabian Sea Process Study. The shaded region delineates the horizontal extent of the quasi-permanent secondary nitrite maximum ($\text{NO}_2^- > 1 \mu\text{M}$) region described by Naqvi (1991).

1.1. Manganese in the Arabian Sea

We report here the horizontal and vertical distributions of “dissolved” ($0.45 \mu\text{m}$ filterable or total dissolvable fractions) and suspended particulate manganese in the Arabian Sea oxygen minimum zone (OMZ) at stations throughout the US JGOFS study area. Samples were collected along the standard US JGOFS Arabian Sea cruise track (Fig. 2) in March and April 1995, during the Spring Intermonsoon period (R.V. *Thomas G. Thompson* cruise TN045). Profiles reported here are nearly identical to those previously observed by Saager et al. (1989).

The Arabian Sea is characterized by an intense, basin-wide oxygen minimum zone at intermediate depths (100–1200 m). Saager et al. (1989) have reported profiles for dissolved Mn at stations in this region, for samples collected during the fall of 1986 (Fig. 3). At stations in the northwestern Arabian Sea, they observed a strong mid-depth dissolved Mn maximum (4.5–6.5 nM) in the OMZ, centered at a depth of 600 m, and a local small maximum at 125 m associated with the Persian Gulf overflow water (Fig. 3; Station N2). The peak d-Mn concentrations at 600 m and the shape of the profiles were very similar to manganese profiles from the eastern Pacific, where a similar oxygen minimum exists (Fig. 1). Saager et al. (1989) attributed this signal to horizontal advection, supported by a flux of dissolved Mn

from Oman slope sediments, with transport northward with the Red Sea outflow water ($\sigma_\theta \sim 27.2$). Data presented in this report tend to refute this supposition, indicating instead that the source of dissolved Mn at this depth is most likely from the more reducing Pakistani margin sediments to the north. Dissolved Mn maxima observed by Saager et al. at two offshore stations (Fig. 3; Stations N7, M1) were thought to be related to another water mass. These maxima occurred at a depth interval of approximately 200–400 m in the upper OMZ, and were associated with secondary nitrite maxima. Similar d-Mn maxima were observed during the present study for stations within the main denitrification zone outlined by Naqvi (1991). Saager et al. (1989) suggested that the in situ reduction of Mn oxyhydroxides was the probable source of the d-Mn maxima at the offshore sites. Our findings are in keeping with this hypothesis.

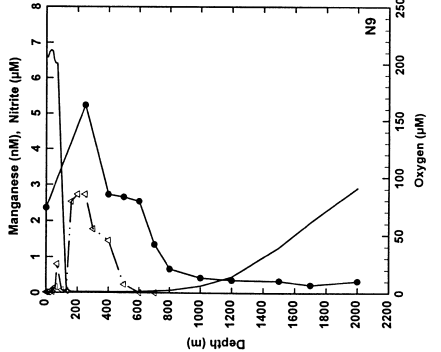
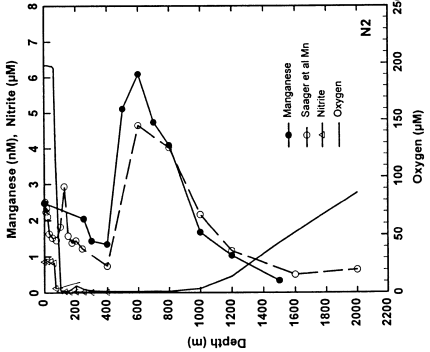
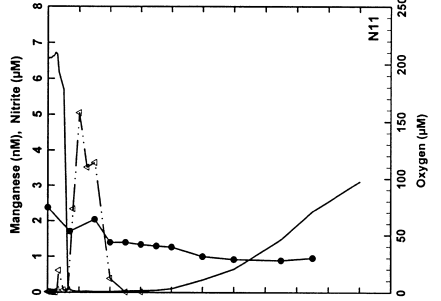
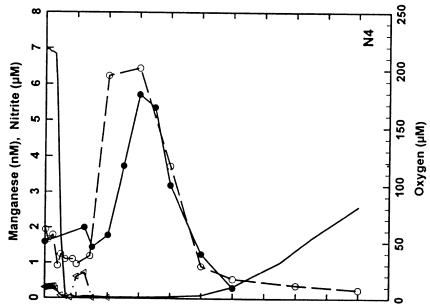
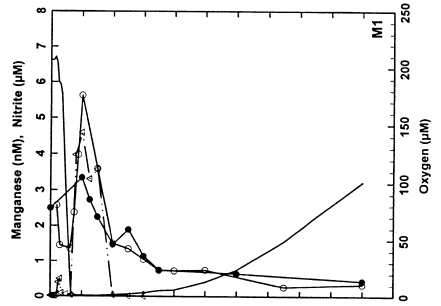
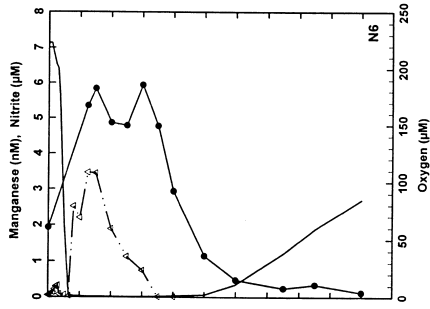
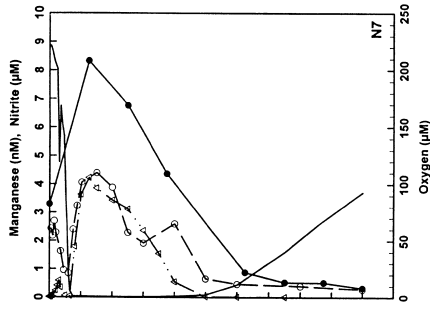
1.2. Study area

The Arabian Sea is a highly dynamic, wind-driven system, characterized by a seasonally reversing monsoonal circulation pattern, high surface water productivity and organic carbon fluxes, and a well-developed oxygen-minimum zone. Oxygen levels in the OMZ decrease northward from 10°S, reaching levels of less than five micromolar north of 15°N. The OMZ is maintained by a balance between oxygen consumption by organic matter oxidation and relatively rapid ventilation of intermediate depths. Although earlier reports (Wyrтки, 1973; Qasim, 1982) suggested restricted horizontal mixing at intermediate depths, more recent estimates of the average renewal time of OMZ waters range from 4 to 20 years, depending upon the total volume of water considered and other factors (Naqvi, 1987; Olson et al., 1994). Suboxic conditions in the OMZ thus appear to be maintained by rapid biological consumption as the oxygen sink and by the input of Indian Central Water (ICW) from the south, a water mass already low in oxygen (Naqvi, 1987; Olson et al., 1994; Swallow, 1984; You and Tomczak, 1993).

Dissolved oxygen concentrations in the core of the OMZ at the time of sampling were less than $\sim 1 \mu\text{M-O}_2$ throughout most of the study area. (See US JGOFS data base for Cruise No. TN045 at: <http://www1.who.edu/>.) The vertical thickness of the OMZ was greatest at stations in the northeast. Oxygen levels in the lower OMZ increased toward the south. Coincident with the OMZ were concentration maxima of nitrite, iodide, and dissolved manganese and iron (Farrenkopf, personal communication; Measures, 1997; Morrison et al., 1999; this study.) Levels observed were similar to those previously reported for the region (Farrenkopf et al., 1997b; Naqvi, 1991; Naqvi et al., 1990; Saager et al., 1989).

2. Methods

Strict attention was given to control of potential contamination sources at all stages of the study. All reagents were of the highest purity available. Sample bottles, plasticware, and filters were acid-cleaned, using procedures described in Landing and



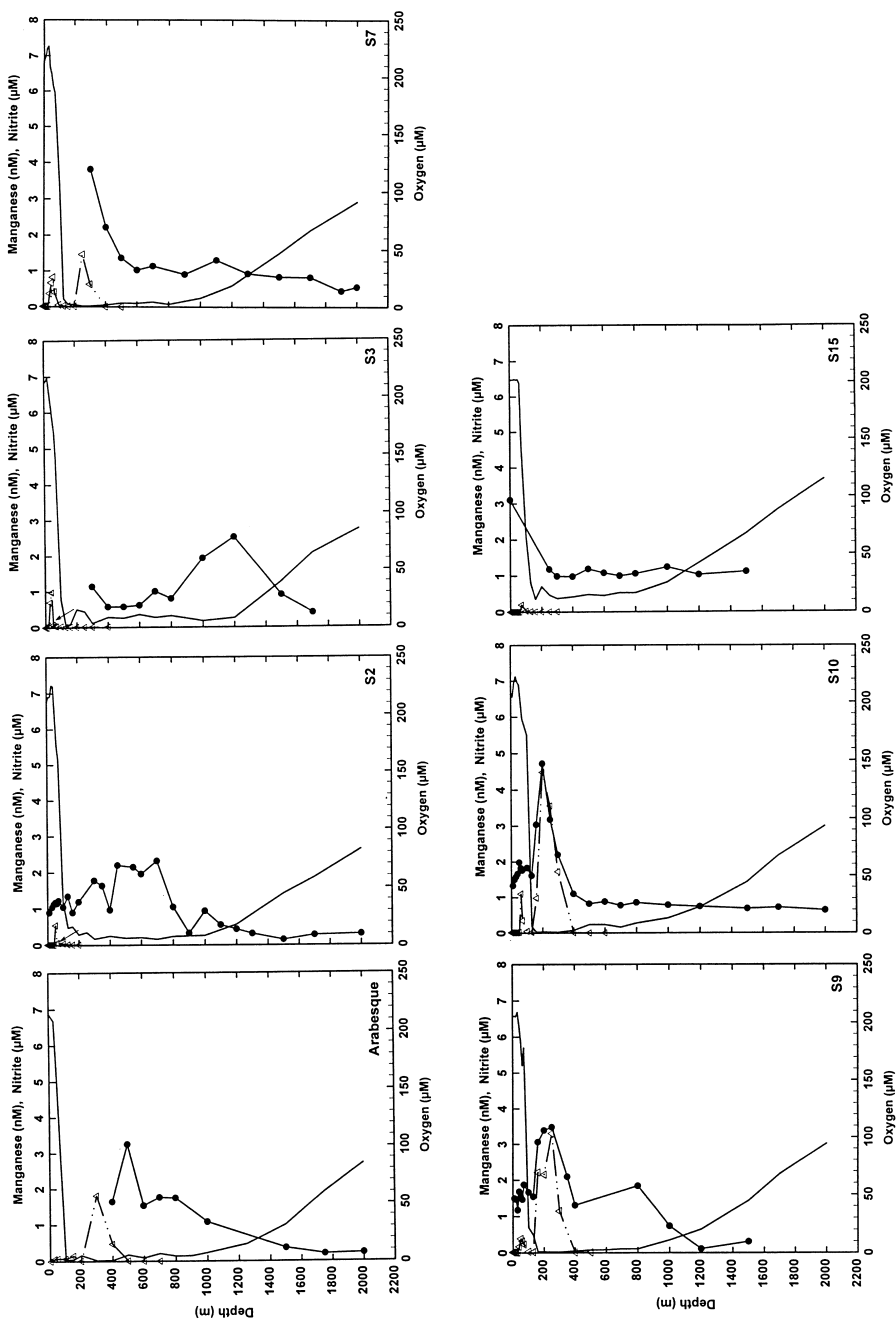


Fig. 3. Vertical profiles of “dissolved” (0.45 µm filtered or total dissolved) manganese (closed circles) versus depth during the 1995 Spring Intermonsoon period (March–April, 1995). Profiles of dissolved oxygen (solid line) and nitrite (open triangles) are also shown (after Morrison et al., 1998, 1999). Shown for comparison are dissolved Mn profiles reported by Saager et al. (1989) (open circles, Stations N2, N4, N7 and M1) for samples collected during the fall of 1986.

Lewis (1991). Ship-board sample processing was carried out in a 2 × 4 lumber and plastic enclosure equipped with Class-100 HEPA blowers to maintain a filtered, positive-pressure air supply within the clean area. Critical ship-board manipulations such as sample acidification and loading of filter sandwiches were carried out in a Class-100 clean bench within the clean enclosure. At the University of Delaware (UDEL) and at Kettering University, sample processing and analysis steps were performed in Class-100 clean benches.

2.1. Dissolved and total dissolvable manganese

Samples for total dissolvable (unfiltered) and dissolved (0.45 µm filtered) Mn were collected using a CTD rosette/bottle system, equipped with Niskin-type bottles constructed of PVC and equipped with silicon O-rings and plastic coated springs. Samples were collected in acid-cleaned Low-Density Polyethylene (LDPE) bottles, acidified to pH < 2 with sub boiling quartz distilled hydrochloric acid (“Q-HCl”; Seastar Chemicals, British Columbia), and stored double-bagged in zipper-seal polyethylene bags until analysis in our laboratory at the University of Delaware. At stations along the northern transect and at M1 and S15 (Fig. 2), subsamples for dissolved manganese were drawn from the Niskins into acid-cleaned polypropylene syringes and filtered through acid-cleaned 0.45 µm PVDF Gelman Acrodisc syringe filters. Although some differences were seen between filtered and unfiltered aliquots, particularly for deep-water samples, the features of the profiles were the same. Both filtered and unfiltered fractions are thus hereafter referred to as “dissolved” manganese (d-Mn). The reader is referred to the US JGOFS website for a compilation of the raw data (<http://www1.whoi.edu/>).

“Dissolved Mn” was quantified by Flow-Injection-Analysis with UV/VIS detection, using the method of Mallini and Shiller (1993). The method involves the Mn-catalyzed oxidation of tiron by peroxide to form a colored semiquinone, which is detected at 440 nM using an ISCO Model 228 LC UV/visible detector with a one centimeter pathlength low-volume flow cell. The signal is enhanced via on-line preconcentration of Mn using a 1-cm column of Toyopearl TSK-immobilized 8-hydroxyquinoline (Landing et al., 1986; Mallini and Shiller, 1993). The reaction is carried out at an optimum pH of ~ 9.6, using a buffered mixed reagent solution consisting of tiron (0.02 M) and 2,2'-dipyridyl (0.02 M) in an equimolar (0.25 M each) buffer of boric acid and sodium borate decahydrate (“Borax”). The pH of the mixed reagent solution is adjusted to pH 10 with small aliquots of Q-NH₃. Reagents were prepared using ASTM Type 1 water (18 megohm; “Q-water”). The reagent blank was determined daily by analysis of acidified Q-water (2 ml Q-HCL/L). Calibration curves (0–10 nM) were determined daily by standard addition of Mn²⁺ into aged Indian Ocean Deep Water (IODW). Manganese concentrations in selected samples (data not shown) were cross-checked by graphite furnace atomic absorption spectrometry following a preconcentration by chelation with APDC/DDDC and extraction into chloroform (Bruland et al., 1979).

2.2. Particulate metals

Samples for metals in suspended particulate matter were collected using a coated rosette equipped with 28.5 L Teflon-coated PVC ball-valve-type sampling bottles provided by the University of Washington. These bottles are modified to allow complete draining of the bottle contents (see Landing and Lewis, 1991, for details). Equipment and logistical problems early in the cruise limited sampling for particulate metals in the OMZ to stations along the southern transect.

Suspended particulate matter was collected by pressure filtration under filtered N₂ gas directly from the samplers. Samples were filtered through acid-cleaned 142 mm, 0.4 μm Nuclepore filters held in Teflon filter sandwiches. Filters were stored frozen for return to the University of Delaware. At UDEL, suspended particulates were extracted with a two-step sequential leaching procedure: (1) 25% Q-acetic acid (Q-HAc) for four hours at room temperature, to dissolve adsorbed cations, carbonate phases, and reactive Mn oxyhydroxides; (2) total digestion of the more refractory (REF) material, primarily detrital aluminosilicates (see Landing and Lewis, 1991). The latter procedure followed the method of Eggiman and Betzer (1976), modified for microwave digestion using PAR Model 4781 digestion bombs. Samples were analyzed at Kettering University by graphite furnace atomic absorption with matrix matching and standard additions, using a Perkin-Elmer Model 5000 AAS spectrophotometer equipped with a HGA 400 graphite furnace.

3. Results and discussion

3.1. “Dissolved” Mn

The distribution of d-Mn throughout the US JGOFS study area is shown in Fig. 3. Also shown are standard hydrographic data for dissolved oxygen and nitrite (Morrison et al., 1998; <http://www1.who.edu/>). For comparison, dissolved manganese data from Saager et al. (1989) are also shown.

Surface mixed layer and deep waters. Concentrations of d-Mn at the surface ranged from approximately 1–3.3 nM throughout the study area, with no apparent differences between northern and southern stations. Measures and Vink (1999) report similarly uniform distributions for surface water Al and Fe during the NE Monsoon and the subsequent Spring Intermonsoon period (Jan.–April). Surface d-Mn concentrations along the northern transect were similar to previously reported levels for the 1986 Fall Intermonsoon period (Saager et al., 1989; 2–3 nM). The surface mixed layer was densely sampled at Stations S9 and S10, in the center of the basin at approximately 15°N. Concentrations of d-Mn were relatively constant through the upper 130 m, below which they increased sharply, coincident with the onset of low oxygen conditions at the top of the OMZ.

Below the OMZ, dissolved manganese levels decrease to relatively constant levels in the 1200–2000 m depth interval, with most values ≤ 0.6 nM, in generally good agreement with values reported by Saager et al. (1989) for the region. Deepwater

d-Mn values at Stations N11 and S15, however, appear to be anomalously high (0.9–1.1 nM). Although the shape of the profiles is as expected for manganese, arguing against random contamination, the possibility of a systematic error for these two stations cannot be ruled out. A deep-water d-Mn maximum centered around 1200 m depth is seen at Station S3 (and perhaps at Station S2). These stations are close to the slope and Station S3 is in the vicinity of the Owens Fracture Zone (bottom depth at S3 was ~ 2400 m). This feature may thus be due to sediment resuspension and lateral advection from slope and/or ridge sediments. A similar feature is seen at a depth of 1700 m for Station N2, another nearshore site.

Oxygen minimum zone. Simultaneous with the decrease in oxygen levels into the OMZ, d-Mn levels at most stations increased by about a factor of two over surface values. The strongest signal was observed at stations along the northern transect, where values as high as 6 to nearly 8 nM were measured. Maximum d-Mn levels along the southern transect were somewhat lower, in the range of ~ 3 –5 nM. Two distinct Mn concentration maxima were observed in the OMZ at the northern stations, with peaks at approximately 250 m and at 600 m depth.

For dissolved Mn in the eastern Pacific, Klinkhammer and Bender (1980) and other investigators (e.g., Martin and Knauer, 1980, 1982) reported increased dissolved Mn levels in the upper water column when oxygen levels drop below $100 \mu\text{M}$, with particularly high d-Mn concentrations at sites where nitrate reduction is evident. A similar scenario is seen in the Black Sea, where dissolved Mn levels increase sharply in the suboxic zone ($[\text{O}_2] < \sim 6 \mu\text{M}$; Lewis and Landing, 1991). Fig. 4 illustrates that elevated Mn levels in the Arabian Sea OMZ correlated with the lowest oxygen concentrations in the OMZ, emphasizing the importance of suboxic conditions to the maintenance of high d-Mn concentrations in the OMZ. (The high Mn values at dissolved oxygen concentrations of $> 150 \mu\text{M}$ are for the surface layer). A similar correlation is found for the occurrence of the secondary nitrite maximum in the upper OMZ of the Arabian Sea, with almost all subsurface nitrite maxima occurring at dissolved oxygen levels well below $5 \mu\text{M}$ (Morrison et al., 1998). During the 1995 Spring Intermonsoon, secondary nitrite maxima and most d-Mn maxima in the upper OMZ occurred at oxygen concentrations $< 1 \mu\text{M}$.

Upper Mn peak. The upper d-Mn maximum in the Arabian Sea OMZ was centered at a depth of 200–300 m, along a potential density surface of 26.4 ± 0.2 . This maximum was previously reported by Saager et al. (1989), at $\sigma_\theta = 26.4 \pm 0.3$ (Fig. 3; Stations N7, M1). Along the northern transect, manganese concentrations at this depth increased dramatically from west to east, reaching a maximum at Station N7. The signal decreased somewhat to the south, but remained strong at stations in the central basin (Stations S7 to S10). The highest Mn concentrations for the upper maximum generally fell within the denitrification zone as delineated by Naqvi (1991), in the central and eastern sectors between approximately 13 – 22°N and 62 – 72°E (Fig. 2). In almost all instances, the signal was coincident with the secondary nitrite maximum (Fig. 3). An anomalously low Mn signal in the upper OMZ was observed at Station N11, the easternmost station sampled, but this was likely due to the sparse sampling distribution over the 100–300 m depth interval rather than to the absence of a Mn peak.

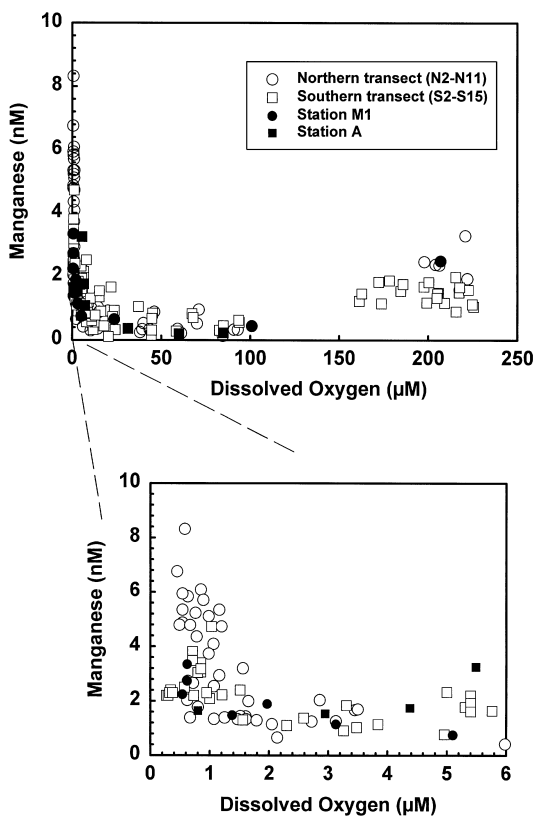


Fig. 4. Dissolved Mn versus oxygen in the upper 2000 m of the Arabian Sea water column. Elevated d-Mn concentrations are observed in the OMZ at oxygen levels below $\sim 2 \mu\text{M-O}_2$ and in the surface layer at levels above $\sim 150 \mu\text{M-O}_2$.

Unlike the broad d-Mn maximum at 600 m, the upper d-Mn peak is very sharp, suggesting fairly rapid cycling between dissolved and particulate phases and back again across the oxic/suboxic interface. The redox cycling of manganese under suboxic conditions has been well-documented for sediments (Froelich et al., 1979), in the eastern tropical Pacific (Landing and Bruland, 1987; Martin and Knauer, 1984) and in marine anoxic basins (Bacon et al., 1980; Jacobs et al., 1985, 1987; Lewis and Landing, 1991; Spencer and Brewer, 1971; Tebo et al., 1984). A typical pattern for manganese at oxic/suboxic interfaces is reductive dissolution of reactive Mn(+ IV/ + III) oxyhydroxide particulate phases, releasing soluble Mn^{2+} to the water column, and an upward flux and oxidative scavenging of Mn^{2+} to balance the reduction. The oxidation is catalyzed by Mn-oxidizing bacteria (e.g., Cowen and Bruland, 1985; Tebo, 1991; Tebo et al., 1984), and results in p-Mn maxima near the top of the oxygen gradient (e.g., Froelich et al., 1979; Lewis and Landing, 1991; Tebo, 1991).

As previously suggested by Saager et al. (1989), we propose that the coincidence of the upper Mn maxima with the secondary nitrite maxima in the OMZ implies in situ reductive dissolution of Mn-oxyhydroxides. Reduction of Mn-oxyhydroxides under suboxic conditions can occur via reaction with sulfide (Burdige and Neelson, 1986) or other chemical reductants, or they can be utilized by microbes as terminal electron acceptors to oxidize organic matter under anaerobic conditions (Myers and Neelson, 1988a,b). No free sulfide was measured in the Arabian Sea OMZ during the 1995 Spring Intermonsoon (Farrenkopf and Luther, unpublished data) nor during the fall of 1992 (Theberge et al., 1997), indicating that chemical reduction by sulfide is not an important process in controlling the Mn cycle in the OMZ. The occurrence of Mn-reducing bacteria in suboxic marine environments has been demonstrated for the suboxic zone of the Black Sea (Neelson et al., 1991; Tebo et al., 1991). Microbially mediated iodate reduction has also been proposed to explain subsurface iodide maxima in the Arabian Sea OMZ (Farrenkopf et al., 1997a,b). Also observed in this study were coincident minima in particulate Mn and in the p-Mn/Al and HAc/REF manganese ratios over this depth interval, as expected for the remobilization of reactive Mn phases (e.g., Landing and Bruland, 1987; Martin and Knauer, 1984).

The occurrence of the secondary nitrite maximum in the Arabian Sea OMZ is taken as a signal of active denitrification (microbial nitrate reduction to N_2 or N_2O), and is accompanied by a microbial activity maximum and light transmission minimum (Naqvi and Shailaja, 1993). Morrison et al. (1999) report intermediate nepheloid layers that correspond well with the regional extent of the secondary nitrite maximum, and hence the occurrence of the upper Mn maximum. These nepheloid layers are interpreted as an increase in particulates due to the presence and activity of bacteria, and it is likely that Mn-reducing bacteria, perhaps the highly versatile facultative anaerobe *Shewanella putrefaciens*, are the primary source of the dissolved Mn maximum (Neelson et al., 1991; Tebo et al., 1991). The same bacterium has been implicated in the reduction of iodate to iodide in the OMZ (Farrenkopf et al., 1997a).

One also may speculate as to the primary oxidant for the oxidation of Mn^{2+} to balance manganese reduction in the upper OMZ. The predominance of nitrate over oxygen in the upper OMZ ($\sim 30 \mu M NO_3^-$ vs. $< 5 \mu M O_2$) suggests that nitrate may be an important oxidant for dissolved manganese. Observations in the suboxic zone of the Black Sea water column (Lewis and Landing, 1991; Murray et al., 1995) and in margin and deep sea sediments (Aller, 1990; Luther et al., 1998; Schultz et al., 1994) have suggested that Mn^{2+} oxidation in suboxic environments in part may be coupled with nitrate reduction to $N_{2(g)}$. Sørensen et al. (1987) postulated such a process, which they termed “chemo-denitrification”, to account for discrepancies between measured microbial denitrification rates and estimated nitrate fluxes into sediments of the Madeira Abyssal Plain. Tebo (1991) speculated about a possible bacterial mediation of Mn^{2+} oxidation by NO_3^- in incubations of samples from the Black Sea suboxic zone. Based upon p_e (log K) values for the pertinent half-reactions, Luther et al. (1998) demonstrated that the oxidation of Mn^{2+} by NO_3^- to produce $N_{2(g)}$ is thermodynamically favorable over all pH's. (Reactions to produce nitrite or ammonia are shown to be possible under basic conditions, but are not as energetically favorable as N_2 production.) These studies support the hypothesis that nitrate may serve as an

oxidant for dissolved manganese in the upper OMZ of the Arabian Sea, although horizontal ventilation and seasonal changes in the depth of the oxic/suboxic interface may supply sufficient oxygen to also account for the manganese oxidation.

Mid-depth Mn peak. The mid-depth (~ 600 m) Mn maximum was very broad, from approximately 400–1000 m depth. This feature was readily apparent along the northern transect for Stations N2–N6 (Fig. 3). It was likely present at N7 as well, but appears to have been masked at this station by the very large upper Mn peak at 300 m. Moving southward from Station N7, the lower boundary of the OMZ began to shoal. With increased oxygen concentrations in the lower OMZ, the deeper Mn peak was absent or greatly decreased south of N7. At Station N9, the peak appeared as a shoulder on the upper maximum, and was reduced in concentration to < 3 nM. It was not observed at all as far south and east as Station N11. Along the southern transect, small Mn peaks below 400 m at Stations M1 and S9 may be the remnants of this feature. As oxygen levels in the OMZ increased southward, this signal disappeared entirely. Station S15, at approximately 10°N , showed constant Mn concentrations below 200 m depth, with no evidence of either an upper or a mid-depth Mn peak, despite oxygen concentrations still as low as 10–20 μM in the OMZ. This likely is due to the absence of active denitrification at this site and its distance from lateral advective sources to the north. Stations S2 and Arabesque also displayed Mn maxima in the OMZ, but the signals were less pronounced than at the northern stations. These stations lie along the Oman Margin, where oxygen levels in the OMZ were somewhat higher than at stations to the east and north.

The mid-depth maximum (~ 600 m) observed during the US JGOFS sampling agrees very well with that observed by Saager et al. (1989) at stations in the northwest Arabian Sea (Fig. 3; Stations N2, N4). This maximum occurs along a potential density surface of approximately 27.1. Since this density is the same as that of the Red Sea outflow ($\sigma_\theta \sim 27.2$), Saager and coworkers postulated that dissolved Mn diffusing from Oman Margin sediments into the OMZ was transported northward with the Red Sea water mass (RSW). However, the RSW is generally confined to south of about 17°N latitude (Rameshbabu et al., 1980), with preferentially southward transport along the Somali coast in winter (Meschanov and Shapiro, 1998). The RSW appears to have had a very minor influence upon the US JGOFS sampling region throughout 1995, with the salinity maximum for RSW evident only at Stations N11 and S15 (Morrison et al., 1998). Furthermore, sediments along the Oman Margin do not appear to be strongly influenced by suboxic diagenetic processes. Compared to other upwelling areas, sulfate reduction in Oman Margin sediments is a less important process than expected, perhaps due to more extensive degradation of organic matter prior to burial (Passier et al., 1997; Pedersen and Shimmield, 1991). Pedersen et al. (1992) have suggested that the preservation of organic carbon in shelf/slope sediments along the Oman Margin is associated with hydrodynamic factors, winnowing and reworking of the sediments, rather than with a low bottom-water oxygen content. During the Netherlands Indian Ocean Programme (NIOP), a boxcore collected on the Oman continental slope within the OMZ ($19^\circ30'\text{N}$, $58^\circ26'\text{E}$; water depth = 527 m) showed no evidence of manganese reduction in the sediments, with no significant

variation in either porewater dissolved Mn or solid phase reactive Mn-oxyhydroxides to a depth of 25 cm in the core (Passier et al., 1997).

The Oman Margin sediments do not then appear to be the most likely source for supporting the Mn maximum at 600 m. Neither is there a coincident nitrite maximum, as is seen for the upper Mn peak at 300 m, suggesting that it does not arise from *in situ* microbial reduction in the water column. We postulate that the primary manganese source supporting the mid-depth maximum at stations along the northern transect is a flux of Mn^{2+} from the more highly reducing Pakistan Margin sediments. During the NIOP sampling program, the Pakistan Margin exhibited significant sulfate reduction. Porewater samples analyzed a month after collection contained significant thiosulfate, in part from the oxidation of sulfide during storage, implying sulfide levels of > 1 mM (Luther, unpublished data). This is compared to undetectable thiosulfate and sulfide (< 1 and < 0.02 μM , respectively) in the upper 20 cm of Oman Margin sediments (Passier et al., 1997). The d-Mn flux appears to be transported southward along a density surface of approximately 27.1, with removal of d-Mn by oxidation and particle scavenging as it is advected southward, resulting in corresponding broad particulate manganese maxima observed at 400–700 m depth at Stations S4–S11 (Fig. 5). Evidence provided by the Indian JGOFS program (Yadav, 1996) suggests that Mn reduction in sediments on the western continental margin of India may also be a significant source of dissolved Mn to the OMZ, particularly for stations along the southern transect.

3.2. Particulate manganese

The biogeochemical and physical processes that control the manganese content of the suspended particulate phase across suboxic boundaries can be implied from vertical profiles of total particulate Mn (p-Mn) and from selective or sequential leaching procedures (Landing and Bruland, 1987; Landing and Lewis, 1991). Treatment of particulate samples with 25% acetic acid allows estimation of the abundance of amorphous Mn-oxyhydroxides. High ratios of “reactive” (HAc-leachable) to refractory (REF) manganese and total p-Mn maxima are indicative of oxidative scavenging of dissolved manganese to the particulate phase, while low HAc/REF ratios and p-Mn minima suggest reductive dissolution (Landing and Bruland, 1987).

Fig. 5 shows profiles for total, HAc-leachable, and refractory suspended particulate Mn (p-Mn) at stations along the southern transect. As noted earlier, suspended particulates were collected using large volume (28.5 L) samplers, modified to allow filtration of the entire sample, rather than the Niskin-type bottles used to collect d-Mn samples. Although the sample depths and stations for p-Mn do not coincide exactly with those for d-Mn, the general patterns observed for each are consistent with the redox processes expected for Mn in suboxic environments. Total p-Mn concentrations along the southern transect were generally less than 0.4 to 0.6 nM, with lower overall concentrations at stations in the center of the basin (S7–S13). Surface layer p-Mn concentrations were highest at the nearshore stations, S2 and S3, decreasing to ≤ 0.2 nM off shore. The p-Mn fractionation in the OMZ was largely dominated by the HAc fraction, indicating the importance of reactive Mn-oxyhydroxides and

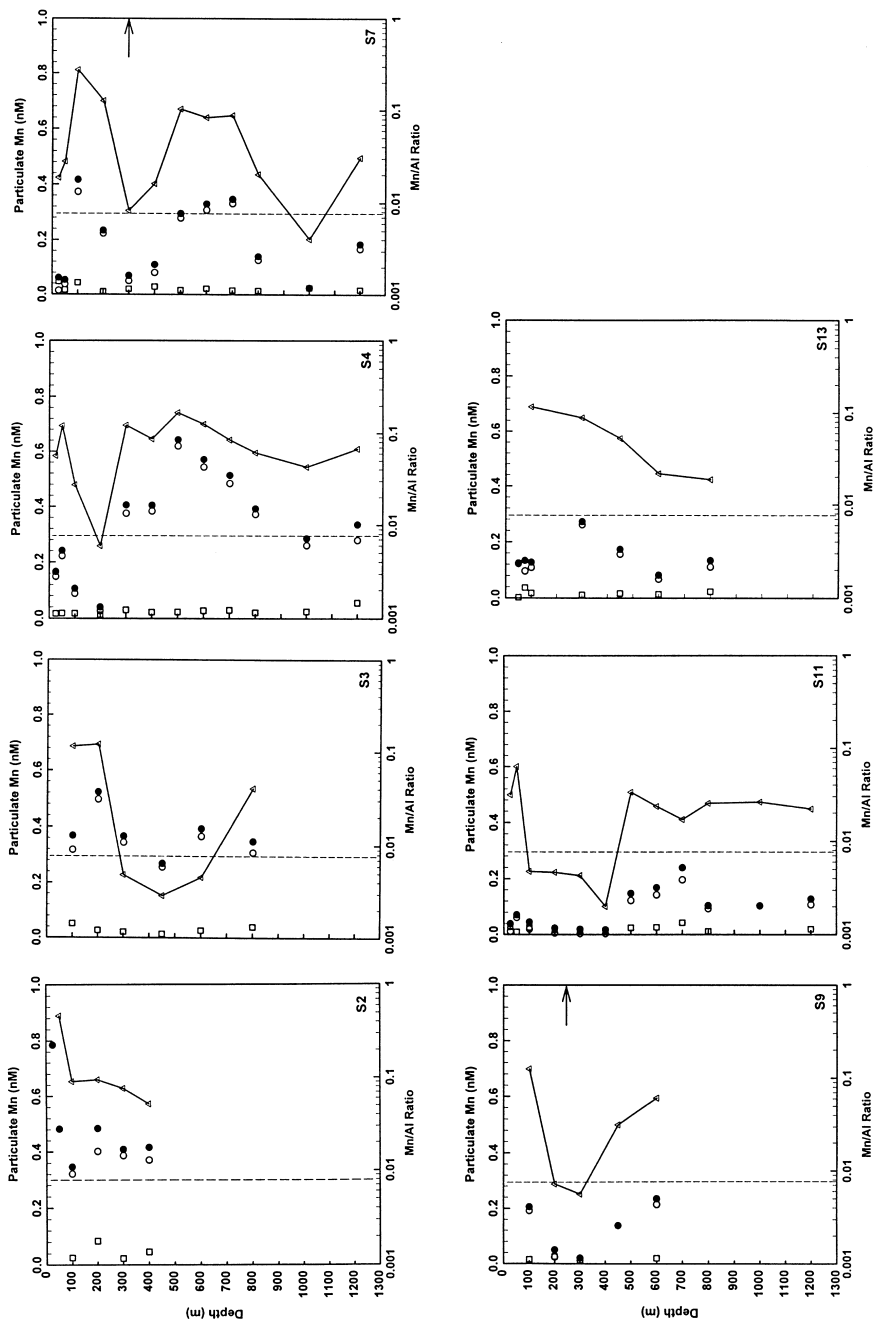


Fig. 5. Vertical profiles of total (closed circles), reactive (HAc-leachable; open circles), and refractory (open squares) manganese in suspended particulate matter. An arrow shows the approximate depth of the d-Mn maximum at Stations S7 and S9. Also shown is the total p-Mn/Al ratio (open triangles). The vertical dashed line is the Mn/Al ratio for average crustal material (see Faure, 1991, Table 10.5).

adsorbed Mn. Refractory manganese concentrations were low (< 0.08 nM) and nearly constant with depth. Stations S2 and S3, located to the west of the denitrification zone, displayed relatively constant p-Mn concentrations throughout the water column. A broad minimum in the Mn/Al ratio is seen at Station S3 at 200–800 m depth. The source of this feature is not readily apparent, but may represent resuspension and horizontal advection of slope sediments. The feature is not observed, however, at Station S2. Stations S4–S11 exhibited distinct p-Mn minima (0.01–0.02 nM) and low HAc/REF Mn ratios in the upper OMZ (100–400 m), coincident with secondary nitrite maxima (Morrison et al., 1999; <http://www1.who.edu>) and the d-Mn maxima observed at stations in this portion of the transect (Figs. 3 and 5). The profiles indicate in situ manganese oxyhydroxide reduction (Landing and Bruland, 1987). Particulate Mn/Al molar ratios at these stations display the same trends, with relatively constant ratios some 2–15 times above average crustal material throughout much of the water column, and a minimum Mn/Al ratio in the upper OMZ at Stations S4–S11. The latter is again indicative of the reductive dissolution of reactive p-Mn phases. Stations S4–S11 also displayed total and HAc p-Mn maxima at 50–100 m, near the top of the oxic/suboxic gradient, and broad maxima deeper in the OMZ at 400–800 m. The upper maxima are likely the result of vertical upward advective–diffusive mixing and microbial oxidation of dissolved manganese from the upper d-Mn maximum, as seen in sediments (Froelich et al., 1979) and anoxic basins (Tebo et al., 1984; Tebo, 1991). Station S13, south of S11, showed a p-Mn maximum at 300 m, perhaps due to southward mixing and oxidation of d-Mn in this same layer. The deeper p-Mn maxima (400–800 m) seen at Stations S4–S11 are also likely a horizontal advective feature, resulting from southward mixing and oxidation of the 600 m d-Mn maxima observed at the northern stations. Vertical mixing from the upper d-Mn peak may also contribute to this maximum.

The p-Mn distribution and fractionation observed along the southern transect support the hypotheses stated previously: (1) active in situ Mn cycling in the central basin at 200–400 m depth, more or less coincident with the top of the suboxic zone and the occurrence of secondary nitrite maxima, and (2) a southward advective flux at approx. 600 m of Mn^{2+} from Pakistan Margin sediments, with oxidation to Mn-oxyhydroxides as oxygen levels in the lower OMZ increase.

4. Summary

During the 1995 Spring Intermonsoon, two distinctly different signals for total dissolvable manganese were observed in the oxygen minimum zone. The major processes maintaining the d-Mn maxima in the OMZ appear to be different. The broad mid-depth maximum, centered around approximately 600 m depth, was largely confined to stations along the northern transect, with the highest observed concentrations in the northwestern section (Stations N2–N6). There was no accompanying nitrite maximum associated with the 600 m Mn peak, suggesting that denitrification was not active at this depth. The signal was greatly decreased or absent at stations along the southern transect, likely due to shoaling of the lower boundary of the OMZ

and subsequent oxidation of manganese to particulate Mn-oxyhydroxides. The broad mid-depth particulate Mn maximum observed at Stations S4–S11 was likely the remnant of this feature. These observations suggest that the source of dissolved Mn maintaining the mid-depth d-Mn maximum is diagenetic reduction of manganese oxides in Pakistan Margin sediments along the northern boundary, with lateral advective-diffusive transport southward into the study region, rather than input from the Oman Margin as previously suggested by Saager et al. (1989).

In contrast, the upper OMZ d-Mn maximum, centered around 200–300 m depth, was more widely distributed and appeared to be a predominantly in situ feature. The highest d-Mn concentrations were observed in the central basin, within the denitrifying zone. The upper d-Mn signal correlated with the secondary nitrite maximum and with intermediate nepheloid layers. Minima in reactive p-Mn were also observed in this layer. Saager et al. (1989) observed a similar correlation between d-Mn and the occurrence of high nitrite for sampling in the fall of 1986 at two stations along 67°E longitude. These observations imply active in situ microbially mediated redox cycling of manganese in the upper OMZ, as observed in other suboxic environments.

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