



Vertical and temporal variability of redox zonation in the water column of the Cariaco Basin: implications for organic carbon oxidation pathways

Tung-Yuan Ho^{a,*}, Gordon T. Taylor^a, Yrene Astor^b, Ramon Varela^b,
Frank Müller-Karger^c, Mary I. Scranton^a

^aMarine Sciences Research Center, State University of New York at Stony Brook, Stony Brook, NY 11794-5000, USA

^bEstación de Investigaciones Marinas de Margarita (EDIMAR), Fundación La Salle de Ciencias Naturales,
Apartado 144, Punta de Piedras, Edo. Nueva Esparta, Venezuela

^cDepartment of Marine Sciences, University of South Florida, St. Petersburg, FL 33701, USA

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Abstract

Temporal and vertical variability in the concentrations of major electron acceptors and donors (O_2 , NO_3^- , particulate Mn and Fe, dissolved Mn^{2+} and Fe^{2+} , and HS^-) were investigated in the water column of the Cariaco Basin between 1995 and 1999. Vertical profiles of the redox species during upwelling and non-upwelling periods reflected the zonation of aerobic respiration, denitrification, metal reduction, and sulfate reduction in the water column and varied widely over time scales of months to years. Comparisons of these profiles with distributions of organic carbon production and acetate uptake suggest that the rate of organic carbon supply was the major control on the variability. Inhibition and enrichment experiments suggested that sulfate reduction was not a dominant pathway for organic carbon oxidation near the oxic/anoxic interface. Instead, the reduction of metal oxides, elemental sulfur, and/or thiosulfate is likely to be more important. Estimates of vertical fluxes showed that vertical diffusive transport of the major electron acceptors (oxygen, nitrate, and metal oxides) only accounted for less than 10% of the oxidation of organic carbon produced near the suboxic/anoxic transition zone. Thus, horizontal oxic mid-water intrusions coupled with strong internal redox recycling of the major redox species occur to supply additional electron acceptors for organic carbon oxidation near the redox transition zone.

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1. Introduction

Redox zonation, the vertical segregation of major electron acceptors and their reduced products, reflects the spatial separation of major organic carbon oxidation pathways in anoxic water columns and sediments. Sequential depletion of the major electron

* Corresponding author. Current address: Institute of Earth Sciences, Academia Sinica, Nankang, Taipei, Taiwan. Tel.: +886-2-27839910x609; fax: +886-2-27839871.

E-mail address: tyho@earth.sinica.edu.tw (T.-Y. Ho).

acceptors and appearance of the reduced products tends to occur in the order of decreasing free energy yield (Froelich et al., 1979; Table 1). Aerobic respiration occurs first, followed by denitrification, metal reduction, and sulfate reduction (Fig. 1). The spatial distribution of these successive reactions in anoxic water columns usually extends from meters to hundred meters (Fig. 1). In comparison with the relatively narrow depth range occupied by the sequence of redox reactions in sedimentary environments, the much wider dispersal of the reactions in water columns offers a major sampling advantage for studies of the redox reactions.

The Cariaco Basin, a permanently anoxic marine basin, is located on the continental shelf of Venezuela in the Caribbean Sea. Coastal upwelling occurs annually between January and May in the region surrounding the Basin, and this triggers elevated primary production and vertical fluxes of organic carbon throughout the region (Müller-Karger et al., 2001). The oxidation of the large amount of organic matter produced in the basin, combined with restricted circulation of the deep water, leads to complete consumption of oxygen in the basin at depth. The suboxic/anoxic

interface (defined as the first appearance of sulfide or the first depth at which oxygen was measured to be undetectable if sulfide was not measured) varied in depth from 220 to 350 m between 1995 and 2000 (Müller-Karger et al., 2001). In addition to primary production in surface waters, carbon also is fixed by chemoautotrophic activity at high rates (factors of 0.1 to 3.3 times of contemporaneous primary production) at and just below the suboxic/anoxic interface (Taylor et al., 2001). This temporal and vertical variability of organic carbon production, as well as the anoxic character of the water column makes the basin an ideal site to investigate the interaction between the distribution of the major electron acceptors/donors and organic carbon diagenesis.

The goal of the present study was to examine the vertical and temporal variability of the redox zonation and its relationship to organic carbon supply. As part of the international CARIACO (Carbon Retention In A Colored Ocean) program, rates of primary production (Müller-Karger et al., 2001), POC fluxes (Thunell et al., 2000), chemoautotrophic production (Taylor et al., 2001), and acetate uptake (Ho et al., 2002) were all measured in the water column. This study capitalizes on these rate and flux data.

A secondary objective of our work was to evaluate the relative importance of major oxidants for organic carbon across the suboxic/anoxic interface in this system. In general, sulfate reduction has been thought to dominate the oxidation of organic matter in marine anoxic water columns. In our work, inhibition and enrichment experiments coupled with the vertical flux estimates of the major electron acceptors have been used to assess the relative importance of organic carbon oxidation pathways in the anoxic Basin.

2. Methods

2.1. Sampling and analysis of the redox species

The sampling site was located in the eastern sub-basin of the Cariaco Basin (10.50°N, 64.66°W) in nearly 1400 m of water. All of the samples were collected aboard the B/O *Hermano Gines*, operated by the Fundación La Salle de Ciencias Naturales, Venezuela. Seawater was collected using 8-l Niskin bot-

Table 1
Terminal electron acceptors with acetate oxidation and corresponding standard state free energy yield

Sequential redox reactions	(kJ/mol acetate)	References
1. Aerobic respiration $\text{CH}_3\text{COO}^- + 2\text{O}_2 \rightarrow 2\text{HCO}_3^- + \text{H}^+$	$\Delta G^{0'} = -854$	Thauer et al., 1989
2. Denitrification $5\text{CH}_3\text{COO}^- + 8\text{NO}_3^- + 3\text{H}^+ \rightarrow 4\text{N}_2 + 10\text{HCO}_3^- + 4\text{H}_2\text{O}$	$\Delta G^{0'} = -802$	Payne, 1981
3. Manganese reduction $\text{CH}_3\text{COO}^- + 4\text{MnO}_2 + 7\text{H}^+ \rightarrow 4\text{Mn}^{2+} + 2\text{HCO}_3^- + 4\text{H}_2\text{O}$	$\Delta G^{0'} = -727$	Lovley and Phillips, 1988
4. Iron reduction $\text{CH}_3\text{COO}^- + 8\text{FeOOH} + 15\text{H}^+ \rightarrow 8\text{Fe}^{2+} + 2\text{HCO}_3^- + 12\text{H}_2\text{O}$	$\Delta G^{0'} = -107$	Thauer and Morris, 1984
5. Sulfate reduction $\text{CH}_3\text{COO}^- + \text{SO}_4^{2-} \rightarrow 2\text{HCO}_3^- + \text{HS}^-$	$\Delta G^{0'} = -63$	Widdel and Pfennig, 1977
6. Sulfur reduction $\text{CH}_3\text{COO}^- + 4\text{S}^0 + 4\text{H}_2\text{O} \rightarrow 2\text{HCO}_3^- + 4\text{HS}^- + 5\text{H}^+$	$\Delta G^{0'} = -39$	Pfennig and Biebl, 1976
7. Methanogenesis $\text{CH}_3\text{COO}^- + \text{H}_2\text{O} \rightarrow \text{HCO}_3^- + \text{CH}_4$	$\Delta G^{0'} = -36$	Müller et al., 1993

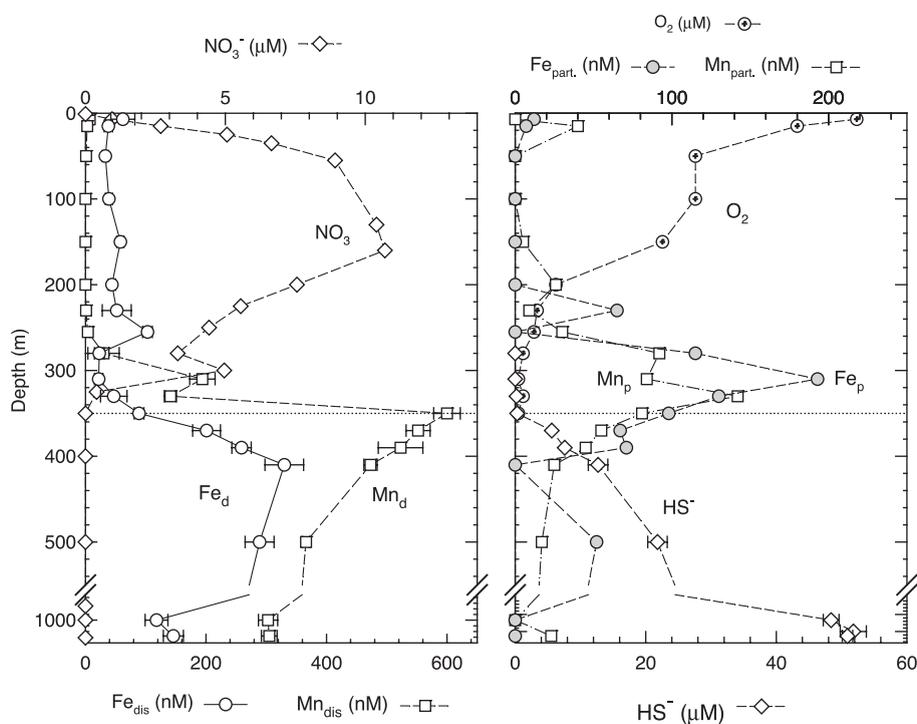


Fig. 1. Vertical profiles of major electron acceptors and their reduced products in the water column of the Cariaco Basin (CAR-29, March 1998). Dotted line represents the suboxic/anoxic interface (defined as the first appearance of sulfide or the first depth at which oxygen was measured to be undetectable if sulfide was not measured). Error bars represent 1 standard deviation ($n=3$).

tles mounted on a rosette equipped with a Seabird CTD. When drawing samples, the top of each Niskin was supplied with N_2 gas to prevent oxygenation of seawater during sampling. For oxygen, samples were fixed on board and were measured at EDIMAR by a modified Winkler method (Aminot, 1983). Precision of replicate analyses of oxygen was better than $1 \mu\text{M}$ at a $10\text{-}\mu\text{M}$ concentration level. Nitrate was determined by standard colorimetric methods (Strickland and Parsons, 1972). Hydrogen sulfide concentrations were measured colorimetrically using a modification of the method of Cline (1969). Seawater samples (4 ml) were collected with no bubbles using a 5-ml Precision gas-tight syringe and were added to vials containing Zn-acetate or $ZnCl_2$ solution. Precision of triplicate measurements was better than 10% for concentrations greater than $1 \mu\text{M}$. Potential temperature, salinity, and density (σ_θ) data were obtained from the CTD profiles for the casts from which samples were collected.

For dissolved metal (Mn and Fe) measurements, seawater was filtered using $0.45\text{-}\mu\text{m}$ acid-washed polycarbonate syringe filters which were first acid-washed and then pre-rinsed with sample. Total Mn and Fe concentrations were obtained from unfiltered samples. All samples for metal analysis were collected and stored in acid-washed polypropylene vials and were treated with concentrated trace metal grade HNO_3 or HCl to yield a final acid concentration of 0.5 N. Metal concentrations were determined by graphite furnace atomic absorption spectrometry (Hitachi Z-8100). Calibration curves were prepared using 25% Cariaco surface water and 75% 1 N trace metal grade nitric acid in a manner similar to the samples. The concentrations of particulate Mn and Fe were calculated as the difference between unfiltered and filtered concentrations (Balistrieri et al., 1992). The metal concentrations in the anoxic zone were two to three orders of magnitude higher than the concentrations in the open ocean. Precision of more than

90% triplicate analysis of Mn was better than 10% relative standard deviation ($100 \times \text{standard deviation}/\text{mean}$) for samples with concentrations exceeding 100 nM; for Fe, the precision of over 80% of the triplicate measurement was better than 20% of relative standard deviation for samples with concentrations exceeding 100 nM, indicating relatively low contamination during sampling and analytical processes.

2.2. Acetate uptake

Acetate uptake rate constants were determined using a radiotracer method modified from Hobbie and Crawford (1969) and Lee (1992). Each acetate uptake rate constant (respiration and incorporation) was based on sacrifice of individual vials at three to five time points. Correlation coefficients (r^2) for time course data were generally good, at 80% better than 0.7. Rate constants determined for time courses with correlation coefficients less than 0.6 were discarded, which were mostly deep water samples (Ho et al., 2002). Acetate concentrations were determined using an HP5890A gas chromatograph with a flame ionization detector and an HP FFAP 530- μm fused silica column (Hordijk et al., 1990). A static membrane diffusion technique was used for preconcentrating samples for acetate concentration measurements (Yang et al., 1993). Details of the methods are described in Ho et al. (2002).

2.3. Inhibition and enrichment experiments

The use of specific inhibitors to block microbial metabolism is a simple and effective method to evaluate the importance of particular microbial reactions. In the present study, the significance of sulfate reduction for organic carbon oxidation across the suboxic/anoxic interface was evaluated using a molybdate inhibition technique (Oremland and Capone, 1988). The effect of molybdate on sulfate reduction can be evaluated by measuring the acetate oxidation rate in the presence and absence of molybdate as acetate is commonly found to be a major substrate for sulfate reducers in anoxic sediments (Christensen and Blackburn, 1982). Both sulfate reduction and acetate oxidation should be inhibited in the presence of molybdate if sulfate reduction is the dominant pathway for organic carbon oxidation. The acetate oxida-

tion rates with and without molybdate added were determined by measuring the production rate of $\text{H}^{14}\text{CO}_3^-$ in the time course incubation samples. The procedures were the same as for the measurement of the acetate uptake rate constant (Ho et al., 2002), except that 1 ml of N_2 -purged molybdate solution was added to the 40-ml incubation vials immediately before the addition of ^{14}C -acetate. Final concentrations of molybdate were 20 mM.

The potential importance of other organic carbon oxidation pathways was examined by enriching samples with other electron acceptors, including MnO_2 , FeOOH , S_0 , and $\text{S}_2\text{O}_3^{2-}$ and measuring acetate oxidation. This approach assumes that the oxidation of organic carbon near the suboxic/anoxic interface is limited by supply of electron acceptors, so addition of extra electron acceptors should enhance the oxidation rate of organic substrates. By comparing the response of acetate oxidation rates to the addition of specific electron acceptors, the potential importance of the organic carbon oxidation pathways may be assessed.

Mn oxides used for enrichment experiments were prepared by oxidation of MnCl_2 with permanganate (KMnO_4) under basic conditions (Burdige and Nealson, 1986). The Mn oxide prepared in this manner is likely to be in the mineral phase vernadite (MnO_x , $x=1.9$) based on X-ray diffraction pattern of manganese oxide prepared by the same method (Balistrieri et al., 1992). Amorphous Fe oxyhydroxide (FeOOH) was prepared by neutralizing 0.4 M FeCl_3 to a pH of 7 with NaOH (Lovley and Phillips, 1986). X-ray diffraction patterns determined at Stony Brook University (Department of Geosciences, K. Bowdwin, personal communication) confirmed that the FeOOH used in this study was amorphous. Solutions of S^0 , $\text{S}_2\text{O}_3^{2-}$, and NO_3^- were individually prepared from reagent grade crystalline elemental sulfur, $\text{Na}_2\text{S}_2\text{O}_3$, and NaNO_3 . As elemental sulfur has a low solubility in water, the sulfur solution was well mixed before use. All reagents were N_2 -purged immediately before use and were added to incubation samples immediately after ^{14}C -acetate was added. Final concentrations of the electron acceptors varied from 100 μM to 1 mM, and were much higher than the background. Thus, the enrichment studies primarily demonstrate the potential for the natural populations to carry out the various reactions. All other procedures for enrich-

ment experiments were the same as for the measurement of the acetate uptake rate (Ho et al., 2002).

3. Results

3.1. Temporal and vertical variability of redox zonation

Based on the vertical distribution of O_2 , NO_3^- , Fe^{2+} , Mn^{2+} , particulate Mn and Fe, and HS^- , four redox zones can be distinguished in the basin (Fig. 1, using March 1998 as an example). Oxygen concentrations were high in the mixed layer and euphotic zone, but decreased rapidly below that. Nitrate concentrations reached maximum values at depths of

100–200 m. Thus, we expect that aerobic respiration occurred in the top 300 m; denitrification was present between 200 and 320 m; metal redox reactions took place between 250 and 410 m; and sulfate reduction was located at and below the suboxic/anoxic interface (350 m).

A comparison of the redox species profiles for all cruises between 1995 and 1999 for which electron acceptor data are available is shown in Fig. 2. Marked temporal and vertical variability was found. In general, the concentrations of oxygen, nitrate, and hydrogen sulfide approached zero at almost the same depths, where microbial activity and organic carbon cycling were highest (Taylor et al., 2001; Ho et al., 2002). The depth of maximum microbial activity usually was at the depth of the highest dissolved Mn concentration.

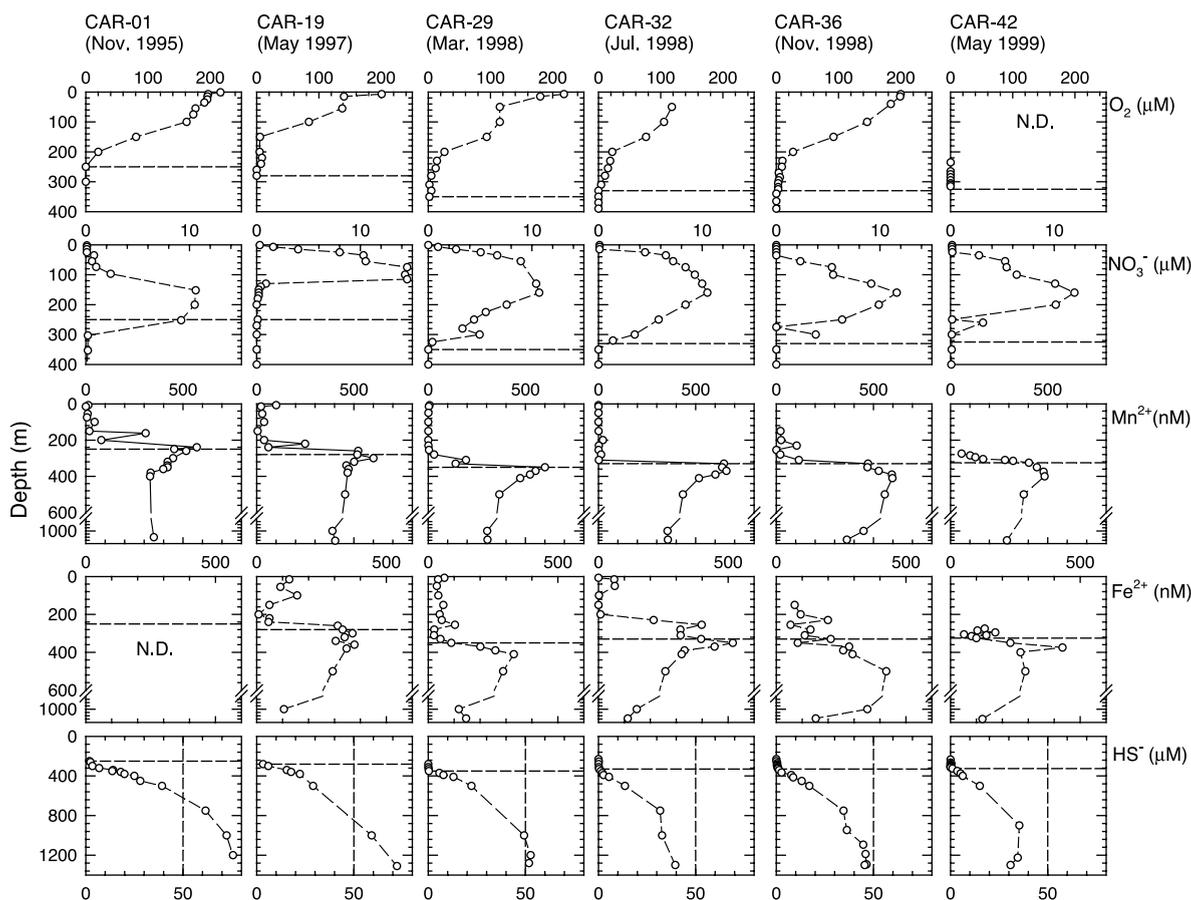


Fig. 2. Vertical profiles of oxygen (μM), nitrate (μM), dissolved Mn (nM), dissolved Fe (nM), and hydrogen sulfide (μM) among all cruises in this study. Horizontal dashed lines represent the suboxic/anoxic interfaces.

However, CAR-19 (May 1997) had a very different distribution pattern from that observed on other dates. Both oxygen and nitrate were almost depleted by 140 m, but hydrogen sulfide was not detected until 300 m. This distribution pattern resulted in a very broad suboxic zone between 140 and 300 m (Fig. 3). This feature was accompanied by a steep nitrate concentration gradient and a maximum concentration of 15 μM , whereas other dates had maximum nitrate levels closer to 10 μM . Similarly, the peaks of dissolved Mn and Fe appeared at shallower depths in CAR-19.

Compared to other oxidants, dissolved Mn profiles were relatively consistent from cruise to cruise. The maximum dissolved Mn concentration varied from 500 nM during CAR-42 to 670 nM during CAR-32, values which were slightly higher than the concentrations (440 nM) determined by Jacobs and colleagues about 15 years earlier (Jacobs et al., 1987). The depth of the maximum metal concentration in each profile was located at or just below the depth of first appearance of sulfide, and lying below a steep

concentration gradient. The depth of maximum dissolved Fe concentration was sometimes located at the interface (e.g., CAR-19 and CAR-32), and sometimes below the interface (CAR-29, CAR-36, and CAR-42). Maximum dissolved Fe concentrations ranged from 320 to 520 nM, values which were similar to or higher than the concentrations (320 nM) determined by Jacobs et al. (1987). Strong vertical and temporal variability of HS^- concentrations also occurred. The depths of first appearance of sulfide varied from 200 m during CAR-1 to 350 m on CAR-32 with bottom water concentrations varying from 75 μM on CAR-1 to 35 μM on CAR-36. A detailed comparison of the bottom water concentrations with decadal historical data is described in Scranton et al. (2001).

3.2. Inhibition and enrichment experiments

Acetate uptake rate constants were not significantly different in the presence or absence of molybdate near the suboxic/anoxic interface (Table 2). This suggests

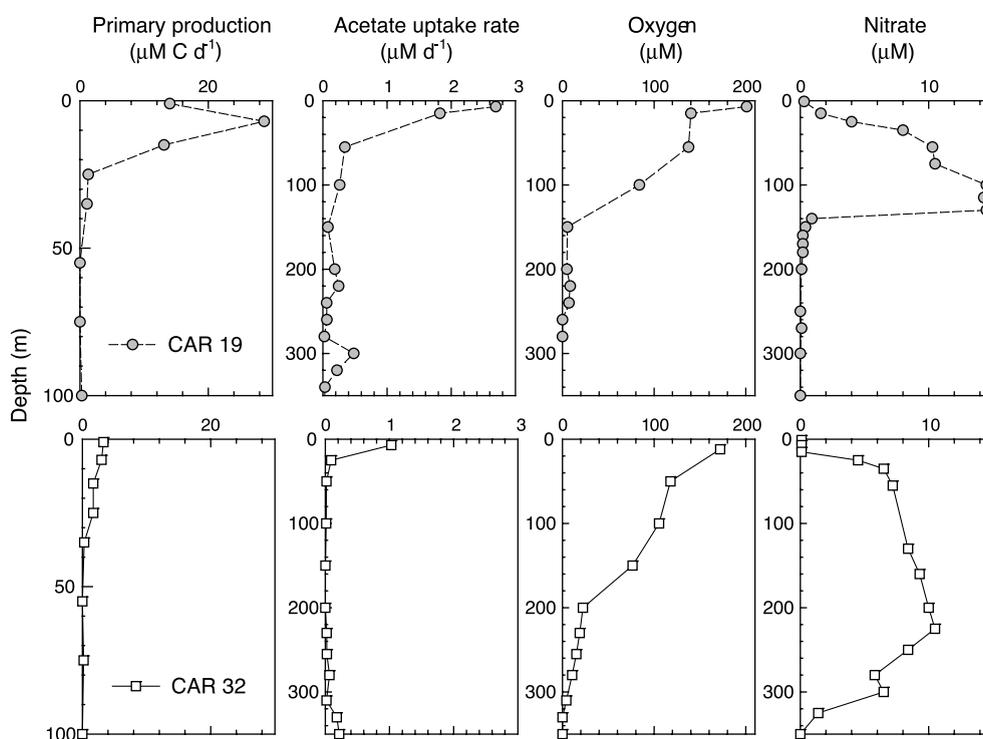


Fig. 3. Vertical profiles of primary production, acetate uptake rates, oxygen, and nitrate during a high primary production cruise CAR-19 (May 1997) and a low primary production cruise CAR-32 (July 1998).

Table 2
Comparison of acetate uptake rate constants for samples near the suboxic/anoxic interface with and without molybdate amendments

Cruise no. and date	Suboxic/anoxic interface (m)	Depth (m)	Control ($\times 10^{-3}$ day $^{-1}$)	Molybdate added ($\times 10^{-3}$ day $^{-1}$)
CAR-9 (July 1996)	~ 280	220	1.2	1.2
		250	1.2	1.2
		270	6.5	6.5
		290	2.1	1.6
		310	3.3	3.1
CAR-19 (May 1997)	~ 280	260	2.5	3.3
		280	2.9	2.7
		300	4.7	6.7
		320	1.7	2.8
		360	1.1	1.7
CAR-32 (July 1998)	~ 330	280	6.0	6.0
		310	1.2	1.6
		330	2.4	2.2

that sulfate reduction was not a dominant pathway for organic carbon oxidation (or at least for acetate oxidation) at these depths. Enrichment experiments, carried out for depths near the interface during three cruises in 1998 showed that addition of the nitrate, iron and manganese oxides, and oxidized forms of S increased the acetate respiration constants (Table 3). However, the effects varied with depth. The acetate uptake constants at depth 285 m of CAR-36 were only slightly enhanced by any added electron acceptors. In contrast, the uptake rate constants were much higher after addition of electron acceptors at 295 m and not much different at 305 m. The marked difference probably was due to the relatively narrow regions inhabited by the various microbial groups around the suboxic/anoxic interface. Addition of elemental sulfur

and thiosulfate, in particular, appears to strongly enhance microbial acetate uptake and the extent of the enhancement was higher than for treatments with metal additions (CAR-36).

4. Discussion

4.1. Organic carbon supply and the variability of redox zonation

The observed temporal and vertical variability of organic carbon production and consumption in the Cariaco Basin (Table 4; Müller-Karger et al., 2001; Taylor et al., 2001; Thunell et al., 2000; Ho et al., 2002) provides some insights into the interaction between the distribution of major electron acceptors/donors and organic carbon supplies. As there are two different organic carbon sources in the water column, we will compare organic carbon supply and redox zonation in two distinct zones.

Fig. 3 compares primary production and acetate uptake with oxygen and nitrate concentrations in the oxic water column for the cruise with the lowest primary productivity (CAR-32) and a cruise with one of the highest productivities (CAR-19). The concentration gradients of oxygen and nitrate during the period of high primary production (CAR-19) were much steeper than during the time of low primary production (CAR-32). Both organic carbon production and acetate uptake were also elevated in the top 100 m during CAR-19. The rapid depth-dependent disappearance of nitrate during CAR-19 coincided with relatively high acetate oxidation rates. In contrast, during CAR-32, a broad nitrate maximum was

Table 3
Comparison of acetate respiration rate constants for samples amended with selected electron acceptor

Cruise no. and date	Suboxic/anoxic interface (m)	Sampling depth (m)	Acetate respiration rate constant ($\times 10^{-3}$ day $^{-1}$)				
			Control	+ MnO ₂	+ FeOOH	+ S ⁰	+ S ₂ O ₃ ²⁻
CAR-29 (March 1998)	~ 350	310	7	74	6	nd	nd
		330	7	95	25	nd	nd
		350	22	209	103	nd	nd
CAR-32 (July 1998)	~ 330	280	8	32	42	nd	nd
		310	2	39	72	nd	nd
CAR-36 (November 1998)	~ 320	285	6	12	18	54	56
		295	32	475	681	1424	1253
		305	20	21	14	15	14

Table 4
Organic carbon production, fluxes, and acetate uptake rates in the Cariaco Basin

Cruise no.	Date	Primary production 0–100 m	Chemoauto. production interface–450 m	POC flux sediment trap depth (m)				Depth-integrated acetate uptake rate*	
				200	265	450	1270	0–200 m	300–450 m
<i>Upwelling</i>									
CAR 05	March 12, 1996	175	nd	13	10	12	3	22–64	3–35
CAR 19	May 8, 1997	208	114	15	10	6	5	110–203	13–32
CAR 29	March 10, 1998	269	12	19	4	1	1	21–43	5–10
CAR 42	May 9, 1999	104	42	8	4	2	2	17–49	6–30
<i>Nonupwelling</i>									
CAR 01	November 14, 1995	nd	nd	nd	3	3	2	5–12	7–24
CAR 09	July 9, 1996	81	nd	6	nd	nd	nd	11–30	1–6
CAR 13	November 8, 1996	147	105	11	3	3	2	6–27	3–13
CAR 25	November 14, 1997	54	80	4	6	3	3	10–29	12–31
CAR 32	July 7, 1998	37	117	3	5	2	1	16–33	13–42
CAR 36	November 7, 1998	50	50	4	5	2	2	6–9	3–13

Comparison of depth-integrated acetate uptake rate with major organic carbon fluxes (in $\text{mmol C m}^{-2} \text{ day}^{-1}$). Data sources: primary production (Müller-Karger et al., 2001); chemoautotrophic production (Taylor et al., 2001); POC fluxes (Thunell et al., 2000; personal communication), and acetate uptake (Ho et al., 2002). POC flux at 200 m is estimated by the empirical function of Pace et al. (1987).

nd: not determined.

*Upper and lower limits of acetate uptake rates.

found between 140 and 300 m, and bacterial abundance and rates of acetate uptake in this zone were very low (Ho et al., 2002). These results suggest that variability in concentration profiles of oxygen and nitrate can be strongly influenced by organic carbon supply from primary production.

Immediately above and below the suboxic/anoxic interface, chemoautotrophic production was the most important source of organic carbon (Table 4). Profiles of dissolved Mn and Fe concentrations, chemoautotrophic production, and acetate uptake rates are compared for the two cruises with the highest (CAR-32) and lowest (CAR-29) chemoautotrophic production (Fig. 4). Near the suboxic/anoxic interface, maxima in dissolved Mn concentrations coincided with those of organic carbon production and oxidation rates (Fig. 4). Similar results were also found during other cruises (Ho, 2000). Slightly elevated concentrations and broader peaks of both dissolved Mn and Fe were observed for the dissolved metals during times when chemoautotrophic production and oxidation of organic carbon were high (CAR-32) as compared to when chemoautotrophic production was low (CAR 29). The maximum concentrations of dissolved Mn and Fe for CAR-32 were 630 and 500 nM, respectively, both being the highest among all cruises, suggesting that

the cycling of the metal redox species around the interface was coupled to organic carbon cycling. The depth of maximum Fe concentration was 50–100 m deeper than the Mn maximum for CAR-29. However, during periods of elevated chemoautotrophic production (CAR-32), maximum Fe and Mn concentrations occurred at the same depth (Fig. 2). This coincidence suggests that iron reduction may become more active near the suboxic/anoxic interface during periods of high carbon supply. This same pattern was also seen on other dates (Ho, 2000). These results indicate that microbes in the water column readily responded to organic carbon supplies and thus mediated changes in the depth distribution of these redox-sensitive chemical species.

4.2. Relative importance of oxidation pathways across the suboxic/anoxic interface

Except for sulfate, most of the major electron acceptors at the suboxic/anoxic interface (oxygen, nitrate, and metal oxides) were present in low concentrations (Fig. 1), while elevated acetate concentrations tended to be found near the suboxic/anoxic interface (Albert et al., 1995; Mopper and Kieber, 1991; Ho et al., 2002). It is natural to consider sulfate

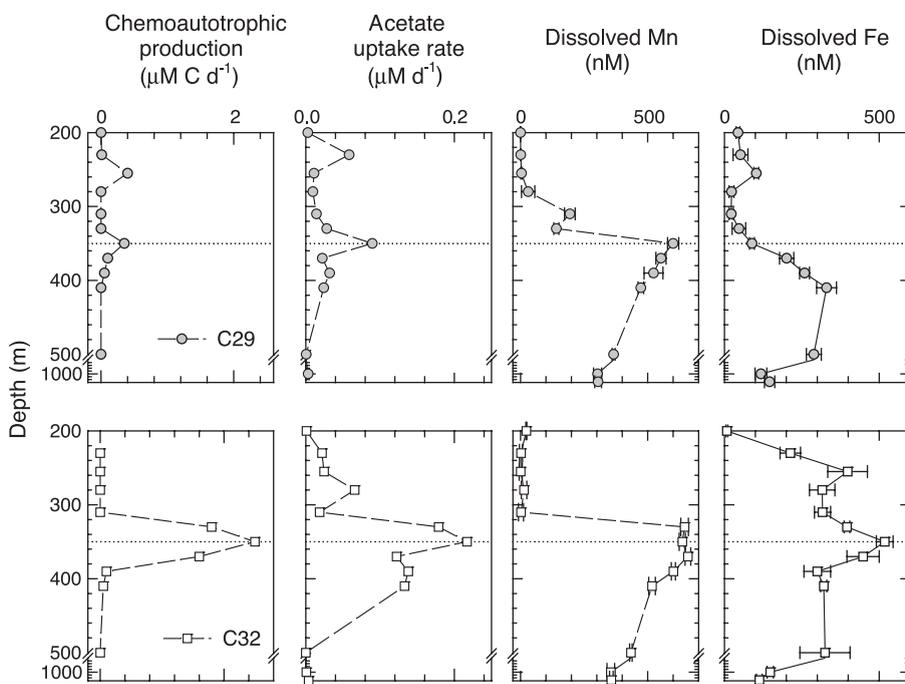


Fig. 4. Vertical profiles of chemoautotrophic production, acetate uptake, dissolved Mn, and dissolved Fe for a low chemoautotrophic production cruise CAR-29 (March 1998) and for a high chemoautotrophic production cruise CAR-32 (July 1998). Dotted line represents the suboxic/anoxic interface.

reduction as a major pathway for organic matter oxidation, given its abundance relative to other electron acceptors. Previous studies in the Cariaco Basin and the Black Sea suggested that sulfate reduction dominates the decomposition of organic matter in the water columns (Spencer et al., 1972; Hastings and Emerson, 1988; Jørgensen et al., 1991; Neelson et al., 1991; Zhang and Millero, 1993; Albert et al., 1995). Although Hastings and Emerson (1988) observed elevated alkalinity and elemental sulfur just above the interface in the Cariaco Basin, sulfate reduction rates were not directly determined. Neelson et al. (1991) reported that no sulfate-reducing bacteria were enriched from Black Sea samples between the suboxic/anoxic interface (85 m) and 500 m during the summer of 1988. In situ production of hydrogen sulfide by sulfate reducing bacteria at the suboxic/anoxic interface in the Black Sea was two to three orders of magnitude slower than the measured rate of sulfide oxidation (Jørgensen et al., 1991). Sulfate reduction rates measured using ^{35}S sulfate were also extremely low ($0\text{--}3\text{ nM day}^{-1}$) in the Black Sea

(Albert et al., 1995). All these findings are inconsistent with the assumption that sulfate reduction plays a critical role in organic carbon oxidation in the water columns. It is likely that much of the sulfate reduction takes place in the sediments rather than in the water columns themselves.

In the Cariaco Basin, the failure of molybdate to inhibit acetate uptake reported here strongly suggests that sulfate reduction is not the dominant pathway for organic matter oxidation near the suboxic/anoxic interface in the water column (Table 2). This result is also supported by phylogenetic information obtained from 16S rDNA libraries created from 320-, 500-, and 1310-m samples (Madrid et al., 2001). Madrid et al. did not find sequences that were most closely related to sulfate reducers in the 320-m library, but rather that 53 of 60 sequences in the 320-m library were closely related to chemoautotrophic symbionts, ϵ -proteobacteria. Based on sequences obtained from the 500- and 1310-m libraries, sulfate reducers and fermenters may be more common at these greater depths. However, organic carbon oxidation rates were

very low in the deep water, on average ranging from <1 to $10 \mu\text{mol C m}^{-3} \text{ day}^{-1}$ between 450 and 1310 m as compared with rates near the interface of up to $500 \mu\text{mol C m}^{-3} \text{ day}^{-1}$. Most of acetate uptake rates samples at the deep water were also too low to be determined (Ho et al., 2002).

If sulfate reduction is not the most important process near the interface, metal reduction or reduction of intermediate oxidation state sulfur species may be important. In anoxic sedimentary environments possessing high concentrations of reactive Mn or Fe oxides and hydroxides or fast recycling mechanisms to reoxidize the reduced metals, a number of studies have revealed that metal reduction can be an important pathway for organic carbon oxidation (Sørensen, 1982; Sørensen and Jørgensen, 1987; Lovley and Phillips, 1988; Aller et al., 1986, 1996; Aller, 1990, 1994; Canfield et al., 1993). In anoxic water columns possessing limited supplies of Mn and Fe oxides, the role of metal reduction has largely been ignored. In Lake Norrviken, however, Sternbeck (1996) found depths of high alkalinity and Mn^{2+} coincided and were comparable in magnitude, suggesting that dissimilatory Mn reduction was a major pathway for organic carbon decomposition. Similar observations have been reported for the Orca Basin, a highly saline anoxic system in the Gulf of Mexico (Van Cappellen et al., 1998).

In addition to metal oxides, intermediate oxidation states of sulfur (S^0 , SO_3^{2-} , and $\text{S}_2\text{O}_3^{2-}$) could also be potential electron acceptors for organic carbon oxidation in marine anoxic water columns (Perry et al., 1993). Elemental sulfur and thiosulfate are major products of H_2S oxidation (Yao and Millero, 1993; Zhang and Millero, 1993) and could be formed during intrusion of oxygenated water into the region of the suboxic/anoxic interface. Elevated concentrations of S^0 , SO_3^{2-} , and $\text{S}_2\text{O}_3^{2-}$ have been observed near the suboxic/anoxic interface and in deeper water in a number of marine anoxic water columns and fjords including the Cariaco Basin (Hastings and Emerson, 1988; Zhang and Millero, 1993).

Our sulfur species and metal oxide enrichment experiments demonstrate that S^0 , $\text{S}_2\text{O}_3^{2-}$, and metal reductions are potentially important pathways for organic carbon oxidation at the suboxic/anoxic interface (Table 3). These results are consistent with the phylogenetic study of Madrid et al. (2001) who found

that that ϵ -proteobacteria were the dominant microbial group (93%) near the suboxic/anoxic interface. The metabolic pathways used by ϵ -proteobacteria include metal, elemental sulfur, and nitrate reduction, as well as sulfide, thiosulfate, and sulfite oxidation.

4.3. Estimation of vertical fluxes of major electron acceptors

To more quantitatively evaluate the relative importance of the major electron acceptors at the interface, the fluxes of the electron acceptors were estimated from the concentration and profiles. If we assume that the system is dominated by vertical processes (Fanning and Pilson, 1972; Scranton et al., 1987; Zhang and Millero, 1993), the major source of electron acceptors for organic carbon oxidation must come from vertical flux which can be estimated using a one dimensional transport-reaction model. The production and oxidation of organic carbon in the suboxic/anoxic zone, as indicated by chemoautotrophic production, acetate uptake, and POC fluxes, appeared to mainly occur between 300 and 450 m (Figs. 4 and 5; Table 4). These two depths may be taken as the upper and lower boundaries of the redox transition zone for flux estimates (Fig. 5).

We use concentration gradients ($\Delta C/\Delta Z$) to estimate the flux (F) of the electron acceptors to the reaction zone. A 1-D advection–diffusion model may be a reasonable approach as the T – S plot in the basin is approximately linear over the depth interval under consideration (300–450 m for CAR-32).

$$F \cong K_z \frac{\Delta C}{\Delta z} + wC$$

where F is the flux due to vertical eddy diffusion and advection, K_z is the vertical eddy diffusion coefficient, C is the concentration of electron acceptor, z is the depth (m), and w is vertical advection velocity.

The volumetric rate of reaction within a layer (R) can be estimated by dividing the fluxes by the thickness of the layer under consideration.

$$R \cong \frac{K_z \Delta \left(\frac{\Delta C}{\Delta z} \right)}{\Delta z} + w \frac{\Delta C}{\Delta z}$$

The vertical eddy diffusion coefficient (K_z) is proportional to the reciprocal of the square root of

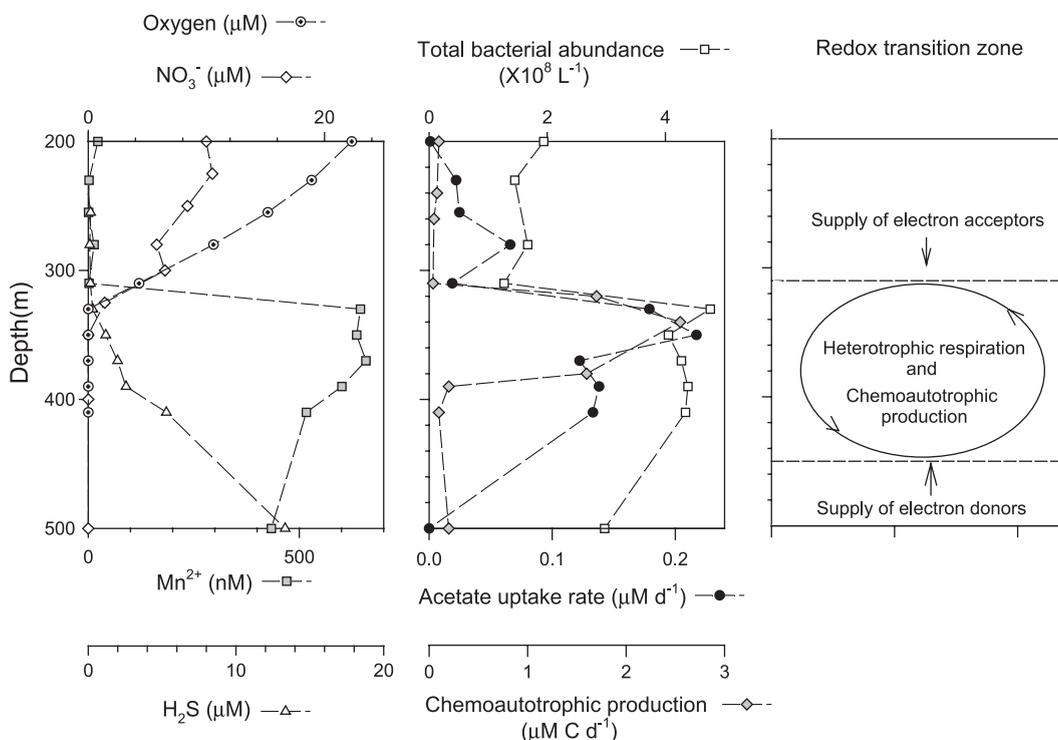


Fig. 5. Schematic diagram of redox transition zone in the water column of the Cariaco Basin (CAR-32). Left panel represents vertical distribution of possible major electron acceptors and their reduced species between 200 and 500 m; middle panel represents vertical distribution of bacterial abundance, acetate uptake rates, and chemoautotrophic production between 200 and 500 m. Right panel represents the assumed upper and lower boundaries of the redox transition zone.

the density gradient and can be estimated from the following equation (Gargett, 1984):

$$K_z = a_0 \left(-\frac{g\Delta\rho}{\rho_z\Delta z} \right)^{-0.5}$$

where ρ_z is density at a given depth, $\Delta\rho/\Delta z$ is the density gradient over a given depth interval, and g is the gravitational constant. The parameter a_0 is a system-dependent constant and is related to energy supplied to the system by internal waves, eddies, and similar phenomena. As the density gradient over the modeling interval was almost constant, K_z is taken as constant. For CAR-32, the density gradient between 300 and 450 m was approximately $0.0002 \text{ g/cm}^3 \text{ m}^{-1}$. This is much smaller than values reported for other systems. In the Black Sea, the density gradient was $0.05 \text{ g/cm}^3 \text{ m}^{-1}$ near the suboxic/anoxic interface (Lewis and Landing, 1991).

Reported values of a_0 range from $0.001 \text{ cm}^2 \text{ s}^{-2}$ in the open ocean to $0.0001 \text{ cm}^2 \text{ s}^{-2}$ in fjords or lakes (Gargett, 1984). Using these upper and lower limits of a_0 to calculate K_z in the Cariaco Basin, a range of $0.7\text{--}0.07 \text{ cm}^2 \text{ s}^{-1}$ can be obtained for K_z . Scranton et al. (1987) previously estimated K_z near 300 m to be about $0.5 \text{ cm}^2 \text{ s}^{-1}$, based on a box model describing temperature and salinity budgets for the deep waters of the Cariaco Basin. If K_z is equal to $0.5 \text{ cm}^2 \text{ s}^{-1}$, the value of a_0 is $0.0007 \text{ cm}^2 \text{ s}^{-2}$. A value of $0.5 \text{ cm}^2 \text{ s}^{-1}$ is used for K_z in this study.

The ratio of vertical advection velocity to vertical eddy diffusion coefficient, w/K_z , can be obtained by curve fitting temperature or salinity profiles (Munk, 1966). For the Cariaco, w/K_z was between -0.0046 and -0.0050 m^{-1} during the CARIACO cruises, close to the value (-0.0043 m^{-1}) determined in the Basin in 1968 (Fanning and Pilson, 1972). Thus, w should be about 8 m year^{-1} (advective flux upward).

By substituting these constants into the flux equation, the downward flux of oxygen to 300 m (the upper boundary of the redox transition zone) can be estimated to be $0.8 \text{ mmol m}^{-2} \text{ day}^{-1}$. Assuming a 1:1 molar ratio of oxygen respiration to organic carbon oxidation, and that all oxygen supplied to the transition zone was used for carbon oxidation, $0.8 \text{ mmol carbon m}^{-2} \text{ day}^{-1}$ would be oxidized. This value is an overestimate since some oxygen is undoubtedly used in chemical oxidations. Thus, the vertical flux of oxygen is small in comparison to both the integrated rate of acetate oxidation for CAR32 ($13 \text{ mmol C m}^{-2} \text{ day}^{-1}$, Ho et al., 2002) and the net rate of chemoautotrophic carbon fixation ($117 \text{ mmol C m}^{-2} \text{ day}^{-1}$, Taylor et al., 2001). Vertical transport of oxygen can account for only 6% of the electron acceptors needed for acetate oxidation or 0.7% of the oxidation of the organic material fixed by chemoautotrophs.

The estimated nitrate flux to this zone also is low ($0.3 \text{ mmol NO}_3^- \text{ m}^{-2} \text{ day}^{-1}$), accounting for 2% of the acetate oxidation or 0.3% of the oxidation of the total carbon fixed in the transition zone if we assume that 0.8 mol nitrate is required to oxidize 1 mol of organic matter. Using this type of calculation for all cruises in this study, oxic respiration and nitrate reduction combined could account for no more than 9% of organic carbon oxidation in the redox transition zone.

Although concentrations of Mn and Fe oxides are low (sub-micromolar) in the water column, the reduction of metal oxides might still be important in carbon cycling if metal oxidation and reduction occur in close proximity and the redox cycling rate is fast. The concept of a 'Mn/Fe redox shuttle' has been previously proposed for anoxic environments (Spencer et al., 1972; Davison et al., 1982; Nealson and Myers, 1992; Aller, 1994). In this model, reduced dissolved Mn and Fe are transported by molecular diffusion (sediments) or by eddy diffusion (water column) from anoxic zone to suboxic zone ($\text{O}_2 < 10 \mu\text{M}$) where they are oxidized to form particulate Mn and Fe, which settle back into the suboxic/anoxic zone and are reduced. Since diffusion and mixing are much faster in water column than in sediments, redox couples of Mn and Fe could be rapidly recycled and may provide electron acceptors for carbon oxidation. If horizontal transport of Mn and Fe oxides is ignored, the upward transport rate of dissolved Mn (Mn^{2+}) is equal to the

downward flux of Mn oxides. Using the one-dimensional steady state transport-reaction model, rates of Mn reduction and oxidation calculated for CAR-32 are shown in Fig. 6. Although Mn oxides are potential electron acceptors for organic carbon oxidation around the interface (Fig. 6), the results show that Mn reduction rates in the Cariaco Basin were very low (about 6 nM day^{-1}) at the interface with an integrated Mn^{2+} flux of around $0.12 \text{ mmol m}^{-2} \text{ day}^{-1}$. A slightly lower value ($0.10 \text{ mmol m}^{-2} \text{ day}^{-1}$) was obtained for the Fe flux using the same approach. Since 2 mol of MnO_2 or 4 mol of FeOOH are required to oxidize 1 mol of organic carbon, the model predicts Mn and Fe reduction rates could account for less than 1% of the respiration of total carbon produced in the zone for all of the cruises. It is clear that the vertical transport of oxygen, nitrate, and metal oxides is too small to explain the measured rate of chemoautotrophic production and acetate uptake in the transition zone (Table 4).

4.4. Internal redox recycling coupled with oxic mid-water intrusion

As the zones of active chemoautotrophic production and heterotrophic respiration overlap in the transition zone (Fig. 5), these processes may be coupled among microbial consortia residing within the same depth range. A similar phenomenon was observed and demonstrated in marine anoxic sediments (Kepkay and Novitsky, 1980). In this scheme, the oxidized products of inorganic electron donors produced during chemoautotrophic production could be used as electron acceptors for organic carbon oxidation by heterotrophic bacteria at the same depth. Thus, this biological production term is neglected in the above-simplified one-dimensional model which only considers a vertical mixing term. An analogous situation is encountered in surface waters when calculating total oxygen consumption rates. The oxygen consumption rates estimated by the 1-D model using vertical concentration gradients cannot account for the total oxygen consumption because of oxygen production through photoautotrophic activity (biological term) is not considered.

In the transition zone of the Cariaco Basin, we use elemental sulfur as an example to elucidate the internal cycling concept and also to evaluate its plausibility

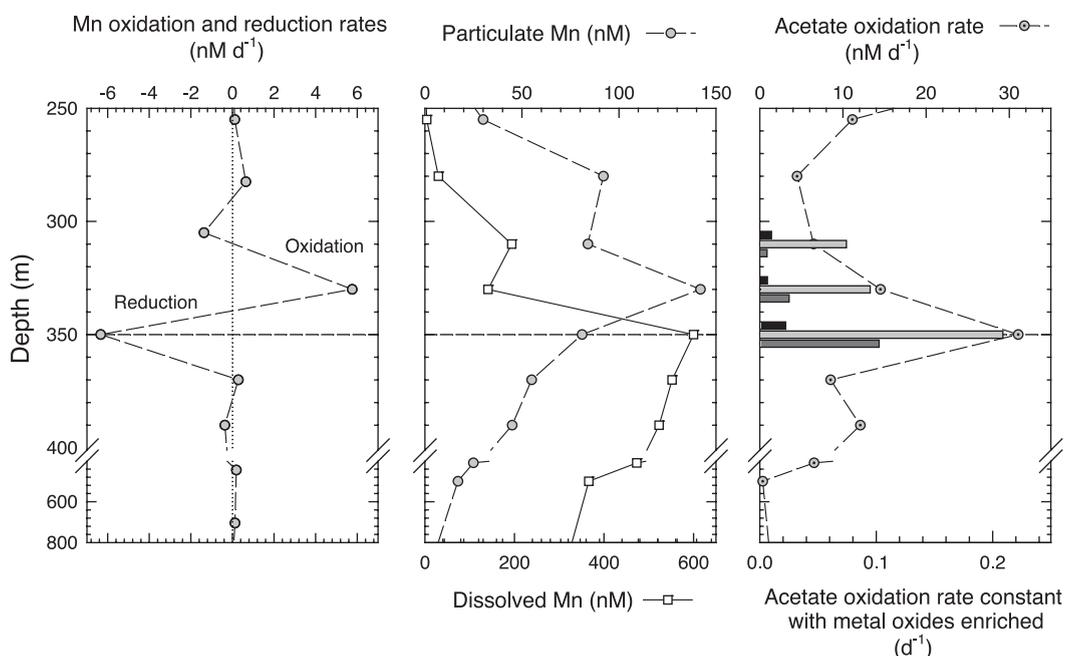
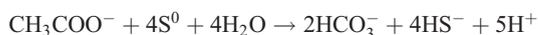


Fig. 6. Profiles of estimated Mn reduction and oxidation rates, particulate and dissolved Mn concentrations, and the comparison of acetate uptake rate constants with metal oxides amendments. Left panel: Positive values represent oxidation; negative values represent reduction. Central panel: The particulate and dissolved Mn profiles. Right panel: The samples at the three depths (310, 330, and 350m) were treated with metal oxides enrichment. Top solid bars at each depth represented the acetate uptake rate constants of the control samples (without metal added); central light-gray bars represented the acetate uptake rate constants of the samples with added MnO₂; bottom dark-gray bars represent the acetate uptake rate constants of the samples with added FeOOH. Grey symbols with line indicate acetate oxidation rate measured in the samples without amendments.

based on free energy yield. At the pH (7.6) measured at the suboxic/anoxic interface in the Cariaco Basin, the oxidation of organic carbon coupled with S⁰ reduction can be expressed as:



$$\Delta G_{\text{pH}=7.6}^0 = -56 \text{ kJ mol}^{-1}$$

The free energy yield is based on the standard value for acetate oxidation ($\Delta G^0 = -39 \text{ kJ mol}^{-1}$; Table 4). The energy yield of the reaction under ambient conditions is:

$$\Delta G_{\text{oxid}} = -56 + RT \ln \left[\frac{[\text{HCO}_3^-]^2 [\text{HS}^-]^4}{\text{CH}_3\text{COO}^-} \right].$$

In the transition zone, we assume $[\text{Mn}^{2+}] = 0.5 \mu\text{M}$, $[\text{HCO}_3^-] = 2 \text{ mM}$, $[\text{HS}^-] = 5 \mu\text{M}$, and $[\text{CH}_3\text{COO}^-] = 3 \mu\text{M}$. Activities of pure solids are taken to be one so

$\{\text{S}^0\} = 1$. The activity coefficients of HCO_3^- , HS^- , and CH_3COO^- are 0.70, 0.70, and 0.68, respectively (Stumm and Morgan, 1996). The value of ΔG_{oxid} would be -179 kJ mol^{-1} meaning that the reaction is thermodynamically favorable. When chemoautotrophic and heterotrophic processes are coupled in the transition zone, the total reduction rate of S⁰ would be underestimated by the calculated flux through vertical concentration gradients. In addition to S⁰, other electron acceptors such as $\text{S}_2\text{O}_3^{2-}$ and SO_3^- are candidates for organic carbon oxidation (Perry et al., 1993). Although we did not measure the concentrations of elemental sulfur, thiosulfate, or sulfite in the Cariaco Basin, active microbial mediation of HS⁻ oxidation has been found at the suboxic/anoxic interface in previous studies both in the Cariaco Basin and in the Black Sea (Tuttle and Jannasch, 1973; Jørgensen et al., 1991). Elevated S⁰ concentrations have been detected near the suboxic/anoxic interface both in the Cariaco Basin and the Black Sea (Hastings and Emerson, 1988;

Luther et al., 1991). As much as $2 \mu\text{M}$ of $\text{S}_2\text{O}_3^{2-}$ and SO_3^- were found below the suboxic/anoxic interface in the Cariaco Basin (Zhang and Millero, 1993). These results suggest that these sulfur intermediates are present to be recycled through the two microbial processes.

Taylor et al. (2001) demonstrated that anaerobic chemoautotrophy in the Cariaco Basin was stimulated by additions of MnO_2 and FeOOH . Enrichment cultures were successfully produced from samples below the interface that reduced MnO_2 at the expense of $\text{S}_2\text{O}_3^{2-}$ under anaerobic chemoautotrophic conditions (Madrid, 2000; Taylor et al., 2001), although attempts to maintain isolates from these enrichments were not successful. These results suggest that metal oxides may be used as electron acceptors in the chemoautotrophic production which combines metal (MnO_2 , FeOOH) reduction, sulfide oxidation, and inorganic carbon fixation. For these reactions to be significant, it appears that external source of electron acceptors and donors is required to support the coupled reactions. Due to energy loss during metabolic activities and the inefficiency of chemoautotrophic production, a larger amount of reducing power is needed to maintain the observed chemoautotrophic production.

One possible mechanism for supplying external electron donors (HS^-) is that the Cariaco Basin is laterally inhomogeneous and sulfide production somewhere else in the basin is higher than our sampling site. Advanced study to investigate the horizontal gradient is needed to verify this possibility. Likewise, a plausible mechanism for supplying large amount of electron acceptors is via horizontal intrusion of oxygenated water containing O_2 and possibly NO_3^- . Astor et al. (2003) and Scranton et al. (2001) have shown that mid-water intrusions are very common in the Cariaco Basin. Layers 10–20 m thick, containing up to 30–120 μM more oxygen than overlying water have been found on occasions near the interface (Astor et al., 2003), but this almost certainly underestimates the amount of oxidant injected as the sill is almost 50 km from our sampling site. The oxygen from the intruding water need not remain in the form of free oxygen but may be stored in the form of other electron acceptors. Horizontal intrusion of oxic water into the suboxic zone would permit conversion of Mn^{2+} , Fe^{2+} , and HS^- to oxidized particulate and colloidal Mn, Fe, S^0 , or to thiosulfate, and sulfite.

The importance of horizontal oxic water intrusion to the geochemical budget at oxic/anoxic interface has been reported in other anoxic water columns (Yao and Millero, 1995; Oguz et al., 2001; Kononov and Murray, 2001; Zopfi et al., 2001). Whether horizontal intrusion of oxic water into oxic/anoxic interface region is a common process for carbon cycling in anoxic water columns deserves further study.

5. Conclusion

Significant temporal and vertical variability in redox zonation occurs in the water column and appears to be related to the changes in organic carbon supply (by primary production in surface waters and by chemoautotrophic production near the oxic/anoxic interface). Sulfate reduction did not seem to be the dominant organic carbon oxidation pathway. Instead, reactions between metals, S^0 , and $\text{S}_2\text{O}_3^{2-}$ reductions appear to be important. Estimated by a vertical transport reaction model, total net vertical diffusive fluxes of oxygen, nitrate, and metal oxides cannot support enough electron acceptors to balance the respiration of organic carbon in the transition zone. Internal redox recycling of the redox species of Mn, Fe, and S, coupled with a lateral oxidant supply, may explain the budget imbalance.

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