Controls on iron, manganese and intermediate oxidation state sulfur compounds in the Cariaco Basin

Dane Percy a, Xiaona Li a, Gordon T. Taylor a, Yrene Astor b, Mary I. Scranton a,⁎

a Marine Sciences Research Center, Stony Brook University, Stony Brook, New York 11794-5000, United States
b Estación de Investigaciones Marinas de Margarita, Fundación de la Salle de Ciencias Naturales, Apartado 144,
Punta de Piedras, Edo. Nueva Esparta, Venezuela

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Abstract

Oxygen, hydrogen sulfide, thiosulfate, sulfite, iron and manganese were measured at three stations in the Cariaco Basin in January and May 2005 to investigate the spatial and temporal variability of the chemistry in the basin as a part of the CARIACO time-series. Sulfide and oxygen profiles at the oxic/anoxic interface differed significantly between the three stations and suboxic zone thickness changed with both space and time. Higher inventories of H2S at a station on the broad sill, and a suboxic zone which varied from 5 to 50 m at this site (most variable among the three stations), may be related to a higher source of sulfide in shallower waters coupled with the effect of an intrusion between the two cruises, causing a large portion of the high sulfide inventory to be oxidized and form thiosulfate and sulfite. Thiosulfate and sulfite concentrations were similar to those previously observed, but, in contrast to previous work, generally exhibited a strong minimum within the suboxic zone. This is consistent with enhanced biological consumption or chemical oxidation/reduction within the suboxic zone following intermediate oxidation state sulfur compound formation. The concentrations of dissolved iron and manganese in the anoxic portion of the basin were ∼50% higher during January 2005 compared to samples from historical data and from May 2004 or May 2005. The source of the metals appeared to be related to high rainfall during late 2004 and early 2005 along the Venezuelan coast which may have resulted in delivery of a large amount of terrigenous material to the system. Saturation calculations suggest that metals were removed between January and May by mineral precipitation, possibly as FeS and CaMn(CO3)2 for Fe and Mn, respectively. Intrusions of oxygenated water and lateral advection of particulate matter from the coast are important processes in providing oxidant to the suboxic zone.

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1. Introduction

The Cariaco Basin, the Black Sea, and probably most other anoxic basins, experience transient water mass intrusions that introduce oxygenated water into the oxygen depleted portions of these systems (Scranton et al., 2001; Zopfi et al., 2001; Konovalov et al., 2003). These intrusions can occur down to depths where sulfide concentrations are normally high. Since sulfide oxidation can occur chemically or biologically and under both oxic and anoxic conditions (Chen and Morris, 1972; Zhang

⁎ Corresponding author. Tel.: +1 631 632 8735; fax: +1 631 632 8820.
E-mail address: mscranton@notes.cc.sunysb.edu (M.I. Scranton).
and Millero, 1993a; Zopfi et al., 2001), intrusions may result in formation of intermediate oxidation state sulfur compounds such as thiosulfate (S$_2$O$_3^{2-}$), sulfite (SO$_3^{2-}$), elemental sulfur (S$^0$), and SO$_4^{2-}$ (Jørgensen et al., 1991; Zhang and Millero, 1993b; Zopfi et al., 2001) near the oxic–anoxic interface.

Sulfur intermediates formed during sulfide oxidation can be utilized to support both chemoautotrophic production and heterotrophic respiration (Tuttle and Jannasch, 1979; Jørgensen and Bak, 1991; Perry et al., 1993; Taylor et al., 2001). For example, thiosulfate can be oxidized biologically to SO$_4^{2-}$, reduced to HS$^-$, or undergo disproportionation to HS$^-$ and SO$_4^{2-}$ (Jørgensen and Bak, 1991; Zopfi et al., 2001). Jørgensen (1990) found that 46% of the sulfur resulting from disproportionation of thiosulfate was in the form of a sulfide (reduced) pool and 24% was in the form of a sulfate (oxidized) pool in anoxic sediments in the Kattegat, Denmark. The free energy yield for thiosulfate disproportionation is low ($\Delta G^\circ_{r} = -21.9$ kJ mol$^{-1}$), but is thermodynamically favorable, if sinks for the HS$^-$ produced by disproportionation are available. In fact, communities using S$_2$O$_3^{2-}$ as a substrate for growth have been identified in the Kattegat and the Black Sea (Jørgensen and Bak, 1991; Perry et al., 1993). Sulfide oxidation in seawater has been studied in the Cariaco Basin since the 1970s, but many aspects of pathways and rates remain unresolved (Tuttle and Jannasch, 1973, 1979; Zhang and Millero, 1993a; Hayes et al., 2006).

Transient events have significant impact on the oxidant budget in the Cariaco system. During the CARIACO time-series, we have noted oxygen concentration anomalies that can only be produced by intrusions that appear to penetrate to depths of up to 330 m, and month to month density changes have been observed much deeper (Astor et al., 2003). Since 1995, the depth at which H$_2$S is detectable (about 1 $\mu$m) has varied from about 250 m to about 350 m. This variability presumably reflects variations in the magnitude and density of intrusions, but details of the intrusion process are still poorly understood (Astor et al., 2003).

Iron and manganese oxides may also play a role as oxidants for microorganisms, may form in situ during intrusion events, may be supplied by aeolian transport or may be advected in after local river discharge as suspended particles. These metals are likely to influence the biogeochemical cycling of sulfur in the Cariaco Basin, as intermediate oxidation state sulfur species may be produced through anoxic sulfide oxidation when Fe and/or Mn hydroxides serve as electron acceptors (Zopfi et al., 2004). MnO$_2$ has been shown to increase rates of sulfide oxidation under anoxic conditions (Burdige and Nealson, 1986; Yao and Millero, 1993). Profiles of Fe and Mn within the water column of many anoxic bodies of water and in anoxic pore-waters often show particulate maxima above the oxic–anoxic interface and dissolved maxima below (Bacon et al., 1980; Jacobs et al., 1987; Canfield et al., 1993; Ho et al., 2004). Lovley and Phillips (1986) isolated a freshwater bacterium from the sediments of the Potomac River which could completely oxidize organic matter using Mn(IV) and Fe(III) as the sole electron acceptors. Reduced Mn (II) and Fe(II) produced from coupled carbon oxidation, and dissimilatory Mn(IV) and Fe(III) reduction can potentially provide energy to support growth of neighboring chemoautotrophic bacteria. Finally, anerobic sulfur species oxidation by chemoautotrophic bacteria using Mn(IV) or Fe(III) is thermodynamically favorable. For example, thiosulfate oxidation can occur via Fe reduction providing 70 times more energy than thiosulfate disproportionation (Jørgensen, 1990):

$$S_2O_3^{2-} + 8FeOOH + 14H^+ \rightarrow 2SO_4^{2-} + 8Fe^{2+} + 11H_2O$$

(1)

In fact, rates of DIC assimilation have been stimulated by Mn(IV) and Fe(III) amendments (Taylor et al., 2001, 2006; Labrenz et al., 2005). However, strict chemoautotrophs capable of mediating these reactions have yet to be isolated.

The CARIACO time-series program has sampled a station in the deepest part of the Eastern Basin of the Cariaco for more than ten years (Muller-Karger et al., 2000, in press). In 2005, we extended our investigations to include two additional stations: a station in the western basin near the site studied by other researchers in the 1970s and 1980s and a station on the broad sill to the northwest of the CARIACO site (Fig. 1). Documenting the spatial distribution of the chemical products of intrusions and sulfide oxidation as well as the relationship of these compounds to microbial activity has extended our understanding of the biogeochemical cycles of S, Mn, and Fe in the Cariaco Basin.

The present study was designed to assess whether horizontal and vertical distributions of major electron donors and acceptors in the water column of the Cariaco Basin are affected by transient, oxygenated intrusions. Dissolved oxygen, hydrogen sulfide, thiosulfate, sulfite, Fe, and Mn were measured on cruises in January and May 2005. We examine factors influencing spatial variability within the basin, finding that intrusions from the western channel may be more important than expected and that river runoff was probably a significant source of metal oxides to the system.
2. Materials and methods

2.1. Study area

The Cariaco Basin (Fig. 1) is a large, marine anoxic system on the continental shelf off the northern coast of Venezuela. The deepest parts of the basin reach 1400 m and are isolated by a shallow (90 to 150 m) sill that restricts the entrance of Caribbean water. Channels to the northeast (La Tortuga channel: about 135 m) and the west (Centinela channel: about 146 m) provide pathways for denser water to penetrate into the deep basin. A 900 m deep, north/south saddle separates the eastern and western basins. The stability of the basin is controlled by temperature but density is uniform to within 0.1 $\sigma_\theta$ units below about 250 m (Richards, 1975). The depth of first appearance of hydrogen sulfide has ranged between about 250 and 350 m (Ho et al., 2004), and a suboxic zone in which oxygen and sulfide concentrations are both below 1–2 $\mu$M has ranged in thickness from zero m to over 100 m over the course of the CARIACO program.

2.2. Sample collection

Water samples were collected in the Cariaco Basin as part of the CARIACO (Carbon Retention in a Colored Ocean) sampling program, an international initiative that has investigated biological production, biogeochemical cycling, and the physical dynamics of the Cariaco Basin since 1995. In CARIACO, a single station (our station A) is occupied monthly for a variety of hydrographic and biological parameters including oxygen, temperature, salinity, nutrients, primary production and CO$_2$ system variables. A general description of the CARIACO program and links to data can be found at the CARIACO web site (http://www.imars.usf.edu/CAR/). In addition to the data available from the monthly cruises, we have undertaken two or three additional cruises a year during which more detailed chemical and microbiological measurements are made. Some of the data from these cruises are described by Hayes et al. (2006), Scranton et al. (2006), Lin et al. (2006) and Taylor et al. (2006) as well as in other publications.

Fig. 1. Map of Cariaco Basin and the sampling sites: station A is the CARIACO time-series station (10°30′ N 64°40′ W); station B is on the broad, shallow region south of the eastern sill (10°40′ N 64°45′ W); station C is in the deep western basin (10°40′ N 65°35′ W).
On January 17–19 and May 23–25, 2005 (CAR-108 and 112, respectively), samples were collected at three locations (Fig. 1) including the CARIACO time-series station (station A: 10°30′ N 64°40′ W), a station southeast of La Tortuga Channel in water about 600 m deep (station B: 10°40′ N 64°45′ W), and a station in the western basin (station C: 10°40′ N 65°35′ W). Water samples were collected in 12 8-l Teflon-lined Niskin bottles mounted on a Seabird rosette system equipped with a CTD, a YSI oxygen probe, a Chelsea profiling fluorometer for chlorophyll-a, and a SeaTec c-beam transmissometer (660 nm). The Niskin bottles were slightly pressurized with N₂ during sampling to minimize O₂ contact.

2.3. Oxygen

Seawater samples for dissolved oxygen were drawn into standard oxygen bottles in duplicate and Winkler reagents were added immediately. The samples were stored in an air-conditioned space with seawater around the caps to minimize oxygen transfer across the stoppers and were run within 48 h of returning to the Fundación LaSalle laboratory. Zhang et al. (2002) have shown that this procedure is effective in preserving oxygen samples. The YSI oxygen probe on the CTD also provided continuous O₂ profiles which were corrected for response time and calibrated with the Winkler data. Yrene Astor and Claudia Paez provided the CTD and dissolved oxygen data. Details of methods are provided in Astor et al. (2003).

2.4. Sulfur species (sulfide, thiosulfate, sulfite)

Seawater samples for sulfide, thiosulfate, and sulfate analyses were collected by placing the tip of a gas-tight syringe below the surface of water flowing upward through a 60 ml plastic syringe barrel which had been attached to the Niskin bottle by a 60 cm length of Tygon tubing. Sampling from flowing seawater was used to minimize contact of samples with O₂.

Sulfide samples were taken in triplicate and were analyzed using a modification of Cline (1969). Four-milliliter samples were collected in a 5 ml Dynatech Gas-Tight glass syringe with Teflon (PTFE) plunger tip (January) or an all-glass Hamilton Gas-Tight 10 ml glass syringe with a PTFE plunger tip (May) and injected into scintillation vials with ZnCl₂ (500 µl; 50 mM) to form a stable ZnS precipitate. Oxygen can chemisorb to Teflon, but the syringe was flushed several times before each sample was dispensed, and the time of contact between sample and plunger was on the order of a few seconds, so we do not expect the short contact represents a serious source of error.

Samples were chilled on the ship and stored refrigerated until analysis. Upon return to the Stony Brook lab, diamine and ferric chloride reagent (50 µl; 4.0 g anhydrous ferric chloride and 1.6 g N,N-dimethyl-p-phenylene diamine sulfate/100 ml of 6 N HCl) were added to samples (Cline, 1969). Samples were diluted with 5 ml of aerated Cariaco Basin seawater from 750 m to keep them in the linear portion of the absorbance calibration curve. The use of ZnCl₂ rather than traditional Zn(Ac)₂ results in less buffering and requires use of seawater diluent. Standards were also prepared in Cariaco Basin seawater to ensure that the standard and sample matrix matched, as the color of the derivative is pH dependent. Based on the relative standard deviation of triplicate samples, the precision of the field samples during analysis was ±3.3%. The detection limit for sulfide analyses was 0.59 µM, calculated as six times the standard deviation of quintuplicate blanks.

While standard curves appeared linear over a large concentration range as determined by a high correlation coefficient (greater than 0.98), close inspection showed they were consistently convex over the entire concentration range (from 0 to ~50 µM). Therefore, we matched concentrations of standards to those in samples and kept total absorbance low to optimize analysis for the concentration range expected in the Cariaco Basin. We used a linear calibration equation to be consistent with previous sulfide measurements. We did not subtract a reagent blank from the samples. In some cases, this has led to small positive values (~1 µM) in the suboxic zone.

Thiosulfate and sulfite samples were collected in triplicate as described above for sulfide and were analyzed using the method of Vairavamurthy and Mopper (1990) as modified by Hayes et al. (2006). Ten-milliliter water samples were collected from Niskin bottles as described above and were transferred within seconds into a glass serum vials containing 0.5 ml sodium acetate buffer (0.2 M). All reaction vials were prepared in advance at the shore-based laboratory by adding buffer, flushing with argon and crimp sealing for transport to the field. To minimize oxidation, the derivatizing agent (5 mM 2,2′dithiobis(5-nitro) pyridine in acetonitrile) was added within seconds of dispensing seawater into serum vials. Derivatization was allowed to proceed for 5 min, after which water was passed through preconditioned Waters SepPak tC18 Solid Phase Extraction (SPE) cartridges. Cartridges were preconditioned immediately before use with 5 ml methanol, 5 ml distilled water, and 5 ml of a mixture of 20 mM sodium acetate and 10 mM tetrabutylammonium hydrogen sulfate (TBAHS).
Vairavamurthy and Mopper (1990) have reported that the DTNP derivative of thiosulfate is unstable in aqueous solution “after a few minutes”. However, they also found (as have we) that derivatives stored on cartridges at low temperatures are stable for relatively long periods. Our samples are transferred to the cartridges immediately after derivatization (within 5–10 min) and are kept in a cooler on deck until the cast is completed. Upon returning to the local laboratory, cartridges were purged with argon and frozen until analysis. Frozen samples are typically thawed for about 10 min prior to elution.

Vairavamurthy and Mopper (1990) reported that, even at room temperature, derivatives on cartridges were stable for at least a day. We have done storage tests on standards preserved frozen on cartridges and have not seen trends of conversion of thiosulfate to sulfite. We have made our triplicate measurements in random order, and see no systematic increase in sulfite with storage time. Comparisons of sub-samples from batches of standards run immediately (few minutes) with standards run days to weeks later also show no shifts.

Upon return of the samples to Stony Brook, thiosulfate and sulfite derivatives were eluted from cartridges with methanol and analyzed on a Shimadzu HPLC consisting of a SCL 10A-VP system controller, two LC-10AT pumps, an SPD-10AV/VP ultraviolet detector, and a SIL-10A auto-injector. Mobile phases for analysis were (A) 100% acetonitrile and (B) a solution of 0.05 M sodium acetate and 7.5 mM TBAHS adjusted to pH 3.5±0.03. The gradient for this method was 1 min with 10% B followed by a gradient to 34% B at 9 min, to 55% B at 23 min, to 100% B at 28 min, continued elution with 100% B for 2 min, then a gradient back to 10% B at 32 min and to 0% B at 40 min. Absorbance of the derivatives was measured at 320 nm.

The laboratory blank for this method consisted of 10 ml of distilled water, buffer and 0.05 ml of the derivatizing agent (DTNP). Lab blanks were concentrated through preconditioned SepPak cartridges and analyzed in the same manner as field samples. Lab blanks were 0.07±0.04 μM for sulfite and 0.3±0.1 μM for thiosulfate. The analytical detection limit (6x the standard deviation of five laboratory blanks) was 0.3 μM for sulfite and 0.6 μM for thiosulfate. The precision of analysis (relative standard deviation of 5 replicates of a 10 μM standard) for thiosulfate and sulfite was ±2.2% and ±1.6%, respectively.

Field blanks were prepared on shipboard prior to and following each cast to account for storage and transport effects and consisted of the same distilled water and derivatizing agent as lab blanks. In January, we used distilled water available in Venezuela. The average field blank for sulfite was 0.8±0.7 μM and 0.4±0.4 μM for thiosulfate, which was considerably higher than our normal lab blanks, particularly for sulfite. In May 2005, we transported commercial HPLC water, as well as our own distilled water, from the US, but continued to have erratic results with the field blanks. Field blanks for May were 0.8±1.0 μM for sulfite and 0.6±0.6 μM for thiosulfate.

Because the field blanks were so much higher than lab blanks, and because a number of samples also were lower than our blanks, blanks were not subtracted from the samples. Upper estimates of the true blanks are the lowest thiosulfate and sulfite value which were measured during a particular cruise and are 0.3 μM and 0.5 μM, respectively.

2.5. Fe and Mn

In addition to the January and May 2005 cruises, samples for Fe and Mn analysis were available from May 2004 (CAR 100). For manganese and iron samples, seawater was collected in Niskin bottles from the CTD that was lowered on a steel cable. Handling of sample bottles on deck was done by two gloved analysts with considerable care taken to avoid touching surfaces, and with gloves and vials kept bagged between samples to maintain cleanliness.

Air-Tite Norm-Ject 10cc luer-lock plastic syringes and Nalgene 15 ml LDPE bottles for sampling were washed in 1 N HNO₃ for 1 month prior to use and kept sealed in double-bagged Ziploc bags until collection. Metal samples were collected directly into acid-cleaned bottles (for total analysis) or into syringes (for dissolved fraction). For dissolved analyses, samples were filtered into LDPE bottles using 0.45 μm Whatman GD/XP 25 mm syringe filters. Particulate metal was determined by difference. Fe and Mn samples were collected in duplicate for each depth and each fraction and then analyzed in triplicate. Plotted error bars were calculated from comparison of duplicate samples at a single depth. Syringe filters and Fisherbrand disposable polyethylene gloves for collection were not acid washed.

After return to Stony Brook, water samples were acidified with 70 μl quartz-distilled Optima grade HCl by Fisher Scientific and stored for at least 1 month. They were then analyzed on a Perkin-Elmer AAnalyst 800 Graphite Furnace/Flame Atomic Absorption Spectrometer. Analytical detection limits for both Fe and Mn analyses on the AAS were less than 2 nM. Standards for Fe and Mn analysis were diluted from concentrated stock solutions obtained from the lab of Sérgio Sañudo-Wilhelmy at Stony Brook University. Prior to each day’s analysis, a calibration curve was made to ensure the
spectrometer was functioning properly. However, calibration of samples was done using calibration curves prepared using standard additions into samples from three different regimes (surface, suboxic, deep) because of concerns that the seawater matrix varied over the water column. The standard addition analysis showed a 22% difference in the slope of the calibration curve between surface waters and depths beneath 250 m. Therefore, different calibration curves prepared using standard additions into Cariaco Basin water were used for calculating the concentrations of Fe and Mn in the two different depth ranges (0–250 m and >250 m).

Analytical precision on the AAS was ±5.4% and ±4.7% for Fe and Mn, respectively. Precision was calculated by determining the standard deviation of six replicates from a 260 nM standard for Fe and 237 nM standard for Mn. Average field precision for dissolved Fe was ±32% if we ignore standard deviations >100% (8 of 43). Average field precision for dissolved Mn was ±8%.

Data for particulate metals (especially for Fe) were much more scattered than for the dissolved metal. The average field precision for particulate Mn was ±16%, while it was 110% for particulate Fe, calculated by averaging the standard deviations for all particulate Mn or Fe samples. Part of these larger errors for particulate metals may result from calculation of particulate metal as the difference between dissolved and total (subtraction of two large numbers). However, inspection of the data also suggests that the metal treatment may not have dissolved all the Fe particles (S. Sañudo-Wilhelmy, personal communication). Because of the extremely high variability in particulate Fe analyses, particulate Fe data are not discussed further.

3. Results

3.1. Oxygen and sulfide

3.1.1. CAR-108

The depth at which dissolved oxygen decreased to about 1 μM varied between stations (Fig. 2). At the CARIACO time-series station A, dissolved O$_2$ reached ~1 μM at 260 m. At station B on the broad shelf to the northwest, oxygen reached this concentration at about 220 m. In the western basin (station C), the 1 μM level was about 245 m. The suboxic zone thickness also varied from station to station. We operationally define the suboxic zone as lying between the shallowest depth where O$_2$ was determined by Winkler titration to be ≤1 μM and the shallowest depth where H$_2$S was greater than 1 μM. Because we sampled at 10 m intervals across the interface, in some cases we did not have measurements at the 1 μM level. In those cases, when there was a clear change in the slope of the oxygen or sulfide profile, we occasionally used an oxygen value of 2 μM. Estimates of the top and bottom of the suboxic zone appear on the figures. The suboxic zone was about 10 m thick at station A during CAR 108, was less than 5 m thick at station B and was about 45 m thick at station C.

The maximum measured sulfide concentration, which occurred at 1300 m, was 53.7 ± 1.8 μM at station A and 54.6 ± 1.4 μM at station C (Fig. 2). At station B, the maximum measured sulfide concentration (10.9 ± 0.8 μM) occurred at 400 m, the greatest depth sampled, which was similar to the concentration observed at 400 m at the other two stations. However, just below the first appearance of sulfide, concentrations at station B were systematically higher than for the other two stations. For example at 270 m, the sulfide concentration at B was about 6 μM while at A and C the concentration was closer to 1 μM. This difference was reflected in the integrated sulfide inventory between 250 and 340 m which was 212 mmol m$^{-2}$ at station A, 496 mmol m$^{-2}$ at station B and 166 mmol m$^{-2}$ at station C (Table 1).

3.1.2. CAR-112

During CAR 112 (May 2005) dissolved O$_2$ concentrations again decreased to zero at different depths among the three stations. At station A, dissolved O$_2$ was approximately 1 μM at 250 m, 225 m at station B, and 255 m at station C (Fig. 3). Suboxic zone thickness was approximately 20 m at station A, ~50 m at station B and ~50 m at station C. The suboxic zone thickness increased most at the sill station between January and May (Table 1), increasing by 10 m at station A, by between 45 and 50 m at station B, and by about 5 m at station C. The maximum measured sulfide concentration at station A (at 1300 m) was 61.6 ± 2.1 μM, which is slightly higher than was seen during January. An increase in sulfide concentrations at station C also was observed at 1050 m, where concentrations were 51.2 ± 0.2 μM in January and 57.8 ± 4.6 μM in May.

The sulfide inventory at station A and B increased from January to May, while decreasing at station C. While station B experienced the largest increase in suboxic zone thickness, station A exhibited the largest sulfide inventory increase. Sulfide inventories integrated between 250 and 340 m were 325, 521, and 85.9 mmol m$^{-2}$ at stations A, B and C, respectively (Table 1).

3.2. S$_2$O$_3^{2-}$ and SO$_3^{2-}$

3.2.1. CAR-108

Maximum concentrations of S$_2$O$_3^{2-}$ and SO$_3^{2-}$ were 1.2 ± 0.4 and 2.3 ± 0.5 μM in the suboxic zone of the
eastern basin, 0.6±0.1 and 0.2±0.03 μM in the suboxic zone at station B and 0.4±0.4 and 0.2±0.03 μM in the suboxic zone at station C, respectively (Fig. 4). The inventories of S\(_2\)O\(_3\)\(^{-}\) and SO\(_3\)\(^{-}\) in the suboxic zone at stations C and B were lower than at station A, and station A was the only station where thiosulfate and sulfite showed a distinct maximum in the suboxic zone. At station A, thiosulfate and sulfite increased from concentrations less than 0.2 μM for both compounds to 1.2±0.7 and 2.6 ± 1.3 μM at 250 m (10 m above the suboxic zone), continued to increase to a maximum level within the suboxic zone, and remained at elevated concentrations for 20 m before decreasing again. Thiosulfate and sulfite data from below 400 m are slightly suspect because sulfide concentrations were high and thiosulfate and sulfite might have been produced during sampling or derivatization (Hayes et al., 2006).

### 3.2.2. CAR-112

In May 2005, maximum concentrations of thiosulfate and sulfite within the suboxic zone at station A were 2.6±0.2 and 1.3±0.1 μM, respectively. At station B, maximum concentrations of S\(_2\)O\(_3\)\(^{-}\) and SO\(_3\)\(^{-}\) in the suboxic zone were 0.1±0.1 and 0.8±0.1 μM. Maximum concentrations of S\(_2\)O\(_3\)\(^{-}\) and SO\(_3\)\(^{-}\) within the suboxic zone at station C were 1.0±0.2 and 2.5± 0.4 μM (Fig. 5). The maximum concentrations of S\(_2\)O\(_3\)\(^{-}\) and SO\(_3\)\(^{-}\) above 400 m occurred in the suboxic zone of stations A and C, but not at station B.

Above and below the suboxic zone at station B, S\(_2\)O\(_3\)\(^{-}\) and SO\(_3\)\(^{-}\) concentrations were approximately three times higher than they were in any of the other stations in either January or May. Thiosulfate and sulfite varied from 2.5 to 6.0 μM in the oxic and anoxic regions at station B and decreased to concentrations of <0.8 μM in the suboxic zone. Previous studies of S\(_2\)O\(_3\)\(^{-}\) and SO\(_3\)\(^{-}\) in the Cariaco Basin showed either local maxima within the suboxic zone or constant and low values throughout the water column (Tuttle and Jannasch, 1979; Zhang and Millero, 1993a; Hayes et al., 2006). This is the first study showing a distinct decrease in the suboxic zone. Station B was the only station to exhibit substantially

### Table 1

Characteristics of the suboxic zone thickness for stations A, B and C for January and May 2005

<table>
<thead>
<tr>
<th>Station</th>
<th>January suboxic zone thickness (m)</th>
<th>May suboxic zone thickness (m)</th>
<th>Change in suboxic zone thickness (m)</th>
<th>January H(_2)S inventory (mmol m(^{-2}))</th>
<th>May H(_2)S inventory (mmol m(^{-2}))</th>
<th>Change in inventory (mmol m(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>10</td>
<td>20</td>
<td>10</td>
<td>212</td>
<td>325</td>
<td>113</td>
</tr>
<tr>
<td>B</td>
<td>&lt;5</td>
<td>50</td>
<td>45–50</td>
<td>166</td>
<td>85.9</td>
<td>−80.1</td>
</tr>
<tr>
<td>C</td>
<td>45</td>
<td>50</td>
<td>5</td>
<td>495</td>
<td>521</td>
<td>26</td>
</tr>
</tbody>
</table>

Sulfide concentrations were integrated from 250 to 340 m (220 to 340 m for station B in January).
lower concentrations for thiosulfate and sulfite within the suboxic zone relative to concentrations in the oxic and anoxic regions. Our data are not yet extensive enough to determine why we sometimes see maxima and sometimes see minima in the suboxic zone for thiosulfate and sulfite. Further sampling will help to resolve this point.

3.3. Iron and Mn

Concentrations of dissolved Fe and Mn measured in the oxic (0 to 185 m) water column on all cruises were higher than expected based on studies in the open ocean and continental margin (Sañudo-Wilhelmy, personal communication) and likely indicate contamination. These data are not discussed further.

3.3.1. CAR-100

Comparison of our data with those of others (Jacobs et al., 1987; Bacon et al., 1980) shows relatively good agreement for values below the oxic/anoxic interface, where concentrations increase as the basin waters become reducing. The maximum measured concentration of dissolved Fe (430±100 nM) at station A was
found at 400 m in May 2004, while the maximum measured concentration of dissolved Mn (610 ± 80 nM) on the same date was found at 500 m (Fig. 6).

3.3.2. CAR-108

Values for dissolved Fe and Mn were generally higher in January 2005 (Fig. 7) than in May 2004. Maximum dissolved Fe concentrations were 740 ± 20, 620 ± 560 and 440 ± 140 nM at stations A, B and C, respectively. Fe concentrations increased near the bottom of the suboxic zone.

Maximum dissolved Mn concentrations were 1170 ± 3, 1110 ± 7 and 940 ± 20 nM at stations A, B and C, respectively, with concentrations increasing below the upper boundary of the suboxic zone at each station.

As mentioned above, the particulate data (particularly for Fe) show signs of substantial contamination and/or incomplete dissolution of particles. The particulate Mn data are less scattered than the particulate Fe data and are presented in Fig. 8. Particulate Mn values were < 25 nM above 200 m and increased at the upper suboxic boundary at the three stations, with values varying from 0.2 to 66 nM between 40 m and 400 m at all three stations. There are hints of particulate Mn maxima in several profiles at or just above the top of the suboxic zone.

3.3.3. CAR-112

Dissolved Fe and Mn concentrations decreased at all three stations between January and May 2005 except for Fe at the sill station. Maximum dissolved Fe concentrations at station A were at 400 m (240 ± 40 nM), at station B were at 330 m (620 ± 290 nM), and at station C were at 305 m (180 ± 10 nM) (Fig. 9). Maximum dissolved Fe decreased from January to May by 504 nM at station A and 261 nM at station C. There was no significant change in maximum dissolved Fe at station B.

Maximum dissolved Mn concentrations were 820 ± 10 nM at 400 m at station A, 650 ± 40 nM at 330 m at station B, and 310 ± 10 nM at 330 m at station C. Maximum dissolved concentrations of Mn at these depths decreased by about 350, 460 and 630 nM at stations A, B and C between January and May. Maximum dissolved concentrations of Fe and Mn occurred at the same depths at station A and at station B.
Maximum concentrations of particulate Mn in May were higher than particulate Mn in January, particularly at station A. Maximum concentrations were 150±70 at 270 m at station A, 60±20 at 400 m at station B, and 130±130 at 400 m at station C. Station A was the only location sampled that exhibited a clear maximum.

4. Discussion

4.1. Suboxic zone variability

Historically the Cariaco Basin has been regarded as a simple system where the vertical distributions of redox-sensitive chemicals, such as sulfide and oxygen, are controlled primarily by vertical diffusion (Scranton et al., 1987; Kessler et al., 2006). However, Holmen and Rooth (1990) noted that deep injection of “young” water was required to maintain observed tritium profiles. Data from the CARIACO program have repeatedly shown that the basin is affected by episodic events, such as earthquakes (Scranton et al., 2001) and mesoscale eddies and other processes which result in intrusions of water from the Caribbean (Astor et al., 2003). Such events would be likely to change concentrations of sulfide, sulfide oxidation products and some trace metals in a complex way, as oxidation products are most likely formed near the channels to the Caribbean and then these products will be transported horizontally within the basin. A similar phenomenon has been described for the Black Sea (Konovalov et al., 2003).

In the Cariaco Basin, density gradients are much more gradual than in the Black Sea. The density contrast between the top of the suboxic zone (about 250 m) and 400 m is typically less than 0.04 $\sigma_\theta$ units in contrast to the Black Sea, where the redoxcline is in a much steeper density gradient. Furthermore, our sample spacing through the redoxcline is between 10 and 25 m, which represents density differences on the order of 0.003 units. Thus we have not found that our understanding of the system is improved by plotting data versus $\sigma_\theta$ rather than depth. However, changes in thickness of the suboxic zone observed in the present study demonstrate the dynamic nature of geochemical fluxes within the Cariaco Basin, and also show that intrusions, other advective processes and episodic events all contribute to spatial variability of chemical properties. This is in contrast to previous reports (e.g. Scranton et al., 1987) where little lateral variability was apparent. In the present case, thickness of the suboxic zone varied at all three stations, but increases were not uniform. Between January and May 2005, the suboxic...
zone thickness at station B increased by 45 m (Table 1), while the western basin station only increased in thickness by 5 m while maintaining one of the thickest suboxic zones (45 to 50 m), and the eastern basin’s suboxic zone increased by no more than 10 m. Examination of ADCP data collected at the CARIACO site indicates a cyclonic gyre in the basin (R. Weisberg, personal communication). An intrusion from the western Centinela Channel may have occurred. Since changes in suboxic zone thickness caused by intruding water likely result in oxidation of sulfide, one would expect that sulfide inventories and concentrations of oxidation products would change as well.

4.2. $\Delta \sigma_\theta$

One way to examine the effect of intrusions is to look at changes in the density structure of the water from month to month. For station A, we have calculated the month-to-month difference (noted here as $\Delta \sigma_\theta$) in potential density, $\sigma_\theta$, between December 2004 to May 2005 to determine if there was evidence for introduction of dense water into the system (presumably from outside the basin) or for the existence of horizontal transport and mixing within the basin. We have used $\Delta \sigma_\theta$, which is calculated from potential temperature, rather than $\Delta \sigma_t$, calculated using in situ temperature, since adiabatic warming is significant at depth in the basin. $\Delta \sigma_\theta$ was calculated by subtracting the $\sigma_\theta$ at each depth in 1 month from the $\sigma_\theta$ in the following month. The $\sigma_\theta$ data were obtained from the CARIACO web site (www.imars.usf.edu).

Between December and January, January and February and between April and May density at depth changed very little. In contrast, Fig. 10 shows that $\Delta \sigma_\theta$ was negative between December 2004 and January 2005, and between March and April, 2005. Interestingly, in January 2005, there was no sign of a suboxic zone at station B.

Geochemical profiles like those observed in January 2005 (Fig. 2) are often interpreted as suggesting the dominance of vertical mixing (Scranton et al., 1987). However, between February and March there was a marked density increase centered at 500 m but also noticeable at other depths below the interface. Previous studies (Scranton et al., 2001) found that density increases accompanied intrusions of oxygenated water from the Caribbean.

We infer that while negative values of $\Delta \sigma_\theta$ (decreases in water density) are associated with mixing within the
basin, a positive $\Delta \sigma_\theta$ most likely indicates the occurrence of an intrusion event introducing denser water at depth as described in Scranton et al. (2001). Fig. 10 shows that there is little evidence for intrusion during most of this period except for between February and March. There is also a small positive peak between 500 and 600 m between January and February.

### 4.3. Sulfide inventory

A thicker suboxic zone suggests localized consumption of both sulfide and oxygen. Sulfide inventories (between 250 (220 m for station B in January) and 340 m for each station) at two of the three stations (A and B) increased between January and May (Table 1). In contrast, the sulfide

![Dissolved Mn or Fe (nM)](image)

**Fig. 9.** Dissolved iron and manganese for CAR-112. Dashed lines (---) indicate the boundaries of the suboxic zone.

![Dissolved Mn or Fe (nM)](image)

**Fig. 10.** Month-to-month changes in $\Delta \sigma_\theta$ at station A. The density increase between February and March probably represents an intrusion. The density decreases at other times (April to May) probably reflect mixing or transport of water by circulation within the basin.
inventory at station C decreased. Clearly temporal variability in sulfide concentrations is a complex product of changes in addition of sulfide (from “upstream” sediments and possibly from in situ production) and removal of sulfide (by chemical oxidation and biological uptake). The greater decrease in inventory in the western basin, station C, suggests that intrusions may be entering through the Centinela Channel. While intrusions may result in sulfide removal at some stations, circulation induced by intrusions or other physical phenomena may also rapidly transport sulfide and sulfur oxidation products from one place to another within the basin.

4.4. Thiosulfate and sulfite production in the suboxic zone

Because both thiosulfate and sulfite can be oxidized abiotically (in reactions that can be catalyzed by the presence of metals such as Fe and Mn) or utilized by chemoautotrophs (Jørgensen, 1990; Jørgensen and Bak, 1991; Perry et al., 1993; Taylor et al., 2001), it is not possible to directly compare accumulation of these products with loss of sulfide. Although we did observe that inventories of thiosulfate and sulfite changed between the two cruises, inventories of these compounds were considerably less than predicted from the loss of sulfide (Table 1). Elemental sulfur and polysulfides (not measured during the cruises discussed here) are also expected to be important oxidation products (see for example, Trouwborst et al., 2006). Hastings and Emerson (1988) previously reported elemental sulfur maxima in the Cariaco Basin’s redoxcline. The high reactivity of thiosulfate and sulfite, which will likely be increased due to the presence of quite high levels of iron and manganese, suggests that production of these compounds must be a continuous and relatively rapid process.

4.5. Iron and manganese

Concentrations of Fe and Mn for CAR 100 (Fig. 7) were similar to previously reported values. For dissolved Fe, maximum concentrations in the eastern basin were about 405 nM in July 1971 (Bacon et al., 1980), 320 nM in November 1982 (Jacobs et al., 1987), and about 300 nM in May 1999 (Ho et al., 2004). Dissolved Mn in the eastern basin was about 460 nM in July 1971 (Bacon et al., 1980), 425 nM in November 1982 (Jacobs et al., 1987), and about 500 nM in May 1999 (Ho et al., 2004). For comparison, the maximum measured dissolved Fe at station A in May 2004 was 430±100 nM, and the maximum measured dissolved Mn was 600±76 nM.

Methods and sampling procedures differed between studies. Bacon et al. (1980) used Chelex-100 resin to preconcentrate samples and then analyzed manganese by atomic absorption spectrometry (AA) and iron colorimetrically. Jacobs et al. (1987) sampled using Go-Flo bottles under nitrogen gas, then analyzed iron and manganese in filtered samples using flameless AA with Zeeman background correction. Ho et al. (2004) used graphite furnace AA to determine metals on filtered samples as well. Therefore, there is some difficulty in making a direct comparison between our data and those of previous workers.

Data from May 2004 were similar to values reported previously considering the different sampling and analytical methods used. In contrast Fe and Mn concentrations in January 2005 were quite different from those previously reported and from those we measured in May 2004. Dissolved Fe and Mn increased between May 2004 and January 2005 by anywhere from about 25 to 100%, depending on the station and metal (compare Figs. 6 and 7). One possibility is that extremely high rainfall during late 2004 and early 2005 along the Venezuelan coast may have resulted in delivery of a large amount of terrigenous material to the system between May 2004 and January 2005. The total annual rainfall in 2004 reported at the Estacion de Meteorologica in Punta de Piedras was 508.2 mm (Arellano et al., 2006), which was the second highest rainfall total since precipitation records started at this site in 1993. The previous year was one of extremely low precipitation and the lowest annual total (141.3 mm) recorded since 1993. The combination of a low precipitation year in 2003 followed by a high precipitation year in 2004 could have increased the amount of terrigenous metals in riverine discharge.

The most recent metal data support the hypothesis that the delivery of terrigenous Fe and Mn is transitory. Average dissolved Fe concentrations in May 2005 (Fig. 9) show that maximum dissolved Fe concentrations decreased by approximately 600 nM at station C and 265 nM at station B while remaining constant at 621 nM at station A between January and May. The May 2005 data also indicate that maximum dissolved Mn concentrations from January to May 2005 decreased by about 600 nM at station B and at station C and by about 300 nM at station A.

Although there are no major rivers on Isla de Margarita where the Estacion de Meteorologica of Punta de Piedras records precipitation, these rainfall records relate well to regional precipitation patterns on the mainland of Venezuela, which has four small rivers discharging near the basin (Lorenzoni, personal communication). Lorenzoni (2005) obtained transmissometer data from a number of stations along the southern boundary of the Cariaco
Basin, and showed that the Neveri and Unare rivers were major sources of particulate matter to the Cariaco Basin with smaller but significant contributions from the Manzanares and Tuy Rivers. She suggested that particle-rich layers present at depths between 150 and 300 m could represent an important path of coastal sediment transport to the central basin. Her study was conducted in the dry year of 2003, which suggests that terrigenous particulate supply to the basin can occur even when rainfall is low. Transport of heavy metals like Mn and Fe could increase significantly if a dry year was followed by a year of heavy rainfall such as 2004.

The temporal fluctuations in Fe and Mn concentrations (and also of sulfide) seem to be a result of water column mineral formation. Jacobs et al. (1987) suggested that changes in iron concentrations between 1971 and 1982 were caused by iron sulfide (greigite) formation associated with increasing sulfide concentrations. Scranton et al. (2001) postulated that iron sulfide precipitation explained the sudden decrease of sulfide concentrations in the basin following the earthquake of 1997 which was accompanied by a large turbidity current. Unfortunately in 1997 we did not have "before" and "after" metal concentrations. In the present case, where we have Fe and Mn data from CAR 108 (following a long rainy period) and CAR 112, it is also likely that mineral precipitation occurred. In Fig. 11, we plot the ion activity products (IAP) of both FeS and CaMn(CO$_3$)$_2$. Kutnahorite has been previously suggested to be the Mn carbonate mineral forming in marine sediments (Aller and Rude, 1988). We used pH measured during monthly CARIACO cruises to estimate pH and [CO$_3$] at each depth, salinity to estimate [Ca$^{2+}$], and our own dissolved Fe, Mn and hydrogen sulfide concentrations. Using $\gamma$Ca$^{2+}=\gamma$Fe$^{2+}=\gamma$Mn$^{2+}$ = 0.26, $\gamma$H$^+$ = $\gamma$H$^-$ = 0.7, and $\gamma$CO$_3^2$ = 0.20 (taken from Morel, 1983), and the following equations, we calculated IAP for each depth.

$$\text{IAP}_{\text{FeS}} = \frac{\gamma_{\text{FeS}}[\text{Fe}^{2+}][\text{HS}^-]}{\gamma_{\text{H}^+}[\text{H}^+]$$}

(2)

$$\text{IAP}_{\text{CaMn(CO}_3^2\text{)}} = \frac{\gamma_{\text{Ca}} \gamma_{\text{Mn}} \gamma_{\text{CO}_3^2}[\text{Ca}^{2+}][\text{Mn}^{2+}][\text{CO}_3^2]}{\gamma_{\text{H}^+}[\text{H}^+]$$}

(3)

These values can be compared with the vertical lines in the graphs which represent literature values for apparent solubility constants ($K'_s$) for FeS and for CaMn(CO$_3$)$_2$ obtained from Dyrssen and Kremling (1990) and Aller and Rude (1988), respectively. Jacobs et al. (1987) earlier suggested that iron concentrations were controlled by greigite precipitation with a log $K_{s1}$ of $-3.6$. Scranton et al. (2001) suggested that the log IAP for iron sulfide in the basin following the earthquake was about $-4.2$, comparable to a number of reported values for solubility of iron sulfide minerals. Values from CAR29 (immediately following the earthquake) plot very close to values from CAR 112, suggesting that in a manner similar to that seen after the earthquake, the system has returned to a state reflecting saturation relatively quickly after the perturbation.

In the above calculation, we compare IAPs calculated with total metal (rather than “free” metal) with reported solubilities for several reasons. First we do not have sufficient information to accurately calculate speciation of metals in this system. Also there is uncertainty in the exact nature of the minerals being formed and in the solubility constants. Nonetheless, the Cariaco water column appears to return relatively rapidly to a state of saturation with these minerals. Apparently water column chemistry in the Cariaco is very sensitive to terrestrial inputs and is more highly buffered by mineral formation than previously believed.

5. Conclusion

The present study has demonstrated the temporal and spatial variability of the concentrations of sulfide, thiosulfate, sulfite, dissolved Fe and Mn and of the suboxic zone thickness. Sampling in the western basin and on the broad sill to the northwest of the CARIACO station has shown that the basin chemistry is neither vertically nor horizontally uniform, and that spatial variability of the major chemical constituents of the basin should be expected. Increased dissolved Fe and Mn concentrations in January 2005 were most likely due...
to anomalously high terrigenous discharge in 2004. The month-to-month differences in $\sigma_\theta$ illustrate that both advective transport of water from outside the basin and circulation within the basin occur. The present data emphasize that lateral intrusions (either of oxygenated water or of sediment-rich plumes) are extremely important in supplying chemical species to mid-depths throughout the basin. Qualitative evaluation of changes in physical and chemical profiles suggests that advective transport of water in the basin is as important to chemical distributions as vertical eddy diffusion.

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