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## Temporal and spatial variability of cobalt in the Atlantic Ocean

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**Abstract**—The spatial and temporal variability of cobalt in the Atlantic Ocean was investigated by means of adsorptive cathodic stripping voltammetry. A vertical profile of total dissolved cobalt at the Bermuda Atlantic Time Series station ranged from 17 to 73 pM and displayed surface depletion indicative of biological utilization. This profile when compared with a cobalt profile from the northeast Pacific shows no increase in deep-water concentrations with thermohaline circulation through the deep ocean basins. Moreover, the middepth maximum observed in northeast Pacific profiles is not present in the Sargasso Sea, perhaps because of the lack of cobalt scavenging by particulate manganese oxides in surface waters and to the absence of a suboxic oxygen minimum zone, which, if present, could dissolve the manganese oxides.

Total dissolved cobalt measurements were also made on a surface transect from the Sargasso Sea to coastal Massachusetts, USA, and on time-series samples from the Moored In Situ Trace Element Serial Sampler. Dissolved cobalt on this transect correlated strongly with salinity ( $r^2 = 0.93$ ) and ranged from 19 to 133 pM, indicating mixing of cobalt from shelf waters into the Sargasso Sea. Time-series samples near Bermuda did not show an obvious response to the summer maximum in aeolian dust deposition, with an annual average of  $20 \pm 10$  pM at 40- to 47-m depths. By use of this annual value and particulate cobalt data from the literature, 100-m surface-water residence times were calculated to be as low as 0.32 yr for cobalt. Several sharp decreases in cobalt were observed in the time series that occurred simultaneously with a shallowing of the thermocline depth. These decreases could be caused by nutrient drawdown associated with higher productivity mesoscale eddy events.

A west–east surface transect across the South Atlantic showed high cobalt concentrations at the boundaries of the transect and low concentrations in the center despite the high precipitation rates in the intertropical convergence zone. Phosphate measurements showed the similar trends as the total cobalt transect. A regression of cobalt vs. phosphate reveals a slope that is an order of magnitude higher than that of the northeast Pacific and that is similar to the slopes observed for zinc vs. phosphate in the Pacific. Copyright © 2002 Elsevier Science Ltd

### 1. INTRODUCTION

Cobalt is an important micronutrient for marine phytoplankton, (Morel et al., 1994), in particular the photosynthetic *Cyanobacteria* (Saito et al., personal communication; Sunda and Huntsman, 1995), yet its surface-water concentrations are very low based on limited available data. The factors controlling the distribution of cobalt in seawater are not well understood. Furthermore, the potential for these low concentrations of cobalt to influence species composition in the oceans is unknown. An understanding of the processes that control the temporal and spatial variability of cobalt in the ocean surface waters are paramount to surmising its potential biologic importance.

The distribution of trace metals in seawater can be categorized into two broad classifications: metals that are cycled via biologic uptake and regeneration (nutrient type), or metals that are removed or cycled via particle adsorption or precipitation (scavenged type; Whitfield and Turner, 1987; Bruland et al., 1994). The input and output mechanisms of a trace element in seawater affects which of these two behaviors the element exhibits. The relative importance of inputs from coastal fluxes

(riverine, release from sediments) and aeolian dust input are difficult to elucidate. Boyle et al. (1984) used <sup>226</sup>Ra and <sup>228</sup>Ra isotopes to show that the relative input of copper to the Gulf of Mexico from diffusion through continental shelf sediments must be less than or equal to the river flux. Bruland and Franks (1983) contend that an increase in concentration and inverse correlations with salinity for Mn, Ni, Cu, Zn, and Cd from the Sargasso Sea to the North American continental shelf are suggestive of riverine input, shelf sediment input, or both. Aeolian dust as a source of trace metals to the Sargasso Sea region is thought to be a major input mechanism (Duce et al., 1991; Jickells et al., 1994, 1998) that could have important implications for surface ocean biotic processes (Falkowski, 1997). There have been few published data concerning the relative influences of coastal and aeolian inputs of cobalt to the Atlantic Ocean.

Cobalt has been generally thought of as a scavenged-type trace element in seawater. Like iron, the low solubility of cobalt when oxidized to inorganic Co(III) seems to prevent the accumulation in deep water of the Pacific that is observed with nutrient-like trace elements such as zinc. The oxidation of Co(II) to Co(III) can be accomplished by coprecipitation with Mn oxides by Mn-oxidizing bacteria (Tebo et al., 1984; Tebo, 1998) and is thought to be an important mechanism for cobalt removal in coastal waters (Moffett and Ho, 1996). In contrast, Co uptake in the surface waters of the oligotrophic Sargasso

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Sea appears to be dominated by phytoplankton uptake rather than Mn oxidation (Moffett and Ho, 1996).

On the basis of the few measurements available of cobalt in seawater, we hypothesize that cobalt can exhibit properties of scavenged-type elements and nutrient-like elements, similar to iron. Co and Fe profiles can be nutrient-like in that at times they display surface-water depletion, yet they do not show deep-water enrichment in the Pacific and Indian Oceans, as is observed for Zn, Ni, and Cd. This surface depletion in profiles has been observed for cobalt in the Pacific on several occasions (Martin, 1985; Martin and Fitzwater, 1988; Martin et al., 1989) and in the North Atlantic (Martin et al., 1993). A previous profile of cobalt near Bermuda showed neither surface depletion nor surface enrichment; however, the authors noted that their values were below the working precision range of their protocol (Jickells and Burton, 1988). Other cobalt profiles from the coastal northeast Pacific, the Mediterranean Sea, and the Philippine Sea have shown low concentrations with surface maxima presumably from aeolian dust input (Knauer et al., 1982; Wong et al., 1995; Vega and van den Berg, 1997). Samples from a depth of 0.2 to 2350 m off central California showed an inverse correlation with salinity suggestive of input from continental weathering (Knauer et al., 1982). A previous Co data set in the northwest Atlantic measured concentrations of 71 to 317 pM and did not have an obvious relationship with salinity (Boyle et al., 1987).

The purpose of this work was to address the sensitivity of cobalt concentrations in the Sargasso Sea to atmospheric inputs relative to riverine and shelf inputs. We use both time-series measurements from the Bermuda Atlantic Time Series (BATS) station and transect data to discuss the importance of shelf and aeolian dust input functions and the residence time of cobalt in the western Atlantic Ocean. In addition, the possibility of upwelling as a source of cobalt is discussed in the context of a transect from the South Atlantic with cobalt, phosphate, salinity, and temperature data. Given the importance of Co and other trace metals such as Fe, Cd, and Zn as micronutrients to marine phytoplankton, determining the input function and residence times is important in understanding how these trace elements influence primary productivity in surface waters.

## 2. SAMPLING AND ANALYSIS

### 2.1. Analytical Methodology

We used an electrochemical method known as adsorptive cathodic stripping voltammetry to make low-level cobalt analyses. Previous work has shown this method to be sufficiently sensitive for oceanic cobalt measurements (Bond et al., 1978; Donat and Bruland, 1988; Bobrowski, 1989, 1990; Bobrowski and Bond, 1992; Herrera-Melian et al., 1994; Vega and van den Berg, 1997). An Eco-Chemie  $\mu$ Autolab system with a Metrohm 663 hanging mercury electrode was operated at 10 V s<sup>-1</sup> scan rates in linear sweep mode between -0.6 V to -1.4 V. Before the scan, a -0.6-V deposition potential was applied to seawater sample for 90 s, followed by a 10-s equilibration period. All samples were purged for 3 min with 99.999% filtered N<sub>2</sub> gas before analysis. Drop size was 0.52 mm<sup>2</sup>, and stirrer speed was set at 5. A sample 8.5 mL in volume was transferred into the Teflon sample cup with a pipette; reagents were then added.

Dimethylglyoxime (DMG) from Aldrich was recrystallized in 10<sup>-3</sup> M Ethylenediaminetetraacetic acid (EDTA) (Sigma Ultra) dissolved in Milli-Q water to remove impurities, dried, and redissolved in high-performance liquid chromatography-grade methanol at a concentration of 0.1 M. N-(2-hydroxyethyl)piperazine-N'-(3-propanesulfonic acid

(EPPS) buffer reagent was prepared at 0.5 M and pH 8.0. Sodium nitrite was prepared to 1.5 M concentration by dissolution in Milli-Q water. The cobalt blank was greatly reduced in the EPPS buffer and nitrite reagent by treating with pretreated Chelex-100 beads (Bio-Rad) as described by Price et al. (1988/1989) for a few minutes and overnight, respectively. Final concentrations of DMG, EPPS, and nitrite in the sample cup were 0.5 mM, 2.5 mM, and 0.15 M, respectively. Cobalt stock solutions for standard additions were prepared from a cobalt nitrite certified stock solution (Fisher) and diluted in polymethylpentene volumetric flasks for 25 pM increment standard additions.

Samples were irradiated with ultraviolet (UV) light for 3.0 ± 0.1 h in quartz tubes to degrade organic complexes of metals. Irradiation times of this length have been shown to be sufficient to degrade organic complexes of cobalt without measurable losses of cobalt as a result of oxidation to Co(III) and subsequent precipitation (Vega and van den Berg, 1997). Moored In Situ Trace Element Serial Sampler (MITESS) samples were irradiated with ultraviolet light while acidified, then neutralized to pH 8 before analysis. The acidified time-series samples were pH adjusted to pH 7.5 to 8.5 between 2 and 24 h after irradiation by means of 0.1 M NaOH (Alfa Aesar metals basis). This dilute base concentration was used to prevent the precipitation of Mg(OH)<sub>2(s)</sub> that appears upon addition of 1.0 M NaOH. Blanks for HCl and NaOH were determined and subtracted from total metal calculations (not detectable and 9 pM mL<sup>-1</sup>, respectively). Four samples from the mooring were run in duplicate to determine precision.

To measure the analytical blank, cobalt-free seawater was created from filtered UV-irradiated Sargasso seawater, followed by equilibration with pretreated Chelex-100 resin beads (Bio-Rad) (Price et al., 1988/1989). This seawater was then UV-irradiated again to degrade any diamino acid groups that were released from the Chelex-100 beads. We observed this last step to be important at these low picomolar Co levels, despite the rigorous protocol used to prepare the Chelex-100 beads.

### 2.2. Accuracy and Precision

The accuracy and precision of our analytical methodology was checked with CASS-3 Coastal Seawater Reference material and NASS-5 (National Research Council Canada-Institute for National Measurements). The CASS-3 seawater was diluted with Milli-Q water from 700 ± 150 pM to 310 ± 69 pM (error is standard deviation of four different analytical techniques), and NASS-5 was analyzed without dilution. The reference materials were UV-irradiated for 3.0 h in covered quartz vessels, then transferred to LDPE bottles, and the pH was raised to between 7.5 and 9 by means of NaOH. Our results were similar and slightly lower than the reported reference material values (Saito and Moffett, 2001).

We were concerned that addition of NaOH to neutralize the acid preservative before analysis might reduce the recovery of cobalt because of scavenging by Mg(OH)<sub>2(s)</sub> precipitates. Precipitates formed when neutralizing the pH 2.5 seawater samples with additions of 1 M NaOH and disappeared after several hours. We decreased the concentration of base as a precaution to 0.1 M NaOH to avoid formation of precipitates. A test of cobalt recovery after acidification and neutralization showed complete recovery of cobalt (98.9% ± 3.2%) relative to a subsample measured before acid and base additions (Fig. 1). Cobalt recovery was determined by the standard additions technique where cobalt concentration was proportional to electrode current (*i*) before the addition of cobalt (0 pM) and was converted to pM by using the slope from cobalt additions. By this method, the absolute value of the x-intercept is equal to the cobalt concentration in the unknown sample before blank correction.

### 2.3. Sample Collection and Storage

Seawater samples were collected for a profile at the BATS station (31.79°N, 64.26°W) and a surface transect (15-m depth) between the Sargasso Sea (Fig. 2) and coastal waters off New England with acid-cleaned 10-L Go-Flo bottles, Kevlar hydrowire, and positive-pressure clean-van. Seawater was pumped into the van with 0.2- $\mu$ m-filtered N<sub>2</sub> gas and Teflon tubing and was immediately filtered through acid-cleaned 0.2- $\mu$ m Nuclepore polycarbonate filters into Teflon bottles. All

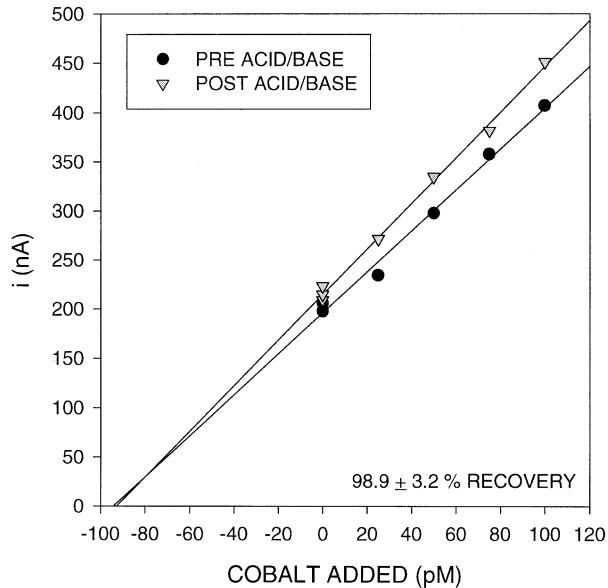


Fig. 1. Standard additions of  $\text{Co}(\text{NO}_3)_2$  to filtered UV-irradiated Sargasso seawater to test for potential artifacts from coprecipitation with carbonates. The 0.1 M NaOH used was dilute enough to avoid visible precipitation at addition. The recovery of cobalt from a sample where the pH was manipulated from pH 8 to 2 and back to 8 again by means of HCl and NaOH was  $98.9 \pm 3.2\%$ , relative to a subsample that was not pH adjusted.  $i$  refers to current from the voltammeter and is proportional to the concentration of cobalt added. Cobalt recovery was calculated by dividing the mean current by the slope of the standard additions and correcting for the blank associated with the NaOH (6 pM).

labware was cleaned with overnight soaking in Citranox detergent, a 2-d 1 M HCl (Baker Instra-analyzed grade) soak at  $60^\circ\text{C}$ , then rinsing and soaking at pH 2 in Ultrex II HCl (Baker). Samples were kept at  $4^\circ\text{C}$  in darkness until analysis within 1 month of collection. These samples were not acidified to minimize artifacts caused by acidification and subsequent neutralization.

Seawater samples for time-series analysis were collected with MIT-ESS automated trace metal samplers developed by Ed Boyle (available at <http://boyle.mit.edu/MITESS/MITESShomepage.html>) and deployed at the Bermuda Testbed Mooring near Bermuda in the Atlantic Ocean ( $31^\circ41.57'\text{N}$ ,  $64^\circ09.04'\text{W}$ ; <http://www.opl.ucsb.edu/btm.html>). The MITESS samplers were deployed at depths between 40 and 47 m throughout 1999. Additionally, occasional 10-m samples were col-

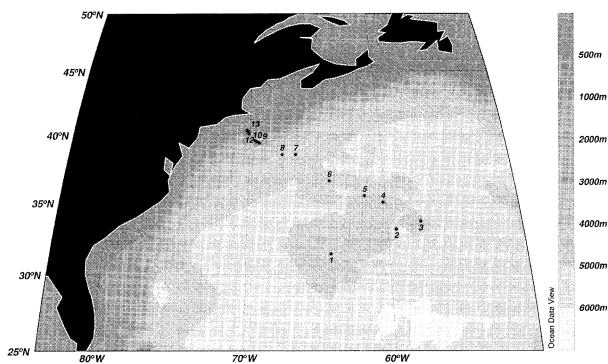


Fig. 2. Cruise track of R/V *Oceanus* cruise 349 on a western North Atlantic transect in September–October 1999. Station 1 is the BATS station.

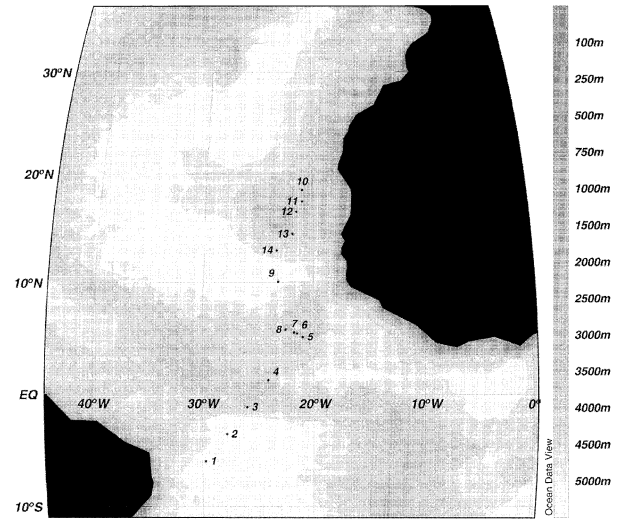


Fig. 3. Cruise track for the South Atlantic transect aboard the R/V *Knorr*, November–December 1999.

lected during retrieval of the mooring. These samples were collected unfiltered and were preserved at the time of collection with triple-distilled HCl (distilled in a Vycor still) to pH  $\sim 2.5$ .

Seawater samples from the South Atlantic transect (Fig. 3) were collected with a clean water pumping system, pumped into a laminar flow hood, and filtered through a  $0.2\text{-}\mu\text{m}$  filter before storage in polyethylene bottles. Samples were stored and analyzed at ambient seawater pH, except for four samples that were acidified to pH 2 (1 M HCl, Baker Ultrex II) before UV-irradiation and neutralized to pH 8 (0.1 M NaOH, Alfa Aesar metals basis) for analysis.

## 2.4. Ancillary Data

Cell numbers of *Prochlorococcus* and *Synechococcus* were determined via flow cytometry on modified FACScan (Dusenberry and Frankel, 1994). Samples were frozen and stored in liquid nitrogen after preservation in 0.125% glutaraldehyde. Samples were thawed at  $35^\circ\text{C}$  for 3 min before analysis and run immediately thereafter. Phosphate measurements were made on samples from the South Atlantic transect by the molybdenum blue method (Parsons et al., 1984).

## 3. RESULTS

### 3.1. BATS Depth Profile

A depth profile of total dissolved cobalt at BATS obtained in September 1999 exhibits nutrient-like behavior with surface depletion of cobalt (Fig. 4A). The water column was stratified at this time, with a mixed layer depth of 50 m. Co depletion in the mixed layer relative to the underlying water reflects a significant biologic demand for this element, consistent with previous radiotracer studies at this location (Moffett and Ho, 1996).

Previous depth profiles of Co reported by Jickells and Burton (1988) from this location under similar stratified conditions do not reveal surface depletion of Co. However, their detection limit was substantially higher than ours and may have obscured surface depletion. Martin et al. (1993), with a detection limit comparable to our method, did report data for Co in the North Atlantic that exhibited surface depletion, with surface- and deep-water values comparable to those we report at BATS (Fig. 4C). Martin and Gordon (1988) also reported a depth profile in

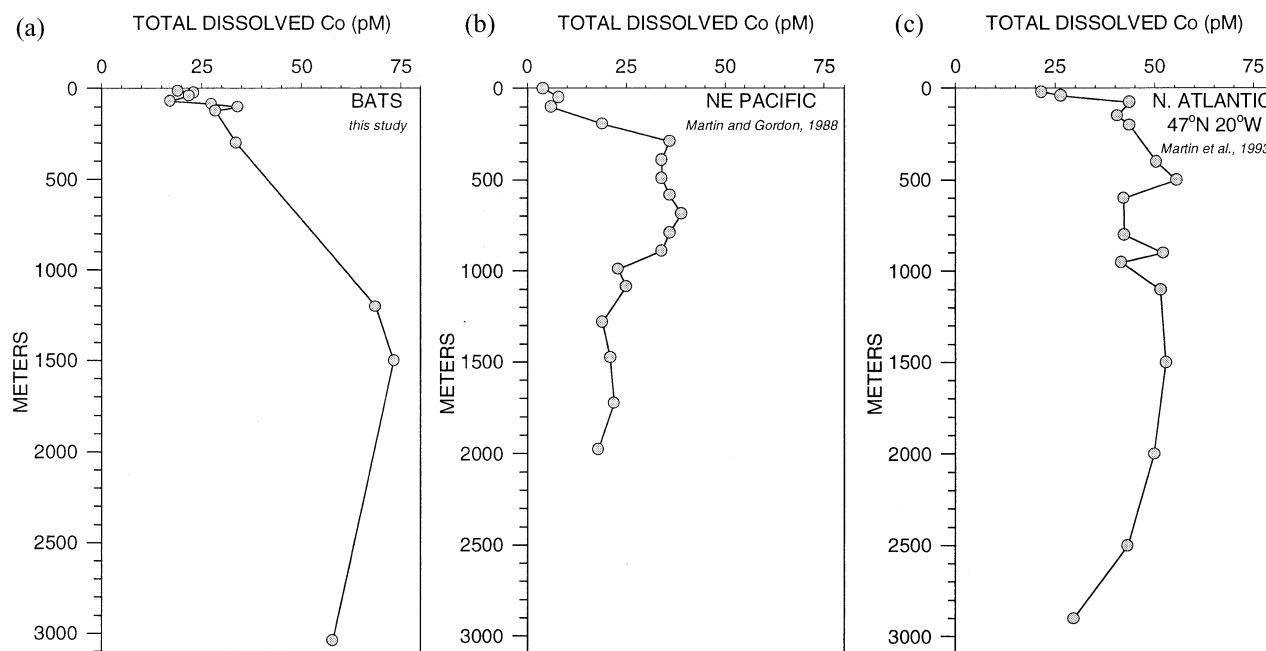


Fig. 4. Comparison of total dissolved cobalt depth profiles from (A) the Sargasso Sea (BATS station September 1999, data from this study); (B) the northeast Pacific (Martin and Gordon, 1988); and (C) North Atlantic 47°N 20°W (Martin et al., 1993). All three profiles show some nutrient-like behavior with surface depletion of cobalt, yet there is no enrichment in deep water from the Atlantic to the Pacific, as is observed with nonscavenged metals such as zinc and cadmium.

the northeast Pacific (Fig. 4B), showing an even stronger surface minimum in dissolved Co concentration. Interestingly, in spite of the nutrient-like characteristics of these profiles, deep-water concentrations of Co do not increase on going from the Atlantic to the Pacific as is observed for other metals that behave like nutrients, such as zinc and cadmium (Bruland and Franks, 1983).

### 3.2. MITESS: Total Cobalt Time Series

Time-series samples from the MITESS trace metal water sampler were measured with biweekly resolution for 1999 (Fig. 5). All samples were less than 50 pM in total cobalt with a mean of  $20 \pm 9.8$  pM, excluding duplicate analyses. The data do not show an obvious seasonal pattern that would be expected with atmospheric dust input. For comparison, Al in surface waters showed a threefold to fivefold increase between June and August in 1981 to 1983 (Jickells et al., 1990) relative to the rest of the year. We do observe several fold oscillations in the data set that are analytically reproducible (replicate samples were analyzed for three of the low values; see the Appendix). However, the pronounced seasonal effect that Jickells et al. observed with Al from aeolian input may not be apparent because of the mooring's location (at  $\leq 40$  m) below the shallow summer thermocline. The shallow summer thermocline should isolate atmospheric inputs in the upper surface waters; yet we do not see an obvious indication of this in the two 10-m samples taken early in the formation of the stratified layers: both of these samples are below the 20 pM annual average. High-resolution samples in the shallow mixed layer would be useful in further resolving this issue.

Temperature data from the mooring at 14 to 15 m and 34 to 35 m show the formation of a seasonal thermocline and significant warming of both depths through the summer (Fig. 5B). There was a decreasing trend in cobalt concentration between Julian day 150 and 267 when MITESS was below the shallow mixed layer. The decrease might reflect isolation from atmospheric sources or underlying waters while biologic scavenging continued. Moreover, several of the sharp decreases in cobalt concentration occur during periods when the thermocline becomes shallower (days 138, 186, and 267). This could result from mesoscale eddies causing upwelling of nutrients followed by an enhanced biologic drawdown of cobalt with the higher productivity (McGillicuddy and Robinson, 1997; McGillicuddy et al., 1998). A significant increase in Co occurred after day 267, associated with deepening of the mixed layer. This could reflect downward mixing of a highly localized near-surface maxima, but could also reflect inputs from underlying waters.

The results suggest that Co depletion to levels at or below 20 pM occurs frequently, indicating that the profile shown in Figure 4A may be fairly typical under stratified conditions. In contrast, Co concentrations are generally higher in the winter under well-mixed conditions, probably because of inputs from deeper waters, where Co concentrations are higher. This is consistent with Co data reported by Martin et al. (1993) for a well-mixed station at higher latitude (59°N 30°W), where surface concentrations were much higher than at the stratified station shown in Figure 4C.

The data indicate that hydrography and in situ removal processes are more significant determinants of Co concentration in surface waters than aeolian inputs, with the aforemen-

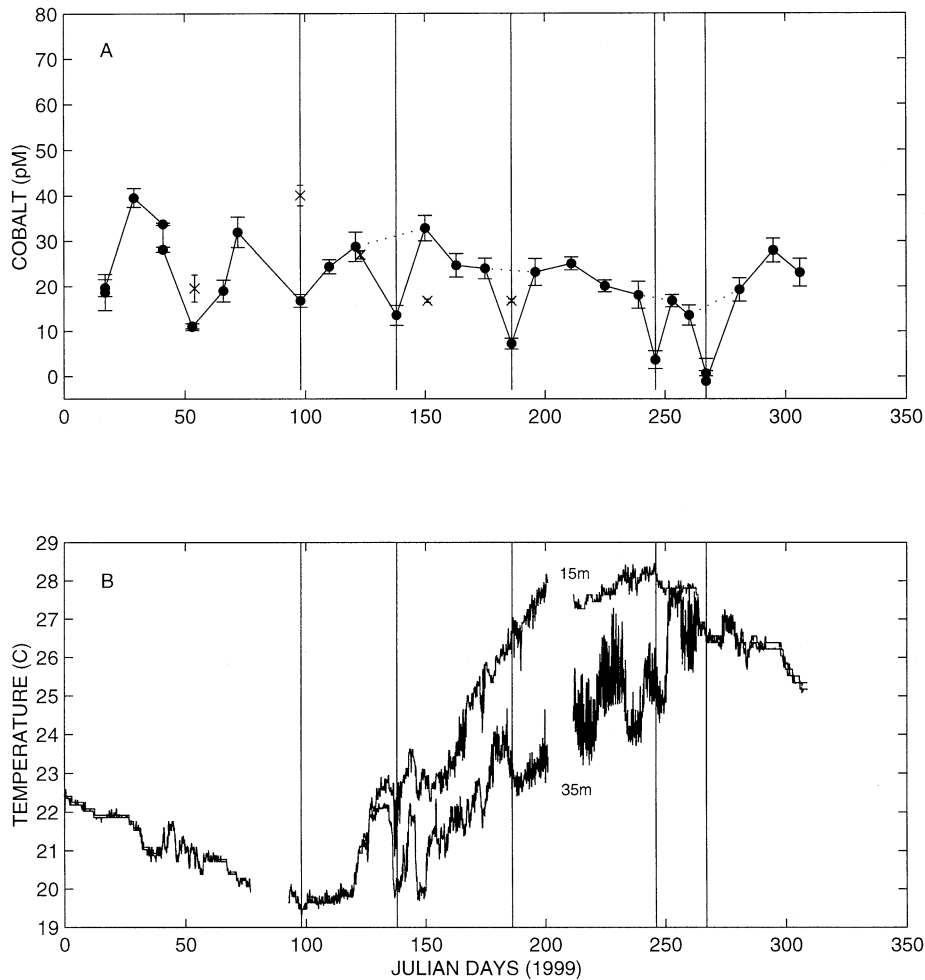


Fig. 5. (A) Time-series cobalt data at the Bermuda Testbed Mooring. Samples were collected by automated trace metal sample collector (MITESS). Biweekly samples were analyzed from a ~40-m depth (circles; see Table A1 for precise sample depths), and several 10-m samples were collected at retrieval of the mooring (crosses). Error bars represent the standard deviation of triplicate scans before standard additions on a sample. Several samples were analyzed twice, in which case both samples were plotted. The dotted line shows relatively consistent cobalt concentration when four sharp cobalt decreases are removed. (B) Temperature data at 14- to 15-m (upper line) and 34- to 35-m depths (lower line) show seasonal stratification with the 14- to 15-m temperature measurements warming relative to the 34- to 35-m depths. Vertical lines indicate simultaneous changes in cobalt concentration and temperature. We hypothesize that these sudden decreases in cobalt may be the result of higher productivity associated with nutrient input from mesoscale cold eddies or mixing events. Temperature data are from the Bermuda Testbed Mooring project using TidbiT instrumentation. (Onset Computer Corp.).

tioned caveat that the mooring depth may result in missing some near-surface features.

### 3.3. BATS—Shelf Transect

Total dissolved Co was determined in samples from 15-m depth along a transect from the BATS station to the Bermuda Rise and toward the shelf region off Massachusetts (Figs. 2 and 6). Cobalt correlated tightly with salinity ( $r^2 = 0.93$ ), similar to the measurements of Mn, Ni, Cu, Zn, and Cd made by Bruland and Franks (1983) on a similar transect between the Sargasso Sea and coastal Massachusetts. In contrast, phosphate and nitrate in that study show highly nonconservative behavior (Bruland and Franks, 1983). And Wu and Luther (1996) reported strongly nonconservative behavior for dissolved Fe on a

transect from Delaware Bay to the Sargasso Sea. Presumably, biologic scavenging of nutrients and Fe in this region is much stronger than for the other trace elements, including Co. Bruland and Franks (1983) used a simple model to demonstrate that the apparent conservative behavior of trace metals across this transect indicates a residence time in surface waters of at least 1 yr.

Extrapolation of the salinity–metal regression to zero salinity provides an estimate of river water concentration if mixing were completely conservative (Table 1). The calculated zero salinity end member for cobalt had a value of 0.785 nM. However, Church (1986) reported highly nonconservative behavior of dissolved Co in Delaware Bay, with a low salinity (1 to 3 ppt) end-member value of 10 to 15 nM and concentrations of 1.5 nM throughout much of the bay. Thus, the apparent

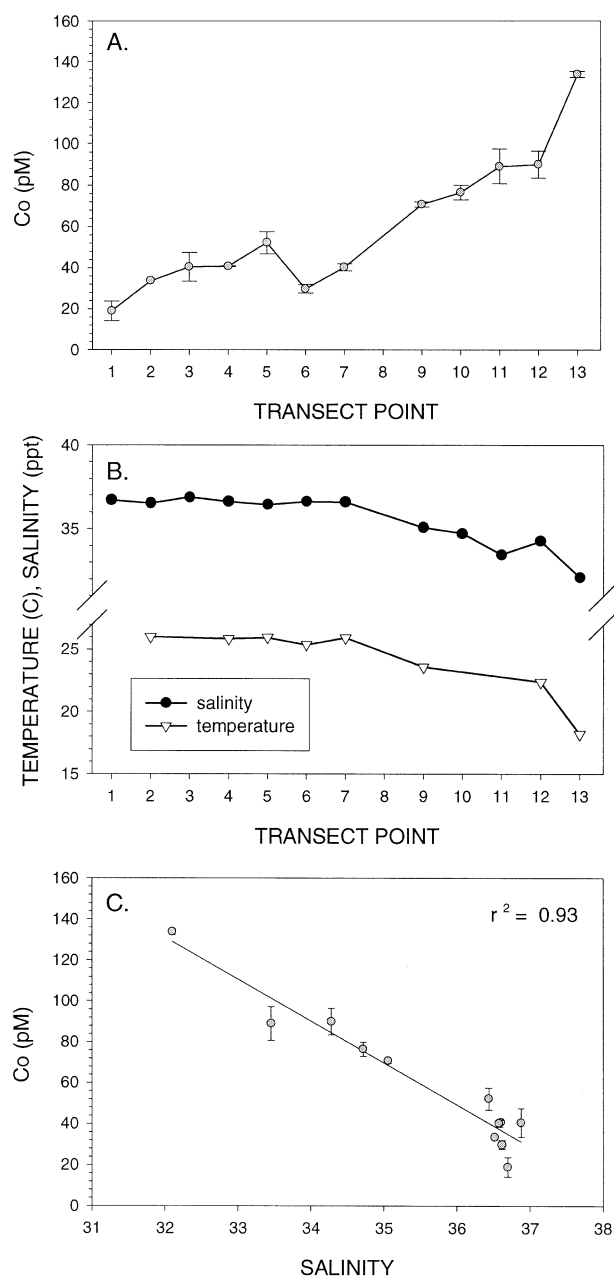


Fig. 6. (A) Transect of total dissolved cobalt from BATS to Coastal Massachusetts, via the Bermuda Rise (station 3) from the R/V *Oceanus*, September 1999. (B) Temperature and salinity data. (C) Inverse correlation between salinity and cobalt was observed.

conservative behavior we observed does not extend to the riverine end member. Church argued that Co was coupled to Mn and Fe in the bay, consistent with Moffett and Ho (1996), who argued that Co and Mn removal is controlled by a common microbial oxidative process. Church contrasted Co with Zn and Cd, which show less drastic removal in estuarine waters than Co. This relative depletion of Co probably contributes to the large differences in the slopes of the concentration vs. salinity plots, expressed as the ratio between the zero-salinity end member and the open ocean in Table 1. For Co, this is 41, significantly lower than the 270 and 550 values of Zn and Cd,

Table 1. Sargasso Sea, shelf water, and extrapolated zero salinity concentrations.

Element <sup>a</sup>	Sargasso Sea end member (nM)	Shelf concentration (nM)	Extrapolated zero salinity end member (nM)	Ratio of end members
Mn	2.3	21	114	50
Ni	2.3	5.9	21	9
Cu	1.2	4.0	19	16
Zn	0.06	2.4	16	270
Cd	0.002	0.20	1.1	550
Co	0.02	0.13	0.79	41

<sup>a</sup> Mn, Ni, Cu, Zn, and Cd transect data from Bruland and Franks (1983).

respectively. These high end-member ratios for Zn and Cd are likely related to the strong effect of biologic drawdown in oceanic surface waters.

### 3.4. South Atlantic Transect

A west-east surface transect across the South Atlantic in November and December of 1998 (5-m depth; see Fig. 3 for map) showed quite high cobalt concentrations on each end, whereas the center of the transect had low cobalt, low salinity, and high temperature (Fig. 7). This central part of the transect is within the intertropical convergence zone where high precipitation and warm temperatures isolate the surface-water masses (Helmers and Schrems, 1995). Interestingly, the pattern of total cobalt distribution on this transect resembles that of phosphate. Of note is the large cobalt and phosphate peak at transect point 2: cell number counts at this site also showed a high concentration of coccolithophore cells (P. Ziveri and M. Conte, private communication), consistent with culture data of Sunda and Huntsman (1995) indicating optimal growth of *Emiliania huxleyi* at high cobalt concentrations.

## 4. DISCUSSION

Co has a unique geochemistry: it is neither a typical nutrient nor a scavenged-type element. The data suggest that seasonal dust inputs in the Sargasso Sea are not a particularly important determinant of surface-water concentrations compared with inputs from upwelled water, in contrast to Al. Dust is considered to be an important source of trace elements to the oceans, as estimated from the relative contribution of aeolian input to dissolved riverine input (Duce et al., 1991). Unfortunately, Duce et al. did not include cobalt in their review of atmospheric deposition.

To assess the importance of aeolian deposition to surface waters, it is important to know the total dust deposition flux, as well as and the fraction of wet deposition that is dissolved and the fraction of material that is solubilized before the dust settles out of the euphotic zone. Aluminum, for example, shows that 3 to 5% of the crustal component is in the dissolved form, and a further 5 to 10% dissolves over 60 h (Prospero et al., 1987). By use of the 2600 Fe:Co ratio in continental crust abundance ratio (Table 2) and atmospheric iron input estimates from Jickells (1999), we estimate the Co

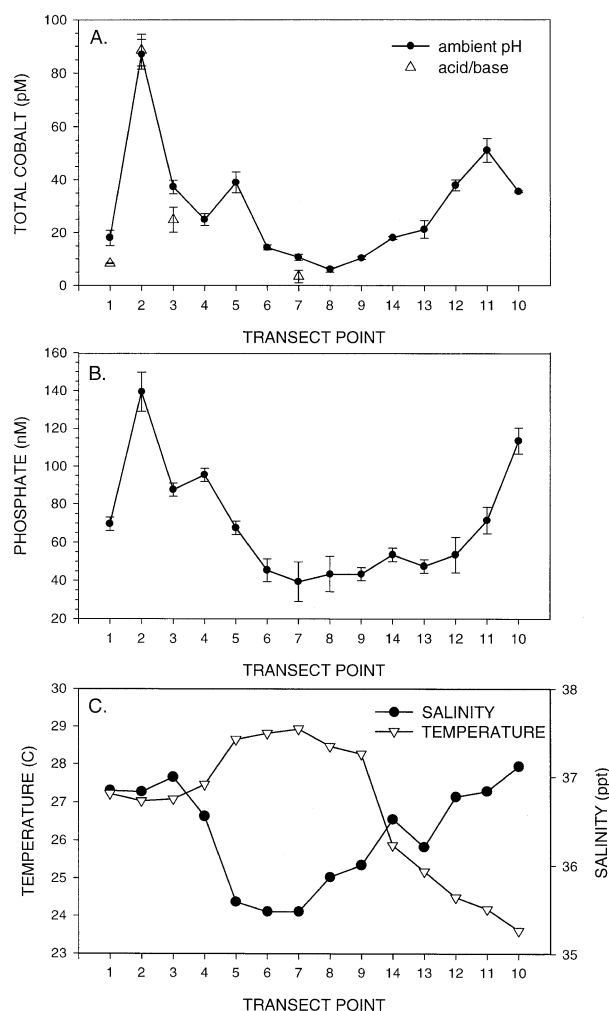


Fig. 7. (A) Total dissolved cobalt along the South Atlantic transect; the transect stations are numbered as shown in Figure 3. (B) Orthophosphate data. (C) Temperature ( $^{\circ}\text{C}$ ) and salinity data.

flux by dust deposition to the Sargasso Sea to be  $1600 \text{ pmol m}^{-2} \text{ d}^{-1}$ . Assuming a soluble fraction of 45% based on Mn solubility (Jickells, 1999), a flux of  $720 \text{ pmol m}^{-2} \text{ d}^{-1}$  results. In a 20-m mixed layer, this would only increase dissolved Co by 3 pM over 3 months. This is probably not contributing to the short-term variability observed in the MITESS data set. It also leads to an upper 100-m surface-water residence time estimate of 7.6 yr, which seems long

Table 2. Crustal composition of transition elements.<sup>a</sup>

Element	Crustal composition (%)	$\log (K_y^{SW})$
Iron	4.0 (FeO)	-8.9
Aluminum	14 (Al <sub>2</sub> O <sub>3</sub> )	-8.0
Cobalt	0.0012	-6.7
Manganese	0.068	-6.3
Zinc	0.0052	-5.2
Nickel	0.0019	-4.6
Cadmium	No data	-3.1

<sup>a</sup> Data from Taylor and McLennan (1985).

Table 3. Particulate metal ratios near Bermuda ( $\mu\text{mol mol}^{-1}$ ).<sup>a</sup>

Metal ratio	10–100 m ( <i>n</i> = 3)	300–4000 m ( <i>n</i> = 17)
Co:P	$403 \pm 128$	$5420 \pm 2440$
Zn:P	$2410 \pm 1050$	$27300 \pm 11800$
Cd:P	$119 \pm 33$	$205 \pm 83$
Co:C	$1.5 \pm 0.6$	$20 \pm 17$
Zn:C	$8.2 \pm 5.6$	$106 \pm 83$
Cd:C	$0.47 \pm 0.17$	$0.71 \pm 0.27$

<sup>a</sup> Calculated from Sherrell and Boyle (1992). Ratios were calculated by means of measured C and P concentrations.

given the low concentrations and drawdown in surface waters we observe. By comparison, residence times in the upper 100-m surface waters for dissolved scavenged-type metals Al and Fe have been calculated to be 1660 to 4750 d and 214 to 291 d, respectively (Jickells, 1999), when measured solubilities of Al and Fe in dust are used. This calculation assumes that the input of Co from dust dominates over upwelled Co, which in light of this study, is an assumption that should be tested. It is important to point out that if upwelled cobalt is significant relative to dust input, then the 7.6-yr residence time is an overestimate.

Rainwater cobalt concentrations are available for the equatorial and South Atlantic, with values of 30 and 28 nM, respectively (Helmers and Schrems, 1995). The equatorial station in the Helmers and Schrems study is also in within the intertropical convergence zone, a region covered by our second transect (Fig. 3). Precipitation in the intertropical convergence zone is extremely high, averaging 1000 to 2000  $\text{mm yr}^{-1}$  (Tchernia, 1980, cited in Helmers and Schrems, 1995). Despite the resultant high estimated flux of cobalt of 28 to 56  $\mu\text{M m}^{-2} \text{ yr}^{-1}$ , the intertropical convergence zone total cobalt surface-water concentrations are the lowest of this transect, ranging from 6 to 39 pM (Fig. 7). Although the study of Helmers and Schrems (1995) was particularly careful about iron contamination, their cobalt data are anomalous compared with all of the other metals they examined (Al, Cd, Cu, Fe, Mn, Ni, Pb, Zn) in that it was the only one to increase between rain storms separated by several hours, with all the other metals showing large to moderate decreases due to atmospheric washout. This leads us to question whether the cobalt rainwater measurement may be overestimated because of analytical considerations or whether cobalt is not susceptible to atmospheric washout effects. Calculations that used wet deposition of this magnitude would result in a 100-m surface residence time as short as 13 d if the average surface Co concentration of the intertropical convergence zone has a similar concentration to that of our Sargasso Sea time-series average. Assuming rainwater concentrations near Bermuda are comparable, the Sargasso Sea would have also have a short residence time of 18 d (0.05 yr) if this approach were used because of the high rainfall at Bermuda ( $1440 \text{ mm yr}^{-1}$ ).

We can also calculate a surface residence time using the flux of carbon export as new production. With cobalt:carbon (Co:C) ratios in particulate matter calculated from Sherrell and Boyle (1992; Table 3), new production at BATS estimated at 4.2  $\text{mol C m}^{-2} \text{ yr}^{-1}$  (Jenkins and Goldman, 1985), and assuming no

preferential release of cobalt from the exported carbon, we can estimate the flux of cobalt from the water column. By use of our 20 pM annual mean total Co concentration, we calculate an upper 100-m residence time of 0.32 yr. The discrepancy between the 100-m surface residence time estimates using estimated dust input (7.6 yr) and the shorter rainwater input (0.05 yr) and particulate matter export (0.32 yr) suggest that input fluxes of cobalt to Atlantic surface waters are poorly constrained and perhaps that aeolian inputs are overestimated relative to other input sources. There is some question as to whether surface-water or deep-water Co:C ratios are better for the surface-water residence time. In the suspended particulates measured by Sherrell and Boyle (1992), cobalt concentrations per liter only increase by a factor of three between surface and deep waters, whereas carbon and phosphorus concentrations per liter decrease by an order of magnitude, forcing the Co:C and Co:P ratios shown in Table 3. Because of this preferential C and P remineralization in deep water, and because surface-water particulate matter may reflect Co:C before significant remineralization, we used the surface Co:C ratio as more accurate reflection of the export ratio. Alternatively, surface-water particulates may reflect the Co:C of the microbial loop, which could have a lower quota than the large phytoplankton that are thought to dominate export flux. If this scenario is true, the surface-water residence time can be recalculated by the deep-water Co:C ratio resulting shorter residence time of 8 to 50 d.

Our residence time calculations should be relatively robust to inaccuracies from episodic events. Estimates of primary productivity have varied by an order of magnitude as a result of sampling of discrete water masses with small in vitro  $^{14}\text{C}$  bottle incubations, vs. geochemical tracer techniques that integrate over large spatial and temporal scales (Jenkins, 1995). The possibility that episodic mesoscale eddies might be a major component of the nitrate supply to surface waters (McGillcuddy et al., 1998) suggests that the Sargasso Sea can be quite dynamic. Our 100-m surface-water residence time calculation should be robust to such short-term variability because we use the tracer-based new production estimate and the average of our time-series data, both of which integrate over long temporal spans. Evidence of this kind of episodic sample heterogeneity is observed in our time series as large decreases in cobalt concentration relative to the mean. Future high-resolution temporal sampling would help to determine whether such fluctuations might indeed be caused by phytoplankton utilization during higher productivity associated with mesoscale eddies.

In laboratory experiments with phytoplankton species, Co cellular quotas can span almost two orders of magnitude (from 0.3 to 11  $\mu\text{mol Co mol}^{-1}\text{C}$ ), depending on the Co concentration in the culture media (Sunda and Huntsman, 1995). These large cellular quota ranges for metals can often occur in a single phytoplankton species with the variability reflecting a physiologic adjustment rather than experimental variability. Particulate Co:C ratios measured by Sherrell and Boyle (1992) are within the range of these laboratory cellular quotas, consistent with our hypothesis that phytoplankton uptake is the predominant pathway for Co incorporation into the particulate matter that is ultimately removed from the upper water column.

Table 4. Regression slopes of Co vs.  $\text{PO}_4$  ( $\mu\text{mol mol}^{-1}$ )

Location	Depth (m)	Co (pM)	$\Delta\text{Co}/\Delta\text{P}$	$r^2$
South Atlantic	5	5–87	560	0.63
Northeast Pacific (T5)	50–150	7.9–32	39.8	0.981
Northeast Pacific (T6)	50–150	28–40	35.5	0.994
Northeast Pacific (T8)	8–50	25–55	38.4	0.977

<sup>a</sup> Northeast Pacific data from Sunda and Huntsman (1995), Martin and Gordon (1988) and Martin et al. (1989).

An analysis of the data of Martin and Gordon (1988) and Martin et al. (1989) by Sunda and Huntsman (1995) showed a strong correlation between zinc and phosphorus until zinc was depleted, at which point cobalt and phosphate begin to correlate. This phenomenon is suggestive of substitution of cobalt for zinc in the phytoplankton community of the northeast Pacific. In the South Atlantic, we can speculate that the biologic demand for cobalt might be more intense relative to that of the Pacific because of the lack of zinc-rich deep waters, and hence a smaller zinc supply from vertical diffusion and advection processes. Following this logic, organisms that can substitute cobalt for zinc may need to make the switch more frequently as zinc becomes depleted. However, on our South Atlantic transect, the surface waters are oligotrophic, with concentrations of phosphate in the low nanomolar range, unlike the micromolar phosphate concentrations of the northeast Pacific. A comparison of the slope of the Co vs.  $\text{PO}_4$  plot ( $\Delta\text{Co}/\Delta\text{P}$ ) between these locations (Table 4) shows that South Atlantic cobalt uptake relative to phosphate uptake is more than an order of magnitude higher than of the northeast Pacific. This high value of  $\Delta\text{Co}/\Delta\text{P}$  ( $560 \mu\text{mol mol}^{-1}$ ) in the South Atlantic is similar to that of  $\Delta\text{Zn}/\Delta\text{P}$  in the northeast Pacific (251, 370 and  $254 \mu\text{mol mol}^{-1}$ ), implying an increased biologic importance of cobalt relative to zinc in this region. The particulate Co, Cd, and Zn profiles near Bermuda by Sherrell and Boyle (1992) show a depletion in Co:C and Zn:C in surface waters and are similar to the surface particulate metal:carbon and metal:P ratios reported by Kuss and Kremling (1999) (Co:C  $1.1 \mu\text{mol mol}^{-1}$ , Co:P  $190 \mu\text{mol mol}^{-1}$ ). In addition, the South Atlantic Co:P ratio in seawater ( $\sim 500 \mu\text{mol mol}^{-1}$ ) is at the upper end of the range of Co:P ratios in phytoplankton (8.5 to  $1200 \mu\text{mol mol}^{-1}$ ; Sunda and Huntsman, 1995).

Cobalt, zinc, and phosphate data from the North Atlantic (Martin et al., 1993) were also examined to see if this relationship between two elements was apparent. No significant correlation was observed for Co and P; however, a correlation between Zn and P was observed in two profiles ( $r^2 = 0.94, 0.67$ ) with  $\Delta\text{Zn}/\Delta\text{P}$  values of 1950 and  $1680 \mu\text{mol mol}^{-1}$ , compared with  $\Delta\text{Zn}/\Delta\text{P}$  values of 251 to  $370 \mu\text{mol mol}^{-1}$  in the northeast Pacific. These calculations suggest the North Atlantic phytoplankton community is using zinc relative to cobalt, and that it is obtaining a higher Zn:P quota in the North Atlantic than the North Pacific. No zinc data are available from the South Atlantic transect for comparison.

The deep-water concentrations of Co provide important insight into its geochemistry. Although Co has a nutrient-like depth profile, concentrations in deeper waters do not increase on going from the Atlantic to the Pacific. In this respect, Co is



similar to Fe (Johnson et al., 1997). For both metals, this reflects scavenging in the deeper waters, coupled with regeneration from settling particles. Johnson et al. (1997) have argued that Fe may be stabilized in deep waters by organic ligands that inhibit precipitation and scavenging. This is supported by direct evidence for metal complexation of Fe in deep waters of the Atlantic (Wu and Luther, 1995) and Pacific (Rue and Bruland, 1995).

We have shown that Co is also organically complexed in deep water (Saito and Moffett, 2001) and argued that such complexation may inhibit scavenging of Co as well. In particular, complexation may inhibit oxidative precipitation by Mn-oxidizing bacteria, an important removal pathway for cobalt in coastal environments (Moffett and Ho, 1996). Comparing the ratios of Co:Mn in Sargasso Sea profiles relative to their crustal abundances (~1:50, Table 2) can give insight into the relative scales of removal processes. For instance, dissolved Co in surface waters is highly depleted relative to dissolved Mn, with respect to crustal abundance. This makes sense in light of the observation that phytoplankton uptake of Co dominates over co-oxidation with Mn in Sargasso surface waters (Moffett and Ho, 1996). In contrast, Co is enriched in deep waters relative to Mn where phytoplankton are absent and Mn concentrations are strongly depleted by microbial oxidation. The organic complexation of cobalt in seawater could serve to stabilize dissolved Co, preventing its microbial co-oxidation with Mn. In addition, organic complexation would stabilize any cobalt in the Co(III) state because  $\text{Co}_{(\text{aq})}^{3+}$  is unstable in seawater. Dissolved Mn, in contrast, is thought to be 100%  $\text{Mn}_{(\text{aq})}^{2+}$  and not influenced by organic complexation (Bruland et al., 1991) and hence would be more reactive toward the predominant removal processes than dissolved Co.

Given the apparent similarities of Co and Fe, it is worth comparing estimates of their whole ocean residence times. An early estimate for Co of ~1000 yr was proposed in 1977 (Bewers and Yeats, 1977). Knauer et al. (1982) calculated an oceanic residence time estimate for cobalt of 52 yr using stream input data and 43 yr using sedimentation rate data. Lacking any open ocean cobalt concentration data, these authors used a 17 pM estimate of world cobalt concentrations based on a prediction that used Mn:Co ratios in coastal waters. Taylor and McLennen (1985) also used a seawater estimate of 17 pM and calculated a residence time of 40 yr based on cobalt abundance in pelagic clays and estimates of sedimentation rates. These seawater estimates of cobalt concentrations are comparable to deep-water concentrations reported in the Pacific (Martin and Gordon, 1988; Martin et al., 1989) and to the time-series surface cobalt numbers reported here, but are lower than those reported for Atlantic deep waters (50 to 70 pM; this work and Martin et al., 1993). Assuming a mean Co concentration between these values would expand Taylor and McLennen's estimate to 40 to 120 yr. These estimates are comparable to estimates of Fe residence times (70 to 140 yr; Bruland et al., 1994).

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## APPENDIX

Table A1. MITESS time series at the Bermuda Testbed Mooring (moored in situ trace element serial sampler).

Date	Depth (m)	Total Co (pM)
1/17/99	44	19
1/17/99	44	20
1/29/99	44	40
2/10/99	44	34
2/10/99	44	28
2/22/99	44	11
2/22/99	44	11
3/7/99	44	19
3/13/99	47	32
4/8/99	47	17
4/20/99	40	24
5/1/99	40	29
5/18/99	43	14
5/30/99	43	33
6/12/99	43	25
6/24/99	43	24
7/5/99	43	7
7/15/99	43	23
7/30/99	40	25
8/13/99	40	20
8/27/99	43	18
9/3/99	43	4
9/10/99	43	17
9/17/99	43	14
9/24/99	40	1
9/24/99	40	ND <sup>a</sup>
10/8/99	43	19
10/22/99	43	28
11/2/99	40	23
2/23/99	10	20
4/8/99	10	40
4/20/99	10	27
5/3/99	10	25
5/31/99	10	17

<sup>a</sup> ND = not detectable.

Table A2. Total cobalt along a South Atlantic surface transect (5 m).

Station	Latitude	Longitude	Date	T (°C)	Salinity	Co (pM)	SD
1	07°09.80'S	31°15.09'W	18-Nov-98	27.2186	36.848	18	2.9
2	03°43.41'S	27°57.74'W	19-Nov-98	27.0271	36.835	87	5.6
3	01°08.42'S	25°56.26'W	20-Nov-98	27.0776	37	37.3	2.6
4	01°35.02'N	25°47.97'W	21-Nov-98	27.4583	36.558	24.9	2.2
5	05°07.12'N	21°00.55'W	23-Nov-98	28.6488	35.591	39	3.9
6	05°25.48'N	21°31.39'W	25-Nov-98	28.8148	35.48	14.4	0.9
7	05°31.87'N	21°48.34'W	26-Nov-98	28.9278	35.479	10.7	1.2
8	05°50.38'N	22°48.37'W	27-Nov-98	28.4683	35.873	6	1
9	10°04.63'N	23°13.53'W	2-Dec-98	28.2679	36.007	10.4	0.5
10	18°28.14'N	21°01.76'W	6-Dec-98	23.6066	37.12	35.5	0.3
11	17°24.67'N	21°05.58'W	11-Dec-98	24.1738	36.841	51.1	4.4
12	16°27.63'N	21°32.28'W	13-Dec-98	24.4887	36.775	37.9	2.1
13	14°25.81'N	21°54.44'W	15-Dec-98	25.1718	36.214	21.2	3.3
14	12°55.83'N	23°20.90'W	16-Dec-98	25.8642	36.526	18 <sup>a</sup>	0.5
1	07°09.80'S	31°15.09'W	18-Nov-98	27.2186	36.848	8.3 <sup>a</sup>	0.2
2	03°43.41'S	27°57.75'W	19-Nov-98	27.0271	36.835	88.5 <sup>a</sup>	5.9
3	01°08.42'S	25°56.26'W	20-Nov-98	27.0776	37	24.8 <sup>a</sup>	4.7
7	05°31.87'N	21°48.34'W	26-Nov-98	28.9278	35.479	3.4 <sup>a</sup>	2.4

<sup>a</sup> These samples are duplicates that were acidified, UV irradiated, then neutralized before analysis.

Table A3. Total dissolved cobalt concentrations in the Sargasso Sea and northwest Atlantic Ocean, September 1999 (R/V *Oceanus* cruise 349).

Station	Depth (m)	Total dissolved cobalt (pM)	Salinity	<i>Prochlorococcus</i> (cells/mL)	<i>Synechococcus</i> (cells/mL)	Picoeukaryotes (cells/mL)
BATS	15	19				
BATS	25	23				
BATS	40	22				
BATS	70	17				
BATS	85	27				
BATS	100	34				
BATS	125	28				
BATS	300	34				
BATS	1200	69				
BATS	1500	73				
BATS	3040	58				
1) 64.10W, 31.40N	15	19	36.7	53,500	7090	—
2) 59.42W, 33.14N	15	34	36.5	125,600	10,100	—
3) 57.62W, 33.69N	15	41	36.9	52,800	6900	—
4) 60.21W, 35.04N	15	41	36.6			
5) 61.51W, 35.50N	15	52	36.4	105,500	5370	—
6) 64.04W, 36.58N	15	30	36.6	59,050	8710	610
7) 66.50W, 38.51N	15	40	36.6	99,600	8260	620
9) 69.27W, 39.38N	15	71	35.1	214,400	23,940	1120
10) 69.43W, 39.46N	15	76	34.7	153,700	31,700	2630
11) 69.57W, 39.56N	15	89	33.5	134,000	24,800	3140
12) 70.07W, 40.10N	15	90	34.3	127,800	27,400	3470
13) 70.23W, 40.31N	15	134	32.1	12,600	122,300	19,400