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Spatial and temporal variability of cadmium in Gulf Stream warm-core rings and associated waters

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ABSTRACT

Seawater samples were collected and analyzed for cadmium during four cruises studying Gulf Stream warm-core rings and associated waters. Warm-core ring (WCR) 82-B was sampled in April (approximately two months after formation), in June (after seasonal stratification), and in August (during its interaction with the Gulf Stream). The September-October cruise studied closure and separation of a meander that formed ring 82-H. The depth of the cadmium maximum varied with the depth of the main thermocline; the maximum occurred at a potential temperature of 7.8 \pm 0.5°C and sigma-theta 27.4 \pm 0.05 in the Slope Water, Gulf Stream, and Sargasso Sea stations. As the upper 100 m of the ring progressed from vertically well-mixed in April to seasonally stratified in June, the mole-ratios of cadmium/nutrient removal in the mixed layer were similar to the calculated slopes of the linear regressions of cadmium with phosphate, nitrate and silicate calculated from spatial distributions. Lateral mixing processes near the boundaries of WCR 82-B markedly influenced the vertical cadmium distribution via intrusions of Shelf/Slope water containing elevated levels of cadmium. Comparison of ASV-labile and total dissolvable cadmium from the August WCR 82-B station indicated essentially 100% ASV-labile cadmium in the waters within and below the main thermocline but non-detectable $(<0.010 \text{ nmol kg}^{-1})$ ASV-labile cadmium in the waters above the thermocline.

1. Introduction

In recent years, improvements in analytical capability and clean sample handling techniques have resulted in accurate oceanic trace metal data. The distribution of cadmium in oceanic waters has been studied extensively during the past several years. The cadmium distribution has been determined in the Atlantic (Bender and Gagner, 1976; Bewers *et al.*, 1976; Boyle *et al.*, 1981; Yeats and Campbell, 1983; Bruland and Franks, 1983), Indian (Danielsson, 1980), Pacific (Boyle *et al.*, 1976; Bruland *et al.*, 1978; Bruland, 1980; Boyle *et al.*, 1981; Knauer and Martin, 1981), and Arctic (Moore, 1981; Danielsson and Westerlund, 1983) Oceans. The behavior of cadmium that emerged from these studies involved removal from surface waters by organisms and subsequent regeneration at depth coincident with the oxidation of particulate organic matter. Cadmium has been found to be strongly correlated with phosphate implying that cadmium is regenerated in a shallow cycle, like the labile nutrients, rather than deeper in the ocean, as is silicate.

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In general, the oceanic cadmium distribution displays surface depletion and enrichment in the deep water. Surface concentrations tend to decrease from the continental boundaries into the central gyres and are elevated in areas of enhanced upwelling. Recent studies of cadmium concentrations in deep water give values of $0.22 \text{ nmol } \text{kg}^{-1}$ for the Sargasso Sea, $0.57 \text{ nmol } \text{kg}^{-1}$ for the Indian Ocean, and $0.82 \text{ nmol } \text{kg}^{-1}$ for the Pacific (Bender and Gagner, 1976; Danielsson, 1980; Bruland, 1980). The higher concentrations in the Indian and Pacific Oceans correspond to an increase in the nutrient concentrations. These trends are a consequence of the general pattern of deep-water circulation with sinking in the Atlantic Ocean and subsequent movement of deep water towards the Pacific.

Warm-core rings form in the Slope Water region between the North American continental shelf and the Gulf Stream. The rings are approximately 100–200 km in diameter and result when a northward meander of the Gulf Stream closes, enclosing a core of warm Gulf Stream or Sargasso Sea water, and separates from the Gulf Stream. Warm-core rings have an average lifetime of 6 months; after formation they tend to travel in a southwesterly direction through the Slope Water region. These rings can draw streamers of water from the continental shelf and transport them into the Slope Water region adjacent to the Gulf Stream. Warm-core rings represent a major mechanism for the exchange of chemical and biological constituents across the Gulf Stream into the Slope Water region (Schink *et al.*, 1982). Thus, the presence of a warm-core ring may have a pronounced influence on the distribution of cadmium in the Slope Water region.

Although cadmium has been termed "one of the most thoroughly studied trace metals in marine environments" (Moore, 1981), there have been very few studies addressing spatial or temporal variability. The development and utilization of "ultraclean" sampling techniques such as the California Institute of Technology common lead sampler (Schaule and Patterson, 1981), Teflon-coated Go-Flo bottles on Kevlar cable and Zodiac surface water collection (Bruland et al., 1978), were necessary steps in the progress of marine trace metal chemistry. These sampling techniques were required to demonstrate the actual levels of trace metals in marine waters. The sampling strategy employed in this study was designed to study small- and large-scale spatial and temporal variability; therefore, the equipment used has to be able to provide high-density vertical samples within a relatively short time period. The sampling equipment consisted of Teflon-lined Go-Flo bottles mounted on a rosette with a CTD-O₂ system. Realizing that such systems using metallic rosettes and electrical conducting cable may contribute contamination, this equipment was compared in surface waters with an "ultra-clean" sampling technique. Our results may also be compared with high quality trace metal data reported by others in the northwestern Atlantic Ocean.

The use of these systems allowed examination of the cadmium distribution with respect to spatial and temporal variability. A study of such variability was also



Figure 1. Locations of two warm-core rings studied during 1982. The core boundaries are outlined by plotting where the 10°C isotherm is 300 m deep. The numbers shown represent Julian days. The shaded circles at left illustrate the changing shape and location of WCR 82-B. The insert in the lower right corner shows the sampling track of the transect during June in WCR 82-B. The location of the Slope Water, Gulf Stream, and Sargasso Sea stations are designated by SW, GS, and SS, respectively.

afforded by the unique environment of warm-core rings in that a given water parcel can be tracked and sampled over time to examine changes during its evolution. This paper describes the larger scale differences in the vertical distributions of cadmium in the Slope, Gulf Stream, and Sargasso Sea parent water masses of warm-core rings, the temporal changes in the cadmium distribution of a warm-core ring during seasonal stratification and localized spatial variability due to the presence of warm-core rings and associated streamer and entrainment features in the Slope Water region.

Samples for trace metals were collected during four cruises in April-May, June, August, and September-October, 1982 (Fig. 1). Warm-core ring 82-B was sampled in April-May (approximately 2 months after formation), in June (after seasonal stratification), and in August (during its interaction with the Gulf Stream). The September-October cruise studied the closure and separation of a Gulf Stream meander to form WCR 82-H.

2. Methods

a. Sampling. Samples were collected primarily with 5-liter Teflon-lined Go-Flo bottles (General Oceanics) mounted on a 24-position rosette sampler and $CTD-O_2$ system. Some samples were collected using 30-liter Teflon-lined Go-Flo bottles on a 12-position rosette, CTD-O₂ system. The Go-Flo bottles were acid-washed prior to use. They were lowered through the sea surface closed; opened at about 10 m beneath the sea surface; and closed electronically at the desired sampling depth during the upcast.

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Experiments to be described in the Results section were conducted to test whether these bottles, on a rosette lowered with electrical conducting cable, would be suitable for uncontaminated low-level measurements of cadmium and other metals in ocean waters.

The samples were drawn into acid-cleaned (4 days 4N HNO₃, 1 day 0.5N HNO₃) 1-liter Teflon bottles (for dissolved samples) or in acid-cleaned 250 ml linear polyethylene (LPE) centrifuge bottles (total metal samples). Filtration and acidification were done onboard ship in a portable positive-pressure, filtered-air laboratory van (Class 1000) that was equipped with a laminar flow clean bench (Class 100) and flameless atomic absorption instrumentation (Zuehlke and Kester, 1985).

The samples for dissolved cadmium were pressure filtered using nitrogen gas in a fully enclosed plexiglass filtration box equipped with Teflon tubing and fittings through acid-cleaned 0.4 μ m Nuclepore membrane filters in clean polycarbonate filter holders. Acidification of the samples to pH 3 (Ultrex HNO₃) using acid-cleaned pipette tips was done in the clean bench within the clean van. Samples to be processed onshore were then double-bagged in plastic. Special care was taken at all times to prevent contamination of the samples.

b. Analytical procedures. A modification of the cobalt-APDC coprecipitation procedure presented by Boyle and Edmond (1975, 1977) and described by Hanson and Quinn (1983) was used for sample preconcentration of dissolved and total cadmium. The procedure can be briefly summarized as follows: 2 ml of 3.5 mmol 1^{-1} clean cobalt chloride reagent were added to 250 ml of seawater at pH 3 and shaken. Two ml of 2% w/w clean APDC were then added, shaken, and the resulting precipitate allowed to develop for two hours. The precipitate was collected onto an acid-cleaned 25 mm 0.4 μ m Nuclepore membrane filter using vacuum-filtration through an all-glass or polysulfone filtration apparatus. After washing the salts through with 20 ml of high purity water, the filter and precipitate were placed in an acid-cleaned polyethylene vial and 4 ml of 3N nitric acid (Ultrex) were added. The samples were sonicated in an ultrasonic generator for $\frac{1}{2}$ hour to aid the dissolution before analysis.

Samples were analyzed at sea and in the laboratory onshore using flameless atomic absorption spectrophotometry (AAS) with a Perkin-Elmer Model 5000 spectrophotometer, Model 500 heated graphite atomizer, and AS-40 Autosampler. The June WCR 82-B radial transect stations were preconcentrated within the laminar flow clean bench in the portable clean van and analyzed at sea for near "real-time" trace metal measurements. Use of the atomic absorption unit at sea allowed for continuous contamination checks and permitted an interaction between sampling and analysis. No loss of analytical precision resulted from the use of the AAS instrumentation onboard ship due to the environment provided by the portable clean laboratory.

There can be serious interference in the cadmium analysis by the high cobalt concentration present in the concentrate (Boyle and Edmond, 1977). This interference

was reduced by: (a) using a 2600°C cleanup step at the end of the atomization cycle, (b) using a high (2300°C) atomization temperature in the maximum power heating mode, (c) recoating the pyrolytically coated graphite tubes in the laboratory using a Perkin-Elmer Pyro-coating unit. Addition of an extra layer of graphite coating not only reduced absorption into the walls but also increased sensitivity and prolonged tube lifetime. The above conditions resulted in negligible interference by the cobalt on the cadmium signal.

Testing of the analytical procedure using standard additions yielded a recovery of 101 \pm 8%. Comparison with NASS-1 Canadian National Research Council Seawater gave a mean and standard deviation of 0.27 \pm 0.03 nmol kg⁻¹ cadmium versus the accepted value of 0.26 \pm 0.04 nmol kg⁻¹. Blank determinations (coprecipitation of 250 gm of high purity water) gave a mean and standard deviation of 0.004 \pm 0.004 nmol kg⁻¹; therefore an average blank value of 0.004 nmol kg⁻¹ was used for all samples. The overall precision of the preconcentration and analytical work was estimated as 5–10%.

ASV-labile cadmium was determined at one station in August. The ASV measurements were done at natural pH using a rotating mercury thin film glassy carbon electrode with a Princeton Applied Research 315 controller, 174A polarographic analyzer, and Hewlett Packard 7045A X-Y recorder. The method was a modification of that described by Huizenga and Kester (1983) and is described in detail by Hanson *et al.* (1987). At this station, AAS analyses for cadmium were done on C_{18} Sep-Pak methanol eluates. This method used a Waters C_{18} Sep-Pak cartridge as a chromatographic column for isolating hydrophobic dissolved organic matter and organically complexed metals in seawater. After passage of seawater through a Sep-Pak, the isolated dissolved organic matter and organically complexed metals were recovered by elution with methanol and the metals analyzed by AAS (Mills and Quinn, 1981; Mills *et al.*, 1981; Hanson and Quinn, 1983).

3. Results and discussion

a. Cadmium in surface waters. Samples were collected aboard the R/V Knorr on all four cruises. To test for possible contamination from the hull of the ship or the sampling equipment, a sampling excursion was conducted using a Zodiac rubber boat to collect surface samples, at various distances from the research vessel, to compare with samples collected from the rosette-mounted Go-Flo bottles. The surface sampling was done using a custom-designed PVC sampling pole. One can place an acid-cleaned Teflon bottle in the apparatus, cap it, submerge it beneath the surface, unscrew the cap, fill, and then recap it; all components are non-metallic. The bottles were rinsed several times before filling. Using this apparatus, potential contamination from the sea surface microlayer was avoided and samples were collected from the bow of the Zodiac while slowly moving forward.

Table 1 is a summary of the Zodiac sampling results from June 1982 in the center of

Sample location relative to ship	Cu	Cd	Ni
0.2 n mile starboard forward	1.4 ± 0.04	0.050 ± 0.001	3.1 ± 0.3
0.2 n mile port forward	1.1 ± 0.1	0.049 ± 0.003	$2.9~\pm~0.3$
0.1 n mile starboard	1.6 ± 0.05	0.059 ± 0.003	2.9 ± 0.2
Adjacent to ship starboard	1.2 ± 0.1	0.067 ± 0.01	3.1 ± 0.5
5-liter rosette 3 meter depth	1.5 ± 0.09	0.039 ± 0.003	2.7 ± 0.04
30-liter rosette 3 meter depth	1.3 ± 0.1	0.048 ± 0.006	$2.7~\pm~0.2$

WCR 82-B. There appeared to be no significant trend of contamination versus distance from the research vessel nor any indication of contamination from the Go-Flo bottles for copper and nickel. The cadmium results appeared to increase toward the ship indicating contamination from the ship; however, the samples collected from the Go-Flo bottles adjacent to the ship, are lower. The copper, nickel, and cadmium results were within the expected range based on recent data for northwestern Atlantic Ocean surface water with a salinity of 35.7‰ (Boyle *et al.*, 1981, 1984; Bruland and Franks, 1983). From this sampling excursion, it appeared that samples collected from the Go-Flo bottles mounted on a CTD rosette could be used for copper, nickel, and cadmium determinations with negligible introduction of contamination. These results are consistent with the sampling experiment conducted by Spencer *et al.* (1982).

The cadmium contents of near-surface waters, collected during this study on different cruises and from various locations in the western North Atlantic Ocean in 1982, were linearly correlated with salinity. This was true for near surface samples collected from a Zodiac or by the Go-Flo bottle/rosette system. The linear relationship between cadmium and salinity in surface waters, determined for this study (Cd(pmol kg^{-1} = -52.2 S(%) + 1931, r = -0.96, n = 20) compared favorably with that of Boyle et al. (1984) (Cd(pmol kg⁻¹) = -51.4 S(‰) + 1870, r = -0.91, n = 16) for a cruise in August 1981 (Fig. 2). However data reported by Bruland and Franks (1983) for the same region in July 1979, exhibit a lower slope (Cd(pmol kg⁻¹) = -31.8 S(%), +1161, r = -0.99, n = 19). The oceanic end members are statistically. equivalent. The cadmium concentrations at 30.2‰ salinity from Bruland and Franks' (1983) data set were derived from samples collected on the continental shelf about 90 km south of Martha's Vineyard, Massachusetts and 110 km from the shelf break. These samples exert a major influence on the lower slope for their July, 1979 Cd-S‰ correlation. Kremling (1983) reported significant variations in the concentration of dissolved cadmium in European shelf waters. It seems likely that estuarine and shelf processes significantly alter the concentration of cadmium in coastal waters, complicating comparisons based upon Cd-S relationships.

b. Cadmium in waters associated with warm-core rings. The hydrographic, nutrient and cadmium data are compiled in tabular form in the Appendix. The nutrient data



Figure 2. Cadmium-salinity relationship for near-surface waters collected from the western North Atlantic during April-October, 1982 (this study) as compared with that of Bruland and Franks (1983) during July, 1979 and with that of Boyle *et al.* (1984) during August, 1980.

used in this analysis were taken from Fox *et al.* (1984a,b; 1985a,b). As part of the study of warm-core rings, the parent water masses in the Sargasso Sea, Gulf Stream, and Slope Water regions were sampled (Fig. 1). Representative profiles of cadmium, phosphate, potential temperature and salinity for these regions are shown in Figure 3. A tabulated summary of the cadmium concentrations for various depth intervals in the water column for these stations is given in Table 2.

Cadmium concentrations in the surface waters were highest in the Slope Water and decreased through the Gulf Stream to the Sargasso Sea. Sargasso Sea surface water, collected by the Zodiac method, had a mean and standard deviation of 0.006 ± 0.003 nmol Cd kg⁻¹ (n = 20). The Slope Water cadmium concentration at the cadmium maximum was slightly higher than that observed in the Gulf Stream or Sargasso Sea, but values in the deep water were similar.

Dissolved cadmium concentrations increased to 0.27 nmol kg⁻¹ in the two deepest samples (2470 and 2533 m) in the Slope Water profile (Fig. 3). This particular cast came within three meters of the bottom. A near-bottom increase of 2 μ mol kg⁻¹ silica was observed in this cast; however, there was a slight decrease in nitrate and phosphate concentrations. A similar near-bottom increase of cadmium has been reported by Yeats and Campbell (1983) which was tentatively attributed to release of cadmium from the sediments. The cause for the near-bottom increase seen in this study remains unclear as samples for total metals or particular phases were not taken at this station.

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Figure 3. Cadmium, phosphate, potential temperature, and salinity from stations in the Slope Water (a), Gulf Stream (b), and Sargasso Sea (c). The Slope Water measurements are dissolved cadmium whereas the Gulf Stream and Sargasso Sea are total dissolvable cadmium.

Table 2. The average \pm one standard deviation of cadmium concentrations (in nmol/kg⁻¹) in several regions of the Northwest Atlantic. The depth intervals of the water column regions are shown in parentheses.

Region of the water column	Slope Water	Gulf Stream	Sargasso Sea	WCR 82-H
Surface waters	0.039 ± 0.004	0.016 ± 0.004	0.011 ± 0.003	0.014 ± 0.003
	(6–56 m)	(20–200 m)	(15–200 m)	(30–150 m)
18° water		0.028 ± 0.016	0.020 ± 0.003	0.019 ± 0.005
		(200–400 m)	(200–490 m)	(150-500 m)
Cadmium maximum	0.33	0.27	0.30	0.28
	(350 m)	(800 m)	(1050 m)	(900 m)
Deep waters	0.22 ± 0.01	0.23 ± 0.005	0.24 ± 0.004	0.22 ± 0.005
-	(750–2450 m)	(10002000 m)	(1600-3000 m)	(1200-2000 m)

The temperature and salinity data suggested that this feature may be associated with Denmark Straits Overflow Water.

The difference in the depths of the cadmium maximum were related to the depth of the main thermocline. The potential temperature and sigma-theta surface at the cadmium maximum for these stations were 7.8 \pm 0.5°C and 27.40 \pm 0.05, respectively.

c. 82-H ring closure. During the September-October 1982 cruise we were able to study events occurring during ring closure. Warm-core ring 82-H developed from an extremely large meander (ring diameter ~ 300 km) with its central waters having chemical and biological characteristics typical of the Sargasso Sea adjacent to the Gulf Stream. Profiles taken in the center of the meander and after closure were not appreciably different. Plots of cadmium, phosphate, potential temperature, and salinity are shown in Figure 4. The cadmium data are summarized in Table 2. The core of 82-H has Sargasso Sea temperature and salinity characteristics, the cadmium distribution was also representative of the northern Sargasso Sea for this time period.

As has been previously documented (Boyle et al., 1976; Bruland et al., 1978; Bruland, 1980; Bruland and Franks, 1983), cadmium showed a high degree of correlation with phosphate. A linear relationship existed between cadmium and the nutrients, nitrate and phosphate, for phosphate values greater than 0.3 μ mol kg⁻¹ and nitrate values greater than 4.5 μ mol kg⁻¹. The linear relationships calculated for phosphate, nitrate and cadmium, by combining the Slope Water, Gulf Stream, Sargasso Sea, and WCR 82-H stations, are presented in Table 3.

The Cd:N:P atom ratio calculated for this study is 1.8×10^{-4} :13:1. In the North Pacific, Bruland (1980) found a Cd:N:P atom ratio of 3.5×10^{-4} :15:1 and found that extrapolation of the regression line predicted that cadmium would be depleted before phosphate. Yeats and Campbell (1983) found a Cd:P ratio of 2.7×10^{-4} for stations in the North Atlantic Ocean between Newfoundland and the Gibbs Fracture Zone and the Labrador Sea, while Bruland and Franks (1983) found a Cd:P ratio of 2.9×10^{-4}

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Figure 4. Total dissolvable cadmium, phosphate, potential temperature, and salinity from a station in the center of WCR 82-H approximately 1 week after formation.

for the Sargasso Sea approximately 200 km northwest of Bermuda. Wallace *et al.* (1983) found a Cd:P ratio of 2.1×10^{-4} from a station in the Gulf Stream adjacent to the southeastern U.S. continental shelf. Danielsson and Westerlund (1983) found a Cd:P ratio of 1.4×10^{-4} in the Arctic Ocean. Danielsson (1980) found different Cd:P ratios for the northern (1.4×10^{-4}) and southern (2.3×10^{-4}) Indian Ocean with the northern Indian Ocean having higher productivity. The comparison of Cd:nutrient ratios for different regions of the ocean may be influenced by the different ranges of nutrient concentrations present. At our stations in the North Atlantic, with a phosphate range of $0-1.55 \ \mu\text{mol} \ \text{kg}^{-1}$, the atom ratios were lower than has been previously determined from central gyre stations and, if the regression lines were

Table 3. Linear cadmium—nutrient relationships calculated for the Slope Water, Gulf Stream, Sargasso Sea and WCR 82-H stations. (Units; NO₃, PO₄ and Si(OH)₄ – μ mol kg⁻¹, Cd-nmol kg⁻¹; slope and intercept include standard deviation).

	Slope	Intercept	Correlation	No. samples
Constituents	m	b	r	n
NO ₃ vs. PO ₄ *	12.7 ± 0.6	4.9 ± 0.6	0.956	49
Cd vs. PO4*	0.18 ± 0.01	0.023 ± 0.01	0.908	49
Cd vs. NO ₃ *	0.014 ± 0.0006	-0.044 ± 0.01	0.951	53
Cd vs. Si(OH)4**	0.019 ± 0.0005	0.0008 ± 0.004	0.982	55

*Calculation limited to samples with NO₃ contents >4.5 μ mole kg⁻¹ and PO₄ contents >0.3 μ mole kg⁻¹.

**Calculation limited to samples collected from the surface down to the depth of the cadmium maximum.

extrapolated to their lower limit, cadmium would be depleted before nitrate but after phosphate.

The depletion of cadmium in surface waters relative to deep waters may be explained via uptake by plankton and subsequent incorporation into the fecal material produced by grazing zooplankton. As the fecal material falls through the water column, microbial decomposition allows cadmium to be released, thus producing the observed profiles. The specific mechanism of cadmium uptake remains unclear, however. The excellent correlations observed between cadmium and the nutrients, nitrate and phosphate, have been used to infer involvement with soft-tissue cycling. However reasonable correlations are also obtained for cadmium and silica, particularly if the calculation is limited to samples from the surface to the depth of the cadmium maximum in the Atlantic.

Work by D. Nelson at Oregon State University, on biogenic silica and silica dissolution rates in the warm-core rings, indicated that most of the biogenic silica dissolution occurs in the waters from the surface to the main thermocline. Below the main thermocline, dissolved silicate continues to increase due to regeneration at the sediment-water interface. The Cd:Si atom ratio of 1.9×10^{-5} from our work (Table 3) is similar to that calculated from the data of Wallace *et al.* (1983) (2.3×10^{-5}) for the Gulf Stream and somewhat lower (2.7×10^{-5}) than that calculated from the data of Bruland and Franks (1983) for the northwestern Atlantic Ocean. Biological investigations of metal uptake sites and selective leaching studies of oceanic particulate phases are required in order to determine if cadmium is primarily associated with the silicate, carbonate, or organic phases of marine particles.

d. Temporal observations in WCR 82-B. Cadmium, phosphate, potential temperature, and salinity profiles for the central waters of WCR 82-B are shown in Figure 5. In April (Fig. 5a), the upper waters were well mixed to nearly 450 m. The average temperature and salinity from 0-400 m was 15.8°C and 36.31‰, respectively. The cadmium and phosphate concentrations were also fairly uniform in this depth range with cadmium concentrations averaging 0.083 ± 0.007 nmol kg⁻¹ and phosphate averaging $0.21 \pm 0.02 \ \mu$ mol kg⁻¹. The higher cadmium and phosphate values in the upper waters of WCR 82-B compared to either the Gulf Stream or the Sargasso Sea were due to deep winter convective mixing of water at depth having higher concentrations of these elements. Intense evaporative cooling from February to April 1982 resulted in deep nitrate, phosphate, and cadmium being mixed to the surface of ring 82-B more rapidly than could be removed by primary production. This resulted in unusual accumulations of these elements in near-surface waters and, with respect to the nutrient elements, set conditions for the phytoplankton bloom that occurred in May.

By the time of the June cruise, seasonal stratification had occurred (Fig. 5b). The average temperature and salinity in the ring-center mixed-layer (30 m depth) were



Figure 5. Cadmium, phosphate, potential temperature, and salinity from a time series study of ring center stations in WCR 82-B sampled in April (a), June (b), and August (c). The April and June measurements are dissolved cadmium, the August samples are total dissolvable cadmium. The ASV-labile cadmium (x) is also plotted for the August station.

18.4°C and 35.59‰ respectively. The increase in temperature was due primarily to surface warming, the decrease in salinity was due to entrainment and mixing into the ring of lower salinity water. Between the April and June cruises the cadmium and nutrient concentrations in the mixed-layer decreased (Table 4). The nutrients were no longer detectable by conventional methods. The molar ratios of cadmium removal to nutrient removal, during the April and June time period, were similar to the slopes of the cadmium-nutrient linear relationships calculated from spatial distribution data (Table 3).

This is the first time in which a given parcel of oceanic water has been tracked and sampled over time to observe cadmium and nutrient removal in the upper waters. The upper ring waters did not represent a completely closed system; the decrease in surface salinity indicated that lower salinity water must have intruded which probably contained elevated levels of cadmium. The removal of 0.048 nmol kg⁻¹ cadmium must therefore be taken as a lower limit of the actual amount removed.

By August, the ring had undergone several intrusions of lower salinity Shelf and Slope water, and was interacting the Gulf Stream. The surface cadmium distribution showed several "spikes" of elevated cadmium concentrations that coincided with lower salinity features (Fig. 5c). These low salinity, high cadmium features were at $\sigma_{\theta} =$ 24.8–25.8 (40–50 m depth) and $\sigma_{\theta} = 26.4$ (64 m depth). The cadmium maximum at this time was at 400 m. The shoaling of the cadmium maximum as well as other parameters (nutrient maximum, 10°C isotherm) was due to the Gulf Stream interactions and an overall loss of gravitational potential energy during the life of the ring. Estimates of cadmium removal in the surface waters from June to August could not be made, because surface entrainment of Slope, Shelf and Gulf Stream waters contributed unknown amounts of cadmium.

ASV-labile cadmium was determined at this station (Fig. 5c). Most of the samples collected above 300 m depth were below the estimated detection limit of 0.010 nmol kg⁻¹. Comparison of ASV-labile cadmium and total cadmium indicated that most of the cadmium in deeper waters (>300 m) was present as labile, probably inorganic, complexes. The percentage (± one standard deviation) of the total cadmium that was ASV-labile for the samples deeper than 300 m was 99 ± 7% (n = 10). Of the eight samples from the waters above 300 m, only one had detectable (0.044 nmol kg⁻¹) ASV-labile cadmium. This sample was associated with a low salinity (35.0%) feature at $\sigma_{\theta} = 24.8$ (40 m depth).

Very little cadmium (<0.005 nmol kg⁻¹) was detected by AAS in the C₁₈ Sep-Pak methanol eluates, which suggested that if the cadmium was organically complexed, it was not bound to the hydrophobic organic ligands that were chromatographically isolated by the octyldecyl silane packing material of a C₁₈ Sep-Pak. The concentration of particulate cadmium was very low (<0.001 nmol kg⁻¹) in Atlantic surface waters (Bruland and Franks, 1983). The ASV-inert cadmium may have been associated with colloidal and small particles that pass through 0.4 μ m filters and/or with hydrophilic

	Mixed						
	layer	Salinity	Temperature	Cadmium	Phosphate	Nitrate	Silicate
	depth m	%00	ç	pmol kg ^{-t}	μmol kg ^{−1}	μmol kg ⁻¹	μmol kg ⁻¹
April	450	36.31 ± 0.02	15.8 ± 0.1	83 ± 7	0.21 ± 0.02	5.7 ± 0.2	2.6 ± 0.2
June	30	35.59 ± 0.28	18.4 ± 0.4	35 ± 5	nd ≤0.01	nd ≤0.1	nd ≤0.1
Difference		-0.44 ± 0.30	$+2.6 \pm 0.5$	-48 ± 12	-0.21 ± 0.02	-5.7 ± 0.2	-2.6 ± 0.2
∆ Cd/∆ Nutr	ient* Based on	above time period.			0.23 ± 0.08	0.008 ± 0.002	0.019 ± 0.006
∆ Cd/ ∆ Nut	rient* Based on	water column data li	inear regressions (Table 3)	0.18 ± 0.01	0.014 ± 0.001	0.019 ± 0.0005
*Cd nmol kg ⁻	1, Nutrients μm	ol kg ⁻¹					

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Table 4. Cadmium and nutrient removal in the mixed layer of central WCR 82-B waters between April and June. (Values are averages ± standard deviations.)

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WCR 82-B TRANSITION ZONE SECTION JUNE 16-17, 1982 KN 95 STATIONS

DISSOLVED CADMIUM (PMOL/KG)

Figure 6. Dissolved cadmium and temperature distributions from a transect of WCR 82-B in June. The distance between stations 3 and 8 is approximately 150 km.

organic complexes that were not isolated by the C_{18} Sep-Pak. The nature of the ASV-inert cadmium in the surface waters merits further investigation.

e. June 82-B radial transect. A transect across the northern portion of WCR 82-B was made during the June cruise (Fig. 1). Figure 6 shows the cadmium and temperature distributions. The temperature section delineated the general hydrographic features of the ring. The deepening of the isotherms toward the central ring waters was reflected in the cadmium concentrations. The central isothermal region of the ring appeared on the cadmium profile as a region of cadmium concentrations less than 0.100 nmol kg⁻¹.

Cadmium concentrations increased with depth; however, samples were not taken deep enough to clearly define the cadmium maximum.

This radial section illustrated some of the spatial variability in cadmium and the gradients which resulted from lateral mixing processes. Three features of particular interest were:

1. The central surface upper 30 m had an average cadmium concentration of 0.087 ± 0.009 nmol kg⁻¹, which was considerably higher than the ring center stations (0.035 nmol kg⁻¹) for this time period. In April, the salinity of the water in this portion of the ring was 36.2%; by June, the salinity of this water was 34.7 to 35.5%. The higher cadmium concentrations were due to lateral mixing into the ring of lower salinity Slope and Shelf Water which had elevated cadmium concentrations.

2. Intrusions of Shelf water at the edges of the ring (primarily stations 3 and 8) have relatively high $(0.15-0.20 \text{ nmol } \text{kg}^{-1})$ cadmium concentrations. These Shelf Water intrusions could be divided into two groupings.

- a) Station 3 at 9 m depth: $\theta = 14^{\circ}$ C, salinity = 33.3‰, $\sigma_{\theta} = 24.8$.
- b) Station 3 at 106 m and Station 8 at 60 m: $\theta = 8.9-10^{\circ}$ C, salinity = 34.1-34.4‰, $\sigma_{\theta} = 26.4$.

3. There was a subsurface dissolved cadmium maximum in the seasonal pycnocline $(\sigma_{\theta} = 26.1-26.7)$ at 40-50 m depth centered at stations 5 and 6. Cadmium concentrations in the maximum averaged 0.18 ± 0.01 nmol kg⁻¹. The isopycnals containing the elevated levels of cadmium sloped upwards from the surrounding Shelf Water intrusions (stations 3, 8) to the central waters. The σ_{θ} values for the pycnocline ranged between 26.1-26.8, the σ_{θ} of the surrounding Shelf Water intrusions was 26.4. Thus it is likely that Shelf Water containing elevated levels of cadmium was advected into the ring along these isopycnals. This transect crossed the northern portion of the ring; it did not go through ring center. At this time in June, a cadmium maximum was not seen in the upper waters of ring center (Fig. 5b). However, the low salinity, high cadmium spikes seen in August in ring center (Fig. 5c) occurred at $\sigma_{\theta} = 24.8-25.8$ (40-50 m depth) and $\sigma_{\theta} = 26.4$ (64 m depth) and were close to the same density as the Shelf Water intrusions seen at the outer portion of the ring in June.

The importance of lateral mixing processes in producing spatial variability was further illustrated in a profile taken in an entrainment feature of WCR 82-B in June (Fig. 7). The salinity was lower (33‰) the cadmium concentration was higher (0.16 nmol/kg) in the surface waters of the entrainment than in the surface waters of the central region of WCR 82-B in June (see Fig. 5b; 35.7‰, 0.04 nmol/kg). The entrainment zone consisted of cold Shelf Water to the north and east of ring center. The entrainment of the Shelf Water streamer into the ring via lateral mixing processes produced definite variations in the profiles of cadmium, phosphate, potential temperature, and salinity.



Figure 7. Dissolved cadmium, phosphate, potential temperature, and salinity from the entrainment feature of WCR 82-B in June. This station was sampled on Julian day 174 at 37°07.0'N, 73°09.0'W. This station was approximately 72 km northeast of the ring center position.

4. Summary and conclusions

The cadmium distribution in warm-core rings reflected both hydrographic features and involvement in biogeochemical cycling. In these waters, as in other parts of the ocean, the cadmium distribution displayed surface depletion and enrichment in the deep water that resulted from uptake by organisms in the euphotic zone and regeneration of organic material at depth. Cadmium and phosphate, as well as cadmium and nitrate, were highly correlated through the water column. Cadmium and silica were highly correlated from the surface to the cadmium maximum. The depth of the cadmium maximum corresponded to the depth of the main thermocline in the Slope Water, Gulf Stream, and Sargasso Sea regions; the cadmium maximum occurred at a potential temperature of $7.8 \pm 0.5^{\circ}$ C and a sigma-theta of 27.4 ± 0.05 .

The surface waters of WCR 82-B displayed removal of cadmium over time as the ring progressed from a vertically well-mixed water column (to \sim 450 m) in April to being seasonally stratified in June. Comparison of the cadmium and nutrient concentrations in the surface waters in April and in June indicated a ratio of cadmium:nutrient removal similar in magnitude to the slopes of the cadmium:nutrient correlation vertically in the water column. This was the first time that a parcel of oceanic surface water had been sampled over a period of time to document cadmium removal along with depletion of nutrients. By August, intrusions of Shelf, Slope, and Gulf Stream waters had altered the cadmium concentrations in the upper 100 m by the addition of low salinity Shelf and Slope Waters with high cadmium concentrations.

Most of the cadmium within and below the main thermocline in WCR 82-B in August was ASV-labile, whereas most of the cadmium above these depths was ASV-inert.

A transect across WCR 82-B in June illustrated the close correspondence of cadmium and the hydrographic regime. Intrusions of Shelf Water at the edge of the ring produced elevated cadmium concentrations. A subsurface cadmium maximum at 40–50 m depth revealed isopycnal transport as an important mechanism for bringing Shelf and Slope Waters into the ring. The role of lateral mixing processes was evident from the spatial variability of cadmium associated with an entrainment feature at the edge of WCR 82-B. Warm-core rings are a major vehicle for the exchange of chemical and biological constituents among the Sargasso Sea, the Gulf Stream, and the Slope Water region. Entrainment features are able to transport chemicals from the continental shelf to the offshore waters. When rings ultimately coalesce with the Gulf Stream, the cadmium they gained and retained in their upper and intermediate depth waters will be injected into the Gulf Stream and into the North Atlantic gyre system.

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REFERENCES

- Bender, M. L. and C. Gagner. 1976. Dissolved copper, nickel, and cadmium in the Sargasso Sea. J. Mar. Res., 34, 327–339.
- Bewers, J. M., B. Sundby and P. A. Yeats. 1976. Distribution of trace metals in the western North Atlantic off Nova Scotia. Geochim. Cosmochim. Acta, 40, 687–696.
- Boyle, E. A. and J. M. Edmond. 1975. Determination of trace metals in aqueous solution by APDC chelate co-precipitation, *in* Analytical Methods in Oceanography, Advances in Chemistry Series 147, Thomas R. P. Gibb, ed., Amer. Chem. Soc., Washington, D.C., 44-55.
- —— 1977. Determination of copper, nickel, and cadmium in sea water by APDC chelate coprecipitation and flameless atomic absorption spectroscopy: Anal. Chim. Acta, 91, 189– 197.
- Boyle, E. A., S. S. Huested and S. P. Jones. 1981. On the distribution of copper, nickel, and cadmium in the surface waters of the North Atlantic and North Pacific Ocean. J. Geophys. Res., 86, 8048–8066.
- Boyle, E. A., D. F. Reid, S. S. Huested and J. Hering. 1984. Trace metals and radium in the Gulf of Mexico: an evaluation of river and continental shelf sources. Earth Planet. Sci. Lett., 69, 69–87.
- Boyle, E. A., F. Sclater and J. M. Edmond. 1976. On the marine geochemistry of cadmium. Nature, 263, 42-44.
- Bruland, K. W. 1980. Oceanographic distributions of cadmium, zinc, nickel, and copper in the North Atlantic. Earth Planet. Sci. Lett., 47, 176–198.
- Bruland, K. W. and R. P. Franks. 1983. Mn, Ni, Cu, Zn, and Cd in the Western North Atlantic,

in Trace Metals in Sea Water, C. S. Wong, E. Boyle, K. W. Bruland, J. D. Burton and E. D. Goldberg, eds., Plenum Press, NY, 395–414.

- Bruland, K. W., G. A. Knauer and J. H. Martin. 1978. Cadmium in northeast Pacific waters. Limnol. Oceanogr., 23, 618–625.
- Danielsson, L.-G. 1980. Cadmium, cobalt, copper, iron, lead, nickel and zinc in Indian Ocean water. Mar. Chem., 8, 199-215.
- Danielsson, L.-G. and S. Westerlund. 1983. Trace metals in the Arctic Ocean, in Trace Metals in Sea Water, C. S. Wong, E. Boyle, K. W. Bruland, J. D. Burton and E. D. Goldberg, eds., Plenum Press, NY, 85-95.
- Fox, M. F., P. P. Bates and D. R. Kester. 1984a. Nutrient data for Warm Core Ring 82-B from R/V *Knorr* cruise 93. Technical Report 84-1, Graduate School of Oceanography, University of Rhode Island, Kingston, 69 pp.
- 1984b. Nutrient data for Warm Core Ring 82-B, R/V Knorr cruise 95. Technical Report 84-2, Graduate School of Oceanography, University of Rhode Island, Kingston, 63 pp.
- 1985b. Nutrient data for Warm Core Ring 82-H, R/V Knorr cruise 98. Technical Report 85-4, Graduate School of Oceanography, University of Rhode Island, Kingston, 81 pp.
- Hanson, A. K., Jr. and J. G. Quinn. 1983. The distribution of organically complexed copper and nickel in the Middle Atlantic Bight. Can. J. Fish. Aquat. Sci., 40 (Suppl. 2), 151-161.
- Hanson, A. K., Jr., C. M. Sakamoto-Arnold, D. L. Huizenga and D. R. Kester. 1987. Copper complexation in Sargasso Sea and Gulf Stream warm-core ring waters. Mar. Chem., (in press).
- Huizenga, D. L. and D. R. Kester. 1983. The distribution of total and electrochemically available copper in the northwestern Atlantic Ocean. Mar. Chem., 13, 281–291.
- Knauer, G. A. and J. H. Martin. 1981. Phosphorus-cadmium cycling in Northeast Pacific waters. J. Mar. Res., 39, 65–76.
- Kremling, K. 1983. Trace metals fronts in European shelf waters. Nature, 303, 225-227.
- Mills, G. L., A. K. Hanson, Jr., J. G. Quinn, W. R. Lammela and N. D. Chasteen. 1981. Chemical studies of copper-organic complexes isolated from estuarine waters using C₁₈ reverse-phase liquid chromatography. Mar. Chem., 11, 355–377.
- Mills, G. L. and J. G. Quinn. 1981. Isolation of dissolved organic matter and copper-organic complexes from estuarine waters using reverse-phase liquid chromatography. Mar. Chem., 10, 93-102.
- Moore, R. M. 1981. Oceanographic distributions of zinc, cadmium, copper and aluminum in waters of the central Arctic. Geochim. Cosmochim. Acta, 45, 2475–2482.
- Schaule, B. K. and C. C. Patterson. 1981. Lead concentrations in the northeast Pacific: evidence for global anthropogenic perturbations. Earth Planet. Sci., Lett., 54, 97–116.
- Schink, D., J. J. McCarthy, T. Joyce, G. Flierl, P. Wiebe and D. Kester. 1982. Multidisciplinary program to study warm core rings. EOS, Trans. Amer. Geophys. Un., 63, 834–835.
- Spencer, M J., P. R. Betzer and S. Piotrowicz. 1982. Concentrations of Cd, Cu, Pb, and Zn in surface waters of the northwest Atlantic Ocean—a comparison of Go-Flo and Teflon water samples. Mar. Chem. 11, 403–410.
- Wallace, G. T., N. Dudek, R. Dulmage and O. Mahoney. 1983. Trace element distributions in the Gulf Stream adjacent to the southeastern Atlantic continental shelf—influence of atmospheric and shelf water inputs. Can. J. Fish. Aquat. Sci., 40 (Suppl. 2), 183-191.

- Yeats, P. A. and J. A. Campbell. 1983. Nickel, copper, cadmium and zinc in the Northwest Atlantic Ocean. Mar. Chem., 12, 43-58.
- Zuehlke, R. W. and D. R. Kester. 1985. Development of shipboard copper analyses by atomic absorption spectroscopy, in Mapping Strategies in Chemical Oceanography, Advances in Chemistry Series No. 209, A. Zirino, ed., Amer. Chem. Soc., Washington, D.C., 117-137.

APPENDIX I

Table A-1. Hydrographic, cadmium and nutrient data for the stations discussed in the paper. D(Cd) is dissolved and T(Cd) is total cadmium determined by atomic absorption spectroscopy.

	CTD No: 40	Loca	tion: WCR 82	-B Center	Cruise: KN	093
	Julian Date: 8	2:118	Latitude: 38	°52.7′ I	ongitude: 71°3.	9.6′
Depth m	Temperature °C	Salinity ‰	D(Cd) pmol kg ⁻¹	NO3 μmol kg ⁻¹	PO₄ µmol kg ⁻¹	Si(OH)4 µmol kg ⁻¹
48	15.88	36.29	_	5.6	0.25	2.8
98	15.87	36.30	75	5.6	0.25	2.8
249	15.88	36.29	89	5.6	0.20	2.8
294	15.82	36.28	70	5.9	0.20	2.8
347	15.63	36.22	86	6.0	0.20	2.7
446	13.95	35.85	179	13.8	0.60	5.8
498	11.61	35.50		20.0	1.00	9.8
543	10.12	35.32	278	23.5	1.25	12.6
697	7.01	35.06	322	24.6	1.30	14.4
796	5.61	35.01	175	20.4	1.15	13.2
896	4.79	34.98	185	19.8	1.05	12.3
1096	4.49	34.98	207	19.3	1.05	12.2
1290	4.30	34.98	244	19.0	1.05	12.4
1496	3.99	34.96	231	18.8	1.05	12.6
1692	3.86	34.96	209	18.8	1.05	13.2
1894	3.72	34.96	161	18.8	1.05	14.2
2096	3.56	34.96	169	19.0	1.05	15.6
2198	3.45	34.95	287	19.0	1.05	16.1
2398	3.31	34.95	206	19.0	1.05	17.7
2478	3.19	34.94	270	19.0	1.05	17.7
2512	3.10	34,94	267	18.7	1.05	17.8

CTD No: 41/42

Location: WCR 82-B Center

Cruise: KN093

	Julian Date:	82:118	Latitude: 38	°53.0′	Longitude: 71°4	1.0′
1	15.89	36.32		5.5	0.25	2.5
2	15.90			5.5	0.20	2.6
6	15.91	36.33		5.5	0.20	2.6
12	15.91	36.33	83	5.5	0.20	2.6
30	15.91	36.33	88	5.6	0.20	2.6
48	15.89	36.33	91	5.7	0.20	2.6
69	15.87	36.33	85	5.8	0.20	2.6
96	15.87	36.33		5.9	0.20	2.6
111	15.87	36.33		5.9	0.20	2.7

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	CTD No:	7 Lo	ocation: Slope	Water	Cruise: KN095	
	Julian Date: 8	82:165	Latitude: 39	°24.0′	Longitude: 71%	9.0′
Depth m	Temperature °C	Salinity ‰	D(Cd) pmol kg ⁻¹	NO3 µmol kg ⁻¹	PO₄ µmol kg⁻¹	Si(OH) ₄ µmol kg ⁻¹
6	18.88	36.13	40	<0.1	<0.10	2.0
47	17.64	36.04	47	3.4	0.10	2.8
66	15.61	35.93	100	8.5	0.35	4.4
94	14.81	35.89	96	11.1	0.55	5.6
114	14.55	35.85	124	12.0	0.55	6.1
145	13.81	35.76	114	12.9	0.65	6.6
168	13.16	35.67	116	14.4	0.75	7.6
195	12.48	35.60	212	16.7	0.90	9.2
244	11.29	35.47	209	20.6	1.20	12.7
269	10.65	35.38	282	21.3	1.30	13.7
343	8.71	35.16	339	25.6	1.45	16.3
385	7.82	35.18	321	25.0	1.45	16.3
491	6.02	35.03	311	20.9	1.30	15.1
736	4.67	34.99	214	19.5	1.15	13.2
988	4.26	34.98	214	19.0	1.15	12.9
1493	3.91	34.98	205	18.5	1.10	13.5
1992	3.53	34.98	203	18.5	1.10	16.0
2240	3.27	34.97	228	18.5	1.10	17.7
2435	3.04	34.96	236	18.5	1.10	18.8
2462	2.97	34.95	262	18.5	1.10	19.5
2527	2.76	34.94	269	18.4	1.10	20.4
	CTD No: 20/2	1 Lo	cation: WCR 8	32-B Section	Cruise: K	N095
	Julian Date:	82:167	Latitude: 3	7°34.6′	Longitude: 74°	8.2'
1	14.09	33.19	207	<0.1	< 0.05	1.4
7	14.12	33.37	184	<0.1	< 0.05	1.3
16	17.09	34.56	108	<0.1	< 0.05	1.0
42	14.83	34.64	138	0.3	<0.05	1.2
62	12.84	34.80	—	3.8	0.15	2.7
96	8.96	34.10		9.7	0.55	7.9
103	8.98	34.10	176	9.6	0.50	7.6
148	10.29	34.56	185	10.3	0.60	7.3
170	11.47	35.06		12.0	0.65	7.2
196	11.78	35.28	264	15.7	0.75	8.4
216	10.34	35.32	346	21.1	1.25	13.4
239	9.03	35.19		21.9	1.40	16.1
345	7.04	35.07	386	21.6	1.35	15.9
397	6.46	35.04		21.2	1.35	15.4
442	5.98	35.02	293	20.4	1.25	14.3
489	5.70	35.01		20.4	1.25	14.6
550	5.49	35.01	370	20.2	1.20	14.5

	CTD No: 22/23	Loc	cation: WCR 8	2-B Section	Cruise: Kl	N095
	Julian Date: 8	2:167	Latitude: 37	°41.7′ L	ongitude: 73°5	8.2′
Depth m	Temperature °C	Salinity ‰	D(Cd) pmol kg ⁻¹	NO_3 μ mol kg ⁻¹	PO₄ µmol kg ⁻¹	Si(OH) ₄ µmol kg ⁻¹
1	16.97	33.83	146	<0.1	< 0.05	1.4
7	18.86	34.97	102	<0.1	<0.05	1.3
21	17.81	35.08	100	<0.1	< 0.05	1.3
34	13.19	34.80	157	<0.1	< 0.05	1.5
71	13.19	35.36	94	4.1	0.10	1.8
94	13.21	35.66	—	4.8	0.10	2.3
104	13.65	35.52	—	8.0	0.25	3.0
118	13.89	35.76	127		_	
144	13.75	35.73	124	8.2	0.25	3.1
208	12.91	35.61	177	13.9	0.60	5.8
234	12.33	35.56	222	17.4	0.80	8.2
284	10.81	35.38	319	23.9	1.30	13.2
318	9.78	35.26		26.0	1.35	15.4
342	9.01	35.19	385	26.0	1.45	16.2
391	7.63	35.08	—	23.9	1.35	15.6
489	5.80	35.02		20.6	1.25	15.0
590	4.97	34.89	280	19.7	1.20	14.0

CTD No: 24/25 Location: WCR 82-B

Cruise: KN095

Julian Date: 82:167

Latitude: 37°38.1'

Longitude: 73°38.7'

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1	18.40	34.89	76	<0.1	< 0.05	0.8
16	18.04	35.19	105	<0.1	< 0.05	0.8
27	15.74	35.45	127	<0.1	< 0.05	1.0
46	14.40	35.78	191	3.4	0.05	1.5
71	14.83	35.99	127	6.5	0.15	2.3
105	14.85	36.02	90	6.9	0.20	2.5
145	14.69	35.98		7.0	0.20	2.6
194	14.51	35.94	100	7.3	0.20	2.9
245	14.11	35.84	110	7.5	0.20	3.1
268	13.55	35.73		8.3	0.30	3.5
294	13.14	35.67	160			—
367	10.61	35.36	284	14.1	0.60	6.0
393	9.67	35.25		23.8	1.25	13.1
441	8.29	35.12	319	25.5	1.40	15.1
490	7.40	35.08	—	26.0	1.45	16.3
543	6.48	35.03	348	23.6	1.35	15.0
596	6.04	35.12	—	23.6	1.35	15.2

	CTD No: 26/27	Loc	ation: WCR 8	2-B Section	Cruise: K	N095
	Julian Date: 8	2:167	Latitude: 379	°33.9′ L	ongitude: 73°2.	0.3′
Depth m	Temperature °C	Salinity ‰	D(Cd) pmol kg ⁻¹	NO3 µmol kg ⁻¹	PO₄ µmol kg⁻¹	Si(OH) ₄ µmol kg ⁻¹
14	18.47	34.76	89	<0.1	< 0.05	0.8
25	17.09	35.42	75	<0.1	< 0.05	0.7
33	15.13	35.50	51	<0.1	0.10	1.0
51	13.72	35.48	180	4.7	0.25	1.7
83	14.53	35.90	_	6.4	0.35	2.9
109	14.83	36.01	114	6.9	0.35	2.6
121	14.53	35.93	—	7.2	0.40	3.0
144	14.49	35.92	82	7.4	0.40	3.0
194	14.07	35.92		7.8	0.45	3.2
247	13.50	35.70	247	_		
300	12.44	35.58	187	_	_	_
337	11.40	35.46	240	20.7	1.25	11.8
398	9.13	35.19	318	24.3	1.55	15.8
446	8.05	35.10	345	25.8	1.55	16.3
499	7.15	35.06		25.9	1.50	15.9
581	5.80	35.01	378	20.0	1.45	14.8
695	5.14	34.99		20.8	1.30	14.1

CTD No: 28/29 Location: WCR 82-B Section Cruise: KN095

	Julian Date:	82:168	Latitude: 37	7°24.4′	Longitude: 73°7.	.0′
10	18.33	34.75	92	<0.1	< 0.05	1.4
18	18.21	34.72	89	<0.1	< 0.05	1.4
30	14.79	35.08	101	<0.1	< 0.05	1.4
40	12.85	35.08	132	2.8	0.10	1.8
51	13.71	35.44	132	3.9	0.15	2.1
109	14.30	35.88	109	7.2	0.25	3.1
146	14.26	35.86		7.5	0.30	3.2
199	14.13	35.84	77	7.7	0.35	3.4
237	13.62	35.73	107	9.0	0.45	4.0
259	13.09	35.66	149			<u> </u>
281	12.68	35.60		15.3	0.70	7.1
317	11.66	35.50	201	20.4	1.10	11.2
369	9.83	35.27	258	23.9	1.35	14.6
447	7.81	35.10	283	24.8	1.50	16.1
498	6.80	35.05		21.6	1.40	16.3
559	6.06	35.02	<u> </u>		1.35	15.1

	CTD No: 30/31	Loc	cation: WCR 8	2-B Section	Cruise: K	N095
	Julian Date: 8	2:168	Latitude: 37	°19.6′	Longitude: 72°4	4 .1′
Depth m	Temperature °C	Salinity ‰	D(Cd) pmol kg ⁻¹	NO ₃ μmol kg ⁻¹	PO₄ µmol kg ⁻¹	Si(OH)₄ µmol kg ⁻¹
1	15.82	33.75	104	<0.1	< 0.05	0.8
17	14.81	34.09	100	<0.1	<0.05	0.8
30	11.28	34.16	123	1.6	0.10	1.3
47	10.03	34.22	200	5.9	0.30	3.4
60	10.38	34.48	154	6.7	0.40	4.4
106	12.17	35.25	178			
123	12.54	35.43	123	10.4	0.50	5.0
142	12.32	35.46	157	14.0	0.65	6.6
167	11.42	35.46	245	20.0	1.05	10.5
192	10.32	35.32	300	24.2	1.30	13.2
242	8.89	35.18	307	26.3	1.45	15.7
439	5.56	34.99	314	20.6	1.25	13.8
592	4.84	34.99		19.7	1.15	12.9
	CTD No: 42	Loca	tion: WCR 82	-B Center	Cruise: KN()95
	Julian Date: 8	2:171	Latitude: 36	°49.5′	Longitude: 73°3	3.3′
11	18.53	35.72	40	<0.1	< 0.05	< 0.3
23	17.37	35.99	30	<0.1	< 0.05	<0.3
41	15.45	36.17	40	5.9	0.10	2.2
55	15.49	36.20	80			
100	15.59	36.25	90	6.6	0.15	2.7
148	15.60	36.25	80	6.7	0.15	2.9
183	15.56	36.24	90	6.6	0.15	2.9
231	15.44	36.20	70	6.7	0.15	2.9
302	15.20	36.13	103	7.1	0.20	3.2
342	14.78	36.03	102	7.9	0.25	3.1
400	12.97	35.77	168	17.6	0.30	7.6
494	10.29	35.35	251	23.5	1.25	13.0
540	8.98	35.24	293	25.5	1.40	15.2
587	7.73	35.14	279	25.3	1.45	15.8
631	6.64	35.06	286	23.2	1.40	15.2
743	5.46	35.02	258	20.9	1.25	13.7
994	4.55	35.00	24 1	19.7	1.15	12.8
1483	4.00	34.98	243	19.2	1.10	13.2
1742	3.84	34.98	238	19.2	1.10	13.7
2005	3.65	34.98	240	19.1	1.10	14.6

CTD No: 58		Location: W	CR 82-B Entr	e Cruise: KN095		
	Julian Date	82:174	Latitude: 37°7.0'		Longitude: 73°9.0'	
Depth m	Temperature °C	Salinity ‰	D(Cd) pmol kg ⁻¹	NO₃ µmol kg ⁻¹	PO ₄ µmol kg ⁻¹	Si(OH) ₄ µmol kg ⁻¹
10	13.72	33.07	164	<0.1	0.05	1.3
16	13.21	33.24	164	<0.1	0.05	1.4
26	12.98	33.61	1 44	<0.1	0.05	1.4
30	13.16	33.83	137	<0.1	0.05	1.4
33	12.65	33.87	121	<0.1	0.05	1.5
38	12.27	34.17	119	0.7	0.15	1.9
49	10.25	33.93	158	3.2	0.30	3.4
77	9.98	34.29	178	7.0	0.45	4.6
99	10.51	34.47	178	7.5	0.50	5.2
119	11.96	34.97	153			
146	12.82	35.37	141	9.4	0.50	4.5
162	12.08	35.35	166	12.1	0.70	6.5
243	7.99	35.13	319	20.9	1.45	15.4
263	7.14	35.09	307	20.4	1.45	15.5
346	6.48	35.12	300	20.2	1.40	15.0
398	5.80	35.03	300	19.5	1.30	14.2
492	5.27	35.02	283	18.8	1.25	13.8
738	4.47	34.99	253	17.6	1.15	13.0
965	4.25	34.99	318	17.5	1.10	12.7
1238	3.98	34.98	294	17.2	1.10	13.2
1491	3.82	34.98	255	17.1	1.10	13.8
1741	3.65	34.98	275	17.2	1.10	15.2
2005	3.44	34.98	301	17.3	1.15	17.7

1987]

	CTD No: 18 L Julian Date: 82:225		ocation: Sargas	so Sea	Cruise: KN097	
			Latitude: 359	°39.9′	Longitude: 71°53	.3′
Depth m	Temperature °C	Salinity ‰	T(Cd) pmol kg ⁻¹	NO3 µmol kg ⁻¹	PO ₄ µmol kg ⁻¹	Si(OH) ₄ µmol kg ⁻¹
14	27.65	36.13	12	<0.1	< 0.05	0.9
30	36.03	36.44	10	<0.1	< 0.05	0.9
51	23.34	36.64	7	<0.1	< 0.05	0.7
75	22.51	36.63	18	<0.1	< 0.05	0.6
101	21.31	36.64	10	<0 .1	< 0.05	0.6
141	20.17	36.63	11	<0.1	< 0.05	0.7
297	13.25	36.53	19	3.8	0.05	1.4
396	17.85		24	_	0.10	1.5
488	17.45	36.43	16	3.9	0.10	1.4
574	16.76	36.30	54	8.0	0.25	2.6
680	15.33	36.06	164	11.5	0.50	4.1
852	11.98	35.54	231	19.0	1.00	9.3
1043	7.87	35.12	297	22.7	1.40	15.1
1258	5.39	35.05	249	18.8	1.25	13.6
1595	4.40	34.99	229	18.3	1.10	12.7
1794	4.14	34.99	237	18.3	1.10	13.1
1996	4.00	34.99	243	_	_	_
2495	3.45	34.96	237	17.9	1.15	16.8
3000	2.93	34.93	236	17.6	1.10	19.1

	CTD No: 19 Julian Date: 82:227		Location: Gulf S	Stream	Cruise: KN097	
			Latitude: 38	°54.7′	Longitude: 63°56	.0′
Depth m	Temperature °C	Salinity ‰	T(Cd) pmol kg ⁻¹	NO3 µmol kg ⁻¹	PO₄ μmol kg ⁻¹	Si(OH) ₄ μmol kg ⁻¹
20	27.62	36.09	19	<0.1	< 0.05	1.1
61	27.13	36.24	18	<0.1	< 0.05	1.1
99	24.45	36.57	10	<0.1	< 0.05	0.7
149	21.07	36.65		<0.1	< 0.05	0.7
199	18.95	36.58	8	2.4	0.05	1.0
281	17.88	36.50	17	4.1	0.05	1.4
349	17.40	36.43	41	5.5	0.10	1.8
396	16.78	36.32	47	7.4	0.20	2.4
470	14.99	36.01		12.6	0.60	4.6
542	12.95	35.68	175	18.6	1.00	8.1
596	11.72	35.52	194	19.9	1.10	9.5
644	10.62	35.38	225	22.5	1.30	11.7
698	9.06	35.20	265	24.8	1.50	15.0
747	7.89	35.10	246	23.8	1.45	15.0
799	7.03	35.06	271	24.1	1.45	15.3
901	5.92	35.03	266	22.3	1.35	14.4
997	5.34	35.02	226	20.7	1.25	13.4
1196	4.65	34.99	222	19.7	1.20	12.7
1402	4.30	34.98	236	18.9	1.20	12.6
1799	3.94	34.97	223	18.1	1.15	12.9
2014	3.78	34.97	222	18.6	1.15	14.3
2301	3.55	34.97		18.9	1.15	16.8
2600	3.25	34.96	254	19.2	1.20	19.7

	CTD No: 42 Locat Julian Date: 82:280		tion: WCR 82-	H Center	Cruise: KN098 Longitude: 65°24.4'	
			Latitude: 39	°32.1′		
Depth m	Temperature °C	Salinity ‰	T(Cd) pmol kg ⁻¹	NO₃ µmol kg ⁻¹	PO₄ µmol kg ⁻¹	Si(OH) ₄ µmol kg ⁻¹
30	25.03	36.19	12	<0.1	< 0.05	0.9
51	25.03	36.19	14	<0.1	< 0.05	0.9
61	24.23	36.54	15	0.1	< 0.05	0.8
76	21.70	36.60	19	0.7	< 0.05	0.7
100	20.42	36.60	12	1.2	< 0.05	0.9
140	19.17	36.58	12	1.7	0.05	0.9
181	18.62	36.56	14	2.4	0.05	1.0
250	18.17	36.54	15	2.4	0.05	1.0
300	18.10	36.54		2.2	0.05	1.1
374	17.97	36.52	19	2.6	0.05	1.2
434	17.64	36.47	26	4.1	0.10	1.5
525	17.19	36.42	27	4.1	0.10	1.6
573	16.72	36.32	60	6.9	0.15	2.4
649	14.75	35.96	124	12.9	0.55	4.8
722	13.03	35.69	176	17.2	0.80	7.6
799	10.97	35.40	244	21.4	1.15	12.0
850	9.63	35.23	277	23.5	1.30	13.9
973	6.86	35.06	273	22.7	1.30	15.2
1249	4.79	35.99	235	1 9.4	1.10	12.7
1500	4.38	34.99	226	18.7	1.05	12.6
1747	4.08	34.97	216	18.2	1.05	12.7
1993	3.87	34.97	215	18.3	1.05	13.7
2200	3.75	34.97	241	18.3	1.05	14.7

	CTD No: 1	CTD No: 11		Location: WCR 82-B Center			7
	Julian Date: 82:222		Latitu	ude: 36°38.1′	Long	4′	
Depth m	Temperature °C	Salinity ‰	T(Cd) pmol kg ⁻¹	ASV-Cd pmol kg ⁻¹	NO3 μmol kg ⁻¹	PO4 µmol kg ⁻¹	Si(OH) ₄ µmol kg ⁻¹
6	27.84	35.49	26	<10		_	·
18	28.16	36.27	15	<10	<0.1	0.05	0.7
24	26.85	36.22	55	<10	<0.1	0.05	0.9
40	19.85	35.01	78	44	<0.1	0.05	1.1
50	18.11	35.80	126	<10	4.8	0.15	2.6
58	16.18	35.70	74		4.7	0.15	2.5
64	15.16	35.66	132	<10	10.3	0.45	4.6
100	15.58	36.22	83		7.2	0.30	2.7
149	15.51	36.21	68	<10	6.8	0.30	2.7
203	15.51	36.21	74	_	6.7	0.35	2.6
249	15.41	36.18	71	<10	6.9	0.35	2.7
271	15.08	36.11	151	_	7.7	0.35	3.0
299	13.02	35.80	151	151	14.1	0.75	6.3
351	11.19	35.43	245	271	21.0	1.25	11.1
382	10.48	35.34	286	306	22.6	1.35	12.4
399	9.92	35.27	295	271	24.2	1.45	14.2
546	6.45	35.04	304	292	22.2	1.35	14.4
638	5.43	35.01	302	292	20.6	1.30	13.4
749	4.89	35.01	287	264	19.6	1.25	12.7
996	4.33	34.97	239	271	18.7	1.20	12.2
1486	3.96	34.97	257	278	18.2	1.15	12.7
2005	3.32	34.95	248	271	18.7	1.15	16.2