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The distribution and preferential biological uptake of cadmium at 6°W in the Southern Ocean

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Abstract

The spatial and temporal distribution of cadmium (Cd) and phosphate in the Southern Ocean are related to biology and hydrography. During a period of 18 days between transects 5/6 and 11, a phytoplankton spring bloom developed in the Polar Frontal region. Upper water Cd concentrations were not depleted and ranged from 0.2 to 0.8 nM at about 10 m depth. These relatively high Cd concentrations are attributed to upwelling of Upper Circumpolar Deep Water (0.5–1.2 nM in the core) in combination with low biological productivity (0.2 to 0.3 mg m⁻³ chlorophyll-*a*, 0.3 g C m⁻² d⁻¹). Total particulate Cd concentrations at 40 m depth were between 0.02 and 0.14 nM with the maximum in concentration in the Polar Frontal region. Most of the particulate Cd at this depth (85–94%) was detected in the first phase of a sequential chemical leaching treatment which includes adsorbed Cd as well as Cd incorporated in algae. The Polar Frontal region was characterized by minima in Cd concentration and Cd/phosphate ratio of seawater at both transects; values were the lowest at transect 11 after development of the spring bloom which was dominated by diatoms. This decreasing Cd/phosphate ratio in seawater during spring bloom development was attributed to preferential Cd gross uptake which more than compensated the process of preferential Cd recycling. Within the Upper Circumpolar Deep Water, Cd showed a maximum in concentration similar to that of the major nutrients. Both the Cd concentration and the Cd/phosphate ratio of the deeper water increased in southern direction, from 0.4 to 0.7 nM and from 0.2 to 0.3 nM/μM, respectively. Antarctic Intermediate Water has a Cd concentration of 0.21 nM with a Cd/phosphate ratio of 0.10 nM/μM. In Antarctic Bottom Water, Cd concentrations ranged from 0.60 to 0.82 nM. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: cadmium; phosphate; Southern Ocean

1. Introduction

Among all trace metals in seawater, dissolved cadmium (Cd) exhibits a distribution which is correlated closest with that of phosphate (Boyle et al., 1976; Martin et al., 1976; Bruland et al., 1978;

Bruland, 1980; Knauer and Martin, 1981; Bruland and Franks, 1983). This close relationship would suggest that Cd behaves similar to phosphate, is incorporated into the plankton, and has a biological function. More recently, the latter was indicated for diatoms (Price and Morel, 1990; Lee et al., 1995) and a variety of other species (Lee and Morel, 1995), where Cd may substitute for Zn and play a role in carbonic anhydrase (Price and Morel, 1990; Lee et

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al., 1995; Sunda and Huntsman, 1997). Free Cd concentrations as low as 10^{-12} M may induce the production of phytochelatin, metal-binding peptides (Ahner and Morel, 1995; Ahner et al., 1995). Walsh and Hunter (1992) found enhanced Cd uptake by *Macrocystis pyrifera* during the formation of polyphosphate bodies. They concluded that in the nutrient-rich Southern Ocean depletion of Cd relative to phosphate could be the result of polyphosphate body formation. This may be true, but there is no

ecological advantage for algae to form polyphosphate stores within the cell when phosphate depletion never occurs in surface waters of the Southern Ocean.

In the surface waters, the Cd concentrations, Cd/phosphate ratios and particulate Cd concentrations were determined during two transects crossing the Polar Frontal region, the southern Antarctic Circumpolar Current (ACC) area and the southern ACC Front. In the period between the two transects, a

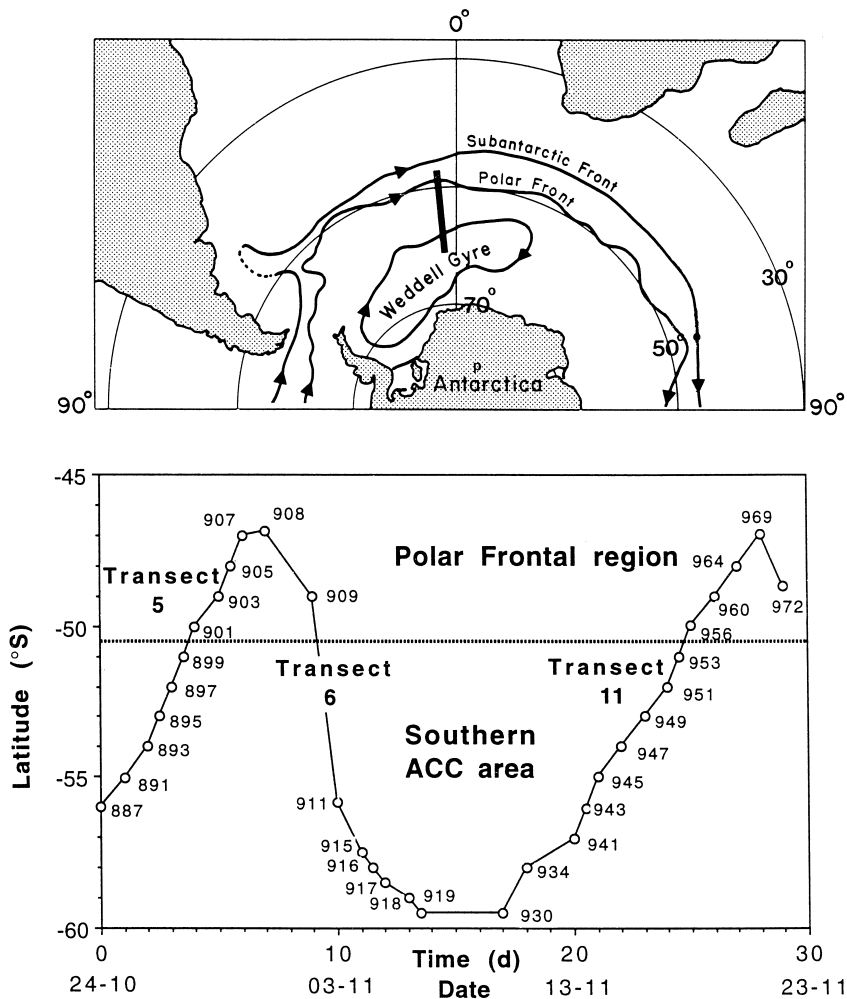


Fig. 1. Chart of the research area with the latitude vs. time cruise track on the 6°W meridian (from Löscher et al., 1997a). During transects 5, 6 and 11 (from 47°S to 59°S), the Polar Front and the ACC Weddell Gyre Boundary were crossed. The numbers on the latitude vs. time plot indicate sampling locations during the compared transects 5, 6 and 11. Not shown is the initial transect 1 at about 57°S from South America towards the 6°W research area. For data see stations 859, 860, 862, 865 and 866 in Tables 1 and 2.

phytoplankton spring bloom, dominated by diatoms, occurred in the Polar Frontal region. Consequently, it was possible to study Cd and phosphate uptake by diatoms in a region replete with phosphate.

2. Sampling and methods

Samples were collected in the austral spring (October and November 1992) during the Joint Global Ocean Flux Study (JGOFS) Antarctic Ocean expedition ANT X/6 aboard RV *Polarstern* (Fig. 1). Between transect 5/6 (stations 887–907) and 11 (stations 930–969) about 18 days passed in crossing the Polar Frontal region (Fig. 1), during which the development of a spring bloom could be followed. A detailed description of the cruise was given by Smetacek et al. (1997).

Deep water (> 400 m) was taken with precleaned GoFlo samplers mounted on an all-Teflon coated CTD/Rosette frame. Upper water (40–400 m) was

collected at standard depths with precleaned GoFlo samplers (12 l) on a 10 mm Kevlar cable and corrected afterwards for the wire angle using a SIS pressure sensor. After recovery, the 12 l GoFlo samplers were connected with Teflon tubes on the outside of the clean air laboratory van. On the top of the samplers, pressure lines with high purity nitrogen gas which passed through fine arrestance filters, were attached. At some stations, logistic constraints did not permit filtration and only unfiltered water was collected (Tables 1–10). At most stations, the seawater was filtered over acid-cleaned NUCLEPORE or PORETICS membrane filters (47 mm, 0.4 μm) with an overpressure of < 1 bar. Particulate matter was sampled at standard depths by filtering 30 to 60 l of seawater through NUCLEPORE filters with a pore size of 0.2 μm . Sea salts were removed by rinsing the filters with about 10 ml nanopure water. Unfiltered surface water at about 10 m depth was occasionally taken in precleaned 2 l GoFlo samplers from a walking bridge extending 10 m

Table 1

Surface water stations on ANT X/6 with data on nutrients, filtered and unfiltered Cd. ALW (German: 'Auslegerwinde') refers to sampling the surface water approximately 10 m in front of the sailing ship with a 2 l GoFlo lowered from a ship's crane. Salinity, potential temperature and density were estimated as the averages of the values of CTD casts between which the Kevlar cable samples were taken at almost the same position and time

Station/Position/ Date	Depth (m)	NO ₃ (μM)	Si (μM)	PO ₄ (μM)	Unfiltered Cd (nM)	Filtered Cd (nM)	Salinity	Potential T (°C)	σ_0 (kg m^{-3})
859	ALW 5	–	–	–	0.658	–	–	–	–
56°59'S	ALW 20	–	–	–	0.081	–	33.94	–1.27	27.31
38°51'W	ALW 35	–	–	–	0.096	–	33.95	–1.30	27.31
04-10-92	200	–	–	–	0.204	–	33.43	0.80	27.60
	300	–	–	–	0.222	–	33.58	1.36	27.68
860	ALW 10	27.9	62.6	1.96	0.198	–	–	–	–
56°59'S	40	27.9	61.6	1.96	0.187	–	33.82	–1.74	27.22
30°27'W	60	28.0	61.7	1.96	0.115	–	33.84	–1.72	27.24
05-10-92	100	33.2	68.7	1.97	0.192	–	34.06	–1.13	27.39
	200	32.9	81.9	2.31	0.138	–	34.55	1.15	27.67
	300	27.9	87.0	2.63	0.289	–	34.61	1.26	27.72
862	ALW 10	27.4	45.8	1.89	0.181	–	–	–	–
57°00'S	40	27.5	45.8	1.87	–	0.155	33.80	–1.02	27.18
23°19'W	60	27.3	45.6	1.95	–	0.905	33.81	–1.02	27.19
07-10-92	100	28.6	50.9	2.01	–	0.769	33.93	–0.70	27.27
	150	28.6	51.1	1.95	–	0.329	33.98	–0.88	27.32
	200	29.4	58.8	2.00	–	0.286	34.23	0.61	27.45
	300	35.5	75.6	2.45	–	1.309	34.51	1.83	27.59

Table 2

Surface water stations on ANT X/6 with data on nutrients, filtered and unfiltered Cd. ALW (German: 'Auslegerwinde') refers to sampling the surface water approximately 10 m in front of the sailing ship with a 2 l GoFlo lowered from a ship's crane. Salinity, potential temperature and density were estimated as the averages of the values of CTD casts between which the Kevlar cable samples were taken at almost the same position and time

Station/Position/ Date	Depth (m)	NO ₃ (μM)	Si (μM)	PO ₄ (μM)	Unfiltered Cd (nM)	Filtered Cd (nM)	Salinity	Potential T (°C)	σ _θ (kg m ⁻³)
865	40	27.9	42.4	1.91	–	0.857	33.82	–1.78	27.22
56°09'S	60	29.5	42.8	1.91	–	0.839	33.82	–1.77	27.22
15°26'W	100	28.5	42.1	2.04	–	0.817	33.82	–1.77	27.22
09-10-92	140	28.5	42.8	1.95	–	0.867	33.84	–1.74	27.24
	200	33.4	58.3	2.24	–	1.055	34.28	0.86	27.47
	300	35.8	80.0	2.45	–	1.136	34.51	1.55	27.61
866	100	33.9	91.5	2.26	1.014	–	34.25	–0.68	27.53
57°45'S	200	33.2	75.5	2.27	1.011	–	34.56	1.48	27.66
06°29'W	300	31.9	74.5	2.36	1.064	–	34.63	1.59	27.71
11-10-92									
879	ALW 10	24.4	18.7	1.65	0.492	–	33.87	1.97	27.07
48°00'S	37	24.8	18.7	1.65	0.552	0.552	33.87 ± 0.00	1.62 ± 0.05	27.10 ± 0.00
06°00'W	74	24.9	19.3	1.71	–	0.416	33.88 ± 0.00	1.49 ± 0.02	27.11 ± 0.00
18-10-92	185	28.0	26.3	1.90	0.557	0.516	34.03 ± 0.01	1.27 ± 0.05	27.25 ± 0.01
	277	32.5	44.0	2.27	–	0.733	34.21	1.67	27.36
887	38	27.6	48.7	1.84	0.475	–	33.88 ± 0.00	–1.77 ± 0.00	27.27 ± 0.00
55°59'S	76	27.5	48.5	1.84	–	0.544	33.90 ± 0.02	–1.76 ± 0.01	27.28 ± 0.01
06°04'W	95	28.1	48.2	1.86	–	0.527	33.92 ± 0.04	–1.73 ± 0.04	27.30 ± 0.03
24-10-92	142	30.9	56.9	2.04	–	0.613	34.14 ± 0.05	–0.77 ± 0.37	27.44 ± 0.03
	189	33.1	68.1	2.22	0.760	0.695	34.34 ± 0.02	0.61 ± 0.12	27.54 ± 0.01
	284	34.8	82.8	2.32	–	0.735	34.56	1.58	27.65
891	ALW 10	27.1	39.9	1.76	0.553	–	–	–	–
55°01'S	40	27.1	40.1	1.79	0.543	0.505	33.88 ± 0.00	–1.49 ± 0.23	27.26 ± 0.00
06°00'W	60	27.1	40.5	1.78	–	0.578	33.88 ± 0.00	–1.64 ± 0.01	27.26 ± 0.00
25-10-92	100	27.2	39.6	1.78	–	0.561	33.88 ± 0.01	–1.69 ± 0.02	27.27 ± 0.01
	150	28.6	44.5	1.87	–	0.561	33.99 ± 0.04	–1.35 ± 0.17	27.35 ± 0.03
	200	31.3	53.4	2.05	0.651	0.618	34.21 ± 0.13	0.10 ± 0.82	27.46 ± 0.06
	300	35.0	77.3	2.32	–	0.673	34.51	1.73	27.60

beyond the bow of the slowly upwind steaming ship, using a small winch with 6 mm Kevlar hydrowire.

Filtered and unfiltered seawater were acidified to pH = 2 with quartz-distilled HNO₃ and stored. The approximately 1 year storage at pH = 2, allowed dissolution of most biogenic fractions and surface oxyhydroxides coatings (Zhuang et al., 1990). Only the most refractory component of land-derived minerals would still be excluded from analysis. For this reason, unfiltered Cd is expressed as 'total dissolvable' Cd and filtered Cd as 'dissolved' Cd.

In a clean air laboratory at the institute, the seawater samples were pre-concentrated (167 ×) by APDC/DDDC chloroform extraction with the method described by Bruland et al. (1979). Instead of back extraction, the extract was evaporated to dryness and the residue dissolved in diluted HNO₃. All reagents were distilled fourfold by subboiling distillation in quartz stills. The thus treated samples were finally measured using a Perkin-Elmer 5100 PC Graphite Furnace Atomic Absorption Spectrophotometer with Zeeman background correction. A de-

Table 3

Surface water stations on ANT X/6 with data on nutrients, filtered and unfiltered Cd. ALW (German: 'Auslegerwinde') refers to sampling the surface water approximately 10 m in front of the sailing ship with a 2 l GoFlo lowered from a ship's crane. Salinity, potential temperature and density were estimated as the averages of the values of CTD casts between which the Kevlar cable samples were taken at almost the same position and time

Station/Position/ Date	Depth (m)	NO ₃ (μM)	Si (μM)	PO ₄ (μM)	Unfiltered Cd (nM)	Filtered Cd (nM)	Salinity	Potential T (°C)	σ _θ (kg m ⁻³)
893	ALW 10	26.8	41.5	1.87	0.519	–	33.91	–1.41	27.28
54°00'S	39	26.9	41.7	1.85	0.561	0.506	33.91 ± 0.00	–1.49 ± 0.02	27.29 ± 0.00
06°01'W	59	26.9	41.9	1.86	–	0.529	33.92 ± 0.00	–1.51 ± 0.02	27.29 ± 0.00
26-10-92	99	27.0	42.1	1.86	–	0.551	33.92 ± 0.00	–1.54 ± 0.02	27.29 ± 0.00
	148	28.5	47.8	1.98	–	0.529	34.02 ± 0.13	–1.24 ± 0.45	27.36 ± 0.09
895	ALW 10	26.5	36.3	1.82	0.738	–	–	–	–
53°00'S	33	26.8	36.3	1.89	0.533	0.516	33.94	–0.64	27.278
06°00'W	82	27.0	37.0	1.90	–	0.492	33.94	–0.68	27.281
26-10-92	123	27.2	37.0	1.90	–	0.538	33.94	–0.72	27.283
897	ALW 10	26.5	28.4	1.83	0.211	–	–	–	–
52°00'S	40	26.7	28.6	1.90	0.533	0.450	33.96 ± 0.00	–0.03 ± 0.00	27.27 ± 0.00
06°00'W	100	26.7	28.8	1.81	–	0.456	33.97 ± 0.00	–0.12 ± 0.01	27.28 ± 0.00
27-10-92	150	28.9	36.8	1.98	–	0.673	33.98 ± 0.01	–0.19 ± 0.03	27.30 ± 0.01
	200	34.2	59.3	2.29	0.927	0.682	34.24 ± 0.02	0.87 ± 0.10	27.45 ± 0.01
	300	35.5	77.1	2.42	–	0.925	34.50	1.82	27.58
899	40	26.4	28.7	1.88	0.545	–	33.96	1.14	27.26
51°00'S	60	26.8	28.4	1.84	–	0.463	33.96	1.04	27.27
06°00'W	100	26.6	29.3	1.87	–	0.445	33.96	0.94	27.27
27-10-92	150	27.1	31.2	1.90	–	0.481	33.98	0.49	27.28
	200	30.5	43.5	2.15	0.645	0.633	34.19	0.52	27.42
	300	36.2	73.1	2.50	–	0.844	34.49	1.79	27.58
901	ALW 10	25.5	18.9	1.63	0.289	–	–	–	–
50°00'S	40	26.9	20.1	1.71	0.360	0.360	33.93	1.14	27.17
06°00'W	60	26.1	20.2	1.72	–	0.277	33.93	1.04	27.18
28-10-92	100	26.6	22.2	1.80	–	0.354	33.93	0.94	27.19
	150	28.6	29.5	1.98	–	0.413	33.96	0.49	27.24
	200	30.8	38.5	2.13	–	0.531	34.05	0.52	27.31
	300	35.8	61.6	2.42	–	0.864	34.37	1.79	27.48

tailed description of the method is given by Nolting and De Jong (1994).

In each session of 1 day, 18 samples and six blanks were extracted. The recovery of Cd was verified daily by addition of four spikes with increasing Cd concentrations to a 3 × extracted seawater matrix. The Cd concentrations were corrected for extraction recoveries. Blanks were between 0.2 and 30 pM and detection limits lower than 3 pM. Results within one session with recoveries less than 90% were rejected and are not reported. The accuracy of the method was verified with certified reference water NASS-4 which was analyzed and had a con-

centration of 164 pM within the certified concentration range of 142 ± 27 pM. The reproducibility of the overall analytical procedure, based on three duplicates and six replicates, ranged from 1 to 5%.

The filters with the particulate matter were leached with a sequential chemical treatment in the clean air laboratory. In order to dissolve organically complexed adsorbed cations, carbonate phases, reactive oxyhydroxides (Landing and Bruland, 1980, 1987; Collier and Edmond, 1984) and metal-activated proteins (Collier and Edmond, 1984), the particulate matter samples were leached in 4.5 M Q-acetic acid for 4 h at room temperature. Afterward, the particu-

Table 4

Surface water stations on ANT X/6 with data on nutrients, filtered and unfiltered Cd. ALW (German: 'Auslegerwinde') refers to sampling the surface water approximately 10 m in front of the sailing ship with a 2 l GoFlo lowered from a ship's crane. Salinity, potential temperature and density were estimated as the averages of the values of CTD casts between which the Kevlar cable samples were taken at almost the same position and time

Station/Position/ Date	Depth (m)	NO ₃ (μM)	Si (μM)	PO ₄ (μM)	Unfiltered Cd (nM)	Filtered Cd (nM)	Salinity	Potential T (°C)	σ _θ (kg m ⁻³)
903	ALW 10	24.1	11.5	1.17	0.246	–	–	–	–
49°00'S	40	24.4	11.7	1.15	0.363	0.205	33.87	1.52	27.10
06°00'W	60	24.5	11.9	1.21	–	0.211	33.87	1.50	27.11
29-10-92	100	25.1	17.9	1.44	–	0.270	33.89	1.04	27.15
	150	26.5	26.6	1.87	–	0.516	33.94	0.56	27.22
	300	33.5	53.3	2.38	–	0.668	34.31	1.76	27.44
905	40	23.0	14.8	1.62	0.469	0.332	33.86 ± 0.00	2.43 ± 0.01	27.02 ± 0.00
48°00'S	60	24.0	17.0	1.71	–	0.363	33.87 ± 0.01	2.00 ± 0.31	27.06 ± 0.03
06°00'W	100	24.7	19.7	1.79	–	0.457	33.89 ± 0.01	1.33 ± 0.12	27.13 ± 0.02
29-10-92	150	26.2	24.3	1.91	–	0.557	33.92 ± 0.01	1.00 ± 0.02	27.18 ± 0.01
	200	27.7	29.3	2.04	0.598	0.551	34.02 ± 0.01	1.11 ± 0.01	27.25 ± 0.01
	300	32.4	43.2	2.25	–	0.715	34.22	1.62	27.38
907	ALW 10	23.6	13.4	1.57	0.301	–	–	–	–
47°00'S	34	23.7	13.2	1.57	0.410	0.343	33.86	2.27	27.04
06°00'W	51	23.7	13.9	1.57	–	0.242	33.86	2.20	27.04
30-10-92	85	24.9	15.9	1.51	–	0.212	33.88	1.63	27.10
	128	26.4	23.7	1.86	–	0.389	33.91	1.22	27.15
	170	27.2	26.3	1.91	0.460	0.425	33.95	0.87	27.21
	255	31.5	40.3	2.24	–	0.484	34.19	1.62	27.35
908	100	32.9	14.2	1.57	–	0.427	33.87	1.72	27.09
46°52'S	150	25.2	18.9	1.69	–	0.598	33.90	1.12	27.16
31-10-92	200	28.2	25.3	1.99	–	0.813	34.04	1.50	27.24
	250	31.8	38.6	2.24	0.975	–	34.17	1.66	27.33
	400	34.4	58.3	2.44	–	–	34.33	1.95	27.44
909	ALW 10	27.4	42.7	1.92	0.568	–	–	–	–
49°00'S									
06°00'W									
02-11-92									

late matter was digested in 2 M Q-HCl/1 M Q-HNO₃ for again 4 h at room temperature to dissolve the more resistant Fe (III) oxyhydroxides (Lewis and Landing, 1991) and the rest of the biological fraction. After both leaching treatments, the acids were evaporated to dryness and the residue dissolved in diluted HNO₃. The residual refractory material was placed in clean digestion vessels and totally digested with 3 ml Q-HCl, 1 ml Q-HNO₃ and 1 ml ultra clean HF (Merck) in a microwave oven. Then, the samples were diluted with 5 ml saturated H₃BO₃ to neutralize the strong acid HF. The Cd concentrations from

the sequential chemical leaching treatment were measured with a Perkin-Elmer 5100 PC Graphite Furnace Atomic Absorption Spectrophotometer with Zeeman background correction. The method of standard addition was used to avoid matrix effects. The total destruction of the last digestion step was tested with the reference material calcareous loam (BCR No. 141) and light sandy soil (BCR No. 142) for the metals Cu and Ni. The obtained values were within the 95% confidence interval of the certified values. The blanks of Cd ranged between 0.01 and 0.06 pM and between 0.03 and 2.15 pM for the second leach-

Table 5

Surface water stations on ANT X/6 with data on nutrients, filtered and unfiltered Cd. ALW (German: 'Auslegerwinde') refers to sampling the surface water approximately 10 m in front of the sailing ship with a 2 l GoFlo lowered from a ship's crane. Salinity, potential temperature and density were estimated as the averages of the values of CTD casts between which the Kevlar cable samples were taken at almost the same position and time

Station/Position/ Date	Depth (m)	NO ₃ (μ M)	Si (μ M)	PO ₄ (μ M)	Unfiltered Cd (nM)	Filtered Cd (nM)	Salinity	Potential T (°C)	σ_0 (kg m ⁻³)
911 55°51'S 06°00'W 03-11-92	ALW 10	–	–	–	0.580	–	–	–	–
915 57°29'S 06°00'W 04-11-92	ALW 10 40 60 100 150 200 300	27.4 27.3 27.6 28.4 31.9 33.6 33.1	59.1 58.9 59.4 64.9 76.4 82.9 88.3	1.91 1.95 1.92 2.03 2.28 2.37 2.34	0.668 0.605 – – – 0.756 –	– – 0.574 0.592 0.662 0.757 0.650	– 33.98 ± 0.00 33.99 ± 0.00 34.12 ± 0.03 34.38 ± 0.04 34.54 ± 0.01 34.63	– –1.67 ± 0.01 –1.72 ± 0.03 –1.50 ± 0.09 0.06 ± 0.29 1.27 ± 0.03 1.50	– 27.35 ± 0.00 27.36 ± 0.00 27.46 ± 0.02 27.61 ± 0.02 27.66 ± 0.00 27.71
916 58°00'S 06°00'W 04-11-92	40 60 100 150 300	28.1 28.8 30.5 28.6 31.5	67.2 71.4 77.4 78.7 90.2	1.95 2.01 2.13 2.03 2.25	0.465 – – – –	0.467 0.449 0.659 0.549 0.688	34.08 34.17 34.23 34.32 34.57	–1.46 –1.60 –1.14 –1.27 0.52	27.43 27.50 27.54 27.61 27.73
918 59°00'S 06°00'W 06-11-92	40 60 100 200 300	28.0 27.8 27.7 30.5 33.1	77.7 78.3 79.9 99.0 117.0	2.01 1.99 2.02 2.16 2.35	0.574 0.604 0.586 0.768 0.650	– – – – –	34.32 34.32 34.34 34.68 34.68	–1.82 –1.81 1.76 0.58 0.45	27.63 27.63 27.65 27.82 27.82
919 59°29'S 06°00'W 06-11-92	40 60 100 150 200 300	27.2 27.3 29.3 32.4 32.5 32.7	76.9 77.7 78.8 – 113.1 118.2	2.06 2.06 2.08 2.36 2.38 2.39	0.592 0.511 0.513 0.803 0.811 0.749	– – – – – –	34.28 ± 0.01 34.29 ± 0.00 34.38 ± 0.10 34.59 ± 0.09 34.68 ± 0.00 34.68	–1.83 ± 0.01 –1.82 ± 0.00 –1.48 ± 0.45 –0.08 ± 0.69 0.67 ± 0.01 0.53	27.60 ± 0.01 27.60 ± 0.00 27.67 ± 0.07 27.78 ± 0.03 27.81 ± 0.00 27.82

ing step and the total destruction step, respectively. The blanks for the acetic acid leaching step were smaller than 0.05 pM. The detection limits, based on $3 \times$ the standard deviation of the blanks, ranged between 0.06 and 0.18 pM, 0.03 and 0.06 pM, and 1.2 and 2.15 pM for the acetic acid leaching step, the second leaching step and the total destruction, respectively.

Analyses of nutrients were performed on board by standard methods with a Technicon AAII autoanalyser as described by Bakker et al. (1994). The detection limit, precision and accuracy at a typical concentration for phosphate were 0.01 μ M, 0.02

μ M and $2.0 \pm 0.05 \mu$ M, respectively (Table 1 of De Baar et al., 1997). Tables 1–10 contain all data on nutrients, dissolved (filtered) and total dissolvable (unfiltered) Cd concentrations for the upper water (< 400 m; Tables 1–8) and deep water (> 400 m; Tables 9 and 10). Data on particulate matter will be reported elsewhere.

3. Regional hydrography

The hydrography of the research area at the 6°W meridian was presented in detail by Veth et al.

Table 6

Surface water stations on ANT X/6 with data on nutrients, filtered and unfiltered Cd. ALW (German: 'Auslegerwinde') refers to sampling the surface water approximately 10 m in front of the sailing ship with a 2 l GoFlo lowered from a ship's crane. Salinity, potential temperature and density were estimated as the averages of the values of CTD casts between which the Kevlar cable samples were taken at almost the same position and time

Station/Position/ Date	Depth (m)	NO ₃ (μM)	Si (μM)	PO ₄ (μM)	Unfiltered Cd (nM)	Filtered Cd (nM)	Salinity	Potential T (°C)	σ _θ (kg m ⁻³)
930	0 (Zodiac)	28.1	78.2	2.07	0.551	–	–	–	–
59°30'S	ALW 10	28.0	78.2	2.06	0.568	–	–	–	–
06°00'W	40	28.0	77.2	2.08	0.516	–	34.29 ± 0.00	-1.84 ± 0.00	27.60 ± 0.00
10-11-92	60	27.8	76.8	2.09	0.486	–	34.29 ± 0.00	-1.84 ± 0.00	27.61 ± 0.00
	100	27.9	77.4	2.10	0.516	–	34.32 ± 0.04	-1.75 ± 0.14	27.63 ± 0.03
	150	32.9	102.9	2.37	0.686	–	34.61 ± 0.02	0.09 ± 0.15	27.78 ± 0.01
	200	33.3	110.8	2.43	0.727	–	34.68 ± 0.00	0.68 ± 0.00	27.81 ± 0.00
	300	33.4	117.0	2.40	0.680	–	34.68	0.55	27.82
934	40	29.0	75.3	2.03	0.551	–	34.15 ± 0.05	-1.29 ± 0.35	27.47 ± 0.03
58°00'S	60	29.4	75.8	2.12	0.557	–	34.17 ± 0.03	-1.51 ± 0.14	27.50 ± 0.03
06°01'W	100	28.9	77.3	2.04	0.580	–	34.24 ± 0.01	-1.66 ± 0.03	27.56 ± 0.00
11-11-92	150	29.2	79.2	2.05	0.580	–	34.38 ± 0.02	-1.28 ± 0.07	27.66 ± 0.01
	200	32.3	87.4	2.26	0.545	–	34.54 ± 0.02	0.40 ± 0.14	27.71 ± 0.01
	300	33.7	95.4	2.30	0.668	–	34.64	0.95	27.76
941	ALW 10	28.0	61.8	1.91	0.574	–	–	–	–
57°03'S	38	27.9	61.8	1.95	–	0.563	33.97 ± 0.00	-1.51 ± 0.01	27.33 ± 0.00
06°01'W	57	28.0	61.7	1.93	–	0.557	33.97 ± 0.00	-1.52 ± 0.02	27.40 ± 0.08
13-11-92	95	28.8	63.6	2.01	–	0.598	34.11 ± 0.04	-1.16 ± 0.29	27.50 ± 0.12
	142	33.5	75.5	2.33	–	0.727	34.36 ± 0.06	-0.14 ± 0.68	27.50 ± 0.12
	190	34.3	83.4	2.41	–	0.715	34.56 ± 0.02	1.33 ± 0.05	27.64 ± 0.04
	285	33.6	89.4	2.36	–	0.750	33.64	1.47	27.72
943	ALW 10	27.6	50.6	1.91	0.574	–	–	–	–
56°01'	40	27.3	50.1	1.88	–	0.545	33.91	-1.23	27.27
06°00'	60	27.6	50.5	2.01	–	0.551	33.91	-1.25	27.28
13-11-92	100	27.7	52.1	1.91	–	0.574	33.92	-1.29	27.29
	150	30.0	98.2	2.04	–	0.621	34.07	-0.81	27.39
	200	32.8	70.3	2.24	–	0.715	34.30	0.31	27.52
	300	34.3	87.6	2.42	–	0.627	34.56	1.44	27.66

(1997). Here, the water masses at station 979 (45°29'S; 01°08'E) are described as well because this station was outside the 6°W meridian area. The potential temperature–salinity plot for this station is shown by Löscher et al. (1997a) in their fig. 2).

3.1. Surface water

The surface waters of the Antarctic Circumpolar Current (ACC) generally flow eastward forced by the West Wind Drift. Within that eastward flowing surface water, fronts stand out with relatively higher geostrophic velocity compared to the surrounding

water masses. Three fronts characterized the surface waters of the research area (Veth et al., 1997):

- the Polar Frontal region north of 50°S with a main frontal jet meandering near 49°S,
- the southern ACC front at the end of the 1.8°C isotherm between 54°S and 56°S (Orsi et al., 1995), and
- the ACC–Weddell Gyre Boundary (AWB) at about 58°S.

Southwards of the Polar Front, Antarctic Surface Water (AASW) was found in the upper 300 m with salinities between 33.2 and 34.4 and potential temperatures between -1.5 and -0.5°C. It included a

Table 7

Surface water stations on ANT X/6 with data on nutrients, filtered and unfiltered Cd. ALW (German: 'Auslegerwinde') refers to sampling the surface water approximately 10 m in front of the sailing ship with a 2 l GoFlo lowered from a ship's crane. Salinity, potential temperature and density were estimated as the averages of the values of CTD casts between which the Kevlar cable samples were taken at almost the same position and time

Station/ Position/ Date	Depth (m)	NO ₃ (μM)	Si (μM)	PO ₄ (μM)	Unfiltered Cd (nM)	Filtered Cd (nM)	Salinity	Potential T (°C)	σ _θ (kg m ⁻³)
945	ALW 10	27.0	43.8	1.86	0.563	–	–	–	–
55°00'S	40	27.1	43.1	1.89	–	0.498	33.90	–1.21	27.24
06°01'W	60	27.1	43.2	1.87	–	0.563	33.90	–1.32	27.25
14-11-92	100	27.7	43.6	1.89	–	0.510	33.92	–1.35	27.28
	150	28.7	46.9	2.01	–	0.545	33.99	–1.39	27.33
	200	31.8	58.2	2.23	–	0.621	34.27	0.17	27.48
	300	34.8	78.1	2.45	–	0.709	34.56	1.44	27.61
947	59	26.7	42.9	1.90	–	0.870	33.90	–1.12	27.27
54°00'S	98	26.9	42.5	1.87	–	0.769	33.90	–1.12	27.27
06°00'W	148	27.1	43.6	1.90	–	0.750	33.91	–1.35	27.28
15-11-92	197	29.8	51.9	2.08	–	0.962	34.12	–0.78	27.43
	296	34.8	76.5	2.49	1.247	–	34.56	1.67	27.65
	394	34.0	86.6	2.39	1.104	–	34.63	1.76	27.69
949	ALW 10	27.8	39.2	1.93	0.486	–	–	–	–
53°00'S	40	27.7	38.5	1.87	–	0.533	33.93 ± 0.00	–0.39 ± 0.02	27.26 ± 0.00
06°00'W	60	27.3	38.8	1.88	–	0.539	33.93 ± 0.00	–0.42 ± 0.01	27.26 ± 0.00
16-11-92	100	27.1	39.2	1.89	–	0.533	33.94 ± 0.00	–0.60 ± 0.07	27.28 ± 0.01
	150	28.5	41.9	1.99	–	0.533	33.96 ± 0.01	–0.98 ± 0.01	27.31 ± 0.01
	200	34.2	66.4	2.37	–	0.738	34.16 ± 0.00	–0.07 ± 0.00	27.43 ± 0.00
953	ALW 10	26.5	27.4	1.85	0.416	–	33.94	0.82	27.20
51°00'S	40	26.7	27.2	1.86	0.467	–	33.94 ± 0.00	0.72 ± 0.03	27.21 ± 0.00
06°01'W	60	26.4	26.9	1.84	0.434	–	33.94 ± 0.00	0.70 ± 0.04	27.21 ± 0.00
17-11-92	150	27.5	32.9	1.94	0.510	–	33.97 ± 0.00	–0.06 ± 0.00	27.28 ± 0.00
	200	31.24	44.1	2.13	0.615	–	34.07 ± 0.09	0.22 ± 0.38	27.34 ± 0.05

remnant layer of Winter Water between 150 and 250 m unaffected by seasonal warming. North of the Polar Front, the Subantarctic Surface Water (SASW) was found. At station 979 (45°29'S; 01°08'E), it extended to a depth of about 160 m with salinity between 34.0 and 34.2 and potential temperature between 5.2°C and 7.2°C.

3.2. Intermediate and deep water

At the site of the Polar Frontal region, the Antarctic Intermediate Water (AAIW) forms from a combination of SASW, AASW and Upper Circumpolar Deep Water (UCDW). It flows northward into the Atlantic, Indian and Pacific Oceans at intermediate depth, while mixing with surface and deep waters.

During transects 5 and 11, no AAIW was sampled Veth et al. (1997). However, at sub-antarctic station 979 (45°29'S; 01°08'E), AAIW could be characterized between 160 and 770 m depth with a salinity between 34.2 and 34.3, and a potential temperature between 2.6 and 5.2°C.

In the Southern Atlantic Ocean, North Atlantic Deep Water (NADW) with a relatively high salinity penetrates into the deep water of the Southern Ocean, the Circumpolar Deep Water (CDW). By this penetration, it splits the CDW up into an upper and a lower part: the Upper Circumpolar Deep Water (UCDW) and the Lower Circumpolar Deep Water (LCDW). UCDW is characterized as the deep water layer between the isopycnals 27.35 kg m⁻³ and 27.75 kg m⁻³ (Orsi et al., 1995) containing an

Table 8

Surface water stations on ANT X/6 with data on nutrients, filtered and unfiltered Cd. ALW (German: 'Auslegerwinde') refers to sampling the surface water approximately 10 m in front of the sailing ship with a 2 l GoFlo lowered from a ship's crane. Salinity, potential temperature and density were estimated as the averages of the values of CTD casts between which the Kevlar cable samples were taken at almost the same position and time

Station/Position/ Date	Depth (m)	NO ₃ (μM)	Si (μM)	PO ₄ (μM)	Unfiltered Cd (nM)	Filtered Cd (nM)	Salinity	Potential T (°C)	σ _θ (kg m ⁻³)
956	ALW 10	23.6	4.8	1.03	0.354	–	–	–	–
49°59'S	39	23.8	7.1	1.11	–	0.212	33.88 ± 0.01	1.86 ± 0.10	27.08 ± 0.02
06°00'W	98	25.3	14.4	1.38	–	0.345	33.91 ± 0.01	1.19 ± 0.27	27.16 ± 0.02
18-11-92	147	28.1	28.4	1.95	–	–	33.96 ± 0.01	0.42 ± 0.07	27.25 ± 0.01
	196	31.1	38.9	2.15	–	1.035	34.07 ± 0.01	0.67 ± 0.09	27.32 ± 0.00
	294	35.2	59.2	2.43	–	1.136	34.33	1.78	27.46
	392	35.9	72.7	2.50	–	1.171	34.47	2.09	27.54
960	ALW 10	23.9	7.9	1.19	0.234	–	–	–	–
49°00'S	39	23.6	6.9	1.22	–	0.170	33.86 ± 0.00	1.90 ± 0.00	27.06 ± 0.00
06°00'W	58	23.5	7.6	1.28	–	0.182	33.86 ± 0.00	1.85 ± 0.01	27.07 ± 0.00
19-11-92	97	25.9	19.9	1.71	–	0.434	33.90 ± 0.00	1.07 ± 0.09	27.16 ± 0.01
	146	28.4	29.8	1.95	–	0.557	33.96 ± 0.01	0.41 ± 0.02	27.25 ± 0.01
	194	30.0	35.1	2.05	–	0.598	34.02 ± 0.00	0.52 ± 0.03	27.29 ± 0.00
	291	35.3	56.6	2.36	–	0.715	34.26	1.47	27.415
964	ALW 10	19.8	1.3	1.28	0.316	–	–	–	–
48°00'S	40	21.0	3.9	1.50	–	0.228	33.82	3.22	26.92
06°00'W	60	23.4	10.4	1.64	–	0.434	33.85	2.78	26.98
20-11-92	100	26.1	18.0	1.86	–	0.322	33.91	2.11	27.09
	150	27.7	22.9	1.95	–	0.463	33.93	1.58	27.14
	200	30.1	28.4	2.08	–	0.574	34.03	1.69	27.22
	300	32.7	40.8	2.29	–	0.563	34.20	2.04	27.33
969	ALW 10	19.2	1.3	1.21	0.322	–	–	–	–
46°59'S	40	20.2	1.0	1.29	0.363	–	33.81 ± 0.00	3.21 ± 0.00	26.91 ± 0.00
06°00'W	60	21.6	4.5	1.45	0.434	–	33.83 ± 0.01	2.97 ± 0.08	26.95 ± 0.01
21-11-92	100	24.7	13.7	1.78	0.545	–	33.92 ± 0.03	2.63 ± 0.05	27.06 ± 0.03
	200	29.5	24.5	2.00	0.609	–	34.09 ± 0.01	2.43 ± 0.01	27.21 ± 0.01
	300	32.4	36.5	2.16	0.691	–	34.19	2.09	27.32
972	ALW 10	19.1	2.8	1.28	0.328	–	–	–	–
48°41'S	39	20.8	4.4	1.32	–	0.227	33.82 ± 0.00	3.48 ± 0.0 2	26.90 ± 0.00
05°59'W	97	24.7	16.1	1.70	–	0.475	33.93 ± 0.02	2.38 ± 0.1 1	27.08 ± 0.00
22-11-92	145	28.0	24.7	1.89	–	0.563	34.02 ± 0.06	2.21 ± 0.5 3	27.17 ± 0.01
	194	30.1	29.8	2.02	–	0.633	34.09 ± 0.03	2.10 ± 0.2 4	27.23 ± 0.01
	290	32.54	42.9	2.21	–	0.639	34.21 ± 0.00	2.10 ± 0.0 9	27.33 ± 0.00
	387	34.3	57.6	2.33	–	0.721	34.31 ± 0.00	2.18 ± 0.0 3	27.41 ± 0.00

oxygen minimum and a nutrient maximum (Whitworth and Nowlin, 1987), whereas NADW contains a salinity-maximum and major nutrient minimum which is followed by the LCDW (Whitworth and Nowlin, 1987). At two stations (956, 979), the influence of recent NADW is discernible within the CDW by a salinity maximum above 34.73 (Whitworth and Nowlin, 1987). Under the LCDW, north-

ward flowing Antarctic Bottom Water (AABW) was identified by a potential temperature lower than 0°C and a salinity above 34.6 (Carmack and Foster, 1975). It is formed from Weddell Sea Bottom Water which flows out of the Weddell Sea.

In this paper, the expression 'upper water' is used for the waters shallower than 400 m, which contain the surface water as AASW or SASW but also the

Table 9

Deep water stations on ANT X/6 with data on hydrography, nutrients, filtered and unfiltered Cd. After recalculation, there appeared to be slight discrepancies between the data shown in Tables 9 and 10 and depth, salinity and potential temperature as reported in Löscher et al. (1997a,b)

Station/Position/ Date	Depth (m)	Salinity	Potential T (°C)	σ_θ (kg m^{-3})	Oxygen (μM)	NO_3 (μM)	Si (μM)	PO_4 (μM)	Unfiltered Cd (nM)	Filtered Cd (nM)
956	497	34.522	2.037	27.586	180.1	36.0	76.4	2.50	–	0.481
50°01'S	997	34.712	2.014	27.740	187.0	32.0	84.7	2.24	–	0.605
05°58'W	1246	34.746	1.877	27.778	197.2	31.0	85.0	2.16	–	0.292
18-11-92	1495	34.744	1.622	27.795	199.9	31.2	91.7	2.16	–	0.540
	1746	34.719	1.156	27.809	201.3	32.3	105.3	2.25	–	0.575
bottom:	1996	34.713	0.941	27.818	205.5	32.0	109.6	2.25	–	0.475
2512–2517 m	2249	34.703	0.735	27.823	207.6	32.6	115.6	2.30	–	5.593
	2413	34.699	0.630	27.827	209.6	32.9	114.9	2.32	–	0.451
	2463	34.698	0.623	27.827	210.9	32.7	118.5	2.30	–	(0.252)
	2494	34.696	0.577	27.828	210.9	33.2	120.2	2.31	–	0.563
	2504	34.696	0.577	27.828	210.9	32.9	119.5	2.31	–	0.424
951	99	33.949	–0.082	27.262	356.6	26.9	33.1	1.85	0.133	–
52°01'S	249	34.446	1.637	27.556	213.3	35.0	66.8	2.42	0.681	–
06°01'W	497	34.628	1.934	27.679	175.6	34.7	86.0	2.38	0.168	–
17-11-92	747	34.702	1.843	27.746	185.0	32.8	89.2	2.26	0.391	–
	999	34.729	1.642	27.782	195.8	31.7	92.3	2.17	0.729	–
bottom:	1249	34.726	1.361	27.800	200.3	32.9	99.3	2.23	0.697	–
2180 m	1497	34.711	1.000	27.813	204.5	32.4	109.7	2.23	0.711	–
	1746	34.701	0.758	27.821	207.5	32.7	115.7	2.27	0.691	–
	1999	34.692	0.542	27.827	212.7	32.7	121.1	2.29	0.782	–
	2098	34.688	0.452	27.829	214.3	32.8	125.6	2.30	0.749	–
	2148	34.688	0.437	27.830	214.8	32.8	126.2	2.31	0.789	–
947	498	34.665	1.718	27.725	183.3	33.3	88.9	2.36	0.375	–
53°58'S	747	34.708	1.554	27.772	192.7	32.1	94.3	2.24	0.198	–
06°00'W	997	34.715	1.301	27.796	198.2	31.7	99.1	2.24	0.782	–
15-11-92	1247	34.707	1.028	27.808	202.0	32.4	107.9	2.28	0.684	–
	1497	34.698	0.768	27.818	204.6	33.6	112.4	2.30	0.756	–
bottom:	1746	34.689	0.516	27.826	209.5	32.7	120.0	2.33	0.691	–
2627 m	2149	34.678	0.216	27.834	215.0	33.0	127.9	2.34	0.789	–
	2347	34.676	0.170	27.836	216.7	33.0	129.6	2.35	–	0.749
	2498	34.674	0.113	27.837	217.8	33.2	132.5	2.35	–	0.769
	2559	34.674	0.094	27.838	218.6	33.3	132.3	2.36	–	0.749
	2599	34.673	0.076	27.838	219.0	33.1	134.9	2.36	–	0.743

upper part of UCDW or AAIW. The expression 'surface water' was used to designate only the AASW or SASW.

4. Results

4.1. Cd concentrations in the upper water column

Concentrations of dissolved and total dissolvable Cd in upper waters (30–400 m) ranged from 0.2 to

1.2 nM. Minima (lower than 0.3 nM) were found within the Polar Frontal region in the upper 80 m (Fig. 2). Concentrations increased with depth to more than 0.7 nM below 300 m (Fig. 3). Cd in the Polar Frontal region was about 0.2 and 0.3 nM lower than in the southern ACC area at 40 m depth (Fig. 3a,b). A concentration maximum of about 1.1 nM dissolved Cd was observed in the southern area of the Polar Frontal region at about 50°S in the lower 250 m at transect 11 (Fig. 3b). This location coincided with the position of an eddy spun out of the mean-

Table 10

Deep water stations on ANT X/6 with data on hydrography, nutrients, filtered and unfiltered Cd. After recalculation, there appeared to be slight discrepancies between the data shown in Tables 1, 9 and 10 and depth, salinity and potential temperature as reported by Löscher et al. (1997a,b). The depth data at station 979 had to be corrected and show changes up to 400 m which caused a change in the definition of the AAIW and the UCDW. The in Löscher et al. (1997b) reported Cd and Cd/PO₄ range for the LCDW is in the right water mass, when describing the NADW influence to a salinity which is larger than 34.8. The reported range ascribed to the UCDW by Löscher et al. (1997b) had a slight overlap with the determined NADW. Omitting the two samples, which are reported here for NADW, would yield a coefficient of variation of the Cd/phosphate ratio of 11%, which is 1% higher than required by the selection criterion in this paper (Löscher et al., 1997b). This small difference does not cause a change in the interpretation of the previous paper

Station/Position/ Date	Depth (m)	Salinity	Potential T (°C)	σ_θ (kg m ⁻³)	Oxygen (μ M)	NO ₃ (μ M)	Si (μ M)	PO ₄ (μ M)	Unfiltered Cd (nM)	Filtered Cd (nM)
866	499	34.690	1.531	27.759	187.6	33.1	107.7	2.22	0.836	–
57°42'S	999	34.698	0.925	27.807	200.2	33.1	111.6	2.20	0.713	–
06°22'W	1499	34.680	0.409	27.825	208.6	34.8	122.5	2.27	0.891	–
10-11-92	1999	34.674	0.155	27.835	213.6	33.6	126.9	2.28	0.658	–
	2498	34.666	-0.079	27.841	225.7	33.8	130.0	2.31	0.718	–
bottom:	3247	34.659	-0.313	27.847	238.1	33.5	131.8	2.28	0.770	–
3760–3518 m	3498	34.658	-0.345	27.848	241.5	33.3	130.5	2.27	0.688	–
	3563	34.658	-0.357	27.848	241.4	33.1	130.5	2.23	0.688	–
	3713	34.658	-0.368	27.849	243.5	38.3	132.5	2.34	0.596	–
865	498	34.643	1.763	27.704	186.9	(51.1)	88.3	2.37	–	0.627
56°11'S	999	34.718	1.538	27.791	197.6	33.4	95.9	2.29	–	0.620
12°24'W	1495	34.690	0.714	27.815	210.8	33.8	111.5	2.38	–	0.411
10-09-92	1998	34.683	0.358	27.830	217.2	34.6	118.9	2.39	–	0.316
	2498	34.675	0.125	27.838	224.6	36.7	123.3	2.39	–	0.847
bottom:	3995	34.656	-0.454	27.851	248.1	33.7	129.7	2.36	–	(0.215)
4887–4885 m	4598	34.654	-0.517	27.852	252.8	38.1	131.5	2.35	–	0.817
	4839	34.654	-0.522	27.852	255.8	35.4	132.0	2.33	–	0.799
979	501	34.189	3.440	27.197	263.4	29.8	22.1	2.06	0.208	–
45°30'S	993	34.440	2.584	27.475	194.7	34.8	55.8	2.41	0.455	–
01°08'E	1248	34.596	2.521	27.605	182.5	34.5	65.5	2.41	0.748	–
25-11-92	1499	34.689	2.487	27.682	187.3	32.3	67.4	2.25	0.673	–
	1749	34.731	2.374	27.731	197.9	30.9	68.8	2.15	0.538	–
bottom:	2002	34.775	2.196	27.775	207.4	29.4	69.6	2.05	0.636	–
4186–4159 m	2147	34.781	2.115	27.787	210.2	29.3	70.9	2.01	0.628	–
	2347	34.774	1.899	27.799	211.0	29.4	77.0	2.07	0.500	–
	2500	34.774	1.798	27.806	210.5	29.8	79.9	2.09	0.681	–
	2650	34.768	1.682	27.810	211.0	29.7	82.5	2.09	0.613	–
	2998	34.754	1.414	27.819	211.4	30.7	90.4	2.15	0.659	–
	3249	34.744	1.202	27.826	213.1	31.2	96.0	2.18	0.636	–
	3249	34.744	1.202	27.826	213.1	31.2	96.0	2.18	0.622	–
	3748	34.714	0.731	27.833	216.4	32.3	109.4	2.28	0.614	–
	3998	34.707	0.601	27.836	219.1	34.3	110.9	2.29	0.695	–
	4149	34.701	0.521	27.836	21.2	32.9	115.4	2.32	0.565	–
	4150	34.701	0.521	27.836	221.4	32.8	115.7	2.34	0.733	–
	4225	34.699	0.488	27.836	222.2	33.4	116.9	2.34	0.666	–

dering frontal jet at 50°S (Veth et al., 1997; their Fig. 13). At 54°S (Fig. 3c), in another area showing eddy motion (Veth et al., 1997), the dissolved Cd concentration was more than 0.3 nM higher compared to concentrations in the other southern ACC water.

Although no filtered data exist for the very near surface (< 40 m), it can be assumed that the concentrations in the upper 40 m are uniform due to wind mixing. The wind-mixed layer averaged 40 m with maxima of 80 m (Veth, personal communication).

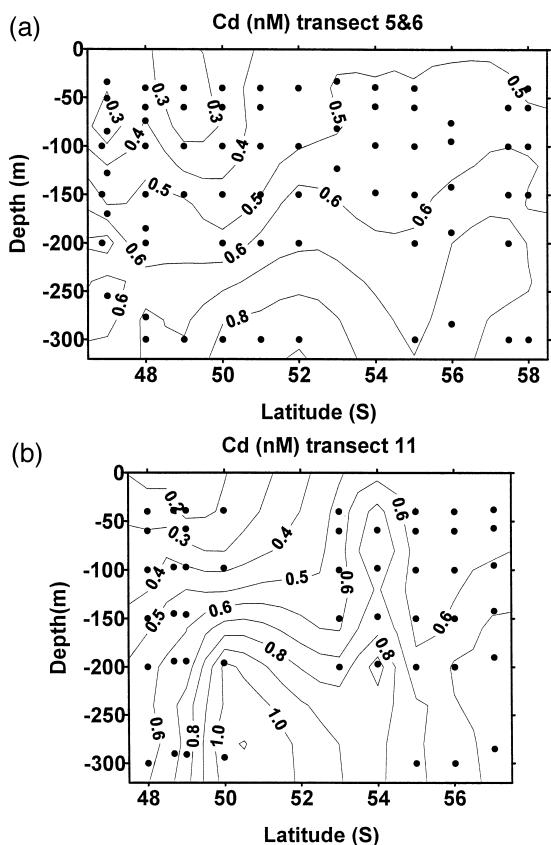


Fig. 2. Section plot of dissolved Cd (nM) in the upper water column along the 6°W meridian. (a) At transect 5 and 6 together with station 879. (b) At transect 11 together with station 972.

Total depletion of Cd at the surface was rarely observed. In contrast the concentrations usually decreased with depth within the first 80 m at most stations (Fig. 3). Only in the Polar Frontal region Cd concentrations exhibited a classical nutrient profile, increasing from 40 m depth (0.2 nM) to 100 m depth (0.5 nM; Fig. 3b). However, total dissolvable Cd concentrations at 10 m depth (Fig. 4) were not depleted, even in the Polar Frontal region. There, concentrations ranged between 0.2 and 0.4 nM whereas in the Southern ACC area, they were between 0.2 and 0.8 nM. In order to estimate the dissolved Cd concentrations at 10 m depth, the particulate Cd concentrations at 40 m depth (Fig. 5) were subtracted from the total dissolvable Cd concentration at 10 m depth. By this method, a low estimate for dissolved Cd at 10 m depth can be calculated because primary production was highest at 40 m depth (Jochem et al., 1995), indicating that biogenic particulate matter concentration can be expected to be highest at that depth. Particulate Cd concentrations at 40 m depth ranged from 0.02 to 0.14 nM in the Polar Frontal region and from 0.02 to 0.06 nM in the southern ACC area at transect 5 (Fig. 5). (Particulate matter data of transect 11 rarely exist.) In the southern ACC area at transect 5, particulate Cd concentrations are one order of magnitude smaller than the total dissolvable Cd concentrations. Subtracting them from the total dissolvable Cd con-

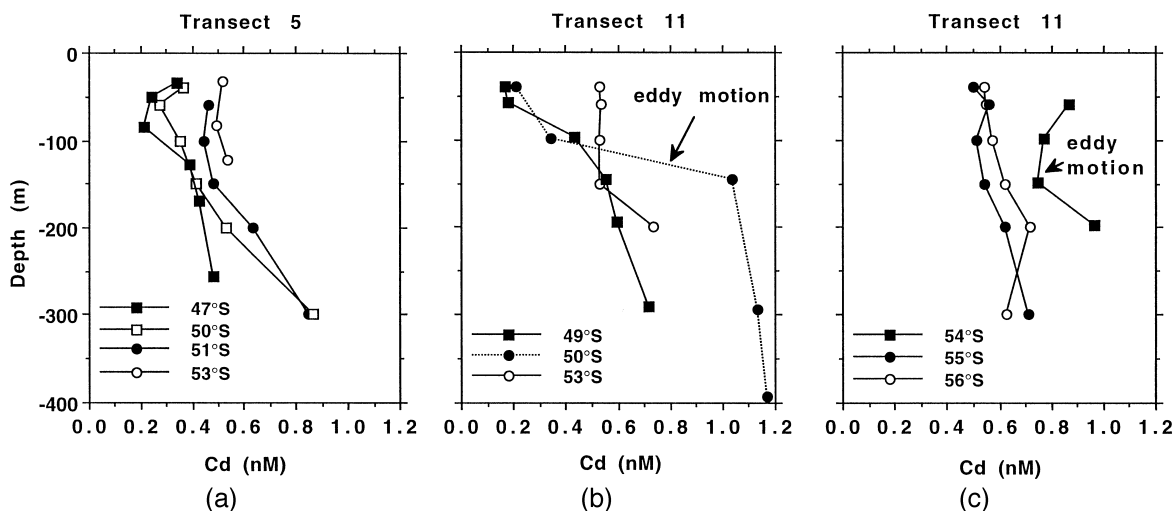


Fig. 3. Vertical profiles of dissolved Cd (nM) in the upper 400 m. (a) At transect 5. (b) At transect 11 between 49°S and 53°S. Positions at 49°S and 50°S are in the Polar Frontal region. (c) At transect 11 between 54°S and 56°S.

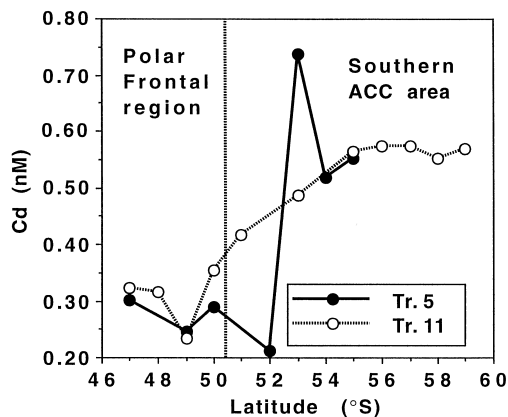


Fig. 4. Total dissolvable Cd concentrations at 10 m depth during transect 5 and 11.

centrations at 10 m depth results in dissolved Cd concentrations which are in the same concentration range as the total dissolvable Cd concentrations. However, in the Polar Frontal region total particulate Cd concentrations (up to 0.14 nM, Fig. 5) were approaching the low end (~ 0.21 nM, Fig. 4) of the range of the total dissolvable Cd concentrations at 10 m depth (about 0.21 nM). By subtracting the total particulate Cd concentration from the total dissolvable Cd concentration in this region, a minimum of about 0.1 nM dissolved Cd can be expected at 10 m depth.

Most of the particulate Cd was found in the first phase of the sequential chemical leaching treatment (85–94%). Particulate Cd which was dissolved in the second leaching step and by total destruction ranged from 2 to 10% and from 0 to 7%, respectively. Total particulate matter concentration and that calculated from the difference between total dissolvable and dissolved Cd at 40 m depth (Fig. 5) show the same dependence on position. However, the measured total particulate matter concentration in the southern ACC area is only about 40 to 70% of the calculated particulate matter concentration. A difference in sampling time (about 1 h) for water used for the determination of the dissolved and the particulate Cd concentration could have led to the larger differences as in the Polar Frontal region. But because of the constancy in difference in the Southern ACC area, another reason must explain the difference between both concentrations. Rinsing of the filters, which

were used for the collection of particulate matter, with nanopure water may have led to a hypotonic osmotic shock (Britten and McClure, 1962; Goldman and Dennett, 1985) as well as to a release of adsorbed organic complexes (Collier and Edmond, 1983, 1984), and this would explain the loss of Cd from particulate matter. The larger filtering-volume per filter surface ($19\text{--}38$ l dm^{-2} for the particulate matter samples compared to about 12 l dm^{-2} for the dissolved samples) as well as the smaller pore size (0.2 μm compared to 0.4 μm) used for sampling of the particulate matter, would cause a greater chance for clogging of the pores by fine-grained material (Sheldon, 1972; Kennedy et al., 1974; Wagemann and Brunskill, 1975; Laxen and Chandler, 1982; Jardine et al., 1986; Taylor et al., 1990; Horowitz et al., 1992). If anything, this would lead to higher concentrations of particulate matter on the filters, but this was not observed.

In general, the dissolved Cd concentrations below 100 m at the stations with eddy motion were higher than in the surrounding area, whereas in the Polar Frontal region the concentration in the upper 40 m was lower ($0.2\text{--}0.3$ nM) than concentrations further south. Thus, the Cd concentration maximum was related to the area showing eddy motion. Surface minima occurred in the Polar Frontal region. Cd was

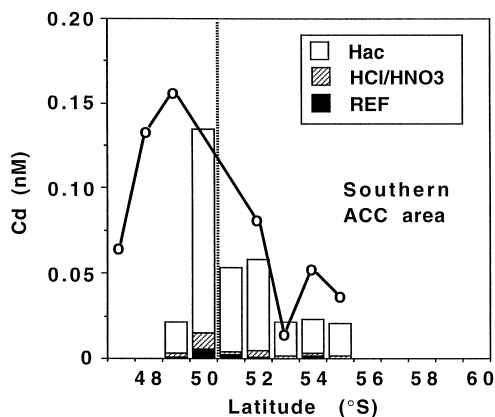


Fig. 5. Sequential chemical leached particulate Cd concentrations (columns) compared with the difference between total dissolvable and dissolved Cd concentrations (circles) at 40 m depth at transect 5. The description of the references for the sequential chemical leached particulate Cd concentrations are: Hac: fraction which was dissolved in 4.5 M Q-acetic acid; HCl/HNO₃: fraction which was leached in 2 M Q-HCl/1 M Q-HNO₃ and REF: residual refractory material, dissolved in aqua regia and HF.

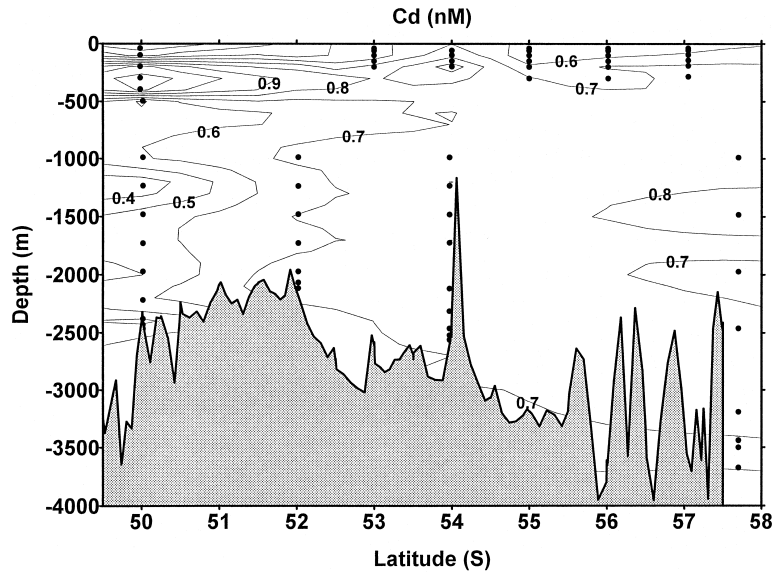


Fig. 6. Section plot of the dissolved Cd concentrations of the upper water column (down to 400 m) at transect 11 together with dissolved and total dissolvable Cd concentrations deeper in water column at transects 5, 11 and 12. At depths lower than 1000 m, totally dissolvable and dissolved Cd concentrations are used together because of the low average contribution from suspended matter relative to the total Cd concentration (ca. 1%) at these depths (Westerlund and Öhman, 1991).

not depleted in the upper water. Some 80 to 95% of the total particulate Cd concentration was found to be in the first fraction of the sequential chemical leaching treatment.

4.2. Deep water Cd concentrations

The deep water Cd concentrations increased to the south from about 0.4 nM to about 0.7 nM (Fig. 6). All profiles exhibited subsurface maxima in the upper part of the UCDW (Fig. 7) whereby at the three most northern stations these maxima were followed by minima in the lower part of the UCDW (Fig. 7a–c). At station 947, this minimum reached into the upper part of the LCDW (Fig. 7c). Concentrations in the deeper water masses remained nearly constant.

5. Discussion

5.1. The upper water column

The relatively high surface water Cd concentrations (0.17–0.86 nM at 40 m) coincided with high

nutrient concentrations (Fig. 8). The Cd concentrations are comparable with those found by Martin et al. (1990) in the Gerlache Strait (0.60 nM at 50 m) and in the Drake Passage (at 30 m, 0.28 nM), by Westerlund and Öhman (1991) in the Weddell Sea (0.49–0.86 nM at 50 m), by Nolting et al. (1991) in the Scotia Sea and Weddell/Scotia Confluence (0.32 to 0.40 nM) and by Frew (1995) in Winter Water (WW) across the Princess Elizabeth Trough (0.45–0.54 nM within the first 30 m). Frew (1995) assumed that the high Cd surface water concentrations in the Princess Elizabeth Trough may be attributed to shelf sources accumulating under the sea-ice and/or from the accumulation of upwelled Warm Deep Water. An explanation for the high upper water concentrations in AASW is UCDW with relatively high Cd concentrations (0.5–1.2 nM; Table 11), rising to the surface at the southern ACC Front. During its flow as AASW to the north (north of the southern ACC front) or to the south (south of the southern ACC front), low primary production ensures that Cd is not removed by incorporation in or adsorption on algae. The continuous decrease northwards of total dissolvable Cd at 10 m depth in the southern ACC area at

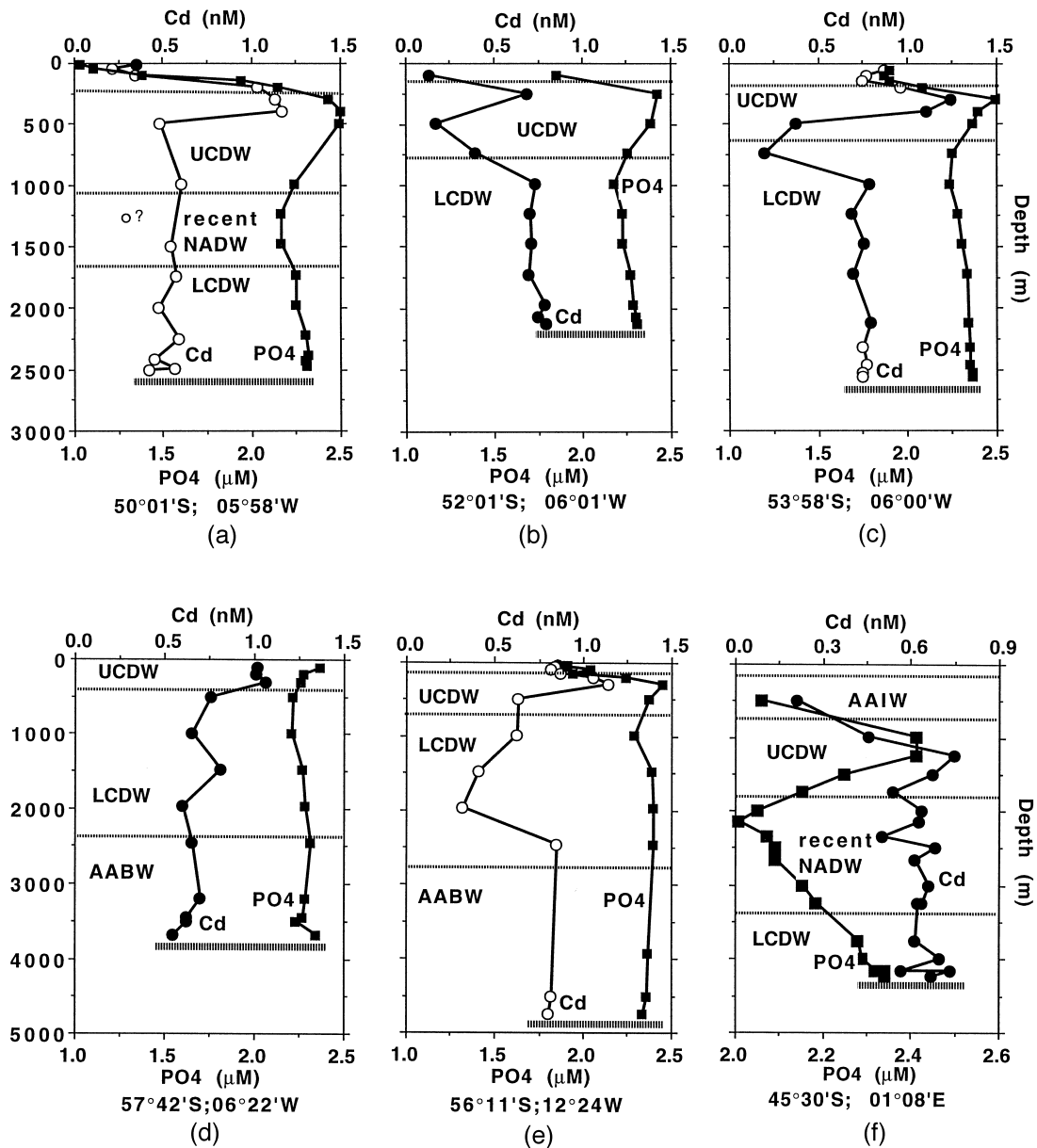


Fig. 7. Vertical dissolved and total dissolvable Cd and phosphate profiles with indicated deeper water masses: Upper Circumpolar Deep Water (UCDW), Lower Circumpolar Deep Water (LCDW), North Atlantic Deep Water (NADW) and Antarctic Bottom Water (AABW). (a) At $50^{\circ}01'S$; $05^{\circ}58'W$, transect 11. The Cd concentration at 1233 m depth may be attributed to recent NADW, which is entering the ACC. (b) At $52^{\circ}01'S$; $06^{\circ}01'W$, transect 11. (c) At $53^{\circ}58'S$; $06^{\circ}00'W$, transect 11. (d) At $57^{\circ}42'S$; $06^{\circ}22'W$, transect 2. (e) At $56^{\circ}11'S$; $12^{\circ}24'W$, transect 1. (f) At $45^{\circ}30'S$; $01^{\circ}08'E$, transect 13. The open circles indicate dissolved Cd concentrations, the closed circles show total dissolvable Cd concentrations.

transect 11 (Fig. 4) supports this statement. Both, upwelling of relatively high concentrated UCDW, which increases in southern direction and an almost

constant primary production can be regarded to be responsible for the continuous decreasing Cd concentration within the northwards flowing AASW.

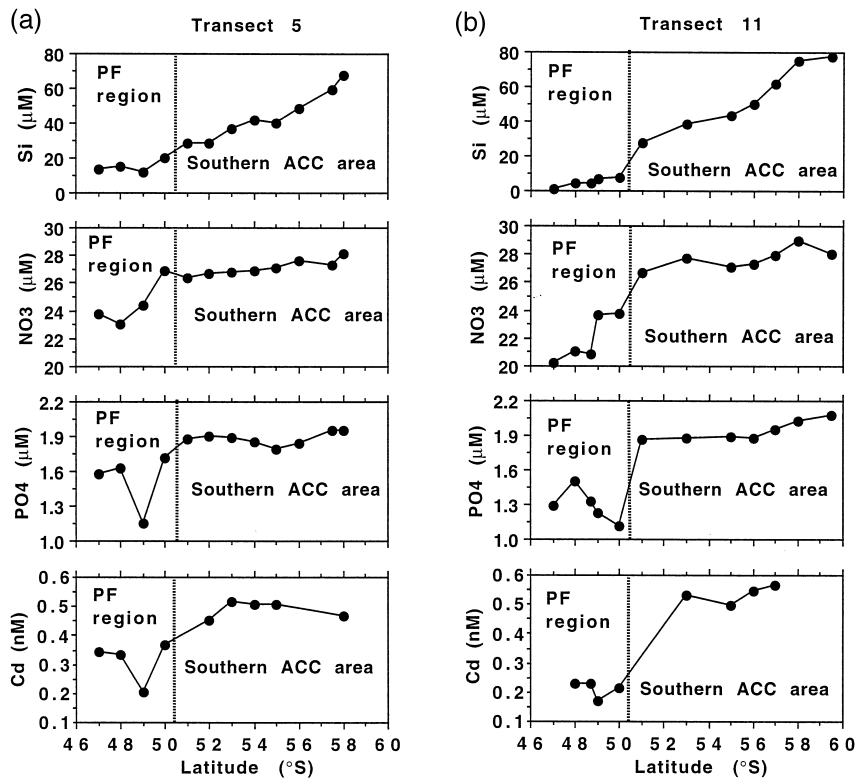


Fig. 8. Concentrations of silicate, nitrate, phosphate and dissolved Cd at about 40 m depth: (a) at transect 5 together with station 908 and (b) at transect 11 together with station 972.

Conditions favouring algal growth developed at transect 5 in the Polar Frontal region (De Baar et al., 1995; Bathmann et al., 1997; Löscher et al., 1997a; Scharek et al., 1997; Van Leeuwe et al., 1997; Veth et al., 1997). At this transect, the chlorophyll *a* concentrations ranged up to $1.5 \mu\text{g kg}^{-1}$ in the Polar Frontal region compared to the southern ACC area which had a lower chlorophyll *a* concentration of about $0.25 \mu\text{g kg}^{-1}$ (Bathmann et al., 1997). At transect 11, a spring bloom was following with chlorophyll *a* concentrations up to $2.5 \mu\text{g kg}^{-1}$ in the Polar Frontal region. In the southern ACC area, the chlorophyll *a* concentration did not change significantly. The development of this spring bloom coincided with a decrease of major nutrients (Fig. 8; see also De Baar et al., 1997) and dissolved Fe (De Baar et al., 1995; Löscher et al., 1997a), which was attributed to uptake by algae. Because Cd can be adsorbed on outer surfaces of biogenic particles (Collier and Edmond, 1983, 1984), can be bound by

phytochelatin (Ahner and Morel, 1995; Ahner et al., 1995) or substitute for Zn in Zn-limited phytoplankton (Price and Morel, 1990; Walsh and Hunter, 1992; Lee and Morel, 1995; Lee et al., 1995; Sunda and Huntsman, 1997), the Cd minima in the surface water in the Polar Frontal region at transects 5 and 11 evolved, like the minima for the major nutrients and for Fe, as a response to the developing spring bloom. In seawater, more than 98% of dissolved Zn (Bruland, 1989) and about 70% of dissolved Cd (Bruland, 1992) is bound on strong organic complexes which are of biological origin. However, the mechanism and selective advantage of ligand (organic complexes) release, remains unknown. Zn might have become limiting in the upper water of the research area, whereas Cd was still available.

The high percentage of Cd in the first phase (85–94%) of the selective leaching treatment (4 h in 4.5 M Q-acetic acid at room temperature) can be explained by dissolution of adsorbed Cd (Collier and

Table 11
Cd- and Cd/phosphate concentration ranges for the deeper water masses including their cores

Water mass position	Depth range (m)	Cd (nM)	Cd/PO ₄ (nM/μM)	PO ₄ (μM)	Depth _{core} (m)	Cd _{core} (nM)	Cd/PO ₄ _{core} (nM/μM)	PO ₄ _{core} (μM)
<i>AAIW</i>								
45°30'S; 01°08'E	501	0.21 *	0.10*	2.1	501	0.21 *	0.10 *	2.1
<i>UCDW</i>								
45°30'S; 01°08'E	993–1749	0.46–0.75 *	0.19–0.31 *	2.2–2.4	993–1248	0.46–0.75 *	0.19–0.31 *	2.4
50°01'S; 05°58'W	294–997	0.48–1.17	0.22–0.47	2.2–2.5	392–497	0.48–1.17	0.19–0.47	2.5
52°01'S; 06°01'W	249–747	0.17–0.68 *	0.07–0.28 *	2.3–2.4	249	0.68 *	0.28 *	2.4
53°58'S; 06°00'W	197–498	0.38–1.25	0.16–0.50 *	2.1–2.5	296	1.25 *	0.50 *	2.5
56°11'S; 12°24'W	200–498	0.63–1.14	0.26–0.46	2.2–2.4	300	1.14	0.46	2.4
57°42'S; 06°22'W	100–300	1.01–1.06 *	0.43–0.47 *	2.3–2.4	300	1.06 *	0.45 *	2.4
<i>Recent NADW</i>								
45°30'S; 01°08'E	2002–3249	0.50–0.68 *	0.24–0.33 *	2.0–2.2	2147	0.63 *	0.31 *	2.0
50°01'S; 05°58'W	1246–1495	0.54	0.25	2.2	1246	–	–	2.2
<i>LCDW</i>								
45°30'S; 01°08'E	2002–4225	0.50–0.73 *	0.24–0.33 *	2.0–2.3	2147 (r.NADW)	0.63 *	0.31 *	2.0
50°01'S; 05°58'W	1246–2504	0.29–0.59	0.14–0.26	2.2–2.3	1246 (r.NADW)	0.29	0.14	2.2
52°01'S; 06°01'W	999–2148	0.69–0.79 *	0.30–0.34 *	2.2–2.3	999	0.73 *	0.34 *	2.2
53°58'S; 06°00'W	747–2599	0.20–0.79 *	0.09–0.35 *	2.2–2.4	997	0.78 *	0.35 *	2.2
56°11'S; 12°24'W	999–2498	0.32–0.85	0.17–0.35	2.3–2.4	999	0.62	0.27	2.3
57°42'S; 06°22'W	499–1999	0.66–0.89 *	0.29–0.39 *	2.2–2.3	999	0.71 *	0.32 *	2.2
<i>AABW</i>								
56°11'S; 12°24'W	4598–4839	0.80–0.82	0.34–0.35	2.3–2.4	4839	0.80	0.34	2.3
57°42'S; 06°22'W	2498–3713	0.60–0.77 *	0.25–0.34 *	2.2–2.3	3713	0.60 *	0.25 *	2.3

* Total dissolvable samples or both dissolved and total dissolvable samples. (For detailed information, whether the values belong to dissolved or total dissolvable samples, see Tables 1–10).

Edmond, 1984) as well of metalloproteins. One metalloprotein might be carbonic anhydrase, with Cd substituting for Zn, in the case of Zn limitation in the

research area. Phytochelatin which is formed in phytoplankton as a reaction to Cd stress, may also be included in the first leaching phase. When subtract-

Table 12
Relationships between Cd (nM) and phosphate (μM) in the upper 400 m at the 6°W meridian, where: [Cd] = a[PO₄] + b, r: coefficient of correlation, n: number of samples

Latitude	a	b	r	n	
<i>Transect 5:</i>					
48°00'S	0.60	–0.63	0.98	6	filtered SASW/UCDW
49°00'S	0.40	–0.27	0.99	5	filtered AASW/UCDW
50°00'S	0.73	–0.96	0.96	6	filtered AASW/UCDW
51°00'S	0.60	–0.66	1.00	5	filtered AASW/UCDW
55°59'S	0.43	–0.25	0.99	5	filtered AASW/UCDW
<i>Transect 11:</i>					
46°59'S	0.36	–0.10	1.00	5	unfiltered SASW/UCDW
48°41'S	0.47	–0.35	0.98	6	filtered AASW/UCDW
49°00'S	0.50	–0.44	1.00	6	filtered AASW/UCDW
51°00'S	0.59	–0.64	0.90	4	unfiltered AASW/UCDW
53°58'S	0.69	–0.51	0.97	3/3	filtered/unfiltered AASW/UCDW
55°00'S	0.36	–0.18	1.00	5	filtered AASW/UCDW

ing the about 70% strong organic complexed Cd, as found by Bruland (1992) for the surface water of the North Pacific, from the dissolved or total dissolvable Cd concentration in the research area, the free Cd concentration would be low enough to induce phytochelatin production in algae ($\sim 10^{-10}$ M; Ahner and Morel, 1995; Ahner et al., 1995). Adding the 2 to 10% Cd of the second leaching step to the first one, results in particulate Cd concentrations which are almost only attributed to adsorbed organic complexes and Cd incorporated in algae.

Plotting upper water Cd concentrations vs. phosphate yields linear relationships ($r > 0.9$; Table 12; Fig. 9). All relationships would have negative intercepts when extrapolating to the hypothetical situation of total Cd depletion. They have the same point of intersection: the Cd–phosphate concentration interval of the UCDW. The only exception is the relationship at the positions of an eddy motion area at transect 11 (Veth et al., 1997). Generally, the strong correlations between phosphate and Cd in the upper water may be attributed to the uptake and remineralization of both Cd and phosphate in the upper water, which in itself has its origin in upwelled UCDW.

In the southern ACC Front (54–56°S), UCDW is rising to the surface. As AASW, it flows northward undergoing Cd- and phosphate-uptake and remineralization, whereby the upper waters in or near the southern ACC front are more influenced by the

rising UCDW (with its high Cd/phosphate ratio) than upper water north of the southern ACC Front. This mixing could explain the decreasing Cd–phosphate slopes from 0.69 (53°58'S) to 0.59 (51°00'S) in the southern ACC transect 11 (Table 12) which was characterized by low biological productivity ($0.3 \text{ g C m}^{-2} \text{ d}^{-1}$; Jochem et al., 1995). In the Polar Frontal region the area of high biological productivity (up to $3 \text{ g C m}^{-2} \text{ d}^{-1}$; Jochem et al., 1995) the Cd/phosphate slopes were even lower. They were lowest at the position of the meandering frontal jet (Veth et al., 1997) at 46°59'S and 48°41'S which was characterized by the highest biological productivity. The low slope at 55°00'S can be explained by the occurrence of the diatoms *Nitzschia prolongatoides* and *N. closterium* at this position (Bathmann et al., 1997).

5.2. Fractionation of Cd vs. phosphate

In the Polar Frontal region at 40 m depth, the depth with the highest primary production (Jochem et al., 1995), Cd/phosphate ratios were less than half the ratio in the southern ACC area (Fig. 10). Between transect 5 and transect 11 in the Polar Frontal region, the Cd/phosphate ratios further decreased from about 0.20 to 0.15 nM/ μM . On the contrary, in the southern ACC area the Cd/phos-

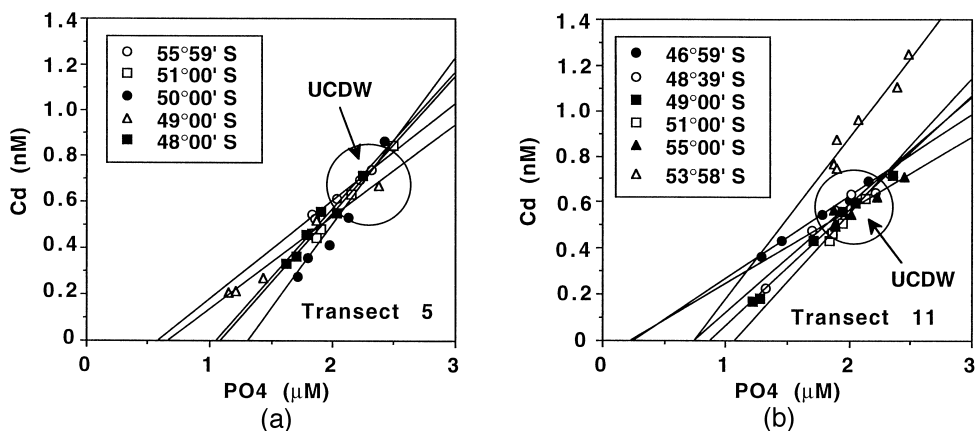


Fig. 9. Relationships between Cd and phosphate in the surface water interpolated to Cd depletion: (a) at transect 5; and (b) at transect 11 and station 972. The large circles indicate the UCDW, which is the origin of the AASW. Biological processes in the surface water alter the slope of the relationships. The one relationship at 53°58'S of transect 11 which does not intersect the large circle (representative of UCDW) was attributed to an area with eddy motion, i.e., where UCDW could have been upwelled more intensively.

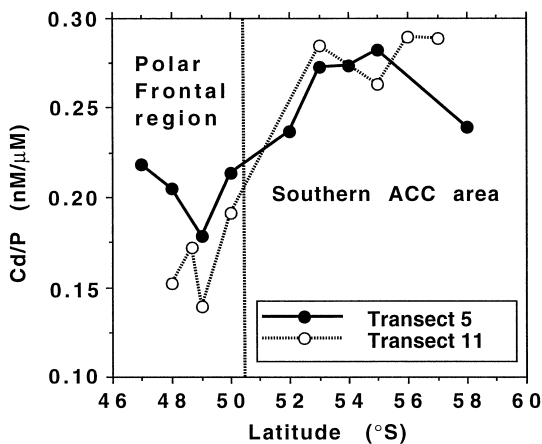


Fig. 10. Cd/phosphate ratio at 40 m depth at transects 5 and 11.

phate ratios were nearly constant (about 0.27 nM/ μ M) in both transects. These observations suggest that during bloom development in the Polar Frontal region, the net uptake of Cd was relatively larger than the net uptake of phosphate in the upper euphotic zone.

From the disappearance of both dissolved Cd and phosphate between Sections 5 and 11, the rate of removal and apparent net uptake ratio Cd/P can be calculated. Because most of the primary production occurred within the upper 50 m depth (Jochem et al., 1995), the concentrations were integrated within 50 m depth. Subsequently, the differences between sections 5 and 11 were divided by the average time period of 21 days between the sections. This led to a net uptake of Cd at 250 nmol m⁻² d⁻¹ and of phosphate at 562 μ mol m⁻² d⁻¹ with an uptake ratio Cd/P at 0.44 nM/ μ M. When comparing this uptake ratio with average ambient ratios in seawater of 0.27 nM/ μ M (southern ACC), 0.20 nM/ μ M (Polar Frontal region, transect 5) and 0.16 nM/ μ M (Polar Frontal region, transect 11), a clear case of preferential net uptake of Cd in the upper 50 m water column during the diatom bloom was observed.

Saager and de Baar (1993) simulated the Cd/phosphate distribution in Interglacial and Glacial oceans. They tested two processes which according to Boyle (1981, 1988) were responsible for the negative intercept of Cd/phosphate relationships in case of extrapolation to hypothetical Cd depletion or, for the kink in the global Cd/phosphate relationship.

The first process was preferential net uptake of Cd in surface waters with sinking particulate organic matter which is enriched in Cd (upper box in Fig. 11). The second process would be in deep waters, namely the fractionated deep remineralization of Cd compared to phosphate. Saager and de Baar (1993) found that both processes would yield realistic model scenario simulations of global Cd/phosphate distributions. However, their scenario for fractionation during deep remineralization was somewhat less realistic but admittedly the model was also very simple.

In this study in the Polar Frontal region, a clear case of preferential Cd net uptake was observed. This may, or may not, be a world-wide trend. In combination with the somewhat less realistic deep remineralization scenario by Saager and de Baar (1993), this would suggest that biological fractiona-

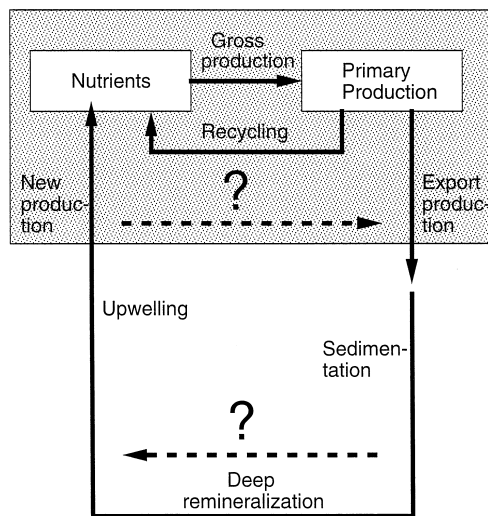


Fig. 11. Scheme of nutrient circulation in the ocean. Two processes, preferential Cd net uptake in the euphotic zone and/or deep fractionated Cd and phosphate remineralization were described to be responsible for the negative intercept of Cd/phosphate relationships when extrapolating them to the hypothetical case of Cd depletion, and the kink in the global Cd/phosphate relationship (Boyle, 1981, 1988). Saager and de Baar (1993) tested the importance of these two processes (here expressed as question marks) by modelling; and found that both of them yield realistic model simulations. Here, it was found that preferential Cd net uptake in the surface ocean box was taking place at the Polar Frontal region. Moreover the Cd/phosphate fractionation of gross production and recycling within the surface box is assessed.

tion in surface waters is driving the global Cd/phosphate distribution in the ocean basins. However, deep remineralization may also play a role.

5.3. Primary vs. net fractionation within surface waters

The observed preferential net-uptake of Cd actually results from either fractionated gross uptake and/or fractionated recycling of Cd and phosphate within the surface waters (Fig. 11). Here, the expression ‘recycling’ is used exclusively for dissolution due to grazing activity within surface waters, as opposed to the above mentioned deep remineralization. Because little information was available on Cd/phosphate uptake by phytoplankton, excretion by grazers, particulate distributions and recycling, Saager and de Baar (1993) were not able to unravel the two processes within the euphotic zone of either preferential gross uptake of Cd, or fractionated recycling.

Here, an attempt was made to unravel the Cd/phosphate gross uptake and recycling within the surface water box (Fig. 11). It was assumed that the Cd- and phosphate decrease between transects 5 and 11 in the Polar Frontal region (Fig. 8) is attributed to uptake and recycling as well as some subsequent sedimentation of diatoms, which dominated the phytoplankton. Cd and phosphate taken up by all other plankton (phyto- and zooplankton) than diatoms as well as bacteria can be assumed to become recycled, because in the southern ACC, where hardly any diatoms and few other phytoplankton and grazers occurred, no decreases in Cd and phosphate concentrations between both transects were observed. The increasing uptake of phytoplankton by grazers as copepods can be regarded to have almost no influence on the Cd:phosphate ratio because both, Cd and phosphate, are assimilated with an efficiency which is directly related to the cytoplasmic content of the diatoms (Reinfelder and Fisher, 1991; Wang et al., 1996). Only the more particle-reactive elements which are bound to structural components of cells, are packed into the rapid sinking fecal pellets (Lee and Fisher, 1994). The small amount of Cd which could be packed into fecal pellets will be recycled for more than 90% after 1 day (Wang et al., 1996).

For the calculation of the Cd and phosphate gross uptakes, the average integrated primary production rates of transect 5 and 11 in the Polar Frontal region (Jochem et al., 1995) were multiplied with estimated Cd:C and P:C ratios (Table 13). The recycling of both was calculated as the difference between estimated gross uptake and above calculation (Section 5.2) of observed net decrease.

For the calculation of the gross phosphate uptake, the molar Redfield C:P ratio of 105 (Redfield, 1934; Hecky et al., 1993) as reported for two oceanic diatoms by Goldman et al. (1992) was used. The C:P ratios described in literature for the Southern Ocean

Table 13

Calculation to evaluate the importance of gross uptake and recycling within upper waters for the Cd/phosphate ratio in the Polar Frontal region in Section 5.3. For the calculation of the net Cd and phosphate decrease, the average concentration differences between transect 5 and 11 were integrated over the upper 50 m where most of the primary production occurred (Jochem et al., 1995)

Primary production (PP)^a:

$$\begin{aligned} \text{PP (transect 5)} &= 588 \text{ mgC m}^{-2} \text{ d}^{-1} \\ \text{PP (transect 11)} &= 1825 \text{ mgC m}^{-2} \text{ d}^{-1} \\ \text{average} &= \phi\text{PP} = 1206 \text{ mgC m}^{-2} \text{ d}^{-1} \\ &= 100 \text{ mmolC m}^{-2} \text{ d}^{-1} \end{aligned}$$

Gross-phosphate-uptake rate by particulate primary production

$$\text{PPP} = \phi\text{PP}/(\text{C:P}) \quad (1)$$

$$\text{C:P} = 105^{\text{b,c,d,e}}$$

$$\text{PPP} = 952 \text{ } \mu\text{mol m}^{-2} \text{ d}^{-1}$$

Observed net-phosphate-decrease:

$$v_{\text{net}}\text{P} = 562 \text{ } \mu\text{mol m}^{-2} \text{ d}^{-1}$$

Gross-Cd-uptake rate by particulate primary production

$$\text{PPCd} = \phi\text{PP} \cdot (\text{Cd:C}) \quad (2)$$

$$\text{Cd:C} = 9 \cdot 10^{-6}$$

$$\text{PPCd} = 900 \text{ nmol m}^{-2} \text{ d}^{-1}$$

Observed net-Cd-decrease:

$$v_{\text{net}}\text{Cd} = 250 \text{ nmol m}^{-2} \text{ d}^{-1}$$

Phosphate-recycling rate ($v_{\text{rec}}\text{P}$):

$$v_{\text{rec}}\text{P} = \text{PPP} - v_{\text{net}}\text{P} \quad (3)$$

$$v_{\text{rec}}\text{P} = 390 \text{ } \mu\text{mol m}^{-2} \text{ d}^{-1}$$

Cd-recycling rate ($v_{\text{rec}}\text{Cd}$):

$$v_{\text{rec}}\text{Cd} = \text{PPCd} - v_{\text{net}}\text{Cd} \quad (4)$$

$$v_{\text{rec}}\text{Cd} = 650 \text{ nmol m}^{-2} \text{ d}^{-1}$$

^aJochem et al., 1995.

^bGoldman et al., 1992.

^cRedfield, 1934.

^dHecky et al., 1993.

^eCopin-Montegut and Copin-Montegut, 1978.

vary between 74 and 105 for the Polar Frontal region of the South Indian Ocean (Copin-Montegut and Copin-Montegut, 1978) and between 47 and 151 for the area of the Weddell–Scotia Seas (Tréguer et al., 1991). The phytoplankton composition of the latter, with exception of one station for which no C:P ratio was recorded, was not dominated by diatoms, and was, for this reason, not included in the calculation. In the Polar Frontal region of the South Indian Ocean (Copin-Montegut and Copin-Montegut, 1978), phytoplankton was dominated by diatoms. The biogenic silicate concentration of the latter was up to 5 μM , which is close to the reported biogenic silicate concentration found in the Polar Frontal region during this study by Quéguiner et al. (1997). The adopted C:P ratio of 105 is consistent with the C:P ratio found in the Polar Frontal region of the South Indian Ocean (C:P = 108) for the station with the largest molar Si:C ratio of 0.35 (Copin-Montegut and Copin-Montegut, 1978) which is closest to the Si:C ratios for the Polar Frontal area during this cruise (0.50–0.96; Quéguiner et al., 1997). Martin et al. (1991) showed in Fe enrichment experiments that more carbon per unit of major nutrients is fixated when Fe is abundant. Diatoms displayed the most benefit from Fe, which ranged between 1.3 and 1.6 nM (Martin et al., 1991), and were comparable with values found in the Polar Frontal region during the described transects (~ 1.5 nM Fe, De Baar et al., 1995; Löscher et al., 1997a). The C:P ratios at these Fe concentrations ranged between 124 and 134, and

are comparable with the estimated Redfield ratio of 105.

For the calculation of the Cd gross uptake (Table 13) the Cd:C ratio (9×10^{-6}) as found for one sample in the Polar Frontal region at transect 5 was used. For this sample the particulate Cd value was consistent with the difference between unfiltered and filtered water. Here, the biogenic particulate Cd concentration (phase 1 and 2 of the selective chemical leaching treatment) was divided by the particulate organic carbon (POC) concentration as reported by Bathmann et al. (1997). The obtained Cd:C ratio is comparable with the ratios reported by Martin et al. (1976) and by Collier and Edmond (1983) but about one order of magnitude higher than the Cd:C ratio described for a diatom sample collected during a diatom bloom (Martin and Knauer, 1973). However, particulate Cd collected on this cruise was sampled with GoFlo's followed by filtering through filters with a pore size of 0.2 μm , whereas the particulate matter described by Martin and Knauer (1973), Martin et al. (1976) and Collier and Edmond (1983) were sampled with nets of mesh sizes larger than 44 μm . With the latter sampling method, only the larger phytoplankton and grazers were collected, whereas the sampling method used during this cruise for the collection of particulate Cd includes smaller phytoplankton as well as protozoa and bacteria. Grazers, phytoplankton and bacteria may have different Cd:C ratios and by this affect the Cd:C ratio of the particulate matter. However, POC due to phytoplankton in

Table 14

Contribution of bacteria, phytoplankton and zooplankton to the total POC in the Polar Frontal region at transect 5 at 40 m depth. For the calculation of the phytoplankton biomass, the observed Chl a (0.8–1.8 $\mu\text{g chl l}^{-1}$; Bathmann et al., 1997) was combined with the C:Chl ratio of 62 ($\mu\text{g}/\mu\text{g}$) reported for the same dominant diatom genera as in the Polar Frontal region (*Chaetoceros*, *Nitzschia fragilariopsis*, *Corethron*, Mikaelyan and Belyaeva, 1995). The irradiance (Smith and Sakshaug, 1990; their Fig. 9.3) as well as the chlorophyll a concentration, factors which influence the C:Chl ratio in algae (Cloern et al., 1995; Mikaelyan and Belyaeva, 1995), can be expected to be the same in the sampling period by Mikaelyan and Belyaeva (1995) and during this study

Category of biomass	Carbon Transect 5 ($\mu\text{g l}^{-1}$)	Reference
Bacteria	6–12	(Lochte et al., 1997)
Nanoprotozoa	0.7–1.2	(Becquevort, 1997; upper 100 m)
Microprotozoa	2–8	(Klaas, 1997; upper 100 m)
Zooplankton	10	(Fransz and Gonzalez, 1997)
Phytoplankton	50–112	(Bathmann et al., 1997), (Mikaelyan and Belyaeva, 1995)
Total POC	134 ± 24	(Bathmann et al., 1997)

the Polar Frontal region at transect 5 was estimated to be up to 85% of the total POC (Table 14) and can be expected to have controlled the Cd:C ratio.

The used Cd:C ratio is in the same range of $0.05\text{--}10 \times 10^{-6}$ as calculated from Tortell and Price (1996) for the cellular Cd:C ratio dependency from the free Cd^{2+} concentration of four *Thalassiosira* cultures, when assuming that the free Cd^{2+} concentrations in the surface water of the Polar Frontal region are in the range of 0.1 and 0.3 nM when about 70% of the dissolved Cd is strong organically complexed (Bruland, 1989). Moreover, it is in the same order of magnitude as found for the diatom *Phaeodactylum tricornutum* by Kudo et al. (1996). They described cellular Cd:P ratios between 0.10×10^{-3} and 0.23×10^{-3} , which correspond with a Cd:C range of $1\text{--}2 \times 10^{-6}$.

Using the above described molar C:P (105) and Cd:C (9×10^{-6}) ratios, the Cd/phosphate gross uptake ratio would be 0.9 nM/ μM , consistent with Cd/phosphate ratios as described by Noriki et al. (1985) during a phytoplankton bloom in time it was dominated by diatoms (0.17–1.57 nM/ μM) and in the same order of magnitude as reported by Kudo et al. (1996) for the diatom *P. tricornutum* (about 0.2 nM/ μM). The Cd/phosphate ratio found by Abe and Matsunaga (1988) during a diatom bloom in the Funka Bay (0.07 nM/ μM) is on the low side of this range. Comparing the calculated Cd/phosphate uptake ratio (0.9 nM/ μM) with the average Cd/phosphate ratio in the ambient seawater of the upper 50 m of the Polar Frontal region at transect 5 (0.20 nM/ μM), the conclusion must be that the gross Cd uptake rate is faster than the gross phosphate uptake rate.

The recycling rates for phosphate and Cd within the upper 50 m at the Polar Frontal region were about $390 \mu\text{mol m}^{-2} \text{d}^{-1}$ and $650 \text{nmol m}^{-2} \text{d}^{-1}$, respectively. About 70% of the Cd and about 40% of the phosphate which were taken up during particulate primary production were recycled. Thus, Cd is, overall, also recycled more efficiently.

Overall it appears, that preferential Cd gross uptake overrides the more efficient recycling of Cd compared to phosphate in the upper 50 m of the Polar Frontal region, and is the process which is responsible for the overall net decrease of the Cd/phosphate ratio of ambient seawater. Major un-

certainties in the calculations of the Cd and phosphate gross uptake are the estimations of the Cd:C and P:C ratios.

5.4. Cd in the deeper water masses

Table 11 shows an overview of the Cd concentrations and Cd/phosphate ratios in the different water masses sampled. AAIW sampled at $45^{\circ}30'S$; $01^{\circ}08'E$ had a Cd concentration of 0.21 nM with a molar Cd/phosphate ratio of 0.10 nM/ μM . The relatively low concentration and ratio were lower than those reported by Frew and Hunter (1992, 1995) for the AAIW core south of New Zealand at $48^{\circ}05'S$; $164^{\circ}30'S$ (0.45–0.48 nM Cd and 0.22–0.23 nM/ μM). After Frew and Hunter (1992, 1995), low Cd/phosphate ratios in the AAIW could be the cause of two different Cd/phosphate relationships in the world ocean, one for the North Atlantic Ocean data and one for the Antarctic–Indo–Pacific Ocean data. However, according to Löscher et al. (1997b), there is lack of evidence whether the global Cd/phosphate data may be described by two different Cd/phosphate relationships or suggest a single linear relationship instead.

Neither the Cd distributions here reported nor the previously known nutrient distributions of the Southern Ocean (Ruud, 1930; De Baar et al., 1997) fit into the classical concept of nutrient profiles which increase with depth in the euphotic zone and remain nearly constant in the deeper water column. For example, the observed maxima of Cd in the UCDW (Fig. 7) coincide with maxima of phosphate. However, the deeper minima (400–800 m) of Cd at the three northernmost stations (Fig. 7a–c) were not expected. Here, one needs to ensure that such extrema are real features and not an artifact of sampling and sample treatment, because the sampling method in the upper waters (GoFlo's mounted on a Kevlar hydrowire) is different from that in deep waters (GoFlo's mounted on a Teflon coated CTD Rosette).

The sampling devices had been used successfully for Cd several times before (Nolting et al., 1991; Nolting and De Jong, 1994; Saager et al., 1997), and there has never been any evidence pointing to contamination during sampling. If anything, than the

shallow water Kevlar wire hydrocasts would likely be less prone to contamination than the deep CTD Rosette casts, in contrast with the observations of maxima in the upper 400 m and minima at 400–800 m depth (Fig. 7a–c). Upon sampling and filtration, all samples were stored in bottles for analyses in the home laboratory. During analyses, no distinction was made between groups of samples. The recovery of the Cd extraction was verified daily by addition of four spikes, and the Cd concentrations were corrected for these recoveries. Recoveries which were lower than 90% were rejected. The accuracy of the method was verified with a certified reference at the end of all extractions. Because always the same standard was used for the checking of the recoveries, the accuracy of all the reported Cd concentrations should be high.

The above described precautions as well as the existence of the Cd concentration maximum and minimum at station 951 (Fig. 7b), where only the Teflon coated CTD rosette was used, lead to the conclusion that different sampling methods cannot be the reason for the detected UCDW maxima and minima. Firstly, the continuity of maxima among all six stations throughout the whole section (Fig. 7a–f) and minima among three northern stations (Fig. 7a–c) cannot be an artifact. Secondly, at four given single stations the maxima (Fig. 7a,c,e,f) and two stations the minima (Fig. 7b,c) comprise more than one sampling point.

A selection-criterion for high quality Cd- and phosphate data as described in De Baar et al. (1994) using data below 1000 m which have a Cd/PO₄ ratio with a coefficient of variation of less than 10%, can ensure that such selected data are of acceptable precision, without suggesting that non-selected data necessarily are of lesser quality (De Baar et al., 1994; Löscher et al., 1997b). In this paper, five of the six presented Cd-profiles fulfilled that 10% criterion and were used for a description of the global Cd/PO₄ relationship (Löscher et al., 1997b). However, deviations in the Cd/PO₄ ratio may occur, because hydrography as well as sedimentary sources (Westerlund and Öhman, 1991) appear to be important for the trace metal distributions (Löscher et al., 1997b). Summarizing, we are confident about the analytical quality of the data, and any strong gradient is, therefore, treated as a real feature.

In the UCDW, the Cd concentration ranges from 0.38 to 1.25 nM with a Cd subsurface maximum (0.46–1.25 nM) occurring within the major nutrient subsurface maximum (here phosphate, 2.4–2.5 μM, Fig. 7) which indicates the UCDW (Whitworth and Nowlin, 1987). The Cd maximum obvious in the Cd contour plot along the 6°W meridian (Fig. 6) coincides with the upper wedge of the UCDW. Like UCDW, the Cd maximum rises to the surface at the position of the southern ACC front at about 56°S where it becomes indistinguishable from the surface water. In this sense, Cd could serve as an indicator for the upper wedge of UCDW. The higher Cd concentrations in surface water than deep waters south of the Polar Frontal region (Fig. 7c,d,e) can be assumed to derive from UCDW which flows northward (North of the southern ACC front) and southward (South of the southern ACC front) as AASW. Low primary productivity ensures that almost no Cd is removed from the previous UCDW.

The persistently detected minima at the three northern stations (Fig. 7a–c) are not correlated with the concentrations in major nutrients. The minimum at station 947 (Fig. 7c) is most pronounced not only in the upper part of the LCDW but also discernible at one point in the overlying UCDW. Thus, the Cd minima are not strictly found only in the UCDW. Nevertheless, there is some consistency as the minima of all three stations are at the same 27.7–27.8 isopycnal (Table 9). Therefore, the minima are real features but we are not aware of the underlying mechanism.

At station 956 in the Polar Frontal region at 50°S (Fig. 7a), the influence of NADW is still discernible through the salinity maximum ($S = 34.74 - 34.75$) and gentle minimum of phosphate and nitrate (Table 9). Unfortunately, in this NADW only two Cd samples were collected with concentrations of 0.29 and 0.54 nM and Cd/phosphate ratios of 0.14 and 0.25 nM/μM, respectively. The 0.29 nM value is comparable to concentrations reported for NADW in the North Atlantic Ocean (Bruland and Franks, 1983; Sakamoto-Arnold et al., 1987; Saager et al., 1997). However, compared to the dissolved Cd concentrations of 0.36–0.49 nM reported by Yeats et al. (1995) for younger (PO₄ = 1.6 μM), more saline ($S = 34.95$), NADW in the Cape Basin (30°S; 8°E), it appears to be quite low. With the small number of

two observations in the NADW, it is not clear whether its Cd concentration truly differs from the adjacent UCDW and LCDW (Fig. 7a).

At the more northerly final station 979 (45°39'S; 01°08'E), near the margin of the Cape Basin, phosphate and nitrate (Fig. 7f) have a minimum in the upper part of the recent NADW ($S = 34.78$; Tables 9 and 10). The Cd concentrations have some scatter, possibly due to the unfiltered samples used for analyses, and it remains uncertain whether they reflect this nutrient minimum. The average Cd ($0.62 \text{ nM} \pm 0.05 \text{ nM}$; $n = 8$) and phosphate ($2.1 \mu\text{M}$) in this NADW ($S > 34.74$) are relatively higher than the average of Cd 0.40 nM and phosphate $1.6 \mu\text{M}$ further North in the Cape Basin (Yeats et al., 1995), and therefore, more consistent with the expectation based on the global trend of Cd vs. phosphate than the anomalously low Cd in NADW at above station 956.

Data from deeper water masses in the Southern Ocean do not coincide with the linear Cd/phosphate relationships of upper water (Fig. 12) because the circulation of water masses with different preformed Cd/phosphate ratios is the most important factor affecting the Cd/phosphate ratio. Such 'non-linear' Cd/phosphate functions in different water masses at one and the same station were also reported by Saager et al. (1992) for the Arabian Sea and Yeats et al. (1995) for the South Atlantic Ocean.

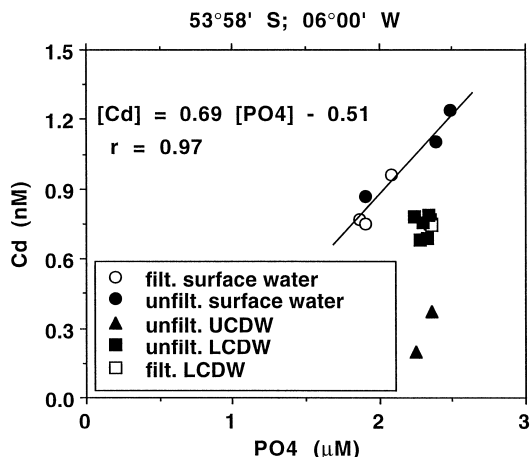


Fig. 12. Example of Cd vs. phosphate concentrations in the surface and deeper water (53°58'S; 06°00'W) showing a linear relationship in the surface but not in the deeper water.

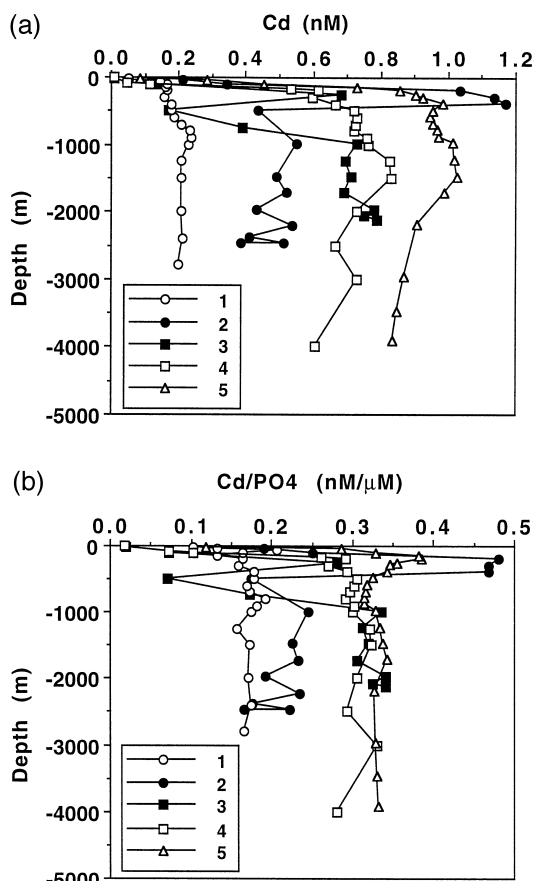


Fig. 13. Global vertical profiles from the literature with profiles from this study, from North Atlantic to Indo-Pacific Ocean waters: (a) for dissolved Cd, and (b) for the Cd/phosphate ratio. References are (1) N.E. Atlantic Ocean, 59°N; 20°W (Martin et al., 1993); (2) 50°S; 06°W (this study); (3) 52°S; 06°W (this study); (4) Indian Ocean, 14°N; 67°E (Saager et al., 1992); and (5) Pacific Ocean, 50°N; 145°W (Martin et al., 1989).

Cd concentrations in the northern Atlantic Ocean (after De Baar et al., 1994; Saager et al., 1997) ranged from about 0.20 to 0.39 nM with Cd/phosphate ratios from about 0.19 to 0.30 nM/ μM . For the Indo-Pacific Ocean, these values were 0.60 to 1.10 nM and 0.21 to 0.40 nM/ μM , respectively. The reported deep water Cd concentrations (Fig. 13a) as well as the Cd/phosphate ratios (Fig. 13b) at the 6°W meridian (48°–57°S) contribute to bridge the gap between North Atlantic Ocean data and the Indo-Pacific Ocean data. This trend was to be expected from a generally increasing deep Cd concen-

tration and Cd/phosphate ratio with age of the deep water (Morley et al., 1993; De Baar et al., 1994).

6. Conclusions

Differences in dissolved upper water Cd concentrations were related to biology and hydrography. It is shown that the high upper water concentrations are a result of: (1) deep water (UCDW), rising to the surface, carrying elevated Cd concentrations (up to 1.25 nM) in combination with (2) relatively low primary production. The low biological activity ensures that Cd does not become depleted in the surface water.

By a comparison of Cd and phosphate data at the beginning and during a phytoplankton bloom, which was dominated by diatoms, preferential Cd net uptake was observed. This net effect resulted from preferential Cd gross-uptake which appeared to override the process of Cd recycling which was about 50 to 95% of the Cd taken up during primary production. It can be assumed that about 35% of the gross phosphate uptake was recycled. If the observed preferential net uptake is a world-wide trend, biological fractionation in the surface waters would largely determine the global deep Cd/phosphate distributions.

Cd/phosphate ratios were not constant through the deeper water column because the circulation of water masses was the most important factor which determined the Cd/phosphate distribution in the Southern Ocean. Deep Cd concentrations indicated UCDW by a maximum concentration within that water mass. Both the concentration of Cd and the Cd/phosphate ratio increased in southern direction at the 6°W meridian and showed a gradual transition between Atlantic Ocean and Pacific/Indian Ocean distributions.

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