Vertical distribution of cadmium in marginal seas of the western Pacific Ocean

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Abstract

The vertical distribution of cadmium at four locations in three marginal seas of the western Pacific Ocean are described. Data show that the surface layers at all stations were depleted (< 0.02 nM Cd) and the concentration of Cd increased with depth up to 1.05 nM at 1000–1200 m. Although the shapes of the profiles for the three seas differ significantly, Cd concentrations show strong correlation with those of nitrate and phosphate. Average molar ratios of $(3.64 \pm 0.02) \times 10^{-4}$ and $(2.50 \pm 0.01) \times 10^{-5}$ ($n = 107$) were found for $d[Cd]/d[PO_4]$ and $d[Cd]/d[NO_3]$, respectively. Unlike previous work reported for the eastern Pacific Ocean, intercepts were almost zero (below the detection limits) on the correlation plots for [Cd], [NO_3], and [PO_4] at the studied locations, and correlation coefficients (Cd vs. NO_3 and PO_4) for all stations were 0.99 or greater. These data are consistent with the nutrient-like behavior of Cd as has been previously observed and significantly expand the Pacific data base for this trace element.

1. Introduction

It is generally known that the concentration of cadmium in the open ocean is closely related to biological activities, and that its distribution is similar to that of nitrate and phosphate. For these reasons Cd has been customarily classified as a nutrient-type element (Bruland, 1983). If the uptake and regeneration cycle of Cd in the ocean is so closely related to that of nutrients, as has been shown by many workers, then there may exist a unique ratio of $d[Cd]/d[PO_4]$ (like dN/dP ratio) for global oceans, at least for the Pacific area.

Unfortunately, limited data have precluded such a determination.

The current Cd data reported for the Pacific Basin cover the northeast Pacific (Bruland et al., 1978; Bruland, 1980; Jones and Murray, 1984), the Bering Sea and the northern Pacific Ocean (Boyle et al., 1976), the western Pacific near Guam (Kanamori, 1985), as well as the Tasman Sea of the Southern Hemisphere (Hunter and Ho, 1991). All authors have agreed that the relationship between Cd and nutrients are linear (except for those at extreme latitudes and up-welling areas), but the molar ratios reported ($d[Cd]/d[NO_3]$ or $d[Cd]/d[PO_4]$) for the open ocean stations vary significantly, and the overlapped profiles plotted from those data show a high degree of scatter.

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Table 1
Detailed information of the sampling sites

Cruise	Station No.	Sampling date (m/d/y)	Location		Bottom depth (m)	Bottle type
			Latitude (N)	Longitude (E)		
ORI-257	17	10/13/1990	21°45.1'	124°00.1'	5500	Niskin
	23	10/15/1990	21°45.0'	127°00.0'	5740	Niskin
ORI-280	4531	05/04/1991	24°50.0'	123°10.0'	1700	GoFlo
ORI-287	17	06/28/1991	21°45.0'	124°00.1'	5500	GoFlo
	157	07/08/1991	16°35.0'	119°00.0'	3500	GoFlo

There are four possible explanations for such variation:

(1) poor precision and accuracy of detecting Cd at such low concentrations (generally less < 1.1 nM), due to the limitation of the method used;

(2) different sampling, storage, pre-treatment, and analytical methods, which lead to imprecise definition of the Cd species measured;

(3) poor nutrient data accompanying the Cd measurements;

(4) natural variation between water masses.

Unless an analyst can ascertain the quality of the data (including nutrient data), there are risks of misinterpretation regarding bias as fact. To examine this potential problem, the acquisition of more reliable data in other unexplored areas was deemed necessary.

The present paper describes our effort of collecting cadmium data, using an extremely careful analytical scheme, in the three marginal seas around Taiwan: the western Philippine Sea, the South China Sea, and the East China Sea. The results for Cd and the related molar ratios with nutrients are presented as a contribution to the Pacific data base.

2. Sampling and methods

2.1 Cruises and locations

Samples were collected during three cruises aboard R/V *Ocean Researcher I* (ORI-257, 280, and 287) during 1990–1991. The location of stations, as well as other hydrographic infor-

mation, are listed in Table 1 (also see Fig 1). Station 17 was visited twice in two separate cruises (ORI-257 and 287). Those cruises were conducted in cooperation with the WOCE (World Ocean Circulation Experiment, 1990–1996) or KEEP (Kuroshio Edge Exchange Processes, 1990–1994) programs. Hydrographic, oxygen, and nutrient data were obtained on-board by the protocols matching WOCE requirements (WOCE, 1988).

2.2 Sampling

Niskin bottles (Type #1010, General Oceanic Inc., Miami, FL, USA) were used only on the first cruise (ORI-257); whereas Teflon-treated GoFlo bottles (Type #1080, also from General Oceanic Inc.) were used for the other two cruises. The GoFlo bottles, coated with a thin layer of Teflon spray as suggested by Bruland et al. (1979), were cleaned first with a neutral detergent, then soaked in mild acid (0.1 N HCl) for several days. The bottles were flushed thoroughly with distilled water, double distilled water, and wrapped with a layer of polyethylene film. After installation on a rosette sampler (supporting a SBE-9/11 CTD unit, SeaBird Electronics Inc., Bellevue, WA, USA), they were flushed during casts before samples were taken.

2.3 Analytical procedure

An on-board Chelex-100 pre-concentration technique was applied throughout this study. The details of the procedure have been described in an earlier paper (Pai et al., 1990). Two modifications of this method were made: (1) the disposable Bio-
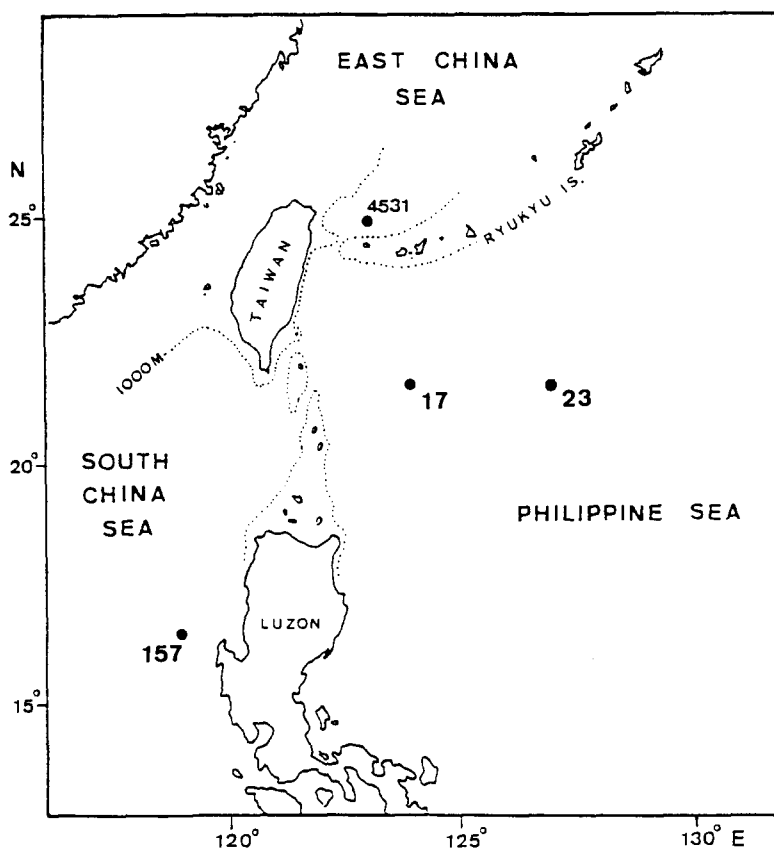
Fig. 1. Location of the sampling stations. Dashed line represents the 1000 m isobar.

Rad chromatographic columns (ca. 8 mm ID, Cat. No. #731-1550) were used instead of the previous self-made Tygon columns; (2) each column set consisted of two columns that were connected in series (see Fig. 2). The sample was allowed to pass through both columns, but elution was carried out separately. The eluate from the upper column represented the sample, whereas the eluate from the lower column was used to examine the blank. The lower column eluate was also used as the blank matrix for constructing calibration curves using standard addition technique.

All samples were unfiltered. Upon retrieving the sampler, seawater was passed directly into 1.28 l PET (polyethyleneteraphthalate) bottles each containing a 30 ml aliquot of ammonium maleate buffer at pH 6.5. The sample bottle was connected to a previously packed pair of columns (each contain-ing 2.0 g 100–200 mesh Chelex-100 resins in ammonium form), and hung upside-down to allow the sample to flow through at a rate of no more than 4 ml min^{-1}. The column pair was brought back to the laboratory for elution with 2 N nitric acid. Measurement of Cd recovered in the final eluate (10 ml) was carried out with a Hitachi Z-8100 Zeeman effect graphite furnace atomic absorption spectrometer (GFAAS). Calibration curves were made by spiking standards into the "blank" eluates (from the second column) containing the same matrix as that of the "sample" eluates (from the first column). Reagent blank was obtained in a separate experiment by passing a double-distilled water, to which ammonium maleate buffer was added, through a column and collecting the eluate in the same way as for the samples.
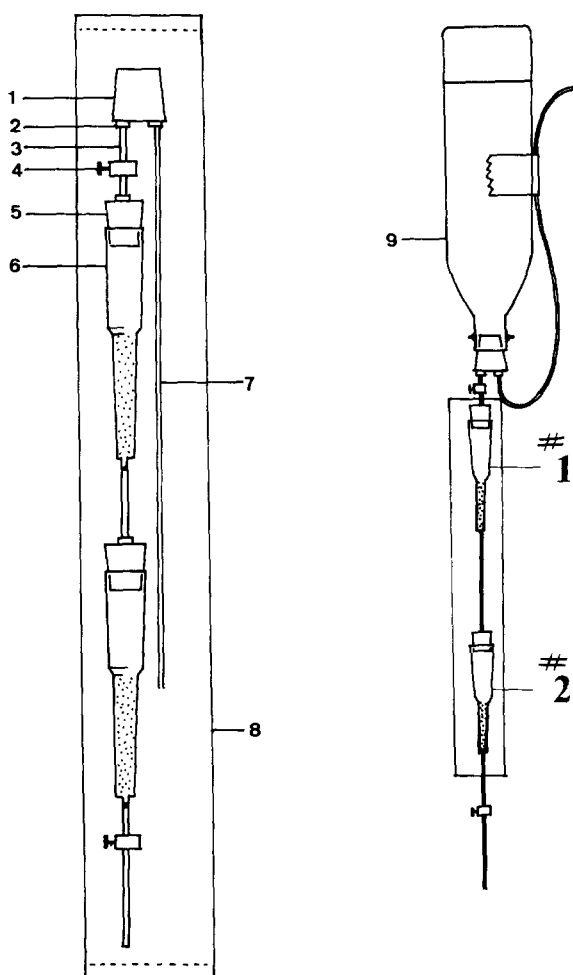
Fig. 2. (a) The pre-packed double-column set consists of two columns each packed with 2 g Chelex-100 resin (100–200 mesh, ammonium form). (b) Hang-bottle technique in operation. Eluate from the first column was analyzed as sample, whereas the eluate from the second column was used for checking the blanks and also for constructing calibration curve. *1* = 5(1/2) silicon rubber stopper; *2* = nipple; *3* = silicon rubber tubing 0.4 mm ID; *4* = tubing clamp; *5* = 4 silicon rubber stopper; *6* = BioRad PP column; *7* = ventilation tube; *8* = PE bag; *9* = 1280 ml PET bottle.

3. Results and discussion

3.1 Calibration, blank, and recovery

The laboratory test of the precision and accuracy for Cd determination using the Chelex-100 pre-concentration-GFAAS method has been performed prior to field sampling. This involved the following: a filtered surface seawater sample was purified by ion-exchange through a large Chelex-100 column (containing 10 g resin) at a low flow rate (1 ml min^{-1}). Recovery test was as follows: aliquots of 1 l of the purified seawater were spiked with 0, 0.445, 0.890, 1.335 nmol Cd, respectively, after adding 25 ml of ammonium maleate buffer each mixture was allowed to pass through the column pair. Known amounts of Cd were spiked to the blank matrix for the construction of the calibration curve (Table 2). The results of GFAAS measurements for the eluates (10 ml aliquots) from both columns are shown in Table 3. It was found that all spikes were recovered quantitatively (98–105%) from the first column. The small but consistent GFAAS signal produced by the second column eluate was equivalent to an original Cd concentration of ca. 0.02 nM, almost the same as that produced by the reagent blank. The average blank value found for over 200 sets of field samples was 0.02 ± 0.004 nmol (in 1250 ml seawater), indicating a detection limit of ca. 0.02 nM Cd (taking 4.65 fold of the deviation of the blank). It should be noted that the blank prepared in this way did not include the bottle and buffer blanks. However, an extended experiment showed that all blanks were no more than the detection limit, so the difference was not significant. An analysis of the precision of the proposed method was also carried out on-board ship on a deep seawater sample spiked with 1 nM Cd. An overall analytical error (including sampling error) of ca. 4% at 1 nM level was achieved, and the recovery of the spike was 99.5 ± 2% (*n* = 4).

3.2 Quality check

To minimize the inclusion of spurious data caused by leakage of the GoFlo bottles, a careful QA/QC scheme was used. Each data set (including CTD data) was first cross-checked by the correlation plots of various physical and chemical parameters, including temperature, salinities (both by CTD and manual methods), concentrations of nitrate and phosphate, as well as the record of bottle numbers. The *T*–*S*, N–P, and *T*–nutrient plots gave primary check of quality of nutrient measurements (see Fig. 4). Any off-set

Table 2
Typical calibration performed by spiking known amounts of Cd
to 10 ml of blank eluate

Spiked amount (nmol)	Final vol (mL)	Raw absorbance ×1000			Mean	RSD (%)
		i	ii	iii		
0	10.0	2	3	3	3	17.7
0.445	10.1	63	65	64	64	1.3
0.890	10.2	128	126	124	126	1.3
1.335	10.3	185	189	188	187	0.9

Spiking was made by added 0, 0.1, 0.2, 0.3 ml of 0.5 ppm Cd
standard solution to 10 ml of the eluate from a Chelex-100
column (1 l purified seawater passed through).

point on the T–nutrient diagram, if not due to the
analytical error, could indicate a possible leakage
due to the faulty closure of the bottle. If the leakage
was obvious, further analysis of Cd was
abandoned. The discard rate for the three cruises
was 8% and was attributed to leaking Go-Flo
bottles.

3.3 Hydrographic and nutrient data

The profiles of temperature, salinity, oxygen,
and nutrients for the three marginal seas are
shown in Fig. 3. The cross-plots of T–S and T–
nutrients at all stations are shown in Fig. 4. It can
be seen that the three seas show strong difference in
hydrography, although they are connected with
each other through channels. The western Philip-
pine Sea covers the largest area. Profiles of tem-
perature, salinity, oxygen, and nutrients at the
three stations from this region are all similar to
each other, and also to those of the nearby stations
on other WOCE cruises and the INDOPAC cruise
Leg 3. Salinity maxima (> 34.9) and minima
(< 34.2) are found within the 100–200 and 600–
700 m layers, respectively. The concentrations of
dissolved oxygen in the upper layer (from surface
to 200 m) are saturated or slightly over-saturated;
whereas nutrients are not detectable above the
thermocline. Obvious concentration maxima have
been found at 1000–1100 m for both nitrate and
phosphate. Below the maxima, the nutrient con-
centrations decrease slightly with depth. Signifi-

Table 3
Recovery test on a purified seawater spiked with known
amounts of cadmium using the double-column technique

Spiked amount (nmol)	Raw absorbance × 1000 for 10 ml eluate from		Recovery (%)
	1st column	2nd column	
Distilled water (1 l)			
0	2	2	–
0	4	2	–
0	2	3	–
Purified seawater (1 l)			
0	3	3	–
0	3	2	–
0	4	3	–
0.445	65	2	102
0.445	66	4	100
0.445	68	3	105
0.890	126	2	99
0.890	128	3	100
0.890	131	2	103
1.335	198	2	103
1.335	190	2	99
1.335	197	3	102

Ammonium maleate buffer (25 ml) was added to each sample.
Each of the data represents the mean value of triplicate
measurements on GFAAS. Recovery was calculated for the
1st column only, using the calibration curve made in Table 2.

cant seasonal variation on any parameter through
the water column has not been found, indicating
that the water mass is fairly stable in those para-
meters over time.

The East China Sea Basin is divided from the
Philippine Basin by the Ryukyu Arc, and the
channels between the island chain are quite
shallow (up to few hundred meters) except for a
deep narrow underwater gap (few km wide,
1000 m deep) between the Yunagoni (Japan) and
Taiwan islands, where the Kuroshio's axis passes
through. The strong current carries the surface and
sub-surface Philippine Sea water into the East
China Sea. The surface water is mixed with shelf
water, but the sub-surface layer (100–700 m)
retains the same properties as those of the Philip-
pine Sea. No nutrient maxima in the deeper layers
(> 800 m) have been observed.

The South China Sea below 1000 m is also like
an isolated basin, with only two narrow channels
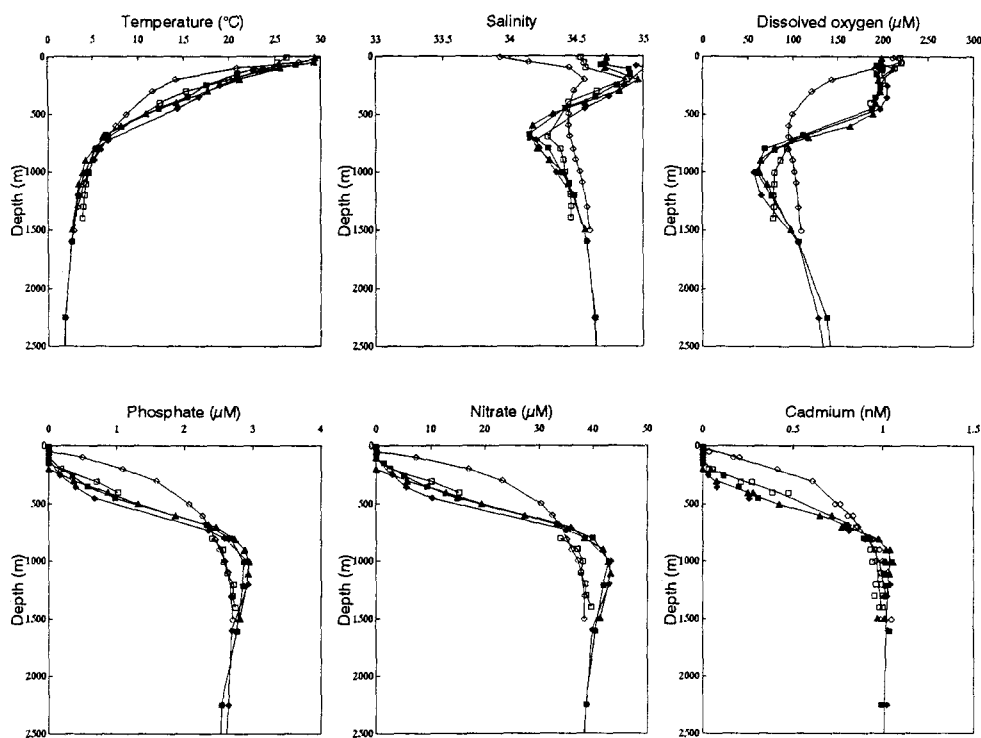allowing the exchange with the Philippine Sea.

Fig. 3. Hydrographic, nutrient, and cadmium profiles for the five stations. *Western Philippine Sea*: ■ = ORI-257 Station 17; ◆ = ORI-257 Station 23; ▲ = ORI-287 Station 17. *East China Sea*: □ = ORI-280 Station 4531. *South China Sea*: ◇ = ORI-287 Station 157.

Both channels are in the N–S direction at the northeast part of the Luzon Channel. Although there is some indication that the Philippine Sea water intrudes frequently into the South China Sea, this circulation is limited only to surface layers (up to 300 m) of the northern area (Shaw, 1989). It is likely that the water column off west Luzon did not receive direct influence from the Kuroshio at the time of this study. The surface mixing layer was comparatively shallow (ca. 75 m), below which the concentration of oxygen decreased rapidly with a sharp increase in nutrient concentrations. Compared to the Philippine Sea, the middle layer (300–1000 m) of the South China Sea was high in nutrients and low in oxygen and temperature. No above-bottom nutrient maxima have been be found at Station 157, nor at other nearby locations (Gong et al., 1992).

The relationship between concentrations of nitrate and phosphate is linear at all stations (Fig.

4), indicating similar cycling of nitrate and phosphate in the three seas.

3.4 Cd profiles

The results of the measurement for cadmium at the 5 stations including hydrographic data, are given in Table 4. Profiles of up to 2500 m are shown in Fig. 3. Some of the samples were replicated (collected from two bottles). Data of Cd each represents the mean value of GFAAS measurements performed in triplicate.

The profiles of Cd in the West Philippine Sea at Stations 257-17, 257-23, and 287-17 show good agreement. It can be seen that in the surface layers Cd is completely depleted, and the concentration increases with depth to a maximum of around 1.05 nM Cd at 1000–1200 m, then maintains at a steady but slightly decreasing trend (0.95–1.00 nM) in deeper waters. No significant differences have been found at Station 17 for the two cruises (even
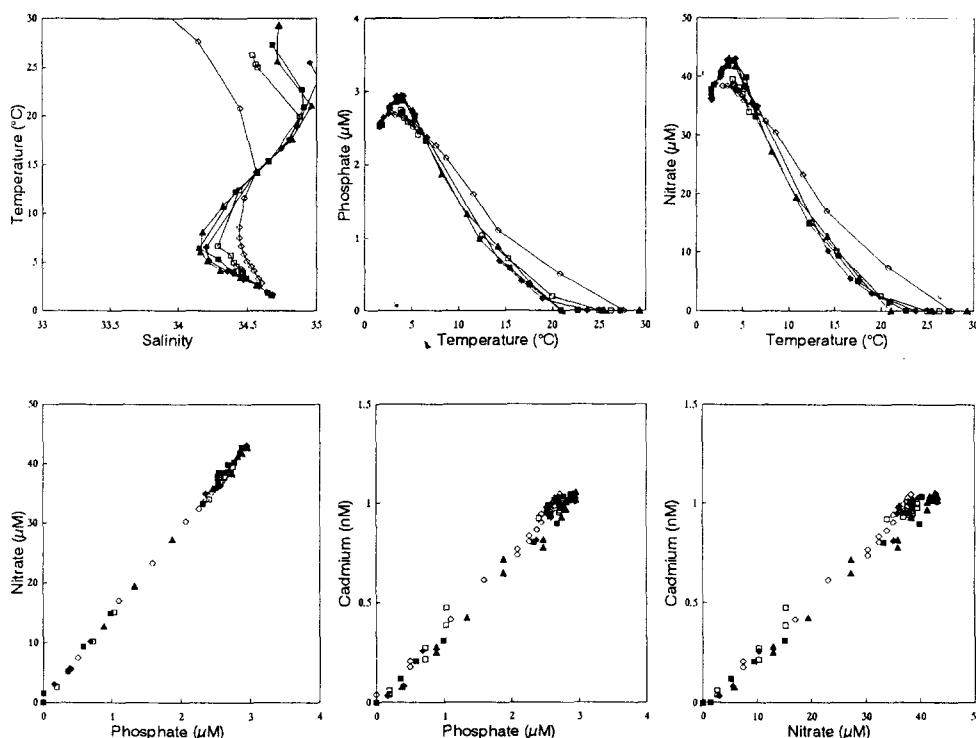
Fig. 4. Correlation plots of T-S, T-nutrient, N-P, and Cd-nutrient obtained at all stations in this study. For legend see Fig. 3.

using different types of bottles), nor for Station 23 which is located 270 km away.

The Cd distribution in the South China Sea also shows surface water depletion followed by an increase in concentration with depth to ca. 1.0 nM at 1000 m. However, the South China Sea profile looks very different from that obtained in the Philippine Sea. The major difference is the strength of Cd gradient within the thermocline. It can be clearly seen that Cd concentrations increased sharply at a depth of ca. 100 m at station 287-157, and reached 0.6 nM at 300 m (Fig. 3). However, in the Philippine Sea, the sharp increase in Cd started deeper, i.e. at 300–400 m, and reached 0.6 nM at around 600 m.

Station 4531 (ORI-280) in the East China Sea has a shallower bottom depth (1700 m). In the upper layer (0–700 m) the Cd distribution pattern was very similar to that found in the Philippine Sea, but the lower part of the profile (700–1500 m) followed the trend of the South China Sea. The highest concentration (ca. 1.0 nM Cd) occurred at 1000–1500 m, without a prominent maximum.

3.5 N/P, Cd/N and Cd/P ratios

The least-square regression coefficients for the concentrations of nutrients and Cd in the three seas are shown in Table 5. In the studied areas, phosphate, nitrate, and cadmium were all depleted in the surface layer; and on the correlation plots all intercepts were below the detection limits and not significantly different from zero. The equations after zero-intercept linear regression for the three parameters are:

$$[NO_3] = (14.53 \pm 0.04) \times [PO_4](r = 0.999, n = 69)$$
$$[Cd] = (0.0250 \pm 0.0001)$$
$$\times [NO_3](r = 0.990, n = 107)$$
$$[Cd] = (0.364 \pm 0.002)$$
$$\times [PO_4](r = 0.992, n = 107)$$

where [Cd] and nutrients are in nM and μM units, respectively.

Although correlation coefficients are high, any

Table 4
Hydrographic data and results of Cd analysis at Stations in the western Philippine Sea, the South China Sea, and the East China Sea (Cruises ORI-257, 280, and 287)

Pressure (db)	Temperature (°C)	Salinity	Oxygen (μM)	[PO$_4$] (μM)	[NO$_3$] (μM)	[Cd] (nM)
ORI-257 Station 17						
75	27.30	34.683	192	nd	nd	nd
111	22.67	34.895	200	nd	nd	nd
151	20.91	34.906	194	nd	1.4	nd
254	17.51	34.802	197	0.35	5.1	0.12
352	15.40	34.647	192	0.58	9.4	0.20
452	12.21	34.411	187	0.98	14.9	0.31
680	6.41	34.151	112	2.32	33.3	0.80
797	5.34	34.290	69	2.67	39.9	0.90
1002	4.03	34.395	61	2.87	42.9	1.05
1207	3.35	34.486	77	2.85	41.8	1.01
1602	2.61	34.579	107	2.77	40.4	1.03
2251	1.84	34.643	139	2.54	38.6	0.99
3301	1.56	34.671	154	2.52	37.8	0.95
4294	1.58	34.678	156	2.53	36.9	0.95
ORI-257 Station 23						
76	25.47	34.949	199	nd	nd	nd
108	23.70	35.012	197	nd	nd	nd
252	18.94	34.858	205	0.16	2.9	0.03
354	16.68	34.744	205	0.40	5.5	0.08
453	14.30	34.565	197	0.68	10.2	0.26
731	6.58	34.201	99	2.36	35.0	0.81
798	5.17	34.219	80	2.59	38.5	0.93
1003	4.11	34.353	58	2.94	43.1	1.01
1199	3.26	34.470	65	2.93	42.8	1.04
1600	2.53	34.582	106	2.69	39.8	1.03
2251	1.94	34.637	129	2.64	38.7	1.02
3298	1.60	34.669	150	2.57	36.3	0.99
4201	1.58	34.678	155	2.52	36.1	0.98
5000	1.65	34.680	154	2.52	35.9	0.95
ORI-287 Station 17						
11	29.36	34.727	198	nd	nd	nd, nd
53	29.28	34.722	198	nd	nd	nd, nd
103	25.60	34.716	212	nd	nd	nd, nd
202	21.07	34.963	195	nd	nd	nd, 0.05
301	17.64	34.822	197	0.37	5.6	0.08, 0.08
401	14.18	34.569	193	0.88	12.8	0.25, 0.28
499	10.82	34.322	189	1.33	19.4	0.43, 0.43
600	8.12	34.174	164	1.87	27.3	0.65, 0.72
701	6.02	34.156	117	2.46	35.9	0.81, 0.78
801	5.12	34.208	80	2.74	38.4	0.98, 0.93
899	4.14	34.298	65	2.88	41.8	1.02, 1.04
1003	3.86	34.408	64	2.95	42.8	1.06, 1.02
1106	3.41	34.444	72	2.94	43.2	1.02, 1.04
1495	2.63	34.562	98	2.81	41.4	1.01, 0.97
ORI-280 Station 4531						
13	26.30	34.535	219	nd	nd	nd, nd
55	25.32	34.561	221	nd	nd	nd, nd

Table 4 (continued)

Pressure (db)	Temperature (°C)	Salinity	Oxygen (μM)	[PO$_4$] (μM)	[NO$_3$] (μM)	[Cd] (nM)
101	25.00	34.574	214	nd	nd	nd, nd
202	19.95	34.882	200	0.19	2.6	0.04, 0.06
304	15.29	34.655	197	0.71	10.2	0.21, 0.27
402	12.45	34.443	187	1.03	15.2	0.39, 0.48
701	6.67	34.286	–	–	–	0.85, 0.81
801	5.68	34.380	94	2.41	34.0	0.92
900	4.97	34.404	87	2.57	37.0	0.95, 0.93
1002	4.57	34.421	81	2.58	38.1	0.94
1101	4.27	34.448	80	2.63	37.7	1.01, 0.99
1200	4.06	34.454	79	2.72	38.5	0.99, 0.96
1299	3.92	34.464	80	2.70	38.7	0.95, 1.00
1400	3.85	34.462	79	2.75	39.6	0.98, 1.00
ORI-287 Station 157						
10	30.32	33.926	212	nd	nd	nd, nd
50	27.66	34.142	220	nd	nd	nd, 0.04
101	20.80	34.446	191	0.50	7.3	0.20, 0.17
202	14.17	34.564	143	1.10	17.0	0.42, 0.42
299	11.57	34.480	121	1.59	23.2	0.61, 0.61
500	8.65	34.441	99	2.08	30.3	0.74, 0.77
600	7.52	34.441	96	2.26	32.4	0.83, 0.81
698	6.66	34.454	95	2.37	33.9	0.86, 0.86
808	5.83	34.476	95	2.45	35.2	0.90, 0.94
897	5.14	34.497	100	2.51	36.0	0.98
996	4.50	34.530	103	2.60	37.1	1.00, 0.96
1094	4.06	34.547	105	2.64	37.8	1.03, 0.99
1303	3.29	34.580	107	2.68	38.3	1.01, 1.02
1507	2.82	34.603	109	2.71	38.4	0.99, 1.05

nd = below detection limits; 0.07 μM for phosphate, 0.5 μM for nitrate, and 0.02 nM for cadmium.
Duplicate measurements: samples were collected by two GoFlo bottles.

systematic error of the measurements of either the nutrients or cadmium could cause significant bias. A further check was needed to ascertain the accuracy of the slope values. The accuracy of nutrient measurements were evaluated by comparing the data from the 2000–2500 m layer obtained for the whole Cruise ORI-257 (WOCE PR-20 Expedition) with that of selected stations (Stations 39–45) obtained from the INDOPAC Leg-3 cruise (1976). The differences of nitrate and phosphate data between the two sets of data were all within 2%. The dN/dP ratios were 14.57 for the ORI-257 and 14.62 for the INDOPAC, respectively. The accuracy of the Cd analysis was checked in the

laboratory with NASS-3 Standard Seawater. The recovery indicated a relative accuracy of ±3%. Thus the possible relative error (±1σ) of the two molar ratios (dCd/dN and dCd/dP) should not exceed ±5%.

3.6 Comparison with east Pacific data

Among all literature data available for the Pacific Ocean, the work by Bruland (1980) has provided probably the best data quality, judging from the smoothness of the profiles and the high correlation coefficients on molar ratios of

Table 5
Regression data for cadmium and nutrients in this study

Cruise/station	Slope	Intercept	n	r
[NO₃] vs. [PO₄]				
ORI-257 Station 17	14.62 ± 0.15	0.45	14	0.9987
ORI-257 Station 23	14.55 ± 0.14	0.11	14	0.9989
ORI-280 Station 4531	14.36 ± 0.10	0.02	13	0.9995
ORI-287 Station 17	14.50 ± 0.10	0.06	14	0.9994
ORI-287 Station 157	14.21 ± 0.11	0.34	14	0.9993
All stations	14.46 ± 0.06	0.17	69	0.9987
All stations[a]	14.53 ± 0.04		69	0.9987
[Cd] vs. [NO₃]				
ORI-257 Station 17	0.02510 ± 0.0006	−0.02	14	0.9937
ORI-257 Station 23	0.02567 ± 0.0008	−0.02	14	0.9876
ORI-280 Station 4531	0.02556 ± 0.0004	0.00	24	0.9955
ORI-287 Station 17	0.02424 ± 0.0004	−0.01	28	0.9934
ORI-287 Station 157	0.02618 ± 0.0004	−0.00	27	0.9951
All stations	0.02529 ± 0.0002	−0.01	107	0.9901
All stations[a]	0.02509 ± 0.0001		107	0.9900
[Cd] vs. [PO₄]				
ORI-257 Station 17	0.367 ± 0.009	−0.01	14	0.9935
ORI-257 Station 23	0.374 ± 0.010	−0.02	14	0.9911
ORI-280 Station 4531	0.367 ± 0.005	0.00	24	0.9954
ORI-287 Station 17	0.352 ± 0.005	−0.01	28	0.9943
ORI-287 Station 157	0.372 ± 0.005	0.01	27	0.9961
All stations	0.366 ± 0.003	−0.00	107	0.9920
All stations[a]	0.364 ± 0.002		107	0.9920

[a] Force-zero linear regression process was used, because all intercepts were apparently less than the detection limits (0.5 and 0.07 μM for nitrate and phosphate respectively; 0.02 nM for cadmium).
Concentration units are nM for Cd and μM for nutrients.

more than 0.99. Other data, either with zigzag shaped Cd profiles or accompanied with poor temperature–nutrient relationships, were not quoted for comparison.

If the d[Cd]/[nutrient] ratios obtained in this study are compared with that reported by Bruland for the eastern Pacific region, it is interesting to see the ratios, representing both sides of the Pacific Basin, agree well within only a few percent. The d[Cd]/d[PO₄] ratio obtained in this study (3.64×10^{-4}) is ca. 4% higher than the 3.47×10^{-4} reported by Bruland, whereas the d[Cd]/[NO₃] ratio (2.50×10^{-5}) is ca. 7% higher than the 2.35×10^{-5} for the Cruise H-77 Station 17 in Bruland's work. The differences were insignificant compared to the relative slope bias of ±5%. The maximum Cd concentrations found

at the 1000 m layer in the two studies were similar, ranging from 1.0 to 1.1 nM.

4. Conclusion

In the present study we have collected high-quality cadmium and nutrient data at four locations (5 stations) in three marginal seas of the western Pacific Ocean (the western Philippine Sea, the South China Sea, and the East China Sea). The highest Cd concentration was ca. 1.05 nM found in the 1000–1200 m layer of the Philippine Sea. Surface depletion was found at all stations for both Cd and nutrients. The relationships between Cd (in nM units) and nutrients (in μM units) were linear and were almost identical for the three seas, to be

$[Cd] = (0.364 \pm 0.002) \times [PO_4]$, and $[Cd] = (0.0250 \pm 0.0001) \times [NO_3]$ ($n = 107$). Intercepts on the cross-plots were not significantly different from zero. It is not appropriate to compare those ratio values with that reported by other workers in other areas without considering the data quality (both Cd and nutrients) in term of accuracy. Nonetheless, since such linear relationships have been consistently found in many parts of the Pacific Ocean, we suggest that the molar ratios of $d[Cd]/d[PO_4]$ and $d[Cd]/d[NO_3]$ are invariant over the whole open Pacific Basin averaging $(3.55 \pm 0.20) \times 10^{-4}$ and $(2.42 \pm 0.15) \times 10^{-5}$, respectively. If this is true then these ratios may be used for identifying the sources or sinks, such as anthropogenic and hydrothermal inputs, of this metal in different areas.

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