NOTE AND CORRESPONDENCE
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Vertical Distributions of Cadmium, Copper, Nickel and Zinc in the Western Philippine Sea and a Comparison With Data From Other Parts of the Pacific Ocean

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ABSTRACT

The concentration profiles of Cd, Cu, Ni and Zn in a water column in the western Philippine Sea (located at 124°00'E, 21°45'N) were investigated. All four elements showed a surface-low and deep-high distribution pattern. The maximum concentrations found between 0-2000 m were 0.97, 2.6, 9.3 and 7.7 nM for Cd, Cu, Ni and Zn respectively. The distributions can be further classified into different types according to their relationships with nutrients. Cadmium was strongly correlated to nitrate and phosphate, whereas nickel and zinc were related to silicate. The concentration of copper increased linearly with depth, but it correlated poorly with either phosphate, nitrate or silicate. A comparison between the present data set and those reported for the northeast Pacific Ocean indicates that those elements follow similar distribution patterns across the Pacific Basin, with a decreasing trend on the maximum concentrations in the deep water from the east to the west.

(Key words: Cadmium, Copper, Nickel, Zinc, Philippine Sea)

1. INTRODUCTION

Although it has been known that cadmium, copper, nickel and zinc exist in oceans at very low concentrations, ranging from pM to up to a few nM (Bruland, 1983), not much field data can be found in the literature. This is probably due to both the analytical difficulties of measuring these elements at such low levels and the associated high costs. More than four-fifths of the presently available data for the Pacific Ocean center upon the northeast Pacific including the near-coast areas off California. Generally, the concentrations of Cd, Cu, Ni and Zn found are either depleted or low in the surface but relatively high in the deep water. Their profiles show similar patterns to that of nutrients (Boyle *et al.*,1976; Bruland, 1980; Jones and

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Murray, 1984). These features along with the assumption that the regeneration of metals may be totally or partially linked to the cycles of nutrients led Bruland (1983) to regard these metals as nutrient- or nutrient-like- type elements. Whether such correlations may also apply to other parts of the Pacific region is still not conclusive because of the lack of high-quality data. In the western marginal seas, such as the Philippine Sea, only cadmium data have been reported (Pai and Chen. 1994). In this paper the distributions of Cd were studied again in the same area, together with three other elements, i.e. Cu, Ni, and Zn. These data were then compared with those found in the eastern and other parts of the Pacific Ocean in order to sketch a general, basin-wide distribution pattern for these elements.

2. SAMPLING AND METHODS

Samples for trace metal analyses were obtained at Sta. 11 (Figure 1) in the Philippine Sea (124°00'E, 21°45'N, bottom depth 5530 m) aboard the *R/V Ocean Researcher I* during Cruise ORI-316a, May 5-15, 1992. Seawater at different depths (0-2000 m) were collected with 2.5 liter Go-Flo bottles mounted on the rosette sampling system (General Oceanic Inc., Miami, FL, USA), which was connected to the Seabird SBE 9/11 CTD (SeaBird Electronics Inc., Bellevue, WA, USA). An oxygen sensor was used. For the determination of metals, a portion of the sub-sample was transferred directly from the GoFlo bottle into a 1.28 L polyethyleneterephthalate (PET) bottle, which has been filled with 30 mL of ammonium maleate buffer at pH 6.5 (Pai *et al.*, 1990). The mixture was allowed to pass through a Chelex-100 double column set (Pai and Chen, 1994). The loaded column sets were brought back to the land-based laboratory, and the metals were recovered by eluting the column with 10.0 mL of 2N nitric acid. A concentration factor of 125-fold was obtained. The contents of Cd, Cu, Ni and Zn in the eluate were detected by a Hitachi Z-8100 graphite furnace atomic absorption spectrometer. The detection limits for Cd, Cu, Ni and Zn with this procedure were 0.02, 0.2, 0.2 and 0.1 nM, respectively. In a laboratory test, the recoveries of spiked metals at 10 nM were within the range of 96-102%. Discrete samples were also collected at two nearby stations (Sta. 10 and 18) for the determination of oxygen, nitrate, phosphate, and silicate.

3. RESULTS AND DISCUSSION

3.1 Hydrography

The distributions of temperature, salinity (by CTD), oxygen (by DO sensor calibrated with manual determination), density, and AOU at the three stations (Sta. 10,11, and 18) are shown in Figure 2. Nutrient data at Sta. 10 and 18 are also plotted. Since the hydrographic patterns at these three stations are almost identical. Thus, although nutrients were not analyzed at Sta. 11, their distributions should be similar to those at Sta. 10 and 18. The profiles in Figure 2 match well with the corresponding data reported previously in the nearby region during INDOPAC Cruise Leg-3, and the WOCE (World Ocean Circulation Experiment) cruises along the observational line PR-20 (Gong *et al.*, 1992). It can be concluded that the water masses in the studied area are very stable without noticeable seasonal variations below the surface mixed layer; therefore the profiles obtained in this study represent the general characteristics of the water column in the west Philippine Sea.

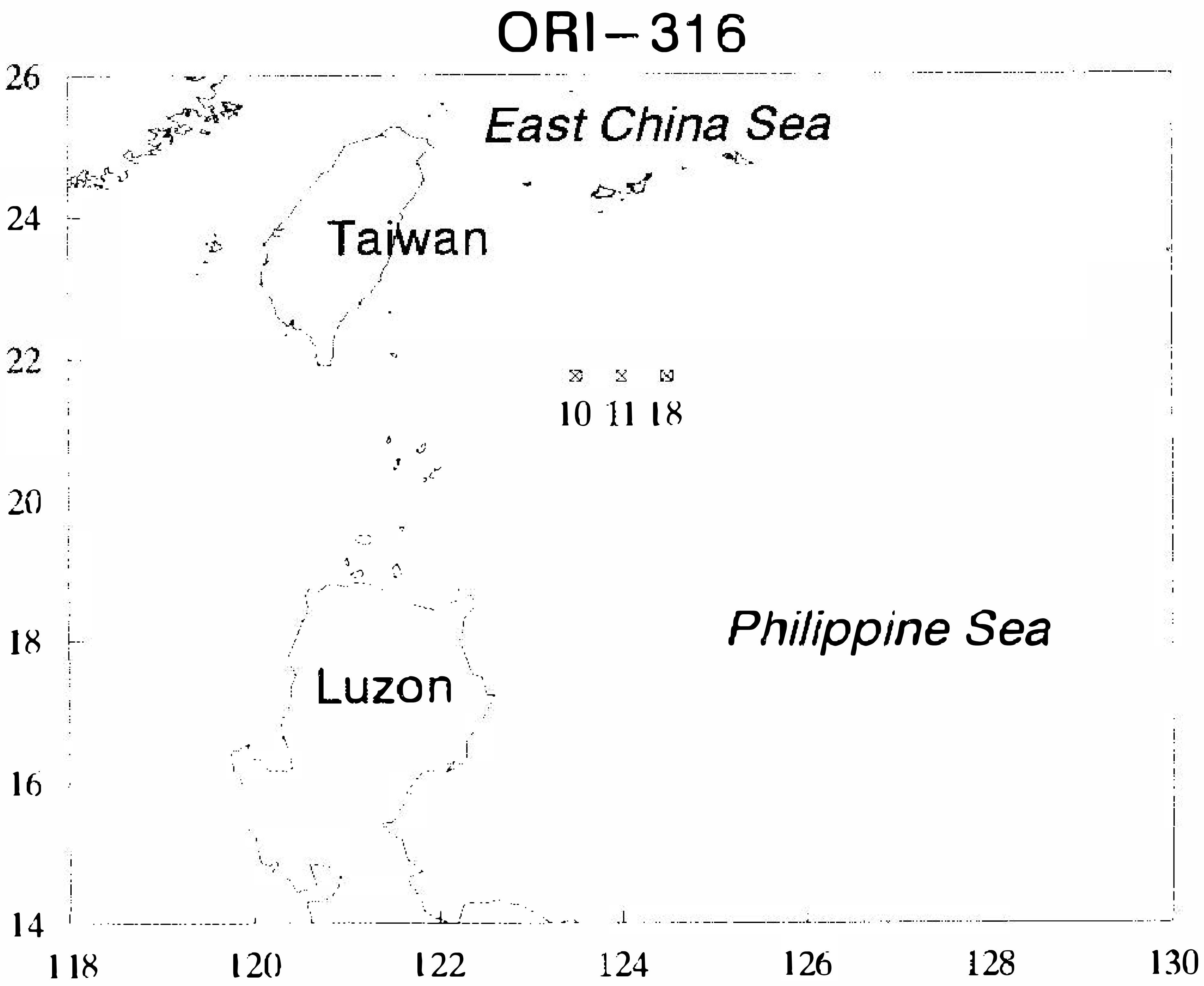

Fig. 1. Location of the sampling stations in this study. CTD and oxygen sensor were used at all stations; metal pre-concentration was performed at Sta. 11; oxygen and nutrients were analyzed at Sta. 10 and 18.

3.2 Cadmium

The vertical profile of cadmium shown in Figure 3A gives an almost identical image to those of phosphate and nitrate. The concentrations (0-0.02 nM) found in the surface layers (0-150 m) were at the detection limit; increasing with depth in the thermocline (200-1000 m) at a gradient (dCd/dZ) of ca. 0.1 nM/100 m, and reaching a maximum of 0.93-0.97 nM at 1000-1200 m layer. Below 1200 m, the concentration leveled off at 0.91-0.95 nM. Both the shape of the profile and the concentration range agree well with previous observations within ± 5% error (Pai and Chen, 1994). Together with the phosphate data, it can be confirmed that cadmium is indeed a nutrient-type element, and that the linearity between Cd and P is almost identical across the whole Pacific Ocean. However, as can be seen from the data in literature (shown in Figure 3B), there exists a distinct difference between the west and the east Pacific Ocean. Two major groups of vertical distribution can be identified from the overlapping-plotted diagram. The group that has a sharp increment in the shallow 0-500 m layer is located generally in the northeast and north Pacific regions. The concentrations of Cd in these areas could be detectable (from 0.05-0.6 nM) in the surface, and the maximum concentration of ca. 1.0-1.1 nM was found at as shallow as ca. 500 m. The other group, with a deeper Cd-cline, is located in the central and western parts of the Pacific. The surface layer (up to 200 m) was almost depleted of Cd, and the maximum concentrations (ca. 1.0 nM) appeared at a depth deeper than 900 m.

When the phosphate data of the two sides of the ocean are compared, the patterns look almost the same as those for cadmium. The concentration of phosphate in the surface layer of the eastern Pacific may be as high as 0.5 μM, whereas it is undetectable in the west. The maximum concentration of phosphate in the eastern side (e.g. 3.3 μM P at 1000 m) appears

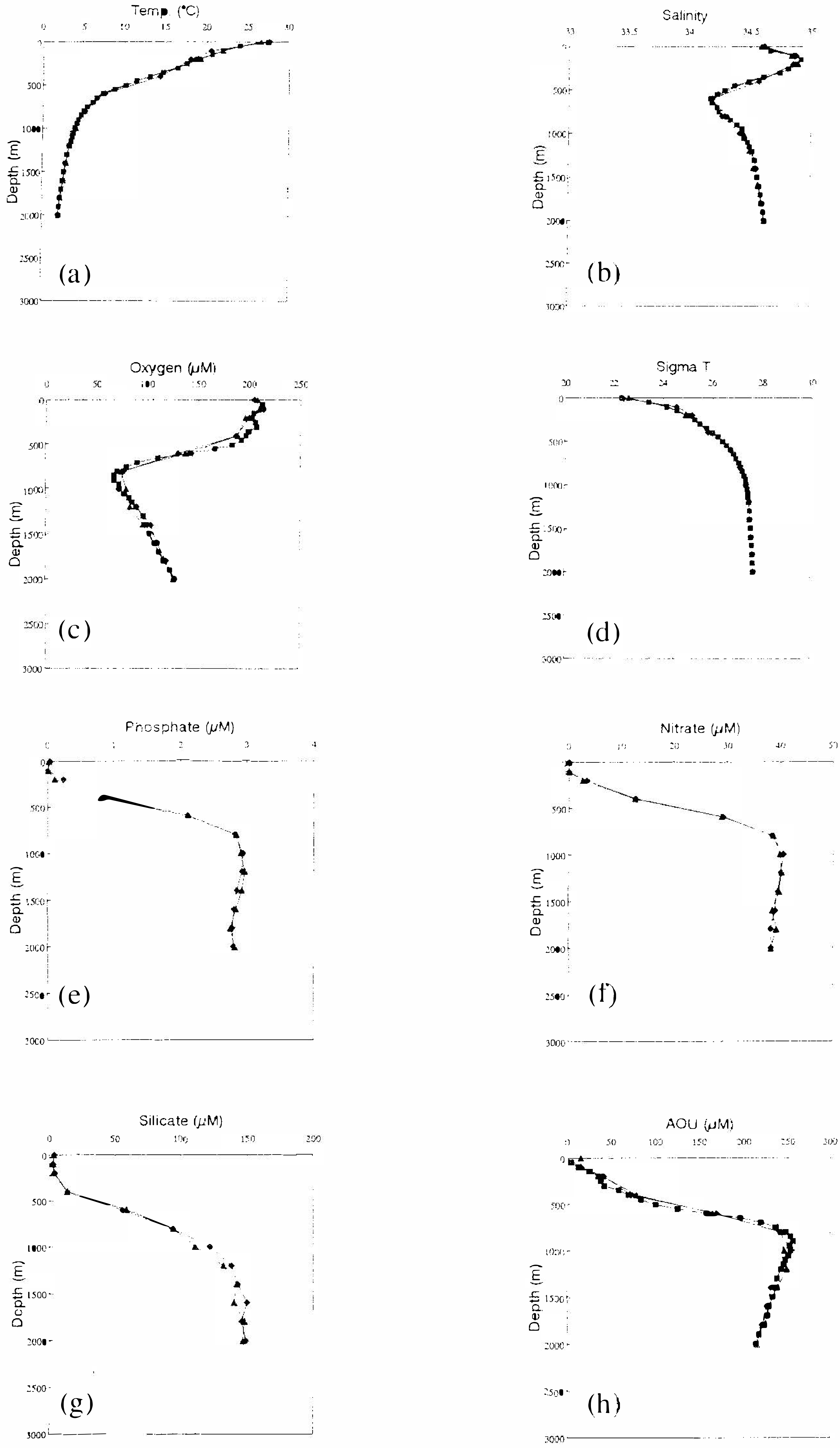

Fig. 2. Vertical profiles of (a) temperature, (b) salinity, (c) dissolved oxygen, (d) sigma-T, (e) phosphate, (f) nitrate, (g) silicate, and (h) AOU at (▲) Sta. 10 ; (■) Sta. 11; and (◆) Sta. 18. Nutrients at Sta. 11 were not measured.

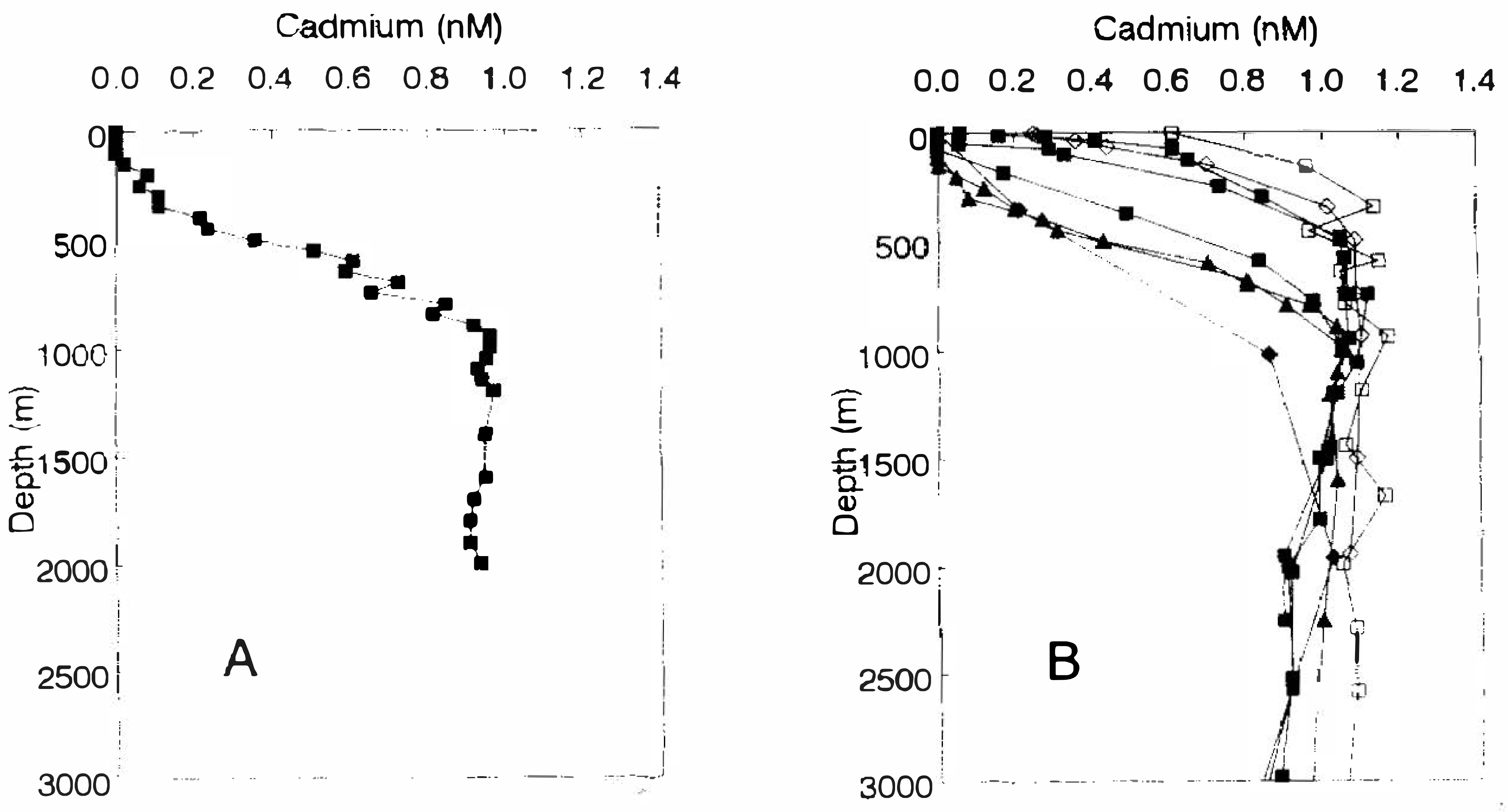

Fig. 3. (A) Vertical profiles of cadmium in the Philippine Sea plotted from the data obtained in this study; (B) overlapping profiles of cadmium plotted from data in the literature for other parts of the Pacific Ocean.(□): from Boyle *et al.* (1976), Sta. 219 in the north Pacific. (■): from Bruland (1980), Sta. C-I/C-II in the northeast Pacific; Sta. 17 in the central north Pacific. (◇): from Knauer and Martin (1981), in the northeast Pacific. (◆): from Murozumi (1983), Sta. M-7 in the west Pacific near Guam. (▲): from Pai and Chen (1994). Sta. 257-17/287-17 in the west Philippine Sea.

a little higher than that found in the western Philippine Sea at the same depth (3.0 μM P). Therefore, it is not surprising to find that the maximum Cd concentration in the Philippine Sea was slightly lower than that reported by previous workers in the eastern parts of the ocean (see Figure 3B).

3.3 Copper

The distribution of copper (Figure 4A) also shows a surface-low and deep-rich trend. The surface layer was not depleted, with a concentration range of 0.5-0.7 nM in the 0-200 m layer. Without taking the spurious data at 250 m into consideration, the concentration increased with depth in an almost linear way. At 1000 m and 2000 m, the concentrations were 1.68 and 2.57 nM respectively, with a gradient (dCu/dZ) of ca. 0.1 nM/100 m. The correlations between the concentrations of copper and nutrients (including phosphate, nitrate, and silicate) were all poor. This indicates that copper might have a slower regeneration than do nutrients during the vertical scavenge process. In fact, in many previous reports (Bruland, 1980; Murozumi,1983), the highest copper concentration were always found near the ocean floor. Their explanation was that the high concentrations in the deep water might have been affected by the release of copper from bottom sediments. The general trend of the profile in this study matches well with that reported by Burland (1980) and Murozumi (1983) but is much lower than that reported by Jones and Murray (1984). The data obtained by the latter authors may well have been contaminated (Figure 4B).

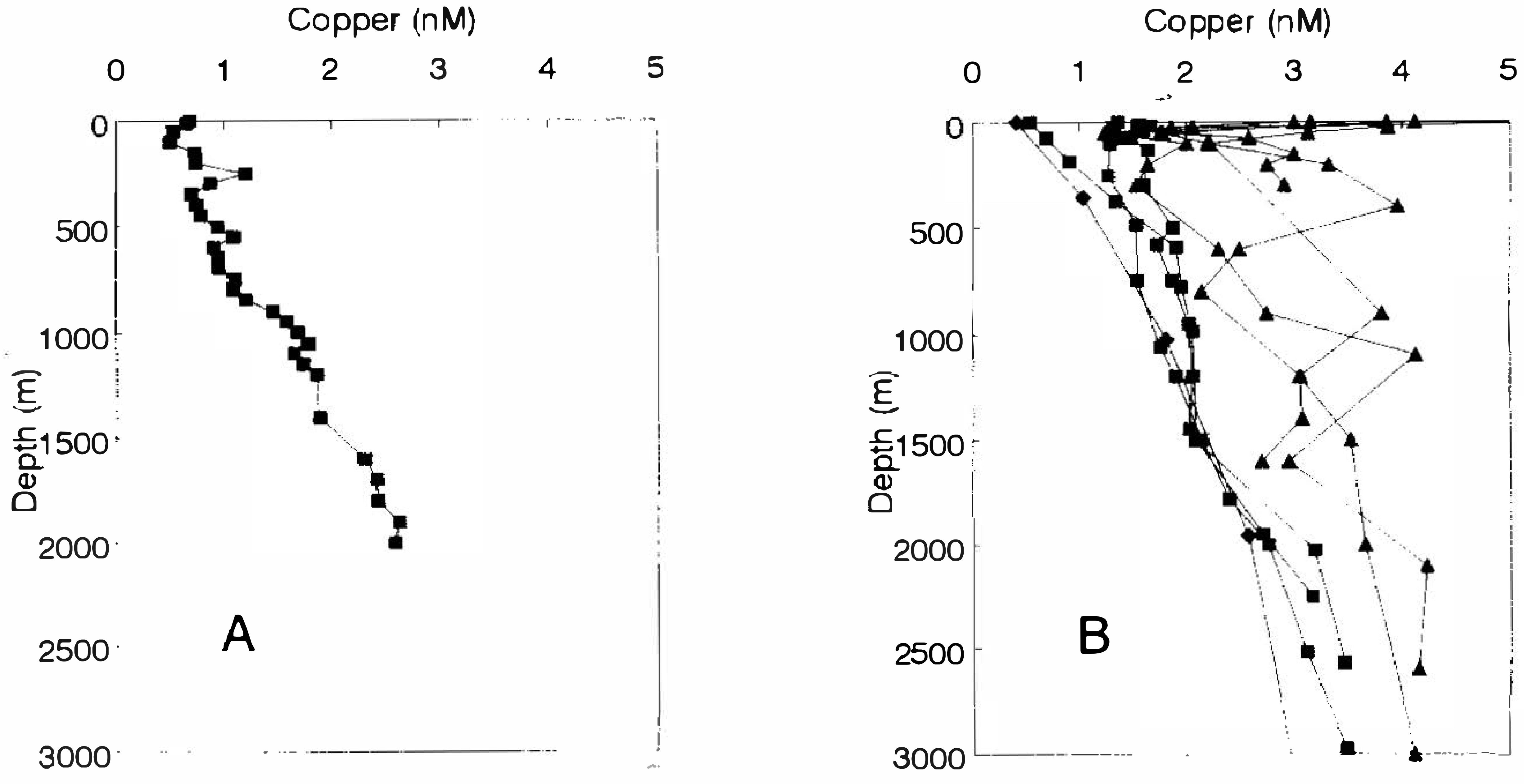

Fig. 4. (A) Vertical profiles of copper in the Philippine Sea plotted from the data obtained in this study; (B) overlapping profiles of copper plotted from data in the literature for other parts of the Pacific Ocean. (■): from Bruland (1980), Sta. C-I/C-II in the northeast Pacific, Sta. 17 in the central north Pacific. (◆): from Murozumi (1983), Sta. M-7 in the west Pacific near Guam. (▲): from Jones and Murray (1984), Sta. 2,3,5 and 7 in the northeast Pacific off the coast of Washington.

3.4 Nickel

The concentration of nickel in the surface layer (0-200 m) was found between 1.9-2.1 nM. It increased sharply with depth in the thermocline and reached ca. 8 nM at 1000-1200 m (Figure 5A). Below 1200 m, the concentration increased more gradually with depth to a 9.34 nM at 2000m. The shape of the profile resembled that of silicate rather than phosphate or nitrate. According to the Bruland's classification, nickel is a labile-refractory nutrient-type element. This means that the distribution may be controlled by a combination of a rapid-regeneration in the thermocline and a slow-regeneration in the deeper layer. The former process should result in a shallow mid-depth concentration maximum, and the latter a deeper maximum at the depth where the maximum of silicate is located (Chester, 1990). This is shown in Figure 5B that a small plume-shaped distribution appeares at the 800-1200 m layer in the eastern Pacific. However, such mid-depth-maximum for Ni was not clearly found in the Philippine Sea, so Ni seems to be only silicate related.

3.5 Zinc

The concentration of zinc measured in the surface layer was low but detectable (ca. 0.3 nM). It increased with depth to ca. 7.6 nM at 1200 m and maintained the same concentration between 1200 m and 2000 m (Figure 6A). It has been noticed that the surface concentration slightly higher than that found in the eastern Pacific being generally less than 0.1 nM in the surface layer (see Figure 6B). Although the difference was small but we suspected that it could have been the result of contamination in the sampling process (e.g. from the hydrowire

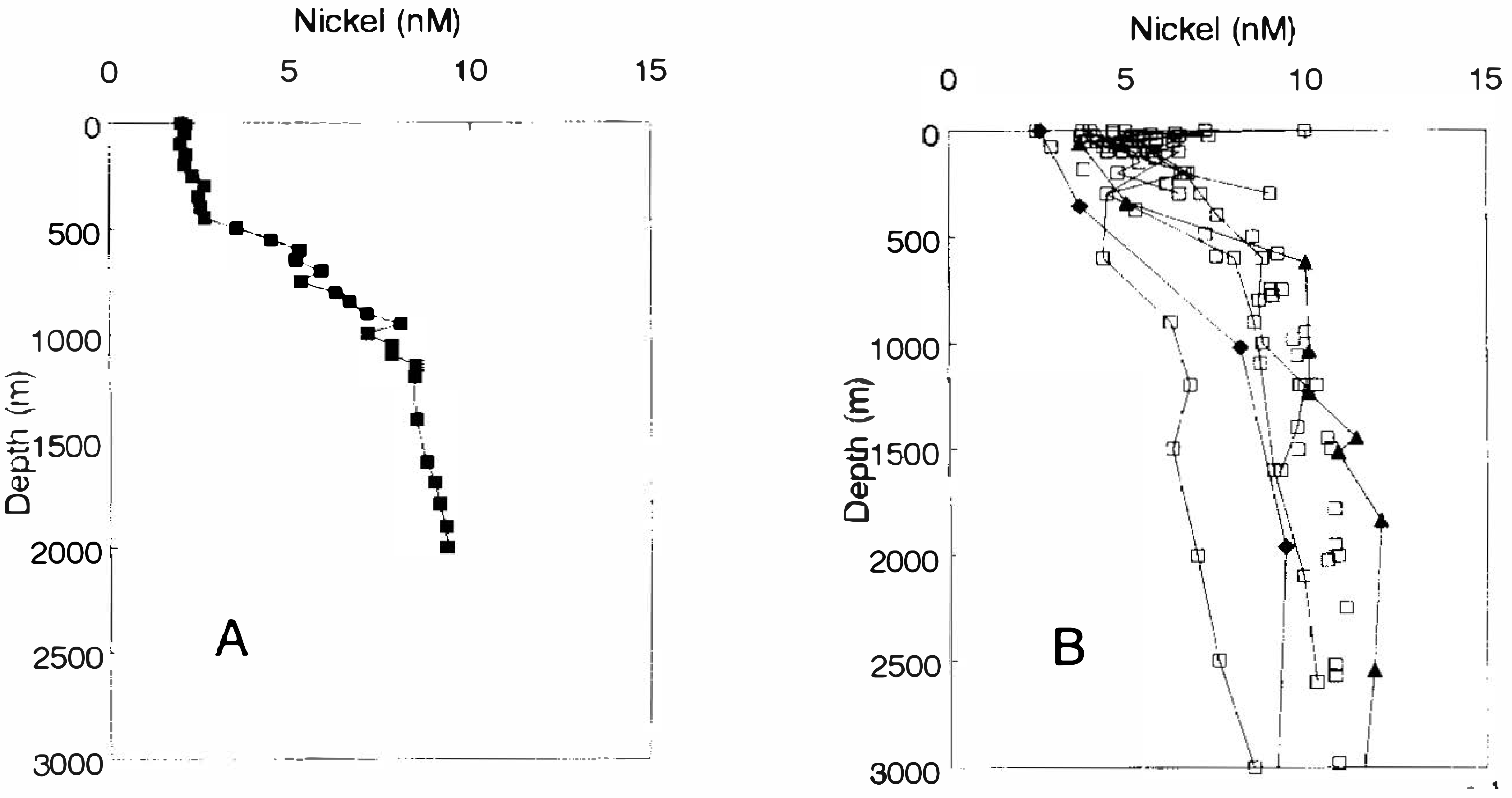

Fig. 5 (A) Vertical profiles of nickel in the Philippine Sea plotted from the data obtained in this study; (B) overlapping profiles of nickel plotted from data in the literature for other parts of the Pacific Ocean. (▲): from Sclater *et al.* (1976), Sta. 204 in the north Pacific. (■): from Bruland (1980), Sta. C-I/C-II in the northeast Pacific, Sta. 17 in the central north Pacific. (◆): from Murozumi (1983), Sta. M-7 in the west Pacific near Guam. (□): from Jones and Murray (1984) Sta. 2, 3, 5 and 7, in the northeast Pacific off the coast of Washington.

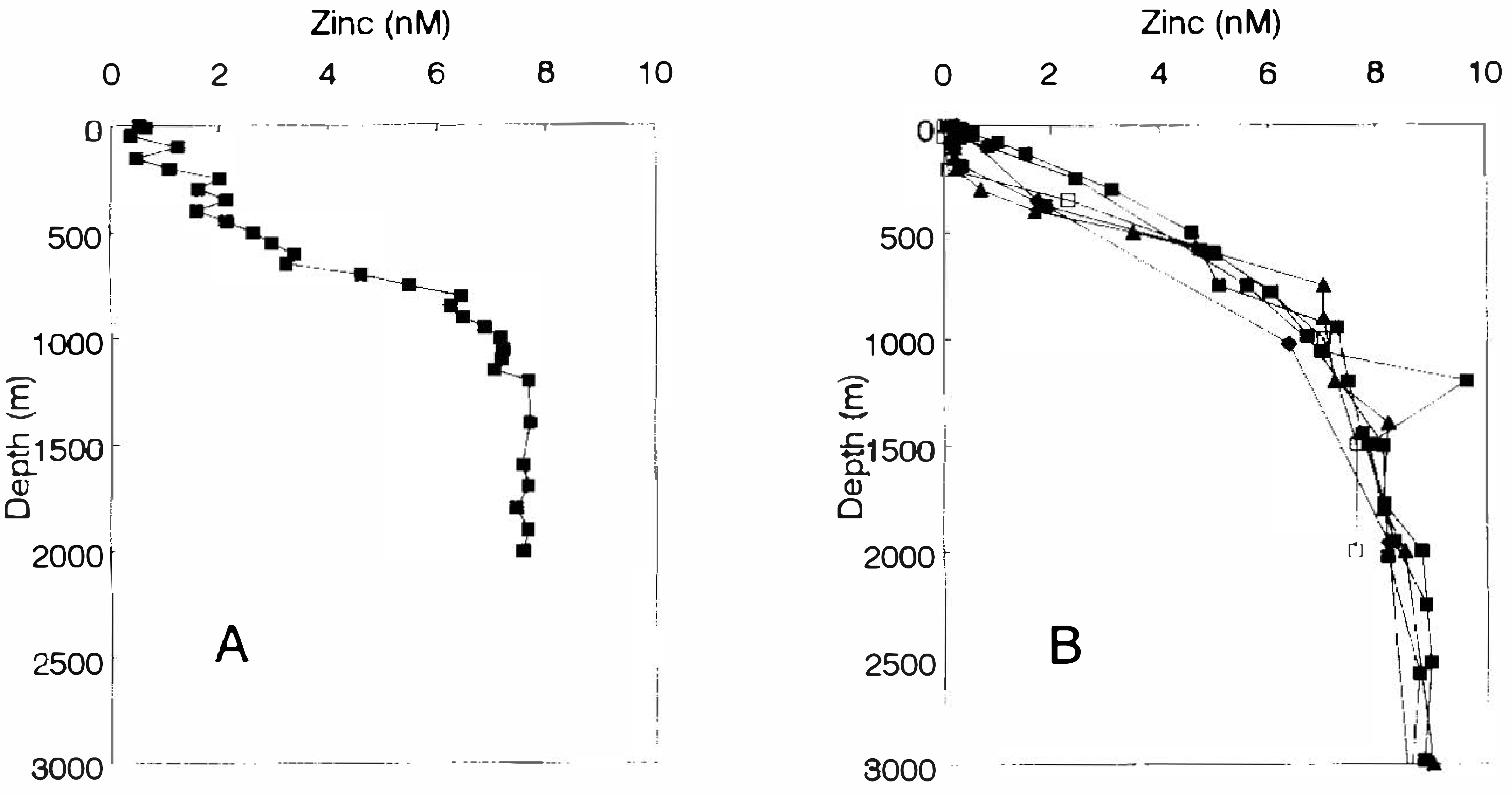

Fig. 6. (A) Vertical profiles of zinc in the Philippine Sea plotted from the data obtained in this study; (B) overlapping profiles of zinc plotted from data in the literature for other parts of the Pacific Ocean. (■): from Bruland (1980), Sta. C-I/C-II in the northeast Pacific, Sta. 17 in the central north Pacific. (◆): from Murozumi (1983), Sta. M-7 in the west Pacific near Guam. ( ): from Nowicki *et al.* (1994), in the north Pacific. (▲): from Bruland *et al.* (1994), in the central north Pacific near Hawaii.

and the bottles). Besides this small uncertainty, the shape of the profile matches that reported by Bruland (1980), Murozumi (1983), and Nowicki *et al.* (1994). The correlation of the Zn concentration to that of silicate was very good in the thermocline. The possible maximum (might at the maximum of silicate concentration), however, could not be identified with the present data due to the limitations of the sampling depth.

4. CONCLUSIONS

The present study provides high quality data of the four elements in the water column of up to 2000 m in the west Philippine Sea . In general the vertical distribution trends are similar to those reported for other parts of the Pacific Ocean. This supports the idea that the basic mechanisms controlling the distributions of these four elements are similar for the whole Pacific Ocean. However, three differences have been observed: (1) the "metal-clines" for Cd, Ni, and Zn were deeper in the west than in the east; (2) the concentrations in the middle layer were slightly lower in the west than in the east at the same depths. The same trends were also found for phosphate, nitrate and silicate; and (3) the so-called "second maximum" for Ni which have been found in the eastern Pacific at the depth of maximum phosphate was not observed in the Philippine Sea.

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