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Baseline

Distribution patterns of six metals and their influencing factors in M4 seamount seawater of the Western Pacific

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ABSTRACT

Metals are crucial to the stability of marine ecosystems, and it is important to analyze their spatial heterogeneity. This study examined the distribution and influencing factors of six metals such as manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu) and cadmium (Cd) in M4 seamount of the Western Pacific. The results showed that the factors affecting the distribution of metals are complex. The concentration ranges of Mn, Fe, Co, Ni, Cu, and Cd in the M4 seamount were 0–0.05, 0–0.44, 0–0.0014, 0–0.082, 0.12–0.16, and 0–0.013 μg/L, respectively, roughly equivalent to those of other open seas, however, there were also some differences. Specifically, the distribution of ferromanganese nodules and Co-rich crusts, resulted in a significant increase in the concentration of metals such as Mn, Fe, and Co in the bottom. This study will significantly contribute to our understanding of the spatial heterogeneity of metals in seamount areas.

Metals, despite their low concentrations in various mediums, play a vital role in maintaining ecosystem stability. For instance, iron (Fe) and manganese (Mn) in the marine environment significantly impact photosynthetic pigment synthesis and carbon fixation. Additionally, an appropriate amount of cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), Fe, and Mn can promote the growth of organisms (Annabi-Trabelsi et al., 2021; Hawco et al., 2022). Conversely, some metals like lead (Pb) and mercury (Hg) exhibit significant toxicity, inhibiting the growth of marine organisms (Henderson et al., 2018; Gutiérrez-Ravelo et al., 2020). This underscores the pivotal role of metals in marine organism growth and material cycling. Therefore, understanding their concentration, distribution, sources, destinations, ecological effect, and related factors is a key focus of marine chemistry research.

The Western Pacific is renowned as a global hotspot for oceanographic research, primarily due to its status as the region with the most significant sea-atmosphere interaction (Hu et al., 2015; Dai et al., 2020a). Moreover, it is a global hotspot for seamounts, which contribute to an exceptionally intricate hydrological environment (Ma et al., 2021b). This area is also known for its abundant mineral resources, including ferromanganese nodules and Co-rich crusts, making it a renowned hub for mineral resource exploration (Du et al., 2017; Marino et al., 2018). The intricate hydrological environment in the seamount area likely enhances the dispersion of metals. Furthermore, the ferromanganese nodules and Co-rich crusts in this region are rich in various metals, significantly influencing the spatial distribution characteristics of metals in seawater. However, current metal research has primarily focused on lakes, rivers, and offshore waters due to constraints in sample collection and other factors (Almeida et al., 2006; Yang et al., 2014; Gao et al., 2016; Zhuang et al., 2019). Regrettably, there is a notable lack of research on metals in the seamount area of the Western Pacific, limiting our comprehensive understanding of the baseline metal distribution in the ocean.

This study explored the spatial distribution characteristics of six metals such as Mn, Fe, Co, Ni, Cu and cadmium (Cd) in M4 seamount of the Western Pacific. It analyzed the impact of environmental factors on these metals, discussed the relationship between biogenic elements and

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metals, and evaluated the impact of seamount on metal distribution. The findings of this study serve as a foundational reference for comprehending the spatial heterogeneity of metals in this area.

In May 2019, a comprehensive survey of the M4 seamount in the Western Pacific was conducted aboard the research vessel "*Science.*" This survey encompassed 16 stations categorized into two sections, A and B, with station O serving as their intersection point (Fig. 1A). The M4 seamount, with its summit situated at a depth of 106 m, is considered a shallow seamount (Ma et al., 2021a; Dai et al., 2022). It is significantly influenced by the North Equatorial Current (NEC), which flows from east to west in the 0–200 m range (Sun et al., 2013; Hu et al., 2015) (Fig. 1B).

At various depths, including 0 m, 50 m, and 75 m, the Deep Chlorophyll Maximum Layer (DCML) at approximately 100 m, 150 m, 200 m, 300 m, 500 m, 1000 m, 1500 m, 2000 m, and the bottom layer (at approximately 2000–2500 m), the Niskin water sampler (KC-Denmark, Denmark) was used to collect water samples. The collected samples were subjected to measurements of the following parameters. Salinity, temperature, and depth: Concurrent measurements of these parameters were taken using the CTD (Sea-bird SBE911, USA). Dissolved oxygen (DO): The Winkler iodometry method was used for determination, and the determination error was ±2 %. pH: The determination of pH values was carried out using a multi-parameter tester (Mettler Toledo S479—B, USA), with an accuracy of ±0.002. Chlorophyll a (Chl a): Chl a concentrations were measured using the Turner fluorescence photometer (Turner Designs, USA). Nitrate (NO_3-N) and phosphate (PO_4-P): The automatic nutrient analyzer (SEAL QuAAtro, Germany) was used for determination with detection limits of 0.02 and 0.01 μmol/L, respectively. Particulate organic carbon (POC): The determination of POC involved employing an element analyzer (Thermo Fisher Scientific Flash EA 1112, USA), with an accuracy of ±0.8 ‰. Metals: The inductively coupled plasma mass spectrometer (Thermo Scientific iCAP-Q ICP-MS, USA) was used for determination. To explore the relationships among metals, environmental parameters, and biogenic elements, the Origin Pro 2022 (Version 9.9.0, USA) was used for the Person Correlation Analysis and Principal Components Analysis (PCA), $P < 0.05$. All the samples were collected and measured in accordance with relevant references and marine survey specifications (GB12763.6–2007), and the detailed methods were showed in the Supplementary data.

The upper waters exhibited high temperature, with readings exceeding 28 °C at depths ranging from 0 m to 50 m. Notably, a significant thermocline was observed in the layer spanning 75 m to 200 m (Fig. 2A). In the 50–300 m range, there was a pronounced area of high salinity, with the highest average salinity recorded at 34.69 at a depth of 150 m (Fig. 2B). The Oxygen Minimum Zone (OMZ), characterized by DO levels falling below 3.2 mg/L (Paulmier and Ruiz-Pino, 2009), extended from 290 m to 1100 m. The lowest DO value within this zone was 2.92 mg/L (Fig. 2C). The pH levels displayed a change pattern that closely mirrored the DO distribution (Fig. 2D). Chl a concentrations peaked in the subsurface layer, with the DCML occurring at around 100 m (Fig. 2E). The nutrient levels in the upper waters of the M4 seamount area were extremely limited. However, between depths of 75 m and 300 m, there was a rapid increase in both PO_4-P and NO_3-N concentrations, resulting in the formation of a nutricline (Fig. 2F, G). In the upper waters, POC levels were high, exceeding an average of 14.50 μg/L in the 0–100 m depth range. However, in the 100–300 m layer, POC concentrations decreased significantly from 17.46 to 8.44 μg/L (Fig. 2H).

The distribution patterns of the six metals exhibited distinct vertical distribution characteristics, which can be categorized into four types (Fig. 3). Type 1: This type shows a decrease in metal concentration with increasing water depth, followed by a gradual increase towards the seabed. Mn exemplifies this pattern (Fig. 3A). At 0 m and 2000 m, the Mn concentrations were measured at 0.017 and 0.004 μg/L, respectively. Type 2: In this category, metal concentrations are lower in the middle layer and higher in the subsurface layer and the bottom layer. Fe and Co illustrate this type (Fig. 3B, C). At various depths, the Fe concentrations were as follows: 0 m - 0.060 μg/L, 75 m - 0.083 μg/L, 1000 m - 0.032 μg/L, and 2000 m - 0.098 μg/L. For Co, concentrations at different depths were: 0 m - 0.00016 μg/L, 150 m - 0.00029 μg/L, 1000 m - 0.00018 μg/L, and 2000 m - 0.00024 μg/L. Type 3: In this type, metal concentrations increase initially and then stabilize with increasing water depth. Ni and Cd fall into this category (Fig. 3D, F). At varying depths, Ni concentrations were recorded as follows: 0 m - 0.010 μg/L, 100 m - 0.010 μg/L, 1000 m - 0.049 μg/L, and 2000 m - 0.064 μg/L. For Cd,

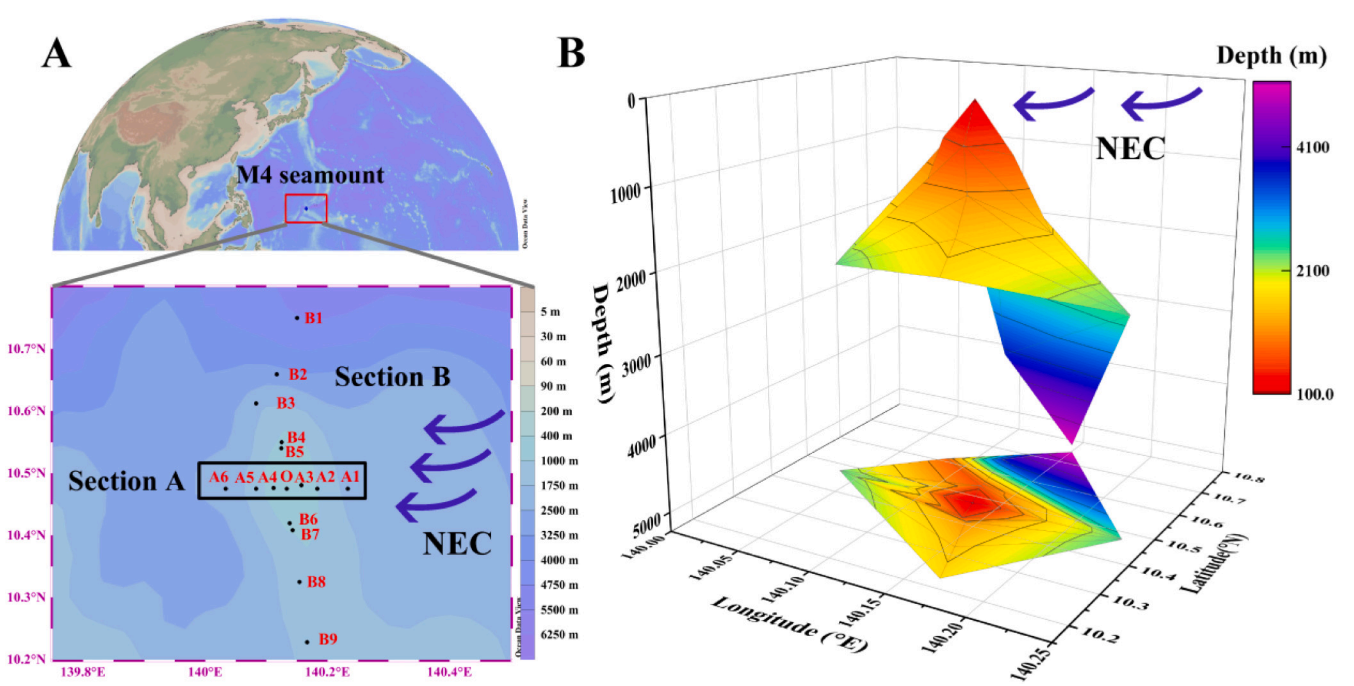

Fig. 1. Station maps of M4 seamount area. (A) The location of M4 seamount area, and the stations were divided into section A and section B. (B) The shape of M4 seamount, and the different color meant water depth. The blue arrows meant the North Equatorial Current (NEC). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

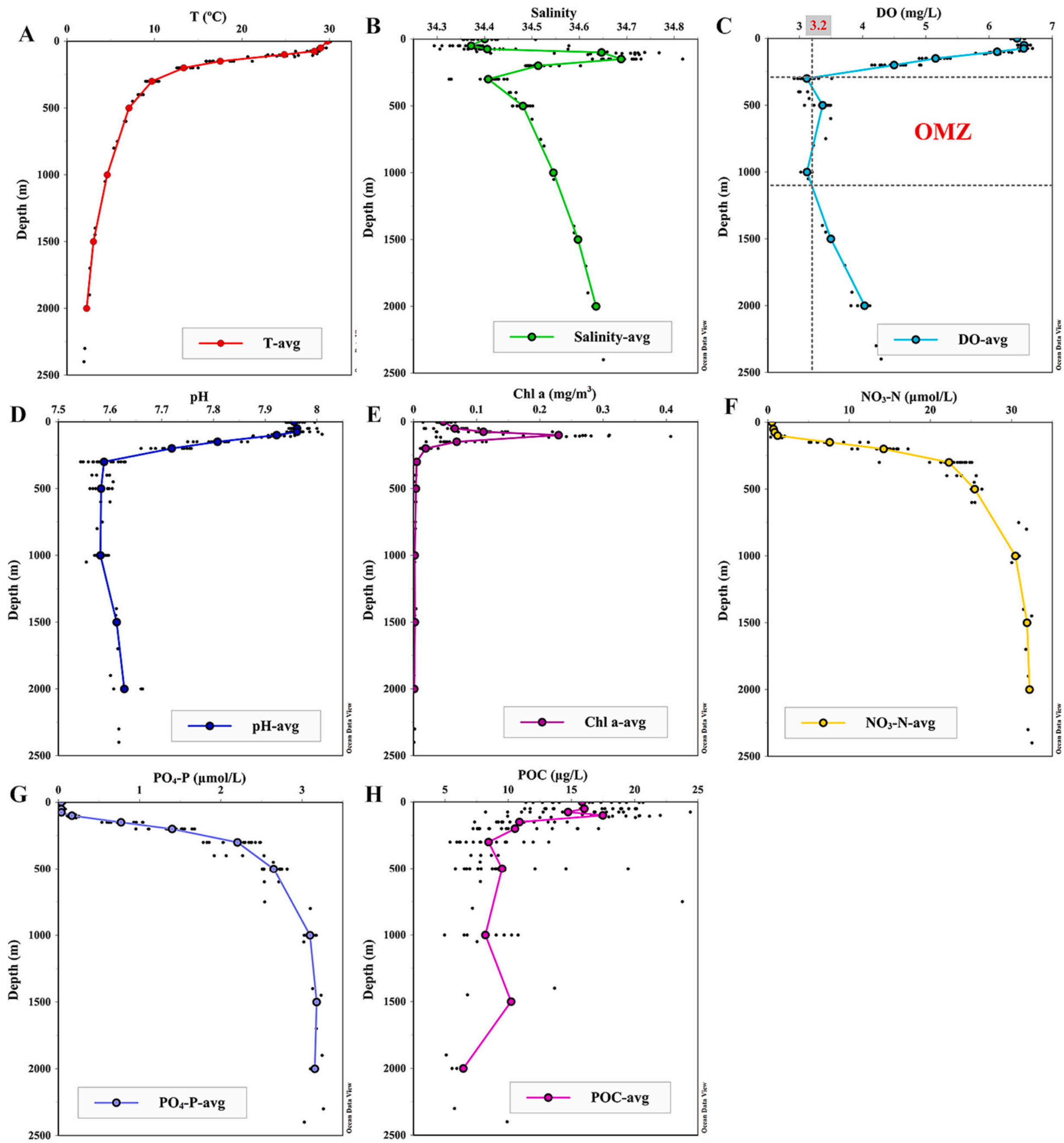

Fig. 2. Vertical distribution of environmental parameters and biogenic elements in M4 seamount area. The dots meant different values of various parameters of each station at different depth, and the lines meant average values of all stations at the same depth. (A) Temperature. (B) Salinity. (C) DO. (D) pH. (E) Chl a. (F) NO_3-N. (G) PO_4-P. (H) POC.

concentrations at different depths were: 0 m - 0.0003 μg/L, 100 m - 0.0006 μg/L, 1000 m - 0.0087 μg/L, and 2000 m - 0.0112 μg/L. Type 4: This type displays minimal changes in metal concentration with increasing water depth. Cu is representative of this pattern (Fig. 3E). At various depths, Cu concentrations were measured as follows: 0 m - 0.154 μg/L, 500 m - 0.152 μg/L, 1000 m - 0.149 μg/L, and 2000 m - 0.141 μg/L.

The vertical distribution of various metals is affected by element characteristics, the marine environment, chemical processes, and marine biological activities, and is mainly divided into seven types: 1) surface enrichment and depletion at depth, 2) mid-depth maxima or minima in the suboxic layer, 3) nutrient, 4) conservation, 5) mid-depth minima, 6) mid-depth maxima, and 7) maxima and minima in anoxic waters (Ellwood, 2008; Annabi-Trabelsi et al., 2021). The vertical distribution of a specific metal can vary significantly based on location, season, depth, and sediment environment. (Salomons and Förstner, 2012; Lagerström et al., 2013). For example, Mn concentrations decrease significantly in areas heavily influenced by atmospheric transport and river input, resulting in a surface enrichment and depletion at depth pattern (Field et al., 2007). In regions with hydrothermal activity, Mn levels rise rapidly in middle or bottom seawater, leading to a mid-depth maxima pattern (Dekov and Savelli, 2004). In the anoxic water column of the Pacific and Indian oceans, Mn reaches maximum values, displaying a mid-depth maxima in the suboxic layer (Konovalov et al., 2004; Tuğrul et al., 2014; Verlaan and Cronan, 2022). The M4 seamount area, contains typical physical, chemical, and ecological structures such as the thermocline, high-salinity zone, OMZ, low pH zone, and DCML (Fig. 2), which may have profound effect on the

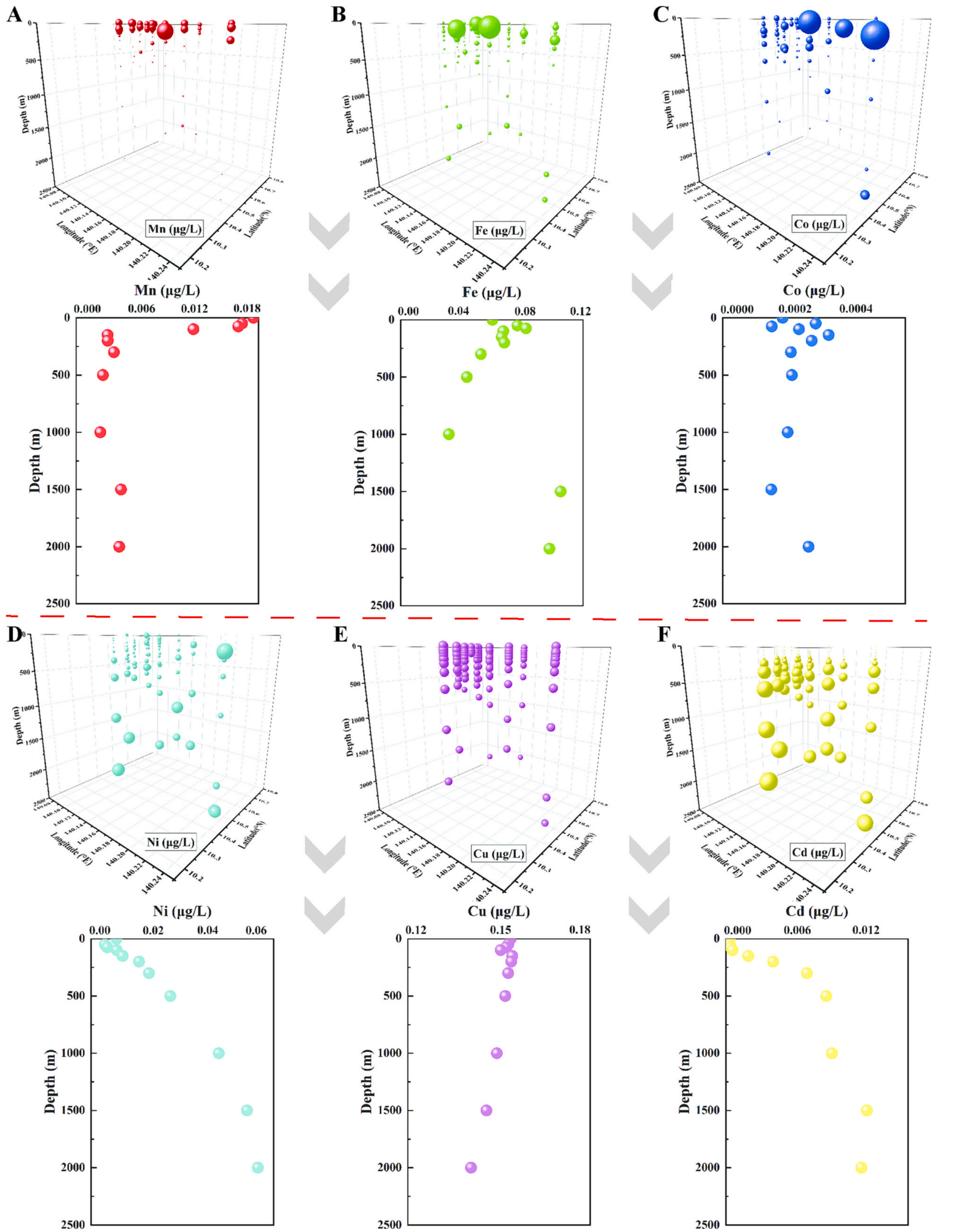

Fig. 3. Vertical distribution of metals in M4 seamount area. In the three-dimensional diagram, the size of the dot meant the relative size of the concentration of metal of each station at different depth. In the two-dimensional diagram, the dots meant the average values of all stations at the same depth. (A) Mn. (B) Fe. (C) Co. (D) Ni. (E) Cu. (F) Cd.

distribution of metals. In this study, the vertical distribution of Mn showed a type of surface enrichment and depletion at depth but rose slowly at depths of 1500 m and 2000 m. Fe and Co showed a type of mid-depth maxima or minima in the suboxic layer. Ni and Cd exhibited nutrient-like patterns, and their vertical distribution characteristics were similar to the distribution of PO_4-P and NO_3-N. Cu demonstrated a conservation pattern, with a relatively small concentration difference between the highest and lowest levels, approximately 30 %. Metal distribution is influenced by various controlled factors, and these patterns vary across environments and regions (Salomons and Förstner, 2012; Lagerström et al., 2013; Twining and Baines, 2013). The vertical distribution structure of metals is relatively complex, except for Ni and Cd, which exhibit relatively simple patterns. In this study, the vertical distribution characteristics of various metals were bound to be closely related to the distribution of environmental parameters and biogenic elements in the M4 seamount area, which will be further discussed in the next section. In this study, the concentration ranges of Mn, Fe, Co, Ni, Cu, and Cd were 0–0.05, 0–0.44, 0–0.0014, 0–0.082, 0.12–0.16, and 0–0.013 μg/L, respectively, while the average concentrations were 0.009, 0.065, 0.0002, 0.02, 0.15, and 0.004 μg/L, respectively. These were roughly similar to the concentration ranges of metals in other sea areas (Table 1), indicating that the concentration range of metals in the open sea areas has little overall change.

In this study, Mn had a significantly positive correlation with other environmental parameters, except for its negative correlation with depth and salinity, and generally decreased with increasing depth (Figs. 3A, 4). Studies have shown that Mn enriched in the surface layer mainly originates from the transport via the atmosphere, rivers, continental shelves, etc. In the seawater, Mn is rapidly and permanently consumed by various biological communities (Field et al., 2007; Lagerström et al., 2013). The M4 seamount area was far from the mainland, with the high surface Mn in this area mainly caused by atmospheric transport. There was a close relationship between Fe and Co ($r = 0.480$, $P < 0.05$), but there was no obvious relationship between these elements and environmental parameters and other metals (Fig. 4). The Fe and Co concentrations were lower in the middle layer and higher in the subsurface layer and bottom layer. The water layer with the minimum value corresponded to the low value zone of DO and pH (Figs. 2C, D; 3B, C). The M4 seamount area had a significant OMZ structure with low DO (minimum: 2.92 mg/L). Low-oxygen structures such as OMZ occur in the sea area with limited circulation and obvious seawater stratification (Wei et al., 2021; Ma et al., 2023), and the low DO and low pH environment in this area has a certain impact on the redox conditions in the waters, thus affecting metal distribution. Studies have shown that in low DO and low pH environments, the vertical distribution of metals such as Mn, Fe, Cr, and Co has changed greatly, often with maximum or minimum values (Delgadillo-Hinojosa et al., 2006; Clement et al., 2009; Ardelan and Steinnes, 2010). It is also necessary to note that the M4 seamount area is also one of the main distribution areas of ferromanganese nodules and Co-rich crusts (Gan et al., 2021; Wang et al., 2021; Xu, 2021). Whether the existence of the seamount has an impact on the distribution of metals such as Fe and Co will be further discussed in the next section. In addition, in this study, the Cu concentration from the surface to the deep layer changed slightly, while the

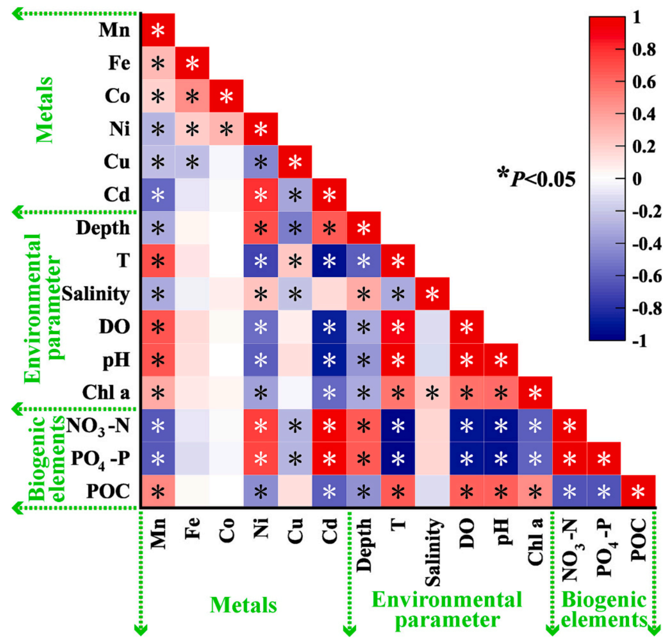

Fig. 4. Person Correlation Analysis result among metals, environmental parameters and biogenic elements in M4 seamount area.
Note: the "*" represented the strong correlation ($P < 0.05$), and the color of the square represents positive (red) or negative (blue) correlation. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

vertical distribution was conservative. There was no obvious relationship between Cu and environmental parameters and other metals (Fig. 4). In some studies, the vertical distribution of Cu had a type of nutrient or mid-depth minima (Wang and Wang, 2007; Salomons and Förstner, 2012), which may be caused by the environmental differences in different research areas.

There was also a close relationship between the vertical distribution of biogenic elements and metals, and the most significant representative was the relationship between nutrients and nutrient-type metals (Song, 2011; Ran et al., 2018). In this study, the vertical distribution of Ni and Cd showed a significant nutrient-type structure. Ni and Cd were not only positively correlated with NO_3-N ($r = 0.746$, $r = 0.965$, $P < 0.05$), but also closely correlated with PO_4-P ($r = 0.736$, r = 0.965, $P < 0.05$) (Fig. 4). Fig. 5 shows the close relationship between Ni and Cd and nutrients; it is evident that Cd has a stronger correlation with NO_3-N and PO_4-P. The bioavailability of nutrient-type metals is similar to that of nutrients; after being absorbed and utilized by phytoplankton in the upper waters, it is transported to the middle and deep oceans by biological pumps, and then decomposed and released, making its concentration significantly higher in the middle and deep oceans (Milne et al., 2010). Notably, although the vertical distribution of Ni and Cd are of the typical nutrient type, there exist certain differences between them. Cd distribution is mainly controlled by the influence of a shallow water

Table 1
Concentration range of metals in different sea areas.

Study area	Depth (m)	Mn (μg/L)	Fe (μg/L)	Co (μg/L)	Ni (μg/L)	Cu (μg/L)	Cd (μg/L)	Reference
Atlantic Ocean	0–1200	0–0.11	0–0.06	0–0.0053	0–0.29	0.06–0.10	0–0.03	Milne et al. (2010)
Atlantic Ocean	0–4000	0–0.09	0–0.04	0–0.0029	0–0.29	0.03–0.13	/	Lagerström et al. (2013)
Southern Ocean	0–1000	0–0.01-0.02	0–0.02	0–0.0014	0.24–0.41	0.06–0.11	0.02–0.11	Wuttig et al. (2019)
Pacific Ocean	0–200	0–0.06	0–0.02	/	/	/	/	Pinedo-González et al. (2020)
Pacific Ocean	0–5000	0–0.04	0–0.04	0–0.0029	0–0.59	0.03–0.32	/	Lagerström et al. (2013)
M4 seamount	0–2500	0–0.05	0–0.44	0–0.0014	0–0.082	0.12–0.16	0–0.01	This study

Note: the "/" represented no data.

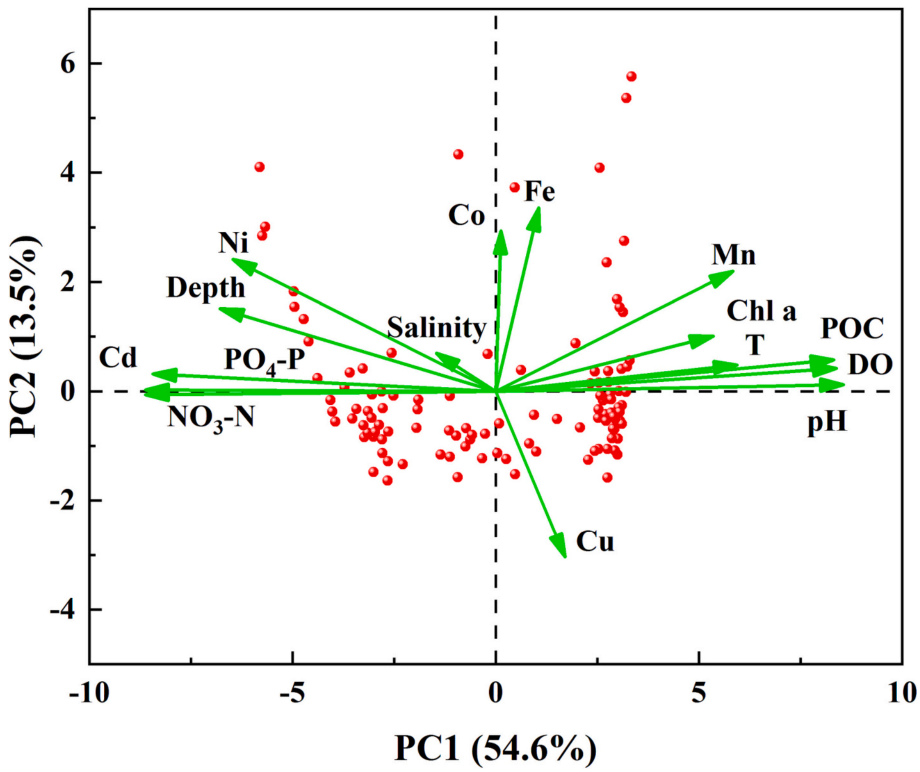

Fig. 5. PCA result among metals, environmental parameters and biogenic elements in M4 seamount area.
Note: the closer the position and length of the arrows represented the closer the relationships.

regeneration cycle, and is more closely related to NO_3-N and PO_4-P, with a maximum value at the middle depths (Sunda and Huntsman, 2000; Hendry et al., 2008). In contrast, Ni may be related to the regeneration cycle combining shallow water and deep water, with its concentration increasing from the middle layer to the bottom layer (Milne et al., 2010; Salomons and Förstner, 2012). In this study, the sampling water depth was only 0–2500 m, while the water depth of 0–5000 m generally describes the distribution characteristics of nutrient-type metals. Therefore, due to the limitation of the sampling water depth, the difference between the vertical distribution of Ni and Cd was not very obvious (Fig. 3D, F). However, as shown in Figs. 4 and 5, as well in relevant reports (Ellwood, 2008; Salomons and Förstner, 2012), there were differences in the distribution of Ni and Cd.

POC is also a typical representative of biogenic elements. POC is closely related to marine biological activities, and is an important parameter to evaluate the productivity level of a certain sea areas (McNichol and Aluwihare, 2007; Malinverno and Martinez, 2015; Ma et al., 2021c). A part of POC is decomposed by microorganisms and returns to the form of inorganic carbon, while the other part is buried in the seabed, which is the main form of carbon output and fixation in seawater. In this study, POC had a significantly positive correlation with Mn ($r = 0.495$, $P < 0.05$). The POC and Mn concentrations gradually decreased and slowly increased with the increase of water depth, t (Figs. 2H, 3A). In addition, POC showed a significantly negative correlation with Ni and Cd ($r = -0.440$, $r = -0.604$, $P < 0.05$; Figs. 4, 5), and had no significant relationship with other metals. POC is also closely related to the productivity of phytoplankton (Song, 2011; Ma et al., 2021c). In this study, POC was closely related to Chl a ($r = 0.476$, $P < 0.05$), and they were closely related to Mn, indicating a similar vertical distribution type of phytoplankton and Mn, thus proving that Mn can be partially absorbed and consumed by phytoplankton and other biological communities (Sunda and Huntsman, 2000; Twining and Baines, 2013).

"Seamount effect" refers to the upwelling, circulation, Taylor column, and other currents around the seamount that cause the high concentration of nutrients in the upper waters, promote the growth of phytoplankton, and then attract zooplankton and fish (Dai et al., 2020a, b; Wang et al., 2023). Upwelling is the most important reason for the formation of the "seamount effect." In seamount research, the existence of upwelling is often determined by the rise of the isotherm (Genin, 2004). In this study, there was no upwelling in depths of 0–2500 m (Fig. 6A). On the contrary, near station O on the seamount summit, the isotherm and isohaline subsided (Fig. 6A, B), and the isolines of Mn, Ni, and Cd also changed simultaneously (Fig. 6C, D, E). In fact, not all seamounts have upwelling near them; even the same seamount may not exhibit upwelling if examined at different times. For example, upwelling was rarely found in deep-sea mountains (Ma et al., 2021b). However, in many surveys of shallow seamounts or medium-deep seamounts such as the Great Meteor, Minami-kasuga, and Cobb, the "seamount effect" was only found in a few studies (MouriÑO et al., 2001; Ma et al., 2021c; Ma et al., 2023). For the M4 seamount area, from the scale of 0–200 m in the upper waters during the survey in August 2017, there was significant circulation and upwelling, which greatly improved the oligotrophic level in this region, and also promoted the aggregation of phytoplankton near the seamount summit, forming the "seamount effect" (Dai et al., 2020a; Ma et al., 2021b). This study serves as the second survey of M4 seamounts in May 2019, focusing on the spatial heterogeneity of metals. No obvious positional relationship between the location of seamounts and the distribution of various metals was observed (Fig. 6C–H). Meanwhile, only from the scale of 0–2500 m, the impact of seamount on the upper waters was weak, and whether there was "seamount effect" in this survey must be further investigated.

Notably, Mn, Fe, and Co in some water layers in contact with the bottom of the seamount increased significantly (Fig. 6C, F, G), indicating that although there is no "seamount effect" in the M4 seamount at depths of 0–2500 m, the existence of seamounts may still have a certain impact on the distribution of metals. Seamounts are also the main distribution areas of mineral resources. Globally, many seamounts have become mining areas and have been undergoing continuous

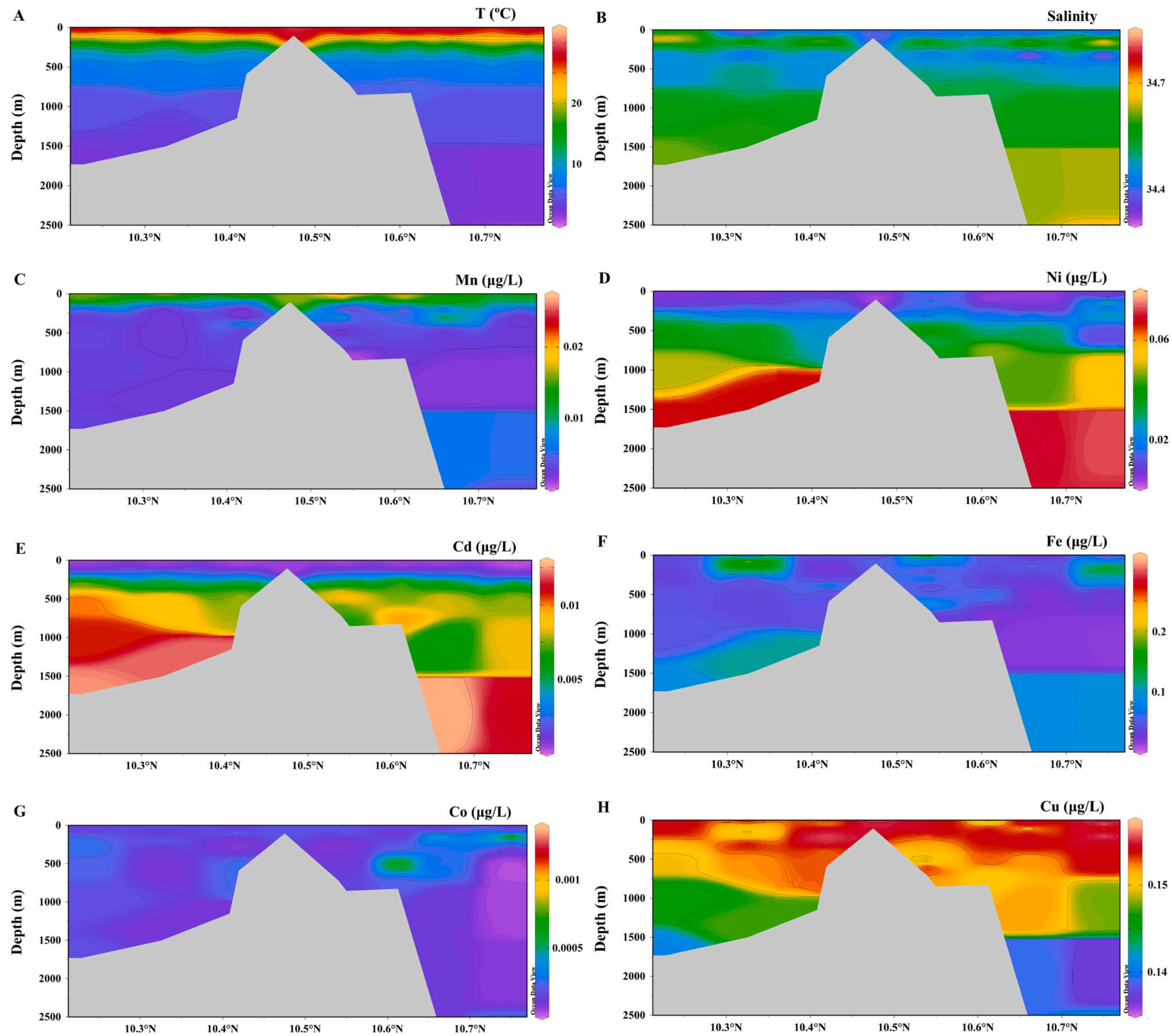

Fig. 6. Metals, temperature and salinity in section B of M4 seamount area. (A) Temperature. (B) Salinity. (C) Mn. (D) Ni. (E) Cd. (F) Fe. (G) Co. (H) Cu.

development (Clark et al., 2010; Rowden et al., 2010). The M4 seamount is located at the edge of the Magellan seamount mining area. Many studies have found that there is a large number of ferromanganese nodules and Co-rich crusts around the seamount (Xu, 2021). Ferromanganese nodules and Co-rich crusts are rich in metals such as Mn, Fe, Co, and Ni, which could be released into the surrounding environment, thus significantly increasing metal concentrations (Zhang et al., 2016; Ren et al., 2022). It was evident that the concentration of metals such as Mn, Fe, and Co in the M4 seamount gradually decreases with water depth (Fig. 3A–C), but significantly increases in the bottom waters. This change may be closely related to abundant ferromanganese nodules and Co-rich crusts in the M4 seamount. Many studies have noted that the vertical change in the concentration of metals is closely related to typical environments such as seamounts, hydrothermal solutions, and cold seepage. A large amount of metals can be released into adjacent waters, thus significantly changing the vertical distribution structure of these metals (German et al., 2016; Keith et al., 2016; Nozaki et al., 2016).

CRediT authorship contribution statement

Jun Ma: Writing – original draft, Visualization, Formal analysis, Investigation, Funding acquisition. **Xuegang Li:** Conceptualization, Project administration, Funding acquisition. **Jinming Song:** Methodology, Resources, Writing – review & editing, Supervision. **Lilian Wen:** Methodology, Formal analysis, Investigation. **Xianmeng Liang:** Investigation. **Kuidong Xu:** Investigation, Funding acquisition. **Jiajia Dai:** Formal analysis, Investigation, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.marpolbul.2023.115664.

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