Distribution of trace elements in the Middle Part of South China Sea deep seawater

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Abstract. During the investigation in the South China Sea in the summer of 2018, the sea water samples were for some trace elements (such as Cu, Zn, Fe, Mn, Ni, Se, Mo, Co and V) analyses from different layers of 12 stations according to the standard sampling specifications. The seawater samples of different depths were directly measured by inductively coupled plasma mass spectrometry. The distribution of trace elements in the South China Sea water was investigated. It could be seen from the analytical results that the contents of Fe, Mo, Co and V in deep seawater at different depths have little change with depth, and other elements vary greatly with depth. There were significant differences in the content of trace elements between different stations, and the contents of Mn, Ni and Se fluctuated greatly. After comprehensive comparative analysis, it can be found that for most trace elements, the sites with lower content were D3 and D5, the depth of trace elements is 500m, and the content of Cu, Zn, Ni and Se is much lower than that of the state. A type of seawater quality standard.

1. Introduction
Deep seawater is another important deep-sea economic resource\textsuperscript{1-4} worth paying attention to in the South China Sea (SCS) after oil and gas fields\textsuperscript{4-6}. Deep seawater refers to the seawater at a depth of less than 200 m, which has the characteristics of low temperature stability, eutrophication, clean and without being polluted\textsuperscript{7-8}. The composition and proportion of deep seawater are similar to human body fluid, and it is an irreplaceable "balanced trace element" resource, with higher extraction, processing and application advantages\textsuperscript{9-15}. Since the 1970s, the developed countries such as America, Japan began to exploit and utilize the deep seawater, some products have reached the commercial and practical level\textsuperscript{11, 16-21}. However, in China, the basic research on the use of deep seawater were still in the blank stage. Compared with the United States, Japan, South Korea, other developed countries and China Taiwan region\textsuperscript{14, 22-25}, China's relevant technology research and product development level gap is huge.  

China is a major maritime country with a coastline of more than 18,000 kilometers. The SCS has the deepest depth area among the China's four big sea area, the average water depth is 1212 meters, the deepest is up to 5377 meters. SCS has a wealth of deep seawater resources, which development potential is huge, especially in central SCS waters, with all the development and utilization, short deep water offshore distance, the advantages of nearshore submarine topography steep, and good condition of exploitation\textsuperscript{26-27}. Previous studies on trace elements in the SCS mainly focused on surface seawater or seabed sediments\textsuperscript{28-32}, and few studies were conducted on the distribution of trace elements in deep
seawater33-35. Due to the lack of basic data such as the distribution of deep seawater resources and the water quality under the jurisdiction, many research are blocked, which seriously restricts the development space of industrial utilization of deep seawater in China 36-37. Therefore, it is urgent to investigate the regional characteristics and water quality characteristics, evaluate the effective utilization of deep seawater resources, promote the development and utilization technology, and enhance the competitiveness of marine science and technology in China.

Deep seawater samples were taken from the central SCS in different depth among 12 stations. The overall objectives of this work were to: (1) analyze content of the trace elements (Cu, Zn, Fe, Mn, Co, Ni, Se, Mo and V); (2) investigate the vertical distribution pattern. This study can provide reliable data of trace elements in deep seawater of the SCS, provide basis for rational selection of water intake point and accurate selection of exploitable and utilized areas for providing available raw water for the development and utilization technology of deep seawater resources development of functional products.

2. Sample collection and testing

2.1. Sample collection and preservation
In May 2018, the seawater samples required for research were collected from the central South China Sea. A total of 12 sample collection stations were selected for this cruise, as shown in Figure 1. The samples were collected at depths of 5 m, 100 m, 200 m, 300 m, 500 m and 800 m, and the elements tested included: copper, zinc, iron, manganese, nickel, selenium, molybdenum, cobalt and vanadium.

The 0.45 µm acid ester filter membrane was immersed in dilute nitric acid for 24 h, repeatedly rinsed with ultrapure water, and dried for use. The sample vial was immersed in nitric acid for more than 24 h and rinsed repeatedly with deionized water for use.

The collected seawater sample was filtered with a 0.45 µm acid ester filter, and then the filtered filtrate was collected. The filtrate was acidified (pure grade) and fixed to pH <2.0, and stored in a polyethylene sample vial, and the vial was sealed and stored in a refrigerator.

2.2. Sample testing
Seawater samples that had been acidified with nitric acid were thawed into the laboratory and then measured using ICP-MS 7500ce ((Agilent, USA).

![Figure 1. South China Sea Trace Element Research Station Map](image-url)
3. Results and Discussion
The concentration and distribution pattern of Cu, Zn, Fe, Mn, Ni, Se, Mo, Co and V in seawater samples in the SCS are shown in Table 1 and Figure 2-9. The results show that there are differences in the concentration range of trace elements in seawater from different depths, which Fe, Mo, Co and V vary little and the contents of other elements fluctuate greatly with the increase of depth. The content of Cu, Zn and Se is lower in 500 m. However, the content of Mn changed disordered with the increase of depth, and the content of Ni was lower in the surface layer. The content of Cu, Zn, Ni and Se is far lower than the national standard of Grade I Seawater Quality.

| Depth (m) | Cu (μg/L) | Zn (μg/L) | Fe (mg/L) | Mg (μg/L) | Ni (μg/L) | Se (μg/L) | Mo (μg/L) | Co (μg/L) | V (μg/L) |
|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| 5         | 0.12-2.12 | 0.1-8.7   | 0.0045-0.0105 | 0.01-0.82 | 0.38-1.01 | 0.59-1.31 | 0.01-0.012 | 0.07-0.11 | 2.58-2.97 |
| 100       | 0.12-1.47 | 0.1-7.1   | 0.0045-0.0077 | 0.01-0.44 | 0.23-0.72 | 0.56-1.07 | 0.01-0.012 | 0.07-0.12 | 2.37-2.97 |
| 200       | 0.13-1.51 | 0.4-6.1   | 0.0045-0.0058 | 0.01-0.69 | 0.27-0.93 | 0.46-1.15 | 0.01-0.012 | 0.07-0.12 | 2.51-2.98 |
| 300       | 0.15-2.63 | 0.3-3.4   | 0.0045-0.0083 | 0.01-0.55 | 0.23-0.82 | 0.64-1.41 | 0.01-0.012 | 0.06-0.13 | 2.44-3.02 |
| 500       | 0.16-1.62 | 0.1-3.5   | <0.0045     | 0.02-0.33 | 0.31-0.59 | 0.63-1.33 | 0.01-0.012 | 0.07-0.13 | 2.32-2.94 |
| 800       | 0.18-1.76 | 0.3-3.3   | 0.0045-0.0083 | 0.01-0.53 | 0.43-0.8 | 0.42-1.38 | 0.01-0.013 | 0.07-0.13 | 2.35-2.96 |
| 1000      | <0.12     | 0.6       | <0.0045     | 0.05 | 0.46 | 1.14 | 0.01 | 0.07 | 2.69 |

Grade I Seawater Quality:
- Cu: ≤5 μg/L
- Zn: ≤20 μg/L
- Fe: < 0.0045 mg/L
- Mg: ≤5 μg/L
- Ni: ≤10 μg/L
- Se: -
- Mo: -
- Co: -
- V: -

Figure 2. Distribution pattern of Cu along the water column.
Figure 3. Distribution pattern of Zn along the water column.
As can be seen from figure 2-9 and table 1, the contents of Mo, Co and V in seawater at the same depth among different stations are similar. At 300 m, the lowest Co content located at D2 (0.12 g/L), and the highest located at D8 (2.63 g/L). Zn lowest content located at D5 (0.1 g/L), the highest located
at D10 (3.8 g/L); Fe content was less than 0.0045mg/L at all sites except D11 (0.0083mg/L). The Mn lowest content located at D8 and D6 (<0.01 g/L), and the highest located D11 (0.53 g/L). The Ni lowest content located at D3 (<0.23 g/L), and the highest located D6 (0.74 g/L). The Se lowest content located at D7 (0.42 g/L) and the highest located at D6 (1.36 g/L).

In 500m, the station with the lowest Cu content was D2 (0.12 g/L), and the station with the highest Cu content was D7 (1.47 g/L). The station with the lowest Zn content was D4 and D6 (<0.1 g/L), while the station with the highest Zn content was D8 (2.3 g/L). Most station with Fe content were less than 0.0045mg/L, and the highest content located at D2 (0.0083mg/L). The lowest Mn content located at D4 and D9 (<0.01 g/L), while the highest located at D5 (0.69 g/L). The lowest Ni content located at D4 (<0.23 g/L), and the highest located at D10 (0.93 g/L). The lowest Se content located D10 (0.46 g/L) and the highest located D9 (1.12 g/L).

At 800 m, the lowest Co content located D4 (0.23 g/L), and the highest located D7 (2.12 g/L). The lowest Zn content located at D8 (1.7 g/L), and the highest located at D11 (6.5 g/L). Fe content at all stations was less than 0.0045mg/L. The lowest Mn content located at D6, D7 and D8 (<0.01 g/L), and the highest located at D10 (0.57 g/L). The Ni lowest content located at D3 and D4 (0.34 g/L), while the highest located at D7 (1.01 g/L). The lowest Se content located at D4 (0.76 g/L) and the highest located D5 (1.38 g/L).

4. Conclusion
Deep seawater contains very rich trace elements and minerals. In fact, deep sea water contains more than 90 kinds of minerals and trace elements needed by the human body. The deep seawater concentration process will affect the preparation process of deep sea functional products. The moderate amount of trace elements is good for the health of the human body; otherwise excessive trace elements are harmful to the human body. Therefore, when the water intake point is selected, the content of trace elements in the raw material water is required to be low. By analyzing and comparing the trace element content of deep seawater at different sites and different depths, it was found that the content of trace elements at 500 m was low. The contents of Mo, Co and V are similar at different sites, and the contents of Fe at most station were very low. After comparative analysis, for most trace elements, the stations with lower contents were located at D3 and D5.

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