A Study on Comprehensive Evaluation of Multiple-depth Sea Water Quality in the South China Sea

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Abstract. During the investigation in the South China Sea in the summer of 2018, the sea water samples were for temperature, salinity, dissolved oxygen, pH, nutrient salts (NO\textsubscript{3}\textsuperscript{-}N, NO\textsubscript{2}\textsuperscript{-}N, NH\textsubscript{4}\textsuperscript{+}-N, PO\textsubscript{4}\textsuperscript{3-}-P, SiO\textsubscript{2}-Si), essential elements (Na, K, Mg, Ca, Sr, Cl, Br, B), trace elements (Cu, Zn, Fe Mn, Ni, Se, Mo and V), heavy metal (Hg, Pb, As, Cd), organic elements (TOC, DOC, GOC), chlorophyll and microorganisms 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 several elements in the South China Sea seawater was investigated. It could be seen from the analytical results that the water temperature, salinity, pH, dissolved oxygen, the content of NO\textsubscript{3}\textsuperscript{-}N, PO\textsubscript{4}\textsuperscript{3-}-P, SiO\textsubscript{2}-Si, K\textsuperscript{+}, Mg\textsuperscript{2+}, Ca\textsuperscript{2+}, Sr\textsuperscript{2+}, Cl\textsuperscript{-}, Br\textsuperscript{-}, B\textsuperscript{3+}, Zn, Mn, V, Cr, GOC and Chlorophyll was significantly correlated with depth of seawater.

1. Introduction
Nowadays, human society faces three major threats, namely, exhaustion of terrestrial resources, deteriorating environment and increasing population, asking for resources from the sea has become an important way to solve the resource crisis in coastal areas and realize sustainable development. Deep seawater refers to the seawater at a depth of less than 200m, which has the characteristics of low temperature stability, eutrophication, clean and without being polluted [1, 2]. 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 [3-5]. These are magnesium, calcium, potassium, zinc, vanadium, selenium, and chromium. [6, 7] It has been documented that the benefits of drinking DSW include the prevention of hyperlipidaemia, [8] hypertension, [9] atopic eczema/dermatitis syndrome,\textsuperscript{[10]} and arteriosclerosis.\textsuperscript{[11]} Moreover, the consumption of DSW reduces the low-density as well as total lipoprotein cholesterol in subjects with hypercholesterolemia [12] and prevents high fat diet induced lipid oxidation and accumulation in liver.\textsuperscript{[13]} In addition, by using high fat diet-induced diabetic animal models, DSW has been proven to exert an antidiabetic effect\textsuperscript{[14]} and protects cardiovascular system.\textsuperscript{[15]} Our previous research demonstrates that the consumption of deep sea minerals possesses several protective effects in a streptozotocin (STZ)-induced diabetic rat model, such as amelioration of apoptotic liver damage\textsuperscript{[16]} and a prolonged life span. 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, 17, 18]} 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, China's relevant technology research and product development level gap is huge [19, 20].

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 [21-23]. Previous studies on trace elements in the SCS mainly focused on surface seawater or seabed sediments [24-26], and few studies were conducted on the distribution of trace elements in deep seawater [14, 24, 25, 27]. Due to the lack of basic data such as the distribution of deep seawater resources and the water quality under the jurisdiction, many researches are blocked, which seriously restricts the development space of industrial utilization of deep seawater in China. 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 [28-30].

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 temperature, salinity, dissolved oxygen, pH, nutrient salts, essential elements, trace elements, organic elements, chlorophyll and microorganisms; (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. Materials and methods

2.1. Surveyed sea area and investigation stations

Southeast, west and southwest of Hainan island, within 100 km of the Xisha islands. A total of 30 survey stations were set up. The distribution of stations is shown in Fig. 1.

**Figure 1** The sea area and station settings of survey
2.2. Time of survey at sea
April 28-May 13, 2018.

2.3. Research ships and detection methods
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. The research ship chosen for this voyage was “Tianlong” scientific research ship of Guangdong Ocean University. SBE917plus (including CTD, chlorophyll, dissolved oxygen and other probes) and SBE32 water sampler (36 bottles ×10L and 12 bottles ×2L each) were used to form a self-contained CTD water sampler system, which was hoisted to the preset depth by Tianlong steel cable winch on the aft deck to conduct observation of temperature and salt depth. The stations that completed the total factor sampling analysis of deep sea water included D2, D5, D10, D12, D14, D15, D16, D18, D19, D20, D24, D25, D26, D28 and D30, and the remaining 15 stations only collected and detected water samples of major elements, trace elements, nutrient salts, pH, dissolved oxygen, temperature and salinity. Samples were filtered and preserved on board and brought back to the laboratory for analysis included dissolved organic carbon, granular organic carbon, chlorophyll, amino acids, and protein peptides. 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.

2.4. Investigation items and test methods
The investigation items included temperature, salinity, dissolved oxygen, pH, nutrient salts, major elements, trace elements, organic elements, chlorophyll and microorganisms. The main elements, trace elements and nutrients, pH and dissolved oxygen were analyzed for the whole site and all samples, the analysis of other factors is 50% of the total number of stations.

2.4.1. Water sample stabilization
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.

2.4.2. The detection of physical property
Depth, temperature, salinity, pH was measured in real time by the water collector with its own electrodes. After seawater was collected, the sample was firstly fixed as 2.5.1, and then determined by HQd Portable multiparameter water quality tester (HACH, Loveland, US).

2.4.3. Determination of nutrients of seawater
The contents of NO$_3$-N, NO$_2$-N, NH$_4$-N, PO$_4$-P were detected by Bran+Luebbe AutoAnalyzer 3 (SEAL Analytical, UK). The content of Si(OH)$_4$ were measured using typical spectrophotometric methods(31). The linear working range we used was 0.16-32 µmolL$^{-1}$ for Si(OH)$_4$. The detection limits for Si(OH)$_4$ were 0.05 µmolL$^{-1}$.

2.4.4. The detection of ion element of seawater
After seawater was collected, the sample was firstly fixed as 2.5.1. Sample aliquots were used to determine the Na, K, Mg, Ca, Sr, Cl, Br, B, Cu, Zn, Fe, Mn, Ni, Mo, Co, V, Se mass fractions by ICP-MS using the Spectrometer X-Series 2 (Thermo Jarrell Ash, USA). Preparation of internal standard solution, a certain amount of Re and Rh standard solution (concentration of 1000 g/mL, National Center for Analysis and Testing of Nonferrous Metals and
Electronic Materials) was absorbed, and the mixed internal standard solution containing Re and Rh of 5 ng/mL was prepared by 1% nitric acid solution. ICP-MS conditions, RF power was 1350 w, plasma gas flow rate was 15.0 L/min, carrier gas flow rate was 1.12 L/min, oxide index (cerium oxide particles/cerium), double charge indicator (bivalent barium ion/barium ion), integration time of 0.1 s, atomizer for high salt atomizer, atomizing chamber temperature is 2 °C, repetitions for 3 times, peristaltic pump speed resolution of 0.1 RPS, sampling depth is 7.0 mm. The chloride ions in seawater were determined by potentiometric titration. 2ml seawater was diluted to 50mL with deionized water and titrated with silver nitrate solution of 0.01mol/L. The determination of heavy metals, using microwave digestion, the contents of Hg, Pb, As, and Cd were determined by graphite furnace atomic absorption spectrometry.

2.4.5. The of detection of organic carbon of seawater
The total organic carbon in the water sample was determined by a 5000TOCi Total organic Carbon analyzer (Mettler Toledo, Zurich, Switzerland). The determination of dissolved organic carbon (DOC) was that the water sample was filtered by 0.45 glass fiber filter membrane, and the TOC content in the filtrate was the DOC content in the water sample. The determination of granular organic carbon (GOC) was as follows: the water sample was filtered by 0.45 glass fiber filter film, which was dried to constant weight at 65 °C, fumigated with hydrochloric acid for 12h, and then dried to constant weight at 65 °C. After high temperature combustion, the carbon content in the sample was oxidized to CO₂, and detected by non-dispersion-infrared detector.

2.4.6. Determination of chlorophyll content and total number of bacterial colonies of seawater
The content of chlorophyll was detected by high performance liquid chromatography (HPLC). Methanol and acetone were used as mobile phases with a volume ratio of 80:20, and glacial acetic acid with a mass fraction of 0.1% was added into the mobile phase at a flow rate of 1.0mL/min. The chromatographic peak area of each pigment was used for quantitative determination of chlorophyll A and chlorophyll B, which could be obtained from the working curve by external standard method. The total number of bacterial colonies was determined by plate counting method. Samples will be made into 4 different increasing 10 times dilution, and then from each in 1 ml put in the sterilization of plating and nutrient agar mix, under a certain temperature, cultivation of 48 hours, each number of colonies formed in the plate, on the basis of dilution ratio, calculated per ml contains the total number of bacterial colonies in the original sample.

3. Results and discussion

3.1. The distribution characteristics of Basic physical and chemical properties of seawater
As the Figure.2 showed, temperature, salinity, pH value and dissolved oxygen of sea water all showed obvious regularity with the change of sea water depth. Among them, the temperature decreased with the increase of the depth of seawater, with the increase of the depth the pH of seawater gradually tended to neutral from weak alkalinity and the dissolved oxygen decreased, and the salinity first increased and then decreased with the increase of the depth. The salinity reaches its maximum at the depth layer of 50-200 meters, and then decreased with the increase of the depth. As the Table.1 showed, the correlation between water temperature, salinity, pH, dissolved oxygen and seawater depth was extremely significant through SPSS Pearson correlation analysis. This is due to the decrease of dissolved oxygen as the depth of the sea increases, the gradual decrease in the temperature of the sea with the decrease in light, the decrease in salinity with the decrease in solubility, and the slow decline in pH to near neutral.
Figure 2. Profile analysis of temperature, salinity, pH and dissolved oxygen in seawater

Table 1. The correlation analysis between the physical and chemical properties of seawater and its depth.

| Depth | Pearson Correlation | Temperature | Salinity | pH | DO |
|-------|---------------------|-------------|----------|----|----|
| Sig. (2-tailed) | 1 | -0.91** | 0.40** | 0.82** | 0.86** |
| N     | 144 | 144 | 144 | 144 | 144 |

**. Correlation is significant at the 0.01 level (2-tailed).
*. Correlation is significant at the 0.05 level (2-tailed).
b. Cannot be computed because at least one of the variables is constant.

3.2. The distribution characteristics of nutrient salts concentration

According to the comprehensive analysis of the line map and section map (Figure 3), there is no obvious trend of change of ammonia nitrogen in seawater with the change of depth, and the ammonia nitrogen content in seawater at each point is at a low level, the contents of nitrate, phosphate and silicate all increased with the deepening of depth. Through SPSS Pearson correlation analysis, the content of phosphate and silicate all had extremely significant correlation with depth, this may be related to the dissolution of phosphate and silicate from the sea floor. According to the profile analysis, the increasing trend of the three nutrient salts was basically the same, approaching the maximum concentration of the seabed.
3.3. The distribution characteristics of essential elements’ concentration

According to the analysis of the line chart and section diagram (Figure 4), the sodium ion concentration did not show regular change with the deepening of seawater depth, which was inconsistent with the change rule of salinity above. The content of potassium and magnesium increased first and then decreased with the increase of seawater depth, which was consistent with the change of salinity. The content of calcium ion and strontium increases gradually with the increase of seawater depth and reaches the maximum value at the bottom of the sea. With the increase of the depth of seawater, the content of chloride ion first increased and then decreased, and the content of bromide ion and boron element reached the maximum at the depth of 100-200 meters, and then showed a small decrease, showing an overall trend of increasing with the depth. The general distribution trend of sodium ion and potassium ion is approximately the same.

Figure 3 Variation tendency of nutrient salt with depth and profile analysis
3.4. The distribution characteristics of trace elements’ concentration

According to the analysis of the line chart and section diagram, the copper ion content in seawater is relatively low, and copper ion content is detected at part stations, and the copper ion content presents a rising trend with the deepening of depth. The zinc ion content in the shallow sea water is low or close to zero, and the zinc ion concentration gradually increases with the deepening of the depth, reaching the maximum at the depth of 500-800 meters and tending to be stable. The content of manganese ions in shallow seawater is relatively high. With the deepening of seawater depth, the content of manganese ions in deep seawater decreases gradually, and the content of manganese ions in some sites tends to zero. With the increase of seawater depth, the nickel ion content showed a regular growth trend and reached its maximum value at the bottom (0.8-1g). The content of molybdenum element did not change regularly with the depth of seawater and the difference between stations was great. The content of vanadium varies greatly among stations, and the vanadium content increases slowly with the increase of seawater depth in the same station. The distribution of cobalt is similar to that of vanadium, but there is no significant correlation between the distribution and depth of cobalt. According to Figure.5, the distribution characteristics of selenium on the seafloor are similar to that of cobalt, and the distribution of selenium varies greatly among stations, and there is no significant correlation between selenium at the same station and the depth of the sea water. The contents of Zn (zinc), Mn (manganese) and V (vanadium) of trace elements detected were significantly correlated with the depth. At the same depth, the contents of Cu, Mn, Ni, Mo, Co, V and Se in different stations were significantly different. The content of iron in seawater is low, and it will fluctuate under the influence of biological elements.

Figure 4: Variation tendency of essential elements’ concentration with depth and profile analysis
3.5. The distribution characteristics of heavy metal

It can be seen from Figure 6 that the lead content in the four heavy metals detected is very low, and only the seawater samples of two stations have detected lead. It can be seen from the profile that the distribution rules of mercury and arsenic are similar, but it can be seen from the line map that the distribution of arsenic in seawater of each station is less different and the change trend is consistent. The distribution of chromium is similar to that of mercury and arsenic. According to the profile analysis, the distribution of the four heavy metals is similar except for Pb.
3.6. The distribution characteristics of organic matter

In this study three kinds of organic elements were investigated, and the distribution rules of total organic carbon and dissolved organic carbon were consistent according to the comparative analysis of the profile. Granular organic carbon was mainly distributed in shallow sea water, and its content tends to be stable with the deepening of sea water.

3.7. The distribution characteristics of biological elements

The contents of chlorophyll and bacteria in seawater were investigated. It can be seen from the figure that chlorophyll exists in the shallow sea water, which decreases rapidly with the decrease of the depth of the sea water. There is no chlorophyll in the sea water with a depth of 200m or more, and the difference in chlorophyll distribution between different stations is not obvious. This is due to a lack of light in the deep ocean, which prevents photosynthesis from producing chlorophyll. The distribution of bacterial total was significantly different between stations, and the variation trend of bacterial total distribution at different depths in the same station was not obvious. Chlorophyll distribution is significantly correlated with seawater depth, but not correlated with station position.
4. Discussion

There is a potential correlation between biological elements and physical and chemical characteristics of seawater. Through SPSS software analysis, among the biological related elements (chlorophyll, total number of bacteria), the distribution of chlorophyll is closely related to the physical and chemical properties of seawater, specifically, it is significantly related to the temperature, salinity, pH and dissolved oxygen of seawater, There was no correlation between the total number of bacteria and the physical and chemical properties of seawater. This is because temperature, sunlight and inorganic salinity are essential for the survival of chlorophyll-rich planktonic microbes.

Among the main elements, the elements significantly related to chlorophyll distribution were magnesium, calcium, strontium, chlorine, bromine, and boron. And the total bacterial population distribution had no significant correlation with the distribution of all the main elements. It’s due to that, compared with fresh water, microorganism quantity of sea water is less, and the survival of microorganisms associated with a number of conditions, for example, temperature, salinity, the species and content of the main elements and trace elements, under the common effect in a variety of conditions, there is no correlation between microorganism in seawater and its quality.

Among nutrient salts, the content of nitrate, phosphate and silicate was significantly correlated with the distribution of chlorophyll, while the total number of bacteria was not correlated with nutrient salts, this is because the survival of autotrophic plankton such as algae requires the absorption of inorganic nitrogen and phosphorus from the environment for cell synthesis. Silicon is the main constituent structure of the cell shell of diatoms, so there is a significant correlation between contents of nitrate, phosphate silicon and chlorophyll. However, the content of nitrogen, phosphorus and silicon was not a limiting factor for the survival of bacterial microorganisms, so there was no significant correlation.

All organic elements (total organic carbon, soluble organic carbon, and particulate organic carbon) showed significant correlation with chlorophyll, and all organic elements have significant correlation with the total number of bacteria. The distribution of bacteria was dependent on the distribution of organic matter. This is because bacteria are heterotrophic microbes, and their growth depends on the organic carbon in the environment, so the distribution of bacteria is significantly correlated with the content of organic carbon. Although the synthesis of chlorophyll is not dependent on the environmental organic carbon, but in the process of the growth of marine organisms which contain rich quantity of chlorophyll can produce secretion of organic carbon such as extracellular polysaccharides to the environment, and the death and disruption process of the microbial cell will along with the release of chlorophyll, organic carbon and nitrogen into environment, so there was a significant correlation between organic carbon and chlorophyll content.

5. Conflict of Interest

None.

6. References

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