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Estimating the Absolute Salinity of China Offshore Seawater Using Nutrients and Inorganic Carbon Data

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Abstract. In June 2009, the Intergovernmental Oceanographic Commission of UNESCO released the international thermodynamic equation of seawater – 2010 (TEOS-10 for short) (IOC et al, 2010) to define, describe and calculate the thermodynamic properties of seawater. Compared to Equation of Ocean State-80 (EOS-80 for short), the most obvious change of TEOS-10 is taking Absolute Salinity as salinity argument, replacing the Practical Salinity used in ocean society for 30 years. Due to the lack of observation data, the applicability of Absolute Salinity algorithm in the offshore and semi-closed sea is not very clear to date. Based on the Marine Integrated Investigation and Evaluation Project of China Offshore, other relevant data together with Pa08 model, we obtain the magnitude, distribution characteristics and formation mechanism of Absolute Salinity in China offshore. As the main composition anomaly relative to SSW, calcium carbonate, originating from terrestrial input of high calcium carbonate content and re-dissolution of sediment of China offshore, raises the Absolute Salinity Anomaly δS_A as high as 0.20 g kg^{-1} and increases the Practical Salinity about 0.04 at most comparing to the chlorinity-based salinity. Moreover, both of them show obvious seasonal variation. Finally, relevant suggestions are proposed for the accurate measurement and expression of Absolute Salinity of the China offshore.

1 Introduction

Absolute Salinity which is traditionally defined as the mass fraction of dissolved material in seawater, replaces Practical Salinity as the salinity argument of TEOS-10 seawater standard for the thermodynamic properties of seawater are directly influenced by the mass of dissolved constituents whereas Practical Salinity depends only on conductivity. Since the

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components of seawater will change with the temperature and pressure, there is still not an appropriate method for frequent and regular measuring the dissolved content directly in ocean studies until now.

At present, the Absolute Salinity of a seawater sample is obtained by adding Absolute Salinity Anomaly δS_A to Reference Salinity S_R, in which S_R is the mass fraction of dissolved material of a stoichiometric composition model (the Reference Composition or RC) of seawater defined by Millero (2008) according to Standard Sea Water (SSW for short), and δS_A is the mass fraction change caused by the composition abnormal of seawater relative to RC. Three algorithms for calculating Absolute Salinity in the open ocean are provided in TEOS-10, detailed in section 2.2 of this paper.

Taking the spatial variation of the composition of seawater into account, Absolute Salinity calculates the thermodynamic properties more accurately than does Practical Salinity. But the applicability and accuracy of the TEOS-10 algorithm are still not very clear for estuary areas and semi-closed ocean where the relative compositions of the seawater may be different from that of the open ocean and relevant research work is still underway. Ryan (2014) revised the algorithm of Absolute Salinity in the open ocean based on 2857 measured sea water conductivity and density data. Pawlowicz (2015) used the chemical composition model and climatological data to calculate the Absolute Salinity Anomaly of the global estuaries, which is one order of magnitude higher than the calculation result of TEOS-10.

China offshore is one of the widest shallow seas in the world, with a large north-south span, numerous estuaries and bays, and a large amount of fresh water and load input from rivers. The relative composition of seawater may not only differ from the open ocean but also varies from place to place. Bao Wanyou (2003) has ever proved there is a significant difference between the Practical Salinity and Absolute Salinity of non-conservative seawater samples through chemical experiments. The influence of relative composition variation on the Absolute Salinity has never been systematically studied in China, although salinity measurement has played an important role in China national ocean survey projects since 1957 (CSTPRC,1964) and the measurement methods also range from chlorination titration to measuring the conductivity of seawater. The research and calculation of Absolute Salinity of the China offshore waters are almost blank. Moreover, in much detection of salinity variations associated with climate change, Practical Salinity S_p is still used as the simplicity of Absolute Salinity and its change caused by the relative composition variation is ignored. That will raise

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obvious problems in the correct presentation of time series and/or transects that begin near the coast and end well offshore (Wright, 2011).

Therefore, this paper firstly clarifies the definition, status and application Absolute Salinity, secondly, based on the measured data and related research results, calculate the magnitude, temporal and spatial distribution characteristics and formation mechanism of Absolute Salinity of the China offshore seawater, thirdly, analyze the Practical Salinity change caused by relative composition variation; finally, based on the above results, put forward relevant suggestions and future research directions for the accurate measurement and expression of absolute salinity of China offshore seawater.

2 Methods and data

2.1 Calculation of Absolute Salinity

According to definition, the Absolute Salinity of seawater is essentially based on adding up the mass of solute in a sea water sample,

$$S_A^{\mathrm{soln}} = \frac{1}{\rho}\sum_{i=1}^{N_c} M_i\, c_i \qquad (1)$$

Where, c_i is the molar concentration of component i in seawater per kilogram, M_i is the molar mass of the component, and N_c is the number of species of component in seawater.

It's impractical to carry out a full chemical analysis for the seawater to get the Absolute Salinity regularly. While the primary and most demanding purpose of oceanographic salinity measurements is the calculation of seawater density to estimate significant ocean currents driven by sometimes tiny horizontal pressure gradients. In TEOS-10, Absolute Salinity is defined as the density of seawater can be accurately calculated by the following equation.

$$\rho = f_{TEOS-10}(S_{\mathrm{A}}, t, p) \qquad (2)$$

Therefore, S_A is also called density salinity in this equation.

It will occur $S_{\mathrm{A}} \neq S_{\mathrm{A}}^{\mathrm{soln}}$ when the salt concentration coefficient change with seawater components. The TEOS-10 have provided the conversion formula to get $S_{\mathrm{A}}^{\mathrm{soln}}$. The S_A in this paper refers to the density salinity unless otherwise specified.

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In order to get S_A, Millero (2008) defines a stoichiometric composition model (the Reference Composition or RC) based on the SSW, and specifies an algorithm to determine a consistent estimate of the mass fraction of dissolved material in a sample of arbitrary salinity with the RC

$$S_R = u_{PS} \cdot S_P , \quad 2 < S_P < 42 \tag{3}$$

In Eq. 3, the factor u_{PS} between the reference salinity of standard seawater and the practical salinity is (35.16504/35) g kg^{-1}, mainly due to original evaporation technique used by Sørensen in 1900 (Forch et al, 1902) lead to some volatile components of the dissolved material were missing in the mass calculation of the dissolved material in the sea water.

For general seawater, it can be considered as the mixture of standard seawater concentrated/diluted with a small amount of other components. The calculation formula of Absolute Salinity (mass fraction of dissolved material) is as follows:

$$S_A = S_R + \delta S_A \tag{4}$$

At present there are three methods for determining Absolute Salinity Anomaly δS_A. First, to obtain it by comparisons with direct density measurements performed in the laboratory (Millero et al, 2008; Wright et al, 2011). According to the density difference $\rho = \rho^{lab} - \rho(S_R, 25°C, 0\ \mathrm{dbar})$ and the haline contraction coefficient which is 0.7519 for SSW, δS_A is determined by

$$\partial\rho/\partial S_A |_{t=25°C,\ p=0\ \mathrm{dbar}} \approx 0.7519\ \mathrm{kg \cdot m^{-3}/(g \cdot kg^{-1})} \tag{5}$$

This procedure is useful for laboratory studies or in situations where ocean water can be obtained from sampling bottles retrieved from certain depths.

Second, to estimate it from an additional correlation equation if chemical measurements of the most variable seawater constituents in the open ocean (carbonate system and macro-nutrients) are also available (Pawlowicz, et al, 2011).

$$\partial S_A^{\mathrm{dens}}/(\mathrm{mg \cdot kg^{-1}}) = 55.6 \times \Delta\mathrm{NTA} + 4.7 \times \Delta\mathrm{NDIC} + 38.9 \times [\mathrm{NO_3^-}] + 50.7 \times [\mathrm{S_i(OH)_4}] \tag{6}$$

In which, the units of each component on the right are all mmol kg^{-1}, $\Delta\mathrm{NTA} = \mathrm{TA} - 2.3 \times S_P/35$ is the standardized ΔTA, and $\Delta\mathrm{NDIC} = \mathrm{DIC} - 2.08 \times S_P/35$ is the standardized ΔDIC.

Third, to calculate δS_A by global Gouretski and Koltermann (2004) hydrographic atlas. Due to the lack of seawater component data, McDougall et al. carried out regression calculation on the practical salinity, density and silicate concentration data of 811 seawater samples worldwide, and found that δS_A is directly related to $\mathrm{S_i(OH)_4}$

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$$\delta S_A/(\mathrm{g\cdot kg^{-1}}) = (S_A - S_R)/(\mathrm{g\cdot kg^{-1}}) = 98.24(\mathrm{S_i(OH)_4}/(\mathrm{mol\cdot kg^{-1}})) \tag{7}$$

Take the effects of evaporation and rainfall on ocean salinity into consideration, Eq.7 can be simplified as:

$$\delta S_A = R^{\delta} S_R \quad \text{(except the Baltic sea)} \tag{8}$$

in which, $R^{\delta} = \delta S_A^{\mathrm{atlas}}/S_R^{\mathrm{atlas}}$, both the S_R^{atlas} and $\delta S_A^{\mathrm{atlas}}$ are from the global Gouretski and Koltermann (2004) hydrographic atlas.

$$S_A = u_{ps} S_P (1 + R^{\delta}) = \frac{35.16504/(\mathrm{g\cdot kg^{-1}})}{35} S_P (1 + R^{\delta}) \tag{9}$$

Eq.9 is adopted in GSW to calculate δS_A with uncertainty in the ocean is less than 0.0047g $\mathrm{kg^{-1}}$. For the semi-closed Baltic sea, Feistel (2011) has fitted an empirical formula for calculating δS_A which is mainly due to rivers bringing material of anomalous composition into the Baltic, it has been also incorporated into GSW algorithm library.

2.2 Pawlowicz model for calculating conductivity based on seawater composition (hereinafter referred to as Pa08 model)

Given the exact ion composition of solution, the Pa08 model (Pawlowicz, 2008) can be used to calculate the conductivity of seawater. The simplified form is as follows:

$$\kappa_{Pa08}(C) = \sum_{i=1}^{N_c} \bar{\lambda}_i c_i^* z_i \tag{10}$$

Where, C is the ions composition of the solution, N_c is the number of species of ions in solution, $\bar{\lambda}_i$, z_i and c_i^* are the equivalent conductivity per mole of i^{th} ion, valence and the corresponding chemical equivalent ion concentration.

Based on the SSW, the Pa08 model calculates the difference ε between the calculated conductivity $\kappa_{Pa08}(C_*)$ and the measured conductivity $\kappa(C_*)$,

$$\kappa(C_*) = \kappa_{Pa08}(C_*) \cdot (1+\varepsilon)^{-1} \tag{11}$$

Then assuming the ratio between the measured conductivity $\kappa(C_*)$ and the calculated conductivity $\kappa_{Pa08}(C_*)$ does not change when the SSW composition has only a small perturbation δC_* relative to the reference seawater, that is,

$$\kappa(C_* + \delta C_*) = \kappa_{Pa08}(C_* + \delta C_*) \cdot (1+\varepsilon)^{-1} \tag{12}$$

Thus, the equivalent electrical conductivity $\bar{\lambda}_i$ of 18 kinds of ions in seawater at 25 °C is calculated.

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When the temperature of the seawater sample $\theta \neq 25$ ° C, ignoring the influence of pressure on the conductivity, and the conductivity calculated from the seawater composition is revised using the following formula:

$$\frac{\kappa(\beta C_0+\delta C_*,25℃)}{\kappa(\beta C_0+\delta C_*,\theta)} = \frac{\kappa(C_0,25℃)}{\kappa(C_0,\theta)} \cdot (1+\tau) \tag{13}$$

2.3 Observation data

The near-synchronous oceanographic and ocean chemical data are from 1,480 stations covering China Offshore that were set up for the Marine Integrated Investigation and Evaluation Project of China offshore (refer to observation) conducted by the State Oceanic Administration of China. These sites give surface, 10m, 30m and bottom layers distribution characteristics of nutrients in four seasons of spring, summer, autumn and winter of 2006 to 2007.

Since in-situ observation of DIC is missing in this project, it is derived from pH and TA data by CO2SYS software released by the department of ecology of Washington State based on the carbonate equilibrium.

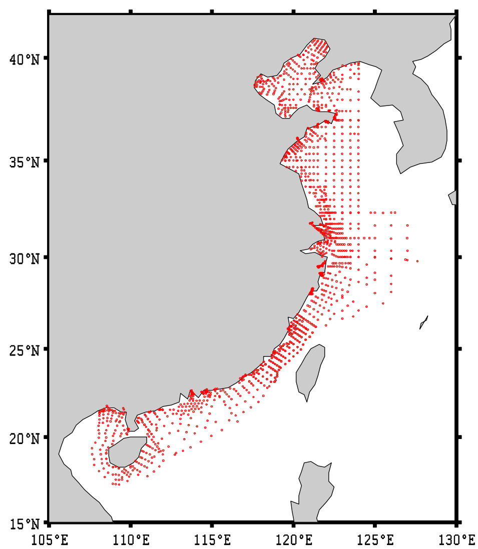

Fig. 1 The geographical distribution map of stations of the Marine Integrated Investigation and Evaluation

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Ocean Science Discussions

3 Results

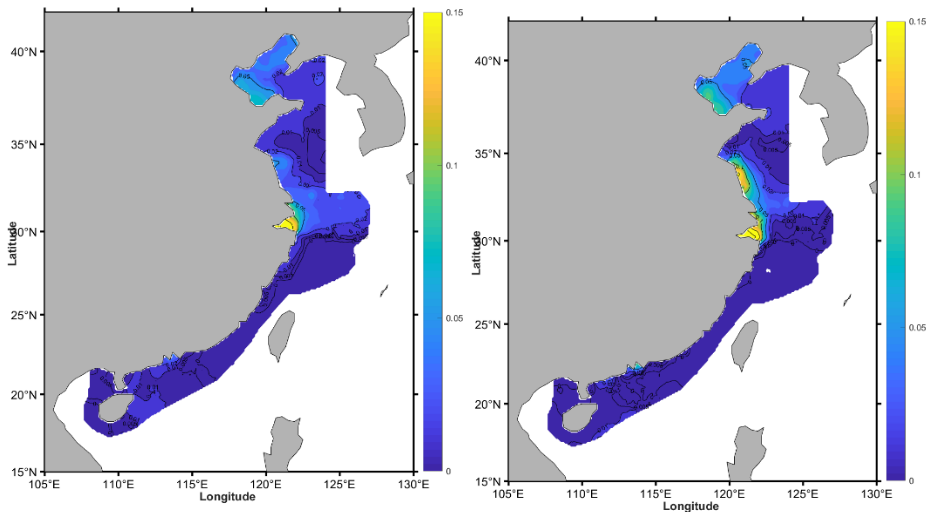
3.1 Reference Salinity S_R of the China offshore seawater

Based on the observation, the Practical Salinity S_P of China offshore seawater diluted by the low salinity river runoff ranges from 12 and 34.5, the minimum of 12 occurs outside the gate of the Yangtze River runoff into the sea, the maximum of 34.5 appears in the Kuroshio way. By the way, an extreme minimum S_P of 0.1 appears in the south branch of Yangtze River in the summer of 2006, since river salinity is beyond the scope of this paper, no further discussion will be made here.

Based on Eq.3, S_R of China offshore ranges from 12 to 34.66 g kg^{-1}.

3.2 Absolute salinity Anomaly δS_A of the China offshore seawater

Using Eq.6 in the section 2.1, the δS_A of China offshore ranges from 0 to 0.2 g kg^{-1}, the largest is one order higher than that of the open ocean. The ΔNTA item in Eq.6 contributes to δS_A as high as 90%, so the largest δS_A appears in the northern Jiangsu shoals, the Yangtze River estuary, the Bohai Sea and the Pearl River estuary where the ΔNTA is high, as shown in Fig.2.



(a) on the sea surface in spring **(b) on the sea bottom in winter**

Fig.2 δS_A isoclines of China offshore seawater

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Due to the lack of complete chemical analysis data, the following researches for different subjects have indicated that the positive ΔNTA in the above areas is caused by the input of high $CaCO_3$ content rivers and the re-dissolution of sediments. Based on the investigation of 13 cruises from April 2011 to February 2012, Qi Di (2013) finds that the mean value of $\Delta N[Ca^{2+}]$ ($\Delta N[\mathrm{Ca}^{2+}] = \mathrm{Ca}^{2+} + -10656.6 * S_P/35/(\mathrm{umol} \cdot \mathrm{kg}^{-1})$, in which Ca^{2+} and S_P are the measured value of Ca^{2+} and Practical Salinity of sea water respectively) is 364±115 umol kg^{-1} in Bohai Sea, 184±33 umol kg^{-1} in North Yellow Sea, 136±46 umol kg^{-1} in South Yellow Sea, 90±54 umol kg^{-1} in East China Sea and 81±24 umol kg^{-1} North South China Sea. In addition, the $\Delta N[Ca^{2+}]$ and ΔNTA is 132~250 umol·kg^{-1} and 245~480 umol kg^{-1} respectively in the north branch of Yangtze River in dry period and transition period. In terms of magnitude, these results are approximately consistent with the following assumption of the Pa08 model in the region mentioned above,

$$\Delta \mathrm{NTA} = 2\Delta \mathrm{N}[\mathrm{Ca}^{2+}] - \Delta[\mathrm{NO}_3^-] \quad (14)$$

Other studies have also indicated that due to the accumulation of materials entering the sea from the old Yellow River and the ancient Yangtze River, the $CaCO_3$ concentration of surface sediments on the seafloor near the coast of northern Jiangsu ranges from 2.8% to 10.5% (Qin, et al, 1989; Yang and Youn, 2007). The NDIC of the Yellow Sea near China has always been high, even when strong biological activity in spring reduces the surface ΔNTA, the sediment of PIC will resuspend and maintain the high dissolved $CaCO_3$ of seawater through the solid-liquid balance (Hong, 2012; Zhang, et al, 1995).

The above research results fully explain the following spatial and temporal distribution characteristics of δS_A of China offshore.

Centered at 33.4 °N and 121 °E, δS_A gradually decreases from the coast to the offshore in the northern Jiangsu shoal. In the central area, δS_A is always greater than 0.05 g kg^{-1} all the year round. The δS_A of the bottom layer is always higher than that of the surface layer except in summer when the carbonate-rich terrestrial input from the Huihe River system is higher than the dissolution $CaCO_3$ of bottom sediments. So the maximum value of 0.15 g kg^{-1} appears on the bottom layer in winter while the minimum value of 0.05 g kg^{-1} appears in the surface layer in spring. In winter, due to the strong Yellow Sea Warm Current invading, the area where δS_A greater than 0.05 g kg^{-1} shrinks towards the shore where the maximum of δS_A locates.

The largest δS_A of the Bohai Sea appears at the estuary of carbonate-rich Yellow River, decreases outwards, is always greater than 0.05 g kg^{-1} and rises to the maximum of 0.1 g kg^{-1} on the bottom in winter. As a semi-closed shallow sea with low exchange with the open ocean, the δS_A in the whole Bohai Sea is always larger than 0.02 g kg^{-1} and the difference between δS_A of the bottom and that of the surface is not obvious.

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As China's largest runoff into the sea, the Yangtze River is rich in freshwater and nutrients from land. At its gate to the sea, the δS_A is greater than 0.1 g kg^{-1} all year round. However, due to the large consumption of phytoplankton, the nutrients decreases rapidly outside the gate, ΔNTA remains the primary contributor to the δS_A. The surface coverage of the 0.05 g kg^{-1} isocline varies with seasons and depths, reach to the maximum in summer and with little variation in other seasons.

The δS_A greater than 0.05g kg^{-1} also occurs at the mouth of the Pearl River and Minjiang River in summer (flood season), and less than 0.02g kg^{-1} in other seasons.

In the rest area, the magnitude of δS_A is below 0.005g kg^{-1}, which is the same as the magnitude of the statistics uncertainty of the Absolute Salinity Anomaly in the open ocean, could be ignored.

3.3 Contrast to the δS_A calculated by GSW

By GSW function library and the corresponding climate silicate and practical salinity data, the δS_A of China offshore ranges from 0 to 0.015 g kg^{-1}, the maximum appears at the bottom near to the Xisha Islands and the Dongsha Islands and the rest is below 0.002 g kg^{-1}. It's one order of magnitude less than that in the 3.2 section, distribution characteristics are also significantly different. These differences mainly come from the following aspects:

(1) $CaCO_3$ is the main relative composition anomaly of China offshore seawater and the primary contributor to the δS_A.

(2) Silicates of the observation is 100μmol·kg^{-1} higher than climatological data of the GSW function library in the mouth of the Yangtze River, Minjiang River and Pearl River at most.

3.4 Practical Salinity change δS_P caused by $CaCO_3$ dissolution

The nitrite and phosphate is temporarily not considered in the calculation for their concentration ranges from 0 to 0.01 mmol kg^{-1} and 0 to 0.005 mmol kg^{-1} respectively in the existing observation which are much smaller than those items in Eq. 6 and Eq.14 above.

First, based on observation, $\Delta N[Ca^{2+}]$, $\Delta N[HCO_3^-]$ and $\Delta N[CO_3^{2-}]$ are derived respectively by Eq.14 and carbonate equilibria; then, the conductivity change $\delta C_{25℃}$ corresponding to these ions change at 25 ℃ by Pa08 is calculated; then, $\delta C_{25℃}$ is converted to the conductivity change δC at seawater sample temperature by Eq.13; finally, δS_P is calculated using Eq.15, in which C_{obs} is conductivity of CTD reading, S_p is the SSW practical salinity corresponding to C_{obs}.

$$\delta S_P = S_P(C_{obs}) - S_P(C_{obs} - \delta C) \quad (15)$$

It can be seen in Fig.3, the relative composition anomaly relative to SSW in China offshore result in a Practical Salinity change δS_P from 0 to 0.04, which greater than 0.01(the accuracy of Practical Salinity in the open ocean) appears in the Bohai sea, northern Jiangsu shoals and the Yangtze River mouth. δS_P also shows a significant seasonal variation, in which the largest appears in winter, followed by autumn and spring, and the smallest in summer, the maximum seasonal

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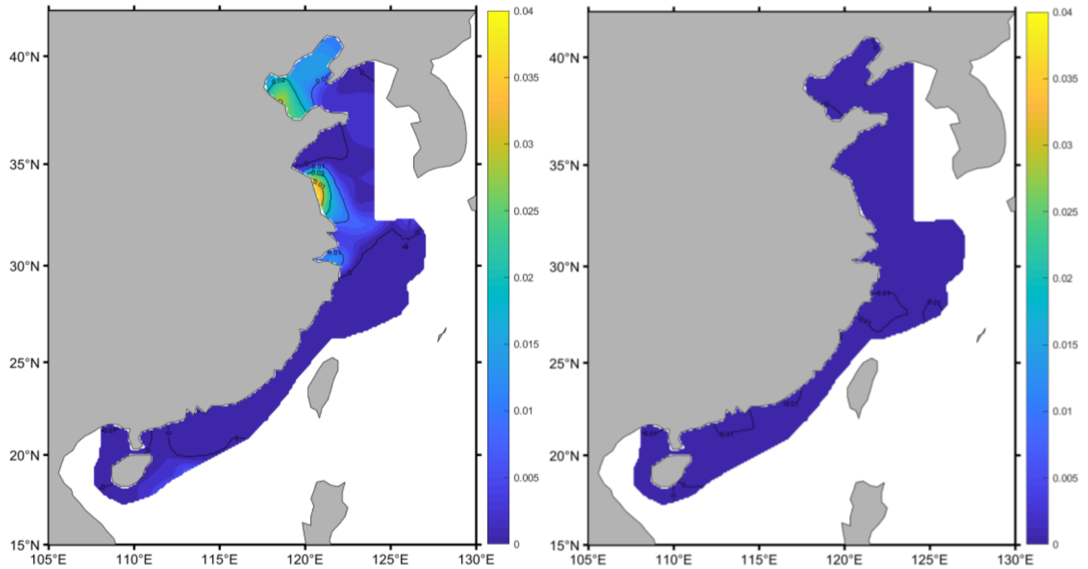
variations can be as high as 0.03.



(a) sea bottom in winter **(b) sea surface in summer**

Fig. 3 The isoclines of practical salinity change δS_P caused by the $CaCO_3$ dissolution in China sea

4 Conclusion and analysis

The proposal and implementation of the concept of S_A in TEOS-10 is to accurately quantify the total mass of inorganic substance dissolved in sea water, ensures the density and related quantities are accurately represented by Gibbs function and corrects errors caused by the measuring the properties of seawater such as chloride and conductivity to get the salinity. In this paper, based on the observation and chemical composition model Pa08, the magnitude, distribution characteristics and formation mechanism of Absolute Salinity in China offshore are obtained:

1) The Absolute Salinity S_A ranges from 12 to 34.66 g kg^{-1}, in which S_R ranges from 12 to 34.66 g kg^{-1} and the Absolute Salinity Anomaly δS_A ranges from 0 to 0.20 g kg^{-1};

2) Calcium carbonate is the main composition anomaly relative to SSW and the primary contributor to the δS_A;

3) The largest δS_A locates in the regions with high calcium carbonate: the northern Jiangsu shoals, Bohai Sea, the Yangtze River mouth, Minjiang River mouth the Pearl River mouth;

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4) Under the combined effects of different water system dynamics, terrestrial input, marine biological activities, and re-dissolution of marine sediments, the δS_A in China offshore seasonal variations are obvious, and the maximum can be as high as 0.05g kg^{-1}; the difference between the surface layer and the bottom layer is also up to 0.1g kg^{-1};

5) The practical salinity will change 0.04 at most due to relative composition variation of sea water.

With the limited observations, this paper only lists the magnitude and distribution characteristics of δS_A in China offshore from 2006 to 2007. At present, we have collated the long-term series of seawater composition data to continue the study on δS_A changes and get an empirical formula to calculate it.

Since δS_P caused by $CaCO_3$ dissolution in China offshore is significantly larger than the precision of 0.002 and the accuracy of 0.01 of the Practical Salinity measurement in the open ocean, issues may arise in the long-term stability and intercomparability of it. The Practical Salinity with δS_P greater than 0.01 in the China offshore requires further tracing, correction and comparison to make it compatible with the one in the open ocean. Moreover, in the study of marine phenomena and laws using the salinity, it is necessary to carefully distinguish the errors introduced by the salinity measurement method.

The current researches are only based on the existing seawater composition data, and the exact influence of other composition is still very clear. Therefore, it is necessary to carry complete chemical analysis for the main components of seawater or the density measurement in the following estuaries of the Yangtze River, Pearl River, Minjiang River, and the semi-closed Bohai Sea.

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