

# Estimating the Absolute Salinity of Chinese Offshore Waters using nutrients and inorganic carbon data

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**Abstract.** In June 2009, the Intergovernmental Oceanographic Commission of UNESCO released the  
10 international thermodynamic equation of seawater – 2010 (TEOS-10 for short) to define, describe and calculate the  
thermodynamic properties of seawater. Compared to the Equation of State-1980 (EOS-80 for short), the most obvious  
change with TEOS-10 is the use of Absolute Salinity as salinity argument, replacing the Practical Salinity used in the  
oceanographic community for 30 years. Due to the lack of observational data, the applicability of the potentially  
increased accuracy in Absolute Salinity algorithms for coastal and semi-enclosed seas is not very clear to date. Here, we  
15 discuss the magnitude, distribution characteristics and formation mechanism of Absolute Salinity and Salinity Anomaly  
in Chinese shelf waters, based on the Marine Integrated Investigation and Evaluation Project of China Offshore and  
other relevant data. The Absolute Salinity  $S_A$  ranges from 0.1 to 34.66 g kg<sup>-1</sup>. Instead of silicate, the main composition  
anomaly in the open sea, CaCO<sub>3</sub> originating from terrestrial input and re-dissolution of shelf sediment is most likely the  
main composition anomaly relative to SSW and the primary contributor to the Absolute Salinity Anomaly  $\delta S_A$ . Finally,  
20 relevant suggestions are proposed for the accurate measurement and expression of Absolute Salinity of the China  
offshore.

## 1 Introduction

An absolute salinity, which is traditionally defined as the mass fraction of dissolved material in seawater, replaces  
Practical Salinity as the salinity argument in the TEOS-10 (IOC et al, 2010) seawater standard for the thermodynamic

25 properties of seawater. This is because these thermodynamic properties are directly influenced by the mass of dissolved constituents whereas Practical Salinity depends only on their conductivity. Since the relative amounts of different constituents change from place to place and from time to time, accounting for the biases that are introduced by these changes may be important. However, appropriate methods for frequent and regular measurements of the dissolved content directly in ocean studies are still a topic of research.

30 At present, the TEOS-10 Absolute Salinity of a seawater sample is obtained by adding Absolute Salinity Anomaly  $\delta S_A$  to Reference Salinity  $S_R$ , in which  $S_R$  is the mass fraction of dissolved material in a stoichiometric composition model (the Reference Composition or RC) of seawater, defined by Millero (2008), for which the reference material known as IAPSO Standard Sea Water (SSW for short), is a good approximation, of the same conductivity as that of the sample.  $\delta S_A$  is the mass fraction change caused by composition variations relative to RC. Three algorithms for calculating  
35 Absolute Salinity in the open ocean are provided in TEOS-10. The two that avoid a direct measurement either make assumptions about the dominant biogeochemical processes in the ocean that affect the Absolute Salinity Anomaly or rely on empirically-determined correlations.

However, the applicability and accuracy of the TEOS-10 algorithms are still not very clear for estuaries and semi-enclosed oceanic basins where the relative compositions of the seawater may be different from that of the open ocean.

40 Although there have only been very few direct measurements of conductivity and density in such areas (Millero 1984, Feistel et al., 2010a), Pawlowicz (2015) used chemical composition/conductivity/density modelling and climatological data to estimate the Absolute Salinity Anomaly near many rivers around the world, finding values of up to one order of magnitude higher than those extrapolated from the open ocean.

The coastal areas of China comprise one of the widest shallow seas in the world, with a large north-south span,  
45 numerous estuaries and bays, and a large amount of fresh water input from rivers. The relative composition of this coastal seawater may not only differ from that of the open ocean but also vary from place to place. However, the influence of relative composition variation on the Absolute Salinity in this area has never been systematically studied, although salinity measurement has played an important role in Chinese national ocean survey projects since 1957 (CSTPRC, 1964) and for metrological purposes a Chinese primary seawater standard has been developed (Li et al.,

50 2016). Moreover, in any efforts to detect salinity variations associated with climate change variability in Bohai and  
northern Yellow Sea(Wu et al., 2004a; Wu et al., 2004b; Xu, 2007; Lv, 2008; Song, 2009) , 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 obvious problems in the correct presentation of time series and/or transects that begin near the coast and end  
well offshore (Wright, 2011).

55 Therefore, in this paper we first clarify the definition, status and application of TEOS-10 Absolute Salinity. Second,  
based on the measured data and related research results, we estimate the magnitude, temporal and spatial distribution  
characteristics and formation mechanisms giving rise to Salinity Anomalies in Chinese coastal seawaters. Finally, based  
on the above results, we put forward relevant suggestions and future research directions for the accurate measurement  
and expression of absolute salinity of Chinese offshore seawaters.

## 60 2 Methods and data

### 2.1 Calculation of Absolute Salinity

The TEOS-10 Solution Absolute Salinity of seawater is essentially based on adding up the mass of solute in a sea water  
sample,

$$S_A^{\text{soln}} = \sum_{i=1}^{N_c} M_i c_i \quad (1)$$

65 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. However, it is impractical to carry out a full chemical  
analysis for the seawater to get the  $S_A^{\text{soln}}$  regularly. 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 instead defined so that the density of seawater can  
70 be accurately calculated by the following equation.

$$\rho = f_{TEOS-10}(S_A, t, p) \quad (2)$$

where  $f_{\text{TEOS-10}}$  is a specified function. Therefore,  $S_A$  is also called a density salinity.

Unfortunately, although for many purposes we can treat  $S_A$  and  $S_A^{\text{soln}}$  interchangeably, at highest precisions  $S_A \neq S_A^{\text{soln}}$  due to small changes in the relative composition of sea salt. In order to get  $S_A$  at this highest precision, Millero

75 (2008) first defines a stoichiometric composition model (the Reference Composition or RC), based on a reference material (IAPSO Standard Seawater), 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. This estimate is based on the widely-used Practical Salinity  $S_P$  (UNESCO, 1981):

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

80 In Eq. (3), the factor  $u_{PS}$  between the Reference Salinity of standard seawater and the Practical Salinity is  $(35.16504/35) \text{ g kg}^{-1}$ , and is not equal to one mainly because an evaporative technique used by Sørensen in 1900 (Forch et al., 1902) led to the loss of some volatile components of dissolved material.

General seawater can be considered as the mixture of standard seawater concentrated/diluted with pure water and a small amount of other components. The calculation formula of Absolute Salinity from Reference Salinity requires the  
85 addition of a correction, the Absolute Salinity Anomaly  $\delta S_A$ :

$$S_A = S_R + \delta S_A \quad (4)$$

At present there are three methods for determining Absolute Salinity Anomaly  $\delta S_A$ . 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  $\rho = \rho^{\text{lab}} - \rho(S_R, 25^\circ\text{C}, 0 \text{ dbar})$  and the haline contraction coefficient which is 0.7519 for SSW,  
90  $\delta S_A$  is determined by

$$\frac{\partial \rho}{\partial S_A} \Big|_{t=25^\circ\text{C}, p=0 \text{ dbar}} \approx 0.7519 \text{ kg} \cdot \text{m}^{-3} / (\text{g} \cdot \text{kg}^{-1}) \quad (5)$$

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

Second, it can be estimated using a correlation equation, if chemical measurements of the most variable seawater

95 constituents in the open ocean (carbonate system and macro-nutrients) are also available (Pawlowicz et al., 2011, IOC et al., 2010).

$$\delta S_A^{\text{dens}}/(\text{mg} \cdot \text{kg}^{-1}) = 55.6 \times \Delta[\text{NTA}] + 4.7 \times \Delta[\text{NDIC}] + 38.9 \times [\text{NO}_3^-] + 50.7 \times [\text{S}_i(\text{OH})_4] \quad (6)$$

The units of each component on the right are all  $\text{mmol kg}^{-1}$ ,  $\Delta[\text{NTA}] = \text{TA} - 2.3 \times \frac{S_P}{35}$  is the standardized change in

Total Alkalkinity (TA), and  $\Delta[\text{NDIC}] = \text{DIC} - 2.08 \times \frac{S_P}{35}$  is the standardized change in Total Dissolved Inorganic

100 Carbon (DIC). Note that the coefficients of this model are calculated using a numerical model for chemical interactions (Pawlowicz, 2008; Pawlowicz et al., 2010; Pawlowicz et al., 2011), which performed well against lab studies, and were shown to have reasonable accuracy for seawater samples by Ryan et al. (2014). An important aspect of this modelling is that, in order to maintain a charge balance in the dissolved constituents, it was assumed that calcium concentrations also changed according to:

$$105 \quad \Delta[\text{NTA}] = 2\Delta\text{N}[\text{Ca}^{2+}] - \Delta[\text{NO}_3^-] \quad (7)$$

In which,  $\Delta\text{N}[\text{Ca}^{2+}] = \text{Ca}^{2+} - 10656.6 * S_P/35/(\mu\text{mol} \cdot \text{kg}^{-1})$ ,  $\text{Ca}^{2+}$  and  $S_P$  are the measured value of  $\text{Ca}^{2+}$  and Practical Salinity of sea water respectively. Calcium was chosen to balance charge since it is a) not usually measured, but b) it is known to vary in its relative composition by a few percent in the open ocean. However, the accuracy of this relationship is not known.

110 Third, it can be found from a global  $\delta S_A$  climatology created by McDougall et al., (2012). 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  $\delta S_A$  can be directly related to  $\text{S}_i(\text{OH})_4$

$$\delta S_A/(\text{g} \cdot \text{kg}^{-1}) = (S_A - S_R)/(\text{g} \cdot \text{kg}^{-1}) = 98.24(\text{S}_i(\text{OH})_4/(\text{mol} \cdot \text{kg}^{-1})) \quad (8)$$

although for further work the numerical coefficient was tuned for specific ocean basins. Taking the effects of

115 evaporation and rainfall on ocean salinity into consideration, Eq.(8) can be simplified as:

$$\delta S_A = R^\delta S_R \quad (\text{except the Baltic sea}) \quad (9)$$

in which,  $R^\delta = \delta S_A^{\text{atlas}}/S_R^{\text{atlas}}$ , both the  $S_R^{\text{atlas}}$  and  $\delta S_A^{\text{atlas}}$  are from the McDougall et al (2012) hydrographic atlas.

$$S_A = u_{ps} S_P (1 + R^\delta) = \frac{35.16504/(\text{g} \cdot \text{kg}^{-1})}{35} S_P (1 + R^\delta) \quad (10)$$

Eq.(10) is adopted in the official Gibbs-SeaWater Oceanographic Toolbox software toolbox (available from [www.teos-](http://www.teos-10.org)

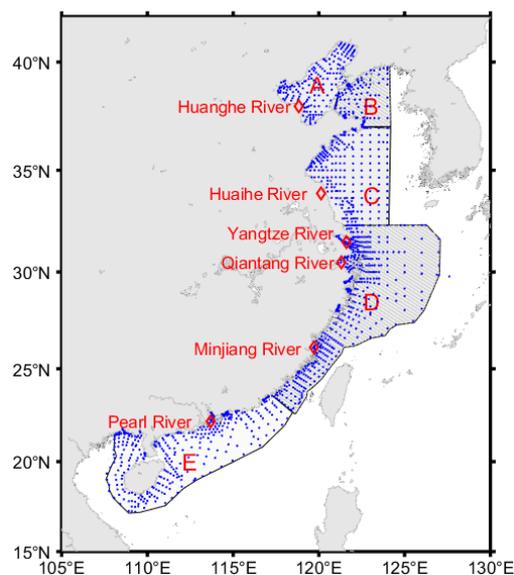
120 [10.org](http://www.teos-10.org), McDougall and Barker, 2011) to calculate  $\delta S_A$  with uncertainty in the ocean is less than  $0.0047 \text{g kg}^{-1}$ . For the

semi-enclosed Baltic sea, Feistel et al. (2010a) have fitted an empirical formula for calculating  $\delta S_A$  which is mainly due to rivers bringing material of anomalous composition into the Baltic, and this formula has also been incorporated into GSW algorithm library.

In the work described here we compare the latter two methods.

## 125 2.2 Observation data

The near-synchronous oceanographic and ocean chemical data used here are from 1,480 stations covering Chinese offshore waters that were set up for the Marine Integrated Investigation and Evaluation Project of China offshore conducted by the State Oceanic Administration of China (Xiong, 2012; Ji, 2016), as shown in Fig. 1. At these sites, surface, 10m, 30m and bottom values for nutrients, as well as TA and pH, are available in four seasons of spring (April - June), summer (July - September), autumn (October - December) and winter (January - March) of 2006 to 2007. Since in-situ observation of DIC is missing in this project, it is derived from pH and TA data using CO2SYS software released by the department of ecology of Washington State based on the carbonate equilibrium (Lewis, et al. 1998).



**Fig. 1** The geographical distribution map of sampling stations

The blue dots are the observation stations of the Marine Integrated Investigation and Evaluation Project of China Sea. "A" is the Bohai Sea, 'B' is the North Yellow Sea, 'C' is the South Yellow Sea, 'D' is the East China Sea, and 'E' is the South China Sea.

### 3 Results

#### 135 3.1 Reference Salinity $S_R$ of the China offshore seawater

The first step in determining salinity anomalies is to estimate the Reference Salinity based on the Practical Salinity.

Because the standard PSS-78 algorithm for Practical Salinity is only valid in the range  $2 < S_p < 42$ , values for samples in the mouth of Yangtze River, Qiantang River and Pearl River (labelled in Fig.1) whose  $S_p$  less than 2 are recalculated with a modified form of the Hill et al. (1986) formula based on the in-situ conductivity, temperature and pressure. Then

140 Eq. (3) is used to get  $S_R$ .

Based on our observations (Fig. 1), the Reference Salinity  $S_R$  of Chinese offshore seawater diluted by low salinity river runoff ranges from 0.01 to  $34.66 \text{ g kg}^{-1}$ . The extreme minimum  $S_R$  of 0.01 appears in the south branch of Yangtze River in the summer of 2006 and the maximum of 34.66 appears in the path of the Kuroshio current (Fig. 2). Low salinities are also seen in the Pearl River estuary and to a lesser degree in shallow areas of the South Yellow Sea, as

145 well as near a few other river mouths.

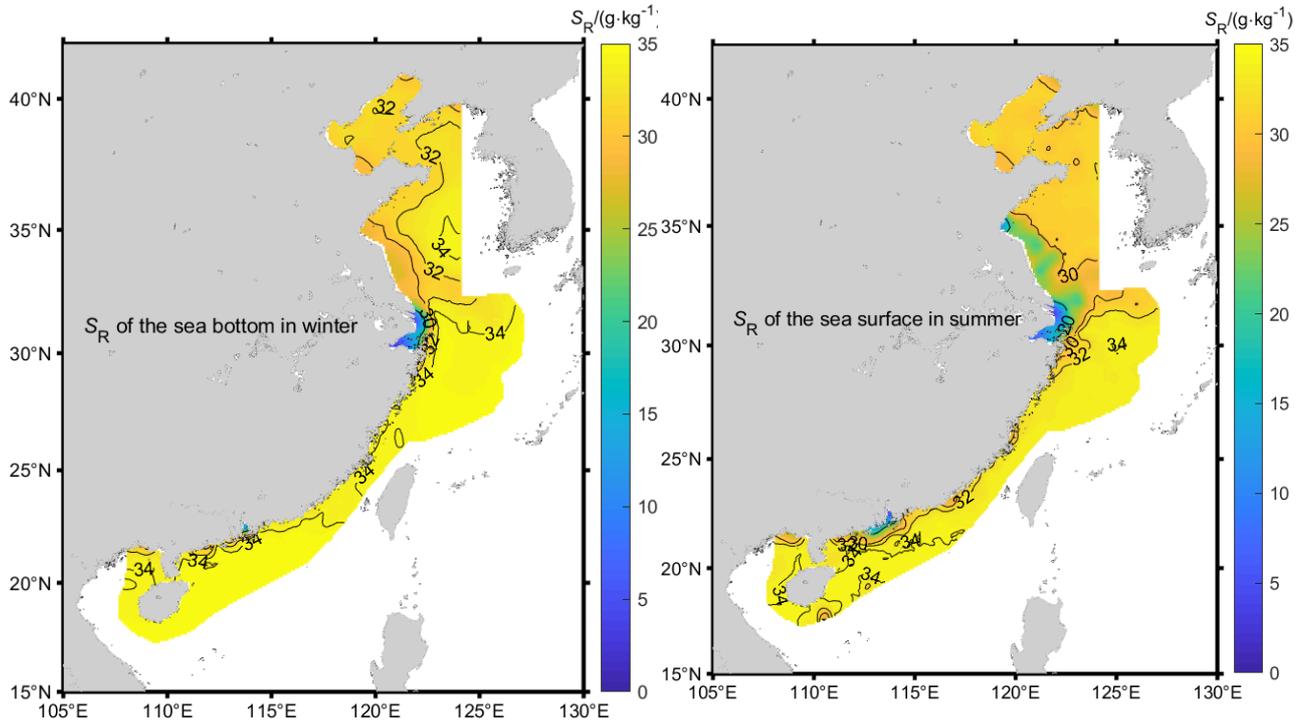
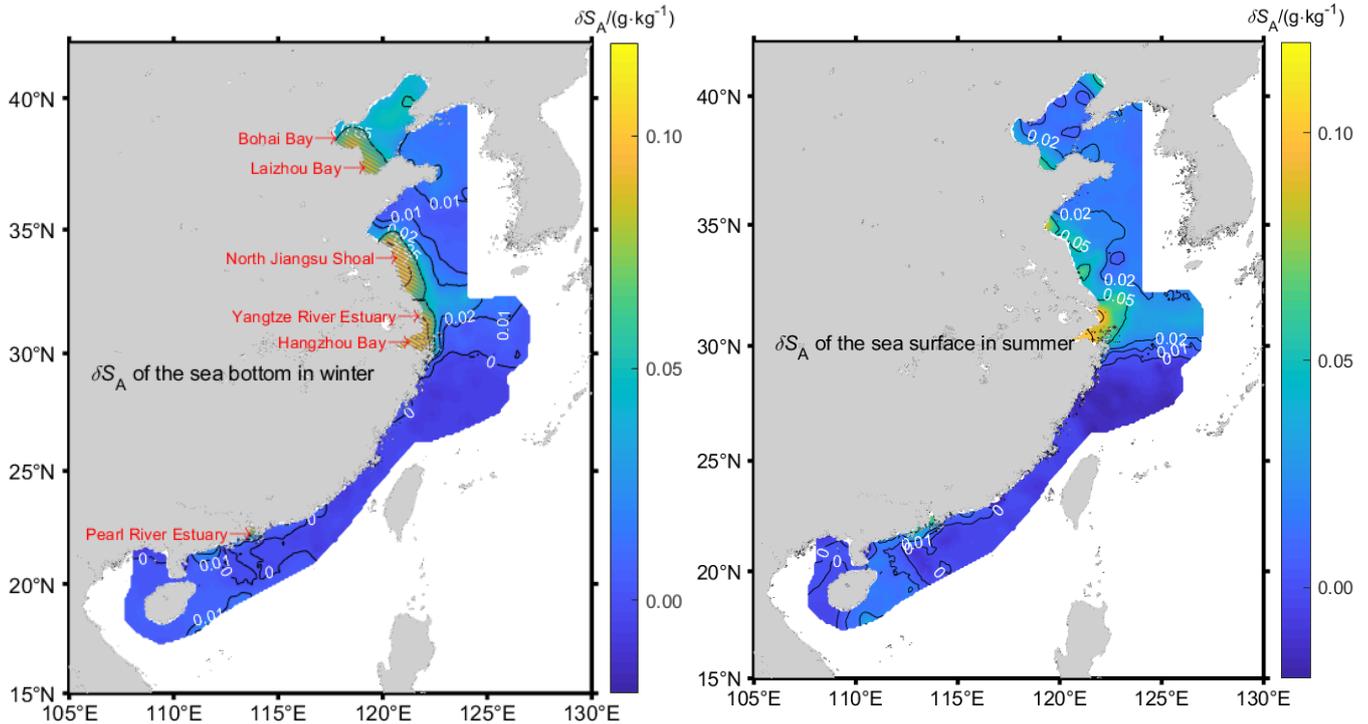


Fig. 2  $S_R$  isoclines of China offshore seawater

### 3.2 Absolute salinity Anomaly $\delta S_A$ of Chinese offshore waters

Using Eq. (6), the estimated  $\delta S_A$  of Chinese offshore waters ranges from  $-0.05$  to  $0.28 \text{ g kg}^{-1}$  (Fig. 3). The largest Salinity Anomalies are one order higher than those of the open ocean. As much as 90% of the calculated  $\delta S_A$  arises from  $\Delta[\text{NTA}]$  term in Eq. (6), so that areas with high  $\delta S_A$  also have high  $\Delta[\text{NTA}]$  (Fig. 4). The largest  $\delta S_A$  values appear in Yangtze River estuary, Hangzhou Bay, Laizhou Bay, Bohai Bay, North Jiangsu Shoals and Pearl River estuary. Hangzhou Bay, which is adjacent to the Yangtze River estuary, has continuously transported water from the Yangtze River estuary due to its current and tidal characteristics (Yuan, 2009) and has almost same water composition with Yangtze River estuary. Thus, in this paper, the waters in Yangtze River estuary and Hangzhou Bay are analyzed as a single water mass. The  $\delta S_A$  in the above coastal regions, which are often in excess of  $0.05 \text{ g kg}^{-1}$ , are given in Table 1.



**Fig.3**  $\delta S_A$  isoclines of Chinese offshore seawater. Hatched areas at left represent Salinity Anomalies more than  $0.05 \text{ g kg}^{-1}$ .

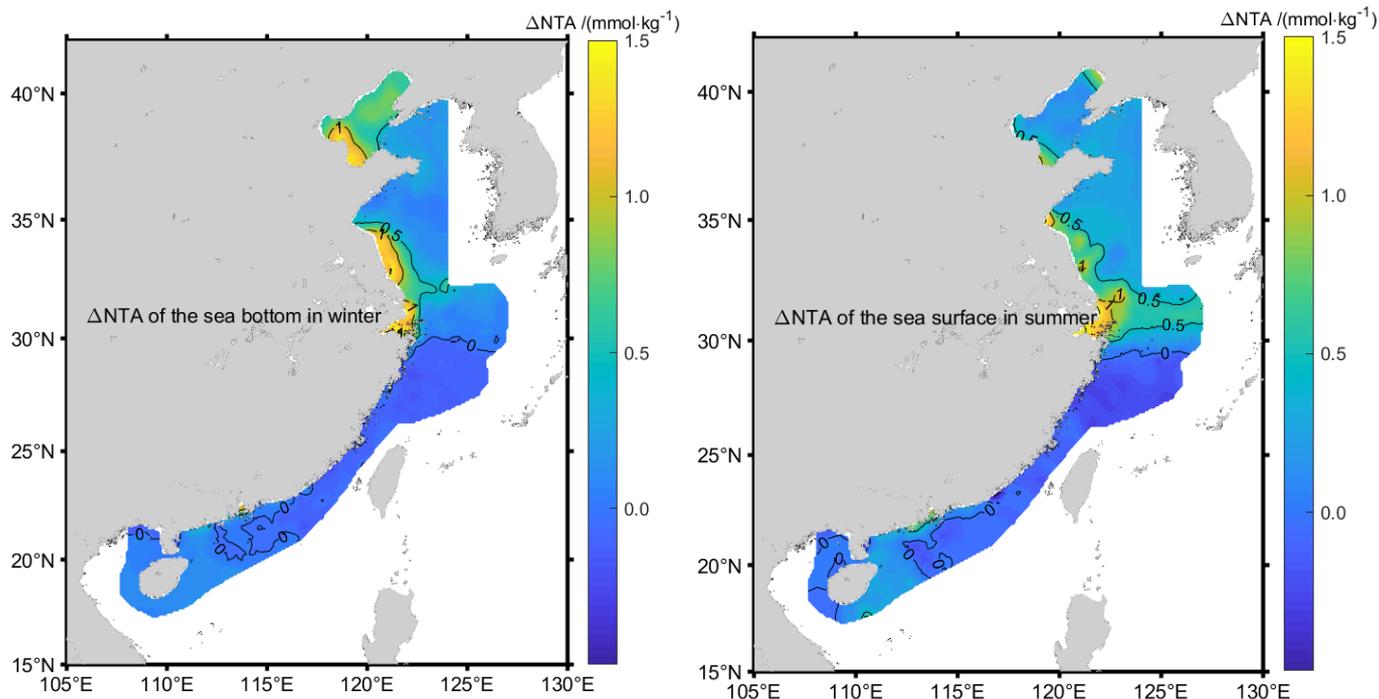


Fig.4  $\Delta$ [NTA] isoclines of China offshore seawater

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Table 1.  $\delta S_A$  in different coastal regions hatched in Fig.3. Units are  $\text{mg kg}^{-1}$ .

Region	Min	Max	Mean $\pm$ Std
Laizhou Bay and Bohai Bay	0	132	54 $\pm$ 23
North Jianguo Shoal	0	228	46 $\pm$ 32
Yangtze River Estuary and Hangzhou Bay	-50	279	86 $\pm$ 63
Pearl River Estuary	0	125	52 $\pm$ 32

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The maximum  $\delta S_A$  of  $0.28 \text{ g kg}^{-1}$  appears at the sea surface of the Yangtze River Estuary and in Hangzhou Bay in summer. As China's largest runoff into the sea, the Yangtze River is rich in nutrients from land. At its entrance to the sea, the silicate concentration exceeds  $100 \text{ umol kg}^{-1}$ ,  $\Delta$ [NTA] is larger than  $1 \text{ mmol kg}^{-1}$  and the  $\delta S_A$  is greater than  $0.1 \text{ g kg}^{-1}$  all year round, but these nutrient concentrations decrease rapidly away from the entrance.  $\Delta$ [NTA] is the primary contributor to  $\delta S_A$ . The surface coverage of the  $0.05 \text{ g kg}^{-1}$  isocline varies with seasons and depths, reaches to the maximum in summer but with little variation in other seasons. In this region, 54% and 26% of negative  $\delta S_A$  appears in spring and winter respectively, which is also mainly arises from  $\Delta$ [NTA].

170 In the northern North Jiangsu Shoal, the maximum  $\delta S_A$  of  $0.23 \text{ g kg}^{-1}$  appears on the bottom layer in winter. Centered at  $33.4^\circ \text{N}$  and  $121^\circ \text{E}$ , many points have  $\delta S_A$  greater than  $0.05 \text{ g kg}^{-1}$  all the year round and gradually decreases from the coast to the offshore. The  $\delta S_A$  of the bottom layer is higher than that of the surface layer in dry season (spring and winter), while smaller in flood (summer and autumn) season in which more terrestrial input is brought by Huaihe River system.

175 The largest  $\delta S_A$  of  $0.20 \text{ g kg}^{-1}$  in the Bohai Sea appears on the bottom of the Laizhou Bay in winter and seasonal characteristics are basically the same as the North Jiangsu Shoal although in summer more terrestrial materials are input by the Yellow River. As a semi-enclosed shallow sea with lower exchange with the open ocean, the  $\delta S_A$  in the whole Bohai Sea is always larger than  $0.02 \text{ g kg}^{-1}$  and the  $\delta S_A$  difference between of the bottom and that of the surface within the same season is not as significant as its seasonal variation in the area.

180 A  $\delta S_A$  of greater than  $0.05 \text{ g kg}^{-1}$  also occurs at the mouth of the Pearl River and Minjiang River in summer, but values are less than  $0.02 \text{ g kg}^{-1}$  in other seasons. However, these values are seen within the estuary with very little presence on the shelf. In the remaining areas, the magnitude of  $\delta S_A$  is below  $0.005 \text{ g kg}^{-1}$ , which is about the same as the magnitude of the statistical uncertainty of the Absolute Salinity Anomaly in the open ocean, and so is essentially zero.

185 Although we have used eqn. (6), which is meant for seawater of relatively high salinity, to estimate the Salinity Anomaly near river mouths where the salinity is far smaller, a more complex calculation of the Salinity Anomaly, based on a full chemical analysis of river water composition, was plotted for some of these rivers (the Yangtze, the Pearl and Minjiang Rivers) in Pawlowicz (2015). The values calculated in that work are consistent with those found here (Table 2).

Table 2.  $\delta S_A$  in some rivers as estimated in this paper, compared with values estimated using a more complete theory in Pawlowicz (2015). Units are  $\text{mg kg}^{-1}$ .

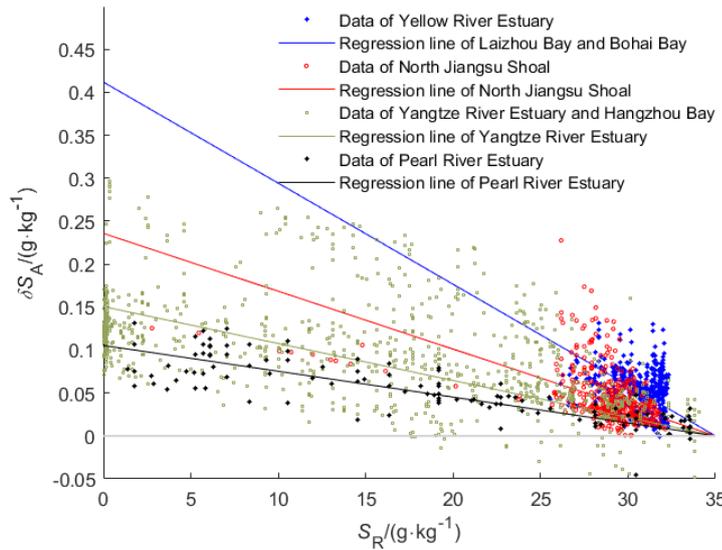
Rivers	Mean $\pm$ Std (our data)	Values from Pawlowicz (2015)
Yellow River	-	200-239
Yangtze River	$90 \pm 23$	105~116
Minjiang	$26 \pm 15$	30
Pearl River	$80 \pm 26$	95~96

190 **3.3 Parameterisation of the Absolute Salinity of the China offshore waters**

Although Salinity Anomalies within rivers are always non-zero, the Salinity Anomaly is significantly nonzero in only four areas along the Chinese coast and river mouths (hatched areas in Fig.3). They are occupied by different coastal water masses (Xiong, 2012) and Salinities Anomalies in each can be parameterized separately.

195 The seawater of China offshore is a mixture of the Kuroshio water originating from the North Equatorial Current and the runoff into the sea. The Salinity Anomaly in Pacific surface waters in any case is generally small; it is the deeper waters that have (relatively) large Salinity Anomalies arising from remineralization in the subsurface branch of the ocean's overturning circulation. In this paper, we ignore the relative composition difference between the Kuroshio and SSW for now. Following Feistel et al. (2010), these four water masses are considered as the mixture of Standard Seawater that has standard-ocean salinity, with the local coastal water which contains unknown amounts of unknown  
 200 solute. The related regression lines of the four water mass between Absolute Salinity Anomaly and the Reference Salinity can be computed from the samples with salinity  $S_R > 2 \text{ g kg}^{-1}$ , in which the seawater endpoints are chosen to be SSW with a  $\delta S_A$  of zero, as shown in Eq. (11) and Fig.5

$$S_A - S_R = \begin{bmatrix} 412 \\ 236 \\ 150 \\ 107 \end{bmatrix} / (\text{mg} \cdot \text{kg}^{-1}) \cdot \left(1 - \frac{S_R}{S_{SO}}\right), \left[ \begin{array}{l} \text{Laizhou Bay and Bohai Bay} \\ \text{North Jiangsu Shoal} \\ \text{Yangtze River Estuary and Hangzhou Bay} \\ \text{Pearl River Estuary} \end{array} \right] \quad (11)$$



205 **Fig.5 The Absolute Salinity Anomaly of the four regions of China offshore as a function of their Reference Salinity**

The linear correlation between Absolute Salinity Anomaly and  $S_R$  in the Pearl River Estuary is the strongest among the four regions, which shows that the mixture between the coastal seawater and that of open ocean is relatively conservative. There are many measurements over all salinities for the Yangtze River water. The strong scatter visible in Fig.5 at low salinities is likely due to the rich (and highly variable) nutrient loading brought by Yangtze River draining from land.

The regressions for the two northernmost areas are less precise, as the oceanographic sampling pattern does not enter into the rivers and measured salinities are larger than  $25 \text{ g kg}^{-1}$ . The fitted curves are somewhat steeper. Note that Pawlowicz (2015) also finds that Salinity Anomalies in the Yellow River of about  $0.2 \text{ g kg}^{-1}$  are also higher than in the other rivers (Table 2), although not as high as our fits in Fig. 5 suggest. The fit for the North Jiangsu Shoal region is heavily influenced by many high values when salinities are between 20 and  $25 \text{ g kg}^{-1}$ , and lies somewhat above a smaller number of values spread over lower salinities.

It can be seen from Fig.5 that the relative composition anomalies decrease from north to south. The exchange of coastal waters with the open ocean waters increases gradually from the northernmost (and somewhat enclosed) Bohai Sea Estuary to the southernmost Pearl River area, which is open to the South China Sea.

### 3.4 Relative composition anomaly of China offshore seawater

In Eq. (6), the coefficients are determined by fitting to the results of a more complete calculations that assume changes to  $\text{Ca}^{2+}$  to maintain a charge balance according to Eq. (7). We cannot directly check the accuracy of this assumption. However,  $\text{Ca}^{2+}$  was directly measured from samples in 13 cruises from April 2011 to February 2012 (Qi Di, 2013). Although these measurements do not occur at the same time as our larger dataset, we can group these measurements in the same regions (labelled in Fig.1) in which we find large Salinity Anomalies. Then, we find the  $\Delta\text{N}[\text{Ca}^{2+}]$ ,  $\Delta[\text{NO}_3^-]$  and  $\Delta[\text{NTA}]$  (first column) values from our dataset (Table 3), are approximately consistent with Eq. (7).

**Table 3.** The mean value of  $\Delta[\text{NTA}]$ ,  $\Delta[\text{NO}_3^-]$ ,  $\Delta[\text{NTA}]^*$ , and  $\Delta\text{N}[\text{Ca}^{2+}]^*$  are given in different areas (marked in Fig.1).

Values obtained from Qi Di (2013) are labelled with ‘\*’. Units are  $\mu\text{mol kg}^{-1}$ .

Region	$\Delta[\text{NTA}]$	$\Delta[\text{NO}_3^-]$	$\Delta[\text{NTA}]^*$ ( Qi Di, 2013)	$\Delta\text{N}[\text{Ca}^{2+}]^*$ ( Qi Di, 2013)
Bohai	$620 \pm 339$	$13.6 \pm 11.3$	-	$364 \pm 115$
South Yellow Sea	$318 \pm 330$	$6.8 \pm 10.1$	-	$136 \pm 46$
East China Sea	$170 \pm 540$	$16.4 \pm 23.0$	-	$90 \pm 54$

South branch of Yangtze River ( $S_P < 1$ )	1727 $\pm$ 301 in Feb. and Apr.	112.06 $\pm$ 18.84	1845	981~1014
	1770 $\pm$ 150 in Jul.	101.45 $\pm$ 4.67	1696~1869	925~936
	1977 $\pm$ 304 in Oct.	81.42 $\pm$ 9.62	1900	992
North branch of Yangtze River Estuary ( $8 < S_P < 20$ )			245~480	132~250

230 The other nutrient of phosphate is not considered in the calculation for their concentrations range from 0 to 0.01 mmol kg<sup>-1</sup> in the existing observation which is much smaller than those items in Eq. (7) above and its effect is negligible. In this case,  $\Delta[\text{NO}_3^-]$  is mostly negligible and  $\Delta\text{N}[\text{Ca}^{2+}]$  is about 43%~58% of  $\Delta[\text{NTA}]$ , in Bohai, South Yellow Sea, East China Sea and Yangtze River.

235 The importation of  $\text{Ca}^{2+}$  and the carbon system suggests that the major source of Salinity Anomalies in shelf areas is the high  $\text{CaCO}_3$  content of rivers. This is consistent with Salinity Anomalies in the Baltic Sea, which were found to be mostly related to the calcium carbonate input from rivers (Feistel et al., 2010a). These rivers would be the Yangtze, Yellow River, and Huaihe Rivers. The importation fluxes of  $\text{Ca}^{2+}$  into the sea of Yellow River and Yangtze River are  $3.6 \times 10^{10}$  and  $6.5 \times 10^{11}$  mol yr<sup>-1</sup> respectively in 2011 (Qi Di, 2013). In addition, there may be re-dissolution of sediments in the Yellow River Estuary and North Jiangsu Shoal. Due to the accumulation of materials entering the sea from the old Yellow River and the ancient Yangtze River, the  $\text{CaCO}_3$  concentration of surface sediments on the seafloor of the North Jiangsu Shoal ranges from 2.8% to 10.5% (Qin, et al, 1989; Yang and Youn, 2007). The  $\Delta\text{NDIC}$  of the south Yellow Sea near China has always been high, even when strong biological activity in spring reduces the surface  $\Delta[\text{NTA}]$ , the sediment of particulate inorganic carbon will resuspend and maintain the high dissolved  $\text{CaCO}_3$  of seawater through the solid-liquid balance (Hong, 2012; Zhang, et al, 1995).

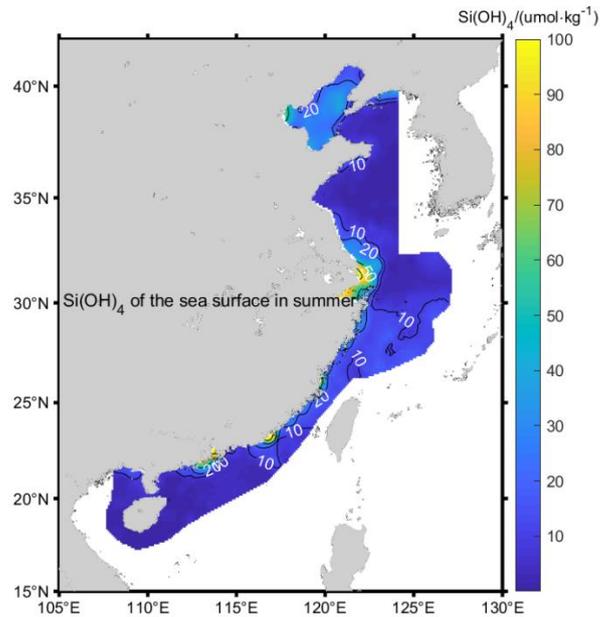
### 245 3.5 Contrast to the $\delta S_A$ calculated by GSW

Using the GSW function library and the corresponding climatological silicate and Practical Salinity data, the calculated  $\delta S_A$  of China offshore ranges from 0 to 0.002 g kg<sup>-1</sup>. This is two orders of magnitude less than values calculated in Section 3.2. The spatial distribution characteristics are also significantly different. These differences mainly come from the following aspects:

250 (1) Instead of silicate,  $\text{CaCO}_3$  is most likely the main relative composition anomaly of China offshore seawater and the primary contributor to the  $\delta S_A$  where it is greater than 0.05 g kg<sup>-1</sup>.

(2) High silicate concentrations (up to  $100 \mu\text{mol}\cdot\text{kg}^{-1}$ ) do appear in Chinese coastal seawaters from the effects of river (Fig 6), but these do not appear in the global silicate climatology used for the GSW calculations. However, even if they did, in these places NTA is even larger, so that the effects of this coastal silicate on the Salinity Anomaly is small.

255 In the remaining areas, the silicate concentration is less than  $20 \mu\text{mol}\cdot\text{kg}^{-1}$ , as shown in Fig.6. At 95 % degree of confidence, the difference between the observation and the GSW climatological dataset is  $[5.46, 6.21] \mu\text{mol}\cdot\text{kg}^{-1}$  which does not change much with the seasons. It can be indicated the GSW climatological dataset basically reflects the distribution characteristics of silicate in these areas.



260 **Fig.6  $\text{Si(OH)}_4$  isoclines of sea surface in summer**

#### 4 Conclusion and analysis

The proposal and implementation of the concept of  $S_A$  in TEOS-10 is meant to accurately quantify the total mass of inorganic substance dissolved in sea water, to ensure that the density and related quantities are accurately represented by the Gibbs function for seawater and correct errors caused by the measuring the properties of seawater such as chloride and conductivity to get the salinity. In this paper, based on observations and calculations, the magnitude, distribution characteristics of Absolute Salinity in China offshore are described:

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1) The Absolute Salinity  $S_A$  ranges from 0.1 to 34.66 g kg<sup>-1</sup>, in which  $S_R$  ranges from 0.01 to 34.66 g kg<sup>-1</sup> and the Absolute Salinity Anomaly  $\delta S_A$  ranges from 0 to 0.30 g kg<sup>-1</sup>, this is an order of magnitude larger than the largest values in the open ocean.

270 2) The largest  $\delta S_A$  are located in four distinct regions: the Yangtze River mouth/Hangzhou Bay, North Jiangsu Shoal, Bohai Sea, and the Pearl River mouth, all of which are areas where the  $\Delta[\text{NTA}]$  is high;

3) Instead of silicate, CaCO<sub>3</sub> is most likely the main composition anomaly relative to SSW and the primary contributor to the  $\delta S_A$  in the above four areas;

4) Under the combined effects of different water system dynamics, terrestrial input, marine biological activities, and re-  
275 dissolution of marine sediments, the  $\delta S_A$  in China offshore seasonal variations are obvious, and the maximum can be as high as 0.05 g kg<sup>-1</sup>; the difference between the surface layer and the bottom layer is also up to 0.1 g kg<sup>-1</sup>;

With the observations available, this paper only lists the magnitude and distribution characteristics of  $\delta S_A$  in China offshore from 2006 to 2007, although it is likely that similar features will occur in other years. At present, we have collated the long-term series of seawater composition data to continue the study on  $\delta S_A$  changes and get an empirical  
280 formula to calculate it.

The current researches are only based on the existing seawater composition data, and the exact influence of other changes to composition is still not very clear. To verify these findings, a complete chemical analysis and/or direct measurements of seawater density would be useful in the estuaries of the Yangtze River, Qiantang River, Pearl River, Minjiang River, and the semi-enclosed Bohai Sea.

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#### **References:**

290 Commission of Science and Technology of the People's Republic of China: Report of the National Comprehensive Marine Survey - Volume I, 1964.

GCOS 2010: Implementation Plan for the Global Observing System for Climate in support of the UNFCCC (2010 Update) (Geneva: World Meteorological Organization) WMO-TD/No. 1532 (GCOS-138), 180.

- IOC, SCOR, IAPSO, 2010. The International Thermodynamic Equation of Seawater— 2010: Calculation and Use of  
295 Thermodynamic Properties. Manual and Guides No. 56. Intergovernmental Oceanographic Commission, UNESCO  
(English), available from (<http://www.TEOS-10.org>).Feistel, R., G. M. Marion, R. Pawlowicz, and D. G. Wright:  
Thermophysical Property Anomalies of Baltic Seawater, *Ocean Science* 6, 949-981, 2010a.
- Feistel, r., s. Weinreben, h. Wolf, s. Seitz, p. Spitzer, b. Adel, g. Nausch, b. Schneider and d. Wright: Density and  
Absolute Salinity of the Baltic Sea 2006-2009, *Ocean Science*, 6, 3-24, 2010b.
- 300 F.J. Millero: *Chemical Oceanography-Fourth edition*, CRC press, Taylor & Francis Group, 2013.
- Gouretski, v. v. and k. p. Koltermann: WOCE Global Hydrographic Climatology. *Berichte des Bundesamtes fur  
Seeschiffahrt und Hydrographie Tech. Rep. 35, 49, 2004.*
- Hong Huasheng: *China Regional Oceanography-Chemical Oceanography*, Ocean Press, Beijing, 2012.
- Ji Weidong: *China Offshore - Ocean Chemistry*, Ocean Press, Beijing, 2016.
- 305 Lewis, E. and Wallace, D. W. R.: Program developed for CO2 system calculations, ORNL/CDIAC-105, Oak Ridge  
National Laboratory, 1998.
- Li, Y., Luo, Y., Kang, Y., Yu, T., Wang, A., & Zhang, C. Chinese primary standard seawater: stability checks and  
comparisons with IAPSO Standard Seawater, *Deep Sea Research Part I: Oceanographic Research Papers*, 113, 101-  
106, 2016.
- 310 Lv Cuilan: *Analysis of Decadal Variability of Salinity Field and its influence to Circulation in Bohai and northern  
Yellow Sea*, The Master Degree Dissertation of China Ocean University, 2008.
- McDougall, T.J. and P.M. Barker: *Getting started with TEOS-10 and the Gibbs Seawater (GSW) Oceanographic  
Toolbox*, 28pp., SCOR/IAPSO WG127, ISBN 978-0-646- 55621-5, 2011.McDougall, T.J., D.R. Jackett, F.J.  
Millero, r. Pawlowicz and P.M. Barker: A global algorithm for estimating Absolute Salinity, *Ocean Science*, 8, 1123-  
315 1134, 2012.
- Millero, F.J.. The conductivity–density–salinity–chlorinity relationships for estuarine waters, *Limnol. Oceanog.* 29 (6),  
1317–1321. (1984)
- Millero, F. J., R. Feistel, D. G. Wright and T. J. McDougall: The composition of Standard Seawater and the definition  
of the Reference-Composition Salinity Scale, *Deep-Sea Research I*, 55, 50-72, 2008.
- 320 Pawlowicz, R.: A model for predicting changes in the electrical conductivity, Practical Salinity, and Absolute Salinity  
of seawater due to variations in relative chemical composition, *Ocean Science*, 6, 361-378, 2010.
- Pawlowicz R., D. G. Wright, and F. J. Millero: The effects of biogeochemical processes on oceanic  
conductivity/salinity/density relationships and the characterization of real seawater, *Ocean Science*, 7, 363-387,  
2011.

- 325 Pawlowicz,R.: The Absolute Salinity of Seawater Diluted by River water, *Deep-Sea Research I*, 101 71-79, 2015.
- Pawlowicz, R., Feistel, R., McDougall, T. J., Ridout, P., Seitz, S., and Wolf, H.: Metrological challenges for measurements of key climatological observables – Part 2: Oceanic salinity, *Metrologia*, 53, R12-R15, 2016.
- Qi Di: Dissolved Calcium in the Yangtze River Estuary and China Offshore, The Master Degree Dissertation of, Xiamen University, 2013.
- 330 Qin Yunshan, Zhao Yiyang, Chen Lirong: *Huanghai Geology*, Beijing: Science Press, 1989.
- Yuan Jianzhong: Study on Water Exchange Characteristics Between Yangtze Estuary and Hangzhou Bay, The Third Yangtze River Forum Proceedings (in Chinese), 183-191, 2009.
- Ryan J. Woosley, Fen Huang, Frank J. Millero: Estimating absolute salinity (SA) in the world's oceans using density and composition, *Deep-Sea Research I*, 93, 14–20, 2014.
- 335 Song Wenpeng: The Analysis of the Structure of T-S and the Current Characteristics in Bohai Sea during Winter and Summer, The Master Degree Dissertation of China Ocean University, 2009.
- Seitz, S., P. Spitzer and R. J. C. Brown: Consistency of practical salinity measurements traceable to primary conductivity standards: Euromet project 918, *Accred. Qual. Assur.*, 13, 601–605, 2008.
- Seitz, S., P. Spitzer and R. J. C. Brown: CCQM-P111 study on traceable determination of practical salinity and mass fraction of major seawater components. *Accred. Qual. Assur.* 15, 9–17, 2010.
- 340 State Ocean Administration of China: *China Offshore Atlas - Ocean Chemistry*, Beijing, ocean press, 2016.
- State Ocean Administration of China: *China Offshore Atlas - Oceanography*, Beijing, ocean press, 2016. UNESCO: The Practical Salinity Scale 1978 and the International Equation of State of Seawater 1980, UNESCO technical papers in Marine Science, 36, 25 pp., 1981.
- 345 Wu Dexing, Mu Lin, Li Qiang, Bao Xianwen, Wan Xiuquan: Characteristics of Long-term Change and Its Possible Dominant Factors in Bohai Sea, *Progress in Nature Science*, 14(2), 191-195, 2004.
- Wu Dexing, Wan Xiuquan, Bao Xianwen, Mu Lin, Lan Jian: Comparison of Temperature-Sallinity Field and Circulation Structure in the Summer between 1958 and 2000, *Chinese Science Bulletin*, 49(3), 287-292, 2004.
- Wright D G, Pawlowicz R, McDougall T J, Feistel R and Marion G M: Absolute salinity, ‘Density salinity’ and the reference-composition salinity scale: present and future use in the seawater standard TEOS-10 *Ocean Sci.* 7, 1–26, 2011.
- 350 Xiong xuejun: *China Regional Oceanography and Marine Meteorology*, Ocean Press, Beijing, 2012.
- Xu Jiangling: The variation characters and formation mechanism of salinity in the Bohai Sea, The Master Degree Dissertation of China Ocean University, 2007.

- 355 Yang S, Youn JS.: Geochemical compositions and provenance discrimination of the central south Yellow Sea sediments. *Marine Geology*, 243(1-4): 229-241, 2007.
- Zhang, J., Huang, W.W., L'écalle, R., Jusserand, C.: Major element chemistry of the Huanghe River (Yellow River), China—weathering processes and chemical fluxes. *Journal of Hydrology* 168 (1-4), 173–203, 1995.