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Surface water $\delta^{18}O$ in the marginal China seas and its hydrological implications

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Surface water $\delta^{18}O$ distribution in the marginal China seas (including the south Yellow and East China Seas, YECS, and the northern South China Sea, NSCS) and its relationship with salinity were investigated to gain insight into the surface hydrological processes in these seas. In the YECS where $\delta^{18}O$ and salinity varied in relatively large ranges, seasonally different slopes of $\delta^{18}O$-salinity linear fits, i.e. 0.26 ± 0.02 in summer and 0.23 ± 0.01 in winter, were observed. In the NSCS, $\delta^{18}O$ and salinity ranged narrower than in the YECS, and exhibited a similar linear relationship in winter but a poor correlation in summer. The saline surface water end-members were nearly identical in $\delta^{18}O$ and salinity in both the YECS and NSCS and showed different values between summer and winter. These saline end-members were distinct from the reported values of the Kuroshio water (KW), which might be related to modification of KW mainly by atmospheric forcing. Using a simple mixing model, we showed that the observed significant linear $\delta^{18}O$-salinity relationships in the YECS were caused mainly by great terrestrial freshwater influx. The observed poor correlation between $\delta^{18}O$ and salinity in the summer NSCS was likely associated with the relatively minor runoff contribution, although in wet period, to the freshwater end-member. The still good relationship in the NSCS during the dry wintertime, however, was attributable to the strong China Coastal Current flowing from the ECS to the NSCS through the Taiwan Strait driven by the prevailing northeast monsoon.

1. Introduction

Marginal seas are important transit zones for the exchange of materials between land and ocean, and they are usually active in air-sea interaction. Despite their moderately-sized surface areas, marginal seas play a crucial role in the ocean carbon cycling and other biogeochemical processes (Dagg et al., 2004; Muller-Karger et al., 2005). A thorough knowledge of the surface hydrological processes along the marginal seas is a primary requirement for understanding ocean circulation, biogeochemical cycling and ecosystem dynamics. Studies over the past decades have shown that marginal seas around the world are experiencing rapid climate change, and consequently the freshwater budgets in these regions are significantly affected (Belkin, 2009; Helm et al., 2010), which is needed to be documented to better understand its consequences.

The stable oxygen isotopic composition ($\delta^{18}O$) is an important tracer of natural hydrological processes. It is imprinted on a water mass in its source area and, once isolated from the surface ocean, altered only by conservative mixing with other water masses of contrasting composition (Craig and Gordon, 1965; Frew et al., 2000). Thus, in modern ocean research, $\delta^{18}O$ measurements have been used to obtain valuable information on the origin and mixing of water masses (e.g., Torgersen, 1979; Zhang et al., 1990; Frew et al., 2000). Besides, a parallel study of $\delta^{18}O$ and surface seawater salinity (SSS) can also provide specific information about sea surface hydrological processes such as (1) evaporation/precipitation, (2) melting/freezing, (3) upwelling/advection, and (4) continental runoff (Craig and Gordon, 1965; Benway and Mix, 2004). Furthermore, the $\delta^{18}O$-SSS relationship has been widely used in paleoclimatology/paleoceanography to determine past SSS changes from the $\delta^{18}O$ measurements of carbonate shells of marine microfossils such as foraminifera (e.g., Rohling, 2000; Jia et al., 2006; Yu et al., 2009).

The marginal seas off China, e.g., the Yellow and East China Seas (YECS), and the South China Sea (SCS), are parts of the western North Pacific and rank among the largest marginal seas in the world (Fig. 1). The northern SCS (NSCS) is connected to the YECS through the Taiwan Strait. Both the marginal seas are occupied by wide

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continental shelves with depth shallower than 200 m. Over these seas, the distribution and variability of water properties (e.g., salinity, temperature and density) are strongly influenced by river discharge from mainland China (including the Yangtze River, the Yellow River and the Pearl River), seasonally reversed summer and winter monsoon winds, and the Kuroshio water (KW) that is a major western boundary current in the north Pacific (Chen et al., 1994; Hu et al., 2000; Chen et al., 2006). Although seasonal variation of the KW is comparatively low, great seasonal contrasts of the river runoff (R), precipitation (P) and evaporation (E) caused by the East Asian monsoon climate may produce relatively large seasonal variation of hydrographic structure of these seas. In the last two decades, seawater $\delta^{18}O$ and its relationship with salinity in the YECS and the NSCS have been investigated (e.g., Zhang et al., 1990; Kang et al., 1994; Hong et al., 1994, 1997; Lin, 2000). However, the available data were mostly from a small spatial coverage and very little has been published about the seasonal differences in seawater $\delta^{18}O$. Moreover, there lack comparative studies discussing possible differences in $\delta^{18}O$-salinity relationship between the two marginal sea systems.

In this study, surface water $\delta^{18}O$-SSS relationships inferred from new and extensive measurements of these tracers in the YECS and NSCS are presented. The wide spatial coverage and two season's sampling allowed us to examine the spatial and temporal variations in the associated surface hydrological processes over the YECS and NSCS. Our results may also be helpful for the paleoceanographic studies based on carbonate $\delta^{18}O$ analysis in these marginal seas.

2. Materials and methods

The sampling was conducted in the YECS and the NSCS during two R/V Dongfanghong II expeditions in July–September 2009 and December 2009–February 2010 (Fig. 1). Seawater samples at ~5 m depth were taken using Niskin bottles mounted onto a rosette system. A total of 217 samples, with 92 in summer and 125 in winter, were collected during the two expeditions. All samples were drawn into glass vials, sealed with wax under air temperature and then kept cool until analysis for $\delta^{18}O$. Sea surface temperature (SST) and salinity were recorded using an SBE19-plus conductivity-temperature-depth (CTD) system. The precision was ± 0.001 °C for SST and ± 0.001 for SSS based on conductivity measurements. Just prior to the cruises, the CTD system was shipped back to Sea-Bird for calibration.

$\delta^{18}O$ analysis was carried out in the laboratory using the standard CO_2–H_2O equilibrium method for $\delta^{18}O$ (Epstein and Mayeda, 1953) in conjunction with a custom headspace auto-sampler connected to an IsoPrime mass spectrometer (GV IsoPrime II). Results were reported in δ-notation ($\delta^{18}O$) relative to the VSMOW in permil (‰). Based on the analysis of random duplicate samples, analytical precision was ±0.08‰ for $\delta^{18}O$. All analyses were performed in the State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, CAS.

3. Results

3.1. Spatial and seasonal distributions

SST and SSS showed clear variations in spatial and seasonal distributions (Fig. 2). Warm waters >24 °C were uniformly distributed across China seas during summer; whereas a nearshore-offshore SST gradient occurred in winter. The SST gradient was small and confined to nearshore area in the low-latitude NSCS, but it became larger and was widely distributed in the YECS. SSS ranged from 25.7 to 33.9 (30.6 ± 2.4 average, $n = 41$)

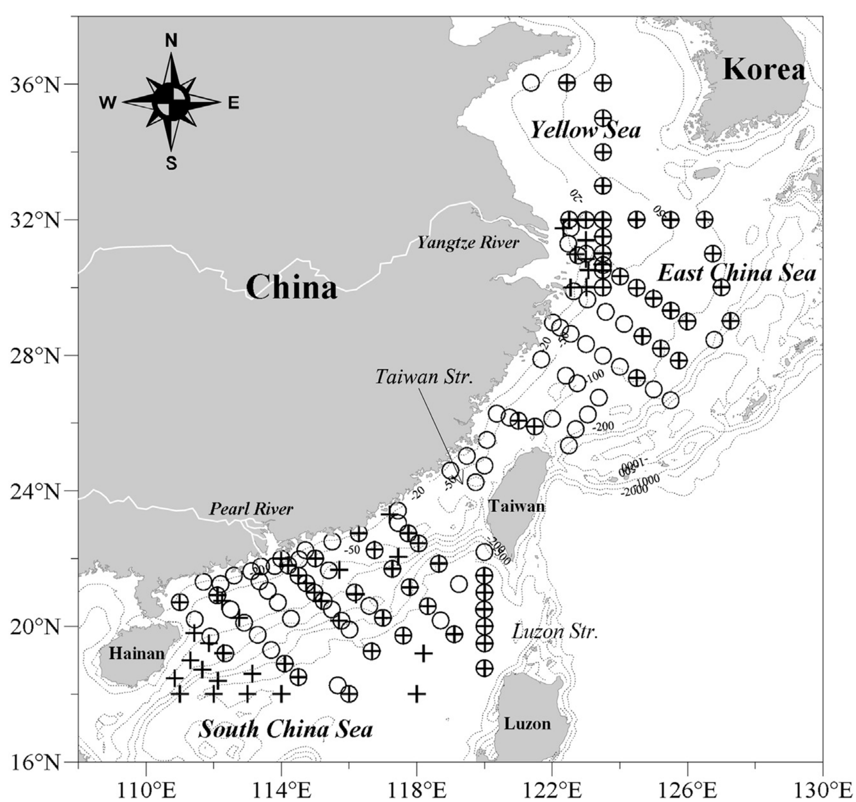

Fig. 1. Map of the marginal China seas showing locations of sampling sites used in this study. Crosses (+) represent sampling sites during summer and open cycles (○) represent sampling stations during winter.

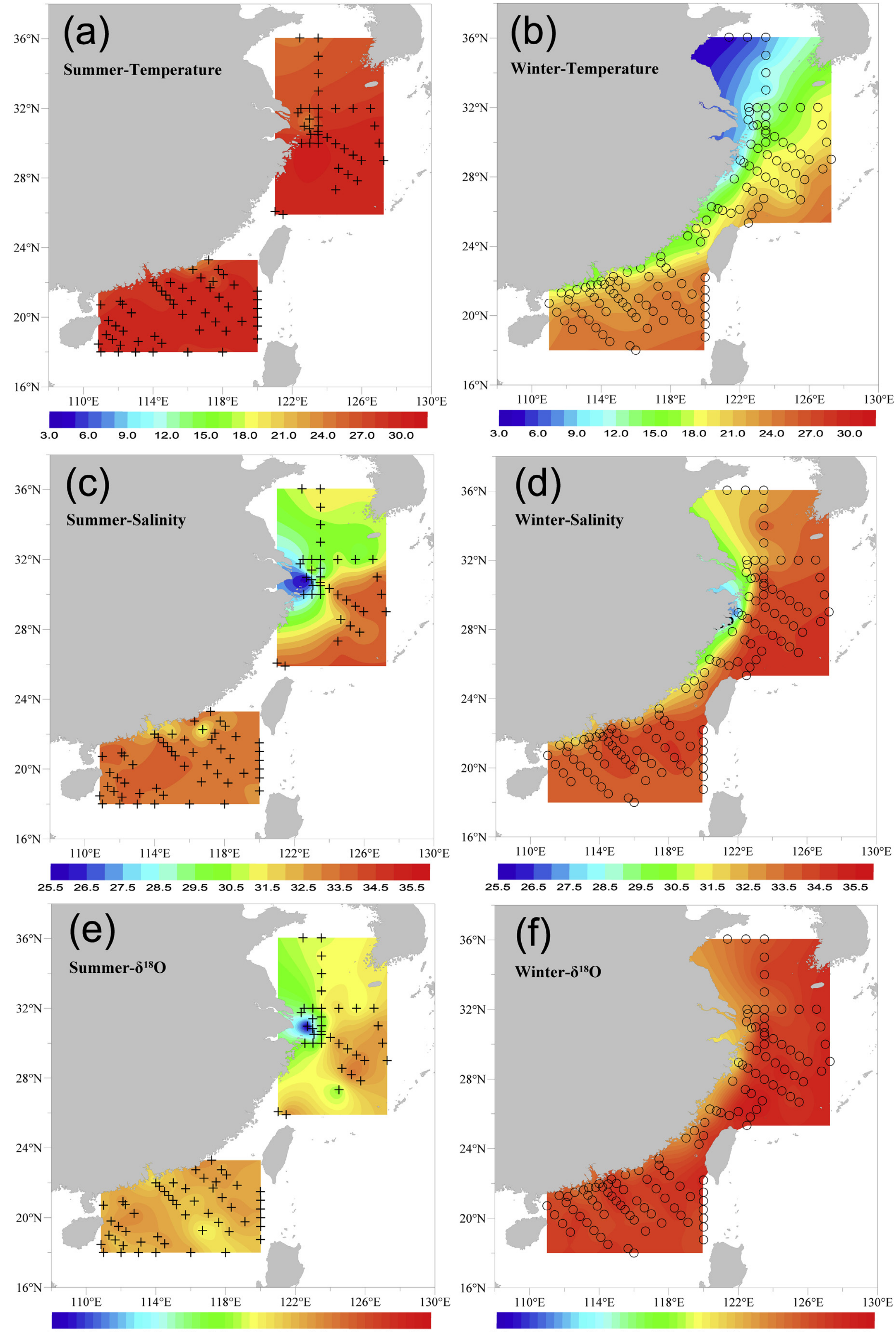

Fig. 2. Surface water distributions of temperature (a, b), salinity (c, d), and $\delta^{18}O$ (e, f) in marginal China seas during summer (left panel) and winter (right panel).

in summer and from 27.1 to 34.6 (33.2 ± 1.6 average, $n = 63$) in winter in the YECS, and its distribution showed roughly inverse seasonal patterns to SST in the YECS. For example, a large area of diluted water (<32.0) extended mainly northeastward from the Yangtze River Estuary to the shelf during summer, but the diluted water became narrower and was confined to nearshore area during winter. In the NSCS, no clear spatial difference can be observed, but there existed a seasonal contrast ($p < 0.01$, *t*-test), with higher SSS in winter (33.8 ± 0.7 average, $n = 62$) than in summer (33.2 ± 0.6 average, $n = 51$). The SSS values in the outer shelf of the YECS were similar to those in the NSCS.

Surface water $\delta^{18}O$ values in the YECS and NSCS ranged from −4.66‰ to −0.31‰, showing significantly heavier values in winter (−0.72 ± 0.31‰ average, $n = 125$) than in summer (−1.90 ± 0.62‰ average, $n = 92$). Similar to the seasonal contrast in SSS distributions in the YECS, waters with lighter $\delta^{18}O$ values occupied a narrow nearshore area in winter but were distributed more widely in summer, with lowest values near the Yangtze River Estuary. Contrary to the YECS, $\delta^{18}O$ values in the NSCS varied in a narrower range from −2.17‰ to −1.31‰ in summer and from −1.13‰ to −0.31‰ in winter with no clear spatial pattern.

3.2. The $\delta^{18}O$-SSS relationship

When being pooled together in one cross plot (Fig. 3a), data of the $\delta^{18}O$ and SSS in the same season from both the YECS and the NSCS overlapped. However, no overlapping occurred between summer and winter data points, with higher $\delta^{18}O$ in winter. So the relationship between $\delta^{18}O$ and SSS in summer and winter was examined separately. Overall, $\delta^{18}O$ positively correlated with SSS, with $\delta^{18}O$-SSS slopes of 0.26 ± 0.02 in summer ($p < 0.001$) and 0.23 ± 0.01 in winter ($p < 0.001$) (Fig. 3b and c). Data in the YECS ranged evidently larger than those in the NSCS, but were similar to the NSCS at the saline-water ends. For example, in winter the average maximum data pair of ($\delta^{18}O$, SSS) were (−0.45‰, 34.56; $n = 5$) in the NSCS and (−0.43‰, 34.60; $n = 5$) in the YECS; and in summer they were (−1.56‰, 33.70; $n = 5$) in the NSCS and (−1.60‰, 33.75; $n = 5$) in the YECS. The intercepts of −10.18 ± 0.54‰ and −8.30 ± 0.30‰ at zero SSS for summer and winter, respectively, could reflect the regionally averaged freshwater end-member $\delta^{18}O$ values. Several most diluted waters in summer YECS, however, deviated evidently from the general linear trend, displaying a secondary relationship (gray dash line in Fig. 3b) with a higher slope of 0.54 ± 0.03 and a very low zero-SSS intercept of −18.35 ± 0.92‰ ($R^2 = 0.96$, $p < 0.001$). If the two most diluted data points are excluded from the linear regression, the $\delta^{18}O$-SSS slopes would be nearly identical between summer and winter. In the NSCS, however, only winter data exhibited a significant linear correlation ($R^2 = 0.67$, $p < 0.001$) between $\delta^{18}O$ and SSS, with a slope of 0.21 ± 0.02 (Fig. 3c). Whereas summer data in the NSCS were clustered at the saline-water end and could not generate a significant linear $\delta^{18}O$-SSS relationship ($R^2 = 0.20$, $p > 0.05$) due to the limited ranges of $\delta^{18}O$ and SSS values (Fig. 3b).

4. Discussion

4.1. Water end-members and isotope–salinity relation

In this study, the saline water end-members in the YECS could not be discerned from those in the NSCS. We believed they originated from the same source of the KW, which stretches northward from the tropic as a western boundary in the Western Pacific and

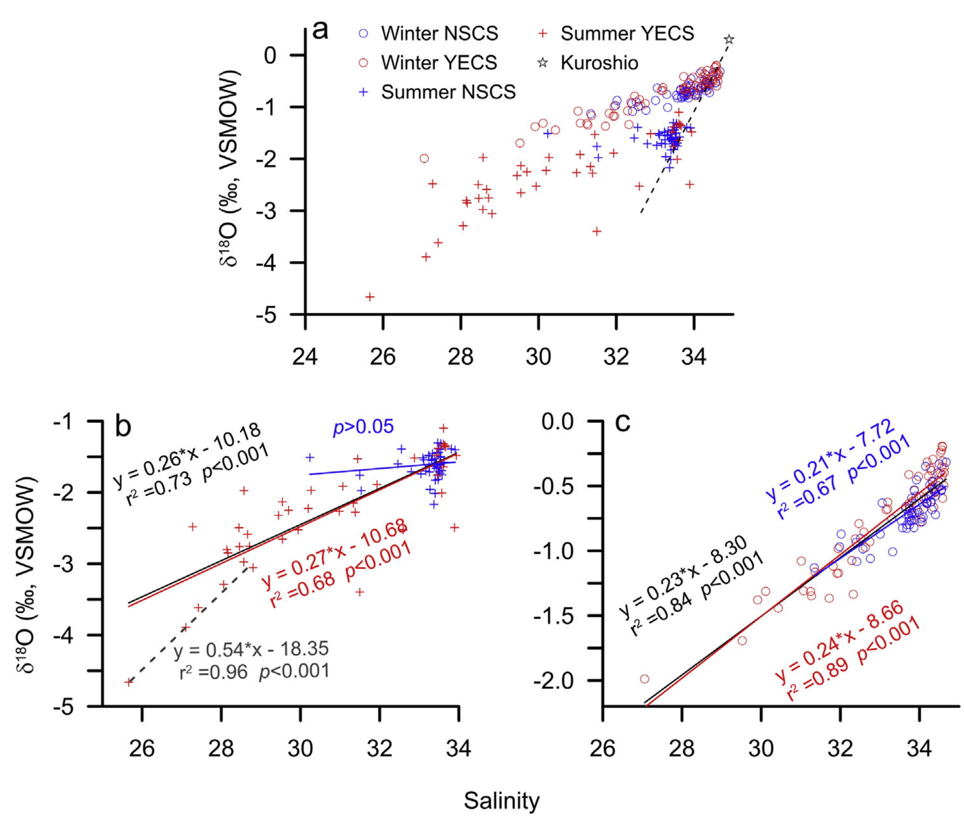

Fig. 3. (a) $\delta^{18}O$-SSS cross plot of all the summer and winter data in the China seas in this study; Star denotes the typical Kuroshio water reported in literature; (b) summer $\delta^{18}O$-SSS data and regressions; (c) winter $\delta^{18}O$-SSS data regressions. The black linear regressions in (b) and (c) are based on the whole dataset, and blue and red regressions are for YECS and NSCS, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

persistently intrudes into the NSCS and YECS (e.g., Hsueh et al., 1997; Matsuno et al., 2009). However, previously reported δ^{18}O-SSS data of KW, e.g. δ^{18}O of 0.2–0.5‰ and SSS >34.4 (star in Fig. 3a) (e.g., Kang et al., 1994; Kim et al., 2005), were higher than our observed saline water data and above the linear mixing lines between the saline and fresh waters. Similar observations have been also noted around Jeju Island in April 1988 by Kim et al. (2005), who attributed the lower saline water end-members to another saline water mass originated from the Taiwan Strait, a modified KW with depleted δ^{18}O. However, our finding of this similar saline water end-member both for the NSCS and YECS suggests that the modification of KW was not locally limited in the Taiwan Strait and Taiwan current. Our results further demonstrated that this modified KW may vary with season. But, seasonal variations in river discharge were unlikely the causes of the modifications, because, by assuming a constant KW, the extrapolated δ^{18}O at zero SSS from the linear trend relating saline end-members to inherent KW would yield unrealistically depleted δ^{18}O (the sketched dash line in Fig. 3a). So, we speculated that the significantly different saline water end-members between winter and summer were likely related to the distinct seasonal modifications by atmospheric forcing in China seas, which is characterized by moist, mild SW monsoon in summer and dry, strong NE monsoon in winter. This seasonal climate change may not only result in higher summer P/E values and lower winter P/E values, but also induce greater vertical mixing in the upper water column in winter, thus causing a lower saline water end-member in summer and a higher one in winter. Nevertheless, the assumption of a constant KW is simplistic. It has been observed that KW may be altered along the flowing path by mixing with surrounding waters along or across isopycnals (Rudnick et al., 2011). Therefore, seasonal changes in subsurface mixing-induced alteration of KW might be an alterative cause for our observed different saline water end-members between winter and summer, and further, responsible for their differences from those reported typical KW values.

The δ^{18}O data and the primary slopes (0.23 ± 0.01 and 0.26 ± 0.02) of the δ^{18}O-SSS relationship obtained in this study are similar to those of previously published slopes of 0.20–0.29 for the YECS (e.g., Zhang et al., 1990; Kim et al., 2005; Du et al., 2012). The projected freshwater end-members identified in this study (−10.18 ± 0.54‰ in summer and −8.30 ± 0.30‰ in winter) are consistent with the typical river water δ^{18}O values (−9.9 to −7.1‰) in the region (Zhang et al., 1990; Wu, 1991; Du et al., 2012). In comparison with surface waters in other seas, the obtained δ^{18}O-SSS slopes are much lower than those at mid-latitudes and high northern latitudes (≥0.50) where the freshwater end-members are more depleted in ^{18}O (Craig and Gordon, 1965; Frew et al., 2000; LeGrande and Schmidt, 2006). In the present study, the low δ^{18}O-SSS slope appears to be also associated with saline surface water end-members characterizing by depleted δ^{18}O relative to inherent KW as discussed above. By using the modified KW instead of the inherent KW as a saline end-member, a lower δ^{18}O-SSS slope would be expected. For comparison, Lin (2000) observed δ^{18}O-SSS linear relationships from a site in the SCS with slopes of 0.66 in April 1998 and 0.33 in April 1999. Such relationships, however, were based on water samples at a certain site with depth range between 0 and 100 m, where the saline end-member was in depth and underwent less modifications by atmospheric forcing.

It is interesting to note that the δ^{18}O-SSS relationship for some low salinity waters in YECS during summer deviated from the main trend with a higher slope and more negative intercept of zero-salinity values (−18.35 ± 0.92‰) (the dash line in Fig. 3b). The contribution of δ^{18}O-depleted freshwater from smaller rivers or submarine groundwater in the Yangtze Delta and the coastal regions can be excluded since these sources of water are characterized by δ^{18}O values heavier than −8.4‰ (Zhang et al., 1990; Jiang et al., 2008). Therefore, we suspected that local heavy precipitation with more isotopically depleted δ^{18}O values was likely the cause for a high slope and more negative intercept observed here. In fact, our summer cruise in the YECS was just after a high rainfall that followed the Typhoon Morakot, which made landfall on 7 August 2009 in central Taiwan and later in mainland China on 9 August (Fudeyasu et al., 2008; Chien and Kuo, 2011). Tropical cyclone rains generally have distinctly lighter δ^{18}O values than normal rains, which may be attributable to the typhoon's high condensation efficiency (Gedzelman and Lawrence, 1982; Lawrence and Gedzelman, 1996; Lawrence et al., 1998).

4.2. Contribution of terrestrial runoff

The observed δ^{18}O and salinity distribution and their relationships in YECS suggest a significant contribution of freshwater, which can be roughly simulated by a simple model. For a simple marine water body with freshwater input (runoff and precipitation) and output (evaporation), the δ^{18}O-SSS relationship can be expressed as a mixing line between the marine end-member ($\delta = \delta_m$, $S = S_m$) and the freshwater end-member ($\delta = \delta_f$, $S = 0$), whose slope is as follows:

$$\Delta\delta/\Delta S = \left(\delta_m - \delta_f\right)\Big/S_m \tag{1}$$

where the δ^{18}O of the freshwater end-member, δ_f, is defined as following:

$$\delta_f = (P\cdot\delta_P + R\cdot\delta_R - E\cdot\delta_E)/(P + R - E) \tag{2}$$

Substituting Eq. (2) into Eq. (1) and making some rearrangements, we got:

$$\Delta\delta/\Delta S = (\delta_m - (\delta_P + R/P\cdot\delta_R - E/P\cdot\delta_E)/(1 + R/P - E/P))/S_m \tag{3}$$

Here, the average values of three most saline data in summer, i.e. SSS = 33.9 and δ^{18}O = −1.4‰, and of four most saline data in winter, i.e. SSS = 34.6 and δ^{18}O = −0.4‰, were used as marine end-member values, respectively. As for the freshwater ends, there are few direct observations of precipitation, evaporation and their oxygen isotopic compositions over the YECS (Chen et al., 1994; Kang et al., 1994). We thus used rainfall and evaporation data from the land weather station at Shanghai (31°N) to estimate the E/P ratio over the YECS. The same treatment was also applied by Chen et al. (1994). Data from 1991 to 2003 (He and Xu, 2006) showed that the E/P ratio over the YECS was about 0.90 in both summer and winter, although seasonal changes in evaporation and precipitation were significant. In terms of precipitation δ^{18}O over the YECS, data from nearby GNIP (Global Network of Isotopes in Precipitation) station of Nanjing was used here, with averaged δ^{18}O values of −9.0‰ and −6.5‰ in wet season and dry season, respectively (Zhang et al., 2004; IAEA, 2008). These data are consistent with previous reports over the YECS (−6.7‰ to −8.8‰) (Kang et al., 1994). As to the river water δ^{18}O, the reported values of the Yangtze River were in the range of −7.1‰ to −9.9‰ (Zhang et al., 1990; Kim et al., 2005; Du et al., 2012), and thus an average value of −8.0 ± 1.0‰ was set here. Evaporation δ^{18}O is also a poorly constrained parameter. A value of $\delta_E = -4$‰ has been proposed as the global mean value under the condition of air temperature of 20 °C, and humidity of 0.75 (Craig and Gordon, 1965; Gat, 2000), and we set the same value in this study.

As shown in Fig. 4, our modelling result using above parameters indicates that increase of runoff relative to precipitation in the river-shelf system may greatly lower the $\delta^{18}O$-SSS slope to ~0.20 in the YECS, a value closer to our observed ones (0.23–0.26). Similar modelling results were also shown in other seas (e.g. Delaygue et al., 2001; Jia et al., 2006). Quantitatively, runoff fluxes approximately 2.3 and 1.6 as large as that of the precipitation are required to reproduce the observed slopes in summer and winter, respectively, demonstrating the predominance of terrestrial runoff over precipitation in the freshwater budget of the surface waters in the YECS. These required R/P ratios fall well within the wide range of previously reported values (about 1.0–3.0) in the ECS (Chen et al., 1994; Chu et al., 2005). Of course, such a box model is very simplified due to the use of a steady-state model in a potentially non-steady state system, poorly constrained parameters and the lack of any oceanic horizontal advections, but it still appears to work reasonably well.

Although the above simulation is appropriate to the YECS, it seems not applicable to the NSCS in summertime when poor correlation between $\delta^{18}O$ and SSS occurred (Fig. 3b). That most sample data were close to the saline end-member indicated a limited contribution of freshwater in surface water budget in the NSCS. This scenario, as well as the poor correlation between $\delta^{18}O$ and SSS, however, was unexpected, as the river discharge from the Pearl River is always largest during summer monsoon period (June to August). In fact, spreading over the whole shelf (1.24×10^6 km^2), the discharge flux from the Pearl River (350×10^9 m^3 yr^{-1}) is only equivalent to about 2.25 cm month^{-1} in the NSCS on an annual basis, with nearly two times (4.50 cm month^{-1}) greater during the high flow periods in summer. However, from the viewpoint of the water budget, the Pearl River discharge is several times smaller than the value of (P–E) there, especially in summer (9.80 cm month^{-1} and 28.9 cm month^{-1} for annual and summer averages, respectively; E and P data from the Hong Kong Observatory: http://www.hko.hk/wservice). These data suggest that a main part of the freshwater budget over the NSCS was controlled by E/P, and the Pearl River input was of secondary importance. The point of minor contribution from river runoff is also consistent with the observation that a large tongue or plume of relatively diluted water was limited only to nearshore areas in summer in the NSCS (Fig. 2). Such a pattern is in contrast to the YECS where the Yangtze River was the most important source of freshwater (i.e., P + R) input as simulated above and reported in literature (Chen et al., 1994, 2006). The poor correlation between $\delta^{18}O$ and SSS in summer NSCS was thus tentatively attributable to the spatially variable E/P values, as well as local upwelling patches induced by the southwest monsoon in the coastal areas (Jing et al., 2009), which may produce inconstant values for the freshwater and marine end-members.

However, the above interpretation of poor $\delta^{18}O$-SSS correlation by minor contribution of runoff in summer NSCS seems contradictory to the occurrence of good linear relationship during winter when runoff would be even less. We believed that the latter occurrence could be associated with the strong China Coastal Current (CCC) flowing from the ECS to the NSCS through Taiwan Strait driven by the prevailing northeast monsoon in wintertime, as demonstrated by a number of studies (e.g., Hu et al., 2000; Jan et al., 2006, 2010). A recent study by Han et al. (2013) not only confirmed that strong coastal current in the ECS can readily run into the NSCS during winter, but also proposed that the transported nutrient from the ECS could be a major nutrient source supporting winter primary production on the NSCS shelf. The surface water connection between the two seas via the CCC can also be read from the distributions of low temperature (<18.0 °C) and low salinity (<33.0) in Fig. 2, evidencing the existence of the CCC in the present study. The good linear relationship between $\delta^{18}O$ and SSS in winter in the NSCS, as well as its similarity to the linear fit in the YECS, therefore, also indicates a significant impact of ECS coastal water on the NSCS .

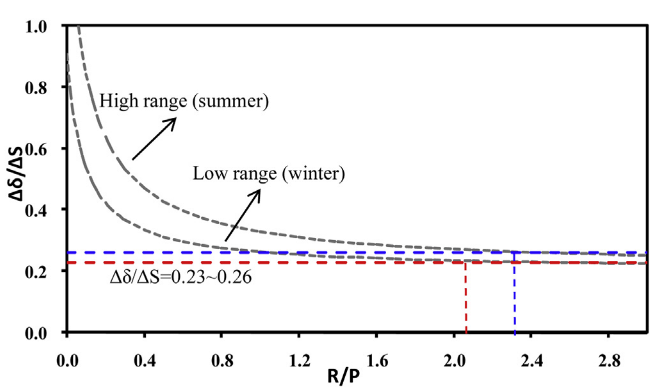

Fig. 4. Modeling of the $\delta^{18}O$-SSS slope in surface waters as a function of the R/P ratio for coastal waters over the YECS.

5. Conclusions

In this study, the wide spread of summer and winter surface water $\delta^{18}O$ data in the YECS and NSCS allowed us to decipher spatial and seasonal variations in $\delta^{18}O$-SSS relationship. The marine end-member for these waters was presumed to be sourced from the KW. However, the extrapolated saline end-members were distinct from the reported typical KW and displayed seasonal variations, which may be associated with the atmospheric forcing on the inherent KW or variations of KW along its flow path. In the YECS, significant linear $\delta^{18}O$-SSS relationships were observed, with slopes of 0.26 ± 0.02 in summer and 0.23 ± 0.01 in winter. These good relationships were attributable to the predominant contribution of the continental runoff to the freshwater end-member. In the NSCS, however, the similar linear $\delta^{18}O$-SSS relationship remained only in the wintertime, but poor relationship occurred in the summertime. The poor relationship in the summer NSCS might be due to the minor runoff contribution to freshwater end-member, as well as variably high E/P ratios. The good $\delta^{18}O$-SSS relationship in the winter NSCS was suggested to be associated with the significant inter-shelf coastal water transport from the ECS to the NSCS, and thus indicate the impact of ECS water masses on the NSCS in winter.

Acknowledgments

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