

A novel method for tracing coastal water masses using Sr/Ca ratios and salinity in Nanwan Bay, southern Taiwan

Chuan-Chou Shen^{a,*}, Kon-Kee Liu^{b,c}, Meng-Yang Lee^d, Typhoon Lee^e,
Chung-Ho Wang^e, Hung-Jen Lee^f

^a Department of Geosciences, National Taiwan University, Taipei 106, Taiwan, ROC

^b Institute of Hydrological Sciences, National Central University, Zhongli 320, Taiwan, ROC

^c National Center for Ocean Research, Taipei 106, Taiwan, ROC

^d Department of Science Education, Taipei Municipal Teachers College, Taipei 100, Taiwan, ROC

^e Institute of Earth Sciences, Academia Sinica, P.O. Box 1-55, Nankang, Taipei, Taiwan, ROC

^f National Museum of Marine Biology and Aquarium, Pingtung 944, Taiwan, ROC

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Abstract

A new method using two tracers, namely, the high-precision Sr/Ca ratio and salinity, has been successfully applied to quantitative determination of mixing proportions of freshwater, intruding surface seawater and upwelled water in a semi-enclosed bay, Nanwan Bay, southern Taiwan, where strong upwelling is induced by tidal forcing. The Sr/Ca ratio of the coastal water is essentially determined by the mixing ratio of the offshore surface water and the upwelled water, which usually have different Sr/Ca ratios. On the other hand, variability of coastal water salinity is strongly influenced by fresh water input. A Sr/Ca-salinity (Sr/Ca-S) diagram can thus be used to decipher the endmember contributions. During the 1994 dry season it was found that the Nanwan water was composed mainly of two components: 75.0% upwelled water from depths of 100–200 m offshore, and 25.0% offshore surface water. In the wet season an additional 2.0–2.5% fresh water, primarily from rainfall and surface runoff, was added to the bay. Validity of this model is confirmed by the agreement between the observed $\delta^{18}\text{O}$ value of the bay water and that calculated from model-derived mixing proportions using the endmember compositions. Once the mixing proportions were determined, the freshwater input rate provided a scaling factor for estimating the turnover rate of the bay water. The case study has thus demonstrated that the Sr/Ca-S relationship may serve as a novel tool for distinguishing different water masses and assessing the upwelling strength in a coastal environment.

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1. Introduction

Understanding coastal systems and assessing anthropogenic perturbations in this zone are key issues for environmental sustainability (Kremer et al., 2004). Some of the most fundamental hydrological properties, such as the mixing ratio of different water masses and their

transports in the coastal zone, are, however, difficult to evaluate because of the dynamic complexity of the coastal environment due to local topography, seasonal climatic forcing, and variable circulation patterns. Tracers, used to characterize different water masses, include temperature and salinity (e.g. Broecker and Peng, 1982; Pickard and Emery, 1990), as well as trace elements, isotopes, and nutrients (e.g. Broecker and Peng, 1982; Measures and Edmond, 1988; Stanev et al., 2002; Volpe and Esser, 2002; Liu et al., 2003; Chen et al., 2004). Most of these parameters are non-conservative,

* Corresponding author. National Taiwan University, Roosevelt Road, No. 1, Sec. 4, Taipei 106, Taiwan, ROC.

E-mail address: river@ntu.edu.tw (C.-C. Shen).

involved in biogeochemical reactions or subject to alteration by anthropogenic derived pollutants in the coastal zones (Liss, 1976; Chester, 1990; Mantoura et al., 1991; Rabouille et al., 2001; James, 2002). Consequently, they may not act as appropriate tracers for accurate assessment of the mixing of water masses. Sr and Ca are more conservative on short time scales than most other elements. The ratio of the two elements can potentially be used as a tool to trace water masses in the coastal ocean.

The contemporary oceanic Sr/Ca ratio remains fairly stable owing to the long residence time of $\sim 10^6$ years for the two elements in the ocean (Broecker and Peng, 1982). Its slight variation in the water column is primarily attributed to the cycling of biogenic minerals (Brass and Turekian, 1974; Chen, 1978; Shiller and Gieskes, 1980; Bernstein et al., 1987; Chen, 1990; Bernstein et al., 1992). Such processes cause the observation that the seawater Sr/Ca ratio increases from 8.50 to 8.52 mmol mol^{-1} at the surface to 8.61 mmol mol^{-1} below 1200 m in the tropical western Pacific Ocean (de Villiers et al., 1994; de Villiers, 1999; Shen et al., 2001). In comparison with fresh water, Sr and Ca are enriched in seawater. By mass balance considerations, fresh water input to the ocean cannot significantly change the seawater Sr/Ca ratio (Dodd and Crisp, 1982; Shen et al., 1996). In contrast, seawater salinity varies proportionally with the input of fresh water. In this paper, a Sr/Ca-S diagram is employed to decipher the mixing proportions of waters from different sources in the coastal seawater in Nanwan Bay, where periodic upwelling is induced by tides. This method can also be used to estimate the residence time of the bay water and the upwelling strength.

2. Site

Nanwan Bay (121°E , 22°N) is a semi-enclosed bay on the southern tip of Taiwan (Fig. 1). The local climate

is typical of that for the subtropics in the East Asian Monsoon area. Precipitation, $2000 \pm 500 \text{ mm year}^{-1}$ (1σ , 1971–2000 A.D.), mostly falls during the wet season from late May to early October. The distinct wet–dry seasonal pattern in rainfall, obvious from the monthly precipitation record, results in salinity variations ranging from 33.5 for the wet season to 34.4–34.6 for the dry season (Fig. 2) (e.g. Su et al., 1991).

Nanwan Bay is bounded zonally by two capes, Oluanbi and Moubitou with the connecting landmass as the northern boundary of the bay (Fig. 1). The bay opens southwards to face the Luzon Strait with a submerged reef about 5 km to the south. The reef, with its top at ~ 50 m below sea surface, partially limits water exchange between the bay and the open ocean. The bay northward of the reef has an area of 33.2 km^2 , an average depth of 37.2 m, and a total volume of 1.23 km^3 ; its terrestrial drainage area is 40.2 km^2 (Shen et al., 1997).

There are two major sources of Nanwan water (NWW) (Liang et al., 1978; Lee et al., 1997, 1999a,b). Offshore surface water (OSW) from the Luzon Strait flows directly into the bay over the submerged reef. Upwelled water (UW) originating from depths of about 100–200 m offshore comes into the bay along the deep channel and its transport is sensitive to the tidal forcing (Lee et al., 1997, 1999a,b). Fresh water (FW) represents a minor component. Its input is significant only during the wet season (Fig. 2).

3. Sampling and analysis

Three water depth profiles from stations, 101 (100 m; $21^\circ 54.00'\text{N}$, $120^\circ 43.00'\text{E}$), 104B (370 m; $21^\circ 15.76'\text{N}$, $120^\circ 44.23'\text{E}$), and 110 (3000 m; $20^\circ 24.30'\text{N}$, $120^\circ 43.00'\text{E}$), in the Luzon Strait, south of Taiwan, were sampled along a transect extending southward from the

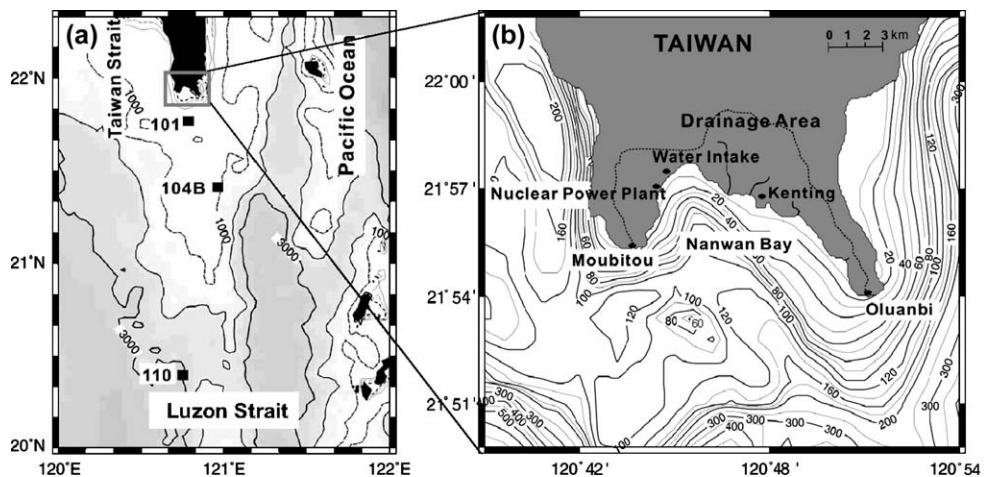


Fig. 1. (a) Map of three stations, 101, 104B, and 110, in the Luzon Strait, where water depth profiles were collected. (b) Map of Nanwan Bay, southern Taiwan. A submerged reef is located south out of bay about 50 m below sea surface. Tidally induced upwelling brings offshore subsurface water from depths of 100–200 m intruding along the deep channel (Lee et al., 1997).

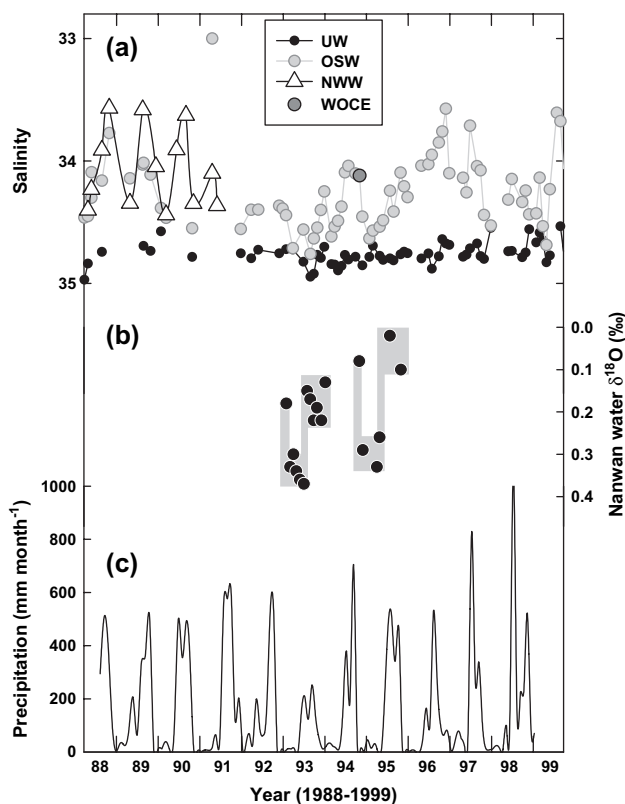


Fig. 2. (a) Salinity records for NWW (solid line with triangles), OSW (gray line with gray circles) and UW (solid line with solid circles) from 1988 to 1999; (b) measured NWW $\delta^{18}\text{O}$ (solid circles and gray area) from 1993 to 1995; and (c) monthly precipitation record in Nanwan area from 1988 to 1998. The measured salinity of OSW during the cruise of WOCE PR21 is shown as a dark gray circle. Rainfall usually is concentrated to the period from May to September and arid with dry weather for other months. The variations of NWW $\delta^{18}\text{O}$ depend on seasonal changes in precipitation. The $\delta^{18}\text{O}$ data are from Shen et al. (2005).

coastal region immediately outside Nanwan. Sampling was done with the CTD-rosette sampler on board *R/V Ocean Researcher I* during cruise 403 on October 5–8, 1994, for surveying the Pacific Repeated Line 21 of the World Ocean Circulation Experiment (WOCE PR21). Station 101 was located just outside Nanwan, station 104B offshore of southeastern Taiwan, and station 110 located in deep water in the middle of the Luzon Strait (Fig. 1). At all stations, the depth profiles of salinity, temperature, $\delta^{18}\text{O}$, [Sr] and [Ca] were measured. Nanwan water samples in the water intake channel of the Third Nuclear Power Plant, located at the northwest side of the bay, were collected from 1993 to 1995. On October 4, 1994, freshwater samples were collected from creeks.

Water samples were stored in 100-ml acid-cleaned Pyrex bottles on board. A preserving agent, 0.1–0.2 g ultrapure HgCl_2 , was added immediately after sampling in order to prevent any possible growth of bacteria and plankton. Potential Sr contamination by the preserving agent is less than 0.04‰. Water samples were filtered

using a 0.45- μm Teflon syringe filter, and were precisely weighed. A 25–50-mg aliquot was mixed with an appropriate amount of ^{42}Ca – ^{44}Ca – ^{84}Sr triple spike solution. Sr and Ca were separated using a cation-exchange resin column and measured on a thermal ionization mass spectrometer, Finnigan MAT-262 (Shen et al., 1996). Analytical errors (1σ) for the concentrations of Sr, Ca and Sr/Ca ratio were 0.35‰, 0.50‰, and 0.22‰, respectively, for laboratory seawater standard. All samples were measured for oxygen isotopic ratios on SIRA-10 and MAT-252 instruments with an external error of 0.06‰ (1σ). Isotopic composition calibration on the two different mass spectrometers was accomplished with five laboratory standards, including MBS, MAS, HPM230, Merck and Hanawa, that were corrected regularly with two international carbonate standards, NBS-19 and NBS-18. The $\delta^{18}\text{O}$ values are expressed relative to SMOW (Craig, 1961). The error given in this paper is one standard deviation unless otherwise noted.

4. Results and discussion

4.1. Hydrography and endmember waters

The hydrographic data of temperature (T), salinity, Sr/Ca and $\delta^{18}\text{O}$ for the three stations are given in Fig. 3. The profiles of T and S at stations 110 and 104B are consistent with long-term (1988–1999) averages of the CTD database of the National Center for Ocean Research (NCOR) in Taiwan (Fig. 2a) and other work along the Luzon Strait for PR21 (Shaw, 1991; Chen and Huang, 1996). Although the profiles of hydrographic and chemical properties differ from station to station, the T – S diagram and the plots of temperature vs. chemical properties (Fig. 4) show that the hydrographic water properties from offshore (station 110) to near-shore (station 101) form a consistent trend, suggesting that the seawater masses originate from similar sources. The T – S diagram further indicates that the upper water column, shallower than roughly 300 m, is more akin to the West Philippine Sea (WPS) water (Gong et al., 1992). In contrast, the water deeper than 370 m may represent a mixture of waters from the South China Sea (SCS) and the WPS, supporting Chen and Huang's (1996) report of the existence of a prevailing mid-depth front within the Luzon Strait. The profiles show the typical water characteristics for those offshore sites in the wet season.

The hydrologic data of stations 110 and B104 with depth less than 50 m were averaged to represent the condition of OSW in the 1994 wet season. Temperature, salinity, Sr/Ca and $\delta^{18}\text{O}$ for OSW are 28.5 °C, 34.12, 8.496 mmol mol⁻¹ and 0.10‰, respectively. In the 1994 dry season the salinity and $\delta^{18}\text{O}$ increase to

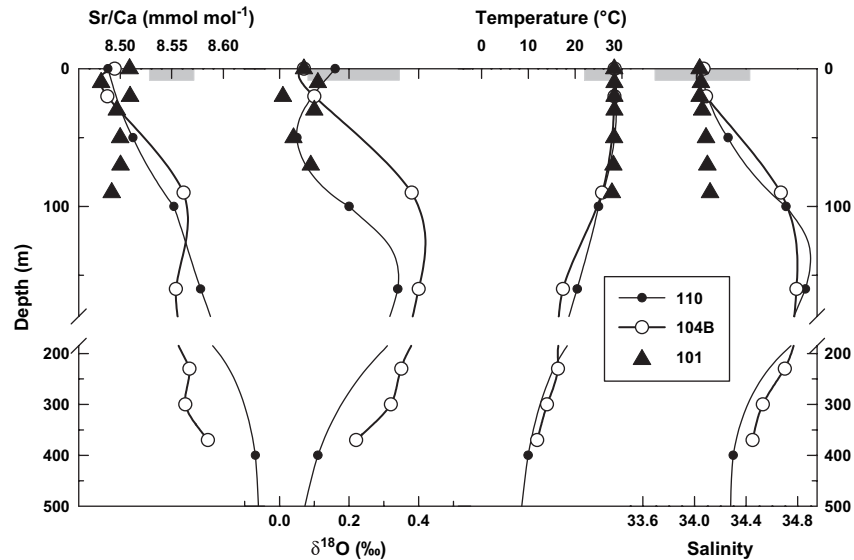


Fig. 3. Depth profiles of hydrographic data, Sr/Ca, $\delta^{18}\text{O}$, temperature and salinity, for three stations, 110 (solid circles), 104B (open circles) and 101 (triangles), and for NWW (gray rectangles). The length of rectangle represents the range of intra-annual variation for this tracer in Nanwan.

34.6 (Fig. 2) and 0.25‰ for OSW. Seawater Sr/Ca is presumed to be unaltered by slight salinity enrichment.

The characteristics of UW tidally intruding Nanwan Bay are derived by averaging hydrographic data at a depth interval between 100 m and 200 m for sites 110 and B104. Temperature, salinity, Sr/Ca and $\delta^{18}\text{O}$ are 18.7 °C, 34.80, 8.569 mmol mol^{-1} and 0.36‰, respectively. Instrumental observations indicate that the seasonal variations of temperature and salinity are minimal for this subsurface water (Fig. 2). The same compositional values are thus used for both dry and wet seasons.

The third source, FW, comes from rain directly falling onto the bay and runoff collected in its small watershed whose size roughly equals that of the bay (Fig. 1). The $\delta^{18}\text{O}$ values of precipitation and runoff around Nanwan area are $-7.53 (\pm 0.31) \text{‰}$ and $-9.09 (\pm 0.37) \text{‰}$, respectively (Wang, pers. comm.). The mean $\delta^{18}\text{O}$ of FW is estimated as $-8.38 (\pm 0.48) \text{‰}$. Sr, Ca, and Sr/Ca in runoff water are $0.007838 \mu\text{mol g}^{-1}$, $0.8880 \text{mmol g}^{-1}$, and $8.827 \text{mmol mol}^{-1}$, respectively. Sr and Ca levels in the direct rainfall are assumed to be negligible. The averaged values of Sr, Ca, and Sr/Ca for FW are estimated as $0.004293 \mu\text{mol g}^{-1}$, $0.4863 \text{mmol g}^{-1}$, and

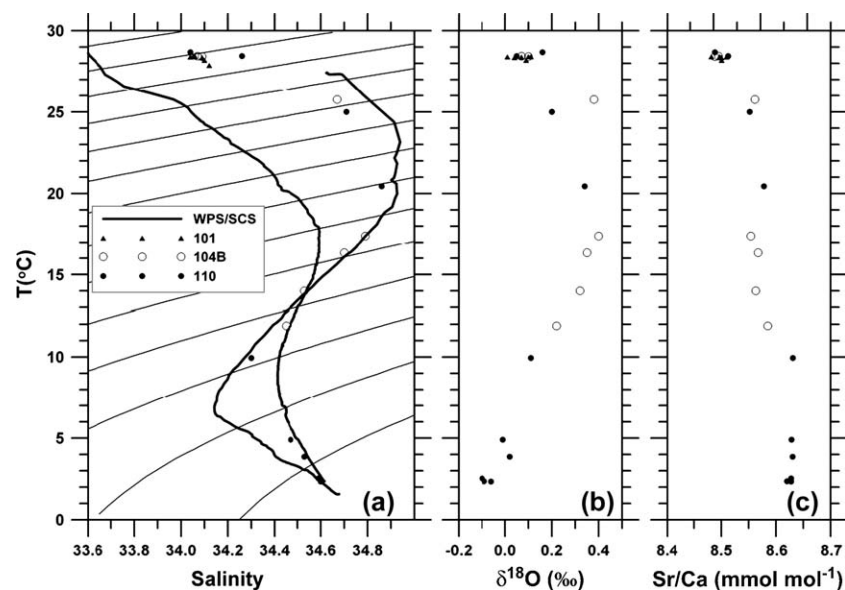


Fig. 4. (a) The T - S diagram of the water samples collected at three stations, 101, 104B and 110. Also plotted are the typical T - S properties of seawaters from the West Philippine Sea and the South China Sea. The thin curves represent isopycnals of σ_T values from 21 near the top to 27.5 near the bottom. (b) The same as (a) except for T - $\delta^{18}\text{O}$. (c) The same as (a) except for T -Sr/Ca.

8.827 mmol mol⁻¹, respectively. The FW temperature is about 25.8–26.8 °C and its salinity is considered to be zero.

The value of NWW Sr/Ca is 8.551 mmol mol⁻¹, the same value as the annual mean measured by Shen et al. (1996) and 0.056 mmol mol⁻¹ higher than that of OSW (Fig. 3). δ¹⁸O value of NWW varies with seasonal precipitation (Fig. 2). Due to FW input, the NWW δ¹⁸O value is 0.08‰, lighter than the value of 0.28–0.32‰ in the 1994 dry season. Temperature of NWW ranges from 28 °C in the summer to 22 °C in the winter (Su et al., 1991; Shen et al., 1996). The daily mean temperature was 26.0 °C on October 4, 1994. The salinity of NWW was 33.74 in the 1994 wet season. For the 1994 dry season, the value of salinity was assumed to be the same as those observed in 1988–1991, 34.4–34.6 (Fig. 2).

A box model, using hydrographic and chemical properties in both wet and dry seasons of 1994, was used to estimate the relative contribution of water masses in Nanwan Bay (Fig. 5). Two assumptions were made: (1) the three water masses are well mixed in the bay; and (2) the characteristics of the out-flowing water are identical to those of NWW. Because of the distinct seasonal rainfall patterns (Fig. 2), the characteristics of variations in hydrographic data were represented by step functions for dry and wet seasons. The dynamic transition between the two states is beyond the scope of this model.

4.2. Sr/Ca-S and T-S diagrams

The expected mixing relationship between Sr/Ca and salinity for mixtures of the three endmembers in the wet season is plotted in Fig. 6a. NWW Sr/Ca is essentially determined by the mixing between UW and OSW. Comparing the measured Sr/Ca of the mixture with the two endmembers thus immediately gives the mixing proportion between the two. The net flux of UW to the

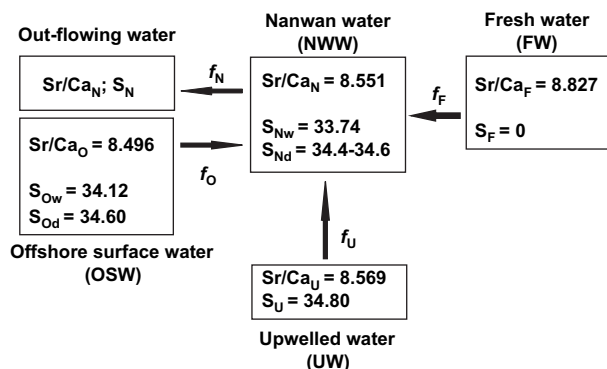


Fig. 5. Box model for estimating the proportion of water components, OSW, UW and FW, in Nanwan Bay. Values in boxes are the characteristics of these waters (see Section 4.1). Unit is mmol mol⁻¹ for Sr/Ca. Subscripts, w, d, N, O, U and F, represent wet season, dry season, NWW, OSW, UW and FW, respectively.

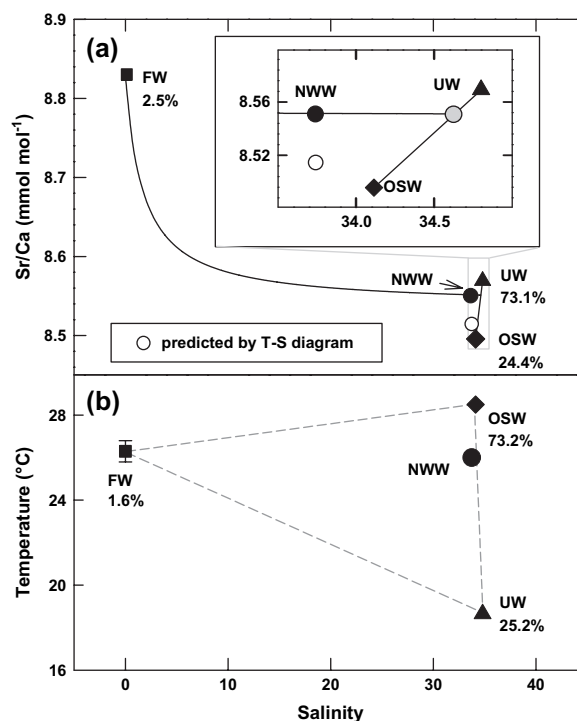


Fig. 6. Modeling the mixing of water masses in 1994 wet season in Nanwan using (a) Sr/Ca-S and (b) T-S diagrams. The NWW (solid circles) is supposed to be stoichiometrically mixed from three endmembers, OSW, UW, and FW (solid squares). On the basis of the Sr/Ca-S diagram, the percentages of these endmembers are: UW 73.1%, OSW 24.4%, and FW 2.5%. If the NWW is mixed by only UW and OSW in dry season, the value of coastal seawater Sr/Ca will be 8.551 mmol mol⁻¹ (gray circle in the inset enlarged plot), the same as the annual one. This indicates that the input of FW does not observably affect the coastal Sr/Ca ratio. The shares of endmembers are estimated as UW 25.2%, OSW 73.2%, and FW 1.6% using T-S diagram. The expected NWW Sr/Ca value by T-S diagram is 8.515 mmol mol⁻¹ (hollow circle), notably lower than the measured of 8.551 mmol mol⁻¹.

bay is found to contribute 75.0% and OSW 25.0%. The resultant salinity of the mixed water is 34.63, 0.89 higher than that of NWW, which has lower salinity due to the input of FW. The FW component is estimated to be 2.5% in the 1994 wet season. The inset in Fig. 6a shows this mixing relationship in detail. The mixing of UW and OSW determines the composition of the Nanwan water in the dry season (gray circle). The addition injection of fresh water during the wet season shifts the mixture point along the the nearly constant Sr/Ca line towards the direction of low salinity.

If a traditional T-S diagram is employed, the contributions of the endmembers in Nanwan are estimated to be 25.2% UW, 73.2% OSW and 1.6% FW (Fig. 6b). The percentages of UW and OSW are significantly different from those, 73.1% and 24.4%, inferred from Sr/Ca-S diagram (Fig. 6a). This discrepancy is mainly attributed to the non-conservative behavior of temperature or heat content of the bay water, which receives heating by solar insolation and

air–sea exchange (Shen et al., 1996) as well as by input of heated seawater, 2 °C higher than that of ambient seawater, from the nuclear power plant. The predicted value of NWW Sr/Ca derived from the T – S diagram is $8.515 \text{ mmol mol}^{-1}$, significantly lower than the observed value of $8.551 \text{ mmol mol}^{-1}$ (Fig. 6a). The results displayed here and in the following section indicate that the Sr/Ca– S diagram is superior to the T – S diagram for deciphering water components in Nanwan Bay.

4.3. $\delta^{18}\text{O}$ –salinity diagram

In order to check whether the modeled mixture using the Sr/Ca– S diagram can describe real hydrographic conditions, the estimated relationship between $\delta^{18}\text{O}$ and salinity for the mixed water was compared to the measured value in Fig. 7. The OSW in the wet season becomes ^{18}O -poor and less salty reflecting the precipitation on the ocean. The seawater coming into Nanwan Bay already has, therefore, a low $\delta^{18}\text{O}$ value of 0.30‰ even if there was no precipitation in Nanwan Bay itself. This corresponds to a shift of 0.05‰ for $\delta^{18}\text{O}$ at 0-mm local precipitation. The addition of FW in Nanwan shifted the $\delta^{18}\text{O}$ of the final mixture to 0.08‰ , identical to the measured value (Fig. 7a).

During dry season, a mixing at a proportion of 75:25 between UW and OSW predicts that the mixed NWW should have a $\delta^{18}\text{O}$ of 0.33‰ and a salinity of 34.75 (Fig. 7b). The $\delta^{18}\text{O}$ value estimated from the mixing model matches the upper bound of the measured values of 0.28 – 0.35‰ (Fig. 2). The predicted salinity is slightly higher than the observed values of 34.4 – 34.6 (Fig. 2). This suggests that up to 0.5% of dry-season NWW might come from freshwater sources, possibly submarine

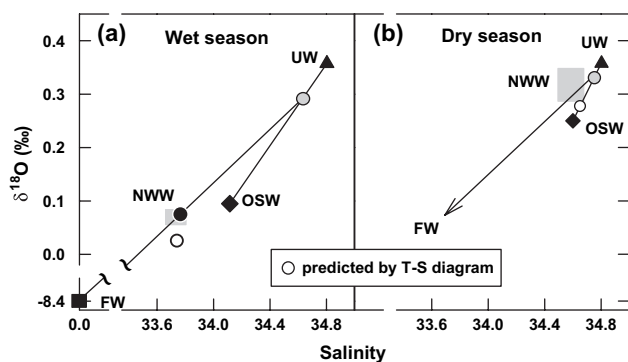


Fig. 7. Predicting the $\delta^{18}\text{O}$ and salinity of the NWW using the $\delta^{18}\text{O}$ –salinity relationship based on the Sr/Ca– S mixing model. (a) In the 1994 wet season, the addition of FW shifts $\delta^{18}\text{O}$ from the supposed point (gray circle) predicted from a mixing of UW (triangle) and OSW (diamond), to the solid circle on the thick solid line, which is close to the observed (gray cube). (b) In dry season, the values of NWW $\delta^{18}\text{O}$ and salinity are expected as 0.33‰ and 34.75 (gray circle) by mixing UW and OSW, somehow larger than the measured data (gray cube). The expected NWW $\delta^{18}\text{O}$ values using the T – S diagram in the wet and dry seasons (hollow circles) are lower than the observed ones.

groundwater discharge (e.g., Burnett et al., 2003) and/or drainage of domestic water. If the flux of the minor sources was seasonally steady, the portion of rainfall in the bay in the 1994 summer was estimated as 2.0 – 2.5% .

Using the composition of water masses in T – S diagram, the predicted NWW $\delta^{18}\text{O}$ in dry season is 0.28‰ (Fig. 7b), slightly lower than the measured of 0.28 – 0.35‰ (Fig. 2). The calculated value of NWW $\delta^{18}\text{O}$ in the 1994 wet season is 0.03‰ , 0.05‰ lower than the observed of 0.08‰ (Fig. 7a). The discrepancies between observed and predicted Sr/Ca (Fig. 6a) and $\delta^{18}\text{O}$ values (Fig. 7) of the NWW during wet and dry seasons suggest that the T – S plot is not suitable for tracing coastal water masses in Nanwan Bay.

4.4. Transports of water masses and residence time of NWW

The total rainfall in the 1994 wet season is estimated to be $0.0221 \text{ km}^3 \text{ month}^{-1}$ by multiplying the mean precipitation of $300 \text{ mm month}^{-1}$ by the total receiving area of 73.4 km^2 . The mean transports of UW and OSW and the residence time of NWW can be then deduced from rainfall flux and its contribution of 2.0 – 2.5% in the bay. Scaled by the steady state proportion from mass balance, the net transports of the UW and OSW flowing into the bay are estimated as 0.62 – $0.74 \text{ km}^3 \text{ month}^{-1}$ and 0.28 – $0.33 \text{ km}^3 \text{ month}^{-1}$, respectively. The residence time of NWW is calculated by dividing the volume of the bay, 1.23 km^3 , by the average monthly rainfall rate during the 1994 wet season plus the influxes of the UW and OSW. The residence time is estimated to be 30 – 40 days, which agrees with the observed time lag of 1 – 1.5 months for NWW $\delta^{18}\text{O}$ between dry and wet seasons (Fig. 2).

It is noted that the simple box model has its limitations due to conditions of the application that may not fulfill the assumptions. An example is the assumption of well mixed water in the box, because the bay water is not entirely uniform despite its strong tidal motion. Hence, one should be cautious about the estimated seawater transports, which are sensitive to the mixing proportion of the freshwater, which in turn depends on the salinity of the bay water measured. Because the salinity was mostly measured at a site rather close to the shore, it is likely that the measured salinity is lower than the mean value. If this is the case, the mixing proportion of the fresh water is overestimated and the seawater transports are underestimated. It is also cautioned that the delay of the freshwater signal after onset of the wet season is partially attributable to the time lag of freshwater discharge from land, where the soil may take up most of the rainfall in the initial stage. In addition, the evaporative loss of water is not considered in the model. However, these limitations are related to the hydrological nature of the environment

rather than the tracer quality of the Sr/Ca-S pair proposed here.

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