Supplement of Biogeosciences, 19, 2397–2415, 2022
https://doi.org/10.5194/bg-19-2397-2022-supplement

Biogeosciences
Open Access

Supplement of

A nitrate budget of the Bohai Sea based on an isotope mass balance model

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Supplement 1: Dissolved oxygen and apparent oxygen utilization

For comparing the spatial and seasonal variability of DO, we use AOU to eliminate the temperature effect on solubility. In spring, the average AOU was -0.77 ± 0.26 mg L^{-1} (n = 57) and ranged from -1.47 mg L^{-1} to -0.48 mg L^{-1} respectively. The AOU pattern was homogeneous over the water column (Fig. S1) and decreased in southeast and eastward direction to the BH strait (Fig. S2).

In summer, the average AOU was 0.82 ± 1.58 mg L^{-1} (n = 76) and ranged between -1.89 to 3.58 mg L^{-1}. AOU vertical distribution mirrored stratification with significant positive values below the thermocline caused by respiration processes such as remineralization and nitrification.

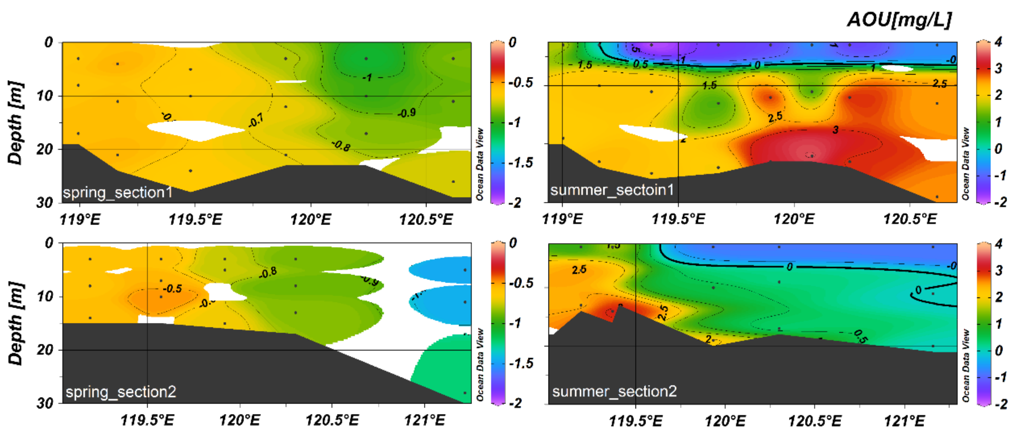

Figure S1. Profiles of AOU in spring and summer of section 1 of spring (a and c) and summer (b and d). (for showing a better pattern, the eastern most station of section 2 in spring was changed from site B36 to site B35 due to missing DO data at B36).

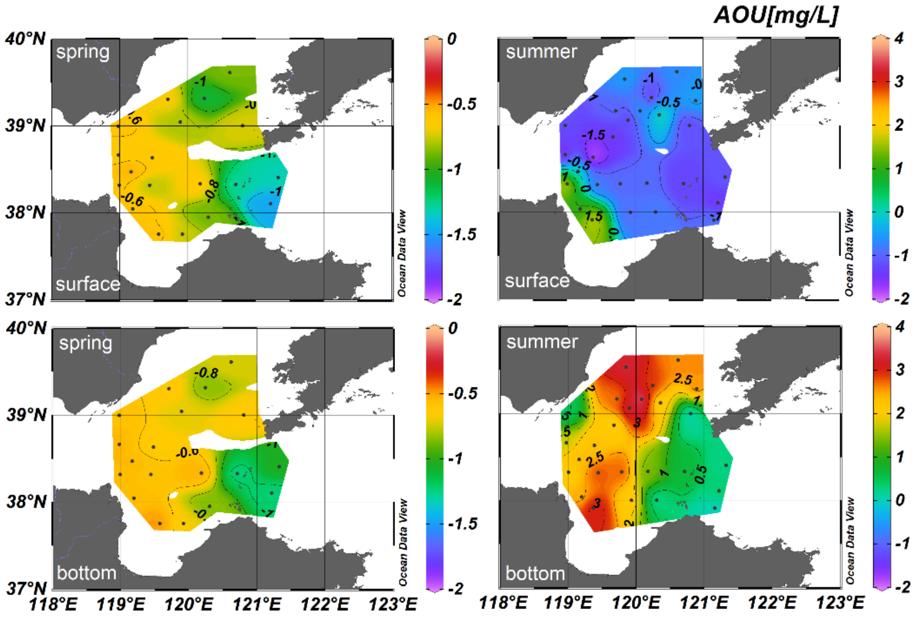

Figure S2. Horizontal distributions of spring and summer in the BHS.

Supplement 2 Summary of results of this study

	Spring		Summer	
	Range	Average ± Std. Dev.	Range	Average ± Std. Dev.
Salinity/psu	29.9–32.8	32.3 ± 0.5 (n = 72)	28.5-32.5	31.6 ± 0.8 (n = 88)
Temperature/°C	2.9–6.7	4.7 ± 0.8 °C (n = 72)	9.5-30.1	22.4 ± 4.2 (n = 88)
NO_3^-/μmol L^{-1}	0.3–31.1	6.5 ± 5.8 (n = 72)	0.1–13.6	1.9 ± 2.7 (n = 85)
NO_2^-/μmol L^{-1}	0.0–1.0	0.2 ± 0.2 (n = 72)	0.0–4.6	0.8 ± 1.1 (n = 85)
NH_4^+/μmol L^{-1}	0.2–2.7	0.8 ± 0.5 (n = 72)	0.1–7.8	1.6 ± 1.9 (n = 85)
PO_4^{3-}/μmol L^{-1}	0.1–0.7	0.4 ± 0.2 (n = 72)	0.0–0.3	0.1 ± 0.1 (n = 85)
SiO_3^-/μmol L^{-1}	0.2–13.9	5.3 ± 3.1 (n = 72)	1.3–17.0	7.7 ± 3.2 (n = 85)
$\delta^{15}N$/‰	5.7–9.7	7.5 ± 1.3 (n = 52)	3.5–23.9	9.9 ± 3.5 (n = 23)
$\delta^{18}O$/‰	5.0–19.8	11.3 ± 2.5 (n = 52)	3. –18.4	8.7 ± 3.3 (n = 23)
SPM/ mg L^{-1}	2.3–44.3	10.6 ± 8.0 (n = 72)	5.7–82.9	22.2 ± 16.5 (n = 85)
TOC/%	0.6–6.9	2.7 ± 1.7 (n = 72)	0.8–6.3	2.1 ± 1.2 (n = 83)
TN/%	0.1–1.8	0.5 ± 0.4 (n = 72)	0.1–1.4	0.4 ± 0.3 (n = 83)
$\delta^{15}N$–SPM/‰	3.2–6.2	4.8 ± 0.9 (n = 14)	3.9–7.2	5.7 ± 0.8 (n = 34)
DO/mg L^{-1}	10.27–11.47	10.84 ± 0.35 (n = 57)	3.84–8.86	6.22 ± 1.37 (n = 57)
AOU/mg L^{-1}	-0.48 to -1.47	0.77 ± 0.26 (n = 57)	-1.89 to +3.58	0.82 ± 1.58 (n = 76)

Supplement 3 The distribution of SPM and its nitrogen isotope

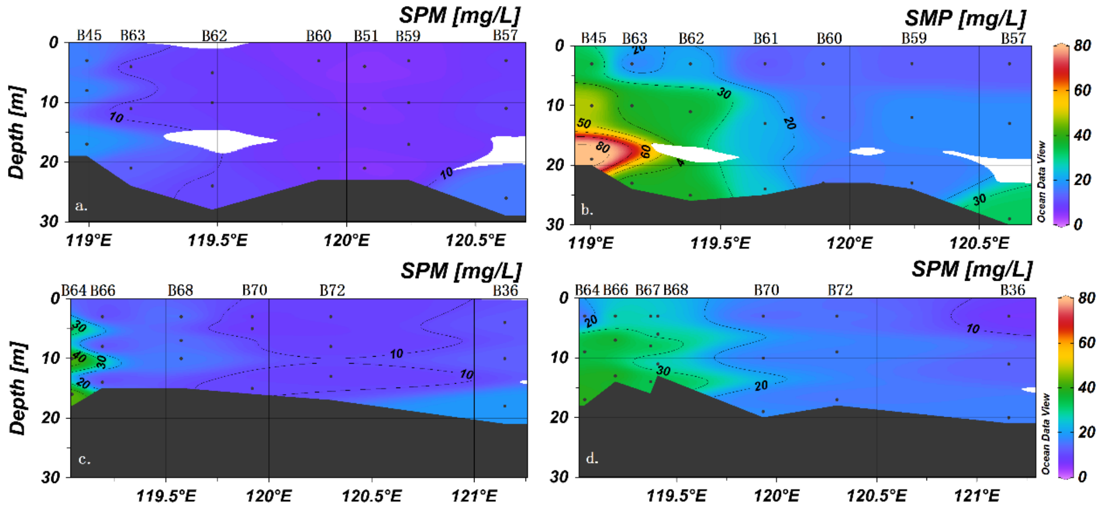

Figure S3. Suspended particulate matter concentrations of section 1 (a) and section 2 (c) of spring and section 1 (b) and section 2 (d) of summer.

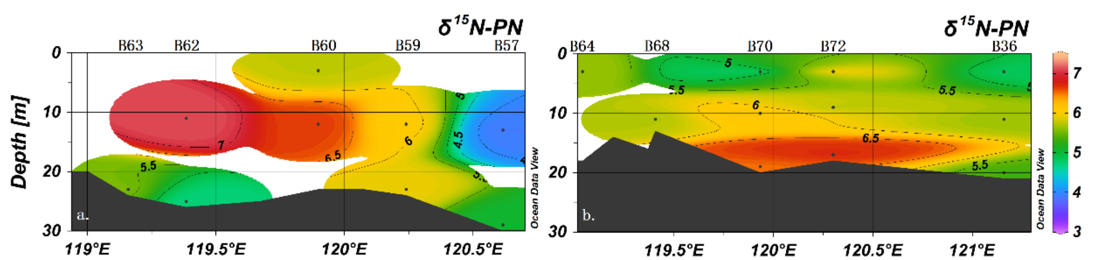

Figure S4. Profiles of δ^{15}N of particulate nitrogen in summer (a. section 1, b. section 2)

Supplement 4 The estimate of two end member mixing of nitrate and impact of underestimate of isotopes in summer

Only a subset of samples could be analyzed due to the low nitrate concentrations in summer, and most of these are from the Yellow River Diluted Water that had $[NO_3^-] > 1.7\mu mol\ L^{-1}$. The average values of $\delta^{15}N$ and $\delta^{18}O$ of the Bohai Sea in summer were 9.9 ± 3.5‰ (n = 23) and 8.7 ± 3.3‰ (n = 23). Although no measurements are available that could better constrain the seasonal range of nitrate isotope values, the lacking isotope data can be roughly estimated:

According to the T–S patten in summer, the Bohai Sea water can be considered as a two–end member mixture between fresh water discharged from Yellow River (YR) and sea water of central Bohai Sea, the nitrate concentration only affected by physically mixing hence can be calculated. The YR provides warm, fresh and nitrate enriched water whereas cold, saline and nitrate depleted water was observed near the area of the outer Liaodong Bay in both spring and summer. Thus, there were two end members to be considered in a mixing model. One should be aware that a contribution of atmospheric nitrogen is included in the marine end member as well.

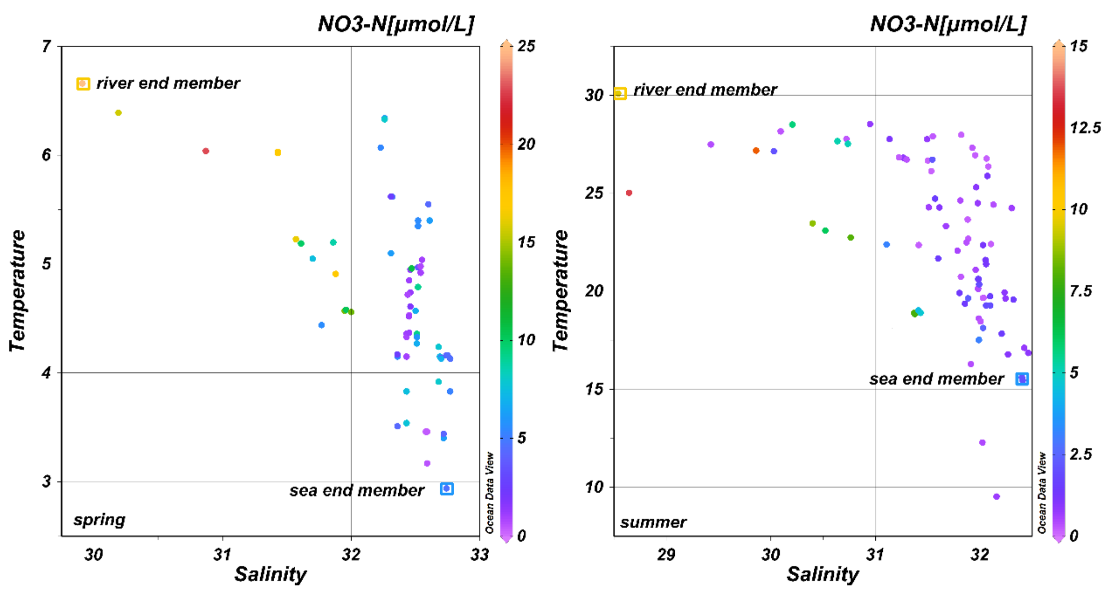

Figure S5. Temperature vs. salinity in Bohai Sea in spring (left) and summer (right). The values adopted for the two nitrate end members were mainly based on this pattern.

The values of these two end members are shown in Table S1. The summer basic pattern of temperature and salinity was similar to that of spring. Thus, the fraction of water originating from YR and the BHS during the mixing process can be calculated follow (1) and (2):

$$S = S_r \times f_r + S_s \times f_s \quad (1)$$

$$f_r + f_s = 1 \quad (2)$$

where S, S_r and S_s refers to the observed salinity in study area, the end member value of river and sea, respectively. f_r and f_s refers to the fraction of river and sea water, respectively. The modeled nitrate concentration and modeled $\delta^{15}N$ and $\delta^{18}O$ values can be calculated following equations (3), (4) and (5):

$$[NO_3^-]_m = [NO_3^-]_r \times f_r + [NO_3^-]_s \times f_s \quad (3)$$

$$\delta^{15}N_m[NO_3^-]_m = \delta^{15}N_r[NO_3^-]_r + \delta^{15}N_s[NO_3^-]_s \quad (4)$$

$$\delta^{18}O_m[NO_3^-]_m = \delta^{18}O_r[NO_3^-]_r + \delta^{18}O_s[NO_3^-]_s \quad (5)$$

where $[NO_3^-]_m$, $[NO_3^-]_r$ and $[NO_3^-]_r$ refers to the modeled nitrate concentration and the end member nitrate concentration values of river and sea, respectively. $\delta^{15}N_m$ / $\delta^{18}O_m$, $\delta^{15}N_r$ / $\delta^{18}O_r$ and $\delta^{15}N_s$ / $\delta^{18}O_s$ refer to the modeled $\delta^{15}N$ and $\delta^{18}O$ values, and the end member $\delta^{15}N$ and $\delta^{18}O$ values of river and sea, respectively.

Table S1 Two end member values in BHS

Seasons	Parameters	Riverine	Marine
Spring	Salinity	29.9	33.0
	Nitrate/μmol L^{-1}	31.1	6.0
	$\delta^{15}N$ ‰	9.5	6.0
	$\delta^{18}O$ ‰	6.8	12.5
Summer	Salinity	28.5	32.5
	Nitrate/μmol L^{-1}	13.6	2.0
	$\delta^{15}N$ ‰	9.9	9.5
	$\delta^{18}O$ ‰	5.3	8.2

The isotope effect of assimilation for nitrate in the Bohai Sea follows the "steady-state model" rather than the Rayleigh model because the Yellow River supplies nitrate continuously (Sigman and Fripiat, 2019). Thus, the estimated dual nitrate isotope values can be calculated according to equation (6) and (7):

$$\delta^{15}N_{reactant} = \delta^{15}N_{initial} + {}^{15}\varepsilon(1 - f) \quad (6)$$

$$\delta^{18}O_{reactant} = \delta^{18}O_{initial} + {}^{18}\varepsilon(1 - f) \quad (7)$$

In Eq.6 and Eq. 7, f is equal to the observed nitrate concentration divided by of result of the two-end member model, $\delta^{15}N_{initrial}$ is equal to the end member of YR, and $\delta^{15}N_{reactant}$ is the estimated value of the residual nitrate, the value we need. The average of $^{15}\varepsilon$ and $^{18}\varepsilon$ adopted here are 5 ‰ (Granger et al., 2010; DiFiore et al., 2009; Liu et al., 2017; Wu et al., 2019; Umezawa et al., 2013; Wang et al., 2016).

The readjusted values of $\delta^{15}N$ and $\delta^{18}O$ for the Bohai Sea in summer is 12.8 ± 2.7 ‰ (n = 85) and 9.1 ± 1.9 ‰ (n = 85), respectively, resulting in seasonally averaged values of $\delta^{15}N$ and $\delta^{18}O$ of 10.3 ‰ and 10.6 ‰, respectively. These values induce about -36 % to 21 % deviations of the mass fluxes in our reference box model.

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