

Nitrate sources and processes in the Bohai Sea: results from seasonal sampling in 2018

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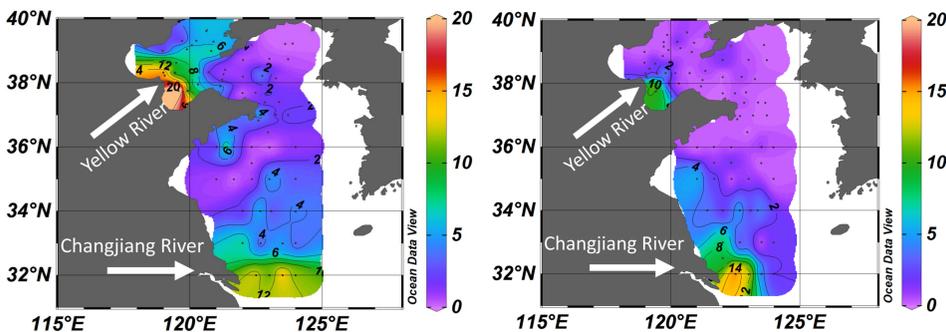
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Introduction

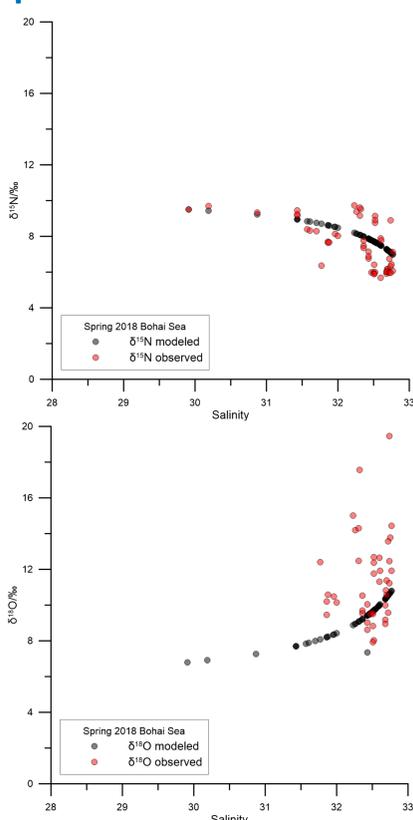
The Bohai Sea (BHS) and the Yellow Sea are semi-enclosed basins strongly affected by human activities due to climate change and growing industries in China. Changes of hydrology, nutrient concentrations, and sources and resulting ecosystem responses are therefore progressively intensifying during the last decades. To characterize nutrient sources and dynamics and to estimate the anthropogenic impact, we investigated nutrient concentrations and dual isotopes of nitrate in spring and summer 2018 in the BHS and the Yellow Sea. A nitrate budget was constrained by the simple box model associated with dual isotopes of nitrate of the BHS.

Distribution of nitrate

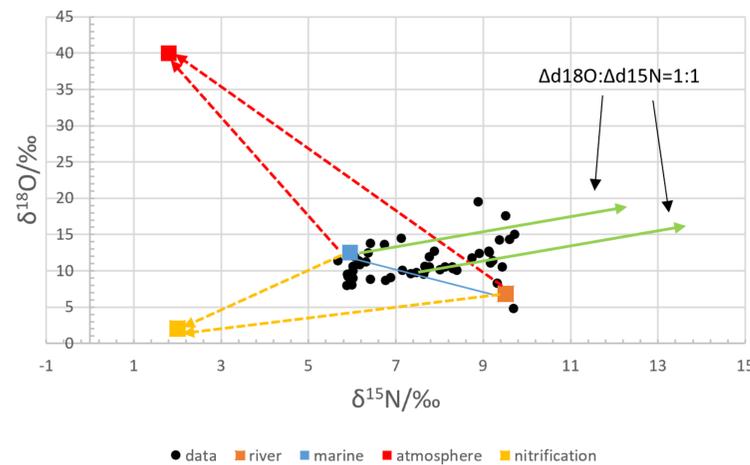


Distribution of nitrate in the surface layer in spring (left) and summer (right). Yellow River and Changjiang River were the terrestrial sources of nitrate. Nitrate concentrations were lower in summer than in spring due to its uptake by organisms..

How do different sources and processes affect the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values of the BHS nitrate pool?

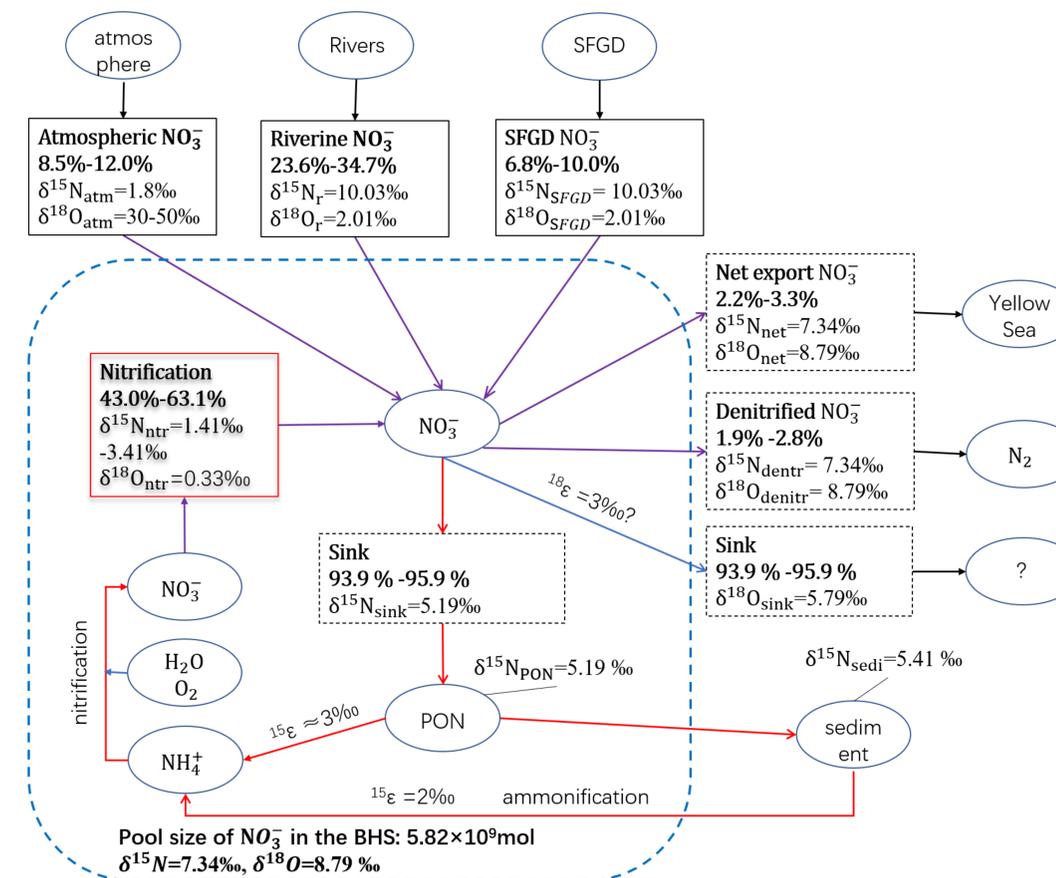


- The dilution curve was simulated with a river-sea two endmember model for $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$, respectively (here only the spring pattern of the BHS is shown).
- $\delta^{15}\text{N}$ higher or lower than the dilution curve is related to assimilation and nitrification, respectively.
- $\delta^{18}\text{O}$ higher or lower than the dilution curve shows the impacts of assimilation, atmospheric deposition, and nitrification, respectively.



- In the BHS, different sources and processes impact $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of nitrate. The black dots are the observed data from the BHS in spring 2018. Squares with different colors refer to different sources and end members of nitrate.
- The green lines refer to assimilation by phytoplankton with a 1:1 ratio of the fractionation factors (ϵ) of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$. Theoretically, assimilation elevates $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of the reactant nitrate along the line with the slope = 1.

A nitrate budget of the BHS constrained with dual isotopes of nitrate



- $^{15}\epsilon$ and $^{18}\epsilon$ of nitrate assimilation by phytoplankton are assumed both as 3‰ in the BHS.
- PON refers to the particles sampled during the two cruises; the $\delta^{15}\text{N}$ values of 5.19‰ is higher than the calculated $\delta^{15}\text{N}$ value of phytoplankton of 4.34‰. This can be attributed to the integrated effects of assimilation (nitrate and ammonium) and ammonification.
- The O atoms are lost during assimilation and are removed from the nitrate pool in masses of 3 times that of N.

The nitrate concentrations and their isotopes are assumed to be in steady state in the BHS. SFGD = submarine fresh groundwater discharge. Inside the dashed blue rectangle the processes of internal cycling of nitrate in the BHS are shown. Outside the dashed blue rectangle the external sources and sinks of nitrate are presented. The red arrows refer to the N pathways, blue arrows refer to the O pathways and the purple arrows refer to the nitrate pathways. Dashed squares denote sinks of nitrate, solid red squares denote sources of nitrate. Numbers in these squares are estimated proportions of mass fluxes of nitrate and the corresponding values of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$.

Conclusions

- The Yellow River accounts for 23%-35% of the nitrate source to the BHS with enriched $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$.
- Nitrification recycles 43%-61% of nitrate from the particulate matter and sediment pool in the BHS.
- Atmospheric nitrate deposition and nitrification contribute ^{15}N depleted nitrate and mask the high $\delta^{15}\text{N}$ of rivers and SFGD discharge to the BHS.

Further questions

- $^{15}\epsilon$ and $^{18}\epsilon$ of nitrate assimilation by phytoplankton need to be better constrained.
- A $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ depleted source of nitrate is probably missing.