Modeling the sediment biogeochemical processes in a semi-enclosed eutrophic sea,

Bohai Sea, China.

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1 Aims

This study focuses on the biogeochemical processes of nutrients (taking nitrogen as an example) in semi-enclosed offshore sediment environments in the Bohai Sea, China, and explores the effects of these processes on Marine nutrient cycling. This will be achieved through the following objectives: (1) quantitative calculation of nitrogen flux and its seasonal variation at the sediment-water interface in the Bohai sea; (2) To reveal the contribution of key processes of nitrogen to the nitrogen exchange flux at the sediment-water interface in the Bohai Sea.

#### 2 Procedure

### 2.1 Model development

Due to shallow water depth of the shelf sea and strong vertical mixing of water, the exchange of nitrogenous nutrients at sediment-water interface is deeply affected by agitation driven by bottom stress. However, this effect is complicated. It is difficult to measure the flux of nitrogenous nutrients at the sediment-water interface with current observation techniques, so it can only be quantitatively calculated by means of numerical simulation. In addition, the concentration of dissolved oxygen varies sharply in the sediment, and only the shallowest surface layer is in an aerobic environment, while the lower layer is in an anoxic environment. This affects the vertical distribution of different aerobic types of organisms, resulting in significant differences in the reaction of nitrogenous nutrients at different depths of sediment. For example, there are more nitrifying bacteria living in the aerobic environment on the surface of sediments, making

nitrification only occur on the surface of coastal sediment. In order to quantify the effect of vertical differences in key nitrogen reaction on the flux of nitrogenous nutrients at the sediment-water interface, and to consider the vertical transport process of nitrogenous nutrients caused by bioturbation, molecular diffusion and burial, we need to construct a vertical one-dimensional shelf sediment model.

Berner proposed the theory of early diagenesis (Berner, 1980), which provides a theoretical basis for the numerical study of material transport in Marine sediments. His theory idealizes the solid and liquid phase of sediment into two fluid systems, and introduces the concept of porosity, so that a one-dimensional vertical transport model can be established for sediments by using Euler method of hydrodynamics. Among them, the burial process driven by gravity makes particle organic nitrogen transport to deep layer, which is advection term; The vertical transport of nitrogenous nutrients is idealized as diffusion term due to bioturbation; Each key nitrogen reaction results in the transfer of different forms of nitrogenous nutrients into source and sink items. Combining this theory with the key processes of nitrogen in shelf sediments, we construct a vertical one-dimensional model and its equation.

The particle organic nitrogen in seawater sinks to the surface of sediment due to gravity, which makes the sediment become an important organic reservoir in coastal waters. These nutrients not only provide a food source for benthic organisms, but also store anthropogenic organic pollutants directly, which do not decompose in the water. The surface sediments, driven by the bottom stress, will undergo a resuspension process, releasing the organic nitrogen stored in the sediment back to the water column. In contrast, dissolved inorganic nitrogen is exchanged between sea water and pore water mainly in the form of diffusion (Paraska et al.,2014). In order to better quantify the nitrogen flux at the sediment-water interface, it is necessary to focus on the concentration of nitrogen in the sediment surface. This concentration is not only affected by vertical transport process, but also controlled by various reactions with obvious vertical differences in sediment. The

particle organic nitrogen in the sediment will be buried deep under gravity, accompanied by the vertical transport process of bioturbation. The dissolved inorganic nitrogen in pore water migrates vertically under the coupling effect of bioturbation and molecular diffusion. Moreover, under the control of complex environmental factors, particle organic nitrogen in sediments mineralizes through the activities of different benthic organisms and form ammonium (Liu et al., 2018). Among them, the vertical distribution difference of varied benthic organisms and oxidants, as well as the mineralization priority of each oxidant, are the main reasons leading to different mineralization approach. For example, aerobic mineralization is dominant in the surface layer of oxygen-rich sediments. In the meantime, ammonium form nitrates under aerobic conditions (Hsiao et al., 2014). Due to the obvious anoxic environment deep in the sediments, nitrates are not only converted to ammonium through dissimilatory nitrate reduction to ammonium(DNRA), but also prone to denitrification and anammox. These reactions form nitrogen and nitrous oxide gases and remove them from the sea, becoming an important nitrogen removal process in the ocean (Brandes et al., 2007).

## 2.2 Study area

The Bohai Sea is a semi-closed inland sea in China, and its water depth is relatively shallow, with an average depth of 18 meters. 26% of the sea area is within 10 meters, so the coupling process between water layer and sediment is strong here. The Bohai Sea is generally divided into five parts: Liaodong Bay, Bohai Bay, Laizhou Bay, central sea area and Bohai Strait. The Bohai Sea is connected to the Yellow Sea only through the Bohai Strait in the east. The Bohai Sea is an important Marine economic zone in China, which has been seriously polluted by human activities around it for many years. The Bohai Sea accounts for less than 3 percent of China's total sea area, but receives more than 30 percent of the total Marine pollution from the Chinese mainland. In addition, the proportion of clay in the sediments of Bohai sea is significantly higher than that of 50 years ago, which

proves the fact that the pollution discharge from the Bohai sea has increased in recent 50 years. Obviously, The Bohai Sea has become one of the most prominent areas in China's coastal environment and ecology, with serious pollution problems such as seawater eutrophication, low oxygen in bottom water and ocean acidification, which will have an important impact on the ecological environment and nutrient circulation in the Bohai Sea. At the same time, human activities changed the spatial and temporal pattern of nutrient transport in the Bohai Sea, making the environmental problems more complex. Studies have shown that organics deposited into the Bohai sea sediments is equivalent to 10%~50% of primary production (Mu et al., 2016). As an important site of nutrient circulation in The Bohai Sea, the response of sediments to ecological environment changes and contribution to nutrient circulation are bound to change correspondingly. Therefore, it is very important to quantitatively study the key processes of nutrient circulation at the sediment-water interface in the Bohai Sea, in order to clarify the contribution of sediment to nutrient structure and effectively control the secondary pollution caused by the rerelease of contaminated sediment (Fennel et al., 2006; Conley et al., 2008).

#### 3 Result

#### 3.1 The amount of nitrogen reactions

The concentration of particle organic nitrogen in the sediments of the central Bohai Sea presents a vertical distribution characteristic, which is higher in surface and lower in bottom. This leads to the same vertical variation of the reaction amount of mineralization. However, due to the high porosity in the sediment surface layer, according to the law of mass conservation, the amount of ammonium generated by mineralization does not reach the maximum value in the surface. On the contrary, it reaches the highest value in the subsurface layer, with about 5 mmol/m²/d.

The maximum reaction amount of anammox occurs in the deeper subsurface layer.

This process converts a large amount of ammonium into nitrogen to remove it from the

sediment, and the amount of this reaction is up to around 5 mmol/m²/d. Nitrification occurs only in the shallow surface determined by the concentration of oxygen and converts a large amount of ammonium to nitrate, up to about 13 mmol/m²/d. Due to the low concentration of nitrate at anaerobic depth, the amount of DNRA is very low. Similar situation also occurred in the denitrification, making the amount of these two processes almost negligible. These reactions together lead to the maximum ammonium concentration in the subsurface layer, while the concentration of nitrate peaks at the surface. They are consistent with the conclusion of relevant observation data.

## 3.2 Budgets

The nitrogen nutrient budget in the sediments of the central Bohai Sea is obtained by vertical integration of reactions of key processes of nitrogen in simulated depth. We divide particle organic nitrogen into two types, fast part and slow part, and unify each reaction. It can be seen from the figure that the sediment is a net sink of particle organic nitrogen with a flux of 0.9 mmol/m²/d. 89% of this amount is formed ammonium through mineralization, and only a small portion of the remaining amount is transported to deeper depths through burial.

For ammonium, 88% of the amount formed by mineralization is removed from the sediment by anammox forming nitrogen, up to 0.7 mmol/m²/d. Moreover, ammonium are nitrated to nitrate or migrate from sediment-water boundary to seawater. The process of DNRA and the flux of ammonium at the bottom of sediment are not important. The source of nitrate is mainly generated by nitrification, at 0.05 mmol/m²/d. 80% of this production (0.04 mmol/m²/d) enters the upper sea water through the sediment-water interface. This makes sediment a net source of dissolved inorganic nitrogen in seawater, as opposed to particle organic nitrogen.

On the other hand, up to 78% of the nitrogenous nutrients in the sediments are converted into nitrogen removal in the anaerobic environment, which played a very

important role in the nitrogen cycle in the Bohai Sea.

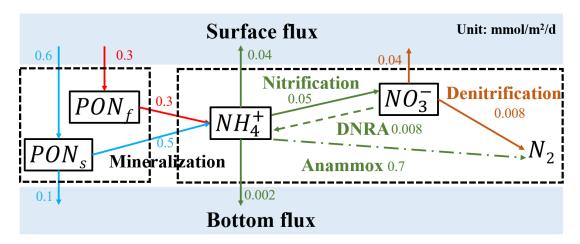


Fig.1 The budget of nitrogenous nutrients in sediments from the central Bohai Sea

# 4 Publication/conference presentation

Currently, the results have not been published.

## **5 Perspectives in future**

In the future, we will pay more attention to the temporal variation of nitrogen flux at the sediment-water interface.