# Seasonal variations and control factors of nutrient fluxes at the benthic-pelagic interface of Harima Nada.

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## **1** Purposes

This study focuses on the biogeochemical processes of nutrients (taking nitrogen as an example) in semi-enclosed offshore sediment in Harima Nada, Japan, and explores the effects of these processes on marine nutrient cycling. This will be achieved through the following objectives: (1) Quantitative calculations of nitrogen fluxes and their seasonal variations at the sediment-water interface in Harima Nada; (2) To explore the environmental factors controlling these seasonal variations.

# 2 Methods

# 2.1 Model development

Based on the theory of early diagenesis proposed by Berner in 1980, we explore the above problems by developing a vertical one-dimensional sediment nitrogen cycle model. This theory provides a theoretical basis for the numerical study of material transport in marine sediments. It 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.

At the sediment-water interface, the exchange of solid mater is controlled by the bottom stress. The solid matter in the water column sinks into the fluff layer when the bottom stress is smaller than a critical value, while resuspension occurs when the bottom stress is larger than that value. The exchange of dissolved nitrogen at the interface is decided by both the diffusive coefficient and the differences between concentrations of the fluff layer and the bottom sea water.

The biochemical processes in the sediment include mineralization, nitrification, denitrification, anammox and the dissimilatory reduction of Nitrate to ammonium. 2.2 Study area

Harima Nada is part of the Seto Inland Sea, which is the largest semi-enclosed sea in Japan, connected to the Pacific Ocean via Bungo Channel and Kii Channel, and to the Japan Sea via the Kanmon Strait. It has an average depth of 38 meters, except for the bays near Bungo Channel and Kii Channel. In the 1960s-70s, the Seto Inland Sea suffered from severe environmental pollution, exhibiting eutrophication with significant accumulation of pollutants in sediments, prompting the Japanese government to

implement environmental protection policies in the 1970s to address the eutrophication issues in the region. After 40 years of environmental restoration, water quality in the Seto Inland Sea has improved, with some areas transitioning from eutrophic to oligotrophic conditions, characterized by nitrogen limitation. However, oligotrophication has led to a lack of fishery resources in the Seto Inland Sea, significantly reducing the production of nori seaweed and fish catches, which are characteristic industries of the region. In order to balance the relationship between the environment and fisheries development to ensure biodiversity and productivity, the Japanese government plans to reassess reasonable ranges of water nutrient concentrations and formulate new management policies.

## **3** Results

3.1 The exchanges of ON and DIN across the sediment-water interface

The exchanges of ON and DIN between sediment and seawater in 2020 are calculated in the model. ON was sank from the overlying water to sediment throughout the year while the amount of resuspension was too small to be ignored compared to the amount of sinking. ON flux was high in fall with 40.66 mg N m<sup>-2</sup> d<sup>-1</sup> as the maximum value in October and low in spring with 14.97 mg N m<sup>-2</sup> d<sup>-1</sup> as the minimum value in May.

In the model, DIN flux is the sum of those of  $NH_4^+$  and  $NO_3^-$ . It was released from sediment to the overlying seawater all the year in Harima Nada, which had its highest value of 14.81 mg N m<sup>-2</sup> d<sup>-1</sup> in September and the lowest value of 5.60 mg N m<sup>-2</sup> d<sup>-1</sup> in February. Both the values and seasonal variations exhibited good agreement between model results and observations, while the abnormal high value observed in April was not reproduced by the model. Separately,  $NH_4^+$  flux was larger than  $NO_3^-$  flux. The seasonal variation of  $NH_4^+$  flux was much similar with DIN flux, with the highest value of 8.75 mg N m<sup>-2</sup> d<sup>-1</sup> and the lowest value of 3.13 mg N m<sup>-2</sup> d<sup>-1</sup>. Unlike  $NH_4^+$  flux,  $NO_3^$ flux had its minimum value of 2.41 mg N m<sup>-2</sup> d<sup>-1</sup> in January, although it also peaked in September with 6.06 mg N m<sup>-2</sup> d<sup>-1</sup>.

3.2 Factors influencing the seasonal variations of the exchanges of ON and DIN

The model results show that the exchanging rates of ON and DIN between the seawater and sediment exhibited obvious seasonal variations. In order to explore the influencing factors, five numerical experiments are carried out by removing the seasonal signals of the ON concentration ( $ON^{bw}$ ),  $NH_4^+$  concentration ( $NH_4^{+bw}$ ),  $NO_3^-$  concentration ( $NO_3^{-bw}$ ), water temperature, and the bottom stress at the overlying water, respectively. The annual mean values of these five factors are used to force the model and the comparisons between the results of experiments and the control case (CONTROL) which represent the reality are shown in Figure.

ON<sup>bw</sup> was the factor controlling the seasonal variation of ON flux between seawater and sediment. The curves of the other four experiments were nearly overlapped to that of CONTROL, indicating there were no effects when removing the seasonal signals of these factors. ON flux was the net value remained the sinking of ON from seawater and resuspension of ON from sediment. Lower bottom stress which indicated slow bottom current made resuspension slightly contribution to the exchange across the interface. Therefore, ON flux was dominated influence by ON<sup>bw</sup>, which mainly controlled sinking. It is consistent with many studies that higher ON<sup>bw</sup> results in more ON conserved in sediment while the bottom current is slow. When neglecting the seasonal variation of ON<sup>bw</sup>, the seasonal variation of ON flux would be decided by bottom stress which was the other factor controlling sinking. In this case, ON flux was higher in July and lower in December exhibited negative correlation with the seasonal variation of bottom stress.

DIN flux was controlled by bottom water temperature because  $NH_4^+$  flux dominated it.  $NO_3^-$  concentration at the sediment surface was equivalent to  $NO_3^{-bw}$  so that the  $NO_3^-$  flux was lower than  $NH_4^+$  flux.  $NH_4^+$  concentration at the sediment surface was much greater than  $NH_4^{+bw}$ , which caused the sediment to continuously dissolve a large amount of  $NH_4^+$  into the overlying water. When the seasonal signal of bottom water temperature was eliminated, the seasonal variation of DIN flux turns to be controlled by  $NO_3^-$  flux affected by  $NO_3^{-bw}$ . The factors of seasonal variations of ON flux and DIN flux were definitely different, which indicated that the change of ON flux controlled by  $ON^{bw}$  cannot get the response of DIN flux. This means that although there was more ON sinking into the sediment if the eutrophication occurred, it could not cause more DIN back to the seawater. After all, the amount of ON sinking was relatively small compared to ON inventory in the sediment so that ON flux cannot significantly altered DIN flux through mineralization.



Fig 9. Comparisons of results of ON flux and DIN flux between the control group representing the reality and the numerical experiments using annual average values of five input data respectively, including the ON concentration ( $ON^{bw}$ ),  $NH_4^+$  concentration ( $NH_4^{+bw}$ ),  $NO_3^-$  concentration ( $NO_3^{-bw}$ ), water temperature, and the bottom stress at the overlying water.

#### 4 Future challenges

In the future, this study will utilize a three-dimensional water-sediment coupled model to further investigate the interannual variations in nitrogen exchange fluxes at the sediment-water interface in the Seto Inland Sea. It aims to reveal the impact of sediment on oligotrophication in the Seto Inland Sea.

#### **5** Publication

The paper will be submitted to Science of the Total Environment soon.