PECULIARITIES IN DISTRIBUTION OF THE N:P RATIO IN SEAWATER OF THE JAPAN/EAST SEA

P. Tishchenko, V.Lobanov, A.Nedashkovskiy, G.Pavlova, S.Sagalaev, M.Shvetsova V.Il'ichev Pacific Oceanological Institute, Vladivostok, Russia and

L.Talley

Scripps Institution of Oceanography, San Diego, USA

Some Results Submitted to the Russian Journal "Oceanologiya"

Objectives: to specify processes which govern peculiarity in distribution of N:P ratios in the Japan/East Sea

Main results:

• Near surface and near bottom of the Sea, N:P ratios reveal low values (significantly less than the Redfield ratio) due to two suggested processes – photolysis and denitrification.

• Within 50–80 m depths vertical distribution of the N:P ratios have maximum which exceed Redfield ratio as a rule. This maximum may be caused by photooxydation of dissolved organic matter by nitrate or result of phosphate scavenging by detritus formation.

• Main body of the Sea is characterized by near constant N:P ration (12.65).

DATA

 International cruises on aboard R/V Roger Revelle and Professor Khromov in summer 1999;
 R/V Akademik Lavrent'ev in October 2003.

July-August, 1999, International Expedition on R/V Roger Revelle (Prof. L.D.Talley – chief scientist), R/V Professor Khromov (Dr. V.A.Luchin – chief scientist) Akademik Lavrent'ev (Prof. A.I.Obzhirov – chief scientist)

In 1999: CTD
Dissolved oxygen
Nutrients (nitrate, nitrite, phosphate and silicate)
PH
Alkalinity
In 2003: CTD, TA, dissolved Ca, Mg and SO4 of pore water



Fig.1. Correlation dependence between concentration of inorganic forms of dissolved nitrogen ([NO3] + [NO2]) and phosphorus for waters of the Sea in summer 1999. (Yellow dots are experimental data. There are four distinct sites designated by green, blue, black and purple lines.

Two distinct views on the stoichiometric ratios of photosynthesis and remineralization exist currently :

1) considerable variation in the composition of organic matter.

2) relative constant stoichiometric ratios. (this view coresponds with the original Redfield ratio concept (Redfield et al., 1963)

After N.Gruber and L.Sarmiento (1997; 2002) arguments, we accept here the second view.

The soft tissue formation/remineralization represents in variations of nitrogen and phosphorous with constant ratio to each other $\Delta N:\Delta P=16:1$ (Redfield Ratio).

Existence of deviations from RR may be caused by processes that have a distinctly different stoichiometry, such as nitrogen fixation and denitrification.

There are two approaches to distinguish nitrogen fixation and denitrification areas:

a) Using of N*-function (N*=N-16P+2.90; N.Gruber and L.Sarmiento, 2002) b) Using of dN:dP- ratios.

 $[N] = a_i + b_i[P] + c_i[P]^2 + d_i[P]^3$ $dN / dP = b_i + 2c_i[P] + 3d_i[P]^2$



Fig.2. Vertical distribution of N* (a) and dN/dP (b). Existence of many negative deviations in N* and dN/dP suggests that denitrifications is occurred in the Sea. However N* and dN/dP reveal distinct different behavior in the upper layer of the Sea.



Fig.3. Vertical distribution of N* and dN/dP for some typical stations. Shapes of the N* and dN/dP are very similar for deep water but quite different for shallow water. Shallow waters reveal very low dN/dP rations which do not reflected in the N* profiles. We prefer dN/dP ratios for recognition of nitrogen fixation and denitrification processes than N* - function because dN/dP parameter has clear sense .



Fig.4. Distribution of dN/dP near surface waters of the Sea.

Most of dN/dP values are lied between 4 and 8 for near surface water.

Main reason of the low N:P ratio in shallow waters is photolysis of nitrate and nitrite ions under natural sunlight irradiation according to reactions (O.C.Zarfiru and M.B. True. 1979. Mar.Chem., V.8, p.9-42.; Y.Zuo and Y.Deng. 1998. Chemisphere, V.36, p.181-188; L.J.Spokes and P.S.Liss. 1996. Mar.Chem. V.54. p.1-10.): $NO_3^- + hv \rightarrow NO_2^- + 0.5O_2$

 $NO_3^- + H_2O + hv \rightarrow NO_2 + OH + OH^-$

 $NO_2^- + hv \rightarrow^* NO_2^- + H_2O \rightarrow NO^+ + OH + HO^-$



Natural surface seawater from the Japan/East Sea has undetectable level phosphate nitrate and nitrite was poisoned by HgCl₂. 1 micromole of NO₂- was added into 1 L of this water. **Obtained solution was** exposed under natural sunlight in Quartz flask, Pyrex flask and Dark flask. **Results demonstrated on the** Fig.5 suggest photolysis of nitrites with rate 0.075 umol/day (10 hours of sunlight per day).

Fig.5. Time course of nitrite photolysis by sunlight in the surface Japan/East Sea water poisoned by HgCl₂.
1- Quartz flask
2-Pyrex flask
3-Dark flask



Fig.6. Distribution of maximum of dN/dP values (a) and depths (b) in the Sea.

- Most of maximum values of dN/dP are lied between 16 and 20 within 50 and 80 m depths.
- Apparently, there are three possible reasons appearance of maximum in the dN/dP values.
- a) Nitrogen fixation by nitrogen fixer.
 b) Photooxidation of dissolved organic matter by nitrate ions in the surface with forming of N-enriched organic matter which is consequently mineralize in deeper layers (50-80m).
 c) Scavenging of phosphate by detritus formation .





Fig.7. Surface temperature of the Sea in summer 1999.



- There are two distinct area with low dN/dP ratios near bottom:
- a) in Ulleung Basin, near Korean Strait
- b) In northern part of the Sea, near Tartar Strait.

Fig.8. Near-bottom distribution of N/P ratio in Summer 1999. Depths less than 500m are filled by grey.

Distribution of Nitrogen/Phosphate ratio in the JES suggests that denitrification is occurred near bottom on interface – "reduced sediments/ oxygenated seawater". It is may be schematically represented as follows:

 $(CH_{2}O)_{106}(NH_{3})_{16}H_{3}PO_{4} + 84.8NO_{3}^{-} + 99.8H^{+} \rightarrow$ 106CO₂ + 148.4H₂O + 16NH₄⁺ + 42.4N₂ ↑ +H₂PO₄⁻

$$NH_4^+ + NO_2^- \rightarrow N_2^+ + 2H_2O$$

Geochemical and hydrochemical properties supported this conclusion are following below



Fig.9. Near-bottom distribution of hydrochemical parameters in summer 1999: oxygen (a); phosphate (b) DIC (C); pCO2 (d). Stars are locations of sediment cores.

Lowest oxygen concentration have been detected in northern part of the Sea (46N Lat.), which has no seasonal variability.



Fig.10. Composition of pore waters: TA (a); dissolved Ca (b); dissolved Mg (C); dissolved SO4 (d). 1- St.33 46°28.808' N; 139°0.294'E 2- St.38 44°52.611' N; 137°10.388'E

Thus, interface between reduced sediments and oxygenated is favorable conditions for denitrification processes.

Data suggest sulfatereduction is occurred in the sediments:

 $(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 53SO_4^{2-} \rightarrow 38H_2S + 16NH_4^+ + H_2PO_4^- + 106HCO_3^- + 15HS^-$



Fig.11. Sections of oxygen, umol/kg (a) and DIC, mmol/kg (b) along near 131° E. Longitude at Summer 1999.

Near Korean Strait, along the continental slope bottom water is depleted by oxygen and enriched by DIC.



Fig.12. Sections of N/P ratio along near 131 ° E.



Fig.13. Sections of oxygen, umol/kg (a) and DIC, mmol/kg (b) along near 46° N. Latitude at Summer 1999.



Western part of the section is Primorye continental slope.

Fig.14. Sections of N/P ratio along near 46 ° E in Summer 1999.

Summary:

- The main water body of the Japan/East Sea has N:P ratio as low as 12.65 due to two processes:
- a) Photolysis of nitrite and nitrate ions in the surface water. This process supported available publications and own experimental data as well.
- b) Denitrification on interface "oxygenated seawater reduced sediments". There are strong geochemical evidences for denitrification into two distinct near bottom area, which are characterized by low oxygen content, high CO2 content and low dN/dP ratios. These are southwestern slope of Ulleung Basin and Continental slope of Primorye in northern part of the Sea.

Maximum of dN/dP ratios was discovered in subsurface waters, within 50-80 meters depth. It was supposed, that this maximum may be formed by photooxydation DOM with participate nitrate or nitrite ions and scavenging phosphate by detritus which form at there depths.



Thank you for attention !