NITRITE IN A DEEP OXYGENATED ENVIRONMENT - SEDIMENTARY DENITRIFICATION IN THE JAPAN/EAST SEA

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During our summer 1999 and winter 2000 hydrographic surveys of the Japan/East Sea (Fig. 1), nitrite (NO_2) above the detection level for standard colorimetric nutrient analyses was found close to the ocean bottom well below the euphotic zone, in an oxygen-rich water column. Careful examination of the nutrient analysis method, the reproducibility of the observations of non-zero NO_2 from three separate cruises, and other biologically-active properties convince us of the robustness of the observation. Different properties taken together suggest sedimentary denitrification. Similar signatures in the Okhotsk and Bering Seas impact the North Pacific's nitrogen inventory, based on World Ocean Circulation Experiment hydrographic surveys. While the Japan Sea process does not affect the Pacific Ocean because of the shallowness of the straits connecting it to the Pacific, examination of the nutrient budget in the Japan Sea can shed light on sedimentary processes in the other marginal seas precisely because the water sources for the Japan Sea are so limited.

Nitrite is a short-lived (3-30 days) intermediate product of both the nitrification and denitrification processes in the oceans. NO_2 is created by bacterial oxidation of ammonium, phytoplankton reduction of nitrate, and bacterial reduction of nitrate in anaerobic environments. The first two processes dominate in the euphotic zone, with bacterial oxidation more important (Olson, 1981; Ward et al, 1989). Nitrate reduction in the water column is found in oxygen-depleted regions such as the eastern tropical Pacific. The nitrogen cycle in the sediments can include coupled nitrification and denitrification, with nitrite production in both processes and a net loss of nitrate in the overlying water due to flux into the sediment (Devol, 1991; Christensen et al., 1987). NO_2 is removed by bacterial oxidation to nitrate, utilization by phytoplankton when the preferred nitrate content is small, and by bacterial reduction.

The primary NO_2 maximum found throughout the world at the base of the euphotic zone is present throughout the Japan Sea, and will be discussed in our complete paper on Japan Sea nitrite. NO_2 is also found to depths of about 500 m along the continental margins and to depths of 1500-2200 meters in some locations, especially in the Ulleung Basin (Fig. 1). The deep NO_2 concentration is less than 0.01 umol/kg. (The detection limit of the colorimetric analysis is 0.004 umol/kg.) Where found, the deep NO_2 is always adjacent to the bottom, in a turbid bottom boundary layer 80-100 meters thick, evident in light attentuation (Fig. 3). Stations that contain deep NO_2 are shown in Fig. 2. Properties at a representative station (southern Ulleung Basin, in the Tsushima Current region) are shown (Fig. 3). This station, which is near the continental slope, also has nitrite extending downward from the euphotic zone to a depth of 600 meters, through the nitracline to the nitrate maximum. Nitrate appears to be somewhat depleted in the turbid bottom boundary layer; oxygen is also depleted, and phosphate is enhanced. The parameter N* (Gruber and Sarmiento, 1997) is depleted in the bottom boundary layer, suggesting denitrification. The biologically inert chlorofluorocarbons have no signature of a bottom boundary layer. The oxygen loss is possibly due to oxidation in the upper part of the sedimentary layer.

The location of the deep continental slope and bottom nitrite signal corresponds with the existence of sediments that are rich in organic carbon (Likht et al., 1983) such as was observed with sedimentary denitrification off the Washington coast (Devol, 1991). Ammonium is produced in these sediments and oxidized to nitrite. Below the nitrification portion of the sediments, it is likely that denitrification is occurring since the overall nitrate content is reduced in the bottom boundary layer. What causes the high turbidity in the bottom boundary layer? We hypothesize that it is due to the strong and variable currents and eddies (since tidal amplitudes are small in the Japan Sea), or to outgassing in the sediments from subsurface methane hydrates (Takeuchi et al., 1998).

The nitrate/phosphate ratio in the Japan Sea (Fig. 4), as well as the nitrate/AOU and phosphate/AOU ratios (Kim et al., 1992), indicate denitrification, by the significant deviation of the deeper waters above the 1/16 Redfield ratio. N* as a function of potential density for the Japan, Okhotsk and Bering Seas (Fig. 5) as well as for the entire Pacific (not shown, from WOCE data set) suggests net denitrification in the NW Pacific marginal seas. High N* in the Japan Sea surface waters is due to the inflow of subtropical waters at Tsushima Strait, whereas the subpolar Pacific waters adjacent to the Okhotsk and Bering Seas are already depleted in nitrate, possibly due to processes within these marginal seas, low nitrogen fixation rates in the subpolar surface waters, and upwelling of N*-poor waters to the surface layer.

The Japan Sea's oxygen minimum appears to derive from the bottom boundary in the same slope regions where nitrite is found. One hypothesis is that oxygen is removed in greater amounts in these sediments than in the water column (for instance in the Japan Basin where the oxygen minimum is at mid-depth, and appears to be lateral extension of the bottom oxygen minimum of the Ulleung Basin and northeastern Japan Sea). Rates for the nitrogen and oxygen sediment processes could possibly be generalized to the Pacific Ocean (e.g. Jahnke and Jackson, 1987).

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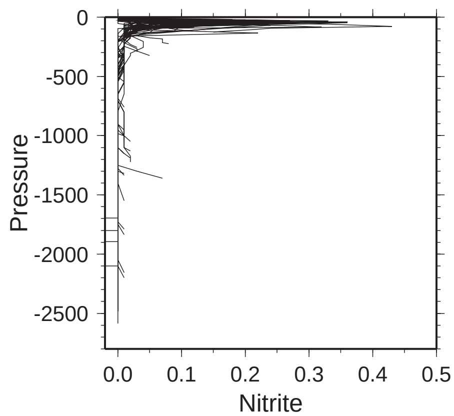

Figure 1. Nitrite profiles for summer 1999 stations (R/V Revelle) in the Ulleung Basin.

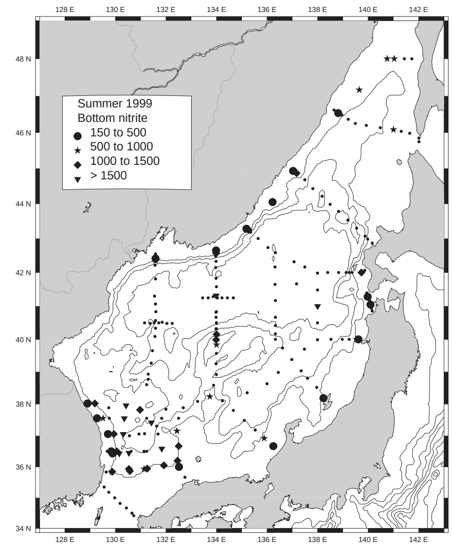

Figure 2. Summer 1999 stations with bottom nitrite.

Figure 3. Properties from summer 1999 in the southern Ulleung Basin (35.9N, 130.6E). "Transmission" is the raw voltage in the shipboard CTD acquisition files.

Figure 4. Phosphate as a function of nitrate for the Japan Sea. Solid line is the Redfield ratio with an offset of .182, (Gruber and Sarmiento, 1997).

Figure 5. N* as a function of potential density for the Japan (X), Okhotsk and Bering Seas (both in dots).