Denitrification

Denitrification is the microbial reduction of nitrate to di-nitrogen gas. Denitrification is sometimes referred to as 'dissimilatory' nitrate reduction because it occurs in association with the dissimilation (decomposition) of organic matter [1]. The denitrification reaction for the oxidation of organic matter with Redfield molar proportions is as follows [2]:

$$106(CH_2O)16(NH_3) + H_3PO_4 + 94HNO_3 = 106CO_2 + H_3PO_4 + 177H_2O + 55.2N_2$$

The nitrate (NO_3^-) is used in the respiratory process of the microbes, and can be derived from the water column or from nitrification occurring during the mineralisation of organic matter in sediments. When nitrate for denitrification is derived from nitrification, the process is called coupled nitrification-denitrification.

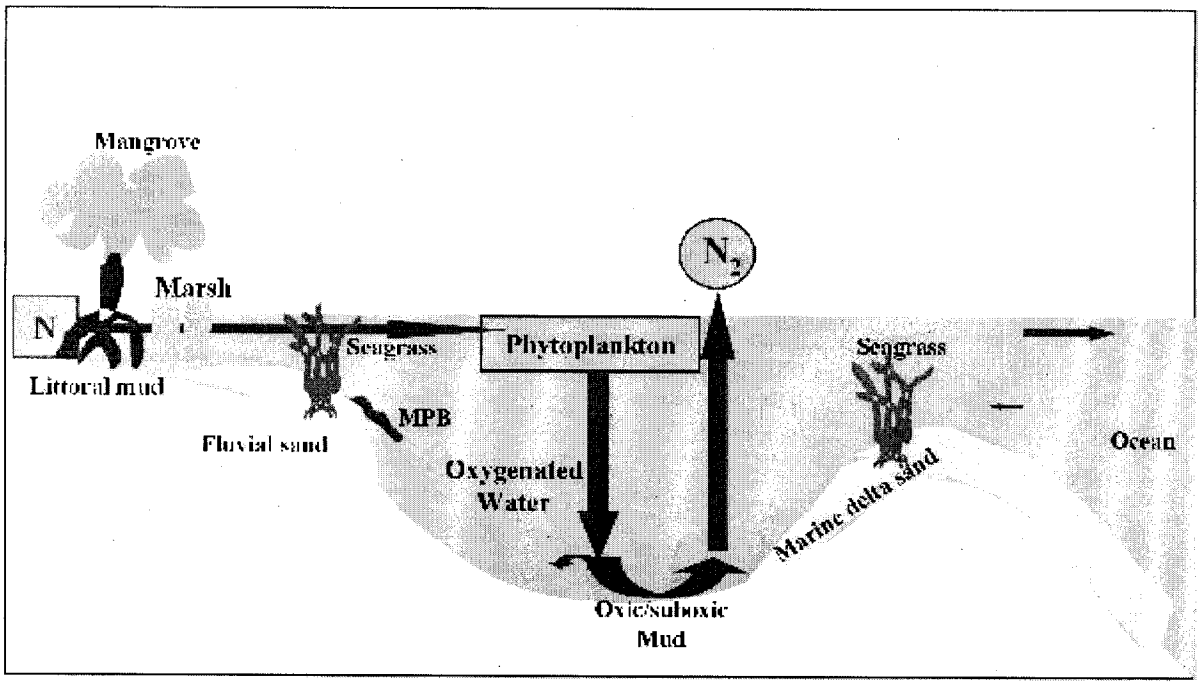

Figure 1. Schematic diagram of N cycling in coastal sediments under relatively low levels of carbon loading. Note that some nitrogen is vented to the atmosphere as dinitrogen gas (modified from Heap *et al.*, 2001 [4]).

Significance of Denitrification in Coastal Waterways

Denitrification is an important reaction in coastal waterways because it can permanently remove nitrogen from the system as di-nitrogen gas (Figure 1). As such, it can counteract the eutrophication process [3,4,13]. If benthic denitrification ceases, flushing by tides or freshwater becomes the only way to eliminate excess nitrogen [5]. The cessation of nitrification and denitrification is also an important cause of hysteresis in the loading response of estuaries to nutrients [6].

Some Controls on Denitrification Rates

Denitrification in sediments appears highly sensitive to carbon loading (*a.k.a* trophic status) [3,9,13,18]. Carbon loading to sediments can be estimated by measuring the carbon dioxide flux

from sediments. Denitrification efficiencies become successively lower as carbon loadings move into the mesotrophic, eutrophic and hypertrophic range [3], and more and more nitrogen is re-cycled in bioavailable forms (such as ammonium). The efficiency of the denitrification process is an 'indicator' of sustainable carbon loading rates in coastal waterways (*e.g. the denitrification efficiency*) [3].

Denitrifying bacteria are anaerobic but they require an oxidised form of nitrogen (*e.g.* nitrate). Denitrification can be enhanced by the presence of benthic infauna which increase sediment surface area (burrows) and enhance irrigation (oxidation) of deeper sediments. Benthic invertebrates thus cause localised increases in concentrations of organic matter and solutes (*i.e.* ammonium) and ultimately enhance microbial activity and oxic / anoxic microenvironments (and therefore coupled nitrification / denitrification) in their burrow linings, excreta and organic particles [7,17].

Seagrasses and other benthic plants and algae may also enhance coupled nitrification-denitrification because they oxygenate the upper sediment layers [8]. However saturating the upper sediment layers with oxygen can also have the reverse effect, and lower denitrification rates during daylight hours. Moreover, if water column nitrogen concentrations are really low, benthic microalgae may inhibit nitrification and denitrification because they compete for nitrate [15].

Denitrifying activity tends to be highest in the summer months coinciding with warmer water temperatures [11]. It also varies inversely with ionic concentration, and is especially high when salinities are <10 ppt [10]. High concentrations of the heavy metals cadmium, copper and zinc in sediment can inhibit denitrification [12].

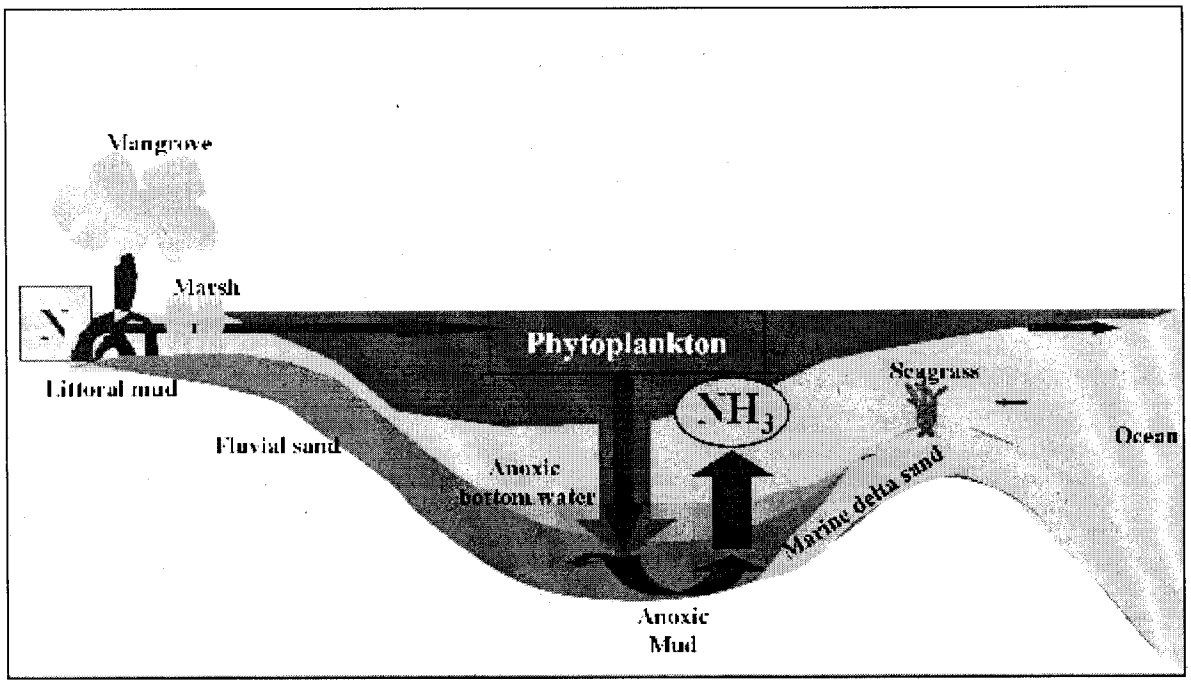

Figure 2. Schematic diagram of N cycling in coastal sediments under relatively high carbon loading rates. Note that denitrification is less important, and most nitrogen is recycled as ammonium (NH_4) which is available to plants (modified from Heap *et al.*, 2001 [4]).

References

1. Postgate, J.R. 1998. Nitrogen Fixation. 3rd Edition. Canbridge University Press, London.

2. Froelich, P. N., Klinkhammer, G. P., Bender, M. L., Luedtke, N., Heath, G. R., Cullen, D., Dauphin, P., Hammond, D., Hartman, B., and Maynard, V. (1979). Early oxidation of organic matter in pelagic sediments of the eastern equatorial

Atlantic; suboxic diagenesis. Geochimica et Cosmochimica Acta Pergamon, Oxford. 43, 1075-1090.

3. Eyre, B. and A.J.P. Ferguson 2002. Sediment biogeochemical indicators for defining sustainable nutrient loads to coastal ecosystems, Proceedings of Coast to Coast 2002 - "Source to Sea", Tweed Heads, pp. 101-104.

4. Heap, A., Bryce, S., Ryand, D., Radke, L., Smith, C., Smith, R., Harris, P. and D. Heggie. 2001. Australian Estuaries & Coastal Waterways: A Geoscience Perspective for Improved and Integrated Resource Management. AGSO Record 2001/07, pp. 118. http://www.ozestuaries.org/oracle/ozestuaries/document/

5. Harris, G.P. 1999. The response of Australian estuaries and coastal embayments to increased nutrient loadings and changes in hydrology, In *Australian Estuarine Systems: Carbon, Nitrogen, and Phosphorus fluxes* (Eds., S.V. Smith and C.R. Crossland), LOICZ Reports and Studies No. 12, LOICZ IPO: Texel, The Netherlands, pp. 112-124.

6. Harris, G.P. 1999. Comparison of the biogeochemistry of lakes and estuaries: ecosystem processes, functional groups, hysteresis effects and interactions between macro- and microbiology. *Marine and Freshwater Research* 50, 791-811.

7. Nixon, S.W 1988, cited in Harris 1999. Comparison of the biogeochemistry of lakes and estuaries: ecosystem processes, functional groups, hysteresis effects and interactions between macro- and microbiology. *Marine and Freshwater Research* 50, 791-811.

8. Risgaard-Petersen, N. and Jensen, K., 1997. Nitrification and denitrification in the rhizosphere of the aquatic macrophyte *Lobelia dortmanna* (L.), *Limnology and Oceanography* 42, 529-537.

9. Seitzinger, S.P., Nixon, S.W. (1985). Eutrophication and the rate of denitrification and N_2O production in coastal marine sediments. *Limnol. Oceanogr.* 30:1332-1339.

10. Rysgaard, S., Thastum, P., Dalsgaard, T., Bondo Christensen, P., and Sloth, N.P. 1999. Effects of salinity on NH_4^+ adsorption capacity, nitrification, and denitrification in Danish Estuarine sediments. *Estuaries* 22(1), 21-30.

11. Carpenter, E.J., Dunham, S. (1985). Nitrogenous nutrient uptake, primary production, and species composition of phytoplankton in the Carmans River estuary, Long Island, New York. *Limnol. Oceanogr.* 30, 513-526.

12. Sakadevan, K., Huang Zheng, and H.J. Bavor. 1999. Impact of heavy metals on denitrification in surface wetland sediments receiving wastewater. *Wat. Sci. Tech* 40(3), 349-355.

13. Heggie, D. T., Skyring, G. W., Orchardo, J., Longmore, A. R., Nicholson, G. J., and Berelson, W M. (1999b). Denitrification and denitrifying efficiencies in sediments of Port Phillip Bay: direct determinations of biogenic N2 and N-metabolite fluxes with implications for water quality. Marine Freshwater Research 50, 589-596.

14. Seitzinger, S.P., Nixon, S.W., Pilson, M.E.Q. (1984). Denitrification and nitrous oxide production in a coastal marine ecosystem. *Limnology and Oceanography* 29, 73-83.

15. Krause-Jensen, D., Bondo-Christensen, P. and Rysgaard, S. 1999. Oxygen and nutrient dynamics within mats of the filamentous macroalga Chaetomorpha linum. *Estuaries* 22(1), 31-38.

16. Sundareshwar, P.V., Morris, J.T., Koepfler, E.K., and B. Fornwalt. 2003. Phosphorus limitation of coastal ecosystem processes. *Science* 299, 563-565.

17. Haese, R.R. 2002. Macrobenthic activity and its effects on biogeochemical reactions and fluxes. In Wefer, G., NBillet, D., Hebbeln, D., Jorgensen, B.B., Schluter, M, Van Weering, T. (eds) *Ocean Margin Systems*. Springer-Verlag Berlin Heidelberg, pp. 219-234.

18. Harris, G.P., Batley, G., Fox, D., Hall, D., Jernakoff, P., Molloy, R., Murray, A., Newell, B., Parslow, J., Skyring, G. and Walker, S. (1996). Port Phillip Bay Environmental Study: final report. CSIRO, Dickson, ACT Australia.

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