



ASSESSMENT OF THE FATE OF ANTHROPOGENIC NITROGEN IN LARGE WATERSHEDS BY ISOTOPIC TECHNIQUES

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Human activity has greatly altered the nitrogen cycle in terrestrial and aquatic ecosystems and increased the nitrogen flow in many rivers. Preliminary work of the International SCOPE Nitrogen Project indicates that only 20 % of the human-controlled nitrogen inputs to large watersheds are exported to the oceans in riverine flows (Howarth, 1998). Therefore, approximately 80 % of the anthropogenic nitrogen inputs are either stored or denitrified in the catchments.

Anthropogenic nitrogen can be retained in forests as a result of increased productivity or in agricultural soils and can potentially be stored in groundwater. These sinks are, however, not large enough to account for the "missing" nitrogen. It is, therefore, assumed that the majority of the human-controlled nitrogen inputs to large watersheds is denitrified in soils, riparian zones, wetlands, lakes, and rivers.

Within the SCOPE Nitrogen Project, preliminary isotope analyses were performed on dissolved nitrates from 15 streams draining into the North Atlantic Ocean. Both $\delta^{15}\text{N}_{\text{nitrate}}$ and $\delta^{18}\text{O}_{\text{nitrate}}$ values were determined in order to identify nitrate sources (Fig. 1). A further objective was to test whether the isotopic composition of dissolved nitrate provides a measure for the extent to which denitrification occurs in the respective watersheds.

Figure 1 summarizes the isotopic compositions of dissolved nitrate from the Hudson River (USA) and the Oder River (Germany). The $\delta^{15}\text{N}$ values of nitrates in the Hudson River ranged between 5.1 and 7.3 ‰ and the $\delta^{18}\text{O}_{\text{nitrate}}$ values varied between 7.2 to 12.3 ‰. These values are indicative of dissolved nitrate, which is derived predominantly from nitrification processes in soils. In contrast, dissolved nitrate in most Oder River samples was characterized by comparatively high $\delta^{15}\text{N}$ (10.4 to 14.8 ‰) and $\delta^{18}\text{O}_{\text{nitrate}}$ values (12.8 to 15.9 ‰). The elevated $\delta^{15}\text{N}$ values could be interpreted as evidence of nitrate derived from manure and/or sewage. However, because of the comparatively high $\delta^{18}\text{O}_{\text{nitrate}}$ values it seems more likely that the isotopic composition of dissolved nitrate in the Oder River is indicative of denitrification. Since ^{14}N and ^{16}O react preferentially during denitrification, $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values in the residual dissolved nitrate increase approximately in a ratio of 2:1 (e.g. Kendall, 1998). Statistical analyses of the presented data set yielded a significant linear correlation ($r^2 = 0.77$, $n = 20$) with a regression line slope of 0.44 (Fig. 1). Therefore, it is hypothesized that the dominant primary source of riverine nitrate in both catchments is NO_3^- generated by nitrification in soils. The

dissolved soil nitrate is subsequently partially denitrified during runoff, presumably in riparian zones, wetlands, lakes, and/or in the river sediments. The data shown in Fig. 1 indicate that denitrification is of minor importance in the Hudson River. In contrast, denitrification appears to be an important factor in the Oder River probably accounting for the removal of a significant portion of the human-controlled nitrogen inputs to its watershed.

The presented hypothesis is currently being tested in 15 watersheds in the mid-Atlantic and New England states (USA), all of them with well-constrained nitrogen budgets.

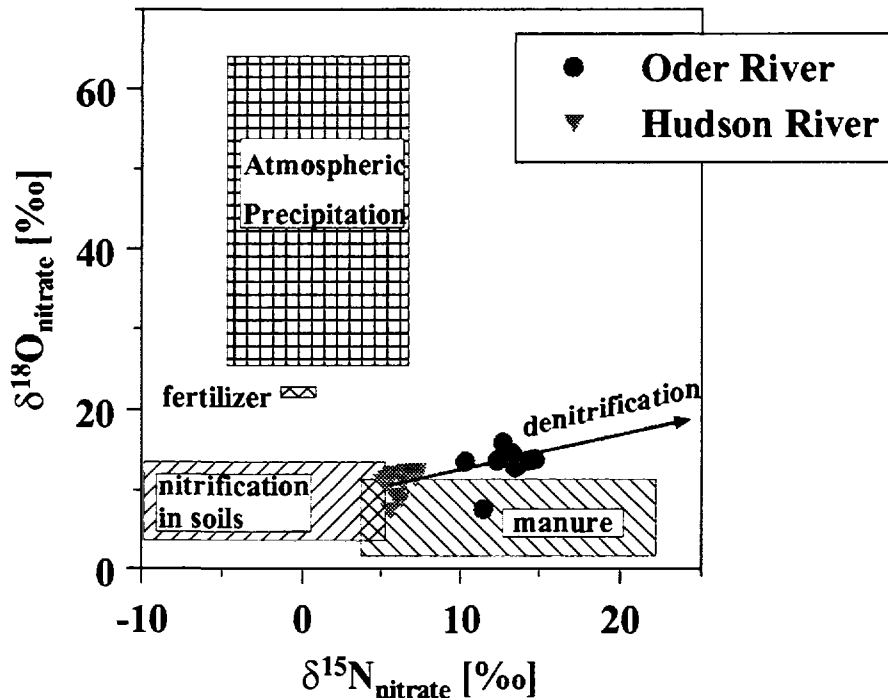


Fig. 1: $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values of dissolved nitrate from the Hudson River (USA) and the Oder River (Germany) with respect to typical isotopic compositions of atmospheric deposition, nitrate-containing fertilizers, and nitrate formed by nitrification in soils and manure.

References:

- Howarth, R. W. (1998): An assessment of human influences on fluxes of nitrogen from the terrestrial landscape to the estuaries and continental shelves of the North Atlantic Ocean. *Nutrient Cycling in Agroecosystems* 52: 213-223.
- Kendall, C. (1998): Tracing nitrogen sources and cycling in catchments. In: *Isotope Tracers in Catchment Hydrology* (Kendall, C. & McDonnell, J. J., eds.), 519-576, Elsevier, New York.