USING DUAL ISOTOPE TRACERS TO LEARN ABOUT THE SOURCES AND TRANSFORMATIONS OF NITRATE DURING TRANSPORT IN THE MOHAWK RIVER BASIN

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The effects of human activities on the nitrogen (N) cycle at regional and global scales is the focus of much research and concern because humans have more than doubled N fluxes, storage, and the rates of many N cycling processes. This human-induced acceleration of the N cycle is linked to myriad environmental concerns including soil acidification, tropospheric ozone, acute ground-water and stream-water pollution, and estuarine eutrophication (Galloway et al., 2003). At the regional scale, much work has focused on the controls of nitrate (NO_3^-) concentrations and fluxes in riverine environments that range in scale from small streams to large rivers (Boyer et al., 2002; Smith et al., 2005). Major uncertainties remain in our understanding of how N from various sources moves through landscapes to rivers and the extent to which N cycling processes alter these sources during transport (Schlesinger et al., 2006). The transport of NO_3^- is of concern in the Mohawk River watershed, because as part of the Hudson River watershed, N loads are transported to estuarine settings such as the Long Island Sound, where eutrophication has been identified as an issue of concern by state and federal environmental regulators.

One approach to learning about the sources and processes that affect the movement of N through the environment is to measure various isotopes of the element or its associated elements. In the case of N, the ratio of the stable isotope ^{15}N to the more common stable isotope ^{14}N can be used to trace sources and transformations through watersheds. In recent years, methods have been developed to measure both $^{15}N/^{14}N$ (reported as $d^{15}N$ relative to a standard) as well as the isotope ratio $^{18}O/^{16}O$ (reported as $d^{18}O$ relative to a standard). This dual isotope method has allowed investigators to better gain insight into the sources and movement of NO_3^- in watershed studies. In multi-land use watersheds such as the Mohawk River, a variety of sources such as fertilizer, human and animal waste, and atmospheric deposition can contribute to river NO_3^- loads. In this study, we measured NO_3^- concentrations as well as $d^{15}N$ and $d^{18}O$ of NO_3^- in the Mohawk River and in five additional streams (either within or near the Mohawk watershed) in differing land uses to learn about the sources and transport of N in the watershed.

Samples were collected monthly from each stream at a range of flow conditions for 15 months during 2004-05 and analyzed for NO_3^- concentrations, $d^{15}N_{NO3}$, and $d^{18}O_{NO3}$. Samples from two streams draining forested watersheds indicated that NO_3^- derived from nitrification was dominant at baseflow. A watershed dominated by suburban land use, but with all waste water discharged outside the watershed had three $d^{18}O_{NO3}$ values > +25‰ indicating a large direct contribution of atmospheric NO_3^- transported to the stream during some, but not all high flow periods. Two watersheds with large proportions of agricultural land use had many samples with $d^{15}N_{NO3}$ > +9‰ suggesting a waste source consistent with direct application of manure to fields associated with regional dairy farming practices. These data showed a linear seasonal pattern with a $d^{18}O_{NO3}$: $d^{15}N_{NO3}$ close to 1:2, consistent with seasonally-varying denitrification that peaked in late summer to early fall with the warmest

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temperatures and lowest streamflow of the year. The large range of d $^{15}N_{NO3}$ values (~10‰) indicates that NO_3^- supply was likely not limiting the rate of denitrification, potentially consistent with ground water and/or in-stream denitrification. Mixing of two or more distinct sources may also have affected the seasonal isotope patterns observed in these two agricultural streams. At a larger basin scale in the Mohawk River watershed that represented the average proportions of land uses in this study, none of the source and process patterns observed in the small streams were evident. These results emphasize that observations at small to medium size watersheds of a few to a few hundred km^2 may be necessary to adequately quantify the relative roles of various NO_3^- transport and process patterns that contribute to streamflow in large basins.

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