Seasonal Variations in Nitrate Flux and Isotopic Composition in the Upper Illinois River Basin

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The $\delta^{15}N$ and $\delta^{18}O$ values of nitrate were measured by the bacetrial denitrification method in 450 water samples (collected between Chicago and Peoria, October 2004 through October 2008) from the Illinois River and its tributaries, including effluent from Chicago's largest wastewater treatment plant (WRP). These data, along with sample nitrate concentrations and USGS discharge records, were evaluated in terms of the influence of land use and climate on nitrate sources, mixing, and transformation within the Upper Illinois River Basin (UIRB) watershed. $\delta^{15}N$ and $\delta^{18}O$ values define nitrate mixing trends indicating that WTP effluent and agricultural drainage waters are the two principal nitrate endmembers within the UIRB. Nitrate flux is correlated with discharge. Isotopic compositions identify the source of nitrate during the annual spring flushing event, when most nitrate export occurs from the UIRB, as being derived from excess fertilizer application. Isotopic compositions of nitrate in tributaries draining agricultural subbasins define an apparent denitrification trend with increases in $\delta^{15}N$ and $\delta^{18}O$ values from spring through fall. This trend is also evident in tributaries having mixed urban-agricultural land use, but less so in those dominated by urban land use where WTP effluent is the dominant source of nitrate. Mass balance of nitrate indicates that the fraction of nitrate from WTP effluent in the Illinois River at Peoria can be <5% during the spring flush (March-May) and much larger during late summer and fall. Input of nitrate derived from WTP effuent is relatively constant year-round, whereas agricultural nitrate flux varies by a factor of 10 or more.