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Tracing nitrate and sulfate in river basins using isotope techniques

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The discipline of Isotope Hydrology has made remarkable scientific advances in the last half century. The understanding of the hydrological cycle was markedly improved by analyzing and interpreting hydrogen ($^{2}H/^{1}H$) and oxygen ($^{18}O/^{16}O$) isotope ratios of ocean water, precipitation, ice cores, surface water and groundwater. Isotope ratio determinations have also been used to identify sources of dissolved constituents in precipitation, surface water, and groundwater such as sulfate ($^{34}S/^{32}S$), nitrate ($^{15}N/^{14}N$), dissolved inorganic carbon ($^{13}C/^{12}C$) and strontium ($^{87}Sr/^{86}Sr$), among others. Furthermore, isotope analyses have provided evidence for the occurrence of physical (e.g. mixing), chemical (e.g. dissolution of salts), and/or microbial processes (e.g. denitrification, bacterial sulfate reduction) in the hydrosphere. This contribution will describe how stable isotope techniques can be used to elucidate the sources and the fate of nitrate and sulfate in river basin studies.

Isotope studies of riverine systems are challenging since sources of water and dissolved constituents will vary both spatially and temporally. This, however, provides an excellent opportunity for multi-isotope approaches, provided that a sufficient number of sampling sites are available. Mixing of river water with tributaries or influent groundwater may be quantified via flow measurements in conjunction with conservative tracers such as $^{2}H/^{1}H$ and $^{18}O/^{16}O$ of water or strontium isotope ratios ($^{87}Sr/^{86}Sr$) along a river flow path. Determination of fluxes and isotope ratios of nitrate ($^{15}N/^{14}N$, $^{18}O/^{16}O$) may reveal admixture of nitrate from diffusive or point sources, or potentially in-stream nitrate consumption by processes such as assimilation or denitrification. Similarly, monitoring of sulfate fluxes and isotope ratios ($^{34}S/^{32}S$, $^{18}O/^{16}O$) may indicate the addition of sulfate from anthropogenic or natural sources, or potentially sulfate removal by assimilation or possibly bacterial sulfate reduction. Based on physi-

cal, chemical, and isotopic measurements on river water from the South Saskatchewan River Basin in western Canada, we will describe the predominant sources and processes controlling nitrate (soil nitrification, manure-derived nitrate) and sulfate fluxes (evaporite dissolution, pyrite oxidation, anthropogenic sources including detergents) in this basin.