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# Seasonal evolution of nitrate isotopic composition in the River Scheldt

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The Scheldt Estuary is the outlet of one of the most densely populated watersheds of Europe (425 inh./km$^2$). Following the implementation of wastewater management measures the Scheldt River has experienced important biogeochemical changes during the last decade. Among others, this resulted in better water oxygenation, and nitrate has become the dominant form of the dissolved nitrogen pool. We present results for the nitrogen and oxygen isotopic composition of nitrate in the River Scheldt and its main tributaries, as sampled monthly from December 2009 till present in the framework of a regional monitoring programme. The method of analysis was based on the denitrifier methodology developed by Sigman and Casciotti (2001), involving bacterial reduction of nitrate and subsequent analysis of the released N2O by Isotope Ratio Mass Spectrometry (IRMS). To that purpose we used a custom build purification and cryofocusing system connected on-line to a Thermo Delta V IRMS.
Along-river sections and tributaries show a clear seasonality with increased [U+F064]15N and decreased d18O signatures in spring-summer, and the inverse in winter. Likewise, d18O vs d15N plots for waters from the Scheldt and its tributaries clearly differentiate winter from spring-summer conditions, the latter having highest d15N and lowest d18O values. While the isotopic composition for winter is expected to represent the condition prevailing in groundwater feeding the river, during spring-summer, within-river transformation processes impact on the isotopic composition. These processes are mainly nitrification, decreasing nitrate d18O and nitrate uptake, increasing both, d15N and the d18O. The fact that seasons are well resolved imply that nitrification occurs early in the season when ammonium is still abundant and uptake by phytoplankton limited, while later in the season, once ammonium drops to very low concentrations and nitrate is the main inorganic N-species, uptake by phytoplankton becomes the predominant process and is witnessed also by decreasing nitrate concentrations on from June.