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Exposure times vs residence times in the hyporheic zone and implications for nitrate processing at reach to catchment scales

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The rate of geochemical turnover associated with natural degradation and transformation processes in hyporheic areas is one of the largest uncertainties in predicting nutrient fluxes from fluvial systems to lakes and the coastal zone. This is especially true at catchment to basin scales. Here we present a combination of natural tracer measurements (222Rn) and a modelling framework that can be used to estimate hyporheic nitrate loss at the catchment scale. In contrast to previous models we use exposure times rather than residence times as the relevant time scale for reactive turnover in hyporheic areas. The exposure time (ET) distribution is generated by removing the portion of the hyporheic residence time (RT) distribution associated with flow paths in the oxic zone. This lag 'a' (hours) was calculated from oxygen respiration kinetics. We apply the method to the Vilqué, a small stream in Brittany (France), which is heavily influenced by agriculture. Hyporheic exchange parameters (e.g. mean residence time) were derived from measured stream 222Rn activities and subsequent 222Rn mass balance modelling. Only a relatively small portion of water entering the hyporheic zone actually flowed through the reactive area and depended on the RTD. The power law distribution had the least water flux through the reactive zone (<5%) due heavy weighting towards shorter flow paths that are confined to the oxic sediments. The gamma and exponential RT distributions where rather similar with \sim 5% flowing through the area conducive to nitrate reduction. Estimated hypothesic nitrate turnover over the 2.5 km stream length ranged between 0.01-0.11 kg d-1 depending on the applied ET distribution. By using exposure times instead of residence times the turnover rates decrease by up to 97% (power law RT/ET distribution) due to removal of the oxic flow paths in the ET distribution. Based on these results, we conclude that hyporheic systems can be very inefficient in removing nitrate from stream water if exposure times are taken into account and the system is characterised by a power law type RT distributions.