



Simultaneous measurement at multiple depths of in situ rates of denitrification in the bed of a groundwater-fed river

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Typically characterised by steep chemical gradients and variable redox conditions, the hyporheic zone is considered a 'hotpot' or site of enhanced biogeochemical activity in the aquatic environment. As such the importance of the hyporheic zone for the attenuation of nutrients such as nitrate in a fluvial network has long been recognised. Controls on nitrogen transformations, however, especially at depths greater than 10cm below the sediment-water interface, remain comparatively less understood. Most work aimed at quantifying denitrification in the hyporheic zone has involved laboratory incubation of recovered sediments which is likely to affect the estimate of the true in situ rate. Results of such studies are usually cited as 'potential' rates of denitrification and have undoubtedly improved the understanding of nitrogen cycling in the aquatic environment. There is, however, a need for in situ measurement to improve our knowledge of nitrogen cycling in the river bed.

Here, rates of denitrification in the hyporheic zone have been measured at multiple depths, simultaneously using "push-pull" methodology (e.g. Snodgrass and Kitanidis 1998). The "push-pull" technique involves injection of a solution containing reactant(s) (e.g. nitrate) and a conservative tracer (e.g. chloride) into the sediment and extraction of pore water samples over time. Recovered samples are screened for the removal of reactant(s) and/or the accumulation of product(s). Temporal changes in the conservative tracer are used to correct the concentration of the reactant(s) and product(s) for dispersion and advection. The disadvantage of the 'traditional' "push-pull" methodology is that rates of nitrate removal are measured rather than rates of denitrification. In this research, comparison of measured and 'corrected' nitrate concentrations allowed the rate of nitrate removal (or production) to be quantified. In order to determine in situ rates of denitrification we used ^{15}N -enriched nitrate as the reactant in the "push-pull" experiments and measured the accumulation of $^{29}\text{N}_2$ and $^{30}\text{N}_2$ over time. Rates of denitrification were then calculated using the isotope pairing technique (as per Nielsen 1992; Sanders and Trimmer 2006).

Measurements have been made at up to 40cm depth in the river bed using a miniprobe system developed from the design of Sanders and Trimmer (2006) in order to validate the experimental approach. Previous work conducted at the study site (R. Leith, Cumbria, UK) suggested that ambient conditions would not be ideal for in situ measurement of denitrification rates using "push-pull" methodology. Slow rates of denitrification were measured during laboratory incubations of the sandy sediment (M. Trimmer, unpublished data), and the velocity of flow in the hyporheic zone would limit the duration of the in situ measurement (Käser *et al.* 2009). Despite difficulties posed by the site, we have measured in situ rates of denitrification at multiple depths in the hyporheic zone simultaneously. We also report measurement of in situ rates of denitrification below the zone of surface water – ground water mixing. In future we will use the experimental technique described in this paper to quantify (i) variation in N transformation rates with depth; and (ii) spatial variation in rates of nitrate consumption/production within the river bed.

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