OR/18/011 Summary

Stuart, M E. 2018. Review of denitrification potential in groundwater of England. *British Geological Survey Internal Report*, OR/18/011.

An understanding of the fate of nitrate in groundwater is vital for managing risks associated with nitrate pollution, and to safeguard groundwater supplies and groundwater-dependent surface waters. One of the main measures to control nitrate is the designation of nitrate vulnerable zones (NVZs). Recent review of the designation process in England has highlighted that in some locations measured groundwater nitrate concentrations were not as high as expected. A possible reason for this is that the nitrate is being transformed through denitrification. This review forms the first stage in the development of a tiered approach to assessing denitrification potential across groundwater in England (and Wales) using three main lines of evidence: groundwater quality indicators, geological mapping of confined aquifers and superficial deposits which can influence redox status and a mass balance approach.

Denitrification can take place either heterotrophically, where microorganisms use a sequence of ions as electron acceptors to enable the consumption of organic carbon, generating intermediates or by-products that can be used as process indicators, or autotrophically where pyrite is used as an electron donor and is oxidised to sulphate. Other nitrogen cycle processes which can produce some similar intermediates can include dissimilatory nitrate reduction directly to ammonia (DRNA), assimilatory nitrate reduction to organic nitrogen, anaerobic ammonium oxidation (anammox) and nitrification.

Demonstrating and quantifying denitrification is difficult, requiring specialist measurements and with different problems in environment and scale. Stable isotopic methods have been the most widely applied. Only a mass balance approach appears to be feasible in groundwater without new specialist measurements.

Groundwater quality indicators
A sequence of threshold concentrations for identifying redox processes have already been developed by other workers and these combined with existing monitoring data should form the basis for identifying areas where denitrification is either likely or unlikely. Groundwater quality from the Environment Agency strategic monitoring network includes nitrogen species, TON or NO_3^-, NO_2^- and NH_4^+ and other parameters that could be indicative of reducing conditions, dissolved O_2, dissolved organic C, Mn^{2+}, Fe^{2+}, SO_4^{2-} and Eh.

Mapping of confined zones and key superficial deposits
Many studies have confirmed the presence of redox boundaries in confined aquifers. Literature data on low redox zones indicating denitrification has focussed predominantly on the confined zones of major aquifers. In England and Wales, these have included the Chalk, Permo-Triassic sandstone and the Lincolnshire Limestone. The boundary occurs some distance down dip from the start of confinement depending on the aquifer flow regime. Both BGS/Environment Agency Baseline reports and the Environment Agency's groundwater quality reports contain qualitative statements about denitrification in areas of confined aquifers. These include the limestones of the Corallian, the Great and Inferior Oolites, the Zechstein Group (Magnesian Limestone) and the Carboniferous, and the sandstones of the Palaeogene, Crag, Lower Greensand, Millstone Grit and the Old Red Sandstone. The confined zones of aquifers or groups of aquifers can be represented by defining aquifer subcrop

from the BGS 3D model and applying a lower depth limit (conventionally 400 m).

Superficial deposits also have a role, both in confinement of underlying aquifers and as a source of organic rich infiltration. The hyporheic zone can also have a role and this needs to be taken into account in assessing the extent of denitrification potential. These can be represented from superficial cover mapping. Predisposing settings include were sediment thickness and permeability, groundwater baseflow index as a measure of groundwate-stream connectivity, and sediment geochemistry.

Mass balance approach
In some areas, inputs of nitrogen do not appear to be reflected in current groundwater concentrations. Inputs could include applications to arable land, urban areas and aerial deposition. One example of this is the area defined during NVZ designation.

Each of these lines of evidence is likely to provide a partial picture of denitrification potential. A tiered approach will be developed to combine these into a useful format together with applicability and limitations for each type of evidence.

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