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Shallow groundwater denitrification capacity at three contrasting hydrogeological environments in Ireland

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Denitrification may be regarded as the dominant nitrate removal or attenuation process in shallow groundwater. A major concern arising from the denitrification process is that it not only serves as a natural pathway for excess NO_3^- removal but its intermediate product, N_2O, is a potent greenhouse gas. A groundwater monitoring network was established on grazed grassland at research farms at Johnstown Castle (JC) and Solohead (SH) on tillage at Oak Park (OP) in Ireland, to investigate the denitrification capacity and N_2O:(N_2O+N_2) ratio within the shallow groundwater zone. The geology of this zone at the 3 sites was i) JC: sand and gravel intermixed with clay, ii) SH: silt and gravel intermixed with dense clay and iii) OP: dense gravel with interbedded clays. Average groundwater table was respectively 3.2, 2.4 and 4.0 m below ground level. Ten piezometers of 50 mm ID with 2 m screen sections were installed at 3.5-6.0 m below ground level using a rotary air drilling method at the three sites. Groundwater sampling was carried out monthly for 6 months (February to July, 2009) using a bladder pump following the USEPA low flow sampling procedures. Dissolved groundwater N_2O was separated by degassing groundwater in a sealed serum bottle (160ml) using high purity He (water:He = 3:1) and the collected headspace equilibrium gas was analyzed on a Varian gas chromatograph. The N_2/Ar ratio, measured using a Membrane Inlet Mass Spectrometer, was used to estimate the denitrified N2 concentrations. The mean NO_3-N concentrations were 7.0, 2.5 and 11.0 mg L^{-1} in JC, SH and OP, respectively. Ground water dissolved N_2O concentrations ranged from 0.01 to 0.05, 0.01 to 0.06 and 0.002 to 0.06 mg L^{-1}, with corresponding mean values of 0.03, 0.02, 0.02 mg N.L^{-1} in JC, SH and OP, respectively. The mean values for total denitrification (N_2O+N_2) were 1.94, 1.03 and 0.38 mg N.L^{-1}, which accounted for 22, 29 and 3% losses of total NO_3^- -N in JC, SH and OP, respectively. The higher denitrification measured on the grassland compared to tillage is most likely related to the hydrogeological conditions e.g. DOC, DO and redox-potential rather than land-use. More importantly, the mean N_2O:N_2O+N_2 ratios, being 0.01, 0.02 and 0.05, respectively in JC, SH and OP indicated that 95-99% of total denitrification was molecular N2 (98-99% in grassland and 95% in tillage farm). With respect to temporal changes, denitrification losses were higher in May in grassland systems and in April in tillage farming systems. Shallow groundwater denitrification appeared to be an important process in reducing NO_3^- , with low N_2O concentrations indicating low losses of this greenhouse gas to the atmosphere upon discharging to surface water.