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Dissolved gas and isotopic tracers of denitrification

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We present results from field studies in California (USA) where tritium-helium age dating is used in conjunction with major gases (N_2, O_2, CH_4, CO_2), noble gases (He, Ne, Ar, Kr, Xe), and stable isotopes ($^{15}N/^{14}N$, $^{18}O/^{16}O$) in order to document nitrate loading and denitrification associated with confined animal agricultural operations and septic systems. Preliminary results show that in-field extraction of the full suite of dissolved gases will be possible using a new Gas Extraction System under development to augment the current Noble Gas Mass Spectrometry and Membrane Inlet Mass Spectrometry techniques.

Ascribing observed groundwater nitrate levels to specific current and past land use practices is often complicated by uncertainty in groundwater age and the degree and locus of dentrification. Groundwater age dating at dairy field sites using the ^{3}H-^{3}He method indicates that the highest nitrate concentrations (150-260 mg/L-NO3) occur in waters with apparent ages of <5 yrs, whereas older waters contain excess N_2 from saturated zone denitrification [1]. At a residential septic system site in Livermore, CA, waters with young apparent ages (<1 yr) proximal to leach line drainage have lower nitrate concentrations and elevated nitrate $\delta^{15}N$ and $\delta^{18}O$ values consistent with denitrification, but little evidence for excess N_2, indicating that denitrification is occurring in the unsaturated zone.

Degassing of groundwater can complicate efforts to calculate travel times [2] and to quantify denitrification. Degassed groundwater underlying dairy operations is formed by two distinct mechanisms: (1) recharge of manure lagoon water affected by biogenic gas ebullition [3] and (2) saturated zone denitrification producing N_2 gas above solubility in groundwater. Gas loss due to both mechanisms is evident in the concentrations of noble gases and major gases in dairy groundwater samples.

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[1] Singleton, M. J., Esser, B. K., Moran, J. E., Hudson, G. B., McNab, W. W., and Harter, T., 2007. *ES&T* **41**, 759-765. [2]Visser, A., Broers, H. P., and Bierkens, M. F. P., 2007. *WRR* **42**, W10434 (1-14) [3] McNab, W. W., Singleton, M. J., Moran, J. E., and Esser, B. K., 2007. *ES&T* **41**, 753-758.