



Concentration Gradients of Excess N₂ and N₂O in the vadose zone and groundwater of the Mid-Atlantic coastal plain, U.S.A.

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We have developed a method to measure excess N₂ and N₂O vertical gradients in the vadose zone of an agricultural riparian buffer strip. Soil gas samples were taken from either buried equilibration chambers (inverted 50 mL open tubes usable only in unsaturated conditions) or silicone membrane diffusion samplers (closed 10 cm silicone tubes that allow sampling in unsaturated and flooded conditions). Excess N₂ concentrations were determined by measuring the N₂/Ar ratios by mass spectrometry, whereas N₂O was measured by gas chromatography. The precision of N₂/Ar ratios was typically < 0.05% (CV) from triplicate injections. N₂/Ar in the vadose zone of one sample set in late fall 2008 ranged from 83.87 in air and increased linearly to 84.31 at 1.5 m; another gradient showed a mid-depth maximum of 84.29. In groundwater at the same site, the equivalent N₂/Ar at the gas/water interface was elevated (91.97-95.24). N₂O concentrations in the vadose zone ranged from 0.1 μ M at 0.25 m to 0.39 μ M at 1.5 m, and N₂O was again considerably higher in groundwater ranging over 8.20 - 8.63 μ M. These preliminary data indicate that the gas gradients in the vadose zone are due to both diffusive losses from the higher concentrations in groundwater as well as originating from internal sources within the vadose zone.