SURFACE-GROUNDWATER MIXING STIMULATES NITROUS OXIDE PRODUCTION IN CARBONATE AQUATIC SYSTEMS

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Extensively developed secondary porosity in eogenetic karst systems allow ample exchange of surface water and groundwater. The exchange delivers vital substrates including surface water derived organic carbon (OC) to subsurface microbes living in low energy environments. The exchange alters aquifer redox conditions and influences nitrogen dynamics, which is often a limiting nutrient in terrestrial ecosystems. One nitrogen species of particular concern is nitrous oxide (N_2O), a long-lived and potent greenhouse gas that originates primarily from heterotrophic denitrification, which couples OC respiration to nitrate (NO_3^-) reduction, with N_2O produced as an intermediate species. Thus, the quantity and quality of OC substrates has the potential to influence N_2O dynamics through heterotrophic denitrification reactions. A natural OC quantity and quality gradient that occurs in the Santa Fe River in north-central Florida provides an ideal site to investigate N_2O dynamics linked to OC variations. The ~120 km river transect can be divided into three main sections: 1) an upstream section where the regional Floridan aquifer is confined by an overlying siliciclastic unit, leading to high OC concentrations of allochthonous origin (recalcitrant), 2) a downstream section, where the confining unit is absent, leading to low OC concentrations of autochthonous origin (labile), and 3) an intermediate section located at the erosional edge of the confining unit where these two endmembers mix. N_2O concentrations in upstream waters are approximately at equilibrium with atmospheric concentration while downstream river waters have N_2O concentrations ~ 2.5 times that of upstream waters. The highest N_2O concentrations, reaching up to 2,000% saturation relative to atmospheric equilibration, occur at these intermediate locations. These elevated N_2O concentrations correlate with mixing of the allochthonous and autochthonous OC sources, suggesting that these mixing zones are hot-spots of N_2O production which may be linked to variations in OC reactivity stimulated by mixing of these distinct OC pools.

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