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Assessment of hydrological and biogeochemical effects on N2O emission factors in river networks of eastern China based on long-term study

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The N_2O emission factors (EF) in river networks remains a major source of uncertainty due to limited data availability. This study integrated three years of multiple stable isotope ($^{15}N\text{-}NO_3^-$/$^{18}O\text{-}NO_3^-$ and $^{2}H\text{-}H_2O$/$^{18}O\text{-}H_2O$) and hydrochemistry measurements for river water and groundwater to evaluate the effects of hydrological and biogeochemical processes on riverine N_2O emission factors in the Yongan watershed (2474 km^2) of subtropical eastern China. The EF in groundwater (0.00195 ± 0.00146) was about one magnitude higher than that in surface water (0.00038 ± 0.00020). The N_2O EF displayed seasonal and spatial variability in surface water and groundwater. The emission factors in surface water showed negative relationship with N levels and positive relationship with dissolved organic carbon: DIN (C:N) ratio. In contrast, N_2O EF in groundwater showed positive relationship with N level and negative relationship with DO concentration, implying quite different processes undergoing in surface water and groundwater. The $^{2}H\text{-}H_2O$/$^{18}O\text{-}H_2O$ information suggested high base flow contribution (~70%) to rivers, implying the potential N_2O contribution from groundwater to riverine N_2O. Information from $^{15}N\text{-}NO_3^-$ and $^{18}O\text{-}NO_3^-$ indicated that N_2O in groundwater were regulated by nitrification and denitrification, while N_2O in river networks was mainly derived from nitrification and may be also regulated by hydrological processes. The strong positive relationship between riverine N_2O concentrations and that in groundwater may indicate the potential high contribution of groundwater N_2O to surface water. This study highlights the importance of combining multiple isotope tracers and hydrochemistry to assess the riverine N_2O dynamics, as well as the necessity to consider the potential impact from groundwater N_2O contribution during the determination of riverine N_2O emission factors in rivers with high groundwater recharge.