Elucidation of the Mechanism of Greenhouse Gas Generation by Abiotic Transformation of Nutrient Ions Flowing into Closed Water Areas with Little Phytoplankton

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ABSTRACT: In Mikawa Bay and Ise Bay, many tidal flats, shallow areas, and seaweed beds have been lost due to land reclamation, and the pollution inflow from domestic and industrial wastewater has increased, causing environmental deterioration such as red and blue tides. To prevent their occurrence, the hyporheic zone of the brackish lake leading to these bays was dredged and covered with sand, and sewerage systems were constructed around the surrounding areas. Furthermore, the water in this lake is regularly substituted with new river water but unregulated agricultural wastewater flows into the lake. Nutrient ions from nitrogen fertilizers in this wastewater are passively decomposed and released into the atmosphere as a greenhouse gas N_2O. We report that ClO_2^- ions, classified as disinfection byproducts detected in this water body, promote the production of ·N and ·NO radicals through the abiotic transformation of NH_4NO_3 from nitrogen fertilizers in aqueous solutions. Because these radicals are highly reactive and have a small energy gap between singly occupied molecular orbital (SOMOs), they generate N_2O through a heterogeneous coupling reaction and release N_2O from water to the atmosphere. Abiotic transformation mechanisms of nutrient ions provide information for resolving biodiversity crises and N_2O emissions problems associated with marine environmental restoration.

KEYWORDS: **N radical, ·NO radical, nitrogen cycle, ClO_2^- ion, nitrogen fertilizer, nutrient ions, greenhouse gas, N_2O*