ORIGIN AND FATE OF NITROUS OXIDE IN A PUTATIVE COUPLED ABIOTIC-BIOTIC DENITRIFICATION PROCESS IN TROPICAL PEATLANDS.

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Methane (CH_4) and nitrous oxide (N_2O) are strong greenhouse gases on Earth. The global warming potentials (GWPs) are ~25 and ~300 times that of CO_2 (1), respectively, which raises the importance to understand the origin and fate of these gases. Beside its role in the climate system, N_2O has drawn attention as a biosignature gas for the detection of life. The ideal biosignature gas is one that does not exist naturally in the planetary atmosphere, is not created by geophysical or geochemical processes, is not produced (or rapidly destroyed) by photochemistry and has a strong spectral signature (2). Findings of the importance of abiotic N_2O production pathways in an Antarctic hypersaline pond have recently challenged N_2O as a canonical, unique-to-life biosignature gas (3).

In 2010, gravity spaceborn data on the atmospheric distribution of methane collected by satellites identified tropical wetlands as a large contributor to global CH_4 emissions (4). Novel peatlands discovered in the Amazon basin revealed large stocks of accumulated organic matter (5). Our analysis showed highly heterogenous CH_4 (-500 to 1204 µg-N m^{-2} h^{-1}) and N_2O (-0.3 to 80 µg-N m^{-2} h^{-1}) fluxes based on geochemically contrasting peatland sites in the Peruvian Amazon. The oligotrophic peats are acidic (2.9-4.8) and have a fluctuating groundwater table dependent on precipitation events. Below the groundwater table the soils are waterlogged and active bacterial fermentation induces steep oxygen depletion gradients to anoxia. In this anoxic regime, a yet uncharacterized archaeal community produces methane. Nitrous oxide is released by denitrifying processes when oxygen is absent. However, the exact mechanism behind a stepwise reduction of nitrous compounds remained mostly enigmatic under the acidic conditions of these tropical soils.

Here, we present early evidence of a putative coupled abiotic-biotic denitrification pathway with a hitherto unknown N_2O reduction potential. We performed anoxic incubation experiments in batch cultures with soils from different sites in the Pastaza-Marañón foreland basin, Peru. Peat soil slurries were treated with nitrite and live soil was compared to killed controls. These controls were sterilized prior to the nitrite injection by either steam sterilization (autoclave) or sodium azide in order to exclude false killed controls. Both live and killed soil revealed rapid nitrite depletion and concomitant N_2O production. The stoichiometry of the nitrous compounds points to a direct conversion from nitrite into N_2O. Reduction of 500 µM nitrite was complete in 5 days. Since nitrite conversion and N_2O accumulation proceeded under live and killed conditions, we conclude a non-enzymatically driven mechanism, which needs additional experiments to be further elucidated. Phenolic rings have been observed to undergo nitrosation in similar environments and form nitrosophenols (6). Nitrite reduction by dissolved ferrous iron at low pH is also possible (3). Interestingly, the N_2O formed is likely biologically removed within approximately 10 days of incubation time. The same set up with live and killed controls showed ongoing N_2O reduction in unsterilized soil only. Nitrous oxide is reduced at a rate of 9-21 µmol g^{-1} wet soil day^{-1}, however, the product and the microorganisms responsible for N_2O consumption are still unclear.

We propose that the investigated tropical peatlands harbor a putative coupled abiotic-biotic denitrification pathway. The question if this pathway is unique to these peatlands or more widespread among wetlands requires further investigation. Recently, several studies compiled evidence on atypical denitrifying microbial guilds and, thus, an overlooked N_2O sink capacity of soils (7, 8). A rapid abiotic transformation of nitrite to N_2O can potentially shape such a non-denitrifier community capable of N_2O reduction. To identify this microbial community, our future efforts will include metagenomic analysis and assessment of nitrous oxide reductase (*nosZ*) gene abundance together with isotopic approaches.

The findings presented are of high astrobiological relevance, because (i) we are characterizing a possibly unknown abiotic N_2O production mechanism and (ii) this abiotic process is closely coupled to microbial N_2O reduction. Nitrous oxide reductases could be more common in microbial genomes than previously thought and, based on the current knowledge, N_2O respiration seems to have evolved prior to the separation of the domains *Bacteria* and *Archaea* (9). Therefore, N_2O could have significantly influenced microbial communities on ancient Earth with implications for its appearance as biosignature gas.

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