Researchers uncover fresh role for nitric oxide

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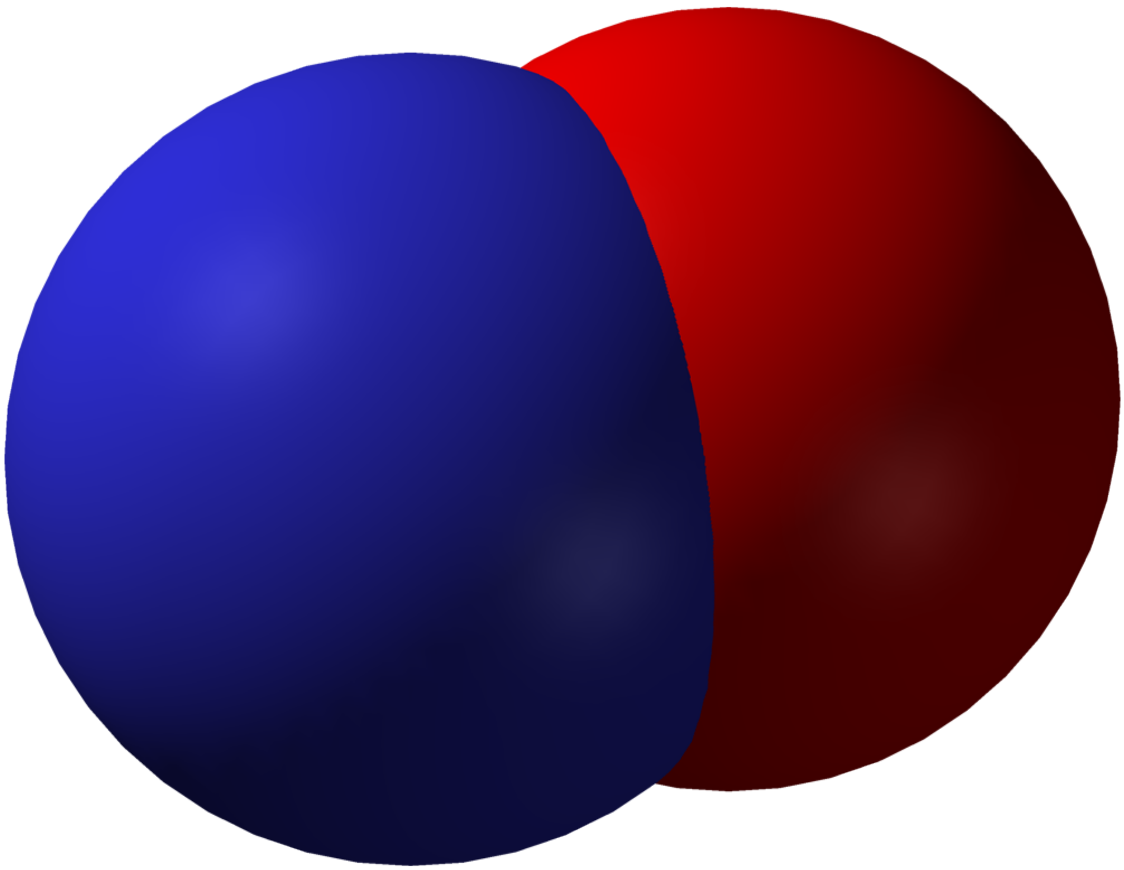

Space-filling model of nitric oxide. Credit: public domain

Cornell University chemists have uncovered a fresh role for nitric oxide that could send biochemical textbooks back for revision.

They have identified a critical step in the nitrification process, which is partly responsible for agricultural emissions of harmful nitrous oxide and its chemical cousins into the atmosphere, contributing to global climate change.

Current biochemical models hold that inorganic hydroxylamine is the only intermediary formed when bacteria convert ammonia - used in commercial agricultural fertilizer - into dormant nitrite. In this new study, the chemists found that hydroxylamine is converted into another intermediary - nitric oxide - which under normal soil conditions acts as the chemical prelude to nitrite. But under imperfect soil conditions, nitric oxide is converted into the potent greenhouse gas nitrous oxide. The work was published in the *Proceedings of the National Academy of Sciences*, July 17.

"We've found a hole in the nitrogen cycle pipeline. As there is nitrous oxide escaping out of the soil into the atmosphere, we now know where the holes are," said co-author Jonathan Caranto, postdoctoral researcher in chemistry. "Nitrous oxide is made from nitric oxide - that's the immediate precursor. If you know where the nitric oxide is coming from, you can make a good guess about nitrous oxide being released."

Understanding how the model works is key to finding greenhouse gas solutions. "This is what the research affords: locating new holes to plug. The holes in the pipeline can be sealed. If you don't fully understand the biochemical pathway, you can't know where the pollutants come from," said co-author Kyle Lancaster, assistant professor of chemistry. "Otherwise, you are shooting in the dark."

In 2015, nitrous oxide comprised about 5 percent of atmospheric greenhouse gas emissions, compared with carbon dioxide at 82 percent, according to the U.S. Environmental Protection Agency. Nitrous oxide, however, is an ozone-depleting gas with a global warming potential more than 300 times greater than carbon dioxide, said Caranto. Nitric oxide also contributes to ground-level ozone and produces acid rain.

Nitric oxide plays an important part in medicine. The journal *Science* named it Molecule of the Year in 1992 for its versatility in heart health. Scientist Robert F. Furchgott, who worked at Cornell Medical College - now Weill Cornell Medicine - from 1941 to 1949, won the 1998 Nobel Prize in physiology or medicine for his role in our understanding of nitric oxide.

The new research shows nitric oxide is formed on the pathway from hydroxylamine to nitrite when soil bacteria use ammonia as chemical fuel. Previously, scientists maintained that hydroxylamine is directly converted to nitrite. "This research could make a huge difference in rearranging predictive nitrogen flux models that scientists use to optimize fertilization practices," said Lancaster.

Greenhouse gas and nitrite production are byproducts of commercial fertilization, and the processes that form them diminish the efficiency of fertilization, said Kyle. "If you can slow down the formation of these species, slow down the oxidation of ammonia in fertilizer, this will raise the 'dwell time' of nitrogen in soil. Agriculture becomes more efficient, more economical and more sustainable."

Knowing this nitric oxide component could help reduce the ratio of cost-to- benefit for farmers and other agricultural producers. Said Lancaster: "This new component to models could lead to better fertilization scheduling."

More information: Jonathan D. Caranto et al, Nitric oxide is an

obligate bacterial nitrification intermediate produced by hydroxylamine oxidoreductase, *Proceedings of the National Academy of Sciences* (2017). DOI: 10.1073/pnas.1704504114

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