Spatiotemporal Variations of Soil Reactive Nitrogen Oxide Fluxes Across the Anthropogenic Landscape

Megan Purchase[1]

[1]Affiliation not available

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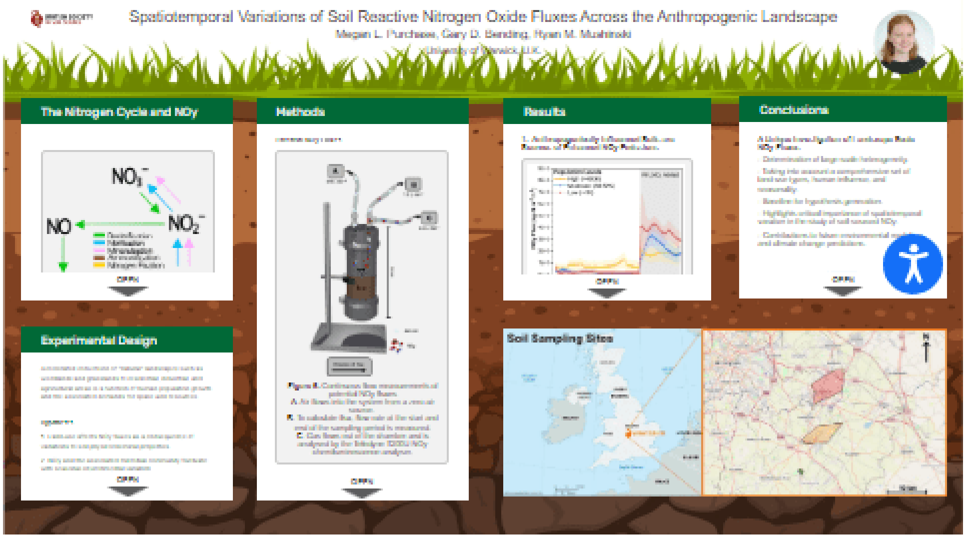


Megan L. Purchase, Gary D. Bending, Ryan M. Mushinski

University of Warwick, U.K.

PRESENTED AT:

THE NITROGEN CYCLE AND NOY

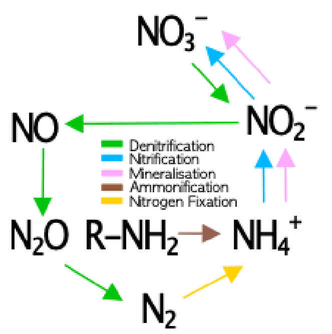


Figure 1. The Nitrogen Cycle

What are NOy?

Volatile reactive nitrogen oxides (NOy) are comprised of NOx (nitric oxide [NO] + nitrogen dioxide [NO_2]) and NOz (nitrous acid [HONO] + nitric acid [HNO_3] + nitrogen trioxide [NO_3] + ...).

Biogenic sources, including soil, account for over 50% of natural NOy emissions to the atmosphere. Soil-sourced NOy generally not included in atmospheric models due to a lack fo mechanistic data.

Impacts of NOy

- Significant atmospheric pollutants

- Contibute to the formation of smog and acid rain

- Reduce air quality

- Exacerbate human respiratory problems

How are NOy formed?

NOy can be produced abiotically, or during microbial processes of the nitrogen (N) cycle (**Fig. 1**). In this study, we focus on nitrification because the soils analysed were all oxygenated aerobic surface soils.

The specific genes analysed were ammonia monooxygenase (*amoA*) (**Fig 2**) and nitrite oxidoreductase (*nxrB*) (**Fig 3**).

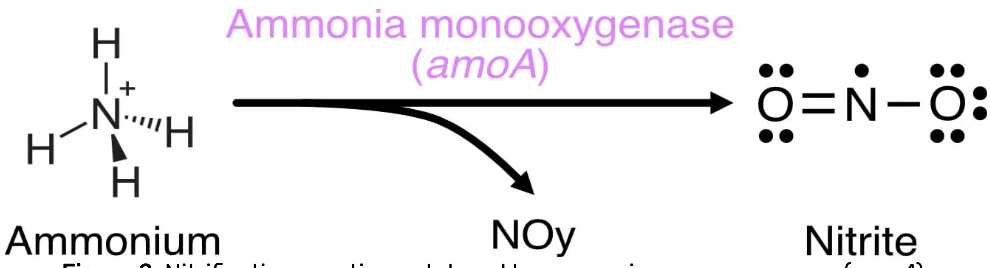


Figure 2. Nitrification reaction catalysed by ammonia monooxygenase (*amoA*).

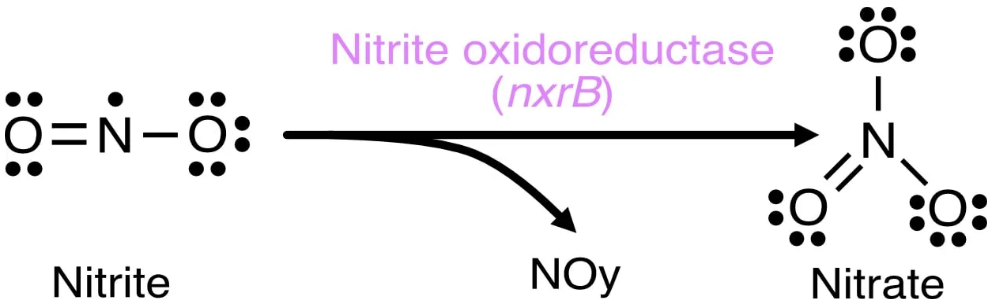


Figure 3. Nitrification reaction catalysed by nitrite oxideoreductase (*nxrB*).

EXPERIMENTAL DESIGN

Accelerated conversion of "natural" landscapes such as woodlands and grasslands to residential, industrial, and agricultural areas is a function of human population growth and the associated demands for space and resources.

Hypotheses

1. Land-use affects NOy fluxes as a consequence of variations to soil physicochemical properties.

2. NOy and the associated microbial community fluctuate with seasonal environmental variation.

3. Human influence on soils, including deposition of N and heavy metals, affects NOy fluxes.

Sampling Strategy

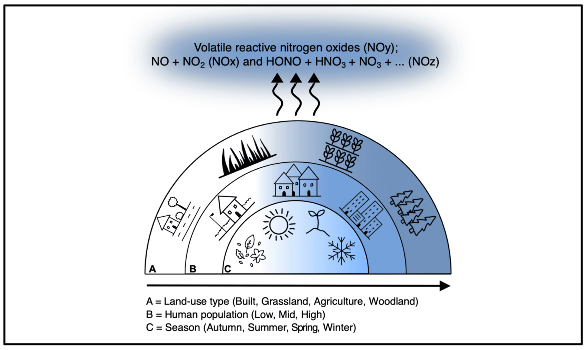


Figure 4. Soil was sampled across a spatiotemporal gradient of the U.K. landscape to determine variations of NOy fluxes.

At each sampling site, soil was sampled using a 7 cm diameter core to a depth of 5 cm. Three samples were taken at each site at 5 m intervals along a 15 m transect and pooled to produce one biological replicate. 10 cm depth intact cores were also taken and used for continuous gas flux measurements. There were three replicates of each land-use type within each location.

METHODS

Potential NOy Fluxes

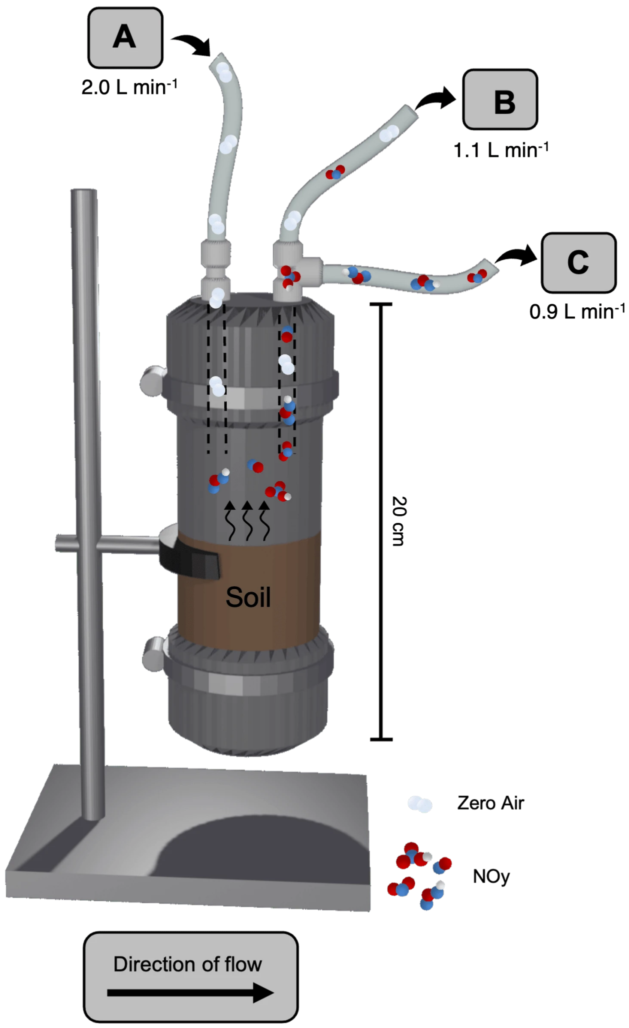


Figure 5. Continuous flow measurements of potential NOy fluxes
A. Air flows into the system from a zero air source.
B. To calculate flux, flow rate at the start and end of the sampling period is measured.
C. Gas flows out of the chamber and is analysed by the Teledyne T200U-NOy chemiluminescence analyser.

Fluxes of total NOy, NO, and $NO_2 + NO_z$ were analysed using a Teledyne T200U-NOy analyser, using a chemiluminescence technique, where NO and ozone (O_3) react, and the resulting luminescence gives a direct concentration measurement of NO. NOy gases other than NO were converted to NO by a flow-through molybdenum converter, and measured as $NO_2 + NO_z$ (NOy−NO) measurements (**Fig. 5**).

To examine the effects of N deposition on the different soil types, ammonium nitrate NH_4NO_3 was dissolved in reagent-grade water and added to soil within chambers and gas flux was analysed for a further 24 h.

Soil Physicochemical Properties

Soils were weighed before and after 48hrs in a 60°C oven to determine moisture content. Soil pH was determined using a pH meter on a solution of 10g soil, air dried for 48 hrs, in 20ml 0.01M $CaCl_2$

Soil Microbiome Analysis

DNA was extracted using the DNeasy PowerSoil Pro kit.16S rRNA gene fragments were amplified from the extracted DNA using primers 515f and 806r. Amplicons were subjected to 250bp, paired-end sequencing on Illumina MiSeq Nano. Specific nitrification genes *amoA* and *nxrB* were analysed using quantitative PCR.

N-Cycle Process Net Rates

Net nitrification, net ammonification, and net total N mineralisation rates were measured using colorimetric analysis to quantify changes in NO_3-(**Fig. 6**) and NH_4+ (**Fig. 7**) over time.

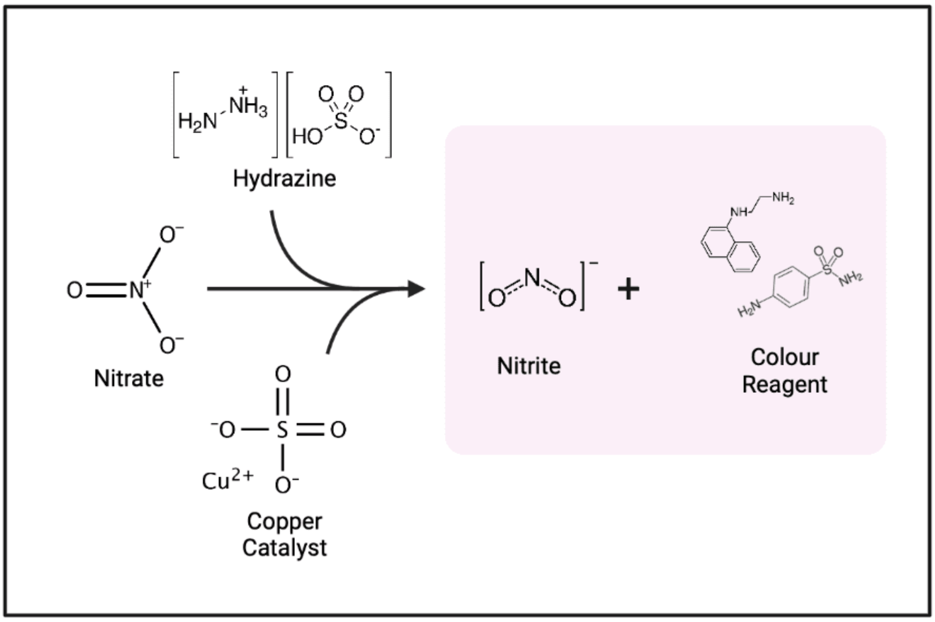


Figure 6. Chemistry of the colorimetric analysis of nitrite and nitrate concentrations.

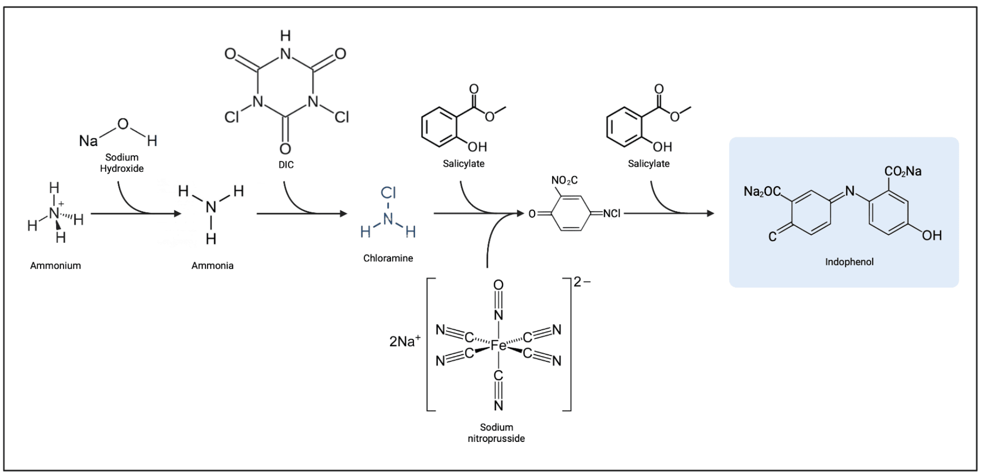


Figure 7. Chemistry of the colorimetric analysis of ammonium concentration.

Heavy Metal Concentrations

Samples were analysed using inductively coupled plasma-optical emission spectroscopy (ICP-OES) to find concentrations of cadmium, copper, lead, iron, nickel, and zinc.

RESULTS

1. Anthropogenically Influenced Soils are Sources of Enhanced NOy Emissions

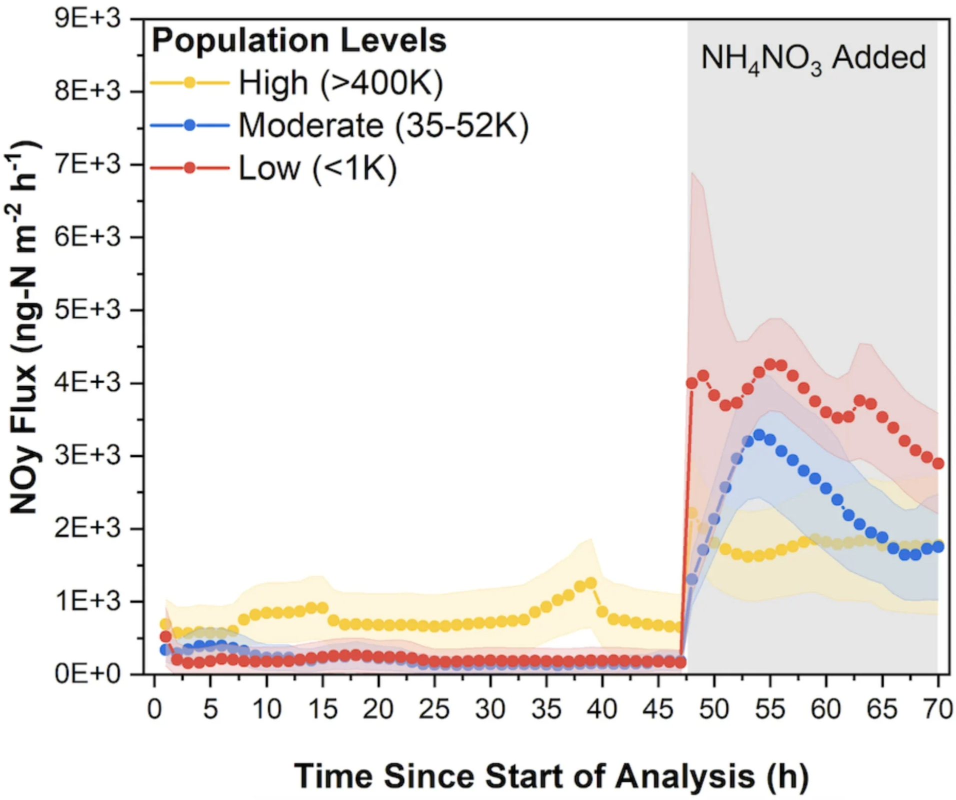


Figure 8. Effect of the addition of NH_4NO_3 to simulate 3 months (one season) worth of N deposition to U.K. soils on potential mean fluxes of total NOy (F_{NOy}) between locations ("low population, Wellesbourne, U.K., <1000", "mid population, Warwick, U.K., 35 000–52 000", and "high population, Coventry, U.K., >400 000")

- Increased N deposition (kg of N per ha per year) in locations with high human population.

- Human population positively correlated with F_{NOY}.

- Higher metal contamination with increasing human population.

- Soils from higher human population locations "buffered" against N deposition.

2. Microbial NOy Production is Dominated by Ammonia-Oxidising Bacteria

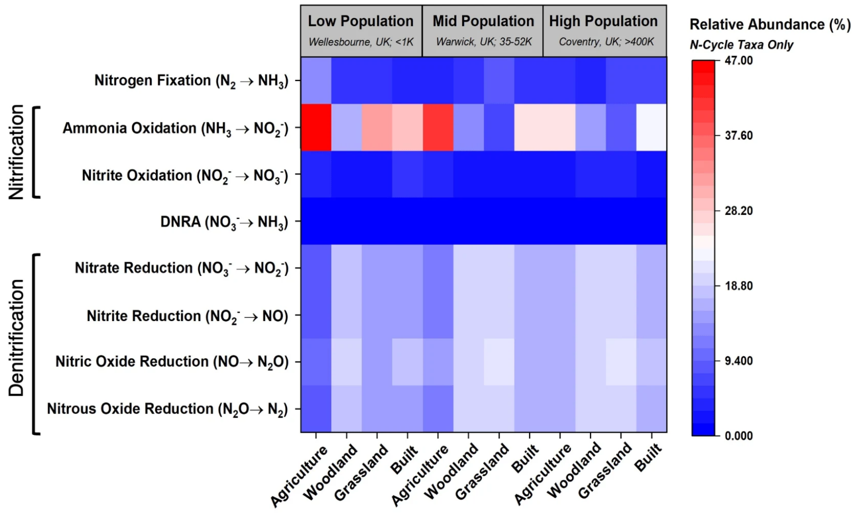


Figure 9. Heat map of relative abundances of microbial orders associated with nitrogen (N) cycling processes compared between locations ("low population, Wellesbourne, U.K., <1000", "mid-population, Warwick, U.K., 35 000–52 000", and "high population, Coventry, U.K., >400 000") and land use (agricultural, woodland, grassland, and built).

- Higher ammonia-oxidising archaea (AOA) abundance compared to ammonia-oxidising bacteria (AOB).

- Increased copies of bacterial *amoA* per g soil positively associated with F_{NOY}.

3. Spatiotemporal Trends in Soil-Sourced N Fluxes

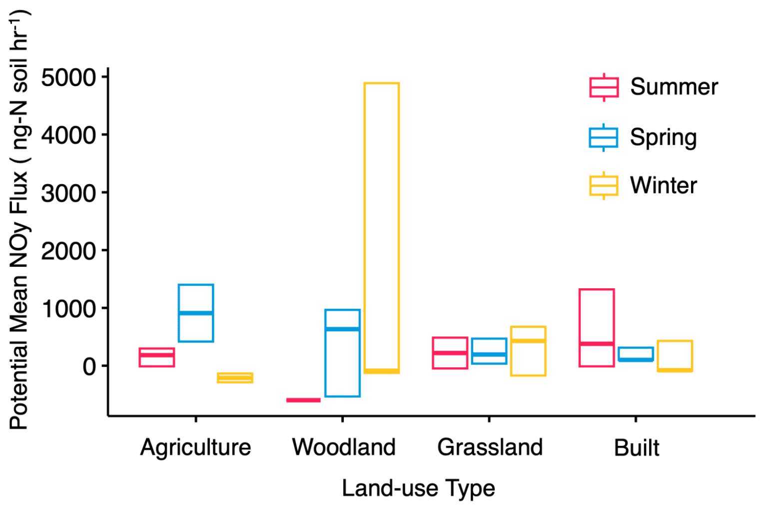


Figure 10. Potential mean fluxes of total NOy (F_{NOy}) across land-use types (agriculture, woodland, grassland, built) and seasons (summer, spring, winter).

- Leaf fall in autumn leads to increased available ammonium from organic matter, thus increasing F_{NO} from woodland soils in winter.

- Fertiliser application in spring leads to increased avaliable nitrate, thus increasing F_{NOY} from agricutural soils in spring.

CONCLUSIONS

A Unique Investigation of Landscape Scale NOy Fluxes

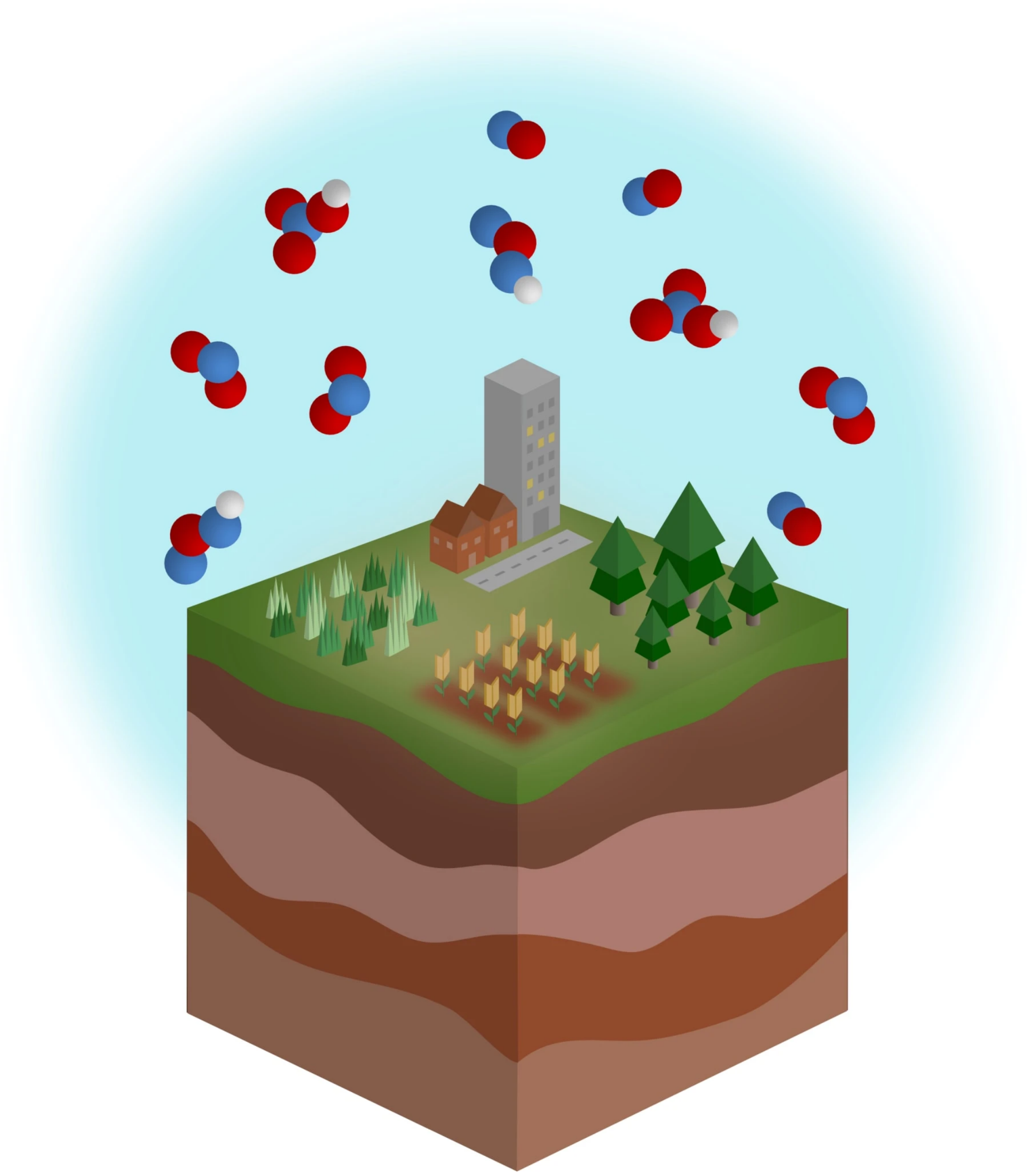
- Determination of large scale heterogeneity.

- Taking into account a comprehensive set of land-use types, human influence, and seasonality.

- Baseline for hypothesis generation.

- Highlights critical importance of spatiotemporal varation in the study of soil-sourced NOy.

- Contributions to future environmental modeling and climate change predictions.



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References and further reading

(1) Purchase, M. L. *et al.* Spatiotemporal Variations of Soil Reactive Nitrogen Oxide Fluxes across the Anthropogenic Landscape. *Environ. Sci. Technol.* **2023.**

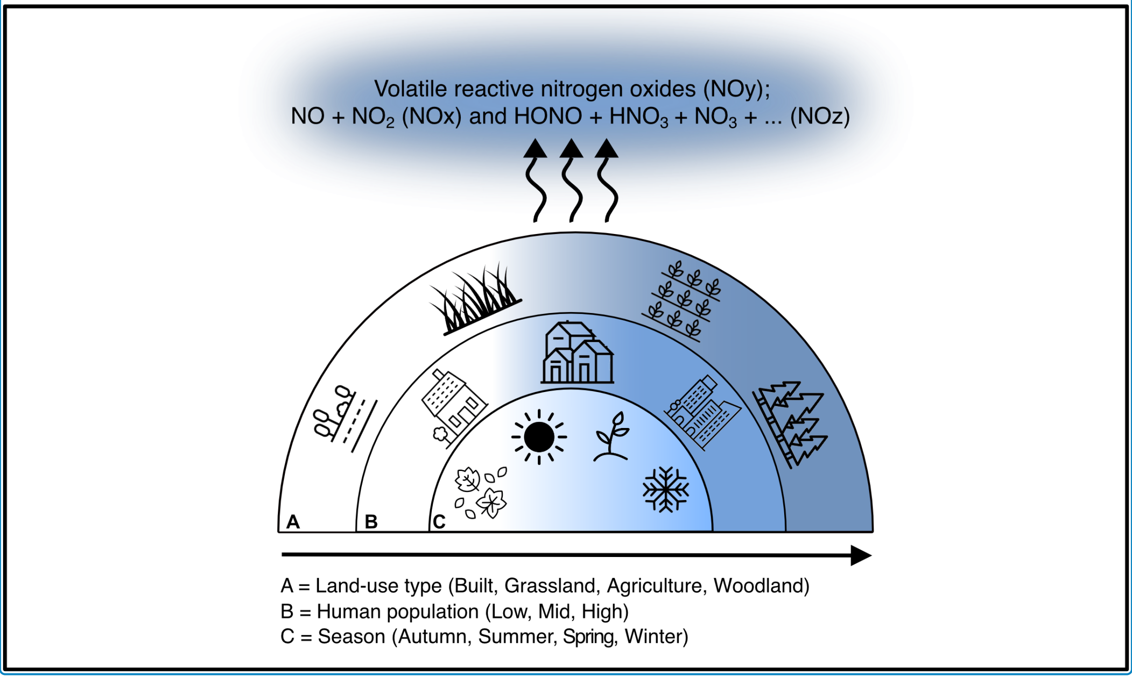
(2) Mushinski, R. M. *et al.* Microbial Mechanisms and Ecosystem Flux Estimation for Aerobic NO_y Emissions from Deciduous Forest Soils. *Proc Natl Acad Sci USA* **2019.**

(3) Mushinski, R. M. et al. Nitrogen Cycling Microbiomes Are Structured by Plant Mycorrhizal Associations with Consequences for Nitrogen Oxide Fluxes in Forests. *Glob. Change Biol.* **2021.**

TRANSCRIPT

ABSTRACT

Volatile reactive nitrogen oxides (NOy) are significant atmospheric pollutants, including NO_x (nitric oxide [NO] + nitrogen dioxide [NO_2]), and NOz (nitrous acid [HONO] + nitric acid [HNO_3] + nitrogen trioxide [NO_3] + ...). NOy species are products of nitrogen (N) cycle processes such as nitrification and denitrification. Biogenic sources, including soil, account for over 50% of natural NOy emissions to the atmosphere, yet emissions from soils are generally not included in atmospheric models due to a lack of mechanistic data. This work is a unique investigation of NOy fluxes on a landscape scale, taking a comprehensive set of land-use types, human influence, and seasonality into account to determine large-scale heterogeneity to provide a basis for future modelling and hypothesis generation. By coupling 16S rRNA amplicon sequencing and quantitative PCR, we have linked significant differences in functional potential and activity of nitrifying and denitrifying soil microbes across a gradient of urbanisation and land-use to NOy emissions from soil. We have assessed soil physicochemical properties characteristic of different land-use types, and as a result of anthropogenic influence. Further, we have identified the response of soil NOy emissions from varying land-use types to N deposition and found soils subject to more human influence to be less microbially active despite increased available N, potentially as a result of poor soil health from anthropogenic pollution. Structural equation modelling suggests human influence on soils to be a more significant effector of soil NOy emissions than land-use type. Results show significant seasonal variation of rates of N cycle processes and reactive N fluxes, demonstrating a need for temporal scale to be considered in future investigations.



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