

The NO₂ Flux Conundrum

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Striking progress has recently been made in understanding the central role of nitrogen oxide radicals, NO_x, in atmospheric processes. NO_x is implicated in the formation of acid rain, tropospheric ozone (the principal toxic component of smog and a greenhouse gas), and the hydroxyl radical (the main atmospheric oxidant responsible for the destruction of many pollutants). Atmospheric models have had some success at reproducing regional and continental acid deposition patterns, ozone profiles, and hydroxyl radical concentrations on the basis of estimated NO_x emissions (1-3). However, atmospheric and biological studies have yielded seriously incompatible results regarding the role of vegetation as a sink or source of NO_x. This is an important problem because we must understand NO_x emission processes to be able to predict future environmental impacts (4-6).

The major known sources of NO_x are fossil fuel combustion, biomass burning, microbial activity in soils, and lightning. Globally, these sources produce a total of 30 to 50 Tg of N year⁻¹, of which microbes in soils contribute 5 to 10 Tg year⁻¹. The vast majority of NO_x is released as nitric oxide, NO, which converts to nitrogen dioxide, NO₂, within minutes by reaction with ozone and peroxy radicals. NO₂ is recycled to NO by photolysis. This cycle is at the heart of tropospheric ozone formation. Typical NO/NO₂ concentration ratios in surface air are 0.2 to 0.5 in the daytime and zero at night when no NO₂ photolysis takes place. Over time scales of hours to days, NO_x is converted to nitric acid and nitrates, which are removed by rain and dry deposition and contribute to acidification and excess nutrients in sensitive ecosystems.

NO_x is also removed directly from the air through uptake of NO₂ by foliage. This process extracts NO_x from the atmosphere and also removes soil-derived NO_x from

the air before it can be exported to the atmosphere. The efficiency of the latter process is crucial for determining the NO_x concentration above landscapes dominated by biological activity. A quantitative



analysis of this effect was made by Jacob and coworkers (7, 8) using data from an Amazonian forest site during the wet season. The authors modeled observed NO_x concentrations in the canopy air with a one-dimensional atmospheric transport and chemistry model constrained by measured NO soil emission fluxes and estimated that only 25% of the NO_x emitted by soils is ventilated to the atmosphere. Globally, the fraction of soil-derived NO_x ventilated out of canopies has been estimated at 50 to 80% (9, 10) by extrapolating Jacob and coworkers' results to canopies of different leaf area indices.

The kinetics of NO₂ uptake by plants have been studied by biologists interested in NO₂ exchange mechanisms and the impact of NO₂ on plant function. In these bottom-up studies, leaf-level exchange of NO₂ is measured across a range of concentrations, and a "compensation point" is calculated assuming first-order uptake kinetics. At ambient concentrations below the compensation point, the plant canopy is a net source of NO₂ to the atmosphere, whereas at concentrations above this point it acts as a net sink. Most studies of leaf-level NO₂ exchange have shown compensation points between 1 and 3 parts per billion by volume (ppbv) (11-15). These results contradict those of Jacob and coworkers (7, 8), who found that at NO₂ concentrations as low as 0.2 to 0.4 ppbv in the canopy air, rapid net uptake of NO₂ by the leaves was needed to reconcile the meas-

ured NO soil emission fluxes with the NO concentrations measured in the canopy air. Because of low sensitivity of the analytical methods available for bottom-up studies, it has been difficult to obtain data at the low concentrations typical of ambient nonurban NO₂ concentrations (0.05 to 1 ppbv), and thus to confirm the assumption of first-order uptake kinetics and the existence of a compensation point.

The discrepancy between top-down and bottom-up approaches has important implications for our understanding of both atmospheric chemistry and plant function. Atmospheric NO₂ concentrations in nonurban surface air are typically much less than 1 ppbv, and the NO₂ compensation points determined in the bottom-up studies would thus imply that vegetation canopies are large NO₂ , with 24-hour average NO₂ emission fluxes on the order of 2×10^{10} molecules cm⁻² s⁻¹ (16). In comparison, soil emissions of NO are typically 10⁸ to 10¹¹ molecules cm⁻² s⁻¹ (9). Inclusion of such a large vegetation source in atmospheric chemistry models would require a hitherto unrecognized NO_x sink to balance the budget.

Resolving the differences in sign and magnitude of leaf-atmosphere NO₂ exchange will require both top-down and bottom-up approaches. Leaf-level measurements will have to be made with techniques that are sensitive at very low NO₂ concentrations. More studies of the key metabolites involved with NO₂ assimilation are needed. NO₂⁻, NO₃⁻, and chloroplast pH measurements during nitrate reduction may help explain the source of NO₂ within leaves. Combined with quantitative biochemical modeling (17), such measurements will improve the accuracy of NO₂ concentration-uptake curves and help determine the true value of the NO₂ compensation point—if such a point does indeed exist. As for top-down approaches, simultaneous measurements of NO fluxes from soils, NO₂ fluxes across leaf surfaces, NO_x fluxes above canopies, and NO_x concentrations in canopy air across a range of ambient NO₂ concentrations are necessary to test the models developed from controlled environment leaf-level studies. Without such measurements, the role of leaf-level exchange and the importance of plant physiological regulation for NO₂ exchange between the surface and the atmosphere cannot be quantified. This issue must be resolved to close the budget of this important atmospheric species.

References and Notes

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[JU2] Refs 4-6 are no longer cited. Please cite them somewhere, or remove them.

Page: 1

[JU3] Okay to say “leading to”? or better “contributing to”?

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[JU4] Not clear what was shown in (7) and what was shown in (8). Please avoid “see also ...”

Page: 1

[JU5] okay as shortened?

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[JU6] NO₂, or NO_x?

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[JU8] I think that this is what you are hinting at above (see JU7), but you are not stating it clearly. Please clarify at JU7

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[JU9] I have moved this here from the final paragraph; it seemed too specialized a point to close the article. Okay?

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