ANONYMOUS REFEREE REPORT

Eddy covariance measurements of nitrogen dioxide exchange at a grazed savanna grassland in South Africa

Hamilton et al. | EGUsphere preprint egusphere-2026-3066

Recommendation: MAJOR REVISIONS

1. Overall assessment

This manuscript presents a rare and potentially important multi-year dataset of ecosystem-scale nitrogen dioxide (NO_2) exchange over an African savanna-grassland system. The geographical setting, the use of a fast-response quantum cascade laser combined with eddy covariance, and the comparison with an inferential dry-deposition model are relevant to the scope of Biogeosciences. Direct flux measurements from African semi-arid ecosystems remain scarce, and the study could make a valuable contribution to regional nitrogen-cycle research and to the evaluation of deposition models.

The manuscript nevertheless has major methodological and interpretative weaknesses in its present form. The eddy-covariance processing chain is insufficiently documented to verify the validity and reproducibility of the NO_2 flux product. Important information is missing on time-lag determination, spectral attenuation, tube losses, coordinate rotation, detrending, dilution or density corrections, random uncertainty, detection limits, storage, advection, and chemical flux divergence. The central analyses are also affected by large and non-random data gaps, inconsistent record counts, uncertain treatment of extreme values, and conceptual problems in the calculation and interpretation of deposition velocity.

The paper has high potential, but publication should be considered only after a substantial reprocessing and reanalysis. The authors should first demonstrate the technical validity and uncertainty of the flux measurements, then reconstruct the temporal analyses using explicit coverage criteria, reformulate the observed-model comparison on a like-for-like basis, and moderate causal interpretations that are not directly tested. If the required high-frequency diagnostics and processing information are unavailable, the main quantitative conclusions cannot be independently verified.

2. Major observations

1. **Eddy-covariance processing and flux validity.** The complete NO_2 eddy-covariance processing chain must be described in a reproducible sequence. The authors should specify the software or code used and document despiking, detrending, coordinate rotation, time synchronisation, time-lag optimisation, covariance calculation, stationarity and turbulence tests, density or dilution corrections, and conversion to the reported mass flux. For the 20 m closed-path inlet, the manuscript must report residence time, Reynolds number, analyser response time, inlet heating, pressure control, filter maintenance, wall-loss tests, cospectra or ogives, high-frequency attenuation corrections, instrument calibration, precision, drift, water-vapour interference, detection limits, and random flux uncertainty.
2. **Reactive chemistry, storage, and advection.** A positive NO_2 covariance at the measurement height represents apparent ecosystem-scale net NO_2 exchange; it does not directly prove biological NO_2 emission by soil or vegetation. The interpretation must account for NO-NO_2-O_3 chemistry, photolysis, turbulent transport, entrainment, storage below the measurement height, and horizontal or vertical advection. Available NO, O_3, radiation, turbulence, wind-sector, fire, plume, and boundary-layer information should be analysed. Biological mechanisms should be presented as hypotheses unless they are quantitatively demonstrated.
3. **Data accounting and temporal representativeness.** The difference between 34,239 final valid half-hourly records and the 21,681 observations used in the analysis must be explained. The authors should provide a transparent data-flow diagram and observation counts by year, month, season, hour, flux sign, and quality-control step. Minimum coverage criteria are required for monthly, seasonal, annual, and diurnal statistics.

Periods with inadequate coverage should be excluded from interpretation, and interannual 'trends' should be described as differences unless a formal trend analysis is performed.

4. **Flux-sign classification and extreme events.** The classification of every positive flux as emission and every negative flux as deposition is not defensible without a measurement-uncertainty threshold. The authors should define a minimum detectable flux or signal-to-noise criterion and quantify how many observations are statistically distinguishable from zero. Extreme fluxes and deposition-velocity values must be checked against raw spectra, lag peaks, analyser diagnostics, stationarity, concentration, precipitation, wind direction, and neighbouring records. Unverified extremes should be removed from the scientific interpretation.

5. **Definition and calculation of deposition velocity.** The exact equation, sign convention, concentration basis, concentration threshold, and uncertainty propagation used to calculate deposition velocity must be provided. A ratio calculated only for downward fluxes is a sign-censored conditional quantity and is not directly equivalent to the deposition velocity of a unidirectional resistance model. Because the manuscript also invokes a non-zero compensation point, the authors should reconsider whether half-hourly observed deposition velocities are physically meaningful for this bidirectional and chemically reactive exchange system.

6. **Observed-model comparison.** The inferential model must be fully described, including code or version, equations, resistance parameterisations, meteorological forcing, temporal resolution, land-cover properties, canopy height, LAI or NDVI treatment, and surface wetness assumptions. Model estimates and measurements should be compared at identical timestamps. The post hoc exclusion of values above the 90th percentile should be avoided or rigorously justified. Robust metrics such as median bias, mean bias, MAE, RMSE, correlation, and normalised bias should be reported with confidence intervals that account for temporal dependence.

7. **Compensation-point analysis.** The ecosystem compensation-point analysis requires stronger statistical support. The authors should report the number of observations per concentration bin, regression weighting, slope significance, confidence-interval method, and sensitivity to bin width and environmental filters. Temporally coherent block bootstrapping is recommended. The result should be called the x-intercept of the fitted relationship, not a zero-intercept. Given the overlapping wet- and dry-season confidence intervals, seasonal differentiation should not be claimed unless it remains robust after sensitivity testing and exclusion of extreme events.

8. **Rainfall analysis and causal interpretation.** Rainfall totals calculated only during valid flux intervals are incomplete and must not be presented as annual or hydrological-year totals. The complete continuous precipitation record should be used independently of flux data. An event-based analysis should compare verified rainfall events with pre-event and post-event fluxes using explicit time windows and adequate sample sizes. Claims that rainfall directly caused NO_2 pulses, including a Birch-effect interpretation, should be replaced by cautious associations unless supported by this analysis.

9. **Footprint heterogeneity and external influences.** A fixed footprint radius is insufficient for a heterogeneous site. Dynamic footprints should be calculated or reconstructed for retained observations and summarised by stability, season, and wind sector. The influence of cropland, the access road, livestock grazing, fire, local activities, and regional plumes should be screened or analysed separately. Grazing intensity and timing should be reported. The back-trajectory analysis also requires a complete methods description or should be simplified and moved to the Supplement.

10. **Statistical methods and uncertainty framework.** A dedicated statistical-methods subsection is required. It should identify each test, null hypothesis, sample unit, effective sample size, treatment of autocorrelation, multiple-testing correction, effect size, and confidence interval. Because the distributions are strongly skewed and temporally dependent, robust or non-parametric methods and block bootstrapping are preferable. Uncertainty should be reported around all central estimates.

11. **Internal consistency and causal overstatement.** The abstract, Results, Discussion, and Conclusions contain contradictions concerning seasonal differences, wet- and dry-season definitions, means versus medians, figure titles, cross-references, and numerical values. These inconsistencies must be systematically corrected.

Causal expressions such as 'confirms', 'direct consequence', 'thermal venting', 'mechanically driven', and 'fundamental shift' should be used only for mechanisms that are explicitly tested.

12. **Data and code availability.** The statement that data are available upon request is insufficient for a study based on a unique long-term dataset and a complex processing chain. A FAIR-aligned repository with a persistent identifier should contain the half-hourly fluxes before and after quality control, concentration and meteorological data, quality flags, lag and spectral diagnostics, uncertainty estimates, footprint calculations, model inputs and outputs at matching timestamps, and scripts reproducing all analyses, tables, and figures. Any restrictions on raw high-frequency data should be clearly explained.

13. **Manuscript organisation and presentation.** After reanalysis, the manuscript should be shortened and reorganised. Repetition between monthly, seasonal, and diurnal descriptions should be reduced; observations should be clearly separated from interpretation; common axis scales should be used where comparisons are intended; sample sizes should be shown; and secondary full-period or monthly diagnostics should be transferred to the Supplement. The main text should focus on a limited number of robust results.

3. Minor observations

1. Use the spelling "savanna" consistently, clarify whether the site is a savanna–grassland ecotone, and use "semi-arid" rather than alternating with "arid".

2. Correct the definition of gaseous dry deposition. It should refer to non-precipitation transfer to surfaces through turbulent transport, molecular diffusion, and surface uptake, rather than gravitational settling of particles.

3. Distinguish NO_2 from the broader term NO_x throughout the Introduction and Discussion because NO and NO_2 have different chemistry and surface-exchange behaviour.

4. State the study objectives and hypotheses explicitly at the end of the Introduction and avoid over-emphasising the compensation point relative to the other analyses.

5. List the supporting measurements actually used, improve the readability of Figure 1, describe the back-trajectory method, and consider adding a site photograph and land-cover map.

6. Present the four-season and wet/dry-season classifications together and apply the same definitions consistently throughout the manuscript.

7. Provide the exact QCL manufacturer and model, optical and sampling-cell specifications, pressure, path length, response time, detection limit, calibration gases, and measurement uncertainty. Complete the unfinished sentence describing the climate-controlled enclosure.

8. Use consistent SI formatting, including m s^{-1}, and explain the choice of the fixed friction-velocity threshold of 0.2 m s^{-1} with a sensitivity analysis.

9. Define every symbol and unit in the deposition-velocity equation, distinguish ppb from mass concentration, and state whether the flux represents mass of NO_2 or mass of nitrogen.

10. Include the Appendix referred to for ancillary measurements or remove the corresponding reference.

11. Explain why the post-processing and final-valid-record rows in Table 1 are identical and report yearly recovery rates.

12. Correct Figure 2: flux cannot be expressed in ppb; clarify the H_2O variable, negative values, axes, units, regression equation, intercept, and outlier treatment.

13. Expand the inferential-model methods to identify meteorological datasets, temporal aggregation, MODIS product and version, spatial resolution, quality filtering, LAI processing, vegetation height, and land-use parameters.

14. Do not call the flux-synchronised meteorological subset a climatology. Report the correlation method, sample size, and treatment of autocorrelation.

15. Improve Figures 3 and 4 by using readable axes, the complete precipitation record, appropriate labels, and a representative event period in the main text while moving the full time series to the Supplement.

16. Reconcile N = 21,681 with Table 1, report uncertainty on the mean and median net flux, avoid declaring a net source until sampling bias is addressed, and exclude months with extremely small sample sizes such as N = 12.

17. Correct the dry-season deposition percentage and avoid annual means or strong interannual interpretation for years with very low or seasonally incomplete coverage.

18. State consistently whether diurnal curves show means or medians, use comparable y-axis ranges, identify local time or UTC, and remove or reframe speculative claims about thermal expansion or advective expulsion of soil gases.

19. Revise the comparison with Brümmer et al. because that study concerned total reactive nitrogen exchange, define NEE at first use, and use "separated by sign" rather than "partitioned".

20. Verify all flux ranges and deposition-velocity values, correct the likely decimal error in the 90th-percentile threshold, and replace the contradictory statement "not statistically significant ($p < 0.05$)" with the correct test result and exact p-value.

21. Correct Figure 10, use "x-intercept" for the compensation point, fix typographical errors, remove the reference to the non-existent Section 3.3.3, and correct the period shown in Figure 12 while adding sample sizes for each bin.

22. Rewrite the Conclusions after reanalysis, explicitly acknowledge fragmented coverage and measurement uncertainty, replace "available upon request" with a repository statement, disambiguate repeated author initials, and standardise references, author names, DOIs, subscripts, symbols, dashes, and English usage.

Final recommendation. Major revisions. The manuscript addresses an important scientific data gap and retains high publication potential. Reconsideration should depend on a demonstrated validation of the eddy-covariance flux product and a complete reanalysis of the source/sink behaviour, deposition velocity, compensation point, rainfall relationships, and model comparison.