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Deriving Cropland N₂O Emissions from Space-Based NO₂ Observations

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Abstract: Croplands are the largest anthropogenic source of nitrous oxide (N₂O), a potent greenhouse gas and ozone-depleting substance. Agricultural emissions produce small atmospheric signals with high spatiotemporal variability presenting a large observational challenge. If capable, space-based observations could characterize cropland N₂O emissions from farmlands across the world. No current satellite can resolve near-surface N₂O variations from cropland emissions. However, satellite observations of nitrogen dioxide (NO₂), a component of NO_x along with nitric oxide (NO), capture cropland emissions. NO, which quickly converts to NO₂ in the atmosphere, and N₂O are co-emitted from soils. Both gases are produced by microbial soil processes and are emitted in large amounts as a result of excess nitrogen from applied fertilizer. Given their co-emission in croplands, we ask: Can satellite NO₂ observations be used to infer N₂O emissions? We examine coincident airborne N₂O and NO_x measurements downwind of California croplands to characterize N₂O:NO_x emission relationships from farms. We use these emission ratios to transform estimates of agricultural NO_x emissions derived from space-based TROPOMI NO₂ observations to N₂O emissions. We compare these estimates to independent ground and airborne studies in the US Corn Belt and Mississippi River Valley. Space-based estimates are broadly consistent with these ground and airborne studies, suggesting that satellite NO₂ observations can be used to infer cropland N₂O emissions. Further refinement of a NO₂ proxy approach for cropland N₂O emissions has the potential to expand observational capabilities to constrain regional and global cropland N₂O emissions and inform process models.

1 Introduction:

Nitrous oxide (N₂O) is a potent greenhouse gas and ozone-depleting substance with sizable anthropogenic emissions. In a 100-year time frame, N₂O has a global warming potential 298 times that of carbon dioxide (Butterbach-Bahl et al., 2013; Ravishankara et al., 2009). With a long atmospheric lifetime (over 100 years) and no tropospheric sink, N₂O emitted from the surface travels to the stratosphere where it can react with excited oxygen atoms to produce reactive nitrogen oxide radicals that deplete stratospheric ozone. N₂O is now the largest contributor to stratospheric ozone depletion of actively emitted anthropogenic gases (Ravishankara et al., 2009). Since the 1700's the atmospheric concentration of N₂O has increased by over 60 parts per billion (ppb) (Tian et al., 2024), with an accelerating rate in recent years (Liang et al., 2022).

Agriculture is a dominant source of N₂O emissions, contributing 3.8 (2.5-5.8) Tg N₂O-N per year, or about 22% (15%-34%) of global emissions, from 2007 to 2016, with a 30% increase over the past four decades due to nitrogen fertilization (Tian et al., 2020). This trend is expected to accelerate due to the growing demand for food and resources that support agricultural industries as well as waste and industrial processes, highlighting the urgent need for mitigation efforts (Davidson and Kanter, 2014).

Much of what we know about agricultural N₂O emissions is the result of near-surface N₂O measurements from soil flux chambers. Observations from chamber systems range from ~10 samples per day (automatic chambers) (Rowlings et al., 2015; Sihi et al., 2020) to as infrequently as daily or monthly scales (manual chambers) (Griffis et al., 2013). The small spatial extent of chamber measurements, along with the availability of coincident auxiliary data (e.g., soil moisture, N application rates), permits robust mechanistic analyses of soil N₂O emissions. However, given the spatial heterogeneity of N₂O emissions (Lawrence et al., 2021), the small spatial resolution (~1m²) of chamber measurements becomes a limitation when assessing emissions at larger spatial scales. Eddy covariance methods can

45 be used to study N₂O emissions at the field scale, with sensitivity to surface emissions from upwind soils of ~10 to 1000 m² (di Marco et al., 2005). Observational constraints at much larger scales are possible with tall (~100's of meters in height) tower measurements of N₂O, which are interpreted with atmospheric transport and inverse modeling to infer N₂O emissions. This provides emissions information integrated over several hundred kilometers at a monthly temporal resolution (Chen et al., 2016; Griffis et al., 2013; Nevison et al., 2018, 2023).

50 More recently, airborne sampling approaches have demonstrated the potential to bridge the scale gap from flux chambers/eddy-flux to tall-towers. Depending on their flight altitude, airborne measurements can resolve N₂O emissions at the farm (~1-2 km) scale (Gvakharia et al., 2020) while sampling an area of several hundred kilometers (Dacic et al., 2024; Desjardins et al., 2015; Eckl et al., 2021; Gvakharia et al., 2020; Herrera et al., 2021; Jimenez et al., 2005; Kort et al., 2008; Xiang et al., 2013). The limitation of airborne observations is that they capture short time windows and sample targeted regions as part of campaigns such as CalNex (2010) (Xiang et al., 2013), FEAST (2017) (Gvakharia et al., 2020) and MAIZE (2021 & 2022) (Dacic et al., 2024; Kort et al., 2022, 2024a, 2024b).

Current observational methods to constrain N₂O emissions for the study of process-level emission controls or mitigation strategies are currently limited to the targeted ground and airborne approaches detailed above. A remote-sensing, space-based solution would have the potential to assess agricultural N₂O emissions at key spatiotemporal scales and broaden the spatial extent of studies beyond those limited by targeted ground and airborne measurements. However, presently, we cannot directly measure surface-level N₂O signals from cropland emissions with a space-based platform. A promising opportunity, however, lies in the widespread remote sensing of nitrogen dioxide (NO₂). Nitric oxide (NO) is co-emitted with N₂O from agricultural soils (Davidson et al., 2000), and the NO is largely oxidized to NO₂ within seconds to minutes after emission (Jacob, 1999). Given that N₂O and NO are co-emitted and their emission patterns are driven by similar variables (e.g., fertilizer application) (Harrison et al., 1995; Sanhueza et al., 1990), variability in atmospheric NO₂ concentrations from agricultural soils may serve as a useful proxy for corresponding N₂O emissions. Space-based NO₂ observations track spatiotemporal variations in NO₂ in both urban (Acker et al., 2025; Adams et al., 2023; Goldberg et al., 2019a, b, 2021, 2024; Ialongo et al., 2020; Park et al., 2022) and agricultural (Ghude et al., 2010; Huber et al., 2020, 2024; Lin et al., 2023) areas, and have done so for decades (Gonzalez Abad et al., 2019). Beyond the existence of NO₂ instrumentation in space, the relatively short lifetime of NO₂ means emissions of NO₂ lead to large enhancements concentrated in the boundary layer, providing a large signal to observe. For N₂O, in contrast, emissions add only a very small enhancement over large background values (often less than 1ppb signals on background over 330ppb, Dacic et al., 2024), which presents an observational challenge.

75 In this work, we explore the potential of using space-based NO₂ observations as a proxy for agricultural N₂O emissions. We first discuss the driving mechanisms for N₂O and NO (NO₂) from managed croplands. We then use coincident airborne observations of NO and NO₂ (NO_x) and N₂O from the California Research at the Nexus of Air Quality and Climate Change (CalNex) campaign conducted in California in 2010 to derive N₂O-to-NO_x emission ratios for large spatial regions commensurate with satellite remote sensing of NO₂. The aircraft sampling captures integrated emissions ratios that include heterogeneity of emissions in response to a number of driving process-level variables. We hypothesize that we can apply the observed emission ratio distribution to NO_x emissions derived from satellite NO₂ observations to obtain an estimate of N₂O emissions from space-based observations. This then enables observational analyses that cover large regions of the world and can track changes over time. We evaluate this possibility for the corn belt and the Mississippi River Valley in the USA.

85 2 Emissions of N₂O and NO from Managed Croplands

N₂O and NO emissions in agricultural soils result from the microbial processes of nitrification and denitrification, with N₂O predominating during denitrification (Baggs, 2008; Chen et al., 1995; Müller et al., 2003) and NO during nitrification (Skiba et al., 1993). Soil moisture influences these processes, where high water-filled pore space (WFPS) favors denitrification and low WFPS favors nitrification. This moisture dependency contributes to large emissions of N₂O and NO following rainfall events (Kim et al., 2012; Scholes et al., 1997), and poorly drained soils

are known to emit more N₂O than well-drained soils, which is an important management consideration for N₂O reduction strategies (Lawrence et al., 2021). Drier soils favor **lower** N₂O:NO emission ratios, often close to or **less** than unity, whereas wet soils can have **higher** emission ratios (Anderson and Levine, 1987; Davidson, 1992; Johansson and Sanhueza, 1988; Lipschultz et al., 1981; Tortoso and Hutchinson, 1990). Crop type also influences the N₂O:NO ratio (Anderson and Levine, 1987).

Fertilizer application is the most important common driver of NO and N₂O emissions, and fertilized soils have higher emissions of both trace gases (Harrison et al., 1995; Liu et al., 2017; Sanhueza et al., 1990; Shepherd et al., 1991). In the atmosphere, NO rapidly converts to NO₂, which together is referred to a NO_x (NO + NO₂). The accumulation of fertilizer is hypothesized to drive large post-rainfall emissions of N₂O (Cardenas et al., 1993; Johansson, 1984; Johansson and Sanhueza, 1988; Levine et al., 1996) and NO_x (Ghude et al., 2010; Jaeglé et al., 2004; Oikawa et al., 2015; Scholes et al., 1997; Smith et al., 1997).

Given the link between fertilizer application and emissions of NO and N₂O, we hypothesize that spatiotemporal patterns in NO_x emissions from croplands may be a useful proxy to estimate agricultural N₂O emissions. Over extended spatial and temporal scales that incorporate a variety of soil conditions and crop types, the variability in N₂O:NO emissions should be reduced compared to shorter, more localized observations, such as those made in chamber studies. This integrating effect may increase the fidelity of using emissions ratios to derive N₂O emissions.

3 Deriving Emission Ratios from CalNex Airborne N₂O, NO, and NO₂ Observations

Satellite observations of NO₂ from TROPOMI or TEMPO, with ground pixel sizes in the range of 5.5x3.5 - 2x4.75 km, used to derive cropland NO_x emissions will be sensitive to the integrated emissions from entire farms and multi-farm conglomerates and counties (~250 km² (Merlos and Hijmans, 2020)). To characterize the cropland emission behavior at comparable spatial scales, we use airborne sampling of N₂O and NO_x to determine an emissions relationship between these gases downwind of agricultural fields. Very few airborne campaigns have been made with continuous, high-accuracy, high-precision measurements of N₂O and NO_x (NO + NO₂) in agricultural regions. For the analysis here we use observations from one of the few campaigns that collected such measurements, the CalNex campaign in 2010 (Fig. 1A), which sampled the San Joaquin and Sacramento Valleys during 6 flights between May 7 and June 18, 2010 (Data available at: <https://esl.noaa.gov/projects/calnex/>). In-flight instrumentation included the Harvard/National Center for Atmospheric Research's (NCAR) Dual Quantum Cascade Laser Spectrometer for measurement of N₂O (Jimenez et al., 2005; Kort et al., 2011), and a chemiluminescence sensor for NO and NO₂ (Pollack et al., 2010; Ryerson et al., 1999, 2001, 2003). During CalNex, measurements of these gases were reported at a 1s rate, and we applied an additional 5-second centered rolling average. In this study, we isolate cropland regions by restricting our analysis to locations >0.04° (~3.7 - 4.4 km) from regions with emissions in the top 1% of the National Emissions Inventory (NEI) (Strum et al., 2017), and to periods when the aircraft was below 500m elevation.

Literature from chamber studies often **report the emission relationships between NO and N₂O**. Chamber measurements of soil emissions typically directly observe NO prior to substantial conversion to NO₂. In this work we determine N₂O:NO_x molecular ratios from the aircraft, in order to provide a factor that can be multiplied directly to a soil NO_x emissions estimate to generate N₂O emissions. The soil NO_x estimate could be generated from a range of different approaches, including from space-based NO₂ observations as we demonstrate here. While soil emissions of NO_x are predominantly NO, when observed from aircraft or satellite downwind of emissions, the majority of this NO has been converted to NO₂ (Goldberg et al., 2024 A; Goldberg et al., 2024 B; Kimbrough et al., 2017; Pilegaard et al., 2013; Seinfeld and Pandis, 2012; Williams et al., 1992).

For the CalNex observations, we consider both the NO₂ and NO measurements to capture the total quantity of NO_x emitted from the agricultural fields. We note the majority of the NO emitted has converted to NO₂ by the time the air has reached the aircraft, so if the subsequent analysis was performed only with NO₂, the results are very similar.

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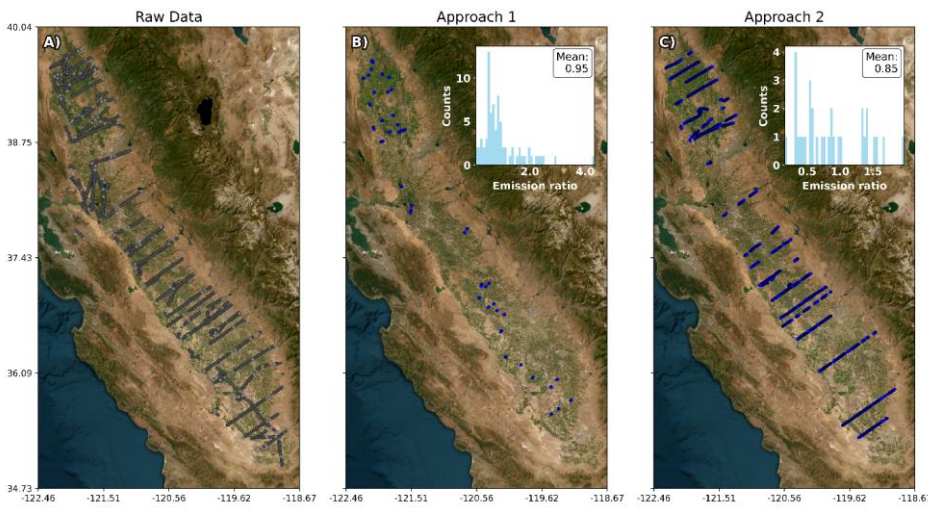
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We apply two methods to characterize $N_2O:NO_x$ emission relationships from the CalNex airborne dataset. Figure 1B and 1C show histograms of derived emission ratios corresponding to each approach overlaid over flight maps with the location of data from those approaches. We use these emission ratios to characterize the heterogeneity in the empirical relationship between N_2O and NO_x at the farm to multi-farm scale. Below, we briefly outline each approach.

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Figure 1: Flight maps corresponding to data remaining after filtering steps in A) the raw CalNex dataset filtered for data within the agricultural fields and away from high NO_2 -emission areas, B) in *approach 1* and C) in *approach 2*. A histogram showing the distribution of **binned** molecular emission ratios determined in each respective approach is overlaid upon the map. Satellite imagery credit: Esri.

Approach 1 seeks to isolate concentration enhancement signals from cropland emissions within ~ 10 km of the aircraft to determine aircraft-derived $N_2O:NO_x$ emission relationships. We isolate concentration enhancements from near-field cropland emissions by filtering for distinct peaks in N_2O concentration and accounting for the chemical loss of NO_2 . A similar method has been performed to isolate plumes from nearby natural gas flares in the Bakken (Gvakharia et al., 2017). First, we determine N_2O , NO and NO_2 enhancements as the concentration above the 5th percentile of a rolling, centered, one-minute window for every data point from the CalNex airborne NO , NO_2 and N_2O dataset. This background approach means enhancements only emerge when they correspond to a plume of this width or narrower. Using a gaussian plume model, a source of this width would be ~ 2 - 4 km in distance upwind of the aircraft assuming moderate instability. Sources further than this will impact the background but not the enhancement. In this way, distant (20-100km) pollution sources do not impact our analysis. We then isolate cases that are separated by at least 5 seconds in time ($\sim 500+$ meters in space) where N_2O concentration is enhanced and NO , NO_2 , and N_2O 's concentration perturbations exceed instrument noise. We require 8 or more observations where the range from minimum to maximum N_2O concentration enhancement exceeds 0.09 ppb. Cases are removed if their slopes are below zero, as these do not imply co-emission.

We account for photochemical loss of NO_2 by estimating the distance from the source to the observed N_2O enhancement. Assuming the width of an observed enhancement represents a plume's width, we estimate the transport distance from the plume's origin using rural dispersion parameters from Zannetti et al., (2013). We assume

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175 a moderately unstable atmosphere during CalNex. Based on daily wind conditions, we estimate the transport time
relative to the average NO₂ lifetime and add this NO₂ lost due to photochemistry back to the observed NO₂
enhancement, creating a chemically corrected NO₂ enhancement. We then add the observed NO enhancement, thus
generating a NO_x enhancement corresponding to emissions from the agricultural field. For each isolated plume, we
180 use the observed N₂O enhancement and chemically corrected NO_x enhancement to calculate a N₂O:NO_x emission
ratio using type-II ranged major axis regression. For each plume, the slope represents a unique emission ratio.

The average chemistry corrected enhancement emission ratio (referred to as the emission ratio from here forward) is
0.95 ppb N₂O / ppb NO_x, a slightly lower value than the ratio (1.36 ppb N₂O / ppb NO_x) if chemical loss is not
accounted for. This adjustment is small compared to the variance we see in the ratio. The final dataset using this
185 approach results in 76 individual plumes observed in the nearfield of croplands to derive the N₂O:NO_x emission
ratio, as shown in Fig. 1B. The resultant molecular emissions ratio distribution will encompass variation due to a
number of variable drivers of emissions in the upwind region (crop type, fertilizer, soil moisture, etc...).

Approach 2 incorporates the airborne measurements at a broader spatial scale. With this method, we isolate
individual flight legs, or portions of the aircraft transects, that are perpendicular to daily wind direction and
downwind of agricultural fields. We then characterize each flight leg's N₂O:NO_x relationship and treat it as a unique
190 concentration enhancement ratio. Similar to *approach 1*, we derive the background by defining the enhancement as
the concentration greater than the 5th percentile of a rolling centered one-minute window around every data point.

Approach 2, rather than isolating small-scale cropland emissions as in *approach 1*, derives an integrated
concentration enhancement relationship of N₂O to NO_x across a portion of the cropland. We assume impacts from
chemical loss are averaged out across flight legs and therefore do not directly correct for the chemical loss of NO₂.
195 Therefore, for *approach 2*, we assume enhancement ratios are equivalent to emission ratios. *Approach 2* yields an
average molecular emissions ratio of 0.85, determined using type-II ranged major axis regression on the N₂O and
NO_x concentration enhancements. Flight legs considered in this method are shown in Fig. 1C. This approach
includes more observational data than *approach 1*, integrating larger domains into the determined emissions ratio.

As seen in Fig. 1, we obtain similar mean N₂O:NO_x ratios from each method, demonstrating that the relationship is
robust to methodological differences and assumptions. The distributions of the derived N₂O:NO_x values for each
200 approach are also comparable. The Kruskal-Wallis test performed between these two distributions yields a p-value
of 0.7827, suggesting no significant difference in median or distribution, and the Welch's t-test, compared between
them, shows there is no significant difference between the emission ratios. Emission ratios range between 0.038 and

205 4.34 ppb N₂O / ppb NO_x for *approach 1* and 0.16 and 1.97 ppb N₂O / ppb NO_x for *approach 2*, reflecting expected
heterogeneity in N₂O:NO_x ratio over agricultural lands, and demonstrating that increasing the spatial scale
aggregated to create these ratios dampens variability. The N₂O:NO_x values we observe are in line with N₂O:NO_x
values in literature from soil-chamber measurements, which report highly heterogeneous emission ratios typically
ranging from 0.1-10, but that in rare cases can be as high as 100. (Johansson and Sanhueza, 1988; Tortoso and
210 Hutchinson, 1990). This variation occurs as a function of factors such as fertilizer application, crop-type, and other
management and environmental factors (Anderson and Levine, 1987; Davidson, 1992; Johansson and Sanhueza,
1988; Lipschultz et al., 1981). As expected with the larger spatial scale of our airborne approach, integrating over
variable soil conditions and crop types, our ratios show less variability than prior soil chamber studies and decrease
in variability as more observations are aggregated (from *approach 1* to *approach 2*). More coincident observations
215 of N₂O and NO_x downwind of a variety of agricultural domains under varied conditions could lead to refinement
and improvement on the approach outlined here. In the following sections, we use emission ratios derived from
approach 2, though there is little sensitivity to this choice.

4 Deriving N₂O from Satellite NO₂ Observations:

With N₂O:NO_x emissions ratios derived from the aircraft measurements, N₂O emissions can be determined from
space if soil NO_x emissions are calculated from space-based NO₂ observations. Many different methods can be
220 applied to derive NO_x emissions estimates from satellite NO₂ observations. For instance, Huber et al., (2020) applied

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a box model to estimate NO_x emissions from TROPOMI-observed NO_2 enhancements within the Mississippi River Valley, Ghude et al., (2010) inferred top-down soil NO_x emissions from OMI by mass balance, and Lin et al., (2023) estimated soil NO_x emissions from TROPOMI based on seasonal variation.

235 Here, we use a simple chemical box model and TROPOMI NO_2 observations to demonstrate quantification of agricultural N_2O using space-based NO_2 observations. We focus our analysis on three regions (Figure 2) in the USA where independent ground and airborne measurement campaigns have previously been conducted to determine N_2O emissions, providing a bases for direct comparison with this new approach. These independent studies of N_2O emissions, conducted in different locations and with different methods, provides an opportunity for evaluation of our emissions ratio method. This evaluation is a strong challenge for this method, as the emissions ratios are determined from aircraft data collected over California in 2010, and crop-type, management practice, soil moisture, and other driving variables can be quite different in these central US regions.

245 In this work, we use TROPOMI Version 02.04.00 (S5P_L2__NO2__HiR_2) NO_2 retrievals (KNMI). TROPOMI observations are filtered for a quality assurance value greater than or equal to 0.75, indicating high-quality data per the operational retrieval (Van Geffen et al., 2020). We use these TROPOMI NO_2 observations in a chemical box model to determine agricultural NO_x emissions in the Mississippi River Valley, Nebraska, and Iowa, employing a similar data-model approach as previously outlined in Huber et al., (2020). The chemical box model defined by equation 1:

$$E_{\text{soil},\text{NO}_2} = \frac{U\Delta(\text{NO}_2\text{VCD})}{X} + \frac{V\Delta(\text{NO}_2\text{VCD})}{Y} + \frac{V_d(\text{NO}_2\text{VCD})}{Z_{\text{PBL}}} + \frac{\text{NO}_2\text{VCD}}{t} - E_{\text{NEI}}, \quad (1)$$

250 The first two terms in Eq. 1 captures advection, representing NO_2 advected into and out of a box model domain. Here, U represents the average zonal wind speed (m/s) across the box of interest and X is the distance of the east-to-west edge of the box model domain. V denotes meridional winds and Y denotes north-to-south edge distance along the box model domain. In this work, $\Delta(\text{NO}_2\text{VCD})$ denotes the mean TROPOMI NO_2 column enhancement above a background, here defined as the 5th percentile of NO_2 within the box. This enhancement is used as a proxy for the spatial gradient across the domain, where the background value is representative of the inflow into the box and the resulting enhancement is representative of the outflow. This is similar to approaches used in previous studies (Godłowska et al., 2023; Huber et al., 2020; Li et al., 2021). The third term denotes deposition, where V_d denotes the deposition velocity (m/s) from Yang et al., (2010) (Deposition velocity by month: DJF, 0.02 c/s; MAM, 0.16 cm/s; JJA, 0.29 cm/s; SON, 0.06 cm/s). NO_2VCD is the average NO_2 vertical column density in the box model domain and Z_{PBL} is the boundary layer height estimate over the box model domain. Similar to Huber et al., (2020), Z_{PBL} is set to 1000m over the course of the study. The fourth term represents chemical loss, where NO_2VCD again denotes the NO_2 vertical column density in the box model domain and “t” represents the lifetime of NO_x . The final term E_{NEI} denotes the average fossil fuel NO_x emissions in the box model domain from the 2014 NEI inventory (Strum et al., 2017), averaged monthly to eliminate noise. This model outputs an estimate of non-fossil fuel NO_x emissions for the box model domain.

265 Lifetime values used for the analyses were derived from Martin et al., (2003). In Huber et al., (2020) lifetimes of 3, 5, and 7 hours were used (also derived from Martin et al., (2003)) to constrain the influence of lifetime on the analysis. We opt to use a lifetime value of 3 hours for this main text, but variation in results due to these lifetime values of 5 (moderate) and 7 (slow) hours can be observed in supplemental figures 1 & 2. As was observed in Huber et al., (2020) lifetime has a large impact on NO_x emission estimates.

270 In this work, we analyze TROPOMI NO_2 retrievals on a daily scale. The size and location of the analysis domain vary depending upon the region of interest, but have a minimum size $0.75^\circ \times 0.75^\circ$ to be consistent with the domain size used in Huber et al. (2020). We additionally exclude TROPOMI overpasses from the study if they incorporate less than 30 TROPOMI NO_2 observations in our box model domain for the Lawrence et al., (2021) and Gvakharia et al., (2020) comparison, or less than 120 TROPOMI NO_2 observations for the larger Dacic et al., (2024) comparison region. Once NO_x emissions are derived using Equation 1, we multiply soil NO_x emissions ($E_{\text{soil},\text{NO}_x}$, units of

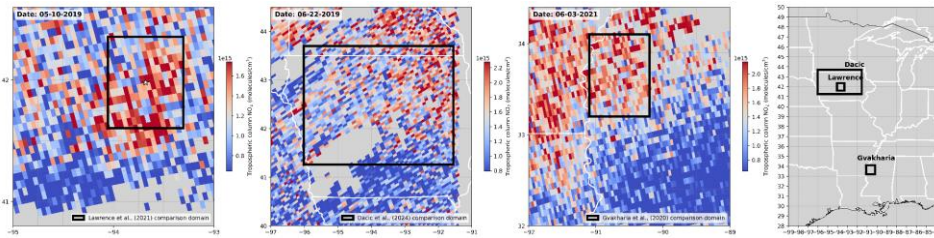
nmole/m²/sec), by the aircraft-derived N₂O:NO_x molecular emission ratio to obtain an estimate of N₂O flux, E_{soil,N_2O} , units of nmole/m²/sec (Equation 2).

$$E_{soil,N_2O} = (ER_{N_2O:NO_x})E_{soil,NO_x} \quad (2)$$

280 To incorporate the variability in the observationally derived emission ratio on estimated N₂O emissions in this analysis, we employ a Monte Carlo resampling approach where we propagate variation in the N₂O:NO_x emission ratio through to N₂O emissions. We iterate through the daily average values of TROPOMI-derived NO_x emissions and multiply each by the distribution of emission ratios shown in Fig. 1C to derive all possible N₂O emissions from the variation in N₂O:NO_x. We then randomly sample one of these N₂O realizations over 10,000 iterations to create a
285 distribution of TROPOMI NO₂-derived N₂O emissions. The 2.5th percentile and the 97.5th percentile define the 95% confidence interval, with the mean providing a central estimate. This confidence interval reflects uncertainty in the analysis reflecting the emission ratio derived in Section 3 and not absolute uncertainty in soil NO_x emissions. Since our focus in this work is evaluating the viability of the emissions ratio proxy approach, we focus on uncertainty of the N₂O:NO_x emission ratios and quantify its impact on resulting N₂O emission estimates. Depending
290 on what approach one takes to generate NO_x emissions estimates from space-based NO₂ observations, other uncertainty would be added. For the box model we use here as an illustrative example, we conduct a sensitivity analysis to lifetime and deposition velocity (model terms 3 & 4), shown in supplementary Fig. 1-4.

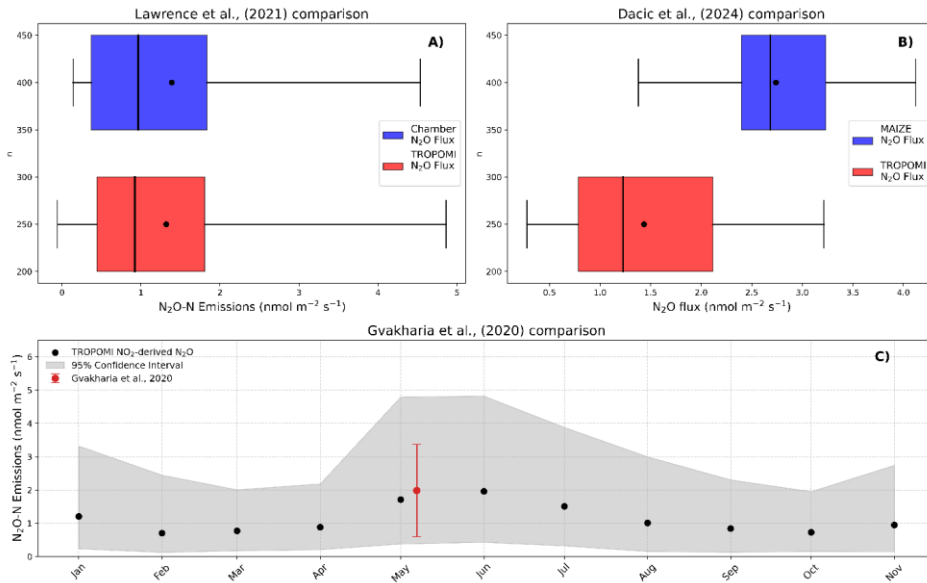
5 Comparison with Independent Estimates of N₂O

295 We compare our space-based N₂O emissions estimates [derived using California-observed N₂O:NO_x emission ratios](#) with N₂O emissions from independent studies. We first compare N₂O emissions derived from TROPOMI-NO₂ observations with those obtained from chamber measurements reported by Lawrence et al., (2021). The chamber measurements, conducted between February 2017 and October 2019 in Iowa crop fields, are compared only for the warm season (May-September) of 2018 and 2019 when TROPOMI was operational, and chamber data was available. The comparison domain spans -94.055 to -93.305 in longitude (0.75°) and 41.605 to 42.355 in latitude (0.75°). The box model domain lies to the north of Des Moines, Iowa, and is centered on the Ames, Iowa field site referenced in Lawrence et al., (2021)(41.98°N, 93.68°W), and is shown in Fig. 2A, with a star indicating the chamber location.



305 **Figure 2: TROPOMI tropospheric NO₂ columns and the box model domains used for comparison with A) Lawrence et al., 2021 with a star denoting the chamber location, B) Dacic et al., 2024, and C) Gvakharia et al., 2020. D) Each corresponding region shown on a map of the central US.**

We calculate the confidence interval for the Lawrence et al., (2021) chamber dataset by randomly sampling daily average values on days that we also have TROPOMI NO₂-derived N₂O estimates and calculating a 95th confidence interval. For the same observational time-window, we derive daily N₂O emission estimates for the box model
310 domain using the proxy-method described in Sect. 4. The distribution of chamber-N₂O emissions and its associated 95% confidence interval against the mean and 95% confidence interval for TROPOMI NO₂-derived N₂O flux are shown in Fig. 3A.



315 **Figure 3: Satellite derived estimates concurrence with independent studies. (A, top left) Box plots of the distribution of**
 320 **daily average N₂O flux derived from chamber observations detailed in Lawrence et al., 2021 and TROPOMI observations**
 325 **from that period. (B, top right) Box plots of N₂O flux observed by TROPOMI across the MAIZE campaign domain, and**
 330 **ensemble averages for coincident days of the MAIZE (2021-2022) campaign. (C, Bottom) TROPOMI-NO₂ derived N₂O**
 335 **flux (gray distribution) compared against the N₂O flux estimate from Gvakharia et al., (2020) (red band).**

320 The confidence interval for the mean chamber-derived N₂O flux largely overlaps with that of the TROPOMI NO₂-
 325 derived N₂O flux (Fig. 3A). The mean values differ by ~4.5% (~7.3 % using *approach 1*), with the chamber-derived
 330 flux averaging 1.38 (0.14, 4.53; 95% CI) nmol N₂O/m²/s and the TROPOMI-derived flux averaging 1.32 (-0.06,
 335 4.86; 95% CI) (1.48 (-0.06, 6.28; 95% CI) nmol N₂O/m²/s using *approach 1*). We evaluate the difference in these
 means with a nonparametric permutation test, which indicates the observed differences between population means
 are not significantly different. These are independent dataset and methods that operate on different scales. The
 relative agreement in mean values and the overlap in confidence intervals suggest that the TROPOMI-based
 approach provides a reasonable estimate of long-term chamber-derived mean N₂O flux in this study.

330 Next, we compare TROPOMI NO₂-derived N₂O fluxes with N₂O emissions derived from aircraft observations
 during the Measurements of Agriculture Illuminating farm-Zone Emissions of N₂O (MAIZE) 2021 and 2022
 335 campaigns (Dacic et al., 2024; Kort et al., 2022, 2024a, 2024b). These airborne campaigns measured N₂O
 concentrations over the Iowa croplands during May and June of both years. Observed N₂O concentrations were
 linked to the surface using an atmospheric transport model, and an ensemble of surface fluxes was derived using a
 Bayesian inversion framework. In this comparison, we use a larger analysis domain to match the area over which the
 MAIZE campaigns took place. For 5 flight days of the MAIZE campaign (2021-05-31, 2021-06-03, 2022-05-18,
 2022-05-20, and 2022-05-21), we produce a TROPOMI NO₂-derived N₂O average flux for the MAIZE domain (S:
 40.398; N: 43.399; W: -96.724; E: -90.044, Fig. 2B). We compare this with MAIZE daily ensemble averages. We
 then randomly sample the MAIZE daily flux ensembles using the previously described Monte Carlo resampling
 approach to obtain a 95% confidence interval for MAIZE N₂O flux. Figure 3B shows the comparison between
 airborne-informed MAIZE N₂O flux and N₂O flux we derive from TROPOMI NO₂ observations and our aircraft-
 derived emission ratios.

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340 While the mean TROPOMI-derived N₂O flux is within the 95% confidence interval of the MAIZE emissions, and
vice versa (Fig 3B), there is less notable agreement than in the comparison with the chamber emissions from
Lawrence et al., (2021) for a similar domain. There exist multiple possible reasons for the larger apparent
discrepancy. 1) The comparison is limited to only five days. 2) The MAIZE aircraft flights captured a heavy-tail
emissions distribution with small number of fields contributing substantially to total emissions. These high
345 emissions events might be missed by chamber observations, and the coarse scale of the satellite observations used
here might reduce sensitivity to small regions with high emissions, thus explaining the TROPOMI and chamber
relative agreement with both values lower than determined by flights in MAIZE. 3) It is also possible the
enhancement ratio approach used here is failing to capture the emissions ratio as well as desired for this place and
time. Still, the mean emissions rate determined from satellite is captured with in the airborne campaign 95%
350 confidence interval, and thus it appears this space-based proxy approach can provide a reasonable mean estimate for
this region with five days of observations.

Finally, we compare N₂O fluxes derived using the proposed space-based NO₂ proxy method to fluxes derived from
airborne mass balance estimates from Gvakharia et al., (2020) over the Mississippi River Valley. During the
Fertilizer Emissions Airborne Study (FEAST) in Spring 2017, Gvakharia et al., (2020) observed N₂O fluxes of 1.98
355 +/- 1.39 nmol N₂O-N/m²/s in May 2017, noting significant spatial variation. The TROPOMI instrument was not
operational until late 2018, so we do not have overlapping data to directly compare TROPOMI NO₂-derived N₂O
flux estimates with those from Gvakharia et al., (2020). Instead, we calculate emissions for a full calendar year for
2021 and compare these estimates with the May 2017 estimate from the FEAST data (see Fig. 2C and 3C). With the
space-based proxy approach, we observe seasonal variation ranging from 0.75 nmol N₂O-N/m²/s in March (0.17,
360 2.0; 95% CI) (0.83 nmol N₂O-N/m²/s using *approach 1*) to a peak of 1.96 in June (0.43, 4.8; 95% CI) (2.22 nmol
N₂O-N/m²/s using *approach 1*), and our spring estimate is in close agreement with the estimate from Gvakharia et
al., (2020) is shown in Fig. 3C. Specifically, we estimate 1.72 nmol N₂O-N/m²/s in May (0.38, 4.8; 95% CI) (14.3%
difference) (1.93 nmol N₂O-N/m²/s in May 2.4% difference using *approach 1*) using TROPOMI NO₂ observations
from 2021.

365 We find the TROPOMI NO₂-derived N₂O flux compares favorably with various independent measures of N₂O flux
and emissions from the corn belt (Dacic et al., 2024; Lawrence et al., 2021) and Mississippi River Valley
(Gvakharia et al., 2020). For two of the ~~comparisons~~, space-based estimates are within ~15% of these independently
obtained N₂O estimates, despite this testing capturing multiple regions and time-periods, and the airborne derived
emission ratios coming from observations in a completely different agricultural region. ~~The N₂O:NO_x ratios used
370 here were observed with aircraft over California croplands – very different from the rainfed agricultural regions in
the Midwest and southern USA. Previous studies have demonstrated strong spatiotemporal variation in emission
ratios in response to soil moisture (Anderson and Levine, 1987; Davidson, 1992; Johansson and Sanhueza, 1988;
Lipschultz et al., 1981; Tortoso and Hutchinson, 1990) and crop variety (Anderson and Levine, 1987) and suggests
in wetter regions N₂O:NO_x ratios would shift upward in general. If that pattern held at the scales observed here, one
375 would expect the satellite method to produce an underestimate of Midwest and southern USA emissions, which is
perhaps another explanation for the comparison between the satellite method and Dacic et al., (2024). The general
agreement of our proxy-based N₂O estimates with those from independent assessments of cropland N₂O emissions
demonstrates the potential of scaling satellite-based NO₂ observations with N₂O:NO_x emission ratios to capture
agricultural N₂O emissions, and that such an approach may provide a viable method to estimate N₂O emissions from
380 agricultural regions around the world, without necessarily needing location specific N₂O:NO_x emission ratios.
Further measurements of N₂O:NO_x emissions at commensurate spatial scales with satellite measurements across
different agricultural regions over time would be invaluable to further evaluate this method's validity to capture
emissions through potentially complex confounding spatial and temporal factors.~~

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6 Conclusion:

385 Constraining global emissions of N₂O is crucial to understanding its spatiotemporal emission distribution, drivers of
emissions, and to guide effective mitigation strategies. Ground-based measurements are inherently limited to the

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390 regions where they are installed, while airborne methods are often limited to targeted, short-duration research
campaigns. North America has been the focus of many studies, but less is known about the other large agricultural
regions around the world. Satellite observations, thus, are an attractive option because they have the potential for
more spatial coverage (~global during the warm season) and relatively fine (~daily) temporal resolution. This can
also serve to bridge the gap that exists between the present point- and region-scale N₂O monitoring. In the absence
395 of direct space-based observations of surface N₂O concentrations, we propose to leverage the well-observed trace
gas NO₂ as a proxy for N₂O emissions to create a pathway to monitor N₂O emissions in global agricultural regions
more comprehensively.

In this work, we derive airborne N₂O-to-NO_x emission ratios from the CalNex (2010) airborne campaign around a
dense agricultural region of California. These ratios represent the molecular emissions ratio of N₂O to NO_x from
400 croplands at spatial scales commensurate with space-based NO₂ observations. We combine these ratios with
satellite-derived NO_x soil emissions to estimate N₂O emissions. We compare our TROPOMI NO₂-derived N₂O
fluxes with N₂O emissions estimates from independent chamber observations and two distinct airborne campaigns
made in Iowa and the Mississippi River Valley. Our space-based N₂O emissions estimates compare favorably with
these independent estimates across different regions and as measured by different methods covering different spatial
405 and temporal scales. In comparison with chamber-derived N₂O flux (Lawrence et al., 2021), our estimate of mean
flux only differs by 3.8% %, or ~0.12 nmol N₂O/m²/s. Mean estimates differ from airborne emission ratios taken in
the Mississippi River Valley (Gvakharia et al., 2020) by ~14.3% %. Comparing emissions derived from Bayesian
inversion of aircraft data (Dacic et al., 2024) yields a larger N₂O flux mean difference by ~60%. In all cases, the
confidence intervals of our space-based N₂O flux estimates and those from independent measurements and
410 approaches overlap.

We have demonstrated that space-based NO₂ observations as a proxy for N₂O cropland emissions compare
favorably to independent estimates across multiple agricultural areas and years. This suggests that space-based NO₂
retrievals are a viable and robust proxy for N₂O flux at scales of at least 0.75 x 0.75 degrees, and over timescales as
short as five days. Further development and refinement of approaches to characterize agricultural NO₂ from satellite
415 observations and link them to N₂O emissions are possible. As presented here, the largest source of uncertainty in the
estimated N₂O emissions derives from the large variability in the observed airborne N₂O:NO_x emissions ratio.
Improved understanding and definition of this ratio, and what controls variation, could improve the fidelity of this
proxy approach. This could be accomplished with airborne observations of NO_x and N₂O. Capturing different crops,
agricultural practices and environmental conditions would provide more insight into emissions ratios and best
practices on how to apply to independent satellite data in new domains. A complementary approach to the use of
420 direct atmospheric observations of cropland N₂O and NO_x in our proxy-based method would be to combine satellite-
based or ground-based estimates of soil moisture with a biogeochemical model, such as DayCent (Li et al., 1992;
Parton et al., 1998), to derive modeled N₂O:NO_x emission ratios. With such an approach one could model emissions,
and uncertainties, over many different regions and conditions where measurements may not be possible. The work
presented here demonstrates a proxy-based approach that may offer a path towards a more spatially comprehensive
constraint on regional and global budgets of agricultural N₂O emissions. ▲

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Data Availability

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All data used in this manuscript are archived in public databases. Airborne data from P3 aircraft during the CalNex
campaign is available from the NOAA Chemical Sciences Laboratory at <https://csl.noaa.gov/projects/calnex/>.
430 TROPOMI Level 2 Nitrogen Dioxide total column products, Version 02, are available from the European Space
Agency at <https://doi.org/10.5270/S5P-9bnp8q8>. The National Emission Inventory is available from the
Environmental Protection Agency at [https://www.epa.gov/air-emissions-inventories/2017-national-emissions-](https://www.epa.gov/air-emissions-inventories/2017-national-emissions-inventory-nei-data)
[inventory-nei-data](https://www.epa.gov/air-emissions-inventories/2017-national-emissions-inventory-nei-data). Chamber flux measurements from Lawrence et al. (2021) are available
at <https://doi.org/10.6073/pasta/e6117972f6a80d5f5a9db354957910ed>. Airborne data from the FEAST campaign
435 and Gvakharia et al. (2020) is available at <https://doi.org/10.7302/Z2XK8CRG>. Posterior fluxes from the airborne
MAIZE campaign and Dacic et al. (2024) are available at <https://doi.org/10.7302/9w5m-mn30>.

Author Contribution

TA developed the box model code, conducted all model simulations, and designed and optimized the aircraft data filtering methods. TA also prepared the manuscript, with significant input from EK and GP. EK conceived the project idea. EK and GP provided guidance on methodology and the presentation of results, and contributed to data collection and modeling for the experimental datasets used for comparison.

Competing Interest

[The authors declare no competing interest.](#)

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