Aircraft observations of wintertime spatiotemporal variability of nitrous oxide (N_2O) in the San Joaquin Valley of California

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ABSTRACT. Nitrous oxide (N_2O) is a long-lived and highly potent greenhouse gas that also destroys stratospheric ozone. N_2O sources are uncertain, with documented differences between bottom-up and top-down emission estimates. We present a unique N_2O dataset that captures the

spatial and temporal variability in N_2O in the atmospheric boundary layer (ABL) in the San Joaquin Valley (SJV) of California during wintertime. N_2O measurements were collected as part of the NASA DISCOVER-AQ (Deriving Information on Surface Conditions from COlumn and VERtically Resolved Observations Relevant to Air Quality) campaign SJV-deployment (January–February, 2013), during which the NASA P-3 aircraft sampled more than 60 N_2O vertical profiles over agricultural, urban, and rural source areas. We describe the influence of diurnal ABL dynamics and source proximity on N_2O spatiotemporal vertical variability at multiple SJV locations. To infer N_2O source type, we investigate enhancement ratios of N_2O, methane, ammonia, carbon dioxide, and carbon monoxide separately within the nocturnal boundary, residual, and convective boundary layers, which show dairy/livestock operations are the primary wintertime N_2O source. We use a nocturnal boundary layer budgeting model, constrained with aircraft vertical profiles, to estimate N_2O emission rates of 60–860 mg N_2O-N ha^{-1} h^{-1} across the SJV.

INTRODUCTION

Nitrous oxide (N_2O) is a long-lived greenhouse gas with a global-warming potential two orders of magnitude larger than carbon dioxide (CO_2).[1] N_2O is also currently the dominant destroyer of global average stratospheric ozone (O_3).[2-3] Increasing at a rate of 0.8 ppb yr^{-1}, N_2O has contributed 7% of the change in radiative forcing on Earth since 1850. N_2O may have a proportionally greater role as a climate forcer in the future because its atmospheric lifetime exceeds 100 years, its emissions are coupled to food production, and because of the current regulatory focus on CO_2.

Approximately 60% of global N_2O is formed by natural nitrogen cycling in soils and oceans.[4] Anthropogenic N_2O is largely emitted by agricultural activities,[5-7] either directly from fertilized fields and animal operations[8-9] or indirectly from leaching and runoff of fertilizer and animal waste.[10-11] N_2O production from microbially-mediated oxidation-reduction reactions in soils and manures is strongly dependent on temperature, water content, oxygen levels, and nitrogen availability.[12-18] Inter-annual trends in tropospheric N_2O concentration follow long-term patterns in synthetic nitrogen fertilizer use,[7, 19] which is expected to increase in the future, with recent trends outpacing even aggressive forecasts,[20-21] and in manure nitrogen production, which has increased 6-fold over 1860–2014.[22] Other sources include water and waste treatment, energy generation, biomass burning, and various industrial activities.[23-24]

Our empirical knowledge around N_2O is mostly built from observations collected at small spatial scales using laboratory incubation experiments and field-deployed soil chambers, especially static chambers with off-line gas-chromatography detection.[25-26] Field-based chamber measurements have the advantage of significant signal amplification, obviating the need for high-precision instrumentation. Because chambers are small in size, N_2O fluxes (F_{N2O}) are well-correlated with specific environmental and microbial factors. Regional bottom-up estimations are then derived by combining flux data with emissions factor parameterizations that scale with one or more environmental variables.[12] However, because of the complexities and heterogeneities of soil biogeochemistry, it has proven difficult to upscale chamber-derived F_{N2O} to landscape/regional scales, and resulting inventories have documented errors.[12] For example, Kort et al.[27] found the EDGAR (Emission Database for Global Atmospheric Research) and GEIA (Global Emissions InitiAtive) inventories were low by factors of 2.6 and 3.1, respectively, over

North America in the summertime and Griffis et al.[28] revealed discrepancies as large as a factor of 1.8 in the U.S. Corn Belt. In agriculturally-intensive Central California, Xiang et al.[4] reported EDGAR was low by a factor of 3–4 in the late spring and Jeong et al.[29] determined multiple inventories were low by seasonally-varying factors of ~2 (versions of EDGAR) and 2.7 (contemporary California estimates). These top-down approaches have uncertainties as well, caused in part by limited atmospheric observations and by transport and process-based model inaccuracies and inconsistencies.[1, 22] Challenges are compounded by N_2O's long tropospheric lifetime and high background mixing ratio, which lead to N_2O enhancements (ΔN_2O) that are spatially distributed away from sources, small compared to the free troposphere concentration, and analytically demanding to detect (low signal to noise). Generally, global nitrogen-cycle and F_{N2O} model development lag progress achieved for CO_2 and methane (CH_4).[22]

California contributes a significant portion of U.S. agricultural productivity, accounting for more than 1/3 of vegetables, 2/3 of fruits and nuts,[30-31] and 1/5 of dairy[32] produced in the U.S. The 2006 California Global Warming Solutions Act, Assembly Bill (AB) 32, requires the state to limit greenhouse gas emissions, including N_2O, defined in terms of CO_2 equivalents (CO_2eq).[33] AB 32, and the subsequent 2016-Senate Bill (SB) 32,[34] mandates timely updates to state inventories, which are fundamental to distributing emission allowances, providing incentives, and reducing state emissions to 40% below 1990 levels by 2030. State-wide F_{N2O} are large enough that F_{N2O} controls are required to achieve California's greenhouse gas reduction targets.[35] Agriculture is thought to be the dominant source of N_2O in the state, and, while there are few N_2O datasets useful for inventory validation, research indicates underestimates in F_{N2O} accounting, particularly from animal operations and crop cultivation,[4, 35-36] but also in cities.[37]

In this paper, we investigate spatially-resolved (horizontally and vertically) N_2O measurements in the San Joaquin Valley (SJV), an agricultural region of California. We describe and interpret the spatiotemporal variability in N_2O mixing ratios measured during the NASA DISCOVER-AQ (Deriving Information on Surface Conditions from COlumn and VERtically Resolved Observations Relevant to Air Quality) deployment in the SJV, which took place January 16–February 10, 2013. We focus on observations of vertical variability in N_2O enhancements above the free-tropospheric mean concentration (ΔN_2O), which we show follow the dynamics of near-surface atmospheric mixing and the location of SJV source regions. We use enhancement ratios of N_2O, CH_4, CO_2, ammonia (NH_3), and carbon monoxide (CO) to infer the identity and diurnal timing of dominant N_2O sources. To produce F_{N2O} on spatial scales relevant to county-level emissions accounting (thousands of km^2), we apply nocturnal mass budgeting and constrain our calculation with N_2O vertical profiles measured during DISCOVER-AQ from onboard the NASA P-3 aircraft.

METHODS

The San Joaquin Valley. The San Joaquin Valley (SJV) is one of the most productive agricultural regions in the U.S., encompassing dairy/livestock operations and crop cultivation.[30] The SJV is also home to major trucking routes for goods transport, spatially distributed oil and gas fields,[38] a number of small towns (e.g., Porterville, Hanford, and Visalia) and the medium-sized cities Fresno and Bakersfield (approximate 2013 populations of 510,000 and 364,000, respectively). According to the California Air and Resources Board (CARB) greenhouse gas inventory, annual N_2O sources state-wide in 2013 were agricultural soil

management (61%), transportation (18%), manure management (11%), and waste water treatment (6%), with many of these types of sources located in the SJV.[36]

NASA DISCOVER-AQ. NASA DISCOVER-AQ collected a suite of airborne observations enabling investigation of spatiotemporal variability of air quality and climate-relevant trace species.[39] As part of DISCOVER-AQ, the NASA P-3 aircraft measured vertical profiles of atmospheric trace composition in the lower half of the troposphere, sampling 2–3 times per day on multiple days with a repeated flight circuit. A typical P-3 flight circuit is shown in Fig. 1, with waypoints usually traveled in the following sequence: Bakersfield (urban/oil and gas), Porterville (rural), Hanford (agricultural), and Fresno (urban). P-3 profile spirals were ~4 km in diameter, traversing the lower troposphere (2–3 km above ground level, AGL) to as low as 10–50 m AGL when missed approaches (flight procedures, in which pilots discontinue landings at very low altitudes) were possible and visibility permitted (Fig. 1d). There were 10 research flights in the SJV; we focus on two consecutive 3-day research flight periods with N_2O measurements, Jan 20–22 and Jan 30–Feb 1, which occurred during distinct air stagnation events.[40]

N_2O, CH_4, and CO were measured with the Differential Absorption CO Measurement (DACOM) instrument, a custom-built, 3-channel, mid-infrared (IR) tunable diode laser spectrometer.[41] During the DISCOVER-AQ SJV deployment, DACOM used cryogenically cooled lead (Pb)-salt lasers to generate tunable IR at 4.5 μm specific to N_2O, 3.3 μm for CH_4, and 4.7 μm for CO. The three beams were combined with dichroic filters and directed through a 0.3 L Herriott cell aligned for a 36-m optical path. Upon exiting the Herriott cell, the beams were spectrally isolated using dichroic filters and sent to individual HgCdTe (MCT) detectors. Each laser's wavelength was continuously, actively controlled using a gas reference cell. Ambient air was pulled into the

aircraft through a Nafion tube dryer to remove water vapor. The Herriot cell pressure was maintained at 120 mbar to minimize interferences from spectral overlap. The 1σ precision at 10-s averaging for N_2O, CH_4, and CO was 0.1 ppb, 0.8 ppb, and 0.6 ppb, respectively. Accuracy was ±1% for N_2O and CH_4 and ±2% for CO, achieved by frequent in-flight calibrations using gas standards assayed by the NOAA Earth System Research Laboratory.

Other trace species measured onboard the NASA P-3 used in this analysis were CO_2, nitric oxide (NO), nitrogen dioxide (NO_2), O_3, NH_3, and water vapor ($H_2O_{(v)}$). CO_2 was measured at 1-s time resolution via non-dispersive IR spectroscopy using the AVOCET (Atmospheric vertical observations of CO_2 in the Earth's Troposphere) instrument.[42] During DISCOVER-AQ, AVOCET reported accuracy of ±0.25 ppm relative to World Meteorological Organization (WMO) standards. NO, NO_2, and O_3 were measured at 1-s time resolution using chemiluminescence to directly quantify NO and O_3, and chemiluminescence coupled to a blue light converter for NO_2. Overall uncertainties were ±10% for NO and NO_2 and ±5% for O_3. NH_3 mixing ratios were quantified by PTR-ToF-MS (proton-transfer reaction time-of-flight mass spectrometry) at 1-s time resolution with an accuracy of ±35%. $H_2O_{(v)}$ was measured by the NASA open-path Diode Laser Hygrometer (DLH) and reported at 1-s time resolution. Static air temperature was measured by a Rosemount model 102 sensor with an accuracy and precision of ±0.2°C and 0.006°C, respectively.

Atmospheric Layer Height Determination. In this paper, we identified the heights (h) of the nocturnal boundary layer (NBL, h_{NBL}), nocturnal residual layer (RL, h_{RL}), and convective boundary layer (CBL, h_{CBL}) with two techniques, described in Schwartz et al.[43] and Heffter,[44]

which employed measurements of either atmospheric trace gases or potential temperature (θ), respectively. Both methods evaluated vertical variability in conserved tracers, with the first definition based on the observation that longer-lived species are generally well-mixed within the atmospheric boundary layer (ABL). These are among many established methods of ABL *h* determination.[45] Turbulence data were not collected onboard the NASA P-3 during DISCOVER-AQ.

Following Schwartz et al.,[43] we defined the ABL *h* by first identifying a full-mixed layer height (h_{FM}), an altitude region in which the species mixing ratio was approximately constant, and the entrainment zone, a visible region of transition to the free troposphere.[43, 46] Complete vertical mixing then equaled h_{FM} plus the height of the top of entrainment zone transition (h_T), with $h = \beta(h_{FM} + h_T)$ and $\beta = 1 - \frac{h_T}{2(h_{FM} + h_T)}$. To determine h_{FM} and h_T, we used aircraft measurements of N_2O, CO_2, CH_4, $H_2O_{(v)}$, NO_x, and NO/NO_x averaged into 10-m altitude bins (Figs. S1–S42). For each P-3 profile, we averaged the h_{FM} and h_T for each gas (Tables S1–S4, S9). If h_{FM} or h_T could not be selected for any individual species, either because an enhancement could not be unequivocally distinguished or because of a data gap, that value was omitted from the mean. NO/NO_x was particularly useful for identifying the height of the nocturnal boundary layer in the polluted SJV, as at night NO/NO_x approached 1.

Following Heffter,[44] we calculated the 3-point running mean lapse rate ($\frac{\partial}{\partial z}$) and averaged $\frac{\partial}{\partial z}$ into 10-m radar altitude bins (the running mean reduced spurious layer identification). We identified layers as continuous vertical regions with $\frac{\partial}{\partial z}$ greater than 0.005 K m^{-1}, recorded the base and top of these layers, and then selected *h* as the radar altitude at which Δθ was greater

than or equal to 2 K (from the base) (Figs. S1–S42, Tables S5–S8, S10). The heights were classified as indeterminate if $z(\Delta\theta = 2)$ was greater than z at the top height. The two methods produced nocturnal and convective boundary layer heights (h_{NBL} and h_{CBL}) that were well-correlated ($r^2 > 0.8$). The Heffter[44] approach consistently gave a factor of 1.5 higher h_{NBL} and 1.3 higher h_{CBL} values (Fig. S43), a result also reported by Department of Energy (DOE) Atmospheric Radiation Measurement (ARM).[47]

Nocturnal Boundary Layer (NBL) Budgeting Methodology. NBL budgeting is a mass balance technique for deriving gas fluxes by treating the near-surface atmosphere as a well-mixed reaction volume and solving Eq. 1,[28, 48-62] where h is the height of the volume's lid, ρ is the air density, and $\frac{\partial \Delta N_2O}{\partial t}$ is the change in N_2O mixing ratio enhancement throughout the night.[28, 55, 63-64] ΔN_2O values were computed relative to background N_2O, defined as daily N_2O mixing ratios measured above 1.5 km. The average background N_2O on our six flight days was 325.9 ± 0.4 ppb, with errors as the 1σ standard deviation, representing the observed natural variability rather than the measurement uncertainty. This approach has been used to estimate fluxes in calm, stable nighttime atmospheres that do not satisfy conditions required for micrometeorological methods.[58, 61] Several observational constraints are required to solve Eq. 1: $\frac{\partial \Delta N_2O}{\partial z}$ and h, the time of NBL formation (t_0), and the N_2O mixing ratio at t_0.

(1) $$F_{N_2O} = \int_0^h \rho \frac{\partial \Delta N_2O}{\partial t} \partial h$$

Past analyses have determined h according to the height of the morning fog layer,[65] the strongest inversion in potential temperature,[66] vertical variability in the slope of the correlation between CO_2 and unreactive co-emissions,[64] and vertical gradients in gas concentration.[61] We defined h as h_{NBL} and integrated $\frac{\partial \Delta N_2O}{\partial z}$ from 0 to h_{NBL}, which assumed ΔN_2O at the surface was represented by ΔN_2O at the lowest altitude sampled. h_{NBL} at t_0 was zero and NBL growth was presumed to be logarithmic for 5 hours after sunset, after which h_{NBL} was constant.

To constrain t_0, we exploited high NO_x concentrations in the SJV. During the daytime, fresh NO emissions react with O_3 to form NO_2. NO_2 subsequently photolyzes forming NO and $O(^3P)$, which combines with molecular oxygen (O_2) to regenerate O_3.[67] Attenuated evening light and high NO concentrations drive this chemistry such that O_3 is titrated to NO_2. Steep decreases in surface-level O_3 are cotemporaneous with NBL formation, as NO concentrations increase because NO emissions occur into the substantially smaller NBL volume (Figs. S44–S45). We defined a daily SJV-wide t_0 by inspecting the coordinated timing of the evening O_3 decrease and NO_2 increase using data collected at Bakersfield, Hanford, and Fresno (there were no data in Porterville). Averaged t_0 equaled 4:50 pm LT, varying by 10 minutes (1σ) between sites and on different days. During DISCOVER-AQ, the mean sunset time was 5:19 pm LT. We estimated ΔN_2O at t_0 as equal to ΔN_2O at the altitude of the NBL h_{FM}, which was typically the lowest ΔN_2O value in each profile.

While not required to solve Eq. 1, knowledge of the surface area influencing F_{N2O} is important for interpreting F_{N2O}. Nocturnal fluxes are influenced by air mass advection, especially when integrated over long winter nights.[61, 68] Quantifying this advection is difficult due to large errors

in nighttime surface footprint calculations, for example, by Lagrangian trajectory models.[61, 69-70] Instead, we visualized F_{N2O} source areas as gridded (0.05° *x* 0.05°) normalized vector wind frequency density maps using ground station measurements at the base of each P-3 profile spiral. Specifically, we counted grid box crossing of 1-s wind vectors, backwards calculating trajectories over a 4-hour period assuming straight-line paths. We consider source areas as encompassing grid boxes with frequencies of at least 10% the maximum occurrence. Maps included all data between 1-h before sunset until the early-morning P-3 profiling (15–17 h). DISCOVER-AQ mean (Jan 20–22 and Jan 30–Feb 1) areas were: Bakersfield, 1.9 *x* 10^3 km^2; Porterville, 2.4 *x* 10^3 km^2; Hanford 2.9 *x* 10^3 km^2; and Fresno 2.8 *x* 10^3 km^2. While Bakersfield and Porterville source areas were spatially distinct, the Hanford and Fresno areas overlapped (Fig. S46), which mirrored source areas inferred from F_{N2O} and enhancement ratio results and are described below.

NEAR-SURFACE ATMOSPHERIC DYNAMICS: OVERVIEW AND CONDITIONS DURING DISCOVER-AQ

N_2O is chemically unreactive in the troposphere and mixing ratio enhancements from the global background (ΔN_2O) are a function of the location and strength of emissions and the dynamics of atmospheric mixing (Fig. 2). Soil microbes can also consume N_2O, but net F_{N2O} are generally upward.[71] The depth of the ABL exerts a large influence over the concentration of recently-emitted moderately and long-lived species.[72-73] ABL dynamics are driven by turbulent and radiative processes,[74] with ABL heights well correlated with surface sensible heat fluxes.[75] In the morning, solar surface heating leads to convective turbulent eddies that efficiently mix surface emissions throughout the convective boundary layer (CBL). Entrainment of less

turbulent layers with lower ΔN_2O dilutes ground-level ΔN_2O[76] and concentration gradients between the CBL and free atmosphere above are often linear through the entrainment zone.[43, 46, 76-77] In the late afternoon/early evening, sunlight attenuation causes the CBL to collapse and a nocturnal boundary layer (NBL) forms. At night, high concentrations of emitted species accumulate in the NBL, which may be just 10s–100s m deep. Vertical mixing between the NBL and nocturnal residual layer (RL) above is weak and multiple RLs may form.[78] In the morning, the nearly statically-neutral RLs are rapidly entrained into the growing CBL[76] and unreactive gases emitted on the previous day are reincorporated into the surface layer.

During DISCOVER-AQ, h_{NBL}s ranged 50–250 m across all sites (values per Schwartz et al.[43]). Despite differences in morning sampling times, higher mean h_{NBL}s were observed in Porterville (147 ± 18 m at 8:57 am LT) and Fresno (138 ± 49 m at 9:57 am LT) than Hanford (59 ± 15 m at 9:15 am LT). The average sunrise time was 6:58 am LT. Bakersfield was the first site in the circuit, but flight conditions did not permit missed approaches for data collection below 300 m on Jan 20–22 or in the early morning of Jan 31. In the afternoon, h_{CBL}s varied as follows: Bakersfield, 627 ± 68 m at 1:43 pm LT; Porterville, 430 ± 142 m at 1:31 pm LT; Hanford, 515 ± 46 m at 1:49 pm LT; and Fresno, 549 ± 27 m at 2:49 pm LT. While Bakersfield was usually the first afternoon profile site, the P-3 visited Bakersfield at the end of the circuit on Feb 1. h_{CBL}s were at the low end of the climatological range presented by Bianco et al.,[79] who found daily maximum h_{CBL}s of 0.5–0.8 km in January–February using 915-MHz radar wind profilers with radio acoustic sounding systems (RASS) at two SJV sites, Chowchilla (37.11°N, 120.24°W), ~50 km northwest of Fresno, and Lost Hills (35.62°N, 119.69°W), ~60 km north-northwest of Bakersfield.[79]

Horizontal mixing in the SJV is controlled by the nonlinear combination of multiple terrain-driven mesoscale and sub-mesoscale flow patterns. Although not prominent during DISCOVER-AQ, typical daytime surface winds follow an extended land-sea breeze pattern, with onshore flow through the Carquinez Strait (near the San Francisco Bay), which then diverges in Central California south into the SJV or north into the Sacramento Valley.[79-81] At night, the direction of flow reverses in a recurring counterclockwise flow pattern known as the Fresno eddy, which recirculates air from the southern SJV (Bakersfield) northward toward Fresno.[80, 82] The valley is bordered by the Pacific Coastal Ranges (to the west), Sierra Nevada Mountains (east), and Tehachapi Mountains (south); interactions between mesoscale and synoptic flows influence SJV air quality. Horizontal transport during the wintertime is generally weak, particularly at night, with slower and more disorganized surface winds than observed in other seasons and frequent air stagnation periods lasting days to weeks.[83] During DISCOVER-AQ, a high pressure system dominated California and synoptic flows were weak.[76] Corresponding to research flight days (Jan 20–22 and Jan 30–Feb 1), mean nighttime (10 pm–6 am LT) surface winds measured at local monitoring stations were: Bakersfield, 1.8 ± 1.2 m s^{-1}; Porterville, 3.7 ± 1.3 m s^{-1}; Hanford, 2.1 ± 1.0 m s^{-1}; and Fresno, 2.2 ± 1.2 m s^{-1}. During the daytime (11 am–4 pm LT), higher wind speeds were typical: Bakersfield, 3.8 ± 1.7 m s^{-1}; Porterville, 5.0 ± 1.7 m s^{-1}; Hanford, 3.5 ± 1.6 m s^{-1}; and Fresno, 3.3 ± 1.2 m s^{-1}.

While not frequent in the winter, nocturnal low level jets (LLJs) are a common phenomenon in the SJV during spring and summer.[79] LLJs are fast moving air currents at the top of radiative inversions[79] known to redistribute trace gases just above the NBL[84-86] and enhance vertical mixing between the NBL and nocturnal RL.[87] Vertical profiles of wind speed and direction were

measured during DISCOVER-AQ using a RASS high-resolution wind profiler (915-MHz) near Visalia (36.310°N, 119.389°W). These data do not suggest significant LLJ influence, with mean wind speeds of 1.8 ± 0.9 m s^{-1} below 0.6 km on nights preceding DISCOVER-AQ flights (Fig. S47). While a fast-moving layer of air descended downward at ~10 m s^{-1} on the night of Jan 30, wind speeds diminished to <4 m s^{-1} below 0.6 km AGL.

Horizontal mixing in the SJV is also affected by diurnally varying mountain-valley flows.[76, 88] During the daytime, differential heating between the air above the valley floor and sidewalls causes upslope flow from the SJV to higher mountain elevations. Mountain flow intensity depends on terrain slope, surface friction, and entrainment of synoptic flows aloft.[89-90] At night, differential cooling causes the direction of flow to reverse. If the NBL is shallow, trace gases in high elevation downslope flows can be incorporated into nocturnal RLs and redistributed horizontally prior to morning entrainment into the surface layer.[91-92] Bakersfield, Porterville, and Fresno experienced winds that were influenced by the diurnal cycle of upslope/downslope flows. During DISCOVER-AQ, median nighttime surface winds were from the south in Bakersfield (from the Tehachapi Mountains) and from the east in Porterville (from the Sierra Nevada Mountains) (Fig. S46). In Fresno, wind patterns were more varied, but downslope flows were observed on Jan 30.

RESULTS AND DISCUSSION

Spatiotemporal Variability. Within the CBL, ΔN_2O were highest near Hanford (Fig. 3), a region of numerous dairies (Fig. 2c). Smaller ΔN_2O were observed near Fresno and in the southern SJV around Bakersfield. Porterville appeared to be at the eastern edge of the Hanford

source area, but not a source location itself. The ΔN_2O distribution away from the Hanford region varied day to day: on some days (Jan 22 and 31), ΔN_2O were largely spatially correlated with Hanford and near zero elsewhere; on other days (Jan 20–21, Feb 1), elevated ΔN_2O were distributed valley wide.

The diurnal evolution of $\frac{\partial \Delta N_2O}{\partial z}$ indicated the vertical ΔN_2O structure in the wintertime SJV was driven by ABL dynamics. Representative ΔN_2O profiles are shown over Hanford in the early-morning, late-morning, and afternoon on Jan 20–22 (Fig. 4). Similar diel patterns were observed for Jan 30–Feb 1. Early morning P-3 sampling occurred before the breakup of the NBL; as a result, substantial N_2O surface enhancements of 18–24 ppb (5–8%) were observed. Slightly smaller NBL ΔN_2O of 5–15 ppb (1.5–5%) were measured Jan 30–Feb 1. On all days there were steep concentration gradients between the NBL and RL above, suggesting weak nocturnal vertical mixing. Within distinct nocturnal RLs (100–600 m AGL), ΔN_2O mixing ratios were enhanced by as much as 3–6 ppb (1–2%). In the late morning, ABL heights increased from 45–75 m up to 180–250 m AGL; at the same time, ground-level ΔN_2O decreased because of dilution. In the afternoon, P-3 sampling captured ΔN_2O as generally well-mixed within the CBL with visible transitions through the entrainment zone. ΔN_2O were lowest in the afternoon, with values of 3–7 ppb (1–2%). CBL mixing ratios were comparable in magnitude to ΔN_2O in nocturnal RLs on the following day.

We observed smaller surface ΔN_2O in Fresno, Porterville, and Bakersfield. In Fresno, ΔN_2O were elevated within the NBL by 2–11 ppb (0.5–3%). Sample Fresno profiles are shown in Fig. 5. Because of the later sampling time (~10 am LT), $\frac{\partial \Delta N_2O}{\partial z}$ were more influenced by entrainment

than in Bakersfield, Porterville, and Hanford.[76] h_{NBL}-normalized ΔN_2O were ~20% (Jan 20), ~60% (Jan 21), and 25–80% (Jan 22, 30–31) lower in Fresno than Hanford. On Feb 1, the h_{NBL}-normalized ΔN_2O was greater in Fresno than Hanford despite similar wind conditions; however, the aircraft sampled only to a depth 75 m AGL over Hanford and it was visually evident that the profile data were incomplete (Fig. S6). In Porterville, NBL ΔN_2O were not consistently elevated versus nocturnal RL ΔN_2O: on Jan 20, ΔN_2O below the h_{NBL} were lower than within the adjacent RL (Fig. 6a); on Jan 21, ΔN_2O below the h_{NBL} were approximately equal to ΔN_2O within the adjacent RL (Fig. 6e). Surface ΔN_2O were always greater than in the free troposphere (Fig. 6).

N_2O Enhancement Ratios. To investigate F_{N2O} sources, we calculated N_2O/CH_4, N_2O/CO_2, NH_3/N_2O, and CO/CO_2 enhancement ratios, equal to the slope of the correlation of mixing ratios using a bivariate linear regression[93] with uncertainties as 1σ standard deviations of measurements above 1.5 km. Daily ratios (i.e. at constant background concentrations) were computed separately within the NBL, lowest-altitude RL, and CBL, and statistically significant ($p < 0.05$) slopes with $r^2 > 0.4$ were averaged for the dates Jan 20–22 and Jan 31–Feb 1 (Table 1). Because aircraft sampling blends spatial heterogeneities in emitters,[94] enhancement ratios are not equivalent to emission ratios, but do reflect patterns in N_2O sources. Spatial variability in enhancement ratios of long-lived gases signaled limited horizontal mixing within all atmospheric layers during DISCOVER-AQ.

In Hanford, enhancement ratios indicated dairy/livestock operations were the dominant F_{N2O} source. N_2O/CH_4 in all atmospheric layers were comparable to, but at the low end, of ratios measured downwind of dairies in Colorado[95] (0.004–0.006) and Idaho (0.005).[96] N_2O/CH_4 were

less variable in Hanford than in Fresno, Porterville, and Bakersfield, consistent with Hanford being a uniform (although integrated) source region. The highest N_2O/CH_4 and N_2O/CO_2 were measured in the CBL (the midday surface layer) and RL (the late afternoon surface layer), with the lowest ratios in the NBL. A comparably subtle N_2O/CH_4 diel pattern was reported for large animal facilities in Colorado, attributed to the diurnal balance of temperature-dependent N_2O and CH_4 fluxes.[95] Likewise, NH_3/N_2O in Hanford were of similar magnitude and comparable temperature dependence to other dairy/feedlot analyses.[94-97] The highest NH_3/N_2O (34 ± 3 ppb/ppb) were observed in the RL (late afternoon). Lower ratios were found at other times of day; however, NH_3 is chemically reactive and NH_3/N_2O are a function of both NH_3 emissions and loss rates. During DISCOVER-AQ, Miller et al.[94] showed distance-dependent decreases in NH_3/CH_4 in the near field (100s m) of dairies due to deposition and chemistry, as well as considerable facility-level variability.

In Fresno, N_2O/CH_4 and CO/CO_2 were higher and N_2O/CO_2 lower than in Hanford at all times of day (in each atmospheric layer), implying influences from distinct N_2O sources. Ratios suggest crop agriculture and/or urban combustion were more prominent N_2O emitters than dairies. There are more cultivated fields around Fresno than Hanford and managed fields directly emit N_2O, but not much CH_4 or CO_2.[98] Fresno County has more cropland that any other California county and is modeled to be responsible for ~8% of the state's N_2O emissions from fertilized soils.[99] Major crops include grapes, alfalfa, corn, cotton, winter wheat, tomatoes, citrus, and almonds.[100] While most of these crops are grown in the summer, with fertilizer application in the spring, SJV growers have reported applying fertilizer to alfalfa (18% of farmers), citrus, cotton (45%), and wheat (75%) fields in January–February.[101] Soil F_{N2O} in nitrogen-rich systems have been

observed to maximize during the daytime,[102] suggesting differences in CBL N_2O/CH_4 in Fresno and Hanford maybe linked to local differences in crop cultivation.

Throughout the SJV, the highest N_2O/CH_4 were observed in Fresno and Bakersfield in the NBL, indicating at least some N_2O contribution from urban combustion. CO/CO_2 is often used to infer combustion source type, as the ratio indicates emitter combustion efficiency. U.S. urban areas are dominated by high-efficiency combustion sources compared to other global cities,[103] with mean CO/CO_2 of 4–12 x 10^{-3} ppb/ppb in U.S. cities[104] and 10–11 x 10^{-3} (ppb/ppb) in California in 2010.[105-106] NBL CO/CO_2 in Fresno and Bakersfield were equal to within uncertainties. CO/CO_2 were as low as ~2 x 10^{-3} ppb/ppb signifying additional CO_2 sources without CO co-emissions. Dairies and soils are known sources of CO_2, with CO_2 emitted by animal, plant, and soil respiration and the decomposition of organic matter in manures and soils.[107] During the growing season, these emissions are offset by carbon assimilation by crops, but CO_2 fluxes are potentially positive in the wintertime. Moreover, upward wintertime CO_2 fluxes maximize at night, which is when plants do not photosynthesize and when we observed the lowest Hanford CO/CO_2. Generally, enhancement ratios in Porterville were most like those measured in Hanford. Bakersfield ratios were similar to Fresno, with lower N_2O/CH_4 explained by CH_4 emissions from nearby oil and gas fields.

***F_{N2O}* Estimates Using NBL Budgeting.** Solving Eq. 1, we calculated location-averaged F_{N2O} across the SJV ranging 60–860 mg N_2O-N ha^{-1} h^{-1} (Table 2). The highest F_{N2O} were computed over agriculturally-intensive Hanford, where the mean F_{N2O} was 740 ± 120 mg N_2O-N ha^{-1} h^{-1}. F_{N2O} were similar day-to-day, consistent with the area being a source region. Because the P-3

was unable to sample h_{FM} on Feb 1, F_{N2O} on that day (200 ± 40 mg N_2O-N ha^{-1} h^{-1}) was underestimated and not included.

Near-zero F_{N2O} were observed over Porterville (rural) and Bakersfield (urban/oil and gas). The California inventory estimated traffic contributed ~20% of state-wide F_{N2O} in 2013, but past research has shown vehicles to be minor local sources,[36] in agreement with dynamometer data of rapidly declining F_{N2O} with improved catalyst technologies and low fuel sulfur content.[108] While enhancement ratio analysis suggested combustion/urban emissions predominated, we found their fluxes were negligible. We anticipated low F_{N2O} in urban Fresno; however, F_{N2O} were comparable to, but not greater than, F_{N2O} in Hanford on 3 of 6 nights. Because F_{N2O} in Bakersfield were small, high fluxes in Fresno were likely not due to transportation or other urban sources. According to nighttime surface wind data, air flowed from Hanford to Fresno on most nights. One exception was Jan 30, when evening and nighttime winds were from the northeast and east, from where air had little interaction with agricultural lands. Correspondingly, F_{N2O} in Fresno on Jan 30 were statistically indistinguishable from zero. On Jan 20 and 22, F_{N2O} were ~340 mg N_2O-N ha^{-1} h^{-1}, approximately half the mean F_{N2O} in Hanford. In the Fresno NBL, different enhancement ratios were observed on days when F_{N2O} were ~340 mg N_2O-N ha^{-1} h^{-1} (Jan 20 and 22) versus >600 mg N_2O-N ha^{-1} h^{-1} (Jan 21, Jan 31, and Feb 1). On Jan 20 and 22, ratios were: N_2O/CH_4, 9.4 x 10^{-3} ppb/ppb; CO/CO_2, 13.9 ppb/ppm; and N_2O/CO_2, 0.07 ppb/ppm. On Jan 21, Jan 31, and Feb 1, ratios were: N_2O/CH_4, 5.9 x 10^{-3} ppb/ppb; CO/CO_2, 5.7 ppb/ppm; and N_2O/CO_2, 0.14 ppb/ppm. Therefore, nights with higher F_{N2O} in Fresno corresponded to NBL enhancement ratios more reflective of Hanford sources, caused by horizontal advection rather than local emissions.

We quantified nocturnal F_{N2O} errors based on uncertainties in defining: h_{NBL}, the h_{NBL} growth form factor, and ΔN_2O at t_0. To determine F_{N2O} sensitivity to h, we compared F_{N2O} estimates using the h_{NBL} values according to Schwartz et al.[43] and Heffter,[44]which agreed to within a factor of 1.5. In Hanford, where large ΔN_2O were present in shallow stable NBLs, a factor of 1.5 change in h_{NBL} caused F_{N2O} to differ by <2%. In Fresno, F_{N2O} differences were up to 6%, but typically much smaller. In Bakersfield and Porterville, F_{N2O} differences were on average 10% and 14%, respectively. Regarding $h_{NBL}(t)$, we compared F_{N2O} assuming 5 hours of logarithmic versus linear growth. Changes in the shape of NBL growth caused F_{N2O} differences of just ~4% everywhere. To constrain errors from the lack of ΔN_2O measurements at t_0, we compared F_{N2O} calculated if $\Delta N_2O(t = t_0)$ equaled $\Delta N_2O(z = h_{FM})$ to F_{N2O} if $\Delta N_2O(t = t_0)$ equaled mean nocturnal RL ΔN_2O. Because Hanford was a major source area, we expected the smallest F_{N2O} differences here, which is what we observed with F_{N2O} uncertainties of 10%. Errors defined in this way were larger in Fresno, Porterville, and Bakersfield, where they were on average 23–100%. Individual uncertainties were considered uncorrelated and added in quadrature.

Accurately calculating F_{N2O} by Eq. 1 using P-3 profiles is predicated on the aircraft having flown low enough to sample NBL ΔN_2O (ΔN_2O below h_{FM}). In the wintertime, h_{NBL}s were typically less than 100 m AGL in Bakersfield and Hanford, an altitude region difficult to access by aircraft. When NBLs were this shallow, interpretation of $\frac{\partial \Delta N_2O}{\partial z}$ required caution as elevated low-altitude surface enhancements may have reflected ΔN_2O at some point through entrainment transition zone, not ΔN_2O below h_{FM}, causing F_{N2O} to falsely vary with h_{NBL}. Visual inspection of measured $\frac{\partial \Delta N_2O}{\partial z}$ indicated representative surface ΔN_2O were captured when there were multiple points with similar mixing ratios below h_{FM}. In Hanford, on Jan 22 and Jan 30–31, $\frac{\partial \Delta N_2O}{\partial z}$ appeared to

extend through the NBL and F_{N2O} were independent of h_{NBL}; however, on Jan 20 and 21, corresponding to nights with h_{NBL}s of <60 m AGL, the P-3 may have missed a portion of near surface ΔN_2O and F_{N2O} may be underestimated.

Upscaling and Atmospheric Relevance. Mean F_{N2O} in Hanford (740 mg ha^{-1} h^{-1}) would equal 3 Gg N_2O yr^{-1} if averaged over the DISCOVER-AQ Hanford area (2.9 x 10^3 km^2) and temporally upscaled assuming no seasonal or diurnal variability. For comparison, Jeong et al.[35] inferred emissions of 20–35 Gg N_2O yr^{-1} for the entire SJV air basin (6.1 x 10^4 km^2) using inverse modeling and data from six monitoring sites throughout California. While the highest F_{N2O} spatially correlated with N_2O enhancement ratios representative of dairies/livestock sources, the Hanford area, as defined here, represented a smaller portion of SJV-wide dairy landcover (Fig. 1c). CARB estimates of dairy manure management are reported annually per animal, and, averaging across waste management practices for cows/heifers, equal ~1 kg N_2O $animal^{-1}$ yr^{-1}.[98] Daily aircraft-based F_{N2O} (in units kg N_2O yr^{-1}), divided by the number of cows/heifers within daily Hanford source area (on average ~275,000 animals),[109] were on average 6–14 kg N_2O $animal^{-1}$ yr^{-1} (no seasonal or diurnal differences). In the larger SJV up to Modesto (region defined by 34.0° N, 121.0° W; 38.0° N, 117.1° W), there were 1.87 x 10^6 dairy cows on record in 2018;[109] using aircraft-based per cow estimates, we would predict 11–26 Gg N_2O yr^{-1}, in approximate agreement with the range of statewide emissions from manure management modeled by Jeong et al.[35] While CARB per cow estimates are uncertain and trace gas emissions vary across facilities from differences in waste management practices,[110] our results suggest they are also underestimated.

Although we were unable to distinguish or attribute F_{N2O} to emissions from cultivated fields, short-duration N_2O pulses as large as ~500–6000 mg N_2O-N ha^{-1} h^{-1} have been measured (using soil chambers) and modeled over fertilized alfalfa and winter wheat fields in California in January–February; however, between pulses, emissions are near zero.[111-114] Estimated fallow season F_{N2O} for almond and grapes are 39% and 64% of total annual emissions (9–290 mg N_2O-N ha^{-1} h^{-1}), respectively, and wintertime dairy forage constitutes 7–97% of annual emissions (440–1400 mg N_2O-N ha^{-1} h^{-1}),[115] but fluxes may be up to an order of magnitude higher.[116] While most of this N_2O would be released during the first winter precipitation event, emissions could continue with subsequent rainfall depending on nitrogen availability, with pulses up to 400 mg N_2O-N ha^{-1} h^{-1} reported over wheat fields January–February.[111] One factor potentially responsible for low F_{N2O} from crop agriculture could have been that from Jan 1–Feb 1, only 0.58 inches of rain fell (data from Fresno), with 0.47 inches falling on Jan 6, weeks before DISCOVER-AQ.[117]

F_{N2O} were derived from measurements representing winter nights and should therefore be cautiously compared to annual emission rates. First, extrapolating hourly nighttime F_{N2O} would likely underestimate daily emission totals. Higher daytime F_{N2O} have been reported in the nitrogen-rich systems of recently fertilized soils.[102] During DISCOVER-AQ, variability in enhancement ratios in different atmospheric layers, which interacted with the surface at different times of day, also suggested higher daytime F_{N2O}, a result observed in other locations with dairy/livestock sources.[95] Second, the biogeochemical factors controlling F_{N2O} from fertilized soils and manures should cause greater F_{N2O} in the spring and summer than in winter. On an annual basis, the largest N_2O sources have been shown to be fertilized soils, with peak emissions

from this sector in March–May.[4, 29] Wintertime studies miss this portion of F_{N2O} and projections from winter emissions potentially underestimate total annual F_{N2O} and over-represent the contribution of animal agriculture. Previously, a positive matrix factorization (PMF) analysis of tower-based data collected near Sacramento, concluded that as much as 95% of December–January F_{N2O} were from dairy/livestock operations.[118] During May–June, Guha et al.[28] estimated dairy contributions of 60–70% (also using PMF) in air masses advected to Bakersfield that passed over Hanford the same day,[99] suggesting some fluxes from cultivated fields are not captured in wintertime experiments. However, there remain uncertainties in F_{N2O} seasonality in the SJV, as marginal winter-spring differences in F_{N2O} have also been found,[35] explained by California's climate allowing for year-round crop agriculture compared to the U.S. Midwest.[119] There were benefits to conducting this study in January–February, as wintertime atmospheric conditions facilitated application of NBL-budgeting, in particular, surface winds were slow and disorganized such that ΔN_2O were mostly co-located with emitters, LLJ influences were minimal, and shallow ABLs contributed to ΔN_2O that were unambiguous from the free troposphere background, even away from sources.

Finally, while F_{N2O} are generally characterized by hot spots and hot moments, making chamber measurements difficult to upscale;[12] during DISCOVER-AQ, we found sources spatially integrated to give a hot region on scales of thousands of km^2 that persisted day-to-day. Elsewhere in the study region, including Fresno and Bakersfield, F_{N2O} were small to zero, which provided additional evidence that urban combustion/transportation were negligible local N_2O sources. Combining enhancement ratio analysis and NBL budgeting, we concluded animal agriculture was the dominant wintertime F_{N2O} source in the DISCOVER-AQ study region. Our results imply

efforts should focus on reducing F_{N2O} from manure management to decrease SJV N_2O emission totals.

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Supporting Information available. Vertical profiles for each day and species used to identify *h*, *h* summary tables and comparison figure, O_3, NO_2, and NO ground-based time series used to

determine t_0, nighttime wind vector frequency map, and RASS wind profiler measurements. This material is available free of charge at http://pubs.acs.org.

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