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Key Points:

- IASI NH_3 columns agree well with those derived from boundary layer, in-situ measurements with no significant biases at the pixel scale
- Validation in a hotspot region shows best agreement at narrow spatiotemporal scales on the order of the pixel size and mean wind speed
- Additional accurate, airborne-based NH_3 datasets are critically needed for improved validations across a range of environments

Abstract

Satellite ammonia (NH_3) observations provide unprecedented insights into NH_3 emissions, spatiotemporal variabilities and trends, but validation with in-situ measurements remains lacking. Here, columns from the Infrared Atmospheric Sounding Interferometer (IASI) were intercompared to boundary layer NH_3 profiles derived from aircraft- and surface-based measurements primarily in Colorado, USA, in summer, 2014. IASI-NH_3 version 3 near real-time dataset compared well to in-situ derived columns (windows ±15 km around centroid, ±1 hour around overpass time) with good correlation (r=0.58), a slope near unity (0.78±0.14), and an intercept of $2.1\times10^{15}\pm1.5\times10^{15}$ molec cm^{-2}. Agreement degrades at larger spatiotemporal windows, consistent with the short atmospheric lifetime of NH_3. We also examined IASI version 3R, which relies on temperature retrievals from the ERA Reanalysis and a third product generated using aircraft-measured temperature profiles. The overall agreements improve slightly for both cases. Because no bias is observed within the combined measurement errors, spatiotemporal averaging of IASI over large windows can be used to reduce retrieval noise. Nonetheless, sampling artifacts of airborne NH_3 instruments result in significant uncertainties of the in-situ-derived columns. For example, large validation differences exist between ascent and descent profiles, and the assumptions of the free tropospheric NH_3 profiles used above the aircraft ceiling significantly impact the validation. Because short-lived species like NH_3 largely reside within the boundary layer with complex vertical structures, more comprehensive validation is needed across a wide range of environments. More accurate and widespread in-situ NH_3 datasets are therefore needed for improved validations of satellite products.

Plain Language Summary

Ammonia is an important species in the atmosphere that creates particulate pollution such as haze, but it is challenging to measure especially from space. Major sources of ammonia include agricultural activities. Improving our estimates of the emissions require widespread and frequent measurements such as those from satellite. To date, satellite-based ammonia measurements have not been extensively validated, particularly on the scale of individual measurements. We have compared satellite ammonia measurements with those from ground-based and aircraft measurements and show that satellite measurements are accurate at the pixel scale of an

individual measurement. However, we also show that it is important to consider the spatial and temporal differences between the measurement scales (satellite vs. ground- and aircraft-based) in regions where ammonia is concentrated, and large sources exist. Improved validations will require advances in airborne ammonia measurement technologies, particularly for the relatively low levels of ammonia that exist above the atmospheric boundary layer. Finally, additional airborne-based measurements are needed to compare to satellite-based measurements in other regions and seasons to extend these results more globally.

1. Introduction

Gas-phase ammonia (NH_3) is a ubiquitous base in the atmosphere and an important component of the nitrogen cycle. Atmospheric NH_3 reacts with sulfuric acid and nitric acid to form ammoniated (NH_4^+) aerosol particles, reducing visibility and causing adverse effects on human health (Mensink & Deutsch, 2008; Ostro *et al.*, 2015; Wang *et al.*, 2006). Ammoniated aerosols also affect the climate by scattering solar radiation, resulting in a negative radiative forcing (IPCC, 2013). Excess NH_3 deposited to ecosystems can cause soil acidification, water eutrophication and losses of biodiversity (Galloway *et al.*, 2004). Research suggests that NH_3 and NH_4^+ have become increasingly important in dry and wet deposition of reactive nitrogen (N_r) in most parts of the United States due to reductions in nitrogen oxides (NO_x) emissions (Li *et al.*, 2016).

Agricultural activities such as fertilizer application and livestock waste management contribute to over 80% of total NH_3 emissions globally (Bouwman *et al.*, 1997; Paulot *et al.*, 2014). Other anthropogenic sources of NH_3 include chemical production, residential waste and vehicle emissions (Behera *et al.*, 2013; Sun *et al.*, 2017; Van Damme *et al.*, 2018). Global NH_3 emissions are expected to increase in the forthcoming decades due to growing food demands (Erisman *et al.*, 2008; Lamarque *et al.*, 2011). NH_3 is unregulated in many countries, but active efforts are being made to quantify NH_3 emissions and understanding their trends and distributions on regional to global scales (Paulot *et al.*, 2014; Van Damme *et al.*, 2018). There remain significant uncertainties in bottom-up NH_3 emission inventories as they require representative measurements to scale from a small subset of sources to the entire global budget (Beusen *et al.*, 2008; Golston *et al.*, 2020; Zhang *et al.*, 2018). On the other hand, top-down approaches that depend on inverse modeling of NH_4^+ wet deposition data require widespread observations, accurate vertical profiles, and chemical and deposition lifetimes (Paulot *et al.*, 2014; Zhu *et al.*, 2013). However, current major monitoring networks such as the Ammonia Monitoring Network (AMoN) in the U.S. and the Nationwide Nitrogen Deposition Monitoring Network (NNDMN) in China lack the spatial coverage and temporal resolution needed to fully resolve the variabilities of NH_3, thereby introducing uncertainties in top-down estimates of NH_3 emissions (NADP, 2019; Xu *et al.*, 2015).

In the past decade, advances in remote sensing techniques have provided unprecedented global coverage and medium-term time series for studying NH_3 on a broader scale not achievable by ground-based measurements. Since the early 2000s, several satellites have been launched into space with infrared sounders to measure atmospheric constituents. Examples of satellite NH_3 instruments are the Tropospheric Emission Spectrometer (TES) (Shephard *et al.*, 2011), Infrared Atmospheric Sounding Interferometer (IASI) (Clarisse *et al.*, 2009; Van Damme *et al.*, 2017; Whitburn *et al.*, 2016), Cross-track Infrared Sounder (CrIS) (Shephard & Cady-Pereira, 2015),

Atmospheric Infrared Sounder (AIRS) (Warner *et al.*, 2016) and Greenhouse Gases Observing Satellite (GOSAT) (Someya *et al.*, 2019). Launched in 2004 and having ended its mission in 2018, TES provided the first satellite-based NH_3 product, though it only performed limited measurements in its later years (Rasmussen, 2018). IASI provides Level-2 (L2) NH_3 products dating back to 2008 with much broader spatial coverage than TES. AIRS has the longest data record of NH_3 on a single satellite between 2002 and 2016 (Warner *et al.*, 2017). CrIS and GOSAT are more recently developed NH_3 products with limited availability at this time (Dammers *et al.*, 2019).

Despite the increasing use of satellite NH_3 products for inventory assessments, nitrogen deposition, and aerosol chemistry, validations of satellite NH_3 measurements, especially those against independent in-situ measurements, remain limited *(Dammers et al., 2019; Van Damme et al.*, 2018; Zhang *et al.*, 2018). Although averaged satellite data over a large domain can be used to study regional and global characteristics of NH_3, validations of individual satellite pixels help further understand the capabilities and constraints of satellite observations. Meanwhile, analyses of satellite NH_3 on fine temporal (e.g. daily and weekly) and local scales, such as fertilizer emissions, require validation for increased confidence (Fortems-Cheiney *et al.*, 2016; Van Damme *et al.*, 2018). Previously, Van Damme *et al.* (2015) used an averaged GEOS-Chem model profile to convert IASI NH_3 columns into surface concentrations and found fair agreements between IASI and ground-based observations on monthly scales, and moderate correlations with hourly airborne data, but the fixed profile shapes used for the conversion introduced certain biases in IASI surface concentration estimations. Dammers *et al.* (2016) validated IASI using column measurements from ground-based high-resolution Fourier-transform infrared spectroscopy (FTIR) at nine locations worldwide with spatial and temporal windows of 25 km and 90 min, respectively. Good agreements ($r \sim 0.8$) were found where NH_3 levels were high, though the study removed outliers during wintertime. In addition, the FTIR measurements themselves have not been validated by in-situ profiles and instead rely upon model a priori and limited surface observations *(Dammers et al.*, 2015). Similarly, a comparison between CrIS and FTIR was conducted by Dammers *et al.* (2017), where an overall good correlation was observed, but the agreements for individual sites varied largely. Using a different method, Sun *et al.* (2015) conducted a validation of TES NH_3 with collocated aircraft and mobile lab measurements in California at the pixel scale and found the agreement to be within 10% for selected dates. Furthermore, the spatial variability of NH_3 columns within a satellite pixel (IASI: ~ 12 km in diameter) has been assessed over Colorado using structure functions analyses of mobile NH_3 column observations conducted on fine spatial scales (few 10 meters; Follette-Cook *et al.*, 2015; Kille *et al.*, 2017). During the time of this study, Kille *et al.* (2017) found 50% of variability in NH_3 columns at distances less than approximately 1.6 km, and 90% of variability at distances less than 6 km. The high atmospheric NH_3 variability poses a fundamental sampling challenge to satellite validation on the pixel scale and illustrates the need for a multi-platform sampling strategy for best results.

To expand the scope and robustness of satellite NH_3 validations, we compare the IASI NH_3 at the pixel scale with a combination of aircraft-based profiles and an assortment of other in-situ and mobile column surface observations taken during the summer of 2014 in Colorado, USA, with some insight on the winter of 2013 in California, USA. The general approach used here can be readily applied to other satellite NH_3 products, provided that NH_3 vertical profiles are nearly collocated with the satellite pixels within a temporal window that is consistent with wind and atmospheric transport.

2. Data and Methods

2.1. IASI Observations

IASI is an infrared sounder onboard the polar-orbiting Metop-A/B/C satellites, which were respectively launched in 2006, 2012 and 2018 (Clerbaux *et al.*, 2009). It is sensitive to NH_3 absorption features mainly between 800 and 1200 cm^{-1} (Clarisse *et al.*, 2010; Coheur *et al.*, 2009). IASI provides twice-daily measurements of NH_3 with overpass times of 0930/2130 local solar time (LST). IASI has a swath of 2400 km and a pixel size of 12 km in diameter at nadir. The first IASI NH_3 product was retrieved using lookup tables (LUTs) based on simulations from a forward radiative transfer model. A hyperspectral range index (HRI) was calculated from each observation and converted to NH_3 columns using the LUTs (Van Damme *et al.*, 2014). A subsequent version (ANNI-NH3-v1) improved the retrieval of NH_3 by using an artificial neural network for IASI (ANNI) to transform the calculated HRI into column densities (Whitburn *et al.*, 2016). Version 2 of the ANNI product further improved the algorithm by introducing separate neural networks for land and sea, and simplified input parameters. With the release of this version, an additional product was made available using meteorological retrievals from the European Centre for Medium-Range Weather Forecasts Re-Analysis (ERA)-Interim ECMWF for better interannual consistency, as opposed to using meteorological data from IASI itself to calculate columns (Van Damme *et al.*, 2017). It is emphasized that the ANNI-NH_3 products do not produce information on averaging kernel (AVK) because the current retrieval method is not based on optimal estimation (Whitburn *et al.*, 2016). Thus, only the unconstrained columns were used here to provide an overview of the agreement between IASI and in-situ measurements.

In this work, we analyze version 3 of the ANNI-NH_3 product from IASI Metop-A/B. This version, processed using the retrieval framework outlined in (Franco *et al.*, 2018), features a slightly increased measurement sensitivity due to small changes in the neural network architecture and training and improved post-filtering. In addition, several debiasing procedures have been introduced to correct for the gradual increase of CO_2 columns over the entire IASI time-period and for IASI instrument calibrations. Despite the significant number of changes from v2 to v3, the changes to the retrieved columns are modest in the mean. For columns above 4×10^{15} molec cm^{-2}, 80% of the data agree to within 20%. As infrared retrievals are known to be quite sensitive to auxiliary input data, we evaluate the following products: (1) The near real-time product, retrieved using meteorological data from the European Organisation for the Exploitation of Meteorological Satellites (EUMETSAT) with cloud coverage < 25%, (2) the reanalysis product, retrieved using meteorological data from ERA5/ECMWF with cloud coverage < 10%, and (3) a dedicated product retrieved using collocated in-situ temperature profiles from aircraft, sonde and mobile measurements (other meteorological data such as skin temperature are from EUMETSAT) with cloud coverage < 25%. We only include the morning observations over land surfaces as IASI has better sensitivity to NH_3 under these conditions.

2.2. In-situ Measurements

The Deriving Information on Surface conditions from Column and Vertically Resolved Observations Relevant to Air Quality (DISCOVER-AQ) field experiment was a multi-year campaign led by the National Aeronautics and Space Administration (NASA) (Crawford & Pickering, 2014). Its mission was to validate collocated satellite observations of atmospheric

pollutants over four regions in the U.S. (Baltimore/Washington, California, Houston, and Colorado). Airborne NH_3 measurements were only available in the California and Colorado campaigns, the foci of this study. The California campaign occurred between January 16 and February 7, 2013 over the San Joaquin Valley. In the following year, the experiment was continued in Colorado from July 16 to August 16, along with a complimentary National Science Foundation (NSF) Front Range Air Pollution and Photochemistry Experiment (FRAPPÉ) that had additional platforms and NH_3 measurements (Flocke *et al.*, 2020). The DISCOVER-AQ flight patterns were specifically designed for satellite validations as the P-3B aircraft made repeated upward and downward spirals at several designated locations for the construction of vertical profiles. A typical P-3B spiral roughly spanned 5 km in diameter, which were particularly advantageous for validations of short-lived species such as NH_3 that exhibits strong spatial gradients near source regions.

A unique aspect of the 2014 Colorado campaign compared to past field experiments was the comprehensive suite of NH_3 measurements on multiple platforms: two aircraft, a tall tower, and four mobile laboratories. The NASA P-3B aircraft measured NH_3 with a proton-transfer time-of-flight mass spectrometer (Müller *et al.*, 2014). The NSF/NCAR C-130 aircraft measured NH_3 with a closed-path, quantum cascade laser-based instrument using a fast-response inertial inlet to minimize sampling artifacts (QC-TILDAS, Aerodyne Research Inc.) (Schiferl *et al.*, 2016). A moving carriage on the Boulder Atmospheric Observatory's (BAO) 300 m tall tower in Erie, Colorado made profiles every hour and was equipped with a closed-path, quantum cascade laser-based NH_3 instrument (QC-TILDAS, Aerodyne Research Inc.) (Tevlin *et al.*, 2017). The mobile laboratories included in-situ measurements from an open-path, quantum cascade laser-based instrument onboard the Princeton Atmospheric Chemistry Experiment, a cavity ring down instrument (Picarro G2103) onboard the NOAA Chemical Sciences Division (CSD) van, and a closed-path, quantum cascade laser-based instrument (QC-TILDAS) on the Aerodyne Mobile Laboratory (Eilerman *et al.*, 2016; Herndon *et al.*, 2005; Tao *et al.*, 2015). These three mobile laboratories conducted a stationary and moving intercomparison and showed agreement to within 10% on average (Golston *et al.*, 2020). Column NH_3 abundances were measured by the University of Colorado Solar Occultation Flux (CU SOF) instrument onboard the CU/NCAR mobile laboratory (Kille *et al.*, 2017). CU SOF couples a digital fast solar tracker (Baidar *et al.*, 2016; Patent No. 10379194, 2019) to a fast scanning FTIR to measure the vertical column integral of NH_3 and other gases above the mobile platform directly in the open atmosphere (Kille *et al.*, 2017). Table 1 summarizes the performances of the NH_3 instruments during the two campaigns.

In addition to the NH_3 measurements, temperature and pressure measurements were taken from the P-3B aircraft and specially launched radiosondes (iMet-1 & Vaisala RS92) timed with aircraft flights. These data allowed for the construction of in-situ derived NH_3 columns and for the generation of IASI NH_3 measurements with in-situ temperature measurements as input. For the determination of atmospheric mixed layer height (MLH) used in the construction of in-situ NH_3 profiles, we examined P-3B aircraft profiles of other short-lived species with sources in this region including nitrogen dioxide (NO_2) (Weinheimer *et al.*, 1994), ethane (C_2H_6) from gas-oil activities (Yacovitch *et al.*, 2014), and the number concentration of particles (CN) with diameters > 10 nm from the LARGE instrument (Beyersdorf *et al.*, 2016). Additional MLH measurements were incorporated from the High Spectral Resolution LIDAR (HSRL2) instrument onboard the

NASA B200 aircraft (Scarino *et al.*, 2014). Table 2 lists the dates on which each platform was functional during these campaigns.

Table 1. *Summary of in-situ NH_3 measurements during DISCOVER-AQ*

Platform	Method	Typical uncertainty	Referenced Work
California (2013)			
NASA P-3B aircraft	PTR-MS	± 35%	(Müller *et al.*, 2014)
NASA P-3B aircraft	CRDS	± (35% + 1.7 ppbv) + 0.2 ppbv[a]	(Schiferl *et al.*, 2016)
Princeton mobile	Open-path QCL	± 20%	(Miller *et al.*, 2015)
Colorado (2014)			
NASA P-3B aircraft	PTR-MS	± 35%	(Müller *et al.*, 2014)
NSF/NCAR C-130 aircraft	QC-TILDAS	± (22% + 0.305 ppbv) + 0.058 ppbv[a]	(Ellis *et al.*, 2010; Schiferl *et al.*, 2016)
Aerodyne mobile	QC-TILDAS	± (22% + 0.305 ppbv) + 0.058 ppbv[a]	(Ellis *et al.*, 2010; Schiferl *et al.*, 2016)
Princeton mobile	Open-path QCL	± 10% + 0.2 ppbv[a]	(Miller *et al.*, 2014; Tao *et al.*, 2015)
CU/NCAR mobile	SOF	± 4.4% + 1×10^{15} molec cm^{-2} [a]	(Kille *et al.*, 2017)
NOAA CSD mobile	CRDS	± 20% + 1 ppbv[a]	(Eilerman *et al.*, 2016)
NOAA BAO tower	QC-TILDAS	± 20% + 0.5 ppbv[a]	(Tevlin *et al.*, 2017)

Note. PTR-MS = proton transfer reaction-mass spectrometer; CRDS = cavity ring down spectrometer; QCL = quantum cascade laser; NSF = National Science Foundation; NCAR = National Center for Atmospheric Research; QC-TILDAS = quantum cascade tunable infrared laser direct/differential absorption spectroscopy; CU = University of Colorado; SOF = Solar Occultation Flux. BAO = Boulder Atmospheric Observatory. Uncertainties are presented as reported in archived field data catalog and/or related publications. Subscripts in the third column: [a] uncertainty + limit of detection.

Table 2. *Availability of in-situ NH_3 measurements in DISCOVER-AQ California in 2013 (upper table) and Colorado in 2014 (lower table). Colored and blank cells represent dates when data from each platform were or were not available, respectively.*

Platform \ Date	1/16	1/17	1/18	1/19	1/20	1/21	1/22	1/25	1/26	1/27	1/28	1/29	1/30	1/31	2/1	2/3	2/4	2/5	2/6	2/7
NASA P-3B (PTR-MS, A.Wisthaler)																				
NASA P-3B (CRDS, J. Nowak & A. Neuman)																				
Princeton mobile (Open-path QCL, M. Zondlo)																				

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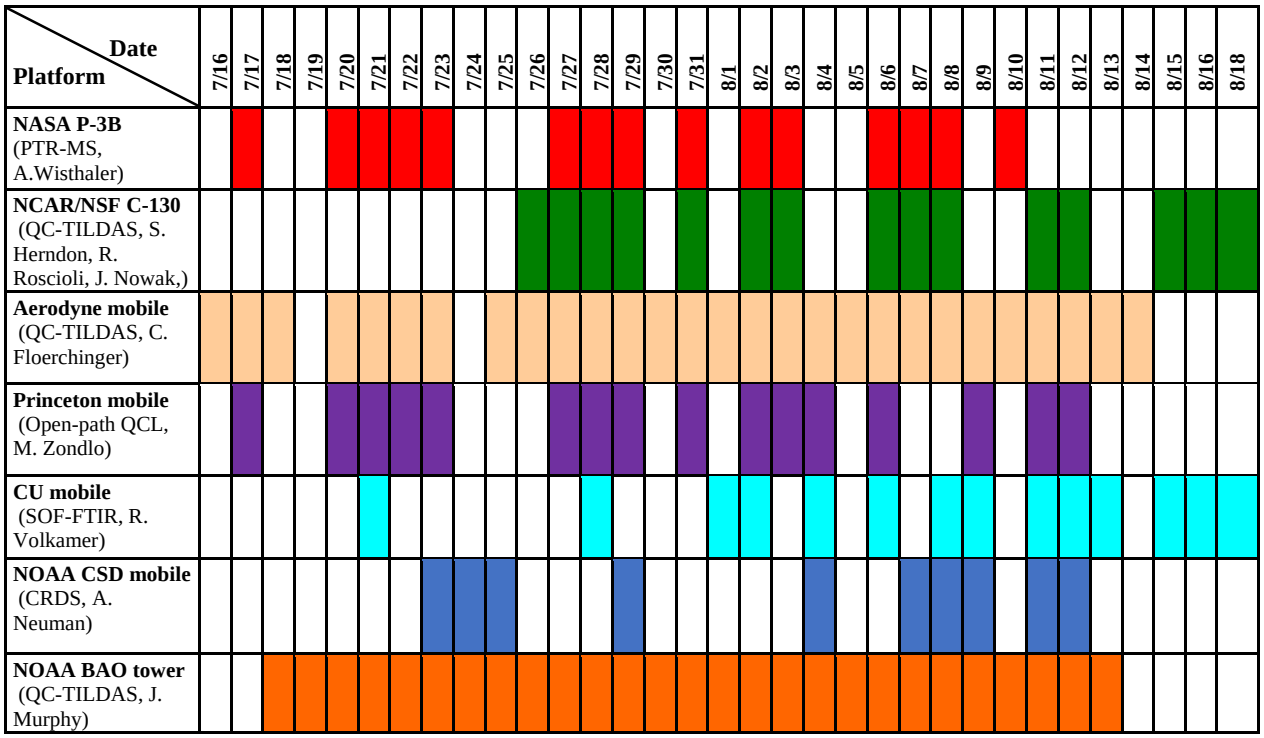
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NASA P-3B (PTR-MS, A.Wisthaler)
NCAR/NSF C-130 (QC-TILDAS, S. Herndon, R. Roscioli, J. Nowak,)
Aerodyne mobile (QC-TILDAS, C. Floerchinger)
Princeton mobile (Open-path QCL, M. Zondlo)
CU mobile (SOF-FTIR, R. Volkamer)
NOAA CSD mobile (CRDS, A. Neuman)
NOAA BAO tower (QC-TILDAS, J. Murphy)

2.3. Validation Algorithm

2.3.1. Spatiotemporal filtering

The general framework of the validation algorithm used in this study is shown in Figure 1. For each valid IASI observation, we applied a spatiotemporal window centered on the pixel's center location and overpass time to filter for DISCOVER-AQ data within the designated window. For example, if an in-situ measurement was made inside a certain spatial distance (e.g. ±15 km) from the center of the IASI pixel, and the time difference relative to the IASI overpass time was within the temporal window (e.g. ±60 min), the measurement was considered valid for comparison. This applied to all in-situ NH_3 measurements and other relevant data (e.g. radiosondes). The only exception was the P-3B aircraft profiles, where we included all the data in a vertical profile if the geographical center (mean latitude and longitude) of the aircraft spiral fell inside the spatial window. Next, in-situ NH_3 measurements located within the spatiotemporal window were aggregated into one dataset. Each collocation between IASI and in-situ measurements required at least one aircraft profile available so that an NH_3 vertical profile could be constructed. Figure 2 shows an example of collocation between IASI and in-situ measurements on July 27, 2014. The location of IASI pixel centroid, denoted as a "+", is positioned in the center with its footprint boundary outlined as a solid white ellipse. The spatial window (in this case, ±15 km) is plotted as a dotted white circle. For demonstration purposes, the ±3 hour temporal window is chosen to include as many measurements as possible. The route of each in-situ platform is marked with a different color. In this example, in-situ NH_3 measurements were available from P-3B, C-130, Princeton mobile lab and BAO tower.

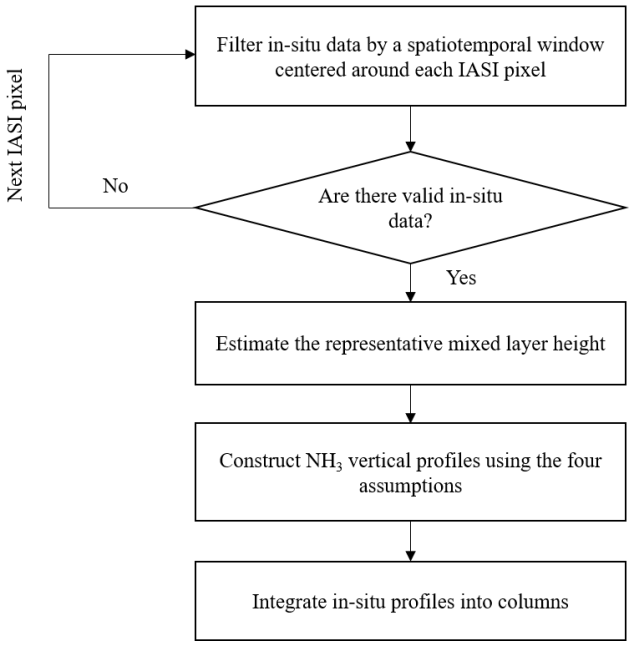


Figure 1. Overview of the validation algorithm. The flowchart is repeated for each valid IASI pixel. If no in-situ data are found near the pixel, the pixel will be skipped, and the next available pixel will be scanned for collocation. The four scenarios in box 4 are described in section 2.3.2 and illustrated with an example in Figure 3.

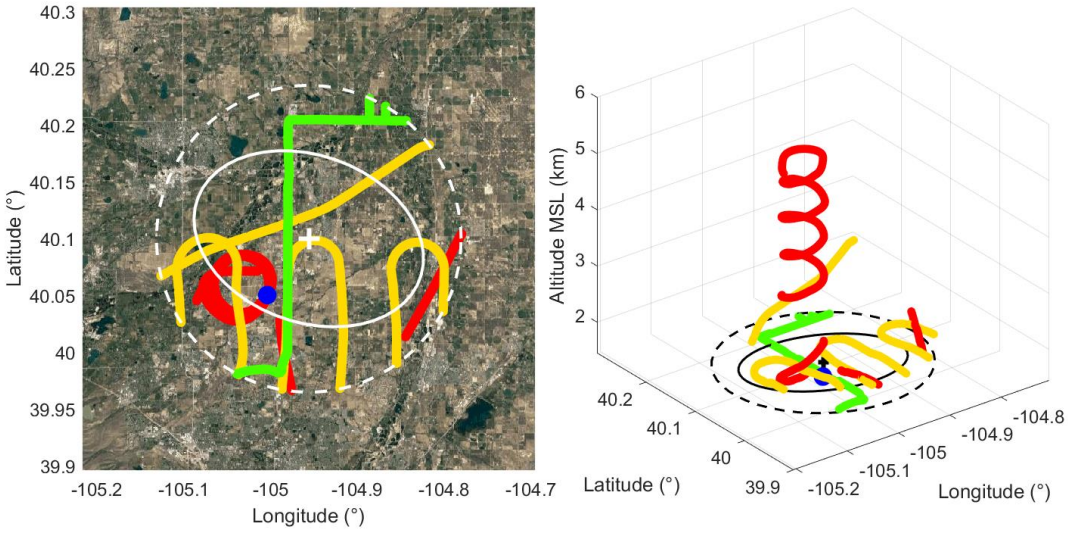


Figure 2. Example of collocated IASI and in-situ measurements on July 27, 2014 at 17:34:09 UTC. The left panel shows a two-dimensional view from the top and the right panel visualizes the movements of the in-situ platforms in a three-dimensional view. The center of the IASI pixel is denoted as "+". The solid ellipse marks the boundary of the IASI pixel. The dotted circle represents the ±15 km spatial window. The temporal window is ±3 hour in this case. Colored lines show the routes of the in-situ platforms: red = P-3B, yellow = C-130, green = Princeton mobile lab, blue dot = BAO tower. The 2D figure is overlaid on Google Maps (Google, Inc.) for better visualization of the geographical location and topography.

2.3.2. Reconciling uncertainties in NH_3 profiles

The combined in-situ dataset was then used to calculate the integrated column density of NH_3. Two issues remained, however, in the construction of the in-situ-derived columns. First, because the aircraft ceiling on most spirals was limited to ~ 5 km above sea level, it was necessary to assume NH_3 concentrations in the middle and upper troposphere. Even though NH_3 is expected to accumulate mostly in the boundary layer because of its short-lifetime on the order of hours to days (Dentener & Crutzen, 1994; Seinfeld & Pandis, 2016), NH_3 has been measured in the middle and upper troposphere previously (Whitburn *et al.*, 2016). Höpfner *et al.* (2016) for instance measured NH_3 levels in the upper troposphere to be tens of parts per trillion by volume (1 pptv = 10^{-12} mol/mol) in the outflow of the active Monsoon system. However, the free tropospheric NH_3 background was below the detection limit (< 3-5 pptv). More recently, Höpfner *et al.* (2019) found that NH_3 concentrations in the upper troposphere could reach up to 1 ppbv in some regions during the Asian monsoon season, but were low in most other places. Other studies that measured NH_3 profiles showed sharp decreases of NH_3 mixing ratio over altitude (Nowak *et al.*, 2010), and low NH_3 (< 1 ppbv) at similar altitudes (Hoell *et al.*, 1980; Ziereis & Arnold, 1986). Based on this evidence, it is reasonable to argue that NH_3 concentrations in the upper troposphere are negligible compared to the lower troposphere. Second, a problem remained on how to deal with NH_3 concentrations measured by the aircraft beyond the MLH. Previously, Sun *et al.* (2015) found that airborne NH_3 sensors (i.e. Picarro

CRDS and PTR-MS on the P-3B aircraft) in DISCOVER-AQ California exhibited sampling artifacts above the MLH due to long and variable instrument response times. Because DISCOVER-AQ CA and CO were in agricultural source regions, a strong gradient existed from very high levels within the boundary layer to nominally-clean free tropospheric levels. Such strong gradients can be problematic for accurately quantifying NH_3 with an instrument or inlet that has a time response slower than the rapid changes in ambient mixing ratios (Fehsenfeld *et al.*, 2002; Von Bobrutzki *et al.*, 2010).

Given these issues on the column construction from the aircraft data, we accounted for the lack of a full tropospheric profile, and sampling artifacts, by bracketing four possible scenarios of NH_3 distributions above the MLH in the troposphere. Figure 3 shows the case studies used to address the vertical profile in the free troposphere: (1) integrating NH_3 only up to the MLH, assuming negligible NH_3 concentrations above. Physically, this corresponds to the assumption that NH_3 is contained within the boundary layer and dominates the column measurement based on its short lifetime. It also assumes that sampling biases of instruments are large in and around the strong gradient of the mixed layer. (2) Integrating NH_3 up to the maximum aircraft altitude, assuming negligible NH_3 at altitudes higher than the aircraft ceiling. This assumes that aircraft NH_3 measurements above the MLH are valid and real signals, but no extrapolation is done beyond the aircraft range. (3) Integrating NH_3 up to the tropopause with linear interpolation of decreasing mixing ratios from the maximum aircraft altitude to zero at the tropopause estimated from sonde temperature profiles. In the real atmosphere, NH_3 is removed from the atmosphere by reacting with nitric and sulfuric acids, and through dry deposition in the gas phase and wet deposition as NH_4^+ by cloud scavenging (Mensink & Deutsch, 2008; Mizak *et al.*, 2005; Nemitz, Milford, & Sutton, 2001). The linear interpolation represents a simplistic mode of decay of NH_3 concentrations over altitude via the removal pathways. (4) Integrating NH_3 up to the tropopause, while assuming constant NH_3 mixing ratio from the maximum aircraft altitude to the tropopause. The last scenario features a well-mixed free troposphere in which NH_3 distributes uniformly in the vertical direction. In all four scenarios, we assumed NH_3 was negligible further beyond the tropopause based on previous studies (Höpfner *et al.*, 2019, 2016). While the truth is not likely to be any of these exact scenarios, these case studies of the free tropospheric NH_3 distribution helped to bracket the magnitude and importance of the full NH_3 vertical profile that was not captured by the aircraft or caused by potential sampling problems in the in-situ measurements.

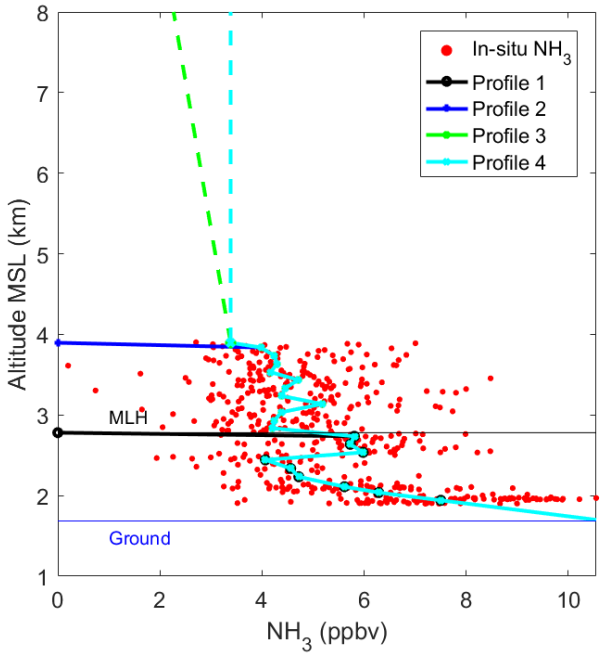
Knowing the representative MLH for each collocation was necessary for the integration of NH_3 profile in the first case. We estimated the MLH using three methods to minimize potential errors and mismatches due to geographical elevation differences within the window: (1) using the altitude of the first inversion of the temperature profile from the nearest timed sonde launch (which may not necessarily be in the exact spatiotemporal window), (2) using aerosol backscatter data from the B200 aircraft within the specified spatiotemporal window, and (3) derived from the vertical profiles of other, short-lived atmospheric tracers (NO_2, C_2H_6 and CN > 10 nm) measured by P-3B. The final MLH was calculated as the average of all available methods for each collocation.

2.3.3. Vertical integration

363 The available in-situ NH_3 measurements at 1 Hz were vertically binned every 100 m to
364 reduce noise, and the median value in each layer was used to build the final vertical profiles.
365 Median values were chosen because in-situ measurements on or near the ground immediately
366 downwind of sources (e.g. feedlots) would skew the mean to be unrepresentative of the overall
367 layer. When there was an altitude mismatch between the lowest in-situ bin and the ground at the
368 pixel's center location (i.e. in-situ altitude > IASI centroid altitude), the NH_3 mixing ratio at the
369 ground level was linearly extrapolated to the ground from the lowest bin. In cases where the
370 IASI centroid ground altitude was higher than in-situ locations, only measurements higher than
371 the ground altitude were included. Using the ideal gas law, the column NH_3 was integrated from
372 gas density over altitude:

373 $$\omega_{NH_3} = \int \frac{C_{NH_3} P_{air}}{k T_{air}} dz$$

374 where ω_{NH_3} is the column density of NH_3 in the same unit as IASI (molec cm^{-2}), C_{NH_3} is
375 the mixing ratio of NH_3 in air, P_{air} is the air pressure, k is the Boltzmann's constant, T_{air} is the
376 air temperature, and z is the altitude.



377

378 **Figure 3**. Four assumed NH_3 vertical profiles in this work. Profile 1 (black): integration up to
379 MLH with zero NH_3 above; Profile 2 (dark blue): integration up to maximum aircraft altitude
380 and zero NH_3 above; Profile 3 (green): integration up to tropopause with linear interpolation of
381 concentrations beyond aircraft altitudes to a value of zero at the tropopause; Profile 4 (turquoise):
382 integration up to tropopause assuming constant NH_3 beyond aircraft altitude. The median profile
383 from each assumption is shown with the interpolated sections above the aircraft altitude plotted
384 as dashed lines. In-situ NH_3 concentrations at 1 Hz are colored in red. The thin blue line

indicates the ground altitude at the IASI pixel center. The thin black line denotes the corresponding MLH in this case. Altitude MSL stands for altitude above mean sea level.

The in-situ temperature profiles used for generating the alternative IASI-NH_3 product described in section 2.1 were aggregated from the in-situ platforms in section 2.2 and filtered using the spatiotemporal window of interest. Sonde measurements of temperature were needed to fill in the gap of aircraft temperature measurements (e.g. near the ground, above the ceiling), yet in many cases a sonde could not be found within the window. Therefore, we always used the nearest sonde in time to construct the temperature profile, whether it was located within the specified spatial window. In California, however, this approach was not ideal in winter. Due to strong yet shallow inversions, there were often large discrepancies between the sonde temperatures and those measured by the aircraft, especially near the surface. To reduce errors due to separation in distance, we used P-3B aircraft temperatures where applicable and sonde measurements outside the aircraft altitude range for California. In Colorado in summer, the horizontal gradients of temperature were less pronounced, and temperature profiles measured by P-3B and a given sonde usually matched up very well. Therefore, temperature data from the two platforms were integrated together, while we further combined them with ground measurements of temperature (e.g. mobile labs) if available. The merged temperatures were grouped in bins of 100 m, and the mean value in each bin was used to make the final temperature profile.

2.3.4. Data coverage

We quantify data coverage contributions from each in-situ platform to the validation dataset using two approaches: (1) by the sum of total measurement time, and (2) by the number of cases when the platform collocated with IASI. Some measurements were counted more than once if they were found to collocate with IASI in multiple windows that we tested. Figure 4 shows that the P-3B aircraft that carried the PTR-MS instrument was the largest contributor to the in-situ dataset in Colorado, because we required each IASI-in-situ collocation to have an aircraft profile from P-3B (the C-130 aircraft, on the other hand, did not perform vertical profiles at fixed locations). The Princeton mobile lab and the BAO tower were operational on most days and became the next major contributors. Although each in-situ NH_3 instrument has a different uncertainty estimate (Table 1), we applied a 30% error to the entire in-situ dataset to approximate the overall instrument uncertainty. Because of potential systematic biases in the in-situ measurements, we did not use a weighted average of errors from different measurements within a given profile layer. Instrument biases were thought to be the limiting factors of the uncertainty in all the in-situ measurements of NH_3 mixing ratio, and unlike random errors, these would not be reduced through averaging.

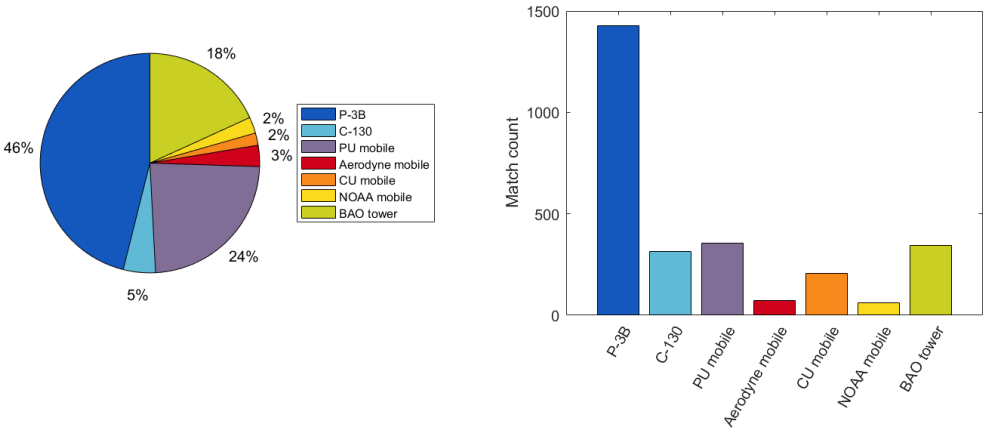


Figure 4. Data contribution from each in-situ platform in DISCOVER-AQ Colorado by (a) sum of total measurement time and (b) number of cases collocated with IASI. Statistics shown here are for all nine spatiotemporal windows tested in this study (total count of collocations = 1,426).

3. Results and Discussion

3.1. Comparison between Different In-situ Profiles

The four different scenarios of NH_3 profiles were quantitatively evaluated and compared based on the data in Colorado, given the larger suite of measurements in this campaign. For comparison purposes, we only show the comparison between in-situ and the reanalysis IASI product, but the overall conclusion holds true for the other two IASI products as well. The IASI reanalysis product versus the four in-situ profiles are plotted in Figure 5 with an orthogonal linear regression fit (MATLAB R2016b, MathWorks) that accounts for uncertainties in both the abscissa and ordinate variables. Profile 1 leads to the lowest column abundance among the four profiles because all the NH_3 measurements above the MLH are excluded. The column abundances increase sequentially from profile 1 to 4 as the contributions from the free troposphere increase. The correlation coefficient and slope between IASI and in-situ in Colorado indeed show a sequential degradation from profile 1 to 4 as extra NH_3 is added into the integration. We hypothesized in section 2.3 that the MLH assumption (profile 1) would be the closest representation of vertical distributions of NH_3 in the real atmosphere based on its short lifetime, emissions at the surface, and negligible amounts measured elsewhere in the free troposphere. Profile 1 shows the overall best agreement between IASI and in-situ, and this is consistent with the expectation that most NH_3 is accumulated within the boundary layer. We note that profile 2, which treats all aircraft data as valid, shows a similar correlation (though a factor of two difference in the slope). However, there are potential caveats associated with using the airborne measurements above the MLH given the sampling artifacts, which will be further discussed in section 3.5. All the correlations shown are tested to be statistically significant ($p<0.05$, same for all the analyses onward).

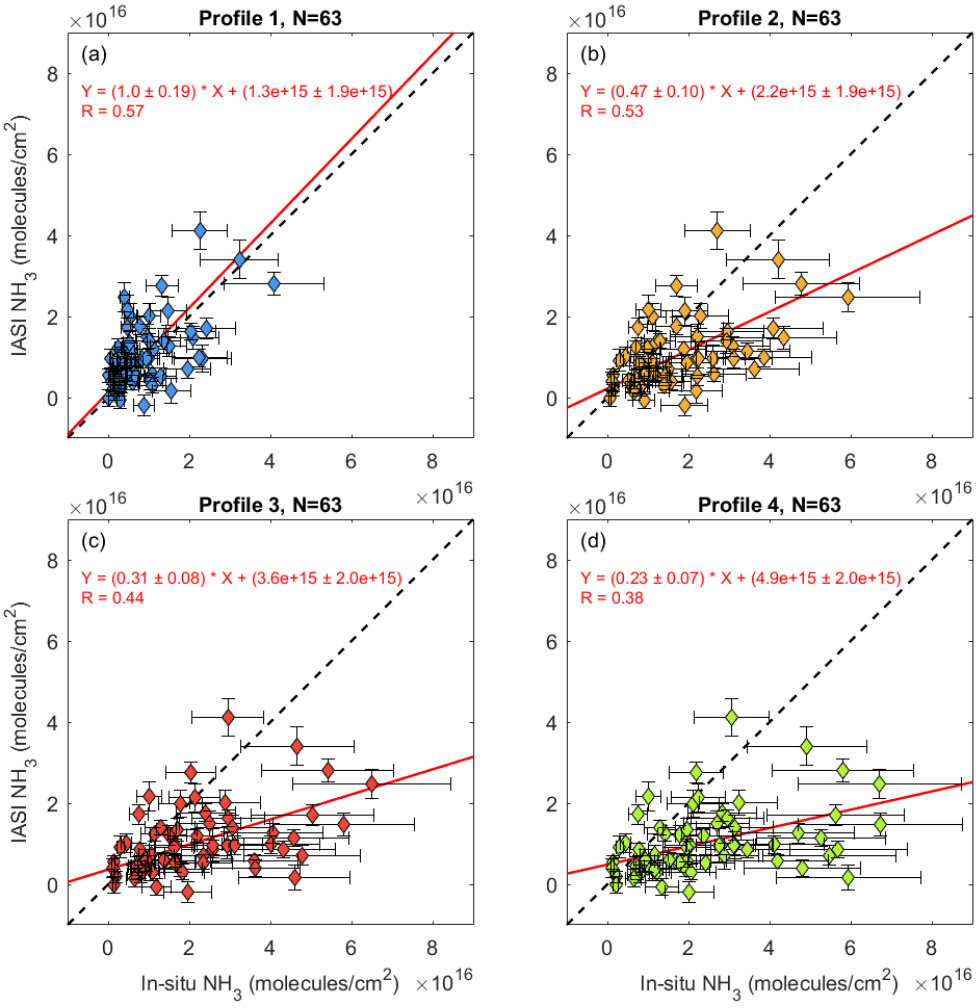


Figure 5. Reanalysis IASI product versus in-situ integrated columns from the four profiles for the ±15 km and ±60 min in Colorado. Profile 1: integration up to MLH; Profile 2: integration up to maximum aircraft altitude; Profile 3: integration up to tropopause assuming a linearly decreasing NH_3 mixing ratio beyond aircraft altitude; Profile 4: integration up to tropopause assuming constant NH_3 beyond aircraft altitude. Error bars indicate the uncertainties of columns.

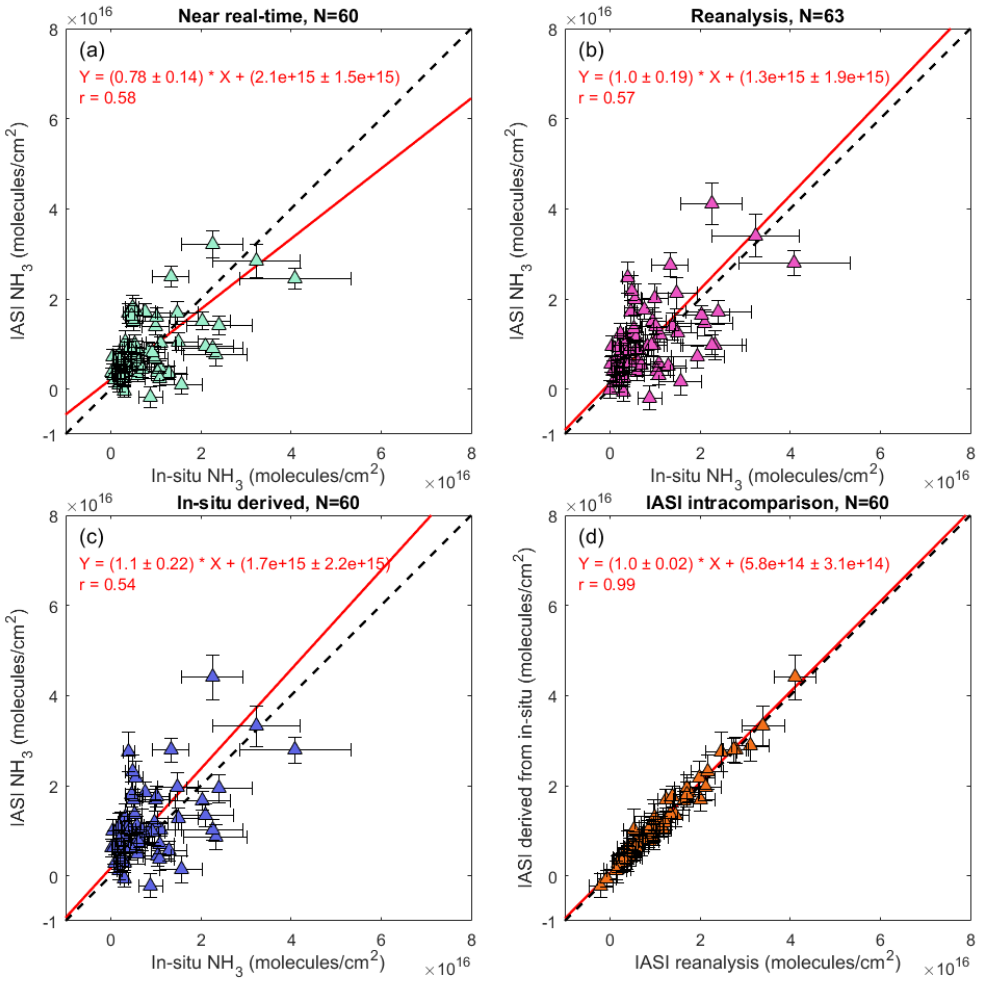
3.2. Comparison between Different IASI Products

The three IASI products described in section 2.1 were compared with vertically integrated in-situ columns under the MLH assumption (profile 1) within the ±15 km and ±60 min window in Colorado (Fig. 6). We determined the optimal size of the spatiotemporal window based on wind speeds in the boundary layer. To calculate typical boundary layer wind speeds, we used wind data measured at 300 m on the BAO tower located in Erie, CO (40.050° N, 105.004° W) from 0600-1200 local time during DISCOVER-AQ to bracket the IASI overpass times, which are always in the morning. The average wind speed during the campaign was 3.5±2.2 m s^{-1} (median: 3.1). The mean value is equivalent to a spatial window of approximately 15 km in diameter on an hourly scale. While we recognize that wind conditions may vary slightly among different regimes, we argue that a spatial window of ±15 km around the IASI centroids and a

temporal window ±60 min around the overpass times were internally consistent with one another and can be used to account for the transport of NH_3 under typical atmospheric conditions during this period.

The near real-time product comparing with in-situ columns integrated up to the MLH and within the ±15 km and ±60 min spatiotemporal window yielded a correlation coefficient of 0.58, an intercept of $2.1\pm1.5\times10^{15}$ molec cm^{-2} and a slope of 0.78±0.14. The reanalysis product showed no real changes in the correlation coefficient (0.57) and intercept ($1.3\pm1.9\times10^{15}$ molec cm^{-2}), but a slope closer to unity (1.0±0.19) was observed. The in-situ derived IASI product showed a similar correlation (0.54), slope (1.1) and intercept ($1.7\pm2.2\times10^{15}$ molec cm^{-2}). All the correlations are statistically significant. The intercepts for the three products are nearly indistinguishable from zero, particularly when compared to column amounts > 10^{16} molec cm^{-2}, suggesting that there is no significant absolute bias between the IASI and in-situ datasets.

Accurate temperature measurements are needed for NH_3 retrievals, especially in the lower layers of the atmosphere where errors in the temperature profile can affect the retrieved NH_3 columns significantly. The reanalysis product relies on gridded ECMWF meteorological data, and our results showed the robustness of this implementation, which allows for long-term consistent time series of IASI. The in-situ derived IASI product shows a slightly deviated slope from unity, but the fact that this product matched well with the reanalysis product (Fig. 6d) suggests that the retrievals are still internally coherent. The deviation may be attributed to the fact that the in-situ temperature profiles largely consisted of sonde data, and sonde measurements were not always representative of the IASI pixel in space and time. Our results are also consistent with previous findings that the historic near real-time product (before the May 4, 2016 and the release of the IASI L2 version 6.2 by EUMETSAT) has a low bias against the reanalysis product in version 2.1 of IASI NH_3 due an underestimation of the thermal contrasts between the surface and the air at the altitude of interest (Van Damme *et al.*, 2017). The differences in temperature inputs are further illustrated in Figure 7, where we plot the mean temperature profile used in the retrieval of each IASI product (left panel) and an example of a single observation (right panel). The different profile shapes and thermal contrast values explain why the retrieved column abundances vary. The largest thermal contrast (TC, shown as inset) between the surface temperature and skin temperature is found in the near real-time product, confirming the reason why the retrieved columns are biased low against the other two products.



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495 **Figure 6.** IASI-NH_3 products (a. near real-time, b. reanalysis, c. in-situ derived) versus the in-
496 situ NH_3 columns in Colorado based on the ±15 km and ±60 min window and MLH assumption.
497 The intracomparison between the reanalysis and in-situ derived IASI products is shown in (d).
498 Red line shows the best fit using orthogonal regression. Dashed line represents the 1:1 slope.

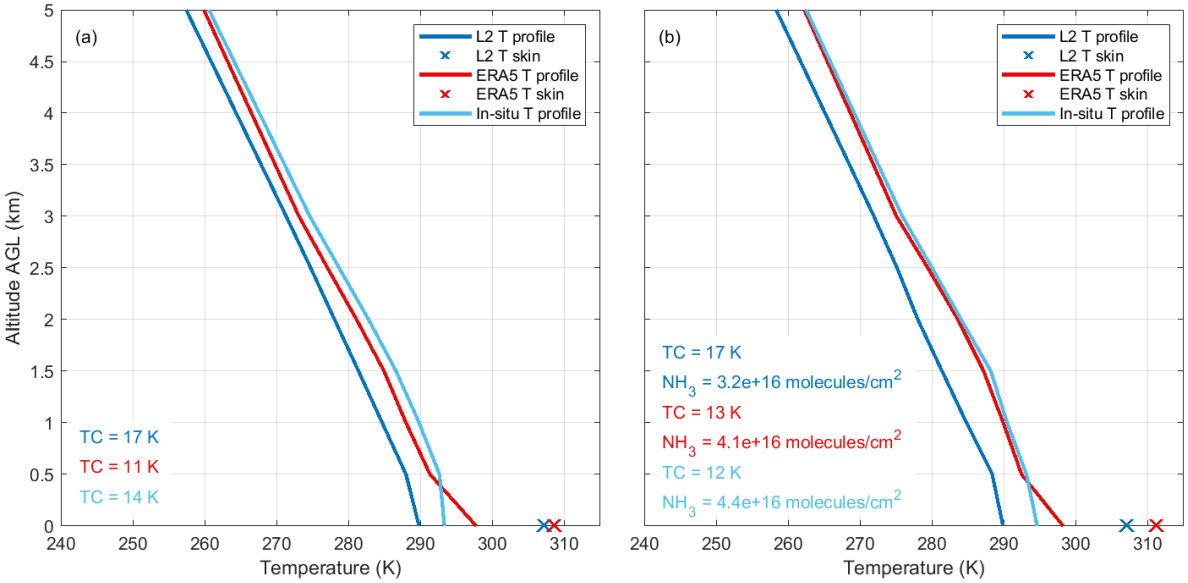

Figure 7. EUMETSAT L2 (dark blue), ERA5 (red) and in situ (light blue) temperature profiles used in the retrieval of near real-time, reanalysis and custom IASI products. Left panel: mean temperature profile in this study; right panel: a single observation on Aug 3, 2014 from IASI Metop-A (39.867° N, 105.205° W).

While linear regression provides a straightforward picture of how two datasets match with each other, the fitted slopes and intercepts can be driven by outliers on either side. We additionally calculated histograms to check for potential differences that may exist between the IASI and in-situ measurements. The remainders obtained from subtracting in-situ columns from corresponding IASI columns are illustrated in Figure 8 (same scenarios as Fig. 6: IASI products versus the in-situ MLH assumption for the ±15 km and ±60 min window in Colorado). The Freedman-Diaconis rule was used to calculate the appropriate bin width and number of bins for each distribution (Freedman & Diaconis, 1981). A Gaussian function was used to fit the remainders for a smoother interpretation of distribution. The histograms show that the remainders were clustered around zero for all three products, with the near real-time product having the smallest mean. This again indicates that the IASI products do not appear to have large systematic biases. Therefore, averaging IASI observations under different scenarios (low/moderate/high NH_3) likely will yield improved detection limits as any random measurement noise become averaged out.

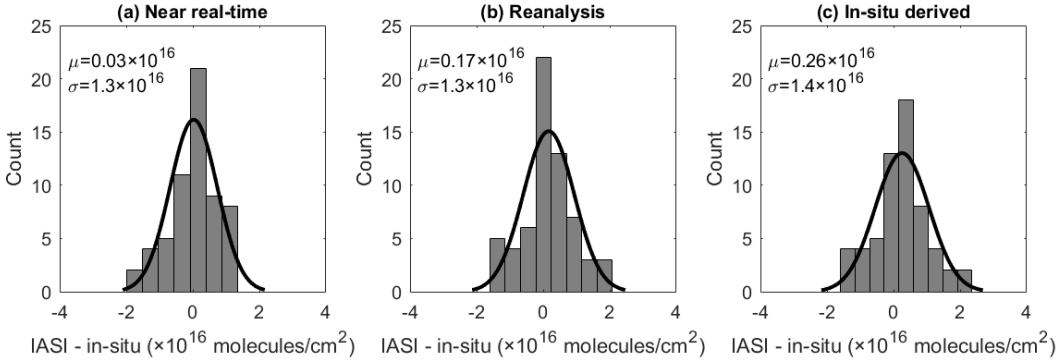

Figure 8. Histograms showing the remainders between IASI and in-situ NH_3 columns in Colorado (±15 km, ±60 min window, MLH assumption) for (a) the near real-time, (b) the reanalysis and (c) the in-situ derived products. The fitted Gaussian distribution is plotted as a black curve. μ and σ denote the mean and standard deviation of the fitted Gaussian function, respectively.

3.3. Comparison between Colorado and California

The DISCOVER-AQ California campaign was conducted over the San Joaquin Valley, the most productive agricultural region in the U.S., with Kern County and Tulare County ranking top in total value of production as of 2017 (CDFA, 2018). Previous studies have found significantly high NH_3 abundances in the San Joaquin Valley (Clarisse *et al.*, 2010; Makar *et al.*, 2009), making it a good area to evaluate the sensitivity of IASI towards surface NH_3. However, using the same criteria as for Colorado, only a limited number of collocated case (N=3, 9, 4 for near real-time, reanalysis and in-situ derived products) were found in California. Part of the reason was that only the Metop-A satellite was available during that time, whereas both MetOop-A and B were operational during the Colorado campaign. The main factor, however, was that the California campaign happened during winter in a valley area, where high cloud coverage, low thermal contrast and strong but shallow temperature inversions were frequently present. These conditions pose a challenge for accurate satellite NH_3 retrievals from an infrared sounder. For demonstration purposes, a test was conducted from January 16 to February 7, 2013 to retrieve NH_3 columns for all IASI Metop-A pixels within the DISCOVER-AQ California domain. Using the near real-time product as an example, only 23% of pixels produced valid columns after cloud filtering (< 25%), and another 14% were removed after accounting for the availability of skin temperature and applying post-filtering, a process that is used to remove erroneous retrievals (Van Damme *et al.*, 2017). In contrast, a similar test between July 17 and August 10, 2014 over the DISCOVER-AQ Colorado domain showed that 52% of the Metop-A and B pixels remained after the retrieval process. The limited sample size makes it extremely difficult to draw any conclusions on the agreement between IASI and in-situ measurements in California. Given this, the scope of this study is limited to Colorado. The California example highlights the fact that validation results in one area may not apply to another area, especially where the conditions are dramatically different for satellite observations. Indeed, the same location may have different seasonality in the validation due to differences in thermal contrast. Similar to the results in Colorado, the reanalysis product in California yielded more datapoints available because of the increased availability of temperature profiles by using gridded, interpolated model data.

3.4. Comparison Between Spatiotemporal Windows

As described in section 3.2, we used the ±15 km spatial window in conjunction with the ±60 min temporal window to account for the transport of NH_3 based on the typical boundary layer wind speed of 3.5±2.2 m s^{-1}. We also evaluated the agreement between IASI and in-situ data using other combinations of spatiotemporal windows that may be relevant. For comparison purposes, we examined windows up to a factor of three apart in space and time to investigate the sensitivity of spatiotemporal windows on the outcomes. Table 3 lists the orthogonal regression results between IASI and the in-situ MLH assumption under nine different spatiotemporal windows. The near real-time IASI product is shown here as an example. The correlations in all nine windows are tested to be statistically significant. Aside from the ±15 km and ±60 min window that has been adopted throughout the analysis, the ±15 km and ±20 min window also showed good performance. The "within pixel" and ±60 min window even outperforms the original window in terms of slope and correlation, which is reasonable since we anticipate that most NH_3 emitted will stay near their sources in a short time frame. However, it should be noted that the ±15 km and ±60 min window has a much larger sample size than the two windows above, providing higher statistical power. From a statistical perspective, none of the remaining windows are comparable to the ones discussed in terms of overall agreement.

Table 3. *Orthogonal regression statistics between the near real-time IASI product and the in-situ MLH assumption for all the spatiotemporal windows tested, including overlapping points*

Temporal window	20 min			60 min			180 min		
Spatial window	Within pixel	15 km	45 km	Within pixel	15 km	45 km	Within pixel	15 km	45 km
m	0.93 ±0.17	0.76 ±0.18	0.60 ±0.17	2.1 ±0.73	0.78 ±0.14	0.85 ±0.13	2.3 ±0.50	2.7 ±0.67	1.1 ±0.15
b	8.0e14 ±2.4e15	1.2e15 ±2.7e15	3.4e15 ±1.5e15	-4.6e15 ±5.1e15	2.1e15 ±1.5e15	1.3e15 ±1.0e15	-3.9e15 ±3.2e15	-7.9e15 ±4.4e15	6.2e14 ±9.2e14
r	0.84	0.68	0.28	0.50	0.58	0.38	0.64	0.41	0.41
N	12	22	150	25	60	245	32	81	258
IASI mean	1.1e16 ±9.7e15	1.1e16 ±9.2e15	8.3e15 ±6.9e15	9.2e15 ±7.6e15	8.8e15 ±7.1e15	7.1e15 ±6.4e15	9.4e15 ±7.8e15	9.2e15 ±8.0e15	6.6e15 ±5.7e15
In-situ mean	1.1e16 ±1.0e16	1.3e16 ±1.1e16	8.1e15 ±8.0e15	6.6e15 ±5.1e15	8.5e16 ±8.2e15	6.8e15 ±6.8e15	5.7e15 ±4.4e15	6.3e15 ±5.0e15	5.5e15 ±5.5e15

Note. "Within pixel" means that the in-situ measurements must be located within the actual IASI pixel (~ 12 km in diameter). m = slope; b = y-intercept (x-axis = in-situ, y-axis = IASI); r = Pearson's correlation coefficient; N = number of datapoints. Standard deviations are shown for slopes, intercepts and means.

3.5. Ascent and Descent Aircraft Profiles

An earlier study on the validation of TES NH_3 suggested that the two airborne NH_3 sensors (PTR-MS and CRDS) in DISCOVER-AQ California exhibited hysteresis during sampling (Sun *et al.*, 2015). Due to the sensors' relatively long response times, the measured

NH_3 concentrations showed long tails of decay when exiting the boundary layer into the free troposphere. On the other hand, the sensors detected almost no NH_3 signals when descending from the free troposphere until reaching the boundary layer, likely due to an extended portion of outgassing in clean conditions prior to the descent. The Colorado campaign only had PTR-MS onboard the P-3B aircraft, but we also examined the differences in validation using the ascent and descent profiles. It is emphasized that NH_3 data were only a side product of the PTR-MS measurements during DISCOVER-AQ. The instrument was primarily measuring volatile organic compounds (VOCs) and thus not optimized for detecting NH_3 (high instrumental background resulting in a poor detection limit, slow time response due to a ~2 m long inlet line).

As an example of the hysteresis in sampling, we selected two pairs of locations relatively close to each other where aircraft profiling was conducted to minimize the influence of NH_3 gradients across the transect. Figure 9a shows the time series on July 23, 2014, of NH_3 for an ascent profile at NREL (Golden), a high-altitude leg near 5.5 km MSL for 22 km (2.5 min) and then a descent spiral profile near the BAO tower (near Erie). The second pair of profiles consisted of an ascent at Denver (La Casa), another high-altitude segment at 5.5 km MSL for 26 km (3 min.), followed by a descent at Chatfield Park south of Denver. MLH was estimated from the aircraft temperature profiles and found to be similar between these locations (difference within 100 m). The geographical locations of the four sites are shown in Figure 9b.

Figure 9c and d show the vertical profiles of NH_3 for the near-adjacent ascent and descent pairs. For comparison, Figure 9e and f show the same pairs of profiles for C_2H_6, a petrochemical tracer with a ~ 2 month lifetime that has sources located in the same general areas as NH_3 emissions in northeast Colorado and has no sampling issues (Kille *et al.*, 2019). The dashed line marks the average boundary layer height averaged between each pair. For the first set of profiles (Fig. 9c), the descent had an average NH_3 mixing ratio of 2.2 ppbv while the ascent averaged over two times higher at 4.6 ppbv. We hypothesize these differences were mainly due to instrument sampling issues because the corresponding C_2H_6 profiles (Fig. 9e) showed no noticeable differences between the two sites, particularly the relative shapes of the profiles around the MLH. This sampling hysteresis for NH_3 is consistent with those reported by Sun *et al.* (2015). We investigated several other profiles and found similar patterns, especially when there were large enhancements of NH_3 (> 5 ppbv) near the ground, suggesting that PTR-MS was subject to artifacts caused by instrument design and sampling method as expected for any inlet-based instrument.

For the second pair (Fig. 9d), the average NH_3 during descent again was lower than the ascent, but there was a difference in air mass between these two sites. Figure 9f shows that C_2H_6 had different boundary layer profiles in the two locations, though were indistinguishable at and above it. Nonetheless, the relative shapes of the NH_3 and C_2H_6 profiles are dramatically different, with C_2H_6 showing an abrupt and large decrease above the MLH while NH_3 shows a more gradual decrease around the MLH. The more gradual transition of NH_3 is again likely related to sampling biases, though real air mass differences certainly play some role at least in the boundary layer.

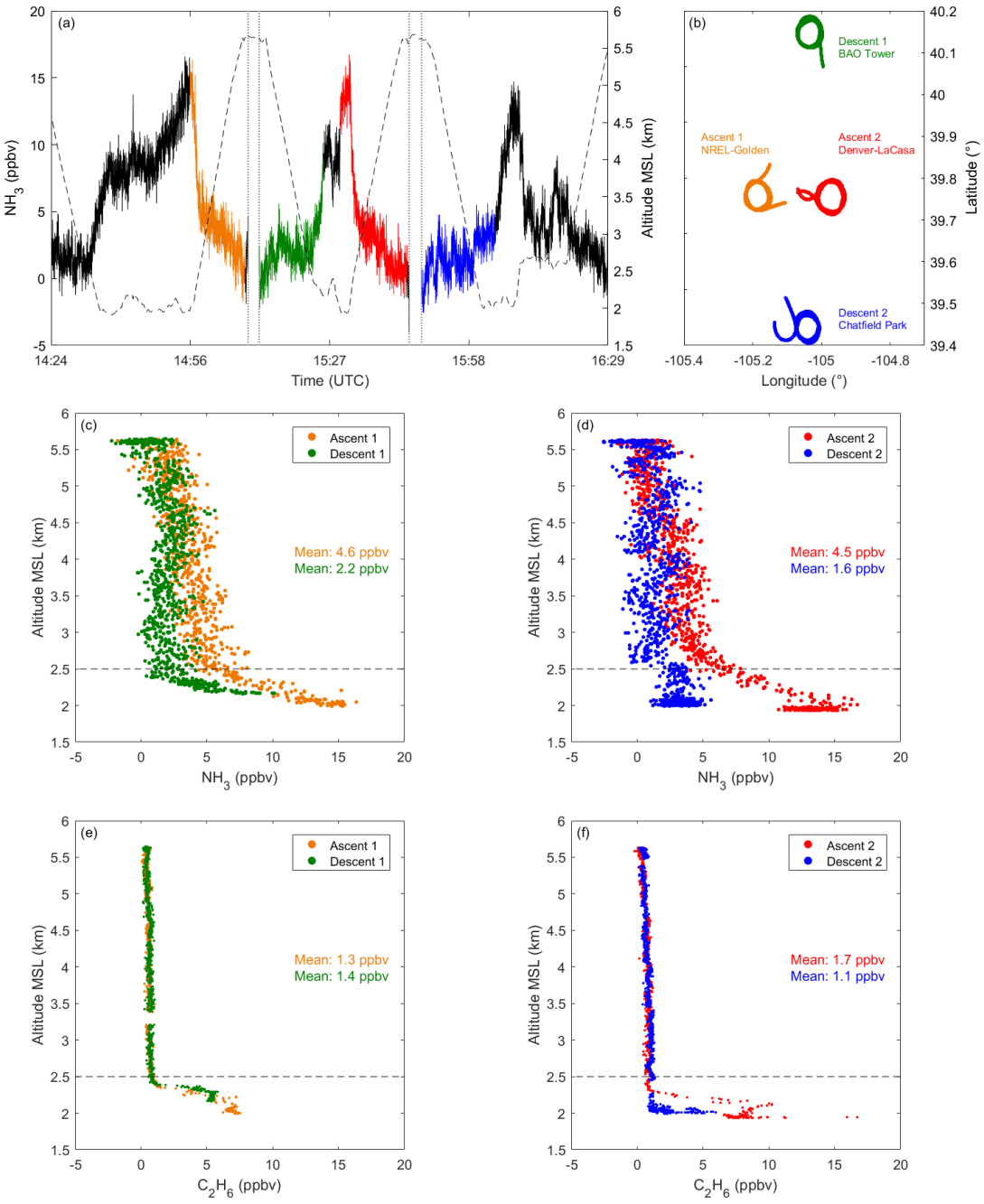

Figure 9. Vertical profiles of 1 Hz NH_3 and C_2H_6 measurements on the P-3B in Colorado on July 23, 2014. Panel (a) shows the time series of NH_3 measured by the PTR-MS. The two pairs of adjacent ascent and descent profiles selected for comparison are highlighted by different colors. The thin dashed line and grey dotted vertical lines show the altitude change during the flight and breaks in the time series, respectively. Panel (b) shows the geographical locations where the aircraft profiles were made. Panels (c) and (d) present the NH_3 profiles during the ascents and descents. Dashed lines mark the MLH averaged across each ascent and descent pair. Panels (e) and (f) are the corresponding C_2H_6 profiles measured simultaneously by a TILDAS instrument.

While we have demonstrated that IASI is comparable to in-situ-derived profiles in general, the differences between ascent and descent profiles due to sampling issues require more examination. To distinguish between ascent and descent aircraft profiles, we now compare the three IASI products against ascents and descents separately (Fig. 10), and key differences are readily observed. For example, the ascent profiles yield higher columns than corresponding IASI columns, consistent with the above observations of instrument artifacts from outgassing. Likewise, descent profiles are generally lower due to surface adsorption upon rapid increases in NH_3 concentrations as one descends. As a result, descent clusters have higher slopes than the ascent clusters. Descents tend to have much better correlations than ascents (0.62-0.68 vs. 0.43-0.46) as well as slopes closer to unity, but their intercepts also tend to be worse. Because sampling biases occur after large concentration changes regardless of the direction (net adsorption vs. net outgassing), it is unclear which of these profiles is more representative of the actual distribution. Therefore, we have opted to aggregate all PTR-MS measurements together regardless of the flight direction. Our findings suggest that attention needs to be paid to the discrepancies between ascent and descent profiles as a metric of in-situ, instrument inlet/sampling performance. Future airborne research campaign targeting NH_3 concentrations should employ sensors with highly quantified instrument responses in-flight, during upward and downward flight profiles in the same location, and with high precisions and low biases for better mapping of NH_3 vertical profiles.

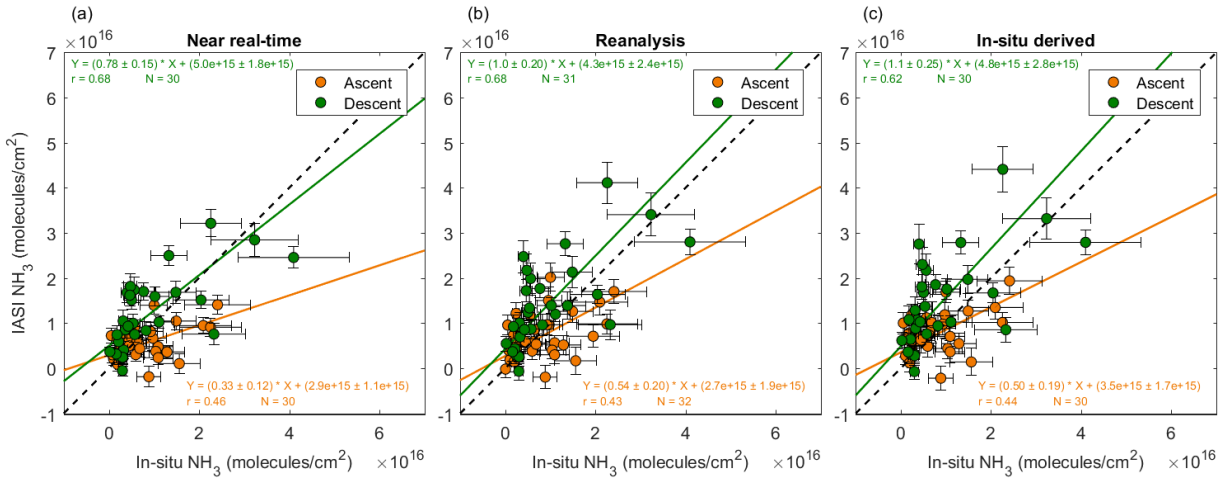

Figure 10. IASI-NH_3 products versus the in-situ NH_3 columns in Colorado (±15 km and ±60 min window and MLH assumption) with ascent (orange) and descent (green) aircraft profiles analyzed separately (same data as in Figure 6).

3.6. Comparison between IASI and CU SOF

Aside from in-situ NH_3 concentrations, ground-based mobile CU-SOF measurements of NH_3 total columns were also available during the DISCOVER-AQ/FRAPPÉ Colorado campaign (Kille *et al.*, 2017). We filtered the FTIR data using the same algorithm as the other in-situ platforms but enlarged the window to ±15 km and ±180 min to include additional data that may be potentially relevant. This was based on the variability of wind speed measured at BAO (3.5±2.2 m s^{-1}), where the ±15 km and ±180 min window is consistent with the lower boundary

of wind speed at 1σ standard deviation (1.3 m s^{-1}). For each collocation, the mean of all CU SOF data within the window was computed. Figure 11 shows that IASI has moderate correlations with FTIR, and the slopes are consistent with the 1:1 line. Given that FTIR retrievals depend only weakly on a priori parameters (< 4% variation in column sensitivities), which also come with large uncertainties (Kille *et al.*, 2019), this comparison shows some promising consistency between the two instruments and independent approaches.

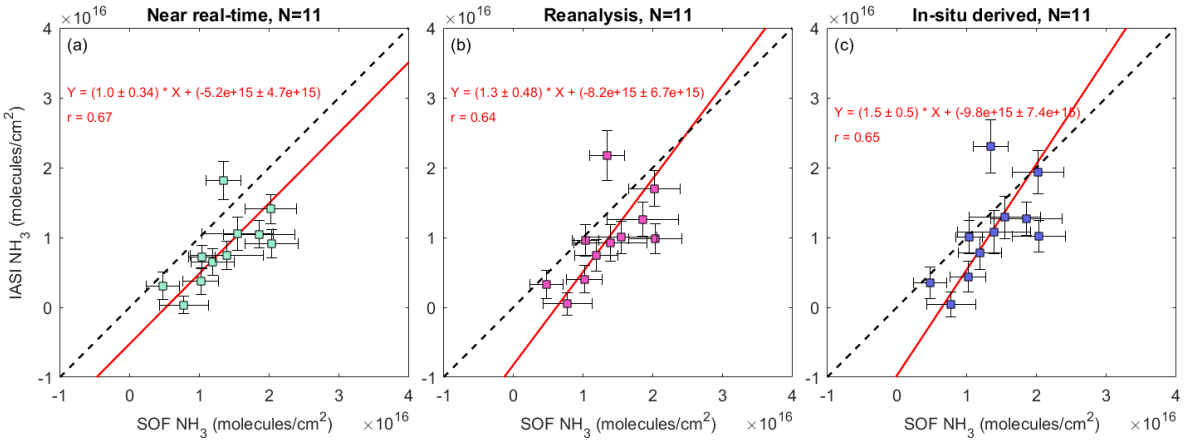

Figure 11. IASI versus CU SOF NH_3 columns using orthogonal regression for (a) the near real-time, (b) the reanalysis, and (c) the in-situ derived products within the ±15 km and ±180 min window in Colorado. All the correlations are statistically significant.

4. Implications

In the past decade, satellite NH_3 measurements have been used to study the trends and distributions of NH_3 owing to their long data record and global coverage (Dammers et al., 2019; Pinder et al., 2011; Van Damme et al., 2018; Warner et al., 2016). Although research has attempted to validate satellite NH_3 using surface concentrations and ground-based stationary FTIR measurements, the accuracies of localized measurements - which are important for studying emission sources and their variabilities - have not been thoroughly validated. In this work, we compared IASI with collocated in-situ-derived profiles and mobile SOF columns from a suite of aircraft, tower, mobile laboratory, and sonde measurements from the NASA DISCOVER-AQ and NSF FRAPPÉ field experiments. We validated version 3 of the IASI NH_3 dataset with three temperature profiles: the near real-time product from EUMETSAT, the ERA5/ECMWF reanalysis product, and one using in-situ temperature profiles from the DISCOVER-AQ/FRAPPÉ campaign.

IASI correlates well with in-situ NH_3 integrated up to the MLH within windows of ±15 km from the IASI centroid and ±60 min of the overpass time. The three IASI products show similar performances, with the reanalysis product showing the overall best agreement (slope = 1.0±0.19, intercept = (1.3±1.9)×10^{15} molec cm^{-2}, r = 0.57). Because IASI has no significant biases compared to the in-situ profiles, IASI columns can be spatiotemporally averaged for improved signal to noise ratios where appropriate. The IASI retrieval depends on accurate temperature inputs, especially in the boundary layer where most NH_3 resides. The near-real time

product showed a slight bias in the slope, which could be readily traced back to a known bias in the IASI L2 temperature profile prior to 2016. Newer data do not exhibit such biases, with near-real time and reanalysis products agreeing in the mean (Van Damme *et al.*, 2017). Limited mobile CU SOF measurements during DISCOVER-AQ/FRAPPÉ Colorado also show overall good consistency with IASI. Our IASI results are demonstrated for summer in Colorado USA but may not be representative of other locations and times. More validations are needed, especially in cases with strong inversions and low thermal contrast such as in valleys and in winter. Large columns ($> 5\times10^{16}$ molec cm^{-2}) could also not be validated with the current set of in situ measurements. We remind here that no AVK information was generated from IASI retrievals or applied to the in-situ data, and therefore this study only presents a comparison between the unbiased IASI columns and in-situ integrated columns. A weighting function is being considered for future IASI versions that can be used to account for the variabilities of vertical sensitivity.

This study is the first validation of IASI NH_3 at the single pixel scale using vertically integrated in-situ concentrations. Nonetheless, as with TES single pixel validation results, sampling artifacts of airborne NH_3 instruments remain a significant barrier for improved validations. Not only are there fewer measurements of free tropospheric NH_3 from airborne science field campaigns compared to other in-situ trace gases, but high accuracy and fast response NH_3 measurements are critically needed for the mapping of NH_3 vertical profiles. This is particularly important for validating in source regions where elevated concentrations in the boundary layer may influence the corresponding free tropospheric values due to sampling biases of existing instruments. Besides, vertical profiles of NH_3 in the boundary layer themselves have complex structures due to emissions, partitioning into aerosol phases, and temperature and relative humidity changes. More boundary layer NH_3 profiles will improve the development of retrieval algorithms for all infrared sounders, and this can be achieved with recent advances in NH_3 measurements techniques and the increased availability of airborne research campaigns (Miller *et al.*, 2014; Pollack *et al.*, 2019).

Vertical profiles of NH_3 in the free troposphere are also a high priority, as the integrated NH_3 concentrations in the free troposphere may be comparable to the overall column abundance in low and moderate NH_3 locations. Spiral, vertical aircraft profiles like those made in DISCOVER-AQ are critical for the validation of short-lived species like NH_3 such that horizontal gradients are not manifested as vertical gradients during altitude changes. In addition, repeated upward and downward transects over the same airmass will provide a measure of confidence in any potential instrument sampling biases. While our study focuses on the measurements from IASI, these generalized conclusions hold for all infrared sounders that are sensitive to boundary layer temperature profiles and thermal contrast. Overall, more robust datasets are needed for validating satellite NH_3 measurements, particularly at the pixel scale as satellite NH_3 datasets are applied toward higher-resolution emission inventories and atmospheric composition analyses.

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Data Availability

All the datasets used in this work are publicly available and archived at the following websites:

DISCOVER-AQ/FRAPPÉ: https://www-air.larc.nasa.gov/missions/discover-aq/discover-aq.html

IASI: https://iasi.aeris-data.fr/NH3/

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