Spatio-Temporal Variations of Atmospheric NH₃ over East Asia by Comparison of Chemical Transport Model Results, Satellite Retrievals and Surface Observations

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Abstract: Atmospheric ammonia (NH₃) plays an important role in the formation of secondary inorganic aerosols, the neutralization of acid rain, and the deposition to ecosystems, but has not been well understood yet, especially over East Asia. Based on the GEOS-Chem model results, the IASI satellite retrievals, the in-site surface observations of a nationwide filter pack (FP) network over Japan and the long-term high resolution online NH₃ measurements at Fukuoka of western Japan, the spatio-temporal distributions of atmospheric NH₃ over East Asia was analyzed comprehensively. A significant seasonal variation with a summer peak was found in all datasets. Comparison between the satellite retrievals and model simulations indicated that the IASI NH₃ vertical column density (VCD) showed good consistency with GEOS-Chem results over North and central China, but had large differences over South China due to the effect of clouds. Over the Japan area, GEOS-Chem simulated NH₃ concentrations successfully reproduced the spatio-temporal variations compared with in-situ observations, while IASI NH₃ VCD retrievals were below or near the detection limit and difficult to obtain a reasonable correlation for with model results. The comprehensive analysis indicated that there were still some differences among different datasets, and more in-situ observations, improved satellite retrievals, and high-resolution model simulations with more accurate emissions are necessary for better understanding the atmospheric NH₃ over East Asia.

Keywords: Atmospheric NH₃; chemical transport model; GEOS-Chem; seasonal variations; surface observation; satellite retrieval

1. Introduction

Atmospheric ammonia (NH₃) is a highly reactive gas and plays an important role in atmospheric chemical processes by reacting rapidly with sulfuric acid (H₂SO₄) and nitric acid (HNO₃) formed from sulfur dioxide (SO₂) and nitrogen oxides (NOₓ) and producing ammonium (NH₄⁺), which is the most important ambient cation [1]. As a result of these reactions, the formed secondary inorganic aerosols (SIAs, e.g., (NH₄)₂SO₄ and NH₄NO₃) significantly contribute to high levels of atmospheric fine
particles or PM$_{2.5}$, especially over China, where there are large amounts of anthropogenic emissions for NH$_3$, SO$_2$, and NO$_x$. The modelling study indicated the control of 20% NH$_3$ emission can affect 5–11% of PM$_{2.5}$ formation in North China [2]. The high concentration of SIAs in China had a wide effect over East Asia through long-range transport [3–5]. Due to rapid decrease of SO$_2$ emission in China in recent years, the formation of (NH$_4$)$_2$SO$_4$ decreased subsequently over East Asia, which created free NH$_3$ that reacts with HNO$_3$ to form NH$_4$NO$_3$, and therefore, the nitrate aerosol significantly increased in the downwind area over East Asia [6]. Since the NH$_3$ could significantly affect the HNO$_3$, it subsequently could affect the heterogenous reactions between HNO$_3$ and dust as well as sea salt to form Ca(NO$_3$)$_2$ and NaNO$_3$ [7,8]. To quantitively understand these component shifts in SIAs, the level of NH$_3$ is critically important.

Because atmospheric NH$_3$ is the most important soluble alkaline gas and can react rapidly with acid gases, it also has an important influence on the acidity of precipitation [9]. Observation analysis based on the Acid Deposition Monitoring Network in East Asia (EANET) data revealed that NH$_3$ has a great neutralization capability toward acid rain, even in the regions with low concentrations, such as Japan [10]. Through wet and dry deposition processes, NH$_3$ and its derivatives can be deposited in ecosystems, increasing eutrophication and reducing biodiversity [11]. Recent multi-model studies indicated that the deposition of total ammonia was about 2–6 kg n ha$^{-1}$ yr$^{-1}$ over marginal seas of East Asia, and could reach as high as 20 kg n ha$^{-1}$ yr$^{-1}$ over North and central China [12,13].

Despite the importance of NH$_3$ in the environment, the atmospheric processes controlling NH$_3$ levels and its related budgets are still poorly understood [1]. One important reason is that the measurement of NH$_3$ is challenging due to the following: (i) strong temporal and spatial variability of ambient levels, (ii) rapid conversion of NH$_3$ between phases (gas/particulate/liquid), and (iii) its tendency to adhere to the surfaces of measurement instruments [14]. Differing with other air pollutants (e.g., SO$_2$ and NO$_x$), there are currently very few monitoring stations that provide daily or hourly resolved NH$_3$ measurements, with most long-term monitoring of NH$_3$ conducted using a passive sampler or dedicated denuder at a time resolution of several weeks.

Over the last few years, satellite instruments capable of detecting NH$_3$ vertical column density (VCD) have been used to study the emission, distribution, and transport of NH$_3$ at global and regional scales [15–17]. Via comparison of satellite retrievals and simulations using a global atmospheric chemistry transport model, it was indicated that NH$_3$ emissions could have been significantly underestimated in the Northern Hemisphere [15]. Also, based on five-year satellite retrievals, the seasonality and interannual variability were examined separately for the Northern and Southern Hemispheres [16]. Via comparison between satellite retrievals and LÖTOS-EUROS model results over Europe and Western Russia, large discrepancies were found over several industrial areas in Eastern Europe and Russia [17]. Since the satellite retrievals may suffer large relative errors, especially in areas with low VCD, detailed evaluations are necessary, especially over East Asia where the studies are limited.

In addition to the measurement of NH$_3$, chemical transport models (CTMs) are useful tools for studying the sources and sinks of NH$_3$, and the processes controlling its levels in the atmosphere. However, model results may have a large bias due to uncertainties of emissions and atmospheric processes, i.e., gas–aerosol partitioning of NH$_3$ and NH$_4^+$. Based on the recent results from the Model Inter-Comparison Study for Asia III (MICS-Asia III), all models failed to reproduce the observed monthly variations in surface NH$_3$ concentrations in the North China Plain region, and most models mismatched the observed peak in July and showed negative correlation coefficients with the observations [18]. Since the MICS-Asia III study only evaluated the simulations of surface NH$_3$ concentrations over North China, more evaluations over other areas of East Asia and comparisons with satellite NH$_3$ retrievals are necessary.

In this study, we analyzed the horizontal distribution and seasonal variation of atmospheric NH$_3$ over East Asia based on the satellite retrievals, the model results, the nationwide filter pack (FP)
observation network over Japan, and the hourly NH$_3$ measurements in Fukuoka of western Japan. The similarities and differences of different datasets were also analyzed comprehensively.

2. Observations

2.1. In-Situ High-Resolution Online Measurement

Concentrations of gaseous NH$_3$ were continuously measured using a semi-continuous microflow analytical system (MF-NH$_3$A; Kimoto Electric Co. Ltd., Osaka, Japan) [19] at the 6th floor of a building in Chikushi Campus of Kyushu University (CC-KU). The open triangle in Figure 1b shows the location of CC-KU site. According to the NH$_3$ emission of the EAGrid inventory [20] shown in Figure 1b, the high NH$_3$ emission (mainly originating from local agriculture and poultry farming) area located 5–10 km south of the observation site may influence the NH$_3$ measurement in CC-KU. Atmospheric NH$_4$ (= gaseous NH$_3$ + aerosol NH$_4^+$) was dissolved in ultrapure water using a continuous air-water droplet sampler and quantified from the fluorescence signal (excitation, 360 nm; emission, 420 nm) of the o-phtalaldehyde-sulfite-NH$_3$ reaction product [21]. The concentrations of NH$_4$ and NH$_4^+$ in liquid samples were measured simultaneously by application with and without a phosphoric acid denuder at the inlet and the NH$_3$ concentration was calculated as the difference between the measured NH$_4$ and NH$_4^+$ concentrations. Atmospheric NH$_3$ was measured hourly between July 31, 2014 and October 19, 2015. The details of the observation system and basic data analysis have been reported previously [22].

![Figure 1. Horizontal distribution of NH$_3$ emission by (a) REAS over East Asia used for GEOS-Chem simulation (Grid = 0.5° × 0.667°) and (b) EAGrid over the North Kyushu area (Grid = 0.01° × 0.01°).](image)

2.2. Japan Environmental Laboratories Association (JELA) Observation Network

We also used the NH$_3$ observations (from 2010 to 2014) from the Japan Environmental Laboratories Association (JELA), which were acquired at 33 sites in Japan [23]. Table 1 shows the site used for the comparison of the NH$_3$ time series later. The locations of Fukuoka (S27) and Dazaifu (S26) sites were shown as open and closed circles in Figure 1b. (A figure later will show the locations of all the sites with observation during the study period).

The JELA dataset provided monthly averaged atmospheric NH$_3$ concentrations measured using the Filter Pack (FP) method (hereafter denoted as FP data) [24]. The FP method used a passive sampler, which was manufactured by Ogawa Shokai Co. Ltd. and had been widely used for NH$_3$ sampling [25]. Captured NH$_3$ on the sampling filter was extracted into pure water (5 mL), and the amount was detected using the Flow Injection Analysis method. We used the JELA NH$_3$ concentration to compare with other datasets and excluded the sites where there was a strong local influence from agriculture and livestock farming.
2.3. Satellite Retrieval

The improved Infrared Atmospheric Sounding Interferometer (IASI) NH$_3$ dataset was used in this study. IASI is a passive remote-sensing instrument, operating in nadir mode that measures the infrared radiation emitted by the Earth's surface and atmosphere. The algorithm used to retrieve NH$_3$ columns from the radiance spectra is described in detail and compared to previous algorithms in the literature [16]. The NH$_3$ VCDs were retrieved based on the hyperspectral range index (HRI, a dimensionless spectral index from IASI Level 1C radiance), thermal contrast (TC, the temperature difference between the earth's surface and the atmosphere at 1.5 km from the IASI Level 2 information), and look-up tables (LUTs, built from forward radiative transfer model simulations). The relative errors were provided by the IASI NH$_3$ product and estimated by considering the uncertainties of HRI and TC, with large errors related to low values of HRI (indicating low values of the NH$_3$ column) and/or TC [16].

The IASI instrument is onboard the polar sun-synchronous MetOp platform, which crosses the equator at a mean local solar time of 9:30 a.m. and p.m. It therefore allows global retrievals of NH$_3$ twice a day. In this study, we only considered the measurements from the morning overpass because they are generally more sensitive to NH$_3$ and have smaller relative errors due to the higher TC at this time of day [16]. The availability of measurements was mainly controlled by the cloud cover, with only observations with cloud cover lower than 25% being processed. It has to be shown that given the strong dependence on TC, the spring–summer months are better suited to accurately measure NH$_3$ from IASI (error below 50%) [17]. As an example of the detection limit (defined as 2$\sigma$ on the HRI) for an individual observation, an NH$_3$-retrieved column was considered detectable when the VCD exceeded $9.68 \times 10^{15}$ molecules cm$^{-2}$ (surface concentration exceeded 1.74 $\mu$g m$^{-3}$) at a TC of 20 K, while the VCD should be larger than $1.69 \times 10^{16}$ molecules cm$^{-2}$ (3.05 $\mu$g m$^{-3}$) at 10 K [17].

The IASI NH$_3$ retrieval dataset used in this study was produced at the Université Libre de Bruxelles (ULB), Belgium (http://www.pole-ether.fr/etherTypo/index.php?id=1700&L=1) [16,17]. And the dataset included: (1) the ammonia total column along the satellite swath path (data only for conditions with cloud cover < 25%), (2) the error on the ammonia total column, (3) the cloud cover on ground pixels, (4) the vertical profile used in the retrieval procedure, and (5) the viewing angle of the satellite. NH$_3$ VCDs were then re-gridded to the GEOS-Chem Asian grid system with 0.5$\degree$ x 0.667$\degree$ resolution.

3. Numerical Model and Emission Inventory

In this study, the three-dimensional (3-D) Goddard Earth Observing System - Chemistry (GEOS-Chem) CTM (version 09-02) [26,27] was run with the full NOx-Ox-VOC-HOx-CO chemistry option to simulate the emissions, chemical reactions, and transport of tracer gases (e.g., NH$_3$, SO$_2$, NO, NO$_2$, CO, and VOCs) and aerosols (e.g., black carbon (BC), organic carbon (OC), mineral dust, sea salt, and secondary inorganic aerosols). To simulate the distribution of atmospheric NH$_3$, the physical processes of advection, diffusion, dry deposition, and wet deposition were considered [26,27]. The partitioning of NH$_3$ and NH$_4^+$ was calculated by the aerosol thermodynamical equilibrium module of ISORROPIA II [28]. The GEOS-Chem model used the assimilated meteorological fields from the
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GEOS of the NASA Global Modeling and Assimilation Office (GMAO). The model had a horizontal resolution of $2^\circ \times 2.5^\circ$ for global runs, and $0.5^\circ \times 0.667^\circ$ for Asian one-way nesting runs ($11^\circ$ S–$55^\circ$ N, $70^\circ$–$150^\circ$ E), with both having 47 vertical levels from the surface to 0.01 hPa. The lowest model layer thickness was approximately 130 m.

We used anthropogenic emissions data from the Emission Database for Global Atmospheric Research (EDGAR) [29] for the global domain and the Regional Emission Inventory in Asia (REAS) (version 2.1) [30] for the Asian domain. REAS NH$_3$ emissions were modified to include seasonal variations in China and Japan based on References [20,31], respectively, and the changes in winter emission amounts as recommended by the literature [32]. This modified NH$_3$ emission inventory, including seasonal variation, is simply referred to as REAS in this manuscript. The horizontal distribution of NH$_3$ emission from REAS over East Asia was shown in Figure 1a, and high NH$_3$ emissions (>15 Gg grid$^{-1}$ year$^{-1}$) could be found over North and central China. The model simulation covered the period from the beginning of December 2013 to October 2015. Other basic numerical settings were as reported previously [33,34].

4. Results and Discussion

4.1. Seasonal/Horizontal Distribution of NH$_3$ Column Density

Figure 2 shows a comparison of the annual average VCDs from IASI retrievals and GEOS-Chem model results. Figure A1 shows the number of satellite data pixels, averaged cloud cover, and relative error. Both IASI and GEOS-Chem data showed a high NH$_3$ VCD over north (Beijing, Tianjin, and the south of Hebei province) and central (Henan and Hubei provinces) China, where the annual mean NH$_3$ VCD could reach $1.5 \times 10^{16}$ molecules cm$^{-2}$. The relative errors over these regions were relatively small (<150%) due to the high NH$_3$ value compared to other areas. Over South China, the IASI NH$_3$ VCD was significantly lower than the GEOS-Chem value due to the small number of measurements and large relative errors resulting from high levels of cloud cover (Figure A1). The NH$_3$ VCD was less than $6 \times 10^{15}$ molecules cm$^{-2}$ over all of Japan. The relative error over Japan was higher than that over central China due to the lower NH$_3$ VCD. The IASI NH$_3$ VCD was below or near the detection limit (as discussed in Section 2.3), except over North and central China. The horizontal distribution of GEOS-Chem NH$_3$ VCD was consistent with REAS NH$_3$ emissions as shown in Figure 1a, which was because NH$_3$ is a primary gaseous tracer with a short life; therefore, the horizontal distribution of NH$_3$ VCD was quite relevant to its sources.

![Figure 2. Horizontal distribution of annual averaged (a) IASI retrieved and (b) GEOS-Chem simulated NH$_3$ vertical column densities (VCDs) over East Asia for the year of 2014.](image-url)
Figure 3 showed the averaged IASI retrieved and GEOS-Chem simulated NH$_3$ VCDs as well as REAS NH$_3$ emission over East Asia in the spring (March–April–May, i.e., MAM), summer (June–July–August, i.e., JJA), autumn (September–October–November, i.e., SON), and winter (December–January–February, i.e., DJF). The horizontal distributions of the IASI and GEOS-Chem NH$_3$ VCDs were generally similar in the different seasons, with high values over North and central China. However, the GEOS-Chem results revealed that the areas downwind of China (e.g., the East China Sea and Japan sea areas) had a higher NH$_3$ VCD in spring than in summer, even though the NH$_3$ VCD over China was significantly higher in summer than in spring. This indicated the importance of long-range transport of NH$_3$ over East Asia in the cold season when northwest winds were dominant.

![Figure 3](image)

**Figure 3.** Horizontal distribution of seasonal averaged IASI retrieved (a1–d1) and GEOS-Chem simulated (a2–d2) NH$_3$ VCDs as well as REAS NH$_3$ emission (a3–d3) over East Asia.

The seasonal variations were significant and consistent in the IASI and GEOS-Chem results, with higher peak values of about 3 × 10$^{16}$ molecules cm$^{-2}$ (central China) in summer and lower peak values of about 5 × 10$^{15}$ molecules cm$^{-2}$ in winter. The major factors affecting the seasonal variation of NH$_3$ VCD included the seasonal variation of NH$_3$ emissions and gas-aerosol partitioning of NH$_3$ and NH$_4^+$. A clear summer peak for NH$_3$ emissions can be found in Figure 3, which resulted from the high NH$_3$ volatilization rate from the soil and livestock due to high temperatures in summer [31]. High temperatures will lead to more gaseous NH$_3$ during the gas-aerosol partitioning process [22]. Due to the low NH$_3$ VCD, IASI retrievals had larger relative errors (>150%) in winter over the East Asia
area (Figure A1). Over the Japan area, IASI retrievals did not show a clear seasonal variation due to the large relative errors (Figure A1), while GEOS-Chem produced a higher NH$_3$ VCD in summer than in winter.

Figure 4 shows the region-averaged monthly IASI NH$_3$ VCD, GEOS-Chem NH$_3$ VCD, and REAS NH$_3$ emission for the six regions shown by black boxes in Figure 1. North China had a clear summer peak of NH$_3$ VCD in IASI retrievals and GEOS-Chem results, but the GEOS-Chem peak in July (1.2 × 10$^{16}$ molecules cm$^{-2}$) was lower than the IASI peak (2.6 × 10$^{16}$ molecules cm$^{-2}$), which may be due to the underestimation of NH$_3$ emissions.

The pattern of IASI NH$_3$ seasonal variation over central China was similar to that over North China, and the GEOS-Chem results also indicated a similar seasonal variation. However, the IASI NH$_3$ level over North China (maximum: 2.6 × 10$^{16}$ molecules cm$^{-2}$) was significantly higher than that over central China (maximum: 1.5 × 10$^{16}$ molecules cm$^{-2}$), while the GEOS-Chem results indicated a similar
NH$_3$ level (maximum: $1.4 \times 10^{16}$ molecules cm$^{-2}$). GEOS-Chem NH$_3$ levels in July were consistent with those of IASI retrievals, but were higher than IASI levels in May. GEOS-Chem NH$_3$ results over South China were higher than IASI retrievals in spring and summer; however, the IASI data did not reveal clear seasonal variation due to the small number of measurements and large relative errors resulting from high levels of cloud cover.

The GEOS-Chem NH$_3$ VCD over South Korea was significantly lower than the IASI levels in June and July due to no monthly variation in REAS NH$_3$ emissions. The GEOS-Chem NH$_3$ VCD over the Kanto region indicated a more significant seasonal variation than that revealed by IASI retrievals, and was consistent with REAS emissions, indicating the importance of Japanese domestic emissions. Over the Kyushu region, the GEOS-Chem NH$_3$ VCD peaked in May, while REAS emissions did not, which may indicate the effect of the long-range transport of NH$_3$ from outside Japan. Based on a sensitivity simulation by GEOS-Chem, we found that only 35% of the NH$_3$ (in May) in the Kyushu region originated from domestic emissions.

4.2. Comparisons between JELA-FP Observations, IASI Retrievals and GEOS-Chem Results

Figure 5 shows the annual averaged FP NH$_3$ data over Japan and a comparison with IASI NH$_3$ and GEOS-Chem NH$_3$ VCDs. Figure 6 shows a scatter plot of (a) FP and GEOS-Chem surface NH$_3$, (b) FP surface NH$_3$ and GEOS-Chem NH$_3$ VCD, (c) FP surface NH$_3$ and IASI NH$_3$ VCD and (d) IASI and GEOS-Chem NH$_3$ VCDs over Japan in 2014. Figure 6 also shows a comparison of IASI and GEOS-Chem NH$_3$ VCDs over (e) North and central China, and (f) South China.

![Figure 5. Horizontal distribution of the annual averaged FP surface NH$_3$ concentrations over Japan (colored circles) and comparison with (a) GEOS-Chem surface concentration, (b) GEOS-Chem NH$_3$ VCD, and (c) IASI NH$_3$ VCD shown as shadings.](image)

The highest level of NH$_3$ concentration (>3 ppb) in Japan was mainly over the Kanto region due to high anthropogenic emissions (Figure 1a). High values of FP NH$_3$ concentration (>3 ppb) were also shown in southern Kyushu, which were due to the large numbers of livestock and high levels of fertilizer use in local agriculture. FP and GEOS-Chem results showed relatively high correlation ($R = 0.69$) as in Figure 6a which indicated that GEOS-Chem captured the gradient of the horizontal distribution of NH$_3$ over Japan (e.g., high NH$_3$ concentration over Kanto region); however, GEOS-Chem NH$_3$ was significantly underestimated in the observations, which might be because the overall amount of NH$_3$ emission in Japan was underestimated. A most important reason for the difference between FP and GEOS-Chem NH$_3$ concentrations was that the GEOS-Chem concentrations represented the mean NH$_3$ concentrations over a grid ($0.5^\circ \times 0.667^\circ$, about 2500 km$^2$), while the FP observations usually represented the NH$_3$ concentrations over a much smaller area due to the short lifetime of NH$_3$. 

![Figure 6. Scatter plot of (a) FP and GEOS-Chem surface NH$_3$, (b) FP surface NH$_3$ and GEOS-Chem NH$_3$ VCD, (c) FP surface NH$_3$ and IASI NH$_3$ VCD and (d) IASI and GEOS-Chem NH$_3$ VCDs over Japan in 2014.](image)
The GEOS-Chem results still showed a summer peak which was constant with the seasonal variation. The range of the IASI NH$_3$ VCD variation at S1 and S2 in 2014 is indicated in Figure 7b by the shaded area. This indicated that the impact of PBLH on NH$_3$ concentrations over Japan was significantly lower than the IASI levels in summer (January to March) was unexpected and might be due to the large relative error and limited observation data as a result of relatively large cloud cover. However, the FP and GEOS-Chem NH$_3$ VCD on grids with FP observations, IASI and GEOS-Chem NH$_3$ VCD for the North China (NC) and central China (CC), and IASI and GEOS-Chem NH$_3$ VCD for the South China (SC). N is the number of data and R is the correlation coefficient.

IASI data did not indicate high values over the Kanto region, but showed higher values over Hokkaido, which was a different pattern to that indicated by the FP and GEOS-Chem results in winter. Scatter plots of the IASI NH$_3$ did not show a positive relationship with FP NH$_3$ (the slope was negative, R = -0.26) and GEOS-Chem NH$_3$ VCD (the slope was -0.03, R = -0.04), due to high relative errors over Japan. Scatter plots for North and central China indicated a relatively strong correlation (R = 0.74) due to there being sufficient IASI observations over these regions. There was a similar correlation (R = 0.75) over South China, although IASI retrieval was only 48% of the CTM value.

For a detailed comparison of NH$_3$ time series, we used two sites (S1 and S2) over the northern Hokkaido Region (Figure 7) and four sites (S8–10, S13) over the Kanto Region (Figure 8). The FP data variation range of S1 and S2 for the period of 2010 to 2014 is shown in the shaded area (Figure 7a). The range of the IASI NH$_3$ VCD variation at S1 and S2 in 2014 is indicated in Figure 7b by the shaded area.

Besides the two factors affecting NH$_3$ VCD, as we discussed in Section 4.1, there was one more factor that could affect the seasonal variation of surface NH$_3$ concentrations, which was the planetary boundary layer height (PBLH). The PBLH in summer was higher than in winter, which may have a dilution effect on surface NH$_3$ concentrations. However, both the FP and GEOS-Chem NH$_3$ concentrations showed similar seasonal variation which peaked in the summer, and the GEOS-Chem NH$_3$ range had a reasonable agreement with FP data. This indicated that the impact of PBLH on the seasonal variation of surface NH$_3$ concentration was much smaller compared to the impacts of emissions and gas-aerosol partitioning.

The winter peak in IASI data (January to March) was unexpected and might be due to the large relative error and limited observation data as a result of relatively large cloud cover (Figure A1). The GEOS-Chem results still showed a summer peak which was constant with the seasonal variation of surface NH$_3$ concentrations.

Figure 6. Scatter plot of (a) FP and GEOS-Chem surface NH$_3$, (b) FP surface NH$_3$ and GEOS-Chem NH$_3$ VCD, (c) FP surface NH$_3$ and IASI NH$_3$ VCD, and (d) IASI and GEOS-Chem NH$_3$ VCD on grids with FP observations, (e) IASI and GEOS-Chem NH$_3$ VCD for the North China (NC) and central China (CC), and (f) IASI and GEOS-Chem NH$_3$ VCD for the South China (SC).
Figure 8 shows similar information for the Kanto area. FP data for various sites (S8, S9, S10, and S13 for 2014) are shown in the shaded area, and these 4 sites are located in 2 grids in GEOS-Chem; therefore, only GC S8 and GC S9 are shown in Figure 8. The FP average was higher than the GEOS-Chem average (i.e., GEOS-Chem was underestimated), but both displayed a clear summer peak (seasonal cycle). Both FP and GEOS-Chem data showed a peak in August, but IASI data did not show a peak at the same time, and the peak of REAS emission was July. The IASI results in August indicated very low levels and did not show a significant summer maximum, which may also be due to a large relative error.

![Figure 7](image_url1)

**Figure 7.** Time series of NH$_3$ in the Hokkaido region (a) FP and GEOS-Chem concentrations, (b) IASI NH$_3$ VCD and GEOS-Chem NH$_3$ VCDs, (c) REAS NH$_3$ emissions for S1 and S2 sites.

![Figure 8](image_url2)

**Figure 8.** Time series of NH$_3$ in the Kanto region (a) FP and GEOS-Chem concentrations, (b) IASI NH$_3$ VCD and GEOS-Chem NH$_3$ VCDs, (c) REAS NH$_3$ emissions for S8 and S9 sites.
4.3. Impact of Local NH₃ Emissions at the Dazaifu and Fukuoka Sites

FP observations in Fukuoka Prefecture were conducted at two sites. S26 (Dazaifu) was located near the CC-KU site, while S27 (Fukuoka) was located in a rural area of Fukuoka city (about 13 km southwest of the Fukuoka City downtown area and surrounded by small forest), and therefore was not significantly influenced by human activities. The locations of these three sites are shown in Figure 1b. Figure 1b also indicated that the NH₃ emissions were quite different in these three sites. The emission rates at the Dazaifu, CC-KU, and Fukuoka sites were 3.68, 2.22, and 0.26 Mg km⁻² year⁻¹, respectively.

Figure 9a shows FP data for Fukuoka and Dazaifu for 2014 and a box-whisker plot of NH₃ measurements at CC-KU (monthly data for January–July 2015, and August–December 2014 was used to show the seasonal cycle). Figure 9b,c show a comparison of IASI and GEOS-Chem NH₃ VCDs over Fukuoka and REAS NH₃ emissions used for GEOS-Chem simulations, respectively (the horizontal resolution of the REAS emission inventory was approximately 50 km; therefore, the three sites could not be distinguished). The FP NH₃ levels were highest at Dazaifu (S27), which was slightly higher than CC-KU and was 2–3 times higher than Fukuoka (S26). This indicated that differences in local NH₃ emissions surrounding the observation site can significantly affect the observed NH₃ concentrations, although the three measurement sites were located in the same GEOS-Chem grid. Therefore, higher resolution simulations were necessary to reproduce the horizontal distributions of NH₃ in urban areas.

Figure 9. Time series of NH₃ in the Kyushu area (a) FP and GEOS-chem concentrations in Fukuoka, Dazaifu and CC-KU (box-whisker), (b) IASI and GEOS-Chem VCDs, and (c) REAS NH₃ emissions.

Both the NH₃ surface concentration and VCD produced by GEOS-Chem displayed peaks in May and July. The peaks in GEOS-Chem NH₃ surface concentration and VCD occurred in different months. The GEOS-Chem surface concentration peaked in summer, while the GEOS-Chem VCD peaked in May. This may be because the long-range transport of NH₃ occurs in elevated layers in spring. The variation of IASI NH₃ VCD in Fukuoka was different from that in Kyushu, as shown in Figure 4. The Kyushu NH₃ VCD had a peak in summer, but there was no peak in May.
Based on the comprehensive analysis and comparison in this study, it can be indicated that although different datasets showed reasonable agreements, there were still some differences among different datasets. As revealed by the observations of 3 sites in Fukuoka, large differences (a factor of 2–3) existed; therefore, more in-situ observations are necessary. Besides in-situ observations, improved satellite retrievals and high-resolution model simulations with more accurate emissions are necessary for a better understanding of the atmospheric NH₃ over East Asia.

5. Conclusions

Atmospheric ammonia plays an important role in the formation of secondary inorganic aerosols, the neutralization of acid rain, and the deposition to ecosystems, but has not been well understood yet, especially over East Asia. In this study, we analyzed the spatio-temporal variation in atmospheric NH₃ using long-term hourly NH₃ measurements made at CC-KU in Fukuoka, the nationwide FP network observation in Japan, GEOS-Chem CTM results, and IASI satellite retrievals over East Asia.

IASI NH₃ data provided useful information for East Asia. IASI retrievals over central and North China were similar to the CTM results. However, over South China, there were fewer IASI observations due to high levels of cloud cover, and the retrieval results were underestimated compared with CTM results (IASI NH₃ was 48% of CTM NH₃). Over Japan, the nationwide FP NH₃ data from JELA and CTM results were strongly correlated (R = 0.65) even when CTM results were underestimated (about half of the FP measurements). It was found that the IASI observations over Japan were below or near the detection limit, and it was difficult to obtain a reasonable correlation between surface measurements and CTM results.

Data from two FP NH₃ measurement sites within Fukuoka Prefecture were examined carefully. Dazaifu FP NH₃ measurements displayed a clear seasonal cycle (spring-summer high and winter low), and were 2–3 times higher than that of the Fukuoka rural site (located 13 km southwest of the Fukuoka downtown area). NH₃ emissions with 1-km resolution identified a 10-fold difference in levels between the Dazaifu and Fukuoka sites (Dazaifu was higher). This indicates that differences in local NH₃ emissions surrounding an observation site play an important role in determining the observed NH₃ concentrations. The CTM underestimation (by about 50%) of the NH₃ might be due to the underestimation of the NH₃ emission inventory at a coarse resolution (50 km) used in the model simulation.

The comprehensive analysis indicated that there were still some differences among different datasets. More in-situ observations, improved satellite retrievals, and high-resolution model simulations with more accurate emissions are necessary for better understanding the atmospheric NH₃ over East Asia.

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Appendix A

Figure A1. Horizontal distributions of NH$_3$ data number per grid (a1, b1, c1, d1, e1), averaged cloud cover (%, a2, b2, c2, d2, e2), and (c) relative error (%, a3, b3, c3, d3, e3) over East Asia for the whole year (a1–a3) and each season (b1–e3) of 2014.
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