1 **The Global Tropospheric Ammonia Distribution as seen in the 13-year AIRS**

2 **Measurement Record**

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Abstract:

Ammonia (NH_3) plays an increasingly important role in the global biogeochemical cycle of reactive nitrogen as well as in aerosol formation and climate. We present extensive and nearly continuous global ammonia measurements made by the Atmospheric Infrared Sounder (AIRS) from the Aqua satellite to identify and quantify major persistent and episodic sources as well as to characterize seasonality. We examine the 13-year period from September 2002 through August 2015 with a retrieval algorithm using an optimal estimation technique with a set of three, spatially and temporally uniform a priori profiles. Vertical profiles show good agreement ($\sim 5 - 15\%$) between AIRS NH_3 and the in situ profiles from the winter 2013 DISCOVER-AQ (DISCOVER-Air Quality) field campaign in central California, despite the likely biases due to spatial resolution differences between the two instruments. The AIRS instrument captures the strongest consistent NH_3 concentrations due to emissions from the anthropogenic (agricultural) source regions, such as South Asia (India/Pakistan), China, the United States (U.S.), parts of Europe, Southeast (SE) Asia (Thailand/Myanmar/Laos), the central portion of South America, as well as Western and Northern Africa. These correspond primarily to irrigated croplands, as well as regions with heavy precipitation, with extensive animal feeding operations and fertilizer applications where a summer maximum and a secondary spring maximum are reliably observable. In the Southern Hemisphere (SH) regular agricultural fires contribute to a spring maximum. Regions of strong episodic emissions include Russia and Alaska as well as parts of South America, Africa, and Indonesia. Biomass burning, especially wildfires, dominate these episodic NH_3 high concentrations.

1. Introduction

Global ammonia (NH_3) emissions are increasing due to the increased agricultural livestock numbers coupled with the increasing use of nitrogen fertilization. Atmospheric ammonia has impacts upon local scales, acidification and eutrophication of the ecosystems, and international (transboundary), as well as local, scales through formation of fine ammonium containing aerosols (Sutton et al., 2007, 2008). Ammonia reacts rapidly with sulfuric (H_2SO_4), nitric (HNO_3), and hydrochloric (HCl) acids to form a large fraction of secondary aerosols, i.e., fine Particulate Matter ($PM_{2.5}$) (particles less than 2.5 micrometers in diameter) (Malm et al., 2004). These ammonium containing aerosols affect Earth's radiative balance, both directly by scattering incoming radiation and indirectly by acting as cloud condensation nuclei (e.g., Adams et al., 2001; Martin et al., 2004; Abbatt et al., 2006; Wang et al., 2008; Henze et al., 2012). A large percentage of $PM_{2.5}$ can penetrate human respiratory systems and deposit in the lungs and alveolar regions, thus endangering public health (e.g., Pope et al., 2002). Ammonia deposition modifies the transport lifetimes, and deposition patterns of sulfur dioxide (SO_2) and nitrogen dioxide (NO_x) (Wang et al., 2008; Henze et al., 2012). Additionally, ammonia increases the concentrations of the greenhouse gas nitrous oxide (N_2O) (EPA, 2011) and, together with NH_4^+ content in soils, NH_3 is involved in CH_4 production and release (Fowler et al., 2009). NH_3 can also contribute to increases in radiative forcing through conversion of organic carbon (OC) into brown carbon (BrC) (Updyke et al., 2012). Therefore, monitoring NH_3 global distribution of sources is important to human health, with respect to air and water quality, and climate change.

Atmospheric ammonia concentrations have been modeled from a three-dimensional coupled-oxidant-aerosol model (GEOS-Chem) (Bey et al., 2001) to estimate natural and transboundary pollution influences on sulfate-nitrate-ammonium aerosol concentrations in the United States (U.S.) (Park et al., 2004). We used the simulated NH_3 fields from GEOS-Chem as the retrieval a priori for this study. A number of ammonia related science studies and top-down inventory studies are based on GEOS-Chem and its adjoint (Henze et al., 2009; Heald et al., 2012; Paulot et al., 2013; Zhu et al., 2013; Paulot et al., 2014; Paulot and Jacob, 2014). The model's ammonia emissions were based on annual data from the 1990 1° x 1° GEIA inventory of Bouwman et al. (1997). Table 1b from Park et al. (2004) shows a summary of global and contiguous U.S.

94   ammonia emissions for 2001. The inventory's categories include anthropogenic sources:

95   domesticated animals, fertilizers, human bodies, industry, fossil fuels, and natural sources:

96   oceans, crops, soils, and wild animals. Additional emissions from biomass burning and biofuel

97   used were computed using the global inventories of Duncan et al. (2003) and Yevich and Logan

98   (2003), with an emission factor of 1.3 g NH_3 per kilogram dry mass burned (Andreae and Merlet,

99   2001). For the emissions from domesticated animals and soils, the GEOS-Chem model used the

100   exponential dependencies on temperature reported by Aneja et al. (2000) and Roelle and Aneja

101   (2002), respectively. Ammonia emissions from crops and fertilizers were assumed to vary

102   seasonally with the number of daylight hours (Adams et al., 1999). Seasonal variations in

103   biomass burning and biofuel emissions in the model were specified based on satellite

104   observations (Duncan et al., 2003) and the heating degree-days approach (Park et al., 2004). The

105   GEOS-Chem model can be used to generate 3-D global monthly mean fields of NH_3

106   concentrations, or higher temporal resolutions (e.g., daily or hourly), for various years.

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108   Satellite remote sensing offers unique opportunities to monitor environmental variables with

109   relatively high temporal and spatial coverages. Ammonia measurements with large, daily global

110   coverage are challenging and lacking, partly due to the relatively short (hours to a day) lifetime

111   of NH_3 near the Earth's surface, and partly because its retrievals require high sensitivity that can

112   be only obtained from areas with high thermal contrast (TC, the temperature difference between

113   that of the surface temperature and of the first discernable atmospheric layer) near the surface

114   (Clarisse et al., 2010). First measurements of ammonia from space were reported over Beijing

115   and San Diego, CA areas, as examples, with the Tropospheric Emission Spectrometer (TES,

116   Beer et al., 2008) and in biomass burning plumes with the Infrared Atmospheric Sounding

117   Interferometer (IASI, Coheur et al., 2009) satellite. Shephard et al. (2011) documented the TES

118   ammonia retrieval methodology. TES NH_3 data has been utilized jointly with GEOS-Chem in

119   various emission source studies (e.g. Alvarado et al., 2011; Pinder et al., 2011; Walker et al.,

120   2012; Zhu et al., 2013). Luo et al. (2014) compared TES NH_3 versus carbon monoxide (CO)

121   ratios, using data from the year 2007, to those of the GEOS-Chem model with a focus on

122   biomass burning emissions using TES representative volume mixing ratio values (Shephard et al.,

123   2011).

124

125 The first global map of ammonia was created from IASI measurements by correlating observed

126 brightness temperature differences between strong NH_3 absorbing channels and weak ones to

127 NH_3 total columns using averaged datasets from 2008 (Clarisse et al., 2009). It was later

128 concluded that this method tends to underestimate the global emission inventories at a number of

129 global NH_3 hotspots using IASI radiances. Clarisse et al. (2010) examined the ammonia amounts

130 in the San Joaquin Valley of California in the U.S. using an optimal estimation (OE) retrieval

131 method (Rodgers, 2000) with a global uniform a priori and IASI radiances and compared them

132 with TES measurements. They studied the factors influencing the ability to use satellite infrared

133 (IR) instruments to retrieve accurate NH_3 columns and concentrations, finding that the main

134 factors were NH_3 concentrations and thermal contrast. They concluded that through retrieval and

135 forward radiative transfer model runs, if both of the NH_3 concentrations and thermal contrast are

136 large enough, it is possible to quantify ammonia near the lowest level of the atmosphere. R'Honi

137 et al. (2013) discussed the elevated concentrations of NH_3 and $HCOOH$ emitted by the 2010

138 Russian wildfires. Heald et al. (2012) used IASI ammonia products jointly with the GEOS-Chem

139 output to study inorganic aerosol loading and atmospheric ammonia concentrations over the U.S.

140

141 Global ammonia sources and variability based on continuous monitoring with longer than a

142 decade record (13 years) have not been hitherto available. This study introduces a newly

143 developed daily and global ammonia product from the Atmospheric Infrared Sounder (AIRS) on

144 the NASA EOS Aqua satellite, spanning September 2002 through August 2015. The AIRS orbit

145 covers nearly the entire globe twice daily, and due to cloud clearing, recovers up to 70% of

146 cloudy coverage (Susskind et al., 2003; Warner et al., 2013). Additionally, AIRS is in the

147 afternoon Equator crossing time; and therefore, it offers high sensitivity due to higher surface

148 temperature and provides higher thermal contrast to NH_3 measurements.

149

150 In the next section, we detail the methodology used to develop the global products of NH_3 and

151 present the discussions for data quality. In Section 3, we show examples of validation cases

152 using in situ data from a recent NASA aircraft mission – DISCOVER-AQ (Crawford et al.,

153 2014) (http://discover-aq.larc.nasa.gov). Section 4 illustrates the global distributions of the NH_3

154 sources. We demonstrate the seasonal variability of NH_3 concentrations using AIRS 13 year

155 measurements in Section 5, before summarizing results in Section 6.

156

2. Methodology

158

159 The AIRS instrument is a grating spectrometer with 2378 separate spectral channels between

160 650-2670 cm^{-1} (15.3-3.8 μm) with a spectral resolving power on the order of 1200. Twelve

161 channels of the AIRS radiances in the window regions (860 – 875, 928 – 932, and 965 – 967 cm^{-}

162 ^{1}) are currently used to retrieve NH_3. These channels are carefully selected so that the retrievals

163 are based on the NH_3 sensitivity, while the effects of the surface and overlapping gases are

164 minimized. AIRS cloud clearing, described by Susskind et al. (2003), increases the data coverage

165 significantly to nearly 50 – 70% of the total measurements, instead of the pure clear coverage of

166 approximately 10 – 15% at a 13.5 km^2 single-view pixel size (Warner et al., 2013). AIRS NH_3

167 retrievals are based on the cloud-cleared radiances (CCRs) from AIRS L2 products. The

168 averaging kernel (AK) peaks at about 918 hPa giving AIRS good sensitivity to lower

169 tropospheric NH_3 because the planetary boundary layer generally extends above this altitude at

170 the overpass local time of 1:30 pm.

171

172 The algorithm used in this AIRS NH_3 study was based on a retrieval module developed for AIRS

173 carbon monoxide (CO) products (Warner et al., 2010). This module was built upon and added to

174 the current AIRS operational system or team algorithm (Susskind et al., 2003), but used a

175 different minimization method. The NH_3 module uses AIRS Version 6 (V6) Level 2 (L2)

176 profiles and errors from the previous retrieval steps (i.e., surface, clouds, water vapor, ozone,

177 methane, CO) as input to the AIRS forward model – the Stand-alone AIRS Radiative Transfer

178 Algorithm (SARTA) (Strow et al., 2003). We used SARTA with the addition of NH_3 as a

179 variable gas, which was carried out by co-author Strow and co-workers, since the official AIRS

180 forward model does not include NH_3 absorption as a variable. AIRS NH_3 retrievals use an OE

181 method following the formulations given by Rodgers (2000), and also described by Pan et al.,

182 (1998). The OE retrieval output quantities not only include the NH_3 concentrations, but also

183 provide the AKs, the error covariance, and the degrees of freedom for signal (DOFS), which

184 benefit model verifications and data assimilation by using well-quantified errors.

185

186 Given a model of the instrument's signals, in the OE method, the forward equation for the NH_3

187 profile retrieval problem can be written as:

188

189 $$\mathbf{y} = \mathbf{f}(\mathbf{x}, \mathbf{b}) + \mathbf{n}_{\iota}, \tag{1}$$

190

191 where $\mathbf{y}$ is the vector of measured radiances, $\mathbf{x}$ is the state vector (variables to be retrieved from

192 the measurements), $\mathbf{b}$ represents all other parameters used by the forward model, $\mathbf{f}(\mathbf{x}, \mathbf{b})$ is the

193 forward model function, and $\mathbf{n}_{\iota}$ is the instrument noise. For the variables that obey a Gaussian

194 distribution, this inverse problem is equivalent to the maximum likelihood solution. By using a

195 Newtonian iteration; the solution to equation (1) can be written as (Rodgers, 2000):

196

197 $$\mathbf{X_{n+1}} = \mathbf{x_a} + \mathbf{C_a}\mathbf{K_n}^{\mathbf{T}}(\mathbf{K_n}\mathbf{C_a}\mathbf{K_n}^{\mathbf{T}} + \mathbf{C_e})^{-1}[\mathbf{y} - \mathbf{y_n} - \mathbf{K_n}(\mathbf{x_a}-\mathbf{x_n})] \tag{2}$$

198

199 where n is the order of iteration and $\mathbf{C_e}$ is the measurement error covariance matrix.

200 $\mathbf{K}n = \partial\mathbf{f}(\mathbf{x},\mathbf{b})/\partial\mathbf{x}$ is the jacobian matrix for iteration n, which is the sensitivity matrix of the

201 forward model to the state vector $\mathbf{x}$. $\mathbf{x_a}$ is the mean of the a priori distribution and $\mathbf{C_a}$ is the a

202 priori error covariance matrix for $\mathbf{x_a}$.

203

204 As defined by the retrieval formulations, the AKs are computed using the following:

205

206 $$\mathbf{A} = \mathbf{C_a}\mathbf{K}^{\mathbf{T}}(\mathbf{K}\mathbf{C_a}\mathbf{K}^{\mathbf{T}} + \mathbf{C_e})^{-1}\mathbf{K} \tag{3}$$

207

208 and,

209

210 $$\mathbf{x'} \approx \mathbf{A}\mathbf{x} + (\mathbf{I}-\mathbf{A})\mathbf{x_a}, \tag{4}$$

211

212 where $\mathbf{I}$ represents the identity matrix and $\mathbf{x}$ is the true state. Equation (4) states that in the

213 absence of other error sources the retrieved state is a weighted mean of the true state and the a

214 priori state, with the weight $\mathbf{A}$ for the true state and $\mathbf{I}$-$\mathbf{A}$ for the a priori. This shows the

215 importance of AKs as diagnostics of the retrieval. The closer the matrix $\mathbf{A}$ is to the identity

216 matrix the more the retrieved state resembles the true state.

217

218 The optimal estimation method requires an a priori mean profile and a corresponding error

219 covariance matrix that represent the current knowledge of the geophysical property, i.e., NH_3,

220 prior to the retrieval. Due to the high spatial variability and short lifetime of NH_3, a simple fixed

221 a priori for all emission scenarios is not appropriate. We developed a global mean, multi-year

222 averaged (2003-2012), three-tier a priori from GEOS-Chem model (v9-02) simulations for high,

223 moderate, and low pollutions. We used GEOS-5 MERRA datasets from the NASA Global

224 Modeling and Assimilation Office (Rienecker et al., 2011) to drive the meteorological fields in

225 the GEOS-Chem simulations. Figure 1 shows the a priori mean profiles (solid curve with

226 squares) and the error covariance matrices (horizontal bars) for the low (left panel), the moderate

227 (middle panel), and the high pollution (right panel), respectively. The high pollution range was

228 defined by profiles with Volume Mixing Ratios (VMRs) greater than or equal to 5 parts-per-

229 billion-volume (ppbv) at the surface. The moderate pollution range includes the profiles with

230 surface VMRs greater than or equal to 1 ppbv but less than 5 ppbv, or greater than 1 ppbv at any

231 level between the surface and 500hPa. The low pollution is then defined as being lower than the

232 lower bounds of the moderate pollution range. The profiles were adjusted to match AIRS

233 forward model levels. The modeled profiles are extrapolated near the surface with additional

234 constraints to eliminate high values in the model near the surface, which are likely seen by

235 satellite sensors.

236

237 The same set of the three-tier a priori profiles is used globally and throughout the AIRS data

238 record. Thus, any spatial and temporal NH_3 variations detected using this algorithm are from

239 AIRS measurements. To select one of the three a priori profiles for each AIRS pixel, we examine

240 the brightness temperature difference between a strong and a weak channel, divided by the

241 measurement noise of the strong channel, defined as a "difference of brightness temperature

242 index" (DBTI). This is similar to the method used by TES NH_3 and described by Shephard et al.

243 (2011). The DBTIs vary with meteorological conditions and, most importantly, the thermal

244 contrast at the surface. To take into account of these effects, we simulate the relationship

245 between the brightness temperature differences and TC under various meteorological conditions

246 using SARTA. We randomly picked 13790 profiles from AIRS L2 products over land from the

247 months of January, April, July, and October in years 2003, 2008, and 2011. We then perturbed

248   the NH_3 values spanning the three a priori mean profiles using the range of $0 - 100$ ppbv

249   multiplied by a random number for each atmospheric profile. The observed brightness

250   temperatures are compared with the simulated values at a given TC to determine the level of a

251   priori for the full retrievals. Figure 2 depicts a relationship between the DBTI and DOFS for the

252   three emission levels with low emissions in blue, moderate emissions in green, and high

253   emissions in red. The higher DBTIs are correlated with higher DOFS, which represent higher

254   surface thermal contrast (Deeter et al., 2007).

255

256   The NH_3 retrieval quality assurance levels are determined based on the retrieval sensitivities

257   under various meteorological and surface conditions using the AKs and the DOFS. We also take

258   into account the performance of the retrievals against surface thermal contrasts from AIRS

259   products. Additionally, we examine the retrieval residuals, χ^2, and the number of iterations to set

260   proper quality assurance flags. The retrieval residuals in Kelvin (K) are defined by the square

261   root of the mean variance of the observed brightness temperatures minus calculated. The NH_3

262   retrieval quality is affected by the meteorological properties, such as the vertical temperature and

263   water vapor profiles, surface temperatures, and emissivity, which are used to model the

264   atmosphere. We also adapt the error information provided by the AIRS CCR for the relevant

265   channels, which includes meteorological quantities that are used in deriving the AIRS CCR

266   (http://disc.sci.gsfc.nasa.gov/AIRS/documentation/v6_docs/v6releasedocs1/V6_Level_2_Cloud_

267   Cleared_Radiances.pdf). This error information is flagged by Q0, Q1, and Q2 with Q0 having

268   the highest quality and Q2 being unusable. In the remaining discussions of this study, we used χ^2

269   between 0.9 and 27, considering that the channels used are not all spectrally independent. The

270   number of iterations limit was set at 10, meanwhile, only the cases with retrieval residuals less

271   than 1 K are used. We also excluded cases with the surface thermal contrast between -4 and +4 K,

272   to avoid ambiguous a priori levels; however, this primarily affects areas over the global oceans.

273   Any additional screening of the data for higher quality requirements, e.g., the use of DOFS, will

274   be discussed case by case. Although we have developed AIRS NH_3 products for all available

275   datasets, only the daytime and land cases are discussed in this study. Additionally, only radiances

276   with quality flag as Q0 are selected for the discussions in the following sections to ensure the

277   best accuracy.

278

279 **3. Validation with in situ measurements**

280

281   Validations of retrievals using in situ measurements are vital to quantifying uncertainties in the

282   concentrations, sources, transport patterns, and trends using satellite data. Direct measurements

283   of tropospheric NH_3 are relatively sparse and in situ measurements above the ground level,

284   necessary to validate satellite retrievals, are available for only limited locations and time periods

285   (e.g. Nowak et al., 2007, 2010, and 2012). Validation of AIRS NH_3 datasets with available in

286   situ measurements is a continuous effort as more in situ measurements become available. As an

287   example of our validation effort, we use the DISCOVER-AQ NH_3 measurements over California

288   (https://www-air.larc.nasa.gov/cgi-bin/ArcView/discover-aq.ca-2013--). The sampling inlet and

289   NH_3 calibration set-up used during DISCOVER AQ with the cavity ring down spectrometer

290   (CRDS) (G2103, Picarro Inc.) is the same as used with the Chemical Ionization Mass

291   Spectrometry (CIMS) and described in Nowak et al. (2007). The CRDS, aboard the NASA P-3B

292   aircraft during DISCOVER-AQ CA, data period covers January 16 to February 06, 2013. The in-

293   situ NH3 vertical profiles were made in the Southern San Joaquin Valley of California. This

294   region inside the central valley of California, between the coastal mountains in the west and the

295   Sierra Nevada Mountains in the east, consists largely of farmland with scattered dairy

296   farms. Although most of the area is rural, the profiles were made near the small cities of Hanford

297   and Corcoran. We only select spiral profiles from the flights within 45 km of the center of the

298   retrieved AIRS profiles, for the closest match, and within 3 hours of the measurement window,

299   similar to the method used for AIRS CO validation (Warner et al., 2006).

300

301   Figure 3 shows four retrieval profiles that show high NH_3 concentrations and meet the matching

302   criteria, where the red curves represent AIRS retrieved profiles, gray curves are the a priori

303   profiles, green solid lines are in situ spiral profiles, and the blue dashed lines are the convolved

304   in situ profiles by AIRS NH_3 AKs. The in situ spiral profiles are taken by flying an aircraft in the

305   spiral shape in descending or ascending order near a central location, hence are the closest to

306   being the true vertical profiles. Note that in Fig. 3, the x-axis is linear from 0 to 25 ppbv and

307   logarithmic from 25 to 150 ppbv. The convolved in situ profiles take into account satellite

308   retrieval sensitivities, making them appropriate to compare against satellite retrievals (Rodgers

309   and Connor, 2003). The convolution calculations follow Eq. (3) and (4) in Sec. 2. The top left

310   panel shows a case measured on January 16, 2013 with the retrieval quality at 0, DOFS at 0.64,

311   χ^2 at 1.91, the retrieval residual at 0.07 K, and the measurement time differences at 1.31 hours.

312   The distance between the in situ profile and the center of the AIRS profile is approximately 13.5

313   km. The top right panel shows four in situ profiles from January 21, 2013 with AIRS retrieved

314   profile quality at 0, DOFS at 0.66, χ^2 at 1.26, the retrieval residual at 0.07 K, the time differences

315   ranging from 0.58 to 1.68 hours, and the distance differences at approximately 56 km for all four

316   profiles. The two profiles in the bottom left panel are also from January 21, 2013, with quality at

317   0, DOFS at 0.83, χ^2 at 0.31, the retrieval residual at 0.06 K. The time differences to the AIRS

318   retrieved profile are 1.02 and -1.25 hours, and the distances are 38.3 and 38.7 km, respectively.

319   In the bottom right panel, there are four profiles taken from February 4, 2013, with the retrieval

320   profile quality at 0, DOFS at 0.84, χ^2 at 1.1, and the retrieval residual at 0.05 K. The time

321   differences between the in situ and the retrieved profiles are 1.63, 1.40, -0.47, and -0.71, and the

322   distances are 5.1, 45.2, 4.9, and 45.2 km, respectively. Some of the AIRS retrievals collocate

323   with several in situ profiles, and these show substantial spatial variability.

324

325   Over regions with high NH_3 in situ concentrations, the convolved in situ profiles agree with the

326   retrievals within <1 to ~3 ppbv (~5-15%) near the top of the boundary layer, as seen in the top

327   two panels in Fig. 3. These two AIRS NH_3 profiles show good retrieval sensitivities with DOFS

328   at approximately 0.64 and 0.66, χ^2 at 1.91 and 1.26, and the residual at 0.07 K, respectively. The

329   top left in situ profile is relatively close (13.5 km) to the center of the AIRS pixel, whereas the

330   top right in situ profiles are further away (~46 km) from the center of the AIRS pixel. When the

331   NH_3 amount is low and there is very little sensitivity in AIRS measurements, the convolved

332   profiles converge to the a priori profiles, as seen in the profiles with low NH_3 concentrations in

333   the top right panel and in the bottom left panel. In the bottom right panel, there are four in situ

334   profiles close to the AIRS profile – the AIRS pixel measures the average effect of the area

335   represented by the four in situ profiles. Below 925 – 950 hPa in height, the in situ NH_3 mixing

336   ratios are significantly higher than the retrieved profiles, indicating a limitation of satellite

337   remote sensing in capturing near surface composition properties. Note again that each AIRS

338   profile covers a surface area of 45 km^2 where in situ observed NH_3 amounts can vary by a factor

339   of ten. The aircraft in situ flights sometimes are biased by their proximity to strong local point

340   sources. Therefore, the differences between the retrievals and in situ measurements are likely due

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341   to sampling issues, although the retrieved profile matches the average of the in situ profiles as

342   discussed above. Nonetheless, the vertical profiles show good agreement (~5 – 15%) between

343   AIRS NH_3 and the in situ profiles in the examples given above.

344

345   **4.   Global Ammonia Concentrations**

346

347   The AIRS global NH_3 VMRs at 918 hPa, averaged from September 2002 through August 2015,

348   are shown in the upper panel of Fig. 4. The lower panel in Fig. 4 shows the total occurrences of

349   elevated concentrations (VMRs ≥ 1.0 ppbv at 918 hPa) for the same dataset. The occurrences, in

350   numbers of days, are good indicators of the types of emission sources either due to recurring

351   agricultural practices or episodic forest fires. It is important to analyze the NH_3 VMRs together

352   with the occurrences to identify major emission sources. Another important quantity used in the

353   NH_3 source analysis is the retrieval DOFS. Figure 5 shows the AIRS NH_3 DOFS values being in

354   a range of 0.1 to slightly above 1.0. The regions with DOFS greater than 0.4 are generally

355   associated with high NH_3 concentrations and strong signal to noise ratios. We used a threshold

356   level of DOFS of 0.1 to screen the retrievals in the Fig. 4 top panel to eliminate noise and to

357   focus on where AIRS sensitivity is high. Areas with DOFS < 0.1 in the whole data record are

358   indicated in white. The AIRS retrievals are sensitive to NH_3 concentrations in the lowest layer of

359   the atmosphere between 850 hPa and the surface, with sensitivity peaking at approximately 918

360   hPa based on the retrieved AKs (not shown). Therefore, we use NH_3 VMRs at this level for all

361   discussions in this study. There are diurnal variations in the datasets (not shown) that may be due

362   to a number of factors including the day-night differences of emissions and chemical reactions

363   and possibly measurement sensitivities, which are beyond the scope of this paper and will be

364   studied at a later time. Also note that the missing data over land in certain regions are either due

365   to high elevation (above the 918 hPa altitude level), and therefore not shown, or persistent

366   cloudy days.

367

368   Globally, AIRS shows strong NH_3 hotspots from biogenic and anthropogenic sources including

369   South Asia (India/Pakistan), East Asia (China), the central U.S., parts of Europe, Southeast Asia

370   (Thailand/Myanmar/Laos), the central portion of South America, and Western and Northern

371   Africa, where both the NH_3 VMRs and the frequent occurrences are high. The primary sources

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372   for these regions are from human activities, e.g., livestock waste management and other

373   agricultural activities. The NH_3 concentrations over these hot spots vary from ~2.5 to above 10

374   ppbv, averaged over 13 years covering both strong and weak emission periods. Also seen are

375   large regions of high NH_3 concentrations due to biomass burning events over Russia, Alaska,

376   South America, Africa, and Indonesia, represented by high VMRs and low occurrences. High

377   concentrations of NH_3 are persistent over South America and reflect emissions from biomass

378   burning that are trapped by the Andes

379   http://earthobservatory.nasa.gov/IOTD/view.php?id=8033&eocn=image&eoci=related_image.

380   The hot spot over South Asia corresponds to the heavily populated Indo-Gangetic Plain with

381   plentiful, fertile croplands and extensive livestock, and bounded on the north by the Himalayas

382   (Yamaji et al., 2004). The absolute maximum on Fig. 4 is found over the Punjab which has the

383   highest population density in Pakistan.

384

385   To understand the persistent emission sources, we filtered the NH_3 VMRs with the collocated

386   occurrences of elevated concentrations (≥ 1.4 ppbv) greater than 40 days; and the results are

387   shown in Fig. 6 top panel. Although a sufficient concentration (≥ 1.4 ppbv) threshold is used to

388   calculate occurrences of the persistent sources, we used all VMR values, with DOFS greater than

389   0.1, for the VMR maps. The persistent NH_3 sources not only include those large regions listed

390   above, but also include small geographical areas such as in the San Joaquin Valley of central

391   California in the U.S. (with low sulfur emissions and where livestock are plentiful); the Po

392   Valley, Italy; Fergana Valley, Uzbekistan; Azerbaijan; the Nile Delta and along the banks of the

393   Nile River in Egypt; and the Sichuan Basin in China. Some of these source locations are

394   consistent with those previously reported by Clarisse et al. (2009). These emission hotspots are

395   compared with the "Pasture and Cropland Map" (see middle panel in Fig. 6), posted by

396   http://OurWorldInData.org, located at the Institute for New Economic Thinking at the Oxford

397   Martin School. AIRS NH_3 source regions are strongly correlated with cropland areas, e.g., over

398   India, China, the middle U.S., Western Africa, eastern South America, and Europe. Note that

399   four of the strongest emission regions correspond to high percentage irrigated agricultural areas

400   (see bottom panel in Fig. 6), i.e., over Pakistan, India, northern Italy, and Azerbaijan adjacent to

401   the Caspian Sea. The irrigated agricultural land includes that irrigated by controlled flooding.

402   These data are provided by the World Bank (data.worldbank.org) where the color values are the

403   percent agricultural irrigated land of total agricultural land. These irrigation activities are

404   associated with periods of fertilization and ammonia release. Sommer et al. (2004) studied the

405   relationship between the fertilizing time and the ammonia release time and indicated that the

406   fertilizers applied in March can be released in the June to August time frame depending on the

407   amount of precipitation. The irrigation practices may have the same effect as high amounts of

408   precipitation.

409

410   Over China, the AIRS retrieval can match high-resolution inventories distinguishing the two

411   major animal husbandry areas in east-central China (Henan, Shandong, and Hebei provinces) as

412   well as Sichuan to their southwest (Huang et al., 2012). Additional weaker, but persistent, NH_3

413   sources are also seen in the Fig. 6 top panel that are likely related to livestock and agriculture

414   practices. These source regions include areas in eastern North Carolina (consistent with Wu et al.,

415   2008), Arizona near Phoenix, in the east coast of Spain near Barcelona and Águilas, and over

416   large areas in the Netherlands, in Mozambique in Africa, and the Gambela National Park region

417   between Ethiopia and South Sudan.

418

419   **5. Seasonal Variability**

420

421   Seasonal variations are shown in Fig. 7 in the four NH_3 VMR maps, averaged between Sept.

422   2002 and Aug. 2015, for December-January-February (DJF, upper left panel), March-April-May

423   (MAM, upper right panel), June-July-August (JJA, lower left panel), and September-October-

424   November (SON, lower right panel), respectively, with DOFS greater than 0.1 and no cutoff for

425   the VMRs. Globally, the highest concentrations are in the NH summer and spring seasons, with

426   the exception from strong biomass burning (BB) sources, i.e., over South America, the Southeast

427   Asia, and Russia in the NH fall season. The highest NH_3 concentrations over non-BB dominant

428   regions occur over India, China, the Mid-West U.S., and part of Europe in the summer months.

429   The longest high concentration seasons are over northern India, collocated with the measurement

430   of high NH_4^+ in the precipitation over India reported by Kulshrestha et al. (2005). The seasonal

431   NH_3 VMR distributions in China, Europe, and the U.S. are also consistent, to a large extent, with

432   the Paulot et al. (2014) study of agricultural emissions inventory derived by high-resolution

433   inversion of ammonium wet deposition data. This is especially true for the spring season, as seen

14

434   in Fig. A1 of Paulot et al. (2014), showing MASAGE_NH3 (Magnitude and Seasonality of

435   Agricultural Emissions for NH_3, https://fpaulot.bitbucket.org/MASAGE/) emissions of NH_3 from

436   fertilizers.

437

438   High average concentrations (Fig. 7) with low frequencies of occurrences (Fig. 8) generally

439   indicate NH_3 from biomass burning (BB). The greatest emissions from BB in the NH appear in

440   the summer months over Siberia and eastern Russia as well as over Alaska, U.S. The highest

441   concentrations due to BB in the SH appear over South America in September to November

442   (spring for the SH) when precipitation is minimal and burning extensive (Oliveras et al., 2014).

443   Over SE Asia where the dry season and most BB occur in March to May, we find another local

444   maximum (Lin et al., 2013). Over Africa high concentrations from BB occur in the Western and

445   Central regions, although both high concentrations and frequencies of occurrences appear in the

446   Sahel just south of the Sahara in the NH winter. In that region persistent burning of agricultural

447   waste has been reported (Haywood et al., 2008); see also http://rapidfire.sci.gsfc.nasa.gov/cgi-

448   bin/imagery/firemaps.cgi.

449

450   Ammonia seasonal variations are presented (Fig. 9) using the monthly mean VMRs averaged

451   over the 13-year period. Simple hemispheric averages of NH_3 concentrations for all cases do not

452   accurately reflect the seasonality of the important agricultural activities in the NH, due to the

453   mixing with BB cases and low NH_3 regions, as well as regions with missing values due to weeks

454   of persistent cloud cover. To understand how NH_3 emissions vary seasonally due to human

455   activities, we focus on the NH_3 concentrations from the continuous emission sources. As in the

456   case of Fig. 6, where we showed continuous sources using screening by the occurrences of

457   elevated concentrations, we select the occurrence thresholds at concentration levels higher than

458   1.4 ppbv on at least 40 days of the 13-year record. Figure 9 shows the monthly mean variations

459   of NH_3 (solid line) in both the NH (upper panel) and the SH (lower panel); the dashed lines show

460   the $\pm 1\sigma$ (standard deviation, STD) and the shaded areas represent the maximum and minimum

461   range of each dataset. In the NH, the high emission period starts in April and the NH_3

462   concentrations peak in June. The NH average of the VMR concentrations from April through

463   July is in the range of 3.7 – 4.0 ppbv; and it gradually decreases to the minimum of below 2 ppbv

464   in November-December-January. The range of monthly mean variability between different years

465   is also larger from April to September (at ~1 ppbv) than in the winter months (at ~0.4 ppbv). The

466   STD decreases from the summer values of 0.6 ppbv to 0.3 ppbv in the winter.

467

468   Seasonal variation in the SH (lower panel in Fig. 9) shows that the primary sources of NH_3

469   emission are from BB, as was seen in the NH_3 seasonal maps (e.g., Fig. 7). Although the filtering

470   for the continuous emission sources eliminated some large occasional fires (i.e., over Indonesia),

471   there are still regularly occurring fires, such as those over the central part of South America. The

472   NH_3 concentrations in the SH peaks in September with an average value near 3.5 ppbv and

473   decreases sharply after the SH spring season. The season of high concentrations in the SH is

474   much shorter than in the NH, as demonstrated by the widths of the seasonal distribution curves.

475   The largest STD occurs in September with a magnitude of 2 ppbv, but the variation between

476   different years in the winter is very small (~0.25 ppbv).

477

478   **6. Summary**

479

480   The AIRS ammonia (NH_3) measurements with a 13-year data record provide global daily maps,

481   identify major source regions, and show seasonal cycles. This enables studies for detailed

482   locations of the sources and their spatial and temporal variations. The AIRS NH_3 products using

483   the optimal estimation (OE) retrievals provide retrieval sensitivity properties, in addition to NH_3

484   concentrations, such as: the averaging kernels (AKs), error covariance matrices, and the degrees

485   of freedom for signal (DOFS). This will facilitate sensor inter-comparisons, model verifications,

486   and data assimilation of satellite retrievals. AIRS measurements can not only capture high

487   biomass burning emissions (e.g., over Russia, Alaska, South America, Africa, and Indonesia)

488   and/or accumulated concentrations such as in various valleys (e.g., San Joaquin Valley,

489   California in the U.S., the Po Valley, Italy, Fergana Valley, Uzbekistan, and the Sichuan Basin in

490   China), but also emissions due to routine animal feeding and agriculture activities (e.g.,

491   Azerbaijan, Nile Delta and along the banks of the Nile River in Egypt, the Mid-West U.S., North

492   Carolina, U.S., the east coast of Spain, in the Netherlands, in Mozambique and Ethiopia, Africa,

493   and especially the Indo-Gangetic Plain of South Asia). Over China, the AIRS retrieval can match

494   high-resolution inventories distinguishing the two major animal husbandry areas in east-central

495   China and the Sichuan Basin. Preliminary validation results show excellent agreement with in

496   situ airborne measurements (to within 5-15% of the retrieved profiles). Note that since each

497   AIRS profile covers a surface area of 45 km^2 where the NH_3 amounts can vary largely, the

498   simple numerical differences may not be the optimal way to validate satellite ammonia products.

499

500   We use frequent occurrences of NH_3 elevated concentrations to select persistent sources. This

501   distinguishes the NH_3 emissions due to human activities versus occasional fires or retrieval noise.

502   We show the persistent ammonia sources correlate well with cropland usage, particularly in

503   regions where irrigation is a routine practice. We show the hemispheric seasonal variation using

504   sources screened by the high NH_3 frequent occurrences. The NH high NH_3 concentrations occur

505   in the spring and summer with highest from April to July and lowest in November through

506   January. In the SH, the NH_3 concentration is highest in September, this is most likely due to BB

507   emissions shown by the high VRMs and relatively low frequent occurrences.

508

509   Detailed examinations of specific regions are needed and will be included in future studies to

510   improve our understanding of the processes that control the NH_3 distribution and variability. The

511   recent NH_3 trends from AIRS 13-year measurements will also be a subject of future studies since

512   the scope of this paper is to focus on the algorithm details and the global distributions. Results in

513   this study are focused on land and daytime only. Future studies will include more complicated

514   surface types, i.e., ocean surfaces and regions with lower thermal contrast. The diurnal variations

515   will also be an important topic in the future studies. We have used the pixels with the highest

516   quality cloud-cleared radiances (at 45 km^2 spatial resolution) defined by the earlier steps of AIRS

517   retrievals, while a future direction will be to also use the higher spatial resolution single-view

518   pixels (at 13.5 km^2) under clear-sky conditions (Warner et al., 2013).

519

520   **Acknowledgement:**

521

527 Program through the NASA Center for Climate Simulation (NCCS) at Goddard Space Flight

528 Center.

529

530 **Reference:**

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749

750 **Figure Captions:**

751

752 **Fig.1.** The *a priori* profiles and the square root of the diagonal terms of the error covariance

753 matrices for the low pollution (left panel), the moderate pollution (middle panel), and the high

754 pollution scenarios (right panel), respectively.

755

756 **Fig. 2.** Correlation between the DBTI (Difference of Brightness Temperature Index) and DOFS

757 (Degrees Of Freedom for Signal) for the three emission scenarios with low pollution in blue,

758 moderate pollution in green, and high pollution in red.

759

760 **Fig. 3.** AIRS NH_3 validation against CRDS (the cavity ring down spectrometer) spiral profiles

761 collected during the DISCOVER-AQ CA (01/16-02/06, 2013). The red curves represent AIRS

762 retrieved profiles, gray curves are the *a priori* profiles, green solid lines are *in situ* spiral profiles,

763 and the blue dashed lines are the convolved profiles using AIRS NH_3 AKs. The x-axis is linear

764 from 0 to 25 ppbv and logarithmic from 25 to 150 ppbv.

765

766 **Fig. 4.** Upper panel: AIRS global NH_3 VMRs at 918 hPa, averaged from September 2002

767 through August 2015. The colorbar is linear from 0 to 5 ppbv and 5 to 10 ppbv, but with

768 different increments. Lower panel: The total occurrences (number of days) of high

769 concentrations (VMRs > 1.0 ppbv at 918 hPa) in the 13-year period. Red/blue colors indicate

770   relatively high/low occurrences of high concentrations, respectively.

771

772   **Fig. 5.** AIRS NH_3 DOFS values averaged over September 2002 – August 2015 period. Red/blue

773   colors indicate relatively high/low DOFS, respectively.

774

775   **Fig. 6.** Top panel: The NH_3 VMRs from the persistent sources filtered with the collocated

776   occurrences of elevated concentrations ($\geq$ 1.4 ppbv) using a threshold of greater than 40 days;

777   Middle panel: Pasture and Cropland Map (http://OurWorldInData.org); and Bottom panel:

778   irrigated agricultural land areas (data.worldbank.org).

779

780   **Fig. 7.** AIRS NH_3 VMRs at 918 hPa averaged between September 2002 and August 2015 for

781   December-January-February (DJF, upper left panel), March-April-May (MAM, upper right

782   panel), June-July-August (JJA, lower left panel), and September-October-November (SON,

783   lower right panel), with DOFS greater than 0.1 and no cutoff limit for the VMRs. Red/purple

784   colors indicate relatively high/low NH_3 VMRs.

785

786   **Fig. 8.** As in Fig. 7 except for the occurrences of high concentrations (VMRs $\geq$1 ppbv). Red/blue

787   colors indicate relatively high/low occurrences of high concentrations.

788

789   **Fig. 9.** The NH_3 monthly mean variations (solid line) in the NH (upper panel) and the SH (lower

790   panel), respectively. The long-dash lines show the 1σ standard deviation (STD); and the shaded

791   areas represent the maximum and minimum range of each dataset.

792

793   **Footnotes for Figure 6:**

794

795   The World Bank provided the statement that the maps displayed on the World Bank web site are

796   for reference only and do not imply any judgment on the legal status of any territory, or any

797   endorsement or acceptance of such boundaries.

798

Pasture   Cropland

100%   100%

0%   0%

0.0   1.0   2.0   3.0   4.0   5.0   10.0 ppbv

0%   76%

DJF   MAM

JJA   SON

Seasonal Variation NH

Seasonal Variation SH