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1 **Atmospheric nitrogen deposition in the Yangtze River basin: Spatial** 2 **pattern and source attribution**

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16 **Capsule:** The total dissolved inorganic nitrogen (DIN) exhibited a significant spatial variation in the
17 Yangtze River basin and fertilizer use is the largest contributor to total DIN deposition over the basin.

18 **Abstract:** The Yangtze River basin is one of the world's hotspots for nitrogen (N) deposition and
19 likely plays an important role in China's riverine N output. Here we constructed a basin-scale total
20 dissolved inorganic N (DIN) deposition (wet plus dry) pattern based on published data at 100
21 observational sites between 2000 and 2014, and assessed the relative contribution of different reactive
22 N (N_r) emission sectors to total DIN deposition using the GEOS-Chem model. Our results show a
23 significant spatial variation in total DIN deposition across the Yangtze River basin ($33.2 \text{ kg N ha}^{-1} \text{ yr}^{-1}$
24 ¹ on average), with the highest fluxes occurring mainly in the central basin (e.g., Sichuan, Hubei and
25 Hunan provinces, and Chongqing municipality). This indicates that controlling N deposition should
26 build on mitigation strategies according to local conditions, namely, implementation of stricter control
27 of N_r emissions in N deposition hotspots but moderate control in the areas with low N deposition
28 levels. Total DIN deposition in approximately 82% of the basin area exceeded the critical load of N
29 deposition for semi-natural ecosystems along the basin. On the basin scale, the dominant source of
30 DIN deposition is fertilizer use (40%) relative to livestock (11%), industry (13%), power plant (9%),
31 transportation (9%), and others (18%, which is the sum of contributions from human waste,
32 residential activities, soil, lighting and biomass burning), suggesting that reducing NH_3 emissions
33 from improper fertilizer application should be a priority in curbing N deposition. This, together with
34 distinct spatial variations in emission sector contributions to total DIN deposition also suggest that,

35 in addition to fertilizer, major emission sectors in different regions of the basin should be considered
36 when developing synergistic control measures.

37 **Keywords:** Nitrogen deposition, Source apportionment, Ecological risks, Mitigation strategy, the
38 Yangtze River basin.

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41 **Introduction**

42 In the past few decades, human activities associated with agricultural and industrial production
43 emitted large amounts of nitrogen (N) oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$) and ammonia (NH_3) to the atmosphere
44 ([Galloway et al., 2008](#)). They can be transported in downwind direction and transformed in the
45 atmosphere to nitric acid (HNO_3) and to particulate ammonium (NH_4^+) and nitrate (NO_3^-) via
46 chemical reactions, and eventually return to earth surface by wet and dry deposition processes. As a
47 consequence, atmospheric N deposition has dramatically increased globally, and this increase is
48 expected to continue over China ([Kanakidou et al., 2016](#)). Meanwhile, a considerable portion of
49 deposited N in land can also be transported to coastal waters and the open ocean via river flow ([Fowler
50 et al., 2013](#)). Excessive N inputs into aquatic ecosystems can cause negative environmental and
51 ecological effects, e.g., eutrophication of water body ([Bergstrom and Jansson, 2006](#)), hypoxia ([Diaz
52 and Rosenberg, 2008](#)), breakout of red tide ([Dai et al., 2010](#)), and a loss of biodiversity (Clark and
53 Tilman, 2008).

54 The Yangtze River basin is a region characterized by rapid economic development and
55 population growth, and generates as much as half of China's gross domestic product (GDP) (Lin et
56 al., 2005). This, in turn, makes the basin suffered from serious reactive nitrogen (N_r) pollution ([Gu et
57 al., 2012](#)). The Yangtze River is the largest river in the Euro-Asian continent and is the third longest
58 river in the world. It is responsible for significant N discharges into its estuary and the adjacent East
59 China Sea, leading to negative ecological effects ([Dai et al., 2010](#)). Dissolved inorganic nitrogen
60 (DIN), which includes oxidized (e.g., NO_x , HNO_3 , NO_3^-) and reduced (e.g., NH_3 , NH_4^+) forms, is
61 often the most abundant and bioavailable form of N and thereby contributes significantly to coastal
62 eutrophication (Veuger et al., 2004; Dumont et al., 2005). Using a mass balance model, [Wang et al.
63 \(2014\)](#) estimated that the contributions of bulk DIN deposition (i.e. wet plus some dry deposition,
64 measured by open [rain collectors](#)) to total N input to the basin increased from 3% in 1980 to 5% in
65 2000. Furthermore, [Chen et al. \(2016\)](#) reported that atmospheric DIN deposition accounts for on
66 average approximately 13% of human-controlled N inputs into the basin during the period of 1980-
67 2012. Using principal components analysis, [Xu et al. \(2013\)](#) estimated that DIN deposition

68 contributed 25-28% of total DIN loads in the river between 1972 and 2010. These estimated
69 contributions, however, are inherently uncertain mainly due to the scarcity of complete observational
70 data on dry N deposition, which accounted for 20%-63% of total N deposition in the Yangtze River
71 basin (Shen et al., 2013; Xu et al., 2015; Kuang et al., 2016), as well as for 60% in northern China
72 (Pan et al., 2012). Indeed, long-term measurement of dry N deposition at a regional scale remains a
73 major challenge because of the wide range of N-containing compounds in gaseous and aerosol phases,
74 and technical difficulties associated with measurement of their deposition, especially in remote areas
75 (Xu et al., 2015). An alternative and widely accepted approach uses a spatial interpolation technique
76 to yield continuous estimates of dry N deposition from discrete data points on a spatial scale (Nowlan
77 et al., 2014; Jia et al., 2016). However, to date no study, based on the interpolation method has
78 provided any information on the magnitude and spatial pattern of total (wet plus dry) DIN deposition
79 over the Yangtze River basin, significantly limiting our knowledge of the N cycle in the basin.

80 Alternatively, chemical transport models (CTMs) are capable of simulating magnitude and
81 spatial pattern of total DIN deposition and was employed at the national scale (Zhang et al., 2012),
82 and on a global scale (Vet et al., 2014; Kanakidou et al., 2016). Recent advances in N deposition
83 modeling include improved estimates of DIN deposition at a continental scale using a nested
84 modeling approach with the GEOS-Chem global chemical transport model to estimate DIN
85 deposition in China (Zhao et al., 2017). However, few studies modeled spatial distribution patterns
86 of total DIN deposition at a regional scale (Huang et al., 2015), mainly due to lack of models with
87 fine resolution. In addition, modeled total DIN deposition should be compared to surface observations
88 to validate and improve models, but few of these datasets are available (Pan et al., 2012; Xu et al.,
89 2015). Thus, application of interpolation method along with modeling method is believe to provide
90 reliable information on the magnitude and spatial pattern of total DIN deposition at a regional scale.

91 To develop emission control strategies to conserve ecosystem health, the emission sources of N
92 deposition needed to be determined. Using the moss $\delta^{15}\text{N}$ method, a previous study determined that
93 the main atmospheric N sources in the Yangtze River basin were excretory wastes for most of the
94 cities and soil emission for forests (Xiao et al., 2010). However, large uncertainties may exist in the
95 results from Xiao et al. (2010), since relevant analysis was built on the $\delta^{15}\text{N}$ signatures of potential
96 atmospheric N sources established for other countries (e.g. Germany); it is unsure whether there is
97 spatial variability of $\delta^{15}\text{N}$ signatures.

98 Fortunately, CTMs are the physical and chemical processes of atmospheric N pollution are useful
99 in providing insights into the relative contribution of emissions sources to N deposition. Existing
100 CTMs such as the Goddard Earth Observing System with chemistry (GEOS-Chem) model (Lee et al.,
101 2016; Zhao et al., 2017), the Community Multiscale Air Quality (CMAQ) model (Qiao et al., 2015)
102 and the European EMEP model (Simpson et al., 2014) have capability to link nitrogen sources with

103 deposition. For example, a current study by some of the present authors used the GEOS-Chem model
104 to show that in China total N deposition is predominantly contributed by domestic anthropogenic
105 sources (86%), followed by trans-boundary import of anthropogenic sources (7%) and natural sources
106 (7%) (Zhao et al., 2017). However, in spite of their effects, the contribution from natural sources tend
107 to be underestimated in part due to the fact that the model used by Zhao et al. (2017) does not account
108 for land-atmosphere bi-directional NH₃ exchange. In addition, relative contributions from different
109 emission sectors (e.g., fertilizer, manure, industry, power plants, and other) to N deposition were not
110 quantified. Source attribution data calculated with CTMs may be used in an integrated assessment
111 modelling framework to calculate the cost-benefit of reduced nitrogen deposition from targeted
112 emission reduction policies (Oxley et al, 2013).

113 In the present study, we use the spatial interpolation technique and available published data to
114 map the spatial distribution of total DIN deposition in the Yangtze River basin. In addition to this, an
115 attempt was made to quantify contributions from different emission sectors (i.e. fertilizer use,
116 livestock, industry, power plant, transportation, and others) to total DIN deposition using the GEOS-
117 Chem model. A comparison of spatial patterns of total DIN deposition obtained with interpolation
118 technique and the GEOS-Chem model was also made using provincial deposition totals. The
119 outcomes of this study are expected to provide the scientific basis for developing an effective policy
120 for N pollution abatement in the basin.

121

122 **2. Methodology and data collection**

123 **2.1 Study area**

124 The Yangtze River basin is located between 24°-35°N and 90°-122°E, originating from the
125 Tibetan Plateau, cross the country from west to east, and finally flowing into the East China Sea (Fig.
126 1). The basin has a total drainage area of approximately 1.8×10^6 km², covering 20% of the total land
127 area of China. The area of the Hubei, Hunan, Jiangxi, and Sichuan provinces, which are totally located
128 within the basin, accounted for about 65% of the total basin area, while that of the other 13 provinces
129 (Qinghai, Gansu, Yunnan, Tibet, Shaanxi, Guizhou, Guangxi, Henan, Anhui, Jiangsu, Shanghai,
130 Guangdong, Fujian) accounted for 35% of the total basin area (Yan et al., 2003). The climate in large
131 parts of the basin is subtropical monsoon. The long-term mean annual precipitation in this region is
132 approximately 1070 mm, but the spatial and temporal distributions are highly uneven, ranging from
133 500 mm in the west to 2500 mm in the east, and more than 60% of the annual precipitation occurred
134 in summer (June, July and August) (Xu et al., 2008).

135 There are nearly 440 million inhabitants in the basin. Main land use types are forest, farmland
136 and grassland (Fig. 1), of which the areas accounted for 40%, 30% and 24% respectively, of the total

137 basin area over the 1980–2012 period (Chen et al., 2016). Agricultural fields are well developed in
138 the Sichuan basin and corresponding regions in the middle and lower reaches of the Hunan, Hubei,
139 Anhui and Jiangsu provinces, where regional NH₃ emission is concentrated compared with low NH₃
140 emissions in northwest remote area of the basin (e.g., Qinghai and Xizang) (Huang et al., 2012). In
141 these regions, a turning cultivation system of rice-wheat, rice-rape, rice-cotton and rice-sweet potato,
142 along with a rotation of rice-peanut, rice-green manure, or double cropping of rice are practiced at a
143 high cropping intensity between 200% and 250% (Liu et al., 2008). High emission density of NO_x
144 occurs in Shanghai and Jiangsu (Zhao et al., 2013).

145

146 2.2. Data collection and description

147 We collected data on from published literature on DIN deposition in the Yangtze River basin
148 during the 2000-2014 period (see **Table S1** in **Supplementary Information (SI)** for a complete
149 reference list). This dataset was built by surveying the peer-reviewed literature with the Web of
150 Science (Thompson-ISI, Philadelphia, PA, USA) and CNKI website (<http://www.cnki.net/>). Briefly,
151 keyword searches used “nitrogen deposition”, “chemical composition” or “precipitation”, and
152 “China”. After rigorous data screening and quality control for the Yangtze River basin, a total of 100
153 sites were included. These sites cover urban, rural and forested areas. The geographical distribution
154 of all selected sites is mapped in **Fig. 1**. Our compiled data set of DIN deposition can be divided into
155 three categories according to the types of deposition and sampling method: dry and bulk deposition
156 data set, wet and bulk deposition data set, and total deposition (dry plus wet) data set. A brief
157 description of those three sub-data sets is given below. The details of all the sites, including site name,
158 site coordinate, monitoring period, and land use type are presented in **Table S1** in SI.

159 The dry and bulk deposition data set was collected from 14 monitoring sites (Fig. 1, and numbers
160 highlighted in red in Table S1, SI) in a Nationwide Nitrogen Deposition Monitoring Network
161 (NNDMN) in China (Xu et al., 2015), which investigated both dry and bulk N deposition
162 simultaneously since 2010. This network focused on five major DIN species (i.e., gaseous NH₃,
163 HNO₃, NO₂, and particulate NH₄⁺ and NO₃⁻) sampled using active and passive samplers, and on NH₄⁺
164 and NO₃⁻ in precipitation collected using precipitation gauge. Dry deposition fluxes were estimated
165 by combining measured N_r concentrations with simulated deposition velocity; Bulk deposition fluxes
166 were calculated by multiplying the precipitation amount with the volume-weighted mean
167 concentrations of NH₄⁺ and NO₃⁻ in the precipitation.

168 The wet and/or bulk deposition data set was collected from 70 monitoring sites (**Fig.1**, and
169 numbers highlighted in blue in **Table S1, SI**), with the former mainly based on automatic precipitation
170 sampling collectors and the latter mainly based on continuously-open collectors (e.g., rain gauge,

171 bucket). In reality, the collected data at those sites were DIN concentrations in precipitation and
172 precipitation amount (**Table S1, SI**). Further, we approximate wet and/or bulk deposition fluxes
173 according to the aforementioned method. It should be noted that data on bulk deposition flux
174 accounted for about 79% of the data set. **Only 4 out of 70 sites had monitoring periods for wet and/or**
175 **bulk deposition that shorter than 1 year, but covered local rainy season (i.e., summer). Therefore, the**
176 **calculated fluxes to some extent can represent their respective annual deposition levels.**

177 The total deposition (dry plus wet) data set was collected from 16 biomonitoring sites (**Fig. 1,**
178 and numbers highlighted in black in **Table S1**) in the study of Xiao et al. (2010), who used moss
179 tissue N contents to estimate total DIN deposition flux for the year 2006 based on a significant linear
180 regression equation between the estimated atmospheric N deposition and moss N content.

181 In line with our previous study (Xu et al., 2015), the term ‘total deposition’ in this study is also
182 defined as the sum of dry and bulk deposition **unless specified otherwise**, although it is in principle
183 defined as the sum of dry and wet deposition. The main reasons for this were given in Text S1 in the
184 Supplement.

185 2.3. Calculation and mapping of total DIN deposition

186 To calculate total DIN deposition at 70 sites with only wet and/or bulk DIN deposition
187 measurements (**Table S1, SI**), it is essential to estimate dry deposition fluxes. Here we calculated dry
188 DIN deposition fluxes by multiplying their measured wet and/or bulk deposition fluxes with a
189 dry/bulk deposition ratio. In brief, the ratios were uniformly assumed to be 0.65, 0.94, and 0.60 for
190 rural, urban and forest sites, which were respectively averaged from the ratios for corresponding land
191 use types at all selected NNDMN sites except for 3 sites in Yunnan province (which show relatively
192 higher dry/bulk ratios due to abnormal (extreme low) precipitation amounts. see details in Table S1,
193 SI). **The variability in the ratios was mainly due to the differences in N_r emission intensity, weather**
194 **conditions (e.g., wind speed, precipitation), underlying surface parameters (e.g., surface roughness**
195 **length and land type) (Xu et al., 2015).** This method has been used elsewhere (Chen et al., 2016),
196 albeit with some uncertainties. To study the spatial pattern of total DIN deposition, we used average
197 annual values of deposition fluxes when there were measurements more than one year in each data
198 set (Table S1, SI).

199 A Kriging interpolation technique was employed to construct a regional-scale map of total DIN
200 deposition in the Yangtze River basin (**Fig. 2a**). One site situated near the boundary of the Yangtze
201 River basin (about 65 km distant, Fig. 1) was included in the analysis to decrease the effect of
202 boundary issues on the spatial interpolation technique. Prior to Kriging interpolation, SPSS 11.5
203 software was used to test whether the original data accorded with normal distribution and thereby
204 determine if a data conversion is required. Then, the Explore Data tool of ArcGIS 10.0 was employed

205 to perform a data analysis including outlier identification and trend analysis; Geostatistics plus
206 (GS+) was applied to determine the optimal variogram model and parameters. The results of the
207 Kriging interpolation were evaluated using a cross-validation analysis, i.e., compared predicted value
208 to the original measured value at all selected sites. For the area of the basin belonging to Qinghai
209 province, we assumed that total DIN deposition was in the range of 1-2 kg N ha⁻¹ yr⁻¹ due to lack of
210 corresponding reported data. This range was extracted from our modeled total DIN deposition to
211 China for the year 2010. Also, a recent modeling study reported that total inorganic N deposition in
212 that area is < 2 kg N ha⁻¹ yr⁻¹ over 2008-2012 period (Zhao et al., 2017). Thus, the flux assumed here
213 can be assumed to be representative of the region.

214 All correlation analyses were performed using SPSS software (version 11.5; SPSS Inc., Chicago,
215 IL, USA), with a significance level of $p < 0.05$.

216 2.4. Source attribution of N deposition

217 In this study, the GEOS-Chem (<http://geos-chem.org>) was used to assess the relative contribution
218 of different emission sectors to the simulated total N deposition over the Yangtze River basin in 2010.
219 The total DIN deposition made up about 96% of the simulated total N deposition (**Table 1**). For
220 consistency when discussing modeled deposition fluxes along with the interpolated deposition fluxes,
221 we refer to the modeled total N deposition as total DIN deposition, although we recognized here that
222 the modeled total deposition included 4% dry organic nitrogen deposition. GEOS-Chem is a 3-D
223 global atmospheric CTM driven by GEOS-5 assimilated meteorological data from the NASA
224 Goddard Earth Observing System with a temporal resolution of 6 h (3 h for surface variables and
225 mixing depths), a horizontal resolution of 1/2° latitude by 1/3° longitude. The model includes aerosol
226 and gas-phase chemistry with heterogeneous aerosol chemistry parameterized using uptake
227 coefficients (Jacob, 2000), and photolysis rates which are dependent on aerosol concentrations
228 (Martin et al., 2003). Tropospheric gas-phase chemistry is represented by the O₃-NO_x hydrocarbon
229 system (Hudman et al., 2007). The ISORROPIA II thermodynamic equilibrium model of Fountoukis
230 and Nenes (2007) is employed to represent the partitioning of total NH₃ and HNO₃ between the gas
231 and aerosol phases. A standard resistance-in-series model is used to calculate dry deposition for gases
232 (Wesely, 1989) and aerosols (Zhang et al., 2001). Wet deposition includes both convective updraft
233 and large-scale precipitation scavenging as for aerosols (Liu et al., 2001) and gases (Mari et al., 2000).
234 The nested version of GEOS-Chem been applied to simulate nitrogen deposition in China and the
235 adjacent ocean (Zhao et al., 2015; 2017). For example, Zhao et al. (2017) conducted a 5-year (2008-
236 2012) comparison of surface observations and model simulations of wet deposition fluxes for China,
237 and their results showed good agreement for wet deposition fluxes of NH₄⁺ (r=0.56, bias=-1%) and
238 NO₃⁻ (r=0.70, bias=-15%), as well as for NH₃ concentration (r=0.65, bias=4%)". . Here we conduct

239 the same GEOS-Chem simulation of nitrogen deposition as [Zhao et al. \(2017\)](#) for 2010 and access
240 the source attribution by model sensitivity tests. Anthropogenic emissions over China are from the
241 MultiResolution Emission Inventory of China (MEIC, <http://meicmodel.org>), except for NH₃
242 emissions that are obtained from the Regional Emission in Asia (REAS-v2) inventory ([Kurokawa et
243 al., 2013](#)). An updated seasonality described by [Zhao et al. \(2015\)](#) was applied to NH₃ emissions to
244 [improve the simulation](#). The detail of the emission settings can refer to [Zhao et al. \(2017\)](#). **Table 2**
245 lists the total NH₃ and NO_x emissions from each source over China and the Yangtze River basin (**Fig.**
246 **1**). The NH₃ and NO_x emissions over the Yangtze River basin are 4.0 Tg N a⁻¹ and 2.2 Tg N a⁻¹ in
247 2010, which respectively, account for 31% and 23% of their total emissions over China. Agriculture
248 sources including fertilizer use and livestock, comprise most of the NH₃ emissions (63% and 18%)
249 while fuel combustion activities, including industry, power plant, and transportation contribute most
250 of the NO_x emissions (40%, 25% and 24%) and small amounts of NH₃ emissions (5%). Both NH₃
251 and NO_x have natural sources (including lightning, biomass burning and soil emissions), but are
252 negligible (3-4%) compared to anthropogenic emissions over the Yangtze River basin.

253 To assess the contributions from main N_r sources (fertilizer use, livestock, industry, power plant,
254 and transportation), we conduct a series of model sensitivity simulations for the year 2010 with the
255 corresponding emission sources turned off. The difference with the standard simulation (with all
256 emissions turned on) represents their individual contribution to N deposition.

257 **3. Results and discussion**

258 3.1. Atmospheric deposition of total DIN in the Yangtze River basin

259 As shown in **Fig. 3**, across the basin total DIN deposition generated from the Kriging interpolation
260 on average was 33.2 kg N ha⁻¹ yr⁻¹, roughly equivalent to the GEOS-Chem simulated deposition value
261 (32.9 kg N ha⁻¹ yr⁻¹) for the year 2010. Evidence from a variety of studies confirms that the three
262 global hotspots for atmospheric N deposition are China, West Europe and North America ([Dentener
263 et al., 2006](#); [Vet et al., 2014](#); [Kanakidou et al., 2016](#)), although there is a clear downward trend in dry
264 N deposition for Europe and North America ([Jia et al., 2016](#)). The total DIN deposition estimated in
265 the present study(33.2 kg N ha⁻¹ yr⁻¹) is approximately 1.4-4 times greater than the estimated values
266 for recent years in the well urbanized and industrialized eastern US ([Li et al., 2016](#)) and the N
267 deposition hotspots of western Europe ([Vet et al., 2014](#)), and is also approximately twice China's
268 average N deposition between 2008 and 2012 ([Zhao et al., 2017](#)) (**Fig. 3**). These results suggest that
269 the basin is subjected to a high level of atmospheric N deposition and associated ecological risks.

270

271 In the basin, the spatial pattern of total DIN deposition varied significantly according to province
272 (**Fig. 2a**). To evaluate this interpolated spatial pattern, we made the cross-validation analysis and

273 calculated the correlation coefficient (r) and the normalized mean bias ($NMB = \sum_{i=1}^N (I_i -$
274 $M_i) / \sum_{i=1}^N M_i$) between the measured (M) and interpolated (I) values over the N sites. As shown in
275 **Fig. 2c**, the interpolation technique fairly reproduces the measured spatial distribution of total DIN
276 deposition fluxes ($r=0.52$, $p<0.001$), with only small annual bias (1%). Nevertheless, the predicted
277 values for some sites (e.g. forest sites) were not ideal because of relatively higher root-mean-square
278 error (14.0) (Table S2 in the Supplement) and mediate r value.

279 As a comparison for the interpolation evaluation, simulated total DIN deposition fluxes at the
280 model $1/2^\circ \times 1/3^\circ$ resolution for the year 2010 was mapped at the same resolution ($1/2^\circ \times 1/2^\circ$) to the
281 mapping of interpolated total DIN deposition (**Fig. 2b**). The model also captures measured total DIN
282 deposition fluxes ($r=0.38$, $p<0.001$) with a relatively high mean bias (10%). This is largely due to
283 underestimates of deposition fluxes measured at the forest sites (**Fig. 2d**). Interestingly, interpolated
284 and modeled deposition fluxes were comparable in most of the areas in corresponding provinces
285 belonging to the basin (note however that the modeled values for Guangdong and Shanghai cannot
286 be extracted due to limitation of spatial resolution) (**Fig. 4a**). Furthermore, a high positive correlation
287 ($r=0.90$, $p<0.001$) was found between interpolated and modeled deposition fluxes across
288 corresponding provinces ($n=17$) (**Fig. 4b**). This interpolation-model comparison further supports the
289 interpolated spatial pattern of total DIN deposition and suggests that the modeled pattern can be used
290 to fill the measurement gaps at a large spatial scale.

291 Based on interpolated results (Fig. 2a), most regions of the basin generally received DIN
292 deposition $> 30 \text{ kg N ha}^{-1} \text{ yr}^{-1}$. The highest fluxes of DIN deposition were concentrated in the central
293 regions, with maximum values of $54.6 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ observed in Chongqing, and the lowest
294 deposition was observed in the underdeveloped regions in the west of the basin (i.e., Qinghai), with
295 the lowest value of $1.0 \text{ kg N ha}^{-1} \text{ yr}^{-1}$. The spatial pattern observed in the present study is driven
296 mostly by differences in many factors, such as usage of N fertilizers, fossil fuel consumption,
297 livestock, and precipitation as well as interregional atmospheric transport (Jia et al., 2014; Zhao et al.,
298 2015). In addition, multiple years of measured DIN may also have a minor influence on the pattern
299 that is discussed later (see Section 3.4). The highest annual N deposition in Chongqing is explained,
300 in part, by the fact that Chongqing is the largest metropolitan area in southeastern China, and is
301 featured by high emission densities of NH_3 and NO_x (Zhao et al., 2013; Kang et al., 2016). In this
302 study, the spatial patterns of total NH_x deposition and total NO_y deposition cannot be mapped using
303 the Kriging interpolation due to limitation of corresponding reported data (Table S1 in the
304 Supplement). Alternatively, the GEOS-Chem model was applied to characterize their spatial patterns.
305 We found that there was a sharp gradient from west to east (Fig. S1 in the Supplement), corresponding
306 well with reported emission patterns of NH_3 and NO_x (Zhao et al., 2013; Kang et al., 2016).

307 The lack of long-term measurement of dry deposition fluxes makes it difficult to explore

308 temporal pattern of total DIN deposition. Dry deposition has recently been included in a national
309 nitrogen deposition monitoring network across China and showed that on average bulk and dry DIN
310 deposition rates based on measurements at 43 *in situ* sites were equally important (50% each) (Xu et
311 al., 2015). This implies that trends in bulk deposition fluxes can be useful to provide guide to trends
312 in total DIN deposition fluxes. As reported by Wang et al. (2014), bulk DIN deposition has increased
313 continuously from 0.24 Tg N in 1980 to 0.89 Tg N in 2010. In the causal relationship between
314 concentration and deposition, change in N_r concentration may provide insight into the trend of
315 deposition. The Atmospheric Infrared Sounder (AIRS)-measured NH_3 concentrations showed a
316 significant increasing trend in period 2003-2015 over major agricultural regions in the Yangtze River
317 basin (Warner et al., 2017). Over Sichuan Basin and Yangtze River Delta (both belong to the Yangtze
318 River basin), the Ozone Monitoring Instrument (OMI)-observed NO_2 columns during the period
319 2005-2015 reached its maximum in 2010 and then remained relatively stable (Krotkov et al., 2016).
320 In this context, we surmise that total DIN deposition over the basin likely exhibited an upward trend
321 since 1980.

322 3.2. Contributions of different processes and emission sectors to total N deposition

323 In the present study, deposition amounts of individual N_r species (e.g., gaseous NH_3 , HNO_3 , and
324 NO_2 , particulate NH_4^+ and NO_3^- , and rainwater NH_4^+-N and $NO_3^- -N$) cannot be separated from
325 interpolated total DIN deposition fluxes. Instead, we examine the different processes and sources
326 contributing to total DIN deposition over the Yangtze River basin by using the GEOS-Chem model
327 results for the year 2010. We evaluate the model simulations by comparing with observed wet (both
328 NH_4^+ and NO_3^-) and total DIN deposition fluxes listed in **Table S1** in the Supplement. The model
329 biases were 22% for wet NH_4^+ deposition, 23% for wet NO_3^- deposition and 9% for total DIN
330 deposition (**Fig. S2** in the Supplement). These biases are reasonable and can be partially explained
331 by the differences in N_r emissions and meteorology conditions. Given that model evaluation is not
332 central to this work, we presented the details in **Text S2** in the Supplement.

333 **Table 1** presents the annual total deposition amounts from individual species and from each
334 process over the basin. On a basin scale, NH_x removal was dominated by wet deposition compared
335 with dry deposition (15.5 versus 6.6 kg N ha⁻¹ yr⁻¹). Gaseous NH_3 accounted for 70% of NH_x dry
336 deposition (4.5 kg N ha⁻¹ yr⁻¹). Similar to NH_x , more NO_y was removed by wet deposition than dry
337 deposition (7.1 versus 4 kg N ha⁻¹ yr⁻¹). Annually HNO_3 (56%) was the biggest contributor to NO_y
338 dry deposition, followed by NO_3^- aerosol (22%), NO_2 (12%) and others (10%). Our results show that
339 wet deposition accounted for 71% of NH_x deposition, 65% of NO_y deposition, and 69% of the total
340 N deposition to the basin, which is consistent with the findings of previous measurements in the basin
341 (Xu et al., 2015). This, in turn, indicates that the basin is likely small in the interpolated spatial pattern
342 of the total DIN deposition, despite uncertainties in bulk measurements (e.g., amount of dry

343 deposition fraction).

344 **Fig. 5** shows the spatial footprint of different N_r emission sectors contributing to total DIN
345 deposition conducted from the GEOS-Chem simulation. Emissions from fertilizer use (40%),
346 followed by industry (13%) and livestock (11%), contribute most to N deposition over the Yangtze
347 River basin. Power plant and transportation contribute 9% each, and other sources, including human
348 waste, residential activities and natural sources (soil, lighting and biomass burning), contribute the
349 remaining 18%.

350 In addition, there were significant spatial variations in contributions of N_r emission sectors to
351 total DIN deposition. To the east of the Qionglai mountains (northwestern rim of the Sichuan basin),
352 the relative contributions from fertilizer use are highest (30-50%). Livestock, industry, power plant
353 and transportation show comparable contribution of 10-20%. To west of the Qionglai mountains,
354 where nitrogen deposition rate is relatively low, most of nitrogen deposition is from livestock (20-
355 30%) and others sources such as human waste and residential activities (20-50%). Contributions from
356 fertilizer use and transportation are generally less than 10% and from industry and power plant are
357 negligible.

358 Many studies have found that anthropogenic activities are main contributors to atmospheric N
359 deposition based on CTMs simulations (L. Zhang et al., 2012; Lee et al., 2016; Zhao et al., 2017),
360 isotope techniques (Xiao et al., 2010), and/or the Positive Matrix Factorization (PMF) model (Liu et
361 al., 2016). For instance, using the PMF method, Liu et al. (2016) determined the main sources of bulk
362 N deposition across China during the period 2003-2014; they reported that agricultural activities were
363 the main contributor for NH_4^+-N (85.9%), and $NO_3^- -N$ was mainly from fossil fuel combustion
364 (86.0%). Furthermore, Zhao et al. (2017) used the GEOS-Chem model to show that 93% of N
365 deposition in China was originated from anthropogenic sources.

366 In the present study, the source attribution results indicate that agricultural activities, either
367 fertilizer use or livestock management, dominate total DIN deposition in the Yangtze River basin.
368 The results also highlight that the intensive agriculture activities may lead to adverse environmental
369 effects such as perturbation to the N cycle in the basin and further threaten the ecology health of the
370 aquatic ecosystems. Recent field measurement also found that more reduced N was deposited than
371 oxidized N in northern China (Pan et al., 2012) and even across China (Xu et al., 2015), although the
372 ratio of $NH_4^+-N/NO_3^- -N$ in precipitation decreased since the 1980s (Liu et al., 2013; 2016).

373

374 3.3. Potential ecological risks of atmospheric N deposition

375 Critical load is a quantitative estimate of exposure to N deposition below which significant
376 harmful ecological effects on an ecosystem do not occur over the long term (Liu et al., 2011) and
377 have been widely used as a useful tool in evaluating the impact of N deposition on ecosystems (Duan

378 [et al., 2002](#); [Ellis et al., 2013](#)). In this study, the basin was divided into five sensitive regions by the
379 critical load of N deposition for terrestrial ecosystems in China (**Table 3**). Regions corresponding to
380 70.3% of the basin were in insensitive areas (i.e., high insensitivity and insensitivity) zones, whereas
381 12.0% of the basin was in sensitive zones. These results indicate that total DIN deposition in
382 approximately 82% of the basin exceeded the critical loads of N deposition in terrestrial ecosystems,
383 which mostly ranged from 10 to 20 kg N ha⁻¹ yr⁻¹ ([Bobbink et al., 2010](#)). By contrast, according to
384 the results from current modeling studies, N deposition rate in 11% of the world's land surface exceed
385 the critical load of 10 kg N ha⁻¹ a⁻¹ ([Dentener et al., 2006](#)), and the area which received this load
386 accounted for between 35% and 47% of the total area of the US ([L. Zhang et al., 2012](#)) and China
387 ([Zhao et al., 2017](#)), respectively. These results indicate that a more serious potential risk of N
388 saturation may exist in the Yangtze River basin compared with other regions in China and the world.
389 A condition of N saturation has been detected in high N deposition areas of the basin, such as
390 Chongqing and the Tuojiang/Minjiang River ([Duan et al., 2016](#)).

391 If the growth rate of N deposition in the entire basin (excluding corresponding areas in Qinghai
392 province) coincides with the annual average growth rate of 0.36 kg N ha⁻¹ yr⁻¹ (unpublished data)
393 derived from 5-year (2011-2015) *in situ* measurements of total DIN deposition at 9 NNDMN
394 monitoring sites (which include NJ, WJ, WX, TJ, ZY, YT, JJ, HN and XS sites, **Fig. 1**) in the basin,
395 all regions will receive N deposition exceeding 10 kg N ha⁻¹ yr⁻¹ after 25 years. The critical loads of
396 N in the basin can be derived from estimated N critical loads for N deposition in various ecosystems
397 in China ([Liu et al., 2011](#); [Zhao et al., 2017](#)). Based on field observations, for example, an empirical
398 N critical load map of N deposition drawn by [Liu et al. \(2011\)](#) shows that estimated values in the
399 basin were generally > 200 kg N ha⁻¹ yr⁻¹ for croplands, and < 100 and 50 kg N ha⁻¹ yr⁻¹ for forests
400 and grasslands, respectively. According to [Zhao et al. \(2017\)](#), the N critical load for soil
401 eutrophication estimated using the steady-state mass balance method varied from 8 kg N ha⁻¹ yr⁻¹ to
402 100 kg N ha⁻¹ yr⁻¹ in the basin. Nevertheless, the critical loads of N in ecosystems are still subjected
403 to some large uncertainties in the calculation methods (e.g., the SSMB), such as plant uptake rate,
404 weathering rate, and denitrification rate ([Zhao et al., 2017](#)).

405

406 3.4. Uncertainty and recommendations

407 Total deposition includes wet deposition (in the form of rainfall and snowfall) and dry deposition
408 (in the form of gases and particles). The present study reported the spatial pattern of total DIN
409 deposition in the Yangtze River basin, the estimated flux here, however, is subject to some
410 uncertainties in our estimation of dry deposition at the selected 70 sites, which were calculated based
411 on dry/wet deposition ratios at their surrounding NNDMN sites. This is because the relative
412 contribution of dry vs. wet deposition to the total deposition at a point scale largely depends on the

413 local environment, such as N_r emissions, weather conditions (e.g., precipitation, wind speed) and
414 underlying surface (Pan et al., 2012). It should be noted that the calculated wet deposition at those
415 sites in fact are mostly bulk deposition. The wet deposition refers strictly to wet-only deposition
416 which is sampled only during rainfall and snowfall events. Bulk deposition should be higher than
417 actual wet deposition. For example, annual difference between bulk and wet deposition was 1.3–9.6
418 kg N ha^{-1} in agroecosystems in northern China, accounting for 5–32% of bulk deposition (Liu et al.,
419 2017). As mentioned earlier (see Section 2.2), the difference between bulk and wet N deposition is
420 likely small in the basin, but the use of bulk deposition may also result in uncertainties in our
421 estimation of total DIN deposition. Furthermore, our study pulled together DIN deposition results
422 from a number of different field studies (Table S1 in the Supplement), which could introduce
423 potential biases in the spatial pattern of total DIN deposition, owing to differences in monitoring,
424 sampling handling and analysis methods. To test whether the use of data measured during 2000-2014
425 period could bias the spatial patterns of total DIN deposition, we summarize data on bulk DIN
426 deposition during the period 2000-2014 from recent publications (Liu et al., 2013; Xu et al. 2015;
427 Song et al., 2017). A total of 126 records on annual bulk DIN deposition fluxes at 43 monitoring sites
428 were obtained (Fig. S3a in the Supplement). A non-significant trend ($p=0.315$) can be seen for annual
429 bulk deposition fluxes at a regional scale (Fig. S3b in the Supplement). Further, annual trends of bulk
430 DIN deposition at five *in situ* monitoring sites (i.e., WJ, GG, JYS, GYQ, NJ) were not significant,
431 and the similar phenomenon was also observed at two *in situ* monitoring sites for wet deposition (Fig.
432 S3a in the Supplement). Based on these findings, we conclude that using DIN deposition measured
433 in different years may have a little influence on the spatial pattern of total DIN deposition. On the
434 other hand, the large-size particulate (e.g. dust or aerosols larger than $10 \mu\text{m}$) N was normally not
435 collected in the dry deposition collection. From this viewpoint, the overestimated "wet" deposition
436 could be partly compensated by the underestimated "dry" deposition. To obtain more accurate
437 information on the spatial pattern, it is crucial to establish a long-term regional N deposition
438 monitoring network covering both wet-only and complete dry deposition using uniform monitoring
439 methods, and to estimated deposition fluxes use a joint method of monitoring, modeling and/or spatial
440 interpolation. In addition, it is indispensable to set up more representative observation sites in
441 corresponding regions in the western Sichuan basin and Qinghai province where observation sites are
442 currently absent.

443 Organic nitrogen (ON), which is an important component of the atmospheric N cycle, is not
444 considered in the present study (Neff et al., 2002). Water-soluble ON contributes on average about
445 25% of the total dissolved N in wet deposition globally (Jickells et al., 2013), and approximately 25%
446 of bulk N deposition in China (Y. Zhang et al., 2012). This soluble ON contains a wide range of N_r
447 compounds (e.g., amino acids, amines, nitrophenols, alkyl amides, and organic nitrates) with different

448 properties and origin (Cape et al., 2011; Jickells et al., 2013). According to the results from the first
449 global model of atmospheric ON (Kanakidou et al., 2012), the major contributors of atmospheric ON
450 were combustion sources (40%), primary biogenic particles (32%), and ocean particulate emissions
451 (20%). However, a national emission inventory of ON species has not yet been developed for China.
452 Further research is required to fill knowledge gaps of organic N emissions, which will be beneficial for
453 source analysis of atmospheric ON deposition, an issue which remains uncertain in China.

454 Uncertainties also exist in the source attribution calculated with the GEOS-Chem simulations,
455 since results largely depend on the emission inventories fed to the model. Zhao et al. (2017) have
456 pointed out that uncertainties in current ammonia emissions inventories (e.g. large range of the
457 emission value in current studies and absence of inclusion of bi-directional NH₃ exchange in land-
458 atmosphere) may influence the nitrogen deposition simulation in China. We also point out here the
459 high contribution (40%) from fertilizer use includes both NH₃ emissions from chemical fertilizer and
460 manure, as they are merged into 'fertilizer use' sector in the REAS-V2 emission inventory. Future
461 work to improve ammonia emission inventories is needed to better simulate the spatial distribution
462 and source attribution of N deposition in China.

463 464 3.5. Conclusions and implications for controlling regional N deposition

465 . In summary, we have presented the spatial pattern of total DIN deposition in the Yangtze River
466 basin based on three data sets on DIN deposition for the period of 2000-2014 at the 100 sites, and
467 also have examined sources of total DIN deposition in the basin for the year 2010 using the GEOS-
468 Chem model at horizontal resolution of 1/2° × 1/3°. We found that there is a significant spatial
469 variation in total DIN deposition across the basin, with the highest fluxes mainly concentrated in the
470 central region. At a regional scale, the total DIN deposition flux was 33.2 kg N ha⁻¹ yr⁻¹. Meanwhile,
471 the deposition fluxes in nearly 82% of the basin exceeded the critical loads for generic terrestrial
472 ecosystems. Based on these findings, we propose that mitigation strategies are urgently needed in the
473 basin and should be developed through a regional strategy according to local economical, ecological
474 and environmental conditions. In other words, more stringent emission controls should be
475 implemented in N emission hotspots near sensitive areas (e.g. the central regions of the basin and the
476 Yangtze Delta) whereas moderate controls in areas near low N deposition levels (e.g. corresponding
477 areas in Qinghai province). In this way, it could achieve a more ideal control effect without affecting
478 the regional economic development.

479 The source attribution conducted by GEOS-Chem model can provide useful information for
480 developing effective measures to reduce the excessive N_r input to the Yangtze River basin. In a regional
481 scale, fertilizer use contributed 40% of total DIN deposition to the basin. This result provides direct
482 evidence that reducing fertilizer NH₃ volatilization over the regional scale, by use of a urease inhibitor

483 (Li et al., 2017) and/or right fertilization pattern (e.g., fertilizing in right type, right amount, right time
484 and right place) is a promising approach to decrease NH₃ emission and subsequent N deposition.
485 Thus, in a sense, the implemented “Zero Increase Action Plan” by the Ministry of Agriculture for
486 national fertilizer use to some extent can suppress the regional N_r pollution and N deposition (Liu et
487 al., 2016). In addition, manure management in feedlots to treat and use it as fertilizer to cropland
488 should be improved. However, the fact that significant variability in emission source contributions to
489 N deposition were observed across the study area suggests that policy-makers should also consider
490 emission reduction from other major emission sectors in addition to fertilizer when developing
491 synergistic control measures.

492 Overall, our results show that the Yangtze River basin is a N deposition hotspot in China and
493 globally, primarily due to high levels of NH₃ emissions from improper fertilize use. Further research
494 at a regional scale to consider both inorganic and organic N in wet and dry deposition is required to
495 assess the spatial pattern of N deposition and optimize control strategy for protecting aquatic and
496 terrestrial ecosystems.

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Figure captions

Fig. 1. Geographic location of the Yangtze River basin and the 100 monitoring sites.

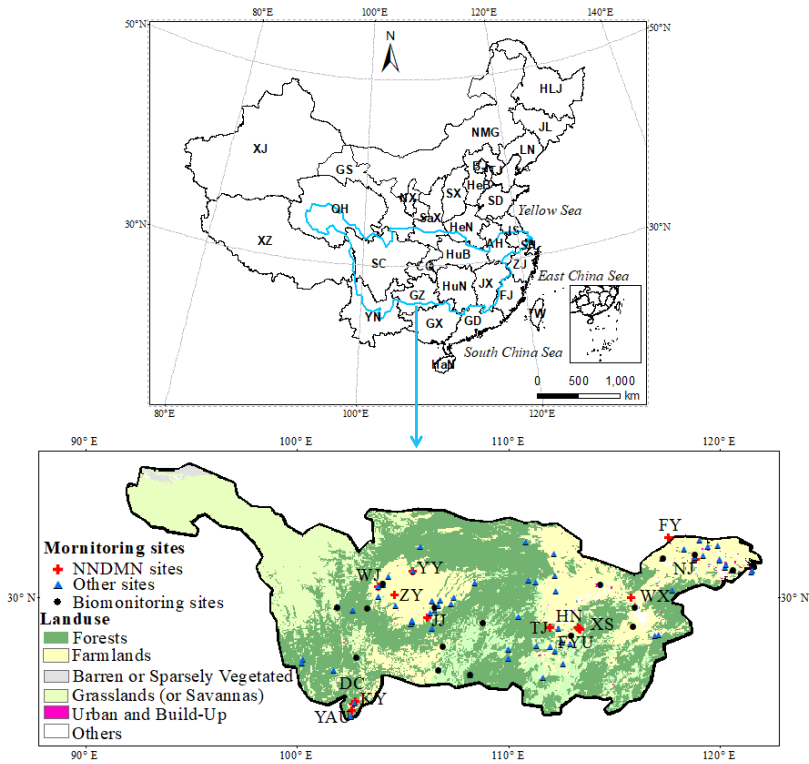
Fig. 2. Spatial patterns of total DIN deposition in the Yangtze River basin derived from the Kriging interpolation during the period of 2000-2014 (a) and the GEOS-Chem model for the year 2010 (b). The Kriging interpolated results and GEOS-Chem model results are compared with measured total DIN deposition (as given in Table S1, SI) as scatter-plots (c and d, bottom panels). The full names of the provinces are successively Hebei, Shandong, Gansu, Shannxi, Shanxi, Henan, Guizhou, Jiangsu, Hubei, Shanghai, Anhui, Ningxia, Jiangxi, Zhejiang, Chongqing, Sichuan, Fujian, Guangdong, Guangxi, Hunan, Yunnan, Xinjiang, Xizang, Qinghai.

Fig. 3. Comparison of total DIN deposition observed in the Yangtze River basin and other areas (red and green bars represent interpolated and modeled values in this study; total N deposition rates in eastern US, western Europe, and China were cited from Li et al. (2106), Vet et al. (2014), and Zhao et al. (2017), respectively).

Fig. 4. a comparison of total DIN deposition from the Kriging interpolation and the GEOS-Chem model for the areas in corresponding provinces belonging to the Yangtze River basin (a) and the correlation between them (b).

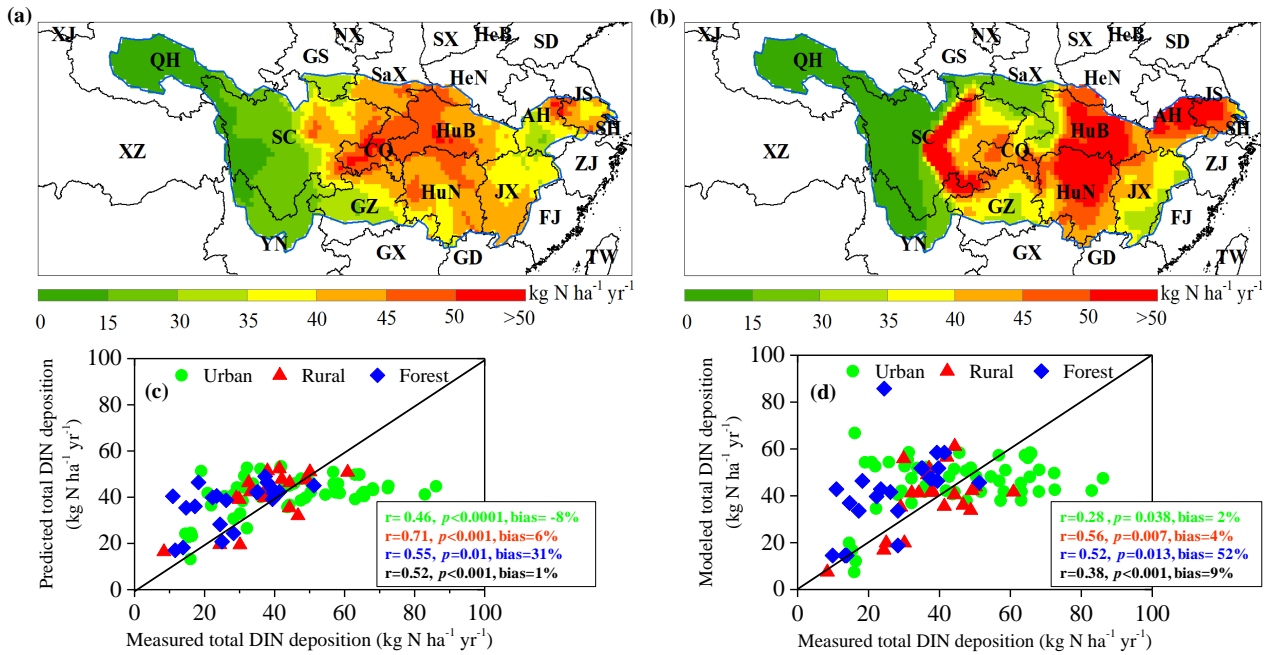
Fig. 5. Fractional contributions to total N deposition from emission sectors (i.e. fertilizer use, livestock, industry, power plant, transportation, and others including emissions from human waste, residential activities, soil, lighting and biomass burning) in the Yangtze River basin.

Figure 1



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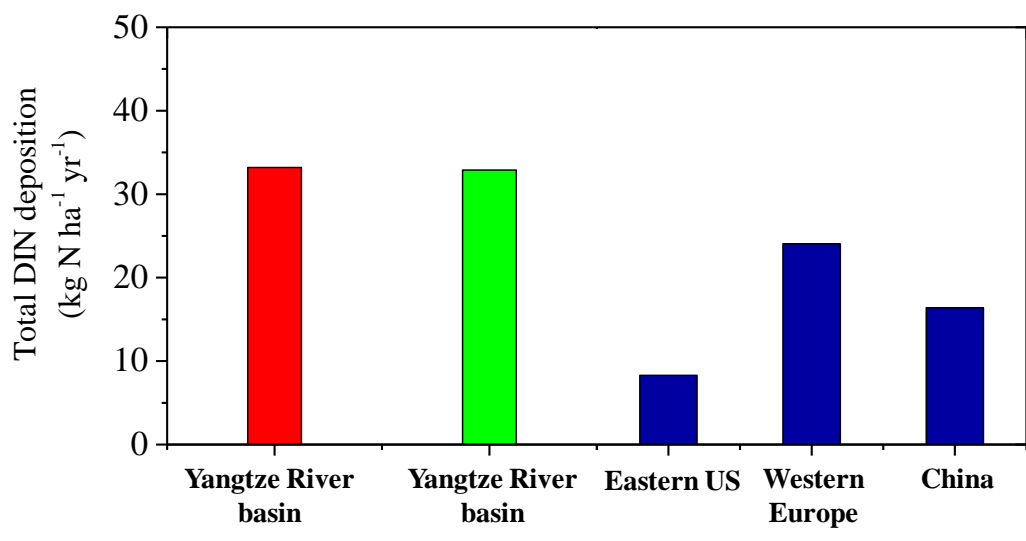
Figure 2



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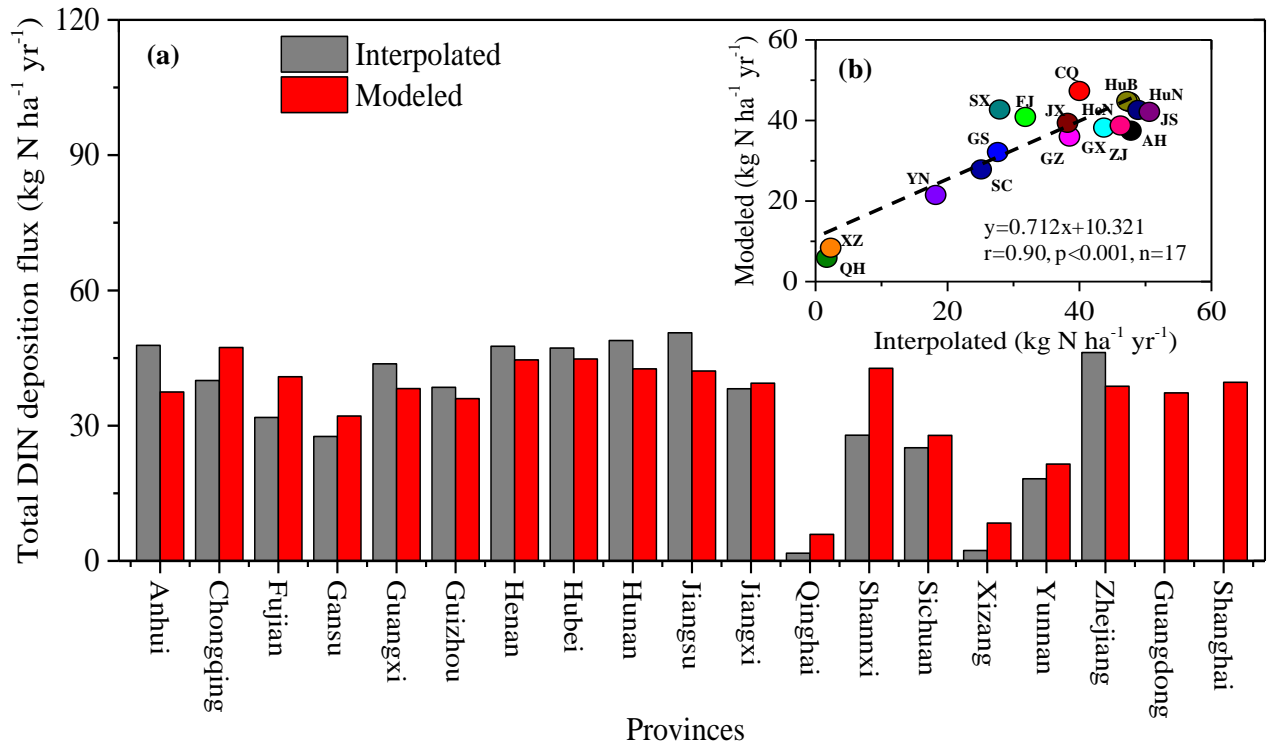
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Figure3



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Figure 4



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Figure 5

838 **Table 1.** Nitrogen deposition over the Yangtze River basin^a

	Deposition process	Deposition (kg N ha ⁻¹ yr ⁻¹)
NH _x	Total	21.9
	Wet NH ₄ ⁺	15.5
	Dry NH ₃	4.5
	Dry NH ₄ ⁺ aerosol	1.9
NO _y	Total	11.0
	Wet NO ₃ ⁻	7.1
	Dry HNO ₃	2.2
	Dry NO ₂	0.47
	Dry isoprene nitrates ^b	0.19
	Dry N ₂ O ₅	0.056
Dry PANs ^c	0.11	

Dry NO ₃ ⁻ aerosol	0.88
Dry alkyl nitrates	0.036

839 ^a Annual total N deposition for 2010 computed with GEOS-Chem model.

840 ^b Isoprene nitrates are formed via the oxidation of biogenic isoprene and are removed by wet and
841 dry deposition at the same deposition velocity of HNO₃ in the model following Zhang et al. (2012).

842 ^c Peroxyacetyl nitrate (PAN) and higher peroxyacetyl nitrates.

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862 **Table 2. Annual total NH₃ and NO_x emissions over China and the Yangtze River basin (Tg N a⁻¹)**

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	Source Type	China	Yangtze river basin
NH ₃	Fertilizer ^a	7.9	2.5
	Livestock	2.4	0.7
	Human waste	1.5	0.5
	Fuel combustion ^b	0.7	0.2
	Natural	0.5	0.1
	Total	12.9	4.0
NO _x	Industry	3.4	0.9
	Power	2.9	0.5
	Transportation	2.3	0.5
	Residential	0.4	0.1
	Natural ^c	0.8	0.1

	Total	9.6	2.2
864	^a Fertilizer NH ₃ emissions include both chemical fertilizer and manure fertilizer.		
865	^b NH ₃ emissions from fuel combustion in power plant, industry, transportation and residential.		
866	^c Natural NO _x emissions from soil, lighting and biomass burning.		

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887 **Table 3.** Sensitivity of atmospheric N deposition in the Yangtze River basin and the percentage of
888 the critical load area to the total river basin area

Sensitivity classification	Critical loads (kg N ha ⁻¹ yr ⁻¹) ^a	Ratio of critical load area to total river basin area
High insensitivity	>40	43.1%
Insensitivity	30-40	27.2%
Slight sensitivity	20-30	12.0%
Sensitivity	10-20	8.8%
High sensitivity	<10	8.9%

889 ^a Critical loads of atmospheric N deposition for terrestrial ecosystem in China (Duan et al., 2002)