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Author(s)	Pavuluri, Chandra Mouli; Kawamura, Kimitaka; Tachibana, Eri; Swaminathan, T.
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1 **Elevated nitrogen isotopic ratios of tropical Indian aerosols from Chennai:**  
2 **Implication for the origins of aerosol nitrogen in South and Southeast Asia**

3

4 **Chandra Mouli Pavuluri<sup>a</sup>, Kimitaka Kawamura<sup>a,\*</sup>, Eri Tachibana<sup>a</sup>, T. Swaminathan<sup>b</sup>**

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6 *<sup>a</sup>Institute of Low Temperature Science, Hokkaido University, N19 W08, Kita-ku, Sapporo*

7

*060-0819, Japan*

8

9 *<sup>b</sup>Department of Chemical Engineering, Indian Institute of Technology Madras, Chennai 600*

10

*036, India*

11

12 \*Corresponding author. Fax: +81 11 706 7142; E-mail addresses:

13 cmpavuluri@pop.lowtem.hokudai.ac.jp (C.M. Pavuluri), kawamura@lowtem.hokudai.ac.jp (K.

14

Kawamura)

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17 **Abstract**

18 To better understand the origins of aerosol nitrogen, we measured concentrations of total  
19 nitrogen (TN) and its isotopic ratios ( $\delta^{15}\text{N}$ ) in tropical Indian aerosols ( $\text{PM}_{10}$ ) collected from  
20 Chennai ( $13.04^\circ \text{N}$ ;  $80.17^\circ \text{E}$ ) on day- and night-time basis in winter and summer 2007. We  
21 found high  $\delta^{15}\text{N}$  values (+15.7 to +31.2‰) of aerosol N ( $0.3 - 3.8 \mu\text{g m}^{-3}$ ), in which  $\text{NH}_4^+$  is  
22 the major species (78%) with lesser contribution from  $\text{NO}_3^-$  (6%). Based on the comparison  
23 of  $\delta^{15}\text{N}$  in Chennai aerosols with those reported for atmospheric aerosols from mid-latitudes  
24 and for the particles emitted from point sources (including a laboratory study), as well as the  
25  $\delta^{15}\text{N}$  ratios of cow-dung samples (this study), we found that the atmospheric aerosol N in  
26 Chennai has two major sources; animal excreta and bio-fuel/biomass burning from South and  
27 Southeast Asia. We demonstrate that a gas-to-particle conversion of  $\text{NH}_3$  to  $\text{NH}_4\text{HSO}_4$  and  
28  $(\text{NH}_4)_2\text{SO}_4$  and the subsequent exchange reaction between  $\text{NH}_3$  and  $\text{NH}_4^+$  are responsible for  
29 the isotopic enrichment of  $^{15}\text{N}$  in aerosol nitrogen.

30

31 **Keywords:** Nitrogen isotopic ratio, Tropical Indian aerosol, aerosol nitrogen origin, South  
32 Asia, Southeast Asia.

## 33 1. Introduction

34 Global biogeochemical cycles of nitrogen (N) have been modified by industrial,  
35 agricultural and other anthropogenic activities. The important N species, such as nitrogen  
36 oxides (NO<sub>2</sub> and NO<sub>3</sub>, together denoted as NO<sub>x</sub>) and ammonia (NH<sub>3</sub>) are short-lived and are  
37 involved in several chemical reactions once they enter into the atmosphere (Olivier et al.,  
38 1998). NO<sub>x</sub> acts as an ozone (O<sub>3</sub>) precursor, affecting the atmospheric oxidizing capability.  
39 NH<sub>3</sub> serves as a neutralizing agent in the atmosphere, influencing the pH of aerosols, cloud  
40 droplets and rainfalls (Olivier et al., 1998). Those gases and their reaction products can be  
41 transported long distances in the atmosphere. After the deposition, N species may enhance  
42 the productivity of lake and coastal/remote ocean waters and raise soil acidity; almost all  
43 open surface areas are now being affected by anthropogenic atmospheric N deposition (Duce  
44 et al., 2008). Thus the increased N loadings likely cause severe damage to the atmospheric  
45 environment on local, regional, and global scales (Rodhe et al., 2002; Vitousek et al., 1997),  
46 including human health effects (Townsend et al., 2003).

47 The emission of N species from human activities into the atmosphere continues to  
48 increase every year (Galloway et al., 2008). Fossil fuel combustion, biomass burning and  
49 animal excreta play an important role in N emission (Bouwman et al., 1997; Lee et al., 1997),  
50 and the extensive use of bio-fuels adds a new and rapidly changing dimension (Galloway et  
51 al., 2008; Oenema, 2006; Streets et al., 2003). Global anthropogenic emissions of N have  
52 significantly increased by a factor of three from 34 Tg N yr<sup>-1</sup> in mid-1800s (1860) to 100 Tg  
53 N yr<sup>-1</sup> in 1990 and are predicted to be further doubled (200 Tg N yr<sup>-1</sup>) by 2050 (Galloway et  
54 al., 2004]. Predictions for 2030 indicate similar deposition patterns, but with a further  
55 increase over the open ocean (Dentener et al., 2006]. In particular, the N deposition of 2030 is  
56 projected to be twice that of 2000 in Southeast Asia, the Bay of Bengal, and the Arabian Sea  
57 (Duce et al., 2008).

58 In South and Southeast Asia, the consumption of fossil energy is highly increasing due to  
59 growing economies, and most of cooking energy (85-90%) comes from bio-fuels (dung cake,  
60 wood, and agricultural waste) and hence the potential for growing pollutant emissions in this  
61 region is large (Lelieveld et al., 2001). Notably in India, bio-fuels account for 47% of the  
62 total energy consumption (Ravindranath and Hall, 1995; TEDDY, 1997). Forest burning and  
63 the field burning of crop residues are also more intensive in this region (Heald et al., 2003;  
64 Streets et al., 2003) and they emit significant amounts of N species to the atmosphere (Levine  
65 et al., 1995; Streets et al., 2003). In addition, India's livestock (~4% of the global livestock;  
66 Bandyopadhyay et al., 1996) is an important source of N species to the atmosphere  
67 (Misselbrook et al., 2001; Oenema and Tamminga, 2005; Yamaji et al., 2004). Conversely,  
68 an enhanced concentration of NH<sub>3</sub> has been reported over India by satellite observation  
69 (Clarisse et al., 2009). However, the sources of N in atmospheric aerosols in South and  
70 Southeast Asia are not well understood.

71 The atmospheric aerosol N contains both inorganic (NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> are major species)  
72 and organic N produced in the atmosphere by several secondary processes (Ottley and  
73 Harrison 1992; Utsunomiya and Wakamatsu, 1996) from gaseous N species emitted from  
74 different sources. Hence, it is difficult to understand the origins of aerosol N from  
75 distributions of N species and/or chemical measurements of specific markers. However, the  
76 measurements of nitrogen isotopic ratios ( $\delta^{15}\text{N}$ ) are helpful in assessing the origin of aerosol  
77 N, because the isotopic ratio in a particular chemical species in the atmosphere is due to the  
78 source or combination of sources from which it originates and is altered by chemical and  
79 physical processes which occur in the atmosphere (Freyer, 1978; Moore, 1977). The use of  
80  $\delta^{15}\text{N}$  as a potential tracer to investigate the origin and atmospheric processing mechanisms of  
81 N species in the atmosphere is well documented and has been used in several studies (Heaton

82 et al., 1997; Kawamura et al., 2004; Kelly et al., 2005; Martinelli et al., 2002; Moore, 1977;  
83 Russell et al., 1998; Turekian et al., 1998; Widory, 2007; Yeatman et al., 2001a, 2001b).

84 In this study, we analyzed tropical Indian aerosols ( $PM_{10}$ ) and cow-dung samples  
85 collected from Chennai for total nitrogen (TN) contents and nitrogen isotopic ratios ( $\delta^{15}N$ ) to  
86 better understand the origins of aerosol N in South and Southeast Asia, where no baseline  
87 study is available for  $\delta^{15}N$  values so far. Here, we report TN and  $\delta^{15}N$  values in tropical  
88 Indian aerosols and their temporal and seasonal variations. Major ionic nitrogen species were  
89 also measured in the aerosols. We discuss the origins of aerosol N in South and Southeast  
90 Asian region by comparing the  $\delta^{15}N$  values in Chennai aerosols with those reported for  
91 atmospheric particles from mid-latitudes and for the particles emitted from point sources,  
92 including a laboratory study as well as the  $\delta^{15}N$  found in cow-dung samples. Further, we also  
93 attempt to assess the plausible atmospheric processes responsible for the elevated  $\delta^{15}N$  ratios  
94 that we found in Chennai aerosols.

95

## 96 **2. Methods**

### 97 *2.1. Sampling site*

98 The geographical features of the sampling site are described in Pavuluri et al. (2010).  
99 Briefly, the tropical mega-city Chennai is located on the southeast coast of India ( $13.04^\circ N$ ;  
100  $80.17^\circ E$ ) (see Figure 2). About 18.6% of the population (total: 7 million, including suburban  
101 area) are living below the standard poverty line (<http://en.wikipedia.org/wiki/chennai>), using  
102 bio-fuel as cooking energy that may emit significant amount of N species.

103

### 104 *2.2. Aerosol and cow-dung sampling*

105 The details of the aerosol ( $PM_{10}$ ) sampling are described in Pavuluri et al. (2010). Briefly,  
106 a day- (~6:00-18:00 IST) and night-time (~18:00-6:00 IST) series of aerosol ( $PM_{10}$ ) samples

107 were collected during winter (January 23 to February 6; n=29) and summer (May 22-31;  
108 n=20) 2007 on a rooftop of the Mechanical Sciences building (~18 m above ground level) on  
109 the Indian Institute of Technology Madras (IITM) campus, Chennai, using a high volume air  
110 sampler and pre-combusted (450 °C, 4 h) quartz fiber filters. The sample filter was placed in  
111 a clean glass jar with a Teflon-lined screw cap and stored in a dark room at -20 °C prior to  
112 analysis.

113 Three cow-dung samples were also collected in May 2009 from Chennai; (1) dung in cow  
114 barnyard, (2) commercially available dung cake containing rice straw residue, and (3) dung  
115 pellets on roadside that were exposed to sun light and traffic emissions for several days. The  
116 samples were packed in aluminum foil and stored in a dark room at -20 °C prior to analysis.

117 During the period of sampling, no rainfall event occurred, and details of the meteorology  
118 observed at the sampling site has been detailed elsewhere (Pavuluri et al., 2010).

119

### 120 2.3. Chemical analysis

121 TN contents and N isotope ratios of samples were determined using elemental analyzer  
122 (EA) (Carlo Erba NA 1500) and EA/isotope ratio mass spectrometer (IRMS) (Finnigan MAT  
123 Delta Plus), respectively (Kawamura et al. 2004; Narukawa et al., 1999). An aliquot of  
124 sample (1.4 cm diameter disc for filter sample and ca. 1 mg cow-dung) was placed in a tin  
125 cup, introduced into EA and then oxidized in a combustion column packed with CuO at 1020  
126 °C. The derived NO<sub>x</sub> (and CO<sub>2</sub>) was introduced into the reduction column to reduce to N<sub>2</sub> at  
127 650 °C. The resulting gasses were then isolated on a gas chromatograph installed in the EA  
128 system and their amounts were measured with a thermal conductivity detector. N<sub>2</sub> and CO<sub>2</sub>  
129 gases were transferred to EA/IRMS via an interface (ConFlo II) for isotopic ratio  
130 measurement. The isotopic composition of N is calculated using the equation;  $\delta^{15}\text{N} =$   
131  $[(^{15}\text{N}/^{14}\text{N})_{\text{sample}} / (^{15}\text{N}/^{14}\text{N})_{\text{standard}} - 1] \times 1000$ . Acetanilide was used as standard to calculate TN

132 and  $\delta^{15}\text{N}$  ratio. The analytical errors for TN and its  $\delta^{15}\text{N}$  measurements based on repeated  
133 duplicate analysis are 4% and 0.4‰, respectively.

134 For the analyses of ion species of interest ( $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ ), an aliquot of filter  
135 sample was extracted with Milli Q water under ultrasonication. The extracts were filtered  
136 using a syringe filter (Millex-GV, 0.22  $\mu\text{m}$ , Millipore), and then injected into ion  
137 chromatograph (761 Compact IC, Metrohm) for measuring ionic species. A calibration curve  
138 was evaluated for each sequence by the analyses of a set of authentic standards, and the  
139 precision fell within 6%.

140 All the data reported here were corrected for field blanks.

141

### 142 **3. Results and Discussion**

#### 143 *3.1. Temporal variations in TN content and N isotopic composition*

144 Concentrations of TN ranged from 0.3 - 3.8  $\mu\text{g m}^{-3}$  (av. 1.7  $\mu\text{g m}^{-3}$ , n=49). The statistical  
145 summary of TN is given in Table 1 for day- and night-time winter and summer aerosols and  
146 their temporal variations are depicted in Fig. 1a. The unpaired two-tailed t-test has also been  
147 performed to check the significance in temporal variations. TN contents were found to be  
148 higher in winter (av. 2.1) than in summer (av. 1.1) with the exception of lower values from  
149 January 27 to 29, except for January 29 night (Fig. 1a) and are significant ( $p = 1.1 \times 10^{-5}$ ).  
150 Whilst the average TN in nighttime (2.4  $\mu\text{g m}^{-3}$ ) was higher than in daytime (1.9  $\mu\text{g m}^{-3}$ ) in  
151 winter, and in summer it was opposite: higher in daytime (1.2  $\mu\text{g m}^{-3}$ ) than in nighttime (0.9  
152  $\mu\text{g m}^{-3}$ ) but not significant ( $p > 0.1$ ). In fact, the diurnal variations were found in winter with  
153 higher concentrations in nighttime, but an opposite trend was generally obtained in summer  
154 (Fig. 1a).

155  $\delta^{15}\text{N}$  ratios were found to range from +15.7‰ to +31.2‰ (av. 23.9‰, n=49). Average  
156  $\delta^{15}\text{N}$  was higher in daytime (25.5‰) than nighttime (23.0‰) in winter ( $p = 0.01$ ). In summer,



157 an opposite trend was observed; higher in nighttime (av. 24.3‰) than daytime (22.2‰)  
158 although the difference is not significant ( $p = 0.24$ ). As seen in Figure 1b, a clear diurnal  
159 trend of  $\delta^{15}\text{N}$  was observed with higher values in daytime during winter, however, during  
160 summer higher  $\delta^{15}\text{N}$  values were often obtained in nighttime. In particular, we detected a  
161 clear diurnal trend in January 23 to 27 and February 1-6 (Fig. 1b). These temporal variations  
162 in  $\delta^{15}\text{N}$  suggest that they are controlled by several parameters including changes in air mass  
163 origins, their transport, contribution of local source and diurnal photochemical  
164 transformations.

165

### 166 *3.2. Backward air mass trajectory analysis*

167 In order to identify the source regions, 10-day backward air mass trajectories were  
168 computed during the sampling period using HYSPLIT model of NOAA as described in  
169 Pavuluri et al. (2010). Briefly, the results showed three major pathways (see Fig. 2). In winter,  
170 the air masses that arrived in Chennai originated mostly from the Middle East and/or the  
171 Indian mainland in January and from Southeast Asia in February passing through the Bay of  
172 Bengal, except for few cases. However, in summer the air masses mostly originated from the  
173 Arabian Sea and/or the Northern Indian Ocean passing over South India. Hence, hereafter we  
174 classify the results into three categories of season; early winter (January 23-28), late winter  
175 (January 29 to February 6) and summer (May 22-31). However, the results of January 31  
176 night and February 1 fall in the category of early winter. Meanwhile, the results of January 29  
177 day, 30 night and 31 day and February 2 day were not included in either categories and  
178 handled as such, because their air masses originated from mixed regions.

179

### 180 *3.3. Seasonal variation in TN and $\delta^{15}\text{N}$*

181 Fig. 3a and b show the box-and-whisker plots of TN and  $\delta^{15}\text{N}$  values, respectively, for  
182 three seasons. The average of TN found to be higher in late winter (av.  $2.5 \mu\text{g m}^{-3}$ ) followed  
183 by early winter (av.  $2.0 \mu\text{g m}^{-3}$ ) and summer (av.  $1.1 \mu\text{g m}^{-3}$ ), although the ranges ( $0.6\text{-}3.8 \mu\text{g}$   
184  $\text{m}^{-3}$ ,  $1.7\text{-}3.5 \mu\text{g m}^{-3}$ , and  $0.3\text{-}2.8 \mu\text{g m}^{-3}$  in early- and late-winter, and summer, respectively)  
185 are similar in the three seasons. Interestingly, the quartiles of TN were also found to be higher  
186 in late winter followed by early winter and summer (Fig. 3a). However, the day- and  
187 nighttime variations in any season are not significant ( $p \geq 0.35$ ).

188 The seasonal changes in TN are highly consistent with the shifts observed in the region of  
189 air masses origin from season to season (Fig. 2). The air masses originated from the Middle  
190 East and the North Indian subcontinent in early winter and Southeast Asia in late winter  
191 might have been enriched with reactive N species emitted from biomass burning, livestock  
192 and agricultural activity (Oenema, 2006; Olivier et al., 1998). The air masses that originated  
193 from the North Indian Ocean and the Arabian Sea over the South Indian subcontinent in  
194 summer probably did not become enriched with reactive N species because the major source  
195 region is only the South Indian subcontinent, and the atmospheric N input from ocean is  
196 minute (Quinn et al., 1988), except from ship exhausts (Sinha et al., 2003; Večeřa et al.,  
197 2008).

198 Whereas, the range and average of  $\delta^{15}\text{N}$  in early winter (range:  $18.0\text{-}27.8\text{‰}$ ; av.  $24.1\text{‰}$ )  
199 and late winter (range:  $22.6\text{-}26.6\text{‰}$ ; av.  $24.8\text{‰}$ ) are comparable although their quartiles and  
200 whiskers are slightly differ with each other (Fig. 3b). The average  $\delta^{15}\text{N}$  in summer ( $23.2\text{‰}$ )  
201 was also close to those observed in early- and late-winter, and interestingly, the quartiles are  
202 highly comparable to early winter (Fig. 3b). But, a significant diversity was detected in the  
203 range of  $\delta^{15}\text{N}$  during summer ( $15.7\text{-}31.2\text{‰}$ ) compared to early- and late-winter. Moreover,  
204  $\delta^{15}\text{N}$  found to be higher in daytime than nighttime during both early- (IQR  $25.6\text{-}27.6\text{‰}$ ; av.  
205  $25.6\text{‰}$  and IQR  $20.0\text{-}25.3\text{‰}$ ; av.  $22.8\text{‰}$ , respectively) and late-winter (IQR  $25.9\text{-}26.5\text{‰}$ ; av.

206 26.0‰ and IQR 23.1-24.2‰; av. 23.7, respectively), but they are significant ( $p = 0.00$ ) only  
207 in late winter. As stated earlier, an opposite trend; higher in nighttime and lower in daytime,  
208 was observed in summer (Table 1).

209 The comparable seasonal distributions of  $\delta^{15}\text{N}$  indicate that the major source(s) of N in  
210 Chennai aerosols might be the same or similar in all seasons. Whilst, the day- and nighttime  
211 variations observed in  $\delta^{15}\text{N}$  during each season can be attributed to local meteorology impact;  
212 land-sea breeze circulation (Pavuluri et al., 2010). In early- and late-winter, daytime, the aged  
213 aerosols those enriched with  $^{15}\text{N}$  by atmospheric processes during long-range transport might  
214 contributed significantly. But in nighttime, local air masses aloft by land breeze might cause a  
215 decrease in  $\delta^{15}\text{N}$  values by mixing with aged air masses. Whereas in summer, it is opposite;  
216 in daytime, the contribution of aged but clean air masses arrived from Oceanic region is high,  
217 those are not enriched well with  $^{15}\text{N}$ . But in nighttime, again the contribution of local air  
218 masses (enriched with biomass/biofuel burning and/or other emissions), those enriched with  
219  $^{15}\text{N}$  compared to oceanic air masses, might be significant and cause to increase the  $\delta^{15}\text{N}$   
220 values.

221 Thus the seasonal distributions of TN and  $\delta^{15}\text{N}$  are highly consistent with the type of  
222 source regions from where the air masses arrived in Chennai during each season. The diurnal  
223 distributions of  $\delta^{15}\text{N}$  in each season clearly indicate the influence of mixing of local and aged  
224 air masses due to local meteorological conditions. In addition, the significance observed in  
225  $\delta^{15}\text{N}$  day- and night-time variations, in particular, during late winter may give further insights  
226 on the influence of meteorological conditions, may be effect of temperature, on atmospheric  
227 processes of N species as discussed in section 3.6.

228 Interestingly,  $\delta^{15}\text{N}$  and TN showed a weak positive ( $r^2 = 0.20$ ) and negative ( $r^2 = 0.14$ )  
229 correlation in early- and late winter, respectively, but no correlation ( $r^2 = 0.02$ ) was found in  
230 summer (see Fig. 4). Moreover, minimum (15.7‰) and maximum (31.2‰)  $\delta^{15}\text{N}$  values were

231 observed only when TN loading was  $<1 \mu\text{g m}^{-3}$  (Fig. 1). These results suggest that  $\delta^{15}\text{N}$   
232 depends mainly on type of source(s) and atmospheric processes (Freyer, 1978; Moore, 1977)  
233 but not on atmospheric loading of aerosol N. In Chennai aerosols,  $\text{NH}_4^+$  is the a major  
234 component of TN as discussed in section 3.6, atmospheric concentrations of  $\text{NH}_4^+$  are  
235 associated with the  $\delta^{15}\text{N}$  ratios of aerosol N. It is likely that the source of N species and their  
236 exchange reactions between gas ( $\text{NH}_3$ ) and particle ( $\text{NH}_4^+$ ) may play an important role in  
237 controlling the  $\delta^{15}\text{N}$  ratios in atmospheric aerosol N.

238

### 239 *3.4. Comparison of $\delta^{15}\text{N}$ ratios in Chennai aerosols with those from mid-latitudes*

240 Table 2 presents the ranges and/or average of  $\delta^{15}\text{N}$  ratios observed in Chennai aerosols,  
241 together with those reported previously for atmospheric aerosols from mid-latitudes and  
242 Brazil. Whilst,  $\delta^{15}\text{N}$  ratios reported for the particles emitted from point sources, located in  
243 mid-latitudes, and a laboratory study of biomass burning as well as those observed in cow-  
244 dung samples collected from Chennai are depicted in Fig. 5. The particles collected from  
245 different kinds of animal barnyards were greatly enriched in  $^{15}\text{N}$  with the  $\delta^{15}\text{N}$  ratios ranging  
246 from 10‰ to 21.0‰ (Fig. 5). The particles emitted during the controlled burning of biomass  
247 were also enriched in  $^{15}\text{N}$ , with variations of  $\delta^{15}\text{N}$  between 2.0‰ and 22.7‰ for different  $\text{C}_3$   
248 and  $\text{C}_4$  plant species (Fig. 5). In contrast, the particles emitted from the combustion of fossil  
249 fuels such as unleaded gasoline, diesel, fuel oil and coal showed a depletion in  $^{15}\text{N}$  with  $\delta^{15}\text{N}$   
250 ratios between -19.4‰ and +5.4‰. However, the  $\delta^{15}\text{N}$  of particles emitted from natural gas  
251 combustion ranges from +3.0 to +15.4‰ (Fig. 5).

252 The aerosols from Piracicaba and the Amazon Basin, Brazil, showed  $\delta^{15}\text{N}$  values ranging  
253 from 8.3‰ to 18.7‰ (Table 2), where a significant contribution from biomass ( $\text{C}_3$  and  $\text{C}_4$   
254 plants) burning was expected (Martinelli et al., 2002). In other urban locations where fossil  
255 fuel combustion was expected as a dominant source,  $\delta^{15}\text{N}$  ranged from -15‰ to +15.9‰

256 (Table 2). In contrast, recent measurements of aerosols in Jeju Island, Korea, showed a  
257 significant enrichment in  $^{15}\text{N}$  with  $\delta^{15}\text{N}$  values of 6.8‰ to 26.9‰ (Table 2), and attributed to  
258 significant atmospheric processing of N species, mainly emitted from China, during long-  
259 range transport (Kundu et al., 2009, submitted). As we expected,  $\delta^{15}\text{N}$  values in Chennai  
260 aerosols are higher (av. 23.9‰) than those (-15.0‰ to 15.9‰) (Table 2) reported for urban  
261 locations from mid-latitudes where fossil fuel combustion was expected as a dominant source  
262 (Kelly et al., 2005; Widory, 2007; Yeatman et al., 2001a). But the lower ends observed in  
263 early winter (18.0‰) and summer (15.7‰) in Chennai aerosols are comparable to those (8.3-  
264 18.7‰) (Table 2) reported from Brazil where a significant contribution from biomass burning  
265 was expected (Martinelli et al., 2002).

266 Interestingly, the average values of  $\delta^{15}\text{N}$  in all three seasons (24.1‰, 24.8‰, and 23.3‰)  
267 are comparable to those reported for point sources including particles emitted from animal  
268 barnyards (range 10.0-21.0‰) and biomass burning (different  $\text{C}_3$  and  $\text{C}_4$  plant species) (2.0-  
269 22.7‰) (Fig. 5), although a few samples from Chennai showed higher ratios (max. 31.2‰).  
270 Further, the comparison of  $\delta^{15}\text{N}$  in Chennai aerosols with those reported for the particles  
271 emitted from animal barnyards is consistent, although temperature conditions are different, as  
272 seen from  $\delta^{15}\text{N}$  found in cow-dung samples collected in Chennai (Fig. 5). In contrast, even  
273 the lowest  $\delta^{15}\text{N}$  (15.7 ‰) observed in Chennai aerosols is higher than those (-19.4‰ to  
274 +15.4‰) for the particles emitted from the combustion of fossil fuels such as unleaded  
275 gasoline, diesel, fuel oil and coal, including natural gas (Fig. 5). These comparisons, together  
276 with air mass trajectories, clearly suggest that animal excreta and bio-fuel/biomass burning  
277 are two major sources of atmospheric N species in the South and Southeast Asian region.

278

279 *3.5. TN content and N isotopic composition of cow-dung cake and comparison to Chennai*  
280 *aerosols*

281 As noted before, the use of bio-fuel (in particular dung cake) for cooking energy is very  
282 common in South and Southeast Asia, which may add a significant amount of N to the  
283 atmosphere. In order to confirm this idea, we measured the  $\delta^{15}\text{N}$  in three cow-dung samples  
284 collected in Chennai. Their TN contents ranged from 1.1-2.2% and their  $\delta^{15}\text{N}$  ratios were  
285 13.4-15.5‰. The dung cake sample collected from the commercial vendor showed lower  
286  $\delta^{15}\text{N}$  (13.4‰) than that collected on the roadside (15.5‰). Another dung sample collected  
287 directly from a cow barnyard showed a medium (14.1‰), although it showed lower TN  
288 content (1.1 %) than in dung cake (1.5 %). These results suggest that the cow-dung is highly  
289 enriched in  $^{15}\text{N}$ , probably due to microbial processes in the animal guts. The highest  $\delta^{15}\text{N}$   
290 value detected in the roadside sample may suggest that emission of  $\text{NH}_3$  occurs during  
291 microbial degradation of the nitrogen compounds of cow dung in the environment, which can  
292 cause higher  $\delta^{15}\text{N}$  ratios in the remaining cow dung.

293 The  $\delta^{15}\text{N}$  values found in cow-dung samples (av. 14.3‰) are comparable to the lower  
294 limit obtained in the Chennai aerosols (Table 1). However, as evidenced from a laboratory  
295 study of biomass burning (Turekian et al., 1998), particles emitted from combustion could be  
296 enriched with the heavier isotope ( $^{15}\text{N}$ ) compared to that of the source substance due to the  
297 partitioning between gas and particles, which may occur between emitted gaseous nitrogen  
298 (e.g.,  $\text{NH}_3$ ) and particulate organic-nitrogen compounds. Turekian et al. (1998) reported an  
299 average  $\delta^{15}\text{N}$  increase of 6.6‰ (range, -1.3‰ to 13.1‰) for aerosol particles collected during  
300 the laboratory burning of plant leaves compared to the source vegetation. Hence if we assume  
301 that the  $\delta^{15}\text{N}$  in particles emitted from the combustion of dung-cake may be enriched in  $^{15}\text{N}$   
302 by ~7‰ during combustion, then the resulting  $\delta^{15}\text{N}$  (approximately 22‰) will become nearer  
303 to the average values of  $\delta^{15}\text{N}$  (23.9‰) that we found in the Chennai aerosols.

304 In fact, the spatial distribution of dung-cake consumption and livestock emission (e.g.  
305  $\text{CH}_4$ ) are higher in Gangetic plains followed by southern India and southeast coastal belt of

306 India (Garg et al., 2001; Reddy and Venkataraman, 2002). Interestingly, the expected  $\delta^{15}\text{N}$   
307 (ca. 22‰) in the particles emitted from dung-cake combustion is very close to the average  
308  $\delta^{15}\text{N}$  found in Chennai aerosols in summer (23.3‰) followed by early- (24.1‰) and late-  
309 winter (24.8‰), and the observed closure is highly consistent with strength of N species  
310 emission of source region from where the air masses were arrived in Chennai during each  
311 season (Fig. 2). Further a little enrichment of  $^{15}\text{N}$  in early- and late winter probably due to  
312 significant contribution of biomass burning emissions and/or atmospheric processing of N  
313 species during long-range transport.

314

### 315 *3.6. Contributions of N species to TN, sources and interpretation of plausible atmospheric* 316 *processes responsible for $^{15}\text{N}$ enrichment in tropical Indian aerosols*

317 The statistical summary of inorganic ( $\text{NH}_4^+\text{-N}$  plus  $\text{NO}_3^-\text{-N}$ ) and organic (TN minus  
318 Inorg-N) N for day- and night-time in winter and summer was given in Table 1. Interestingly,  
319 the Org-N was observed only during winter but not in summer, and the average Org-N in  
320 early- ( $0.36\pm 0.14 \mu\text{g m}^{-3}$ ) and late-winter ( $0.31\pm 0.12 \mu\text{g m}^{-3}$ ) are comparable. As stated  
321 earlier, during early- and late-winter, air masses were come from the South and Southeast  
322 Asian region where biomass burning, including forest fires, are higher (Streets et al., 2003).  
323 During summer, the air masses were come from the oceanic region passing over southern part  
324 of Indian subcontinent where the consumption of biofuel, in particular cow-dung, is higher  
325 (Reddy and Venkataraman, 2002). These results indicate that Org-N might contribute from  
326 biomass burning emissions but not from cow-dung combustion, and could have influenced  
327 the  $\delta^{15}\text{N}$  of TN in Chennai aerosols during winter.

328 Further it is clear from linear regression plot drawn between  $\text{NH}_4^+\text{-N}$  and TN and  $\text{NO}_3^-\text{-N}$   
329 and TN that  $\text{NH}_4^+$  is the main nitrogen species (78% of TN) in Chennai aerosols, whereas  
330  $\text{NO}_3^-$  contributes only 6% of TN (see Fig. 6). Oenema and Tamminga (2005) estimated that

331 contributions of  $\text{NH}_4^+$  and  $\text{NO}_x^-$  emissions from animal manure to global N are 40-60% and  
332 0-10%, respectively. Hence, the higher contribution of  $\text{NH}_4^+$  to TN may be associated with a  
333 significant emission of  $\text{NH}_3$  to the atmosphere from animal barnyards, dung-cake combustion  
334 and biomass burning. Of course, the  $\text{NH}_3$  emitted from sewage and landfills (Sutton et al.,  
335 2000) might have also contributed at minor level because the sewage spreading into water  
336 streams and dumping of municipal solid waste into open landfills is higher in India (Jha et al.,  
337 2008).

338 The emitted  $\text{NH}_3$  may be less enriched with  $^{15}\text{N}$  (Turekian et al., 1998) and should react  
339 with acids in the air to form aerosol particles, probably  $(\text{NH}_4)_2\text{SO}_4$  (Ottley and Harrison,  
340 1992). The reaction of  $\text{NH}_3$  with  $\text{H}_2\text{SO}_4$  is unidirectional (kinetic) at the onset, favoring  
341 lighter isotope ( $^{14}\text{N}$ ) in particles, but stoichiometric equilibrium is attained in several minutes  
342 (ca. 6 min), in which  $\text{NH}_3\text{--NH}_4^+$  exchange (equilibrium) reaction occurs (Heaton et al., 1997).  
343 Under equilibrium conditions,  $\text{NH}_4^+$  stabilizes rapidly with  $\delta^{15}\text{N}$  values being higher than that  
344 of  $\text{NH}_3$ , where the isotopic enrichment factor ( $\epsilon_{\text{NH}_4\text{--NH}_3}$ ) was estimated to be +33‰ (Heaton  
345 et al., 1997). Hayasaka et al. (2004) also observed higher  $\delta^{15}\text{N}$  values of aerosol  $\text{NH}_4^+$  (av.  
346 +22.1‰) than that of gaseous  $\text{NH}_3$  (av. -8.3‰) in the atmosphere at the Maki monitoring  
347 station, Niigata, Japan.

348 In fact, Chennai aerosols are rich in  $\text{SO}_4^{2-}$  (av.  $6.9 \mu\text{g m}^{-3}$ ,  $n=49$ ), and average molar ratios  
349 of  $\text{SO}_4^{2-}/\text{NH}_4^+$  were found to be 1.3, 0.7 and 0.6 in early- and late-winter and summer,  
350 respectively. The enrichment of  $^{15}\text{N}$  in TN was found to correlate positively with  $\text{SO}_4^{2-}$ ,  
351 although it is weak in early- ( $r^2 = 0.31$ ) and late winter (see Fig. 7a) and negligible in summer  
352 ( $r^2 = 0.04$ ). As discussed in Heaton et al. (1997), enrichment of  $^{15}\text{N}$  may be enhanced when  
353  $\text{NH}_3$  is in stoichiometric equilibrium with  $(\text{NH}_4)_2\text{SO}_4$ . However, the lesser  $\text{SO}_4^{2-}/\text{NH}_4^+$  molar  
354 ratios and weak/negligible correlation between  $^{15}\text{N}$  of TN and  $\text{SO}_4^{2-}$  suggest that an  
355 enrichment of  $^{15}\text{N}$  in aerosols in the stoichiometric equilibrium for the  $\text{NH}_3\text{--NH}_4^+$  exchange



356 reaction may be more efficient with  $\text{NH}_4\text{HSO}_4$  rather than  $(\text{NH}_4)_2\text{SO}_4$ . Alternatively, another  
357 acid group, i.e., organic acids, may involve with the stoichiometric equilibrium by forming  
358  $\text{RCOONH}_4$ .

359 Because, sulfate aerosol become more acidic than  $\text{NH}_4\text{HSO}_4$  and accumulate when the  
360  $\text{NH}_3$  source strength is insufficient to maintain an ambient  $\text{NH}_3$  partial pressure greater than  
361 the equilibrium vapor pressure of  $\text{NH}_3$  over the partially neutralized  $\text{H}_2\text{SO}_4$  droplet  
362 (Huntzicker et al., 1980). On the other hand, the organic compounds such as fatty acids are  
363 known to form surface films and inhibit the neutralization of  $\text{H}_2\text{SO}_4$  aerosol by  $\text{NH}_3$  (Junge  
364 and Scheich, 1969), and thus suppress the stoichiometric equilibrium between  $\text{NH}_3$ – $\text{NH}_4^+$ . In  
365 fact, we found high concentrations (up to  $1440 \text{ ng m}^{-3}$ ) of oxalic acid and other dicarboxylic  
366 acids in Chennai aerosol samples (Pavuluri et al., 2010). Our hypothesis is also corroborated  
367 by seasonal variations observed in correlations between  $\delta^{15}\text{N}$  and molar ratios  $\text{SO}_4^{2-}/\text{NH}_4^+$   
368 and ambient temperature as discussed below.

369 First, we found that  $\delta^{15}\text{N}$  values correlate well ( $r^2 = 0.81$ ) with molar ratios of  $\text{SO}_4^{2-}/\text{NH}_4^+$   
370 in late winter (see Fig. 7b), but weak ( $r^2 = 0.34$ ) in early winter and not in summer. In late  
371 winter, air masses arrived from Southeast Asian region, where biomass burning occurs more  
372 frequently than in South Asia (Streets et al., 2003). Streets et al. (2003) estimated that  
373 amounts of vegetation burned in Southeast Asia (331 Tg dry matter) are almost twice those of  
374 South Asia (178 Tg), and the subsequent emissions of  $\text{NH}_3$  in Southeast Asia (416 Gg) are  
375 also twice those of South Asia (229 Gg). Further, biomass-burning emissions (e.g., CO) are  
376 more enhanced in February to April than in January and May (Streets et al., 2003).  
377 Conversely, a larger contribution of biomass burning emissions to Chennai aerosols in late  
378 winter is further confirmed by higher concentrations of levoglucosan (an excellent biomass  
379 burning tracer) in late winter (av.  $0.17 \mu\text{g m}^{-3}$ ) than early winter (av.  $0.07 \mu\text{g m}^{-3}$ ) and  
380 summer (av.  $0.11 \mu\text{g m}^{-3}$ ) (Fu et al., 2009).

381 Secondly, we found a good correlation between  $\delta^{15}\text{N}$  values and ambient temperature in  
382 late winter (Figure 5c) although no correlation exists between these parameters in early  
383 winter and summer. This relation may suggest that the gas-to-particle ( $\text{NH}_3 \rightarrow \text{NH}_4^+$ )  
384 conversion is intensified with increasing temperature, and may reach to the equilibrium  
385 quickly causing a significant enrichment of  $^{15}\text{N}$  in the particles during long-range  
386 atmospheric transport. However, the effect of ambient temperature on atmospheric processing  
387 of aerosol N may be relatively weakened when the temperatures are high in early winter  
388 (range: 16.5-32.1; av. 24.8 °C) and summer (range: 25.3-36.1; av. 31.8 °C) compared to late  
389 winter (range: 18.4-24.5; av. 21.2 °C). In fact, the effective separation factors, which are  
390 defined by  $(^{15}\text{N}/^{14}\text{N})_{\text{soln}}/(^{15}\text{N}/^{14}\text{N})_{\text{g}}$  for the ammonia-ammonium carbonate system from  
391 single stage equilibrations, were reported to be 1.015, 1.019, 1.021 and 1.022 for the  
392 temperatures of 15.6, 25.8, 35.9 and 44.3 °C under the atmospheric pressure, respectively  
393 (Begun et al., 1956).

394 Further as discussed in Utsunomiya and Wakamatsu (1996), it is known to dissociate the  
395 particulate  $\text{NH}_4\text{NO}_3$  into its precursor gases  $\text{NH}_3$  and  $\text{HNO}_3$  at high atmospheric temperature,  
396 but the fate of isotopic fractionation is not known. Based on our observations, we presume  
397 that  $^{15}\text{N}$  may preferably associate with  $\text{HNO}_3$  and might have also been caused depletion in  
398  $\delta^{15}\text{N}$  of TN during high ambient temperature conditions, although the content of  $\text{NO}_3^-$ -N is  
399 minor in Chennai aerosols as noted before.

400 It is clear from these observations that amounts of the fine particles emitted and enriched  
401 with  $^{15}\text{N}$  (Turekian et al., 1998) may be enhanced in late winter compared to two other  
402 seasons. Potentially high  $\delta^{15}\text{N}$  values of organic nitrogen in Chennai aerosols could also  
403 contribute to the higher ratios, although its fraction is rather minor (ca. 17% of TN). Further,  
404 we believe that  $\text{NH}_3$ - $\text{NH}_4^+$  exchange reactions are proportionally enhanced with an increase

405 in the temperature when ambient temperatures (i.e., 15-25 °C) are moderate but such trend is  
406 not effective on further increase in the temperature.

407 Thus, this study becomes a piece of evidence for the origins of aerosol N in South and  
408 Southeast Asia, and also shows that availability of acid species (e.g., H<sub>2</sub>SO<sub>4</sub>) and the  
409 emission rate of NH<sub>3</sub> from animal barnyards, bio-fuel combustion and biomass burning play a  
410 vital role in <sup>15</sup>N enrichment in the atmosphere.

411 However, very high δ<sup>15</sup>N values (29.8‰ and 31.2‰) observed in May 23 day- and  
412 nighttime samples, although TN was found to be only <1 μg m<sup>-3</sup> in both the samples, are  
413 much higher than those of expected potential sources. It indicates that the contributions from  
414 other anthropogenic sources such as industrial activities cannot be ignored in this region.  
415 Because NH<sub>3</sub> is used as raw material for multiple products but the fate of reactive N in  
416 industrial activities is unclear (Galloway et al., 2008), and also the NH<sub>3</sub> emission from  
417 fertilizer manufacturing and other industrial units is significant (Sutton et al., 2000). Recently,  
418 Clarisse et al. (2009) reported elevated NH<sub>3</sub> column concentrations (up to 7 mg m<sup>-2</sup>) over  
419 India by satellite observations. Hence, it is a subject of further research in future.

420 Finally, lower δ<sup>15</sup>N values observed in nighttime particularly in winter (Fig. 1) are  
421 possibly caused by local NO<sub>x</sub> emissions from fossil fuel combustion whose δ<sup>15</sup>N values are  
422 significantly low as described above. Local or regional emissions from bio-fuel burning may  
423 contribute to lower the isotopic ratios of aerosols. In both cases, land breeze at night should  
424 enhance a transport of the anthropogenic particulate nitrogen over the coastal city Chennai.

425

#### 426 **4. Summary and Conclusion**

427 The aerosol TN contents were determined to be high (up to 3.8 μg m<sup>-3</sup>) in the tropical  
428 Indian aerosols from Chennai, but they did not show a systematic diurnal variation. We found  
429 very high δ<sup>15</sup>N values in the aerosols (max. 31.2‰), which are comparable to those reported

430 for particles emitted from animal barnyards and biomass burning. The measured  $\delta^{15}\text{N}$  values  
431 in cow-dung samples were also equivalent to the lower range of  $\delta^{15}\text{N}$  ratios of Chennai  
432 aerosols. The assumed  $\delta^{15}\text{N}$  values from the combustion of dung-cake based on a laboratory  
433 study conducted for vegetation burning are close to the average  $\delta^{15}\text{N}$  ratio in Chennai. We  
434 also found that  $\text{NH}_4^+$  is the major species (78%) of TN, which is probably produced by gas-  
435 to-particle conversion of  $\text{NH}_3$  in the atmosphere. The equilibrium  $\text{NH}_3\text{-NH}_4^+$  exchange  
436 reaction probably play the most important role in the enrichment of  $^{15}\text{N}$  in TN. Hence, we  
437 conclude that animal excreta, bio-fuel and biomass burning are the important sources of  
438 aerosol N in South and Southeast Asia.

439

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Fig. 1.

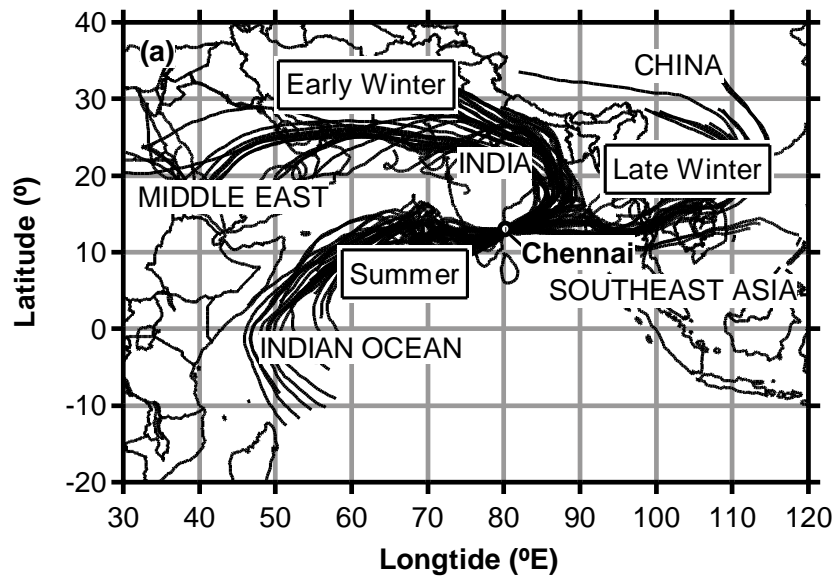


Fig. 2

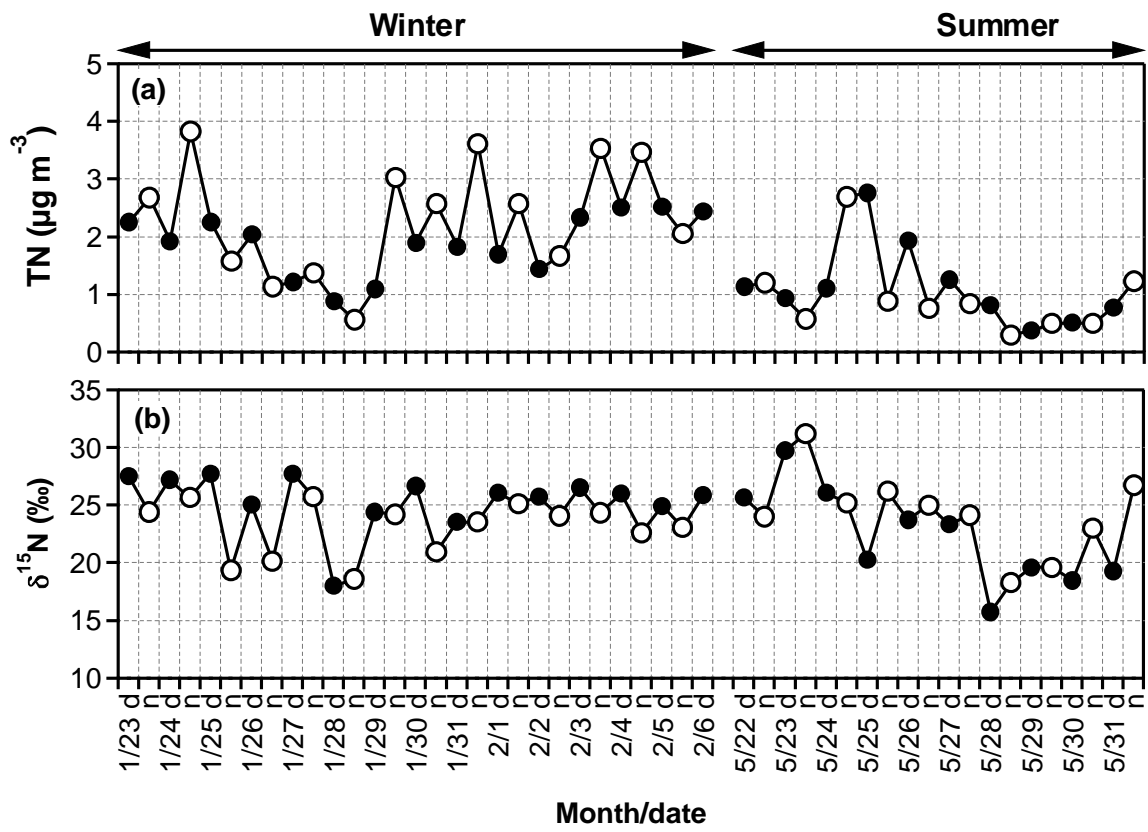


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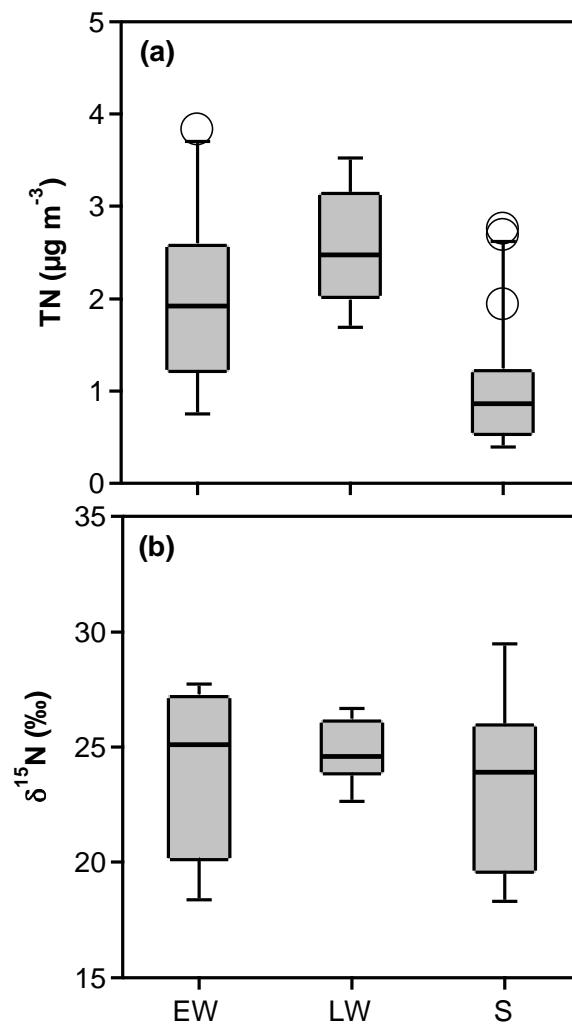


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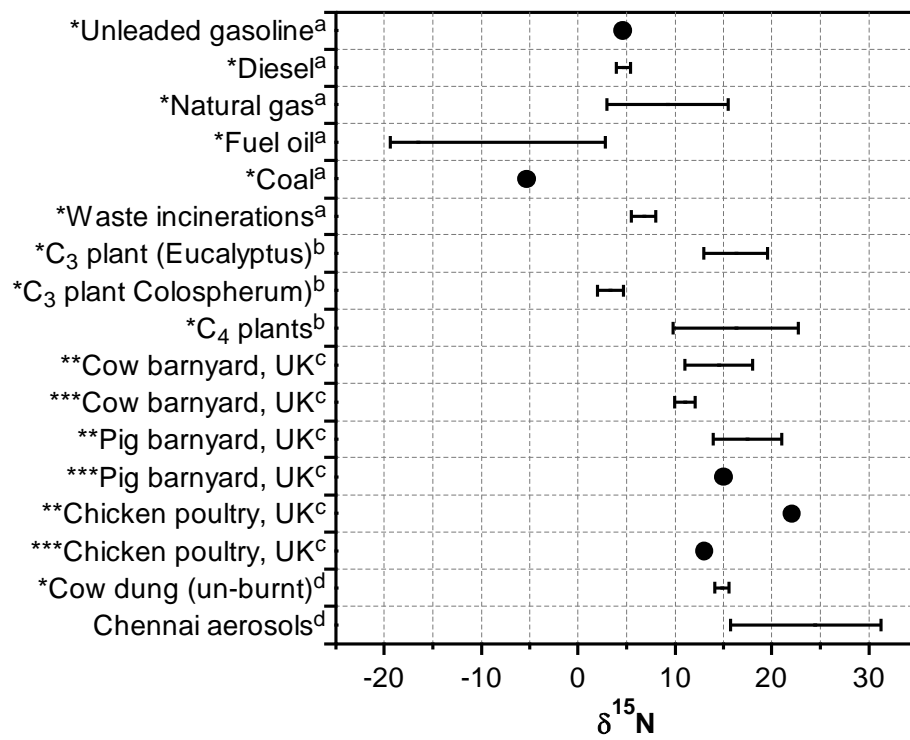


Fig. 5.

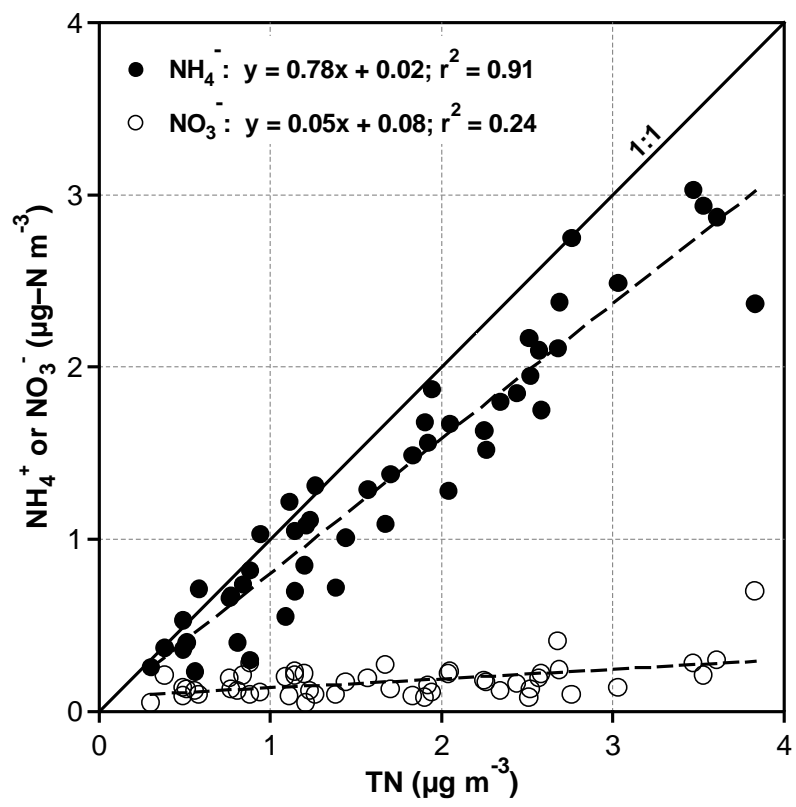
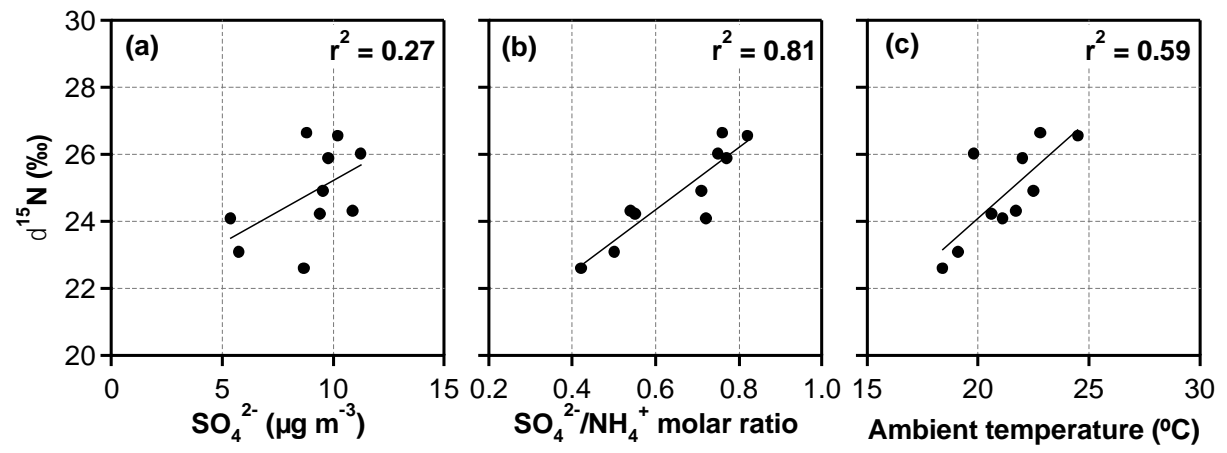


Fig. 6.





### Figure captions

Fig. 1. A map of South and Southeast Asia with sampling location Chennai (13.04°N; 80.17°E) on the southeast coast of India together with plots of air mass back trajectories arriving at 500 m above Chennai in winter (January 23 to February 6) and summer (May 22-31) 2007, showing three major pathways reflecting early winter (January 23-29), late winter (January 30 to February 6) and summer (May 22-31).

Fig. 2. Temporal variations in the (a) concentration of total nitrogen (TN) and (b) its stable isotope ratios ( $\delta^{15}\text{N}$ ) in tropical Indian aerosol ( $\text{PM}_{10}$ ) samples collected on day- (d; closed circle) and night-time (n; open circle) bases in winter and summer 2007 from Chennai.

Fig. 3. Box-and-whisker plot of seasonal variations in (a) total nitrogen (TN) and (b) its stable isotope ratios ( $\delta^{15}\text{N}$ ) in tropical Indian aerosol ( $\text{PM}_{10}$ ) samples collected on day- and night-time basis in early winter, late winter and summer from Chennai. Lower and upper ends of box and the lower and upper bars show the quartiles at 25% and 75% and the whiskers at 10% and 90%, respectively, and the cross bar in the box and open circles show the median and outliers, respectively.

Fig. 4. Range or mean nitrogen isotope ratios ( $\delta^{15}\text{N}$ ) in the particles emitted from point sources in different locations over the world, including a laboratory study, and in cow-dung (source substance) and aerosol samples collected at Chennai, India. \*, \*\* and \*\*\* show form of nitrogen; TN,  $\text{NH}_4^+$  and  $\text{NO}_3^-$ , respectively. <sup>a</sup>Widory, 2007; <sup>b</sup>Turekian et al., 1998; <sup>c</sup>Yeatman et al., 2001a; <sup>d</sup>this study.

Fig. 5. Linear relations of ammonium nitrogen ( $\text{NH}_4^+\text{-N}$ ) and nitrate nitrogen ( $\text{NO}_3^-\text{-N}$ ) to total aerosol nitrogen (TN) in tropical Indian aerosol ( $\text{PM}_{10}$ ) samples collected from Chennai on day- and night-time bases during winter and summer 2007.

Fig. 6. Correlation plots of  $\delta^{15}\text{N}$  values (‰) as a function of (a)  $\text{SO}_4^{2-}$  ( $\mu\text{g m}^{-3}$ ), (b) molar ratios of  $\text{NH}_4^+$  to  $\text{SO}_4^{2-}$ , and (c) ambient temperature for the tropical Indian aerosol ( $\text{PM}_{10}$ ) samples collected from Chennai during late winter 2007.

Table 1. Concentrations of total nitrogen (TN) and its isotope ratios ( $\delta^{15}\text{N}$ ) in tropical Indian aerosols ( $\text{PM}_{10}$ ) collected from Chennai on day- and night-time basis in winter (January 23 to February 6) and in summer (May 22-31) 2007.

	Winter										Summer									
	Daytime					Nighttime					Daytime					Nighttime				
	Range	IQR	Med.	Av.	SD	Range	IQR	Med.	Av.	SD	Range	IQR	Med.	Av.	SD	Range	IQR	Med.	Av.	SD
TN ( $\mu\text{g m}^{-3}$ )	0.9– 2.5	1.6– 2.3	1.9	1.9	0.5	0.6– 3.8	1.6– 3.4	2.6	2.4	1.0	0.4–2.8	0.78–1.2	1.0	1.2	0.7	0.3–2.7	0.51– 1.1	0.8	0.9	0.7
$\delta^{15}\text{N}$ (‰)	18.0– 27.8	25.0– 26.9	26.0	25.5	2.4	18.6– 25.7	21.3– 24.4	23.8	23.0	2.3	15.7– 29.8	19.3– 25.2	21.8	22.2	4.3	18.3– 31.2	23.3– 25.9	24.6	24.3	3.6
Inorg-N ( $\mu\text{g m}^{-3}$ )	0.58– 2.3	1.3– 1.9	1.7	1.6	0.48	0.35– 3.3	1.4– 2.96	2.13	2.07	0.97	0.52– 2.9	0.63–1.4	1.2	1.2	0.73	0.31– 2.62	0.71– 1.0	0.89	0.99	0.64
Org-N ( $\mu\text{g m}^{-3}$ )	0.08– 0.57	0.23– 0.44	0.30	0.32	0.15	0.09– 0.76	0.17– 0.42	0.29	0.34	0.20	(0.20)– 0.30	(0.18)– (0.03)	(0.11)	(0.08)	0.15	(0.23)– 0.13	(0.11)– 0.03	(0.03)	(0.04)	0.11

IQR = Inter Quartile Range; Med. = Median; Av. = Average; SD = Standard Deviation.

Table 2. Nitrogen isotope ratios ( $\delta^{15}\text{N}$ ) in atmospheric aerosols collected at different locations over the world.

Location/Source	Form of N	$\delta^{15}\text{N}$ ratios (‰)		Reference
		Range	Av. $\pm$ SD	
Chennai, India	TN	15.7 to 31.2	23.9 $\pm$ 3.3	This study
Jeju Island, Korea	TN	-3.7 to 12.4		Kawamura et al., 2004
Jeju Island, Korea	TN	6.8 to 26.9		Kundu et al., 2009 (submitted)
Piracicaba, Brazil	TN	9.0 to 18.7	10.6	Martinelli, et al., 2002
Amazon Basin, Brazil	TN	8.37 to 15.45	11.5	"
Paris, France	TN	5.3 to 15.9		Widory, 2007
East Anglia, UK	Org. N	-15.0 to 12.5		Kelly et al., 2005
Waybourne, UK	$\text{NH}_4^+$		6 $\pm$ 6	Yeatman et al., 2001a
"	$\text{NO}_3^-$		7 $\pm$ 6	"
Mace Head, Ireland	$\text{NH}_4^+$		-9 $\pm$ 8	"
"	$\text{NO}_3^-$		-1 $\pm$ 3	"
Atlantic Ocean	$\text{NH}_4^+$	-11		"
"	$\text{NO}_3^-$		-1 $\pm$ 3	"

Av. = Average; SD = Standard Deviation