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**Elevated nitrogen isotopic ratios of tropical Indian aerosols from Chennai:
Implication for the origins of aerosol nitrogen in South and Southeast Asia**

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Abstract

To better understand the origins of aerosol nitrogen, we measured concentrations of total nitrogen (TN) and its isotopic ratios ($\delta^{15}\text{N}$) in tropical Indian aerosols (PM_{10}) collected from Chennai (13.04°N ; 80.17°E) on day- and night-time basis in winter and summer 2007. We 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 NH_4^+ is the major species (78%) with lesser contribution from NO_3^- (6%). Based on the comparison of $\delta^{15}\text{N}$ in Chennai aerosols with those reported for atmospheric aerosols from mid-latitudes and for the particles emitted from point sources (including a laboratory study), as well as the $\delta^{15}\text{N}$ ratios of cow-dung samples (this study), we found that the atmospheric aerosol N in Chennai has two major sources; animal excreta and bio-fuel/biomass burning from South and Southeast Asia. We demonstrate that a gas-to-particle conversion of NH_3 to NH_4HSO_4 and $(\text{NH}_4)_2\text{SO}_4$ and the subsequent exchange reaction between NH_3 and NH_4^+ are responsible for the isotopic enrichment of ^{15}N in aerosol nitrogen.

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

1. Introduction

Global biogeochemical cycles of nitrogen (N) have been modified by industrial, agricultural and other anthropogenic activities. The important N species, such as nitrogen oxides (NO_2 and NO_3 , together denoted as NO_x) and ammonia (NH_3) are short-lived and are involved in several chemical reactions once they enter into the atmosphere (Olivier et al., 1998). NO_x acts as an ozone (O_3) precursor, affecting the atmospheric oxidizing capability. NH_3 serves as a neutralizing agent in the atmosphere, influencing the pH of aerosols, cloud droplets and rainfalls (Olivier et al., 1998). Those gases and their reaction products can be transported long distances in the atmosphere. After the deposition, N species may enhance the productivity of lake and coastal/remote ocean waters and raise soil acidity; almost all open surface areas are now being affected by anthropogenic atmospheric N deposition (Duce et al., 2008). Thus the increased N loadings likely cause severe damage to the atmospheric environment on local, regional, and global scales (Rodhe et al., 2002; Vitousek et al., 1997), including human health effects (Townsend et al., 2003).

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

In South and Southeast Asia, the consumption of fossil energy is highly increasing due to growing economies, and most of cooking energy (85-90%) comes from bio-fuels (dung cake, wood, and agricultural waste) and hence the potential for growing pollutant emissions in this region is large (Lelieveld et al., 2001). Notably in India, bio-fuels account for 47% of the total energy consumption (Ravindranath and Hall, 1995; TEDDY, 1997). Forest burning and the field burning of crop residues are also more intensive in this region (Heald et al., 2003; Streets et al., 2003) and they emit significant amounts of N species to the atmosphere (Levine et al., 1995; Streets et al., 2003). In addition, India's livestock (~4% of the global livestock; Bandyopadhyay et al., 1996) is an important source of N species to the atmosphere (Misselbrook et al., 2001; Oenema and Tamminga, 2005; Yamaji et al., 2004). Conversely, an enhanced concentration of NH_3 has been reported over India by satellite observation (Clarisse et al., 2009). However, the sources of N in atmospheric aerosols in South and Southeast Asia are not well understood.

The atmospheric aerosol N contains both inorganic (NH_4^+ and NO_3^- are major species) and organic N produced in the atmosphere by several secondary processes (Ottley and Harrison 1992; Utsunomiya and Wakamatsu, 1996) from gaseous N species emitted from different sources. Hence, it is difficult to understand the origins of aerosol N from distributions of N species and/or chemical measurements of specific markers. However, the measurements of nitrogen isotopic ratios ($\delta^{15}\text{N}$) are helpful in assessing the origin of aerosol N, because the isotopic ratio in a particular chemical species in the atmosphere is due to the source or combination of sources from which it originates and is altered by chemical and physical processes which occur in the atmosphere (Freyer, 1978; Moore, 1977). The use of $\delta^{15}\text{N}$ as a potential tracer to investigate the origin and atmospheric processing mechanisms of N species in the atmosphere is well documented and has been used in several studies (Heaton

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

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

2. Methods

2.1. Sampling site

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

2.2. Aerosol and cow-dung sampling

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

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

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

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

2.3. Chemical analysis

TN contents and N isotope ratios of samples were determined using elemental analyzer (EA) (Carlo Erba NA 1500) and EA/isotope ratio mass spectrometer (IRMS) (Finnigan MAT Delta Plus), respectively (Kawamura et al. 2004; Narukawa et al., 1999). An aliquot of sample (1.4 cm diameter disc for filter sample and ca. 1 mg cow-dung) was placed in a tin cup, introduced into EA and then oxidized in a combustion column packed with CuO at 1020 °C. The derived NO_x (and CO₂) was introduced into the reduction column to reduce to N₂ at 650 °C. The resulting gasses were then isolated on a gas chromatograph installed in the EA system and their amounts were measured with a thermal conductivity detector. N₂ and CO₂ gases were transferred to EA/IRMS via an interface (ConFlo II) for isotopic ratio measurement. The isotopic composition of N is calculated using the equation; $\delta^{15}\text{N} = [({}^{15}\text{N}/{}^{14}\text{N})_{\text{sample}}/({}^{15}\text{N}/{}^{14}\text{N})_{\text{standard}} - 1] \times 1000$. Acetanilide was used as standard to calculate TN

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

For the analyses of ion species of interest (NH_4^+ , NO_3^- and SO_4^{2-}), an aliquot of filter sample was extracted with Milli Q water under ultrasonication. The extracts were filtered using a syringe filter (Millex-GV, 0.22 μm , Millipore), and then injected into ion chromatograph (761 Compact IC, Metrohm) for measuring ionic species. A calibration curve was evaluated for each sequence by the analyses of a set of authentic standards, and the precision fell within 6%.

All the data reported here were corrected for field blanks.

3. Results and Discussion

3.1. Temporal variations in TN content and N isotopic composition

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

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

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

3.2. Backward air mass trajectory analysis

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

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

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

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

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

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

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

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

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

observed only when TN loading was $<1 \mu\text{g m}^{-3}$ (Fig. 1). These results suggest that $\delta^{15}\text{N}$ depends mainly on type of source(s) and atmospheric processes (Freyer, 1978; Moore, 1977) but not on atmospheric loading of aerosol N. In Chennai aerosols, NH_4^+ is the a major component of TN as discussed in section 3.6, atmospheric concentrations of NH_4^+ are associated with the $\delta^{15}\text{N}$ ratios of aerosol N. It is likely that the source of N species and their exchange reactions between gas (NH_3) and particle (NH_4^+) may play an important role in controlling the $\delta^{15}\text{N}$ ratios in atmospheric aerosol N.

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

Table 2 presents the ranges and/or average of $\delta^{15}\text{N}$ ratios observed in Chennai aerosols, together with those reported previously for atmospheric aerosols from mid-latitudes and Brazil. Whilst, $\delta^{15}\text{N}$ ratios reported for the particles emitted from point sources, located in mid-latitudes, and a laboratory study of biomass burning as well as those observed in cow-dung samples collected from Chennai are depicted in Fig. 5. The particles collected from different kinds of animal barnyards were greatly enriched in ^{15}N with the $\delta^{15}\text{N}$ ratios ranging from 10‰ to 21.0‰ (Fig. 5). The particles emitted during the controlled burning of biomass were also enriched in ^{15}N , with variations of $\delta^{15}\text{N}$ between 2.0‰ and 22.7‰ for different C_3 and C_4 plant species (Fig. 5). In contrast, the particles emitted from the combustion of fossil fuels such as unleaded gasoline, diesel, fuel oil and coal showed a depletion in ^{15}N with $\delta^{15}\text{N}$ ratios between -19.4‰ and +5.4‰. However, the $\delta^{15}\text{N}$ of particles emitted from natural gas combustion ranges from +3.0 to +15.4‰ (Fig. 5).

The aerosols from Piracicaba and the Amazon Basin, Brazil, showed $\delta^{15}\text{N}$ values ranging from 8.3‰ to 18.7‰ (Table 2), where a significant contribution from biomass (C_3 and C_4 plants) burning was expected (Martinelli et al., 2002). In other urban locations where fossil fuel combustion was expected as a dominant source, $\delta^{15}\text{N}$ ranged from -15‰ to +15.9‰

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

Interestingly, the average values of $\delta^{15}\text{N}$ in all three seasons (24.1‰, 24.8‰, and 23.3‰) are comparable to those reported for point sources including particles emitted from animal barnyards (range 10.0-21.0‰) and biomass burning (different C_3 and C_4 plant species) (2.0-22.7‰) (Fig. 5), although a few samples from Chennai showed higher ratios (max. 31.2‰). Further, the comparison of $\delta^{15}\text{N}$ in Chennai aerosols with those reported for the particles emitted from animal barnyards is consistent, although temperature conditions are different, as seen from $\delta^{15}\text{N}$ found in cow-dung samples collected in Chennai (Fig. 5). In contrast, even the lowest $\delta^{15}\text{N}$ (15.7 ‰) observed in Chennai aerosols is higher than those (-19.4‰ to +15.4‰) for the particles emitted from the combustion of fossil fuels such as unleaded gasoline, diesel, fuel oil and coal, including natural gas (Fig. 5). These comparisons, together with air mass trajectories, clearly suggest that animal excreta and bio-fuel/biomass burning are two major sources of atmospheric N species in the South and Southeast Asian region.

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

As noted before, the use of bio-fuel (in particular dung cake) for cooking energy is very common in South and Southeast Asia, which may add a significant amount of N to the atmosphere. In order to confirm this idea, we measured the $\delta^{15}\text{N}$ in three cow-dung samples collected in Chennai. Their TN contents ranged from 1.1-2.2% and their $\delta^{15}\text{N}$ ratios were 13.4-15.5‰. The dung cake sample collected from the commercial vendor showed lower $\delta^{15}\text{N}$ (13.4‰) than that collected on the roadside (15.5‰). Another dung sample collected directly from a cow barnyard showed a medium (14.1‰), although it showed lower TN content (1.1 %) than in dung cake (1.5 %). These results suggest that the cow-dung is highly enriched in ^{15}N , probably due to microbial processes in the animal guts. The highest $\delta^{15}\text{N}$ value detected in the roadside sample may suggest that emission of NH_3 occurs during microbial degradation of the nitrogen compounds of cow dung in the environment, which can cause higher $\delta^{15}\text{N}$ ratios in the remaining cow dung.

The $\delta^{15}\text{N}$ values found in cow-dung samples (av. 14.3‰) are comparable to the lower limit obtained in the Chennai aerosols (Table 1). However, as evidenced from a laboratory study of biomass burning (Turekian et al., 1998), particles emitted from combustion could be enriched with the heavier isotope (^{15}N) compared to that of the source substance due to the partitioning between gas and particles, which may occur between emitted gaseous nitrogen (e.g., NH_3) and particulate organic-nitrogen compounds. Turekian et al. (1998) reported an average $\delta^{15}\text{N}$ increase of 6.6‰ (range, -1.3‰ to 13.1‰) for aerosol particles collected during the laboratory burning of plant leaves compared to the source vegetation. Hence if we assume that the $\delta^{15}\text{N}$ in particles emitted from the combustion of dung-cake may be enriched in ^{15}N by ~7‰ during combustion, then the resulting $\delta^{15}\text{N}$ (approximately 22‰) will become nearer to the average values of $\delta^{15}\text{N}$ (23.9‰) that we found in the Chennai aerosols.

In fact, the spatial distribution of dung-cake consumption and livestock emission (e.g. CH_4) are higher in Gangetic plains followed by southern India and southeast coastal belt of

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

3.6. Contributions of N species to TN, sources and interpretation of plausible atmospheric processes responsible for ^{15}N enrichment in tropical Indian aerosols

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

Further it is clear from linear regression plot drawn between $\text{NH}_4^+\text{-N}$ and TN and $\text{NO}_3^-\text{-N}$ and TN that NH_4^+ is the main nitrogen species (78% of TN) in Chennai aerosols, whereas NO_3^- contributes only 6% of TN (see Fig. 6). Oenema and Tamminga (2005) estimated that

contributions of NH_4^+ and NO_x^- emissions from animal manure to global N are 40-60% and 0-10%, respectively. Hence, the higher contribution of NH_4^+ to TN may be associated with a significant emission of NH_3 to the atmosphere from animal barnyards, dung-cake combustion and biomass burning. Of course, the NH_3 emitted from sewage and landfills (Sutton et al., 2000) might have also contributed at minor level because the sewage spreading into water streams and dumping of municipal solid waste into open landfills is higher in India (Jha et al., 2008).

The emitted NH_3 may be less enriched with ^{15}N (Turekian et al., 1998) and should react with acids in the air to form aerosol particles, probably $(\text{NH}_4)_2\text{SO}_4$ (Ottley and Harrison, 1992). The reaction of NH_3 with H_2SO_4 is unidirectional (kinetic) at the onset, favoring lighter isotope (^{14}N) in particles, but stoichiometric equilibrium is attained in several minutes (ca. 6 min), in which $\text{NH}_3\text{--NH}_4^+$ exchange (equilibrium) reaction occurs (Heaton et al., 1997). Under equilibrium conditions, NH_4^+ stabilizes rapidly with $\delta^{15}\text{N}$ values being higher than that of NH_3 , where the isotopic enrichment factor ($\epsilon_{\text{NH}_4\text{--NH}_3}$) was estimated to be +33‰ (Heaton et al., 1997). Hayasaka et al. (2004) also observed higher $\delta^{15}\text{N}$ values of aerosol NH_4^+ (av. +22.1‰) than that of gaseous NH_3 (av. -8.3‰) in the atmosphere at the Maki monitoring station, Niigata, Japan.

In fact, Chennai aerosols are rich in SO_4^{2-} (av. $6.9 \mu\text{g m}^{-3}$, $n=49$), and average molar ratios 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, respectively. The enrichment of ^{15}N in TN was found to correlate positively with SO_4^{2-} , although it is weak in early- ($r^2 = 0.31$) and late winter (see Fig. 7a) and negligible in summer ($r^2 = 0.04$). As discussed in Heaton et al. (1997), enrichment of ^{15}N may be enhanced when 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 ratios and weak/negligible correlation between ^{15}N of TN and SO_4^{2-} suggest that an enrichment of ^{15}N in aerosols in the stoichiometric equilibrium for the $\text{NH}_3\text{--NH}_4^+$ exchange

reaction may be more efficient with NH_4HSO_4 rather than $(\text{NH}_4)_2\text{SO}_4$. Alternatively, another acid group, i.e., organic acids, may involve with the stoichiometric equilibrium by forming RCOONH_4 .

Because, sulfate aerosol become more acidic than NH_4HSO_4 and accumulate when the NH_3 source strength is insufficient to maintain an ambient NH_3 partial pressure greater than the equilibrium vapor pressure of NH_3 over the partially neutralized H_2SO_4 droplet (Huntzicker et al., 1980). On the other hand, the organic compounds such as fatty acids are known to form surface films and inhibit the neutralization of H_2SO_4 aerosol by NH_3 (Junge and Scheich, 1969), and thus suppress the stoichiometric equilibrium between NH_3 – NH_4^+ . In fact, we found high concentrations (up to 1440 ng m^{-3}) of oxalic acid and other dicarboxylic acids in Chennai aerosol samples (Pavuluri et al., 2010). Our hypothesis is also corroborated by seasonal variations observed in correlations between $\delta^{15}\text{N}$ and molar ratios $\text{SO}_4^{2-}/\text{NH}_4^+$ and ambient temperature as discussed below.

First, we found that $\delta^{15}\text{N}$ values correlate well ($r^2 = 0.81$) with molar ratios of $\text{SO}_4^{2-}/\text{NH}_4^+$ in late winter (see Fig. 7b), but weak ($r^2 = 0.34$) in early winter and not in summer. In late winter, air masses arrived from Southeast Asian region, where biomass burning occurs more frequently than in South Asia (Streets et al., 2003). Streets et al. (2003) estimated that amounts of vegetation burned in Southeast Asia (331 Tg dry matter) are almost twice those of South Asia (178 Tg), and the subsequent emissions of NH_3 in Southeast Asia (416 Gg) are also twice those of South Asia (229 Gg). Further, biomass-burning emissions (e.g., CO) are more enhanced in February to April than in January and May (Streets et al., 2003). Conversely, a larger contribution of biomass burning emissions to Chennai aerosols in late winter is further confirmed by higher concentrations of levoglucosan (an excellent biomass burning tracer) in late winter (av. $0.17 \text{ } \mu\text{g m}^{-3}$) than early winter (av. $0.07 \text{ } \mu\text{g m}^{-3}$) and summer (av. $0.11 \text{ } \mu\text{g m}^{-3}$) (Fu et al., 2009).

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

Further as discussed in Utsunomiya and Wakamatsu (1996), it is known to dissociate the particulate NH_4NO_3 into its precursor gases NH_3 and HNO_3 at high atmospheric temperature, but the fate of isotopic fractionation is not known. Based on our observations, we presume that ^{15}N may preferably associate with HNO_3 and might have also been caused depletion in $\delta^{15}\text{N}$ of TN during high ambient temperature conditions, although the content of NO_3^- -N is minor in Chennai aerosols as noted before.

It is clear from these observations that amounts of the fine particles emitted and enriched with ^{15}N (Turekian et al., 1998) may be enhanced in late winter compared to two other seasons. Potentially high $\delta^{15}\text{N}$ values of organic nitrogen in Chennai aerosols could also contribute to the higher ratios, although its fraction is rather minor (ca. 17% of TN). Further, we believe that NH_3 - NH_4^+ exchange reactions are proportionally enhanced with an increase

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

Thus, this study becomes a piece of evidence for the origins of aerosol N in South and Southeast Asia, and also shows that availability of acid species (e.g., H₂SO₄) and the emission rate of NH₃ from animal barnyards, bio-fuel combustion and biomass burning play a vital role in ¹⁵N enrichment in the atmosphere.

However, very high $\delta^{15}\text{N}$ values (29.8‰ and 31.2‰) observed in May 23 day- and nighttime samples, although TN was found to be only <1 $\mu\text{g m}^{-3}$ in both the samples, are much higher than those of expected potential sources. It indicates that the contributions from other anthropogenic sources such as industrial activities cannot be ignored in this region. Because NH₃ is used as raw material for multiple products but the fate of reactive N in industrial activities is unclear (Galloway et al., 2008), and also the NH₃ emission from fertilizer manufacturing and other industrial units is significant (Sutton et al., 2000). Recently, Clarisse et al. (2009) reported elevated NH₃ column concentrations (up to 7 mg m^{-2}) over India by satellite observations. Hence, it is a subject of further research in future.

Finally, lower $\delta^{15}\text{N}$ values observed in nighttime particularly in winter (Fig. 1) are possibly caused by local NO_x emissions from fossil fuel combustion whose $\delta^{15}\text{N}$ values are significantly low as described above. Local or regional emissions from bio-fuel burning may contribute to lower the isotopic ratios of aerosols. In both cases, land breeze at night should enhance a transport of the anthropogenic particulate nitrogen over the coastal city Chennai.

4. Summary and Conclusion

The aerosol TN contents were determined to be high (up to 3.8 $\mu\text{g m}^{-3}$) in the tropical Indian aerosols from Chennai, but they did not show a systematic diurnal variation. We found very high $\delta^{15}\text{N}$ values in the aerosols (max. 31.2‰), which are comparable to those reported

for particles emitted from animal barnyards and biomass burning. The measured $\delta^{15}\text{N}$ values in cow-dung samples were also equivalent to the lower range of $\delta^{15}\text{N}$ ratios of Chennai aerosols. The assumed $\delta^{15}\text{N}$ values from the combustion of dung-cake based on a laboratory study conducted for vegetation burning are close to the average $\delta^{15}\text{N}$ ratio in Chennai. We also found that NH_4^+ is the major species (78%) of TN, which is probably produced by gas-to-particle conversion of NH_3 in the atmosphere. The equilibrium $\text{NH}_3\text{-NH}_4^+$ exchange reaction probably play the most important role in the enrichment of ^{15}N in TN. Hence, we conclude that animal excreta, bio-fuel and biomass burning are the important sources of aerosol N in South and Southeast Asia.

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Fig. 1.

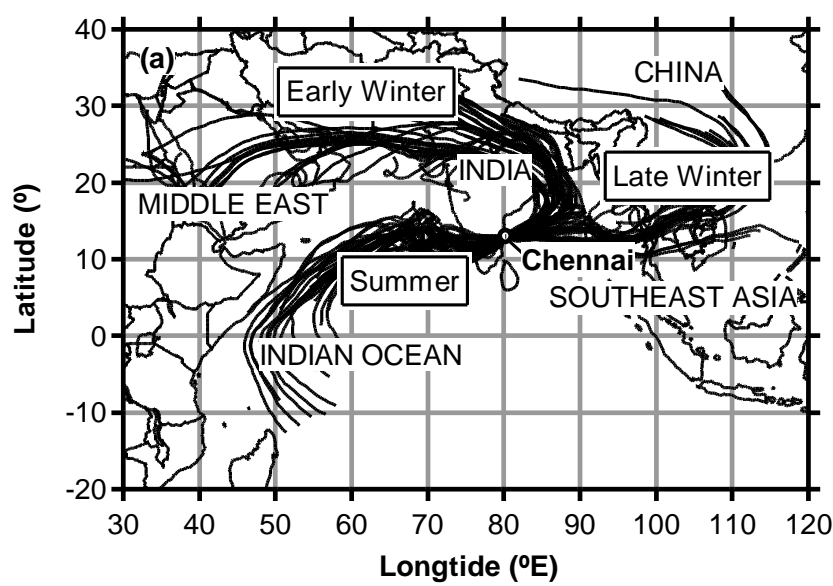


Fig. 2

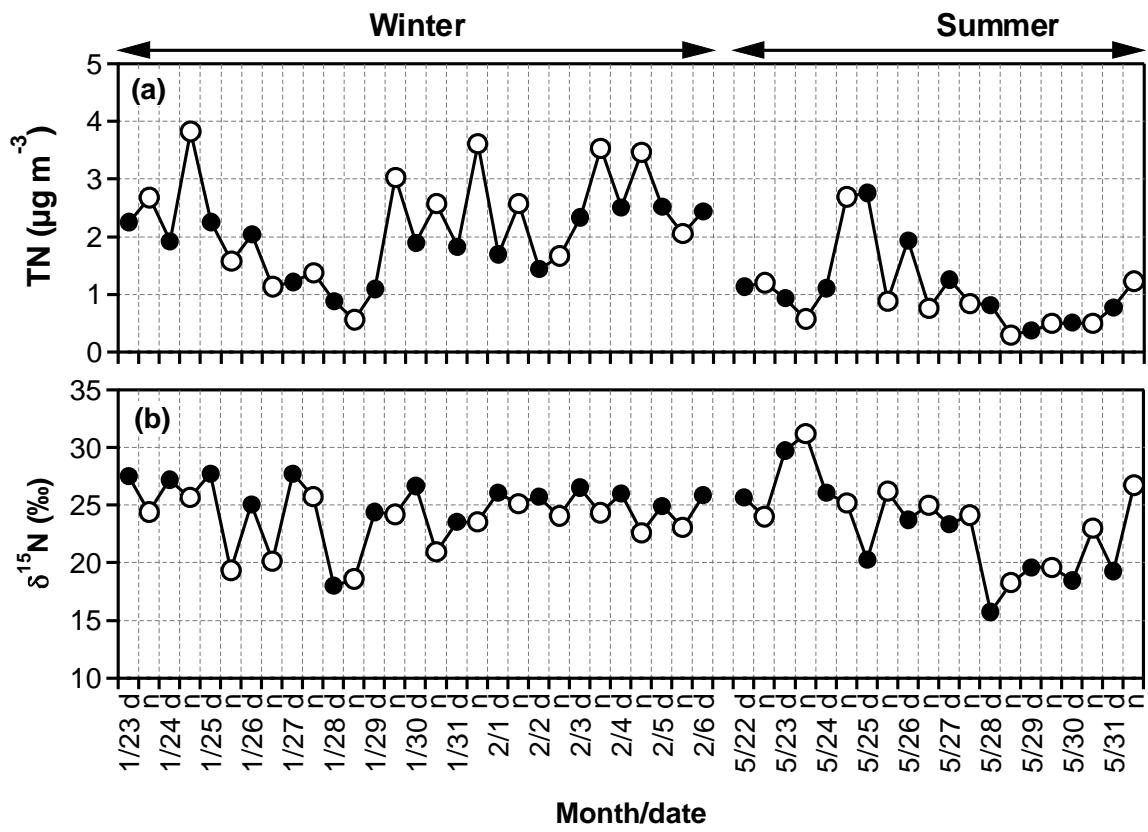


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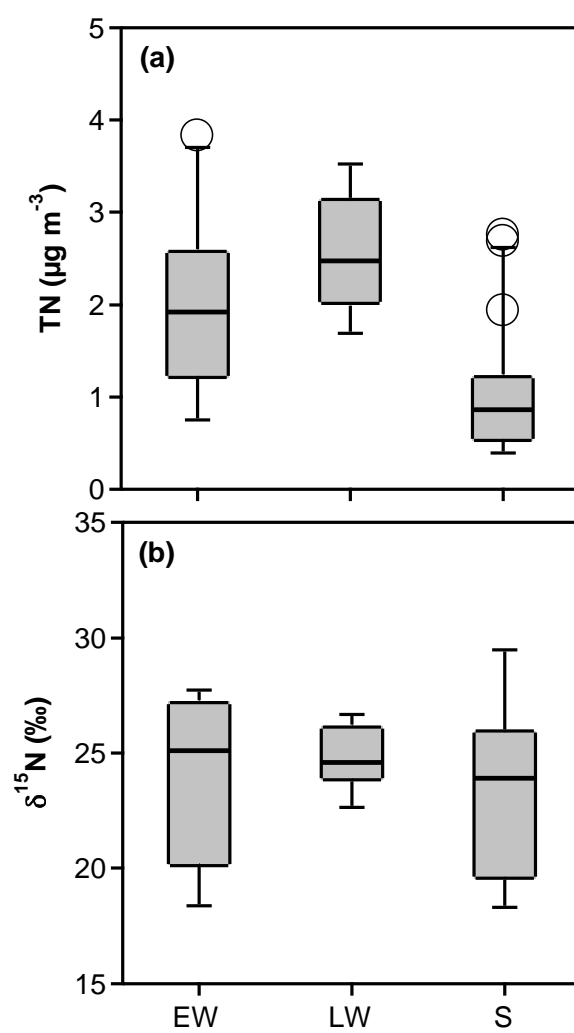


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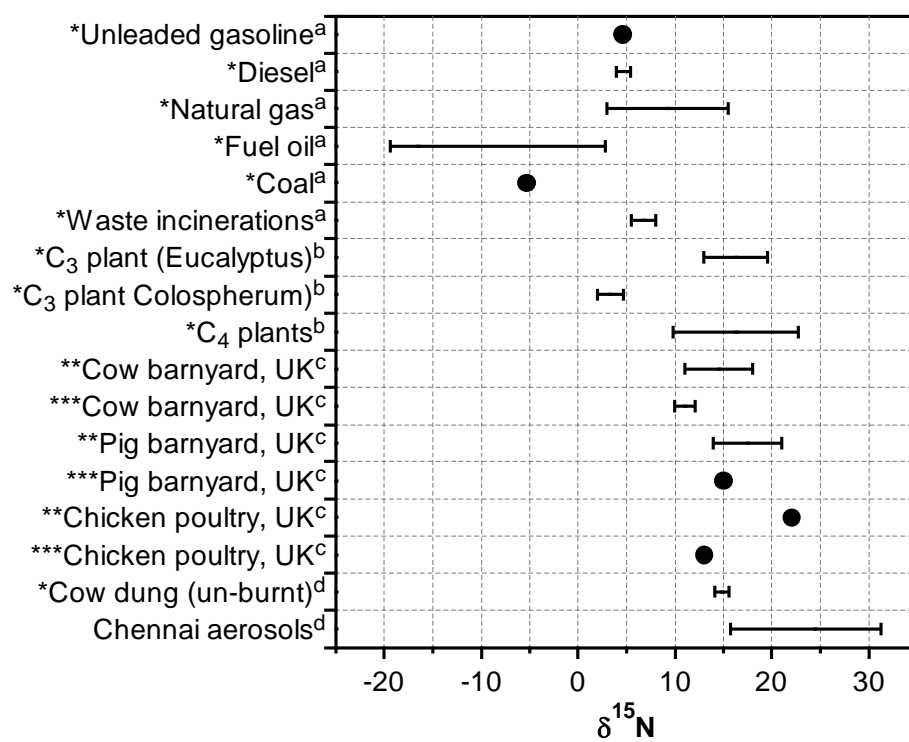


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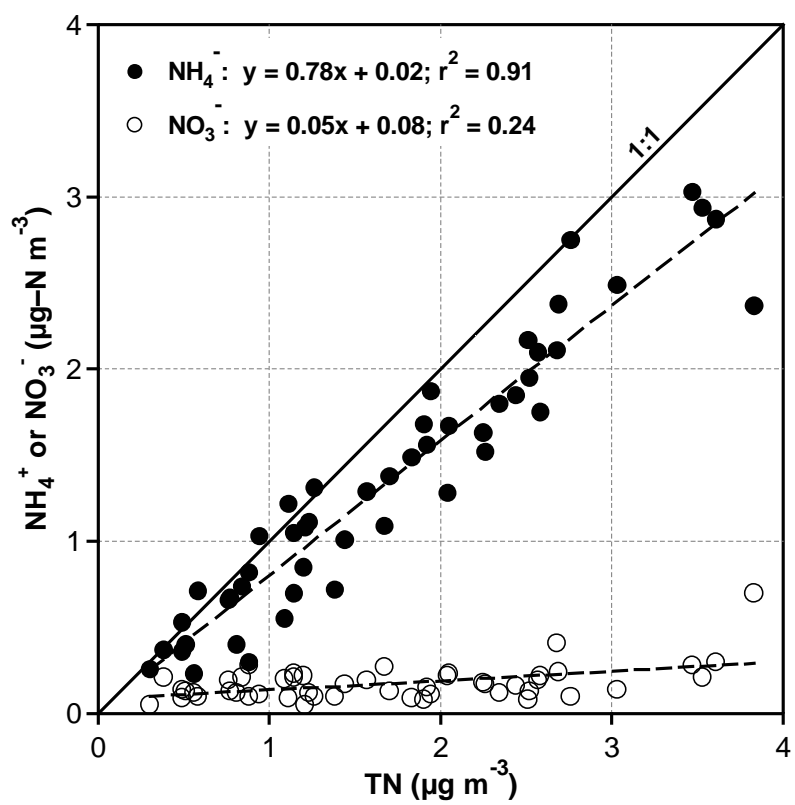


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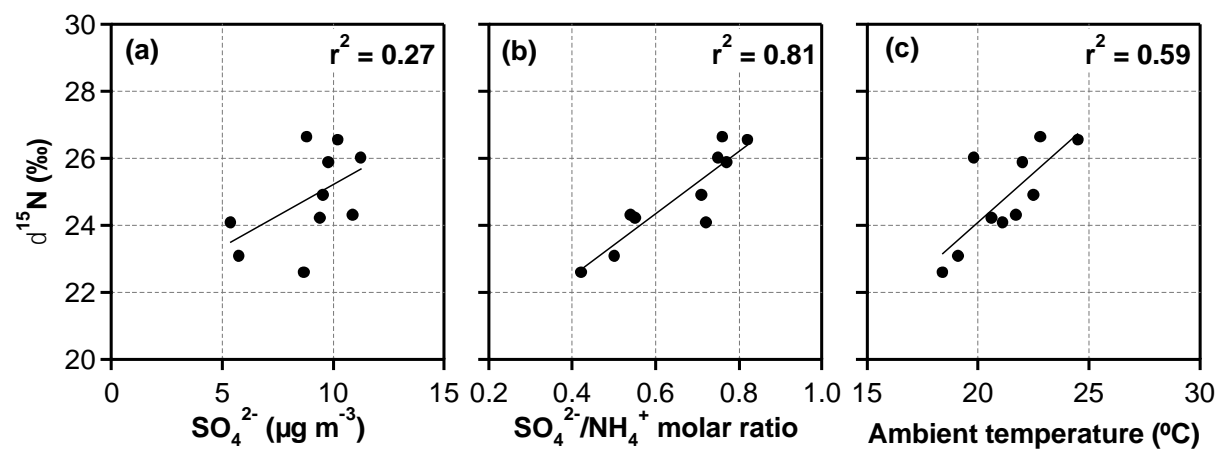


Figure captions

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 (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 (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, NH_4^+ and NO_3^- , respectively. ^aWidory, 2007; ^bTurekian et al., 1998; ^cYeatman et al., 2001a; ^dthis 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 (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) SO_4^{2-} ($\mu\text{g m}^{-3}$), (b) molar ratios of NH_4^+ to SO_4^{2-} , and (c) ambient temperature for the tropical Indian aerosol (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 (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–	1.6–				0.6–	1.6–										0.51–			
	2.5	2.3	1.9	1.9	0.5	3.8	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	1.1	0.8	0.9	0.7
$\delta^{15}\text{N}$ (‰)	18.0–	25.0–				18.6–	21.3–				15.7–	19.3–				18.3–	23.3–			
	27.8	26.9	26.0	25.5	2.4	25.7	24.4	23.8	23.0	2.3	29.8	25.2	21.8	22.2	4.3	31.2	25.9	24.6	24.3	3.6
Inorg-N ($\mu\text{g m}^{-3}$)	0.58–	1.3–				0.35–	1.4–				0.52–					0.31–	0.71–			
	2.3	1.9	1.7	1.6	0.48	3.3	2.96	2.13	2.07	0.97	2.9	0.63–1.4	1.2	1.2	0.73	2.62	1.0	0.89	0.99	0.64
Org-N ($\mu\text{g m}^{-3}$)	0.08–	0.23–				0.09–	0.17–				(0.20)–	(0.18)–				(0.23)–	(0.11)–			
	0.57	0.44	0.30	0.32	0.15	0.76	0.42	0.29	0.34	0.20	0.30	(0.03)	(0.11)	(0.08)	0.15	0.13	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	NH_4^+		6 \pm 6	Yeatman et al., 2001a
"	NO_3^-		7 \pm 6	"
Mace Head, Ireland	NH_4^+		-9 \pm 8	"
"	NO_3^-		-1 \pm 3	"
Atlantic Ocean	NH_4^+	-11		"
"	NO_3^-		-1 \pm 3	"

Av. = Average; SD = Standard Deviation