

Role of atmospheric ammonia in the formation of inorganic secondary particulate matter: A study at Kanpur, India

Mukesh Sharma · Shyam Kishore · S. N. Tripathi · S. N. Behera

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Abstract Levels of fine Particulate Matter (PM_{fine}), SO_2 and NO_x are interlinked through atmospheric reactions to a large extent. NO_x , NH_3 , SO_2 , temperature and humidity are the important atmospheric constituents/conditions governing formation of fine particulate sulfates and nitrates. To understand the formation of inorganic secondary particles (nitrates and sulfates) in the atmosphere, a study was undertaken in Kanpur, India. Specifically, the study was designed to measure the atmospheric levels of NH_4^+ , Ca^{2+} , Mg^{2+} , Na^+ , K^+ , NO_3^- , SO_4^{2-} , Cl^- , NH_3 (gas), HNO_3 (gas), NO_2 and PM_{10} ($PM_{2.5}/PM_{10}$ ratio = 0.74) covering winter and summer seasons and day and night samplings to capture the diurnal variations. Results showed NO_3^- , SO_4^{2-} , NH_4^+ , K^+ are found to be significantly high in winter season compared to the summer season. In winter, the molar ratio of NH_4^+ to SO_4^{2-} was found to be greater than 2:1. This higher molar ratio suggests that in addition to $(NH_4)_2SO_4$, NH_4NO_3 will be formed because of excess quantity of NH_4^+ present. In summer, the molar ratio was less than 2:1 indicating deficit of NH_4^+ to produce NH_4NO_3 . The nitrogen conversion ratio (NO_2 to NO_3) was found to be nearly 50% in the study area that suggested quick conversion of NO_2 into nitric acid. As an overall conclusion, this study finds that NH_3 plays a vital role in the formation of fine inorganic secondary particles particularly so in winter months and there is a need to identify and assess sources of ammonia emissions in India.

Keywords Inorganic secondary particles · Ammonia · Sulfate · Nitrate · Water soluble ions · India

1 Introduction and objective

In a broad sense, out of pollutants monitored under National Air Quality Monitoring Program in India, there are two major issues of air quality: (1) consistently high particulate matter (PM) levels and (2) consistently rising levels of oxides of nitrogen (NO_x) (Sharma et al. 2004). The levels of SO_2 in India have dropped considerably after the introduction of low sulfur diesel (less than 0.25% sulfur) in the year 2000 (CPCB 2001). PM has been widely studied in

M. Sharma (✉) · S. Kishore · S. N. Tripathi · S. N. Behera

Department of Civil Engineering, Indian Institute of Technology, Kanpur 208016, India
e-mail: mukesh@iitk.ac.in

recent years due to its potential health impacts and need for its control (e.g. Schwartz et al. 1996). To understand the health effects and formation/emission of PM, it is essential to know physical characteristics and chemical composition of particles. For example, the mean composition range (in western and eastern US) of PM_{2.5} (particle with aerodynamic diameter of less than 2.5 μ) is: organic carbon (20–40%), metals (<1%), nitrates and sulfates (25–35%), elemental carbon (4–15%) minerals (4–15%) and unknown (0–22%) (USEPA 1996). However, such composition analysis for North India is lacking.

The particulate concentration has shown statistically significant seasonal variability at various locations in India (Sharma et al. 1995). The seasonal variation in PM levels could be due to variations in soil dust emissions, photochemistry responsible for formation of inorganic secondary particles (nitrates and sulfates) and other anthropogenic sources including biomass burning. The variation in inorganic secondary particles (which will mostly be in fine fraction) is of greater significance from public health point of view and needs to be examined.

The primary precursors for formation of nitrate and sulfate are NH₃, SO₂ and NO_x. In other words, levels of PM and NH₃, SO₂ and NO_x are interlinked through atmospheric reactions to a large extent. It has been established that most of the reactions are inorganic in nature (for formation of sulfate and nitrate), complex and competing with each other. These reactions mostly depend on solar insolation, temperature, humidity and presence of other constituents in the atmosphere (Utsunomiya and Wakamatsu 1996). Kumar et al. (2004) and Gupta et al. (2003) have measured concentration of SO₂, NO₂, NH₃ and HNO₃ at urban and suburban sites of Agra and Rampur, India. They interestingly found NH₃ levels (7–10 μg m⁻³) to be comparable or higher than levels of SO₂ and NO₂ signifying the role that NH₃ can play in atmospheric chemistry. Kaneyasu et al. (1995) reported that NO₃⁻ and NH₄⁺ exhibit marked seasonal variation with winter maxima and summer minima.

In summary, there are a few studies that have measured NO_x, NH₃, HNO₃, PM_{fine}, and PM₁₀ (particles having aerodynamic diameter less than 10 μ) simultaneously in the ambient air. Most of the studies reported an apparent seasonal variation in NO_x, NH₃, HNO₃ and PM₁₀ levels. Composition of precursor pollutants and those of inorganic secondary particles are location specific and show seasonal and diurnal variations and one needs to study/measure these parameters at local and regional levels.

NO_x and SO₂ are mainly emitted through combustion processes, which are subsequently transformed into HNO₃ and H₂SO₄ in the atmosphere. NH₃ in the atmosphere results primarily from the decomposition and volatilization of animal wastes. As agricultural livestock numbers have dramatically increased together with increases in nitrogen fertilization, NH₃ emissions have increased substantially (Sutton et al. 1993). The major global anthropogenic sources are from domestic/wild animal wastes and fertilizer uses (e.g. urea). About half of the global emissions of NH₃ come from Asia, and about 70% of the total, is related to food production (<http://www.ars.usda.gov/research/programs>). The regions with highest geographically-localized emission rates are found in Europe, the Indian subcontinent, China, and parts of the U.S (<http://www.ars.usda.gov/research/programs>).

The primary objective of this study was to understand the science behind formation of inorganic secondary particles. Although role of OH radical is vital in formation of SO₄ and NO₃, its direct measurement is very difficult. Therefore, role of NO_x, NH₃, SO₂, HNO₃, temperature and humidity in formation of particulate sulfate and nitrate has been examined. The study area was city of Kanpur (latitude 26° 26' N and Longitude 88° 22' E), North India. Specifically, the study was designed to measure the atmospheric levels of NH₄⁺, Ca²⁺, Mg²⁺, Na⁺, K⁺, NO₃⁻, SO₄²⁻, Cl⁻, NH₃ (gas), HNO₃ (gas), NO₂, SO₂ and PM₁₀ covering winter and summer seasons. Separate day and night samplings were undertaken to capture the diurnal variations in two seasons.

In this study measurements of PM_{10} was only done. However, interpretation of results in terms of chemical composition of PM_{10} can indicate formation of inorganic secondary $PM_{2.5}$. The primary reasons for considering PM_{10} over $PM_{2.5}$ include: (1) $PM_{2.5}/PM_{10}$ ratio=0.74 at the sampling site (Sharma and Maloo 2005 and Bartonova and Sharma 2005) and (2) high gas flow rate for PM_{10} sampler ($1\text{ m}^3\text{ min}^{-1}$) than $PM_{2.5}$ sampler ($1\text{ m}^3\text{ h}^{-1}$). that enables further accurate chemical characterization of collected particulate matter. In another study (Shukla 2007) at the same sampling site, it was noted that the ratio of SO_4^{2-}/Ca^{2+} and NO_3^-/Ca^{2+} in PM_{10} (0.75 and 0.52 during monsoon and 0.47 and 0.21 in non-monsoon season) was substantially high compared to the ratios of SO_4^{2-}/Ca^{2+} and NO_3^-/Ca^{2+} in soil (0.026 and 0.003 respectively); clearly suggesting that atmosphere is enriched with SO_4^{2-} and NO_3^- formed in the atmosphere as secondary particles in fine mode. Tare et al. (2006) for the same sampling site has reported that major part of sulfates and nitrates is in fine mode.

2 Study area, materials and methods

2.1 Site description

The sampling was done during winter (December 2004 and January 2005; n (number of samples)=44) and summer (May 2005; $n=18$) in an open area at a height of 12 m at the Indian Institute of Technology (IIT) in Kanpur, India (Fig. 1). IIT is an educational institute having residential campus with no commercial or industrial activities. The campus lies at about 15 km north of city with minimum emissions. Within the campus, vehicular population mainly comprises two-wheelers (motorcycles and scooters, mostly four stroke engine) and cars. The heavy-duty vehicle population is negligible. For most of the year, campus lies on the upwind side and receives no air pollution from Kanpur city. This site can ideally be taken as a relatively clean site.

2.2 Measurements

2.2.1 PM_{10} sample collection and storage

The 24-h desiccated filter papers (Whatman Quartz Micro fiber filter (size $8''\times 10''$)) were weighed twice on the balance (APM 440, Metler; sensitivity 0.00001 g). The conditioned and weighed filter papers were taken to the field in closed envelopes for sampling to avoid contamination of the filter papers on the way. PM_{10} sampling was done on High Volume Sampler (Envirotech, New Delhi) at a flow rate of $1\text{ m}^3\text{ min}^{-1}$. Before starting the sampling, initial volume, timer and the manometer readings for PM_{10} sampler were recorded in field monitoring sheet. The sampler was operated to obtain day (9 AM to 5 PM) and night (10 PM to 6 AM) samples separately. After sampling, the filter paper was again desiccated for 24-h and weighed. Before and after each set of sampling, data was entered in the field data sheet in the predefined format and concentrations of PM_{10} were calculated gravimetrically.

The sampled filter papers were stored in aluminum foil and preserved in freezer until further chemical analysis for water soluble ions was undertaken.

2.2.2 Water soluble ions (WSI)

The reference method for extraction of WSI was as prescribed in NILU EMEP/CCC (1995). One forth filter paper was taken and cut into small pieces and kept in reagent

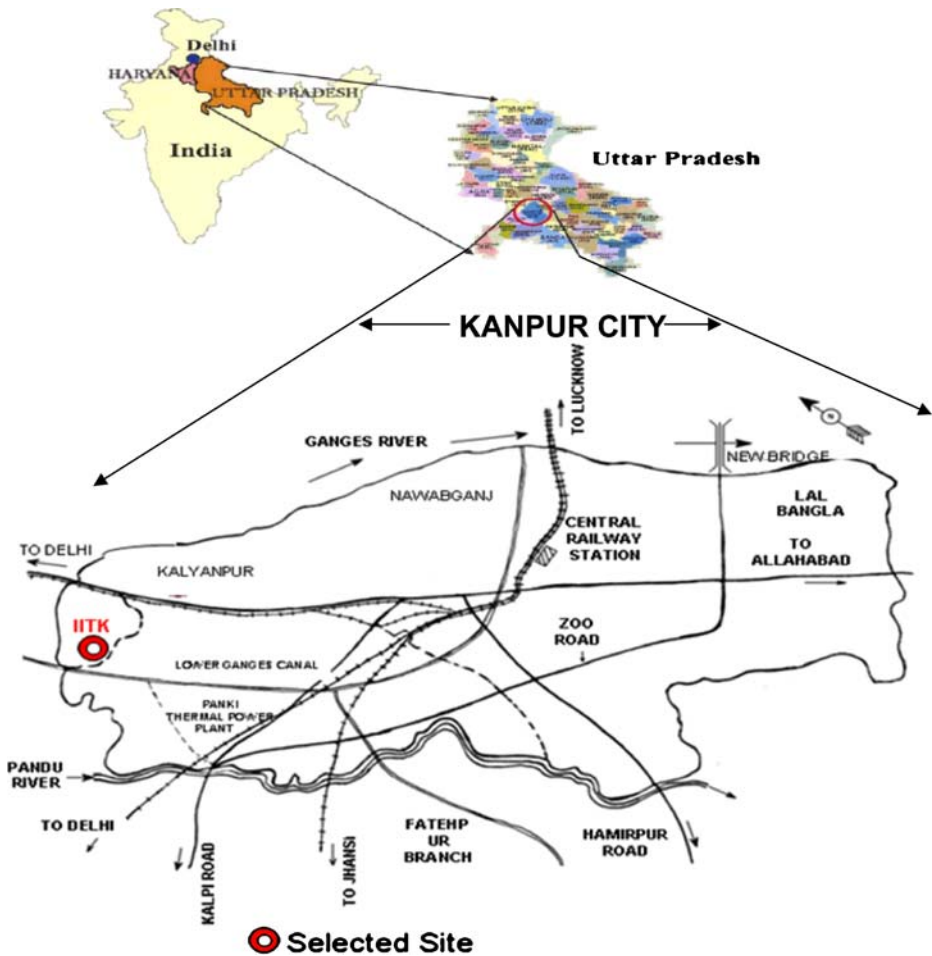


Fig. 1 Sampling location in Kanpur city

bottles. Then, 40 ml deionized (ultra pure) water was added to reagent bottles and bottles were kept in ultrasonicator for 30 min. After digestion, sample was filtered through 0.22 μ filter paper to remove insoluble matter and made up to 50 ml. The filtered sample was transferred to plastic bottle and kept in refrigerator to preserve the sample until further analysis.

The water soluble ions i.e. NO_3^- , SO_4^{2-} and Cl^- were analyzed by Ion Chromatograph (Metrohm761Compact, USA) whereas cations Na^+ , K^+ , Ca^{2+} , Mg^{2+} were analyzed by Atomic Absorption Spectroscopy (Varian, Spectra AA 220 FS, USA). Indo-phenol blue method was used for analysis of the NH_4^+ ions by using UV spectrophotometer (Varin, USA).

2.2.3 Gaseous species

SO_2 was measured by absorbing it in tetra-chloro-mercurate (TCM) solution and then analyzing it using West and Gaeke Method (Lodge 1989). For collection of sample, 20 ml of 0.04 M TCM absorbing solution was taken in a midget impinger. The rate of air

Table 1 Metrological parameters during sampling period

Metrological Parameters	Winter (January)		Summer (May)		Winter (Overall) (including Dec)	Summer (Overall)
	Day	Night	Day	Night		
Temperature (°C)	16.6	14.2	38.4	27.8	17.6	33.4
Humidity (%)	80.6	81.7	32.2	52.9	70.6	41.9
Wind speed (m s ⁻¹)	–	–	–	–	0.66	1.12

sampling was kept at 1 LPM. SO₂ was analyzed colorimetrically using spectrophotometer (Systronics Instrument, India) at 548 nm wavelength.

NO₂ was measured by absorbing it in the solution of sodium-hydro-oxide and sodium arsenate and then analyzing it using Jacob and Hochheiser Method (Lodge 1989). For collection of sample, 20 ml of absorbing solution was taken in a midget impinger. The rate of air sampling was kept at 1 LPM. NO₂ was analyzed colorimetrically using spectrophotometer (Systronics Instrument, India) at 540 nm wavelength. The color was developed using H₂O₂, sulfanilamide and NEDA solution.

NH₃ samples were collected according to the method prescribed in Methods of Air Sampling and Analysis (Lodge 1989). Air was aspirated through a measured volume (30 ml) of 0.1 N H₂SO₄ in a standard impinger. The collected NH₃ samples were transferred into plastic bottles, preserved in refrigerator and analyzed colorimetrically at 625 nm by catalyzed Indophenol- blue method using spectrophotometer (Systronics Instrument, India).

HNO₃ samples were collected by aspirating air through a measured volume of (30 ml) deionized water in a standard impinger (Kumar et al. 2004). The collected samples were transferred to plastic bottles, preserved in a refrigerator and analyzed by ion chromatographic (Metrohm 761Compact) method for NO₃.

2.2.4 Meteorological parameter

During the sampling period, meteorological parameters (Temperature, Relative Humidity, and Wind speed and wind direction) were recorded. Temperature and relative humidity were measured by temperature and relative humidity sensor, whereas wind speed and direction was measured by wind vane and three Cup Anemometer (Wind Monitor WM251 Envirotech, New Delhi). Summary of the meteorological parameters is presented in Table 1.

3 Overall results

The levels of PM₁₀ are presented in Table 2. The levels of WSI in PM₁₀ (collected on filter paper) and levels of gaseous species are presented in Fig. 2 (winter and summer concentration), Fig. 3 (diurnal variation in winter) and Fig. 4 (diurnal variation in summer).

Table 2 Concentration of PM₁₀ in winter and summer

Season	Day (µg m ⁻³)	Night (µg m ⁻³)	Overall (µg m ⁻³)
Winter	175±78	123±19	169±61
Summer	369±128	347±73	359±84

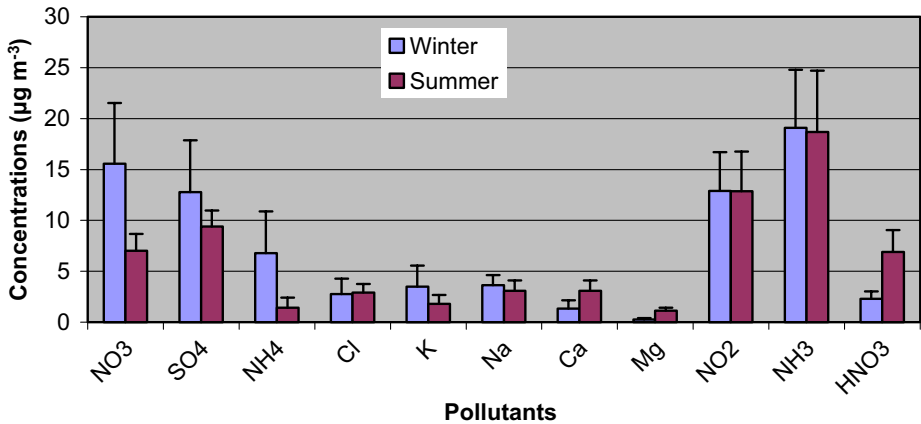


Fig. 2 Concentration of WSI and gaseous pollutants in summer and winter

The SO₂ levels for all samples were below the detection limit of the method (i.e. 4 µg m⁻³) and are not reported here. Results of WSI were examined for electro neutrality. It was found the difference in cation and anion were 17% in winter and 24% in summer. This deficit in anion is attributed to carbonates and bicarbonates, which were not measured. Cation and anion difference found in this study is within the acceptable range in rainwater samples (15–30%) (Ayers 1995).

4 Discussion of results

4.1 Seasonal variation

4.1.1 Winter vs summer

The summer levels of PM₁₀ are statistically higher than winter levels due to higher wind speed (Table 1) experienced in summer that makes the soil dust airborne, which is very dry

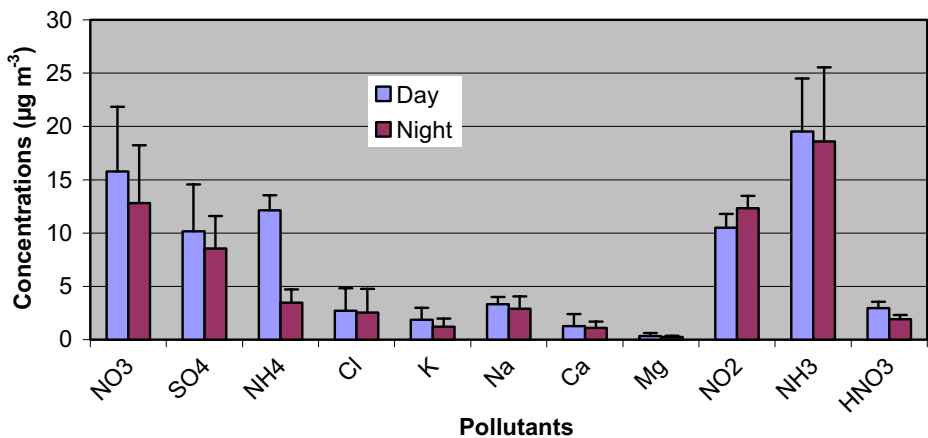


Fig. 3 Diurnal variations of WSI and gaseous pollutants (winter)

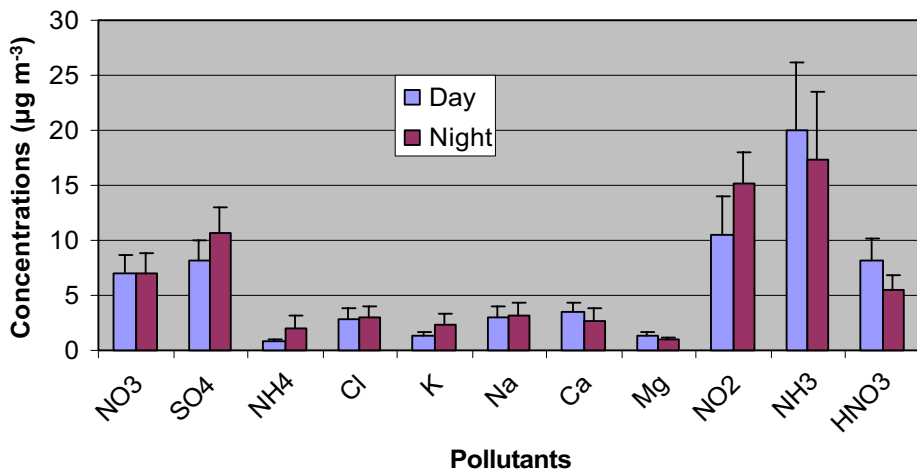


Fig. 4 Diurnal variations of WSI and gaseous pollutants (summer)

and loose (in summer). In winter, the daytime PM₁₀ levels are higher than the night time level, this may be due to reduced emission/activity in night time. Similarly, the daytime PM₁₀ levels are slightly higher than nighttime levels in summer.

NO₃⁻, SO₄²⁻, NH₄⁺, K⁺ are found to be significantly high in winter season compared to the summer season (Fig. 2). Ca²⁺, Mg²⁺ are found higher in summer compared to winter (Fig. 2). There is no significant seasonal difference in chloride and sodium (Fig. 2). The reasons for higher winter concentration of NO₃⁻, SO₄²⁻, NH₄⁺, K⁺ are examined below.

Earlier studies (Kaneyasu et al. 1995; Utsunomiya and Wakamatsu 1996; Mészáros et al. 1984; Willison et al. 1985) have reported high winter time concentration of NO₃⁻ (compared to summer). Under the conditions of high temperatures and low relative humidity in summer (Table 1), particulate ammonium nitrate is volatile, and as a result, NH₄NO₃ will be in gaseous phase. Adams et al. (1999) reported that the temperature >25°C prevents formation of significant amount of particulate NH₄NO₃. The average summer temperature and relative humidity were 33±7°C and 42±18% respectively, limiting the formation of particulate ammonium nitrate in the study area. This implies formation of inorganic secondary fine particulate in winter will be high. This also signifies the role of NH₃, which is a precursor pollutant for formation of NH₄NO₃ and (NH₄)₂SO₄. It is expected that SO₄²⁻ concentrations increases in summer due to high rate of photochemical activity and high OH· concentration, which increases the oxidation of SO₂ and its conversion rate to sulfate (Stockwell and Calvert 1983; Khoder 2002; Utsunomiya and Wakamatsu 1996; Cadle 1985; Gupta et al. 2003). In aqueous phase, largely it is H₂O₂ and O₃, which are responsible for oxidation of SO₂ to sulfates. However, we have found higher concentration of SO₄²⁻ in winter (Fig. 2). There are two possible reasons for this (1) higher emissions of SO₂ due to biomass burning in winter and (2) Kadowaki (1986) has reported that for the conversion of SO₂ to sulfate, high oxidant concentration (i.e. OH· and sunlight) as well as relative humidity is an important factor. Since SO₄ production rate is much higher in aqueous phase, high relative humidity will enhance sulfate formation in winter. The low relative humidity (42±18%) in summer, at this site, may be the reason of low concentration of sulfate in summer compared to winter.

NH₄⁺ generally combines with NO₃⁻ and SO₄²⁻ in atmosphere and forms ammonium nitrate and ammonium sulfate respectively (Appel et al. 1981; Utsunomiya and Wakamatsu

1996). However in summer time, NH_4^+ will be transformed to NH_3 due to high temperature and low relative humidity (Seinfeld and Pandis 1998). Thus, NH_4^+ is not available in significant quantity for formation of NH_4NO_3 in summer. Nonetheless, it is noteworthy that nitrate in summer will remain in gaseous form as HNO_3 and levels of HNO_3 will be higher in summer as shown in Fig. 2.

The other probable reason for higher sulfate and nitrate levels in the winter is higher emission of SO_2 , NO_x , and NH_3 in winter due to additional source of biomass burning, which is prevalent in the study area. This issue of seasonal variability of sulfate and nitrate formation is further discussed in Sections 4.4 and 4.5 on Stoichiometric Analysis of Formation of $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 and NH_3 and HNO_3 equilibrium.

K^+ ions are significantly high in the winter month (Fig. 2). It may be noted that K^+ is released into the atmosphere from vegetation (Kleinman et al. 1979) and biomass burning (Penner 1995). At high humidity, when the rate of transpiration is low, plants emit sub-micron K^+ through the respiration mechanism, known as guttation (Stokes 1954). In this process, K^+ is transported from root to leaves and released into atmosphere through hydathodes (Parmar et al. 2001). Also, the biomass burning in the winter season increases for local heating. These are the main reasons for high potassium concentration in winter season compared to the summer. It may be noted that in the upwind of the sampling site, there are extensive agriculture activities in winters. Also, it is a common practice to burn agriculture residue in winter to clear the field of unwanted vegetation and that will enhance emission of K^+ .

Ca^{2+} , Mg^{2+} are dominant in summer seasons because they are mainly soil driven. During summer, the wind speed is more compare to the winter (Table 1) and high wind speed contributes more wind blown dust to PM_{10} , which increases the concentration of the Ca^{2+} , Mg^{2+} from soil.

4.2 Diurnal variation

4.2.1 Day vs night (winter)

In winter, mainly NO_3^- , SO_4^{2-} , NH_4^+ ions show significant diurnal variations, with higher levels in daytime (Fig. 3). In daytime, the production of gaseous precursors (i.e. HNO_3 and H_2SO_4) for formation of ammonium nitrate and ammonium sulfate are found to be high compared to nighttime. In daytime, the gas phase oxidation of NO_2 by OH radical is predominant, whereas in night, aqueous phase chemistry involving the uptake of N_2O_5 and NO_3 radical (formed as a consequence of reaction of NO_2 with O_3) in cloud water at high relative humidity (Foltescu et al. 1996) is predominant. It has also been reported that homogeneous reaction of N_2O_5 with water vapor and other trace gases are believed to be extremely slow (Seinfeld and Pandis 1998), as a result, night time level of NO_3^- are much lower than the day time. Kadowaki (1986) has concluded that the oxidation NO_2 to HNO_3 is predominant in gas-phase, that is why higher concentration of nitrates is found in daytime.

In case of SO_2 also, daytime oxidation is mainly by OH radicals, whereas at high relative humidity, dissolved SO_2 is mainly oxidized to SO_4^{2-} by the three other dissolved species, H_2O_2 , O_3 and O_2 . Being relatively insensitive to pH, oxidation by H_2O_2 seems to be dominant for lower pH ($\text{pH} < 5$) normally encountered in clouds, rainwater and remote aerosol. Since oxidation of SO_4^{2-} from day time OH radical is overwhelmingly higher than night time aqueous phase oxidation, SO_4^{2-} levels in winter are higher in day time.

In winter, day–night, variations of Ca^{2+} , Mg^{2+} , K^+ , Cl^- , Na^+ ions are not significant in a statistical sense (Fig. 3). The Ca^{2+} , Mg^{2+} generally comes from wind blown dust, which is

not common in winter season because of low wind speed. Also, the relative humidity is almost same during day (81%) and night (82%) time so the production of K^+ ion from vegetation is not going to change much, this may be the reason for no significant variation in K^+ .

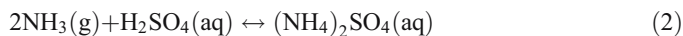
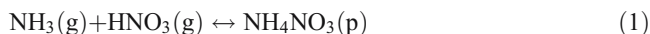
4.2.2 Day vs night (summer)

In summer, NH_4^+ shows statistically significant diurnal variation with high concentration in night compared to the day, whereas Ca^{2+} ion concentration is more in day time compared to night time (Fig. 4). It is noteworthy that in spite of high temperature (38°C) in day time, which enhances the oxidation of NO_2 and SO_2 , and increases the production of gaseous precursors (H_2SO_4 and HNO_3), particulate SO_4^{2-} and NO_3^- are lower in day time. This is due to the low relative humidity in day time (i.e. 33%), because formation of sulfate depends upon both the oxidant concentration as well as relative humidity (Kadowaki 1986). In night time, the temperature and relative humidity are 28°C and 53% (much higher than day time), which helps in the formation of SO_4^{2-} ion more in night. In addition, as the temperature drops in night time, there may be equilibrium shift from NH_3 to NH_4^+ in presence of higher humidity (in night time) resulting in higher SO_4^{2-} formation. The high day time concentration of Ca^{2+} is mainly from wind blown dust due to relatively high wind speed and active atmospheric convection in day time (Matsumoto and Tanaka 1996).

4.3 Correlation analysis

4.3.1 Winter

Table 3 presents the correlation matrix for NO_3^- , SO_4^{2-} , NH_4^+ , Ca^{2+} and PM_{10} for winter and summer seasons. Both SO_4^{2-} and NO_3^- ions show significant correlation with NH_4^+ ion ($r = 0.85$ and $r = 0.63$) and with PM_{10} . This indicates that both $(NH_4)_2SO_4$ and NH_4NO_3 are formed in the atmosphere and contribute significantly to PM_{10} . The possible routes of formation are:



It may be noted that that the Ca^{2+} ion neither correlate with SO_4^{2-} and NO_3^- nor with PM_{10} . This indicates that NH_3 plays a far more important role in inorganic secondary particle formation than do the Ca^{2+} ions. Since Ca^{2+} ions do not correlate with PM_{10} , it may be argued that contribution of soil in winter months is not significant because low wind speeds (in winter) prevents soil getting reborn in the atmosphere.

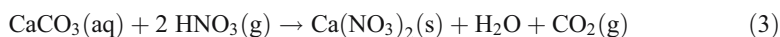
4.3.2 Summer

In summer, while SO_4^{2-} ions show significant correlation (Table 3) with NH_4^+ ($r = 0.75$) NO_3^- is not correlated strongly with NH_4^+ ($r = 0.42$). This indicates that it is largely $(NH_4)_2SO_4$ that is formed in the atmosphere. However, it is noteworthy that unlike winter,

Table 3 Correlation coefficient matrix for WSI

	NO ₃ ⁻		SO ₄ ²⁻		NH ₄ ⁺		Ca ²⁺		PM ₁₀	
	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer
NO ₃ ⁻	1	1	0.68	0.71	0.63	0.42	-0.10	0.35	0.71	0.25
SO ₄ ²⁻			1	1	0.85	0.75	-0.03	0.25	0.73	0.25
NH ₄ ⁺					1	1	-0.02	-0.02	0.69	0.14
Ca ²⁺							1	1	0.02	0.48
PM ₁₀									1	1.00

Ca²⁺ correlates with NO₃⁻ and with PM₁₀. It signifies possible route for formation of Ca (NO₃)₂ and also the fact that in summer the soil dust contributes to PM₁₀ levels due to dry soil and high wind speeds in summer. The possible route of formation of Ca(NO₃)₂ is:



The above reaction is the route for forming coarse fraction of inorganic secondary particles. Although we have not studied the particulate coarse fraction separately, the statistical correlation analysis is largely indicative of possible routes for formation of inorganic secondary particles in coarse fraction in the form of Ca(NO₃)₂. However, to fully understand the mechanism for formation of secondary fine particulate (inorganic), there is a need to understand the science/chemistry, which has been discussed in the following section.

4.4 Stoichiometric analysis of formation of (NH₄)₂SO₄ and NH₄NO₃

4.4.1 Winter

The strong correlation of SO₄²⁻ with NH₄⁺ in winter suggests that ammonium sulfate is formed (Wall et al. 1988; Zhuang et al. 1999). The fine mode ammonium sulfate ions are generated by the reaction of H₂SO₄ (g) with NH₃ (g). The reaction rate constant of formation of ammonium sulfate aerosol is 1.5 × 10⁻⁴ sec⁻¹ (Harrison and Kitto 1992) is much higher than the rate constant for formation of CaSO₄ (1.73 × 10⁻⁹ sec⁻¹; Pervez and Pandey 1992). As the reaction rate of CaSO₄ is less (by several orders of 10) than that of ammonium sulfate aerosols, as long as sufficient amount of NH₃ is available (for neutralization of H₂SO₄ and HNO₃), fine mode (NH₄)₂SO₄ and NH₄NO₃ will be formed. It is only when sufficient amount of NH₃ is not present, coarse mode sulfates and nitrates can be formed through reaction (3).

4.4.2 Sulfate vs ammonium

In atmosphere, H₂SO₄ and HNO₃ both compete for reacting with NH₃ to form the ammonium sulfate and ammonium nitrate but reaction rate of NH₃ and H₂SO₄ is much faster. It is only the excess ammonia that reacts with nitric acid. In (NH₄)₂SO₄, the molar

ratio of NH_4^+ to SO_4^{2-} is 2:1. If observed molar ratio is greater than 2, it signifies that excess NH_4^+ is present which has possibly combined with NO_3^- or other anion. At this site, the molar ratio of NH_4^+ to SO_4^{2-} is 2.83, which indicates the complete neutralization of H_2SO_4 and a predominance of $(\text{NH}_4)_2\text{SO}_4$ aerosol during the winter season (Fig. 5).

4.4.3 Nitrate vs ammonium

The nitrate ion shows significant correlation with ammonium ion and PM_{10} in winter (Table 3). This indicates that ammonium nitrate (NH_4NO_3) is formed in winter season. In winter, the temperature and relative humidity are $18 \pm 4^\circ\text{C}$ and $71 \pm 18\%$ respectively. The low temperature and high relative humidity favors formation of particulate ammonium nitrate (Stelson and Seinfeld 1982) as particulate nitrates are volatile under condition of high temperature and low relative humidity (Utsunomiya and Wakamatsu 1996). The insignificant correlation of nitrate ion with calcium indicates that the ammonium nitrate is present in fine mode, because calcium nitrate ($\text{Ca}(\text{NO}_3)_2$) is found in the coarse mode by the reaction of HNO_3 with NaCl and CaCO_3 respectively (Alastuey et al. 2004; Matsumoto and Tanaka 1996; Utsunomiya and Wakamatsu 1996). Kadowaki (1977) also confirmed that the fine mode nitrate mainly consist of the ammonium nitrate generated by the reaction between gaseous nitric acid, which is produced by the photo-oxidation of nitrogen dioxide, and ammonia gas. As explained earlier, only excess ammonia gas (after reaction with H_2SO_4), react with nitric acid and form ammonium nitrate. This has been examined in Fig. 6. Fig. 6 shows that there are a few days during sampling period in which complete neutralization of nitric acid occurred and on other days NH_4^+ is in deficit and NO_3^- must associated with other alkaline species or be part of acidic aerosol.

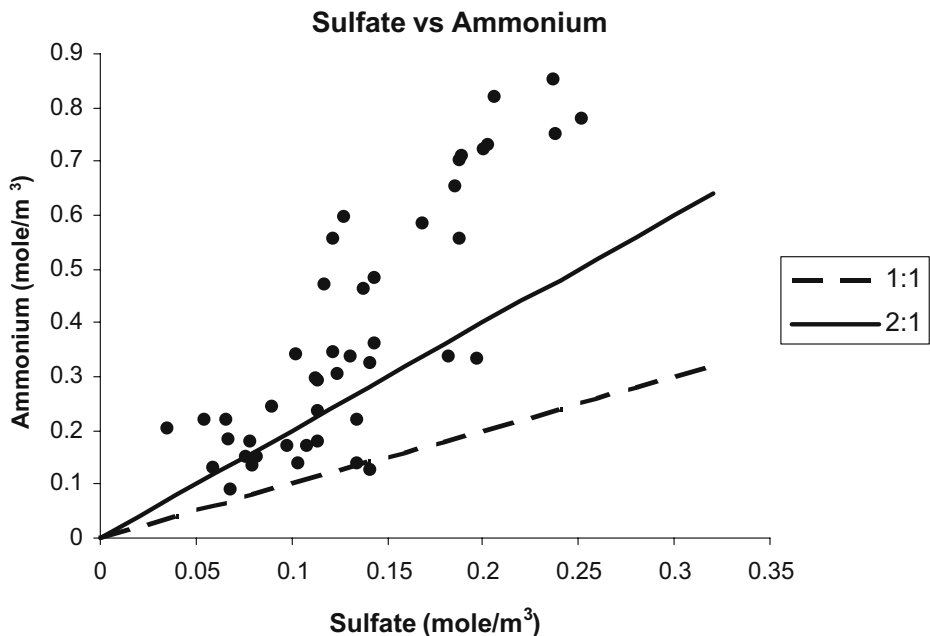


Fig. 5 Comparison of NH_4^+ and SO_4^{2-} ion with stoichiometric ratio of $(\text{NH}_4)_2\text{SO}_4$. (The 2:1 line reference line represents complete H_2SO_4 neutralization)

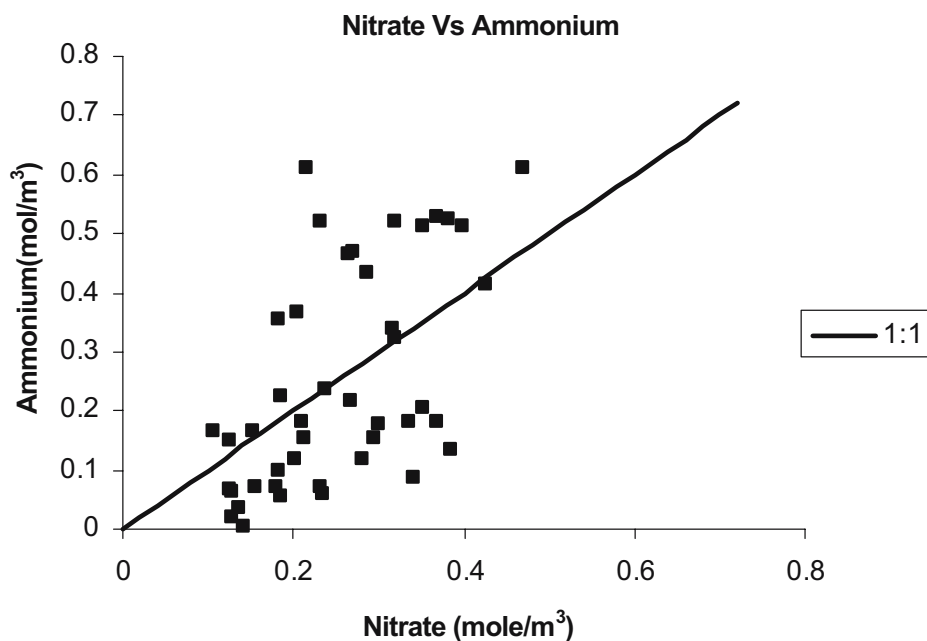


Fig. 6 Comparison of excess NH_4^+ and NO_3^- ion with stoichiometric ratio of NH_4NO_3 (The 1:1 line reference line represents complete HNO_3 neutralization)

5 Summer

5.1 Sulfate vs ammonium

Sulfate ion correlate well with ammonium ion in summer season as well, but not the NO_3^- . Since $(\text{NH}_4)_2\text{SO}_4$ is less volatile than NH_4NO_3 , in summer, there is a relatively higher concentration of $(\text{NH}_4)_2\text{SO}_4$ compared to NH_4NO_3 (Utsunomiya and Wakamatsu 1996). The average molar ratio of NH_4^+ to SO_4^{2-} is found to be 0.81, which is less than stoichiometric molar ratio of 2. The low molar ratio indicates that the neutralization of H_2SO_4 is not complete in summer unlike winter.

5.2 Nitrate vs ammonium

In summer, nitrate ion does show correlation with ammonium ion but to a lesser extent compared to winter season. This is due to the high temperature ($33 \pm 6^\circ\text{C}$) and low relative humidity ($42 \pm 18\%$). At high temperature, the fine mode nitrate, which is formed by the reaction of nitric acid and ammonia are volatile and equilibrium shifts to gaseous products (reaction (1)). Increasing temperature and decreasing relative humidity limit the production of NH_4NO_3 aerosol (Utsunomiya and Wakamatsu 1996; Alastuey et al. 2004; Kaneyasu et al. 1995; Chang et al. 1986; Matsumoto and Tanaka 1996). The overall (day and night) correlation of nitrate with calcium has become significant in summer season as NH_4^+ is not available and neutralization of HNO_3 may occur on coarse soil-driven particle rich in calcium and magnesium.

5.3 NH₃ and HNO₃ equilibrium

The equilibrium in NH₃ and HNO₃ concentrations in the atmosphere is examined for reaction (1). The equilibrium constant (K) for this reaction can be estimated as follows (Stelson and Seinfeld 1982):

$$\ln K = 84.6 - 24220/T - 6.41 \ln (T/298) \quad (4)$$

Where, T is temperature in Kelvin.

The estimation of equilibrium constant for winter and summer seasons can clearly establish if conditions are favorable for formation of NH₄NO₃ or not

- (I) Winter: [NH₃]=26.74 ppb, [HNO₃]=0.90 ppb, Temperature=290K
 [NH₃] [HNO₃]=24 ppb² > K (=3.5 ppb²)
 Conditions are favorable for formation of NH₄NO₃.
- (II) Summer: [NH₃]=27.72 ppb, [HNO₃]=2.69 ppb, Temperature=306K
 [NH₃] [HNO₃]=76.56 ppb² < K (=306.5 ppb²)
 Conditions are not favorable for formation of NH₄NO₃.

This issue of formation of NH₄NO₃ can be examined for each data point (depending on the temperature of the day). Figure 7 presents equilibrium line and measured NH₃ and HNO₃ in winter. It is clear that almost on all days NH₄NO₃ will be formed. Figure 8 presents equilibrium line and measured NH₃ and HNO₃ in summer. It is clear that only on few days, NH₄NO₃ will be formed.

This shows that summer condition is not as much favorable as the winter for the formation of particulate nitrate. The conditions of NH₄NO₃ formation have been compared with a study reported in the US by Baek and Aneja (2005). They have shown formation of NH₄NO₃ takes place in the atmosphere. As per their data: [NH₃] [HNO₃]=32.2 ppb² > K (=21.59 ppb²), confirming formation of particulate nitrate.

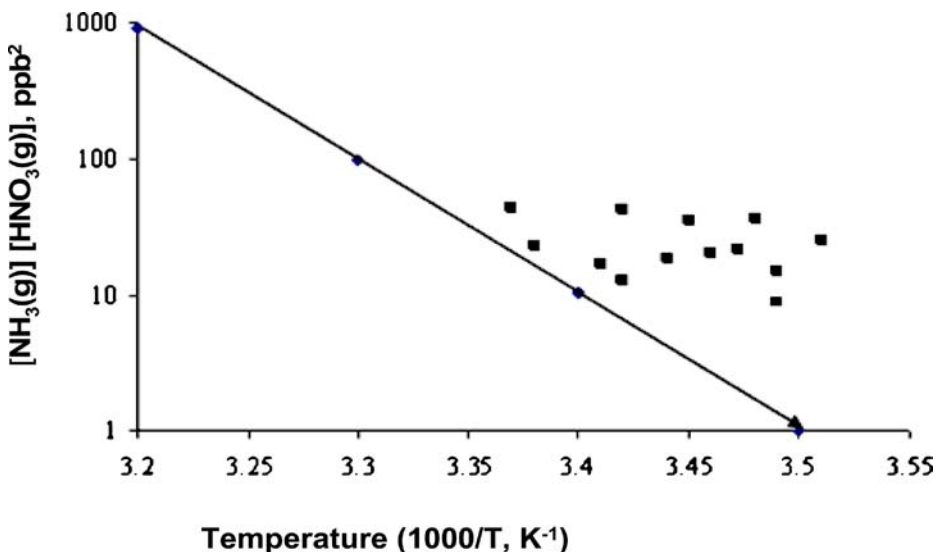


Fig. 7 Relation between [NH₃ (g)] [HNO₃ (g)] product and temperature (winter)

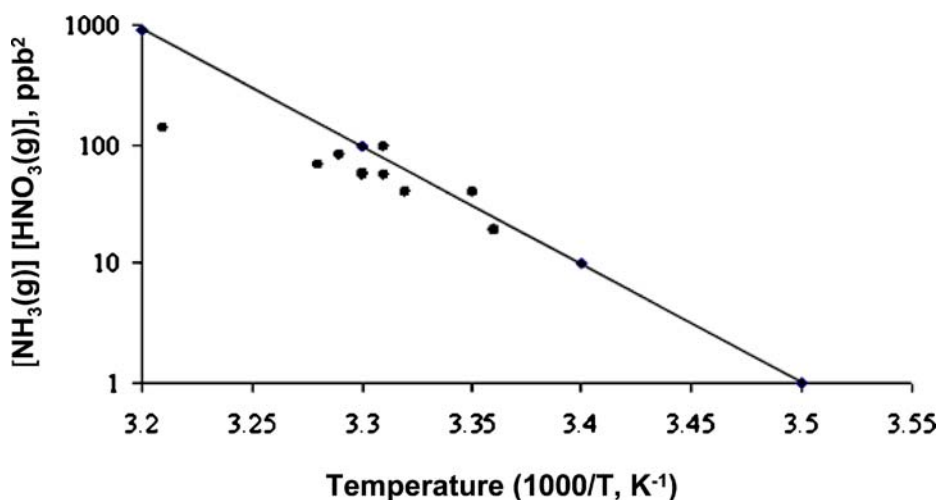


Fig. 8 Relation between $[\text{NH}_3(\text{g})][\text{HNO}_3(\text{g})]$ product and temperature (summer)

6 HNO_3 and NH_3 seasonal variation

HNO_3 showed seasonal variation, with highest concentration in summer compared to winter (Fig. 2). Higher HNO_3 concentration in summer have been explained by increase production of nitric acid from gaseous precursors during photochemical activity and shift of equilibrium from particulate phase ammonium nitrate to gas-phase ammonia and nitric acid ($\text{NH}_3 + \text{HNO}_3 \leftrightarrow \text{NH}_4\text{NO}_3$) (Seinfeld and Pandis 1998; Moya et al. 2004). The higher concentration of HNO_3 in summer may be due to high solar radiation, which leads to higher concentration of OH radical, thereby more formation of HNO_3 . Hoek et al. (1996) reported that HNO_3 concentration during summer was about twice as high as measured during winter. At this station, HNO_3 in summer was found to be nearly three times the winter concentration. There was not much difference in the concentration of NH_3 during summer and winter, but NH_3 concentration was found higher than other places (Table 4). This may be due to extensive agriculture activity in the upwind of the sampling site.

6.1 Nitrogen conversion ratio

It is generally seen that in spite of large emission of NO_x , the air concentration of NO_x remains low in Indian condition and particularly in Kanpur ($10\text{--}35 \mu\text{g m}^{-3}$; unpublished)

Table 4 Comparison of seasonal variations (HNO_3 and NH_3)

Sampling site	HNO_3		NH_3	
	Summer ($\mu\text{g m}^{-3}$)	Winter ($\mu\text{g m}^{-3}$)	Summer ($\mu\text{g m}^{-3}$)	Winter ($\mu\text{g m}^{-3}$)
Rampur, India ¹	1.3	0.3	2.5	8.1
Dayalbagh, India ²	2.1	1.0	10.8	8.9
Cairo, Egypt ³	6.70	1.14	–	–
Present Study at IITK	6.90	2.39	18.69	19.09

¹ Gutpa et al. (2003); ² Parmar et al. (2001); ³ Khoder (2002)

Table 5 Nitrogen conversion ratio (F_n) during winter and summer seasons

Pollutant	Winter	Summer
NO_2 ($\mu\text{g m}^{-3}$)	11.37	12.87
PNO_3^- ($\mu\text{g m}^{-3}$)	14.37	7.03
GNO_3^- ($\mu\text{g m}^{-3}$)	2.39	6.90
$\text{PNO}_3^- + \text{GNO}_3^-$ ($\mu\text{g m}^{-3}$)	16.76	13.93
$\text{PNO}_3^- / \text{PNO}_3^- + \text{GNO}_3^-$ (%)	85.7	50.46
$\text{GNO}_3^- / \text{PNO}_3^- + \text{GNO}_3^-$ (%)	14.26	49.53
F_n (%)	52.26	44.61

data from CPCB Vikas Nagar station). Therefore, it has been examined to see the conversion of NO_x to nitrate in Kanpur. Nitrogen conversion ratio is defined as:

$$F_n = (\text{PNO}_3^- + \text{GNO}_3^-) / (\text{NO}_2 + \text{PNO}_3^- + \text{GNO}_3^-) \quad (5)$$

Where PNO_3^- is particulate nitrate concentration as NO_2 , $\mu\text{g m}^{-3}$, GNO_3^- is the gaseous nitrate concentration, as NO_2 , $\mu\text{g m}^{-3}$, and NO_2 is the gas phase NO_2 concentration, $\mu\text{g m}^{-3}$. Nitrogen conversion ratio (F_n) calculated from the above equation is summarized in Table 5.

The highest ratio of particulate nitrate to total nitrate is found during the winter season (Table 5), consistent with increased production of particulate nitrate as mentioned previously. In contrast, the highest concentration ratio of gaseous nitric acid to total nitrate was found during the summer season. The F_n level in summer may be attributed to the high photochemical reaction and dissociation of already formed fine mode nitrates under the effect of high temperature during the summer season, which may lead to an increase in the formation of gaseous nitric acid (Khoder 2002). The same trend was reported by Kadowaki (1986) in an urban area. They also reported that nitrogen conversion ratio is higher in summer compared to the winter season but at this station average nitrogen conversion ratio is higher in winter compared to summer but not statistically significant. This may be due to more nitrate formation in winter compared to summer because of high humidity that enhances nitrate formation. However, as far as intermediate step of formation of HNO_3 is concerned, it is high in summer. It appears that high concentration of NH_3 in study area compared to other locations, is playing an important role (in winter season) in formation of particulate nitrate. The high NH_3 concentration is perhaps due to extensive agriculture activity in the upwind of the sampling site. It may be noted that the current level of NO_x may not fully suggest the problem of NO_x pollution; one must account for NO_3 conversion and examine the health implications of higher NO_3 in a comprehensive analysis.

It may, therefore, be concluded from this research that NH_3 is playing a very significant role in neutralization of atmospheric acids and in formation of inorganic secondary fine particles (ammonium sulphate in summer and winter and ammonium nitrate in winter). The major sources responsible for NH_3 emission are from the agricultural (urea application) activities and intensive animal production facilities. India and most developing countries are primarily agricultural economy and have very high number of cattle population (an estimated 219.6 million cattle alone in India) (<http://dahd.nic.in/stat.htm>).

7 Conclusions

In this research, both knowledge of statistical correlation and chemistry fundamentals were combined to understand the formation of inorganic secondary particles in the atmosphere.

Since the atmospheric conditions (temperature humidity, wind speed etc.) vary from day to night and from one season to other, the scientific explanations have been developed for seasonal and diurnal variations in the concentrations of ions responsible for formation of inorganic secondary particles. NO_3^- , SO_4^{2-} , NH_4^+ , K^+ (in PM_{10}) are found to be significantly high in winter season compared to the summer season and Ca^{2+} , Mg^{2+} are found to be higher in summer season. In winter, the molar ratio NH_4^+ to SO_4^{2-} was found to be greater than 2:1 suggesting excess NH_4^+ is present which possibly combined with NO_3^- to produce NH_4NO_3 . In summer time the molar ratio less than 2:1 indicating deficit of NH_4^+ to produce NH_4NO_3 . The nitrogen conversion ratio was found to be nearly 50% in the study area that suggest quick conversion of NO_2 into nitrates.

As an overall conclusion, this study finds that NH_3 play a very significant role in the formation of fine inorganic secondary particles and there is a need to study ammonia emissions and develop proper emission factors for its emission assessment.

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