



## A study on major inorganic ion composition of atmospheric aerosols at Tirupati

P. Chandra Mouli<sup>a</sup>, S. Venkata Mohan<sup>b</sup>, S. Jayarama Reddy<sup>a,\*</sup>,<sup>1</sup>

<sup>a</sup> *Electrochemical Research Laboratories, Department of Chemistry, Sri Venkateswara University,  
Tirupati 517502, India*

<sup>b</sup> *Biochemical and Environmental Engineering Center, Indian Institute of Chemical Technology (IICT),  
Hyderabad 500007, India*

Received 11 March 2002; received in revised form 3 June 2002; accepted 19 July 2002

### Abstract

Atmospheric aerosol samples were collected from an urbanized area (Tirupati, South India) during the period April to September 2001 and were analyzed for major inorganic ions—F, Cl, NO<sub>3</sub>, SO<sub>4</sub>, Na, K, Mg, Ca and NH<sub>4</sub> by employing the ion chromatograph. The average mass of the aerosol was found to be 55.64 μg m<sup>-3</sup> with a total water-soluble load (total anion + total cation) of 5.74 μg m<sup>-3</sup>. Seasonal distribution of the aerosol mass and temporal variations of the ion concentrations present a clear trend of lowering atmospheric levels during the rainy season due to washout effect. Composition of the aerosols showed higher concentration of SO<sub>4</sub> followed by NO<sub>3</sub> and NH<sub>4</sub> and found to be influenced by local terrestrial sources. The presence of SO<sub>4</sub> and NO<sub>3</sub> may be due to re-suspension of soil particles (formation by heterogeneous oxidation). Ca, Mg and Cl are mainly soil derived ones. The presence of NH<sub>4</sub> may be attributed to the reaction of NH<sub>3</sub> vapors with acidic gases such as H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub> and HCl or ammonia vapor may react or condense on an acidic particle surface of anthropogenic origin. Equivalent ratios of NH<sub>4</sub>/(NO<sub>3</sub> + SO<sub>4</sub>) varied between 0.62 and 0.74. It shows the aerosol to be slightly acidic due to the neutralization of basicity by SO<sub>2</sub> and NO<sub>x</sub>. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Aerosol; Major inorganic ions; Ion chromatography; Sources; India

### 1. Introduction

Aerosols are natural constituents of the earth atmosphere with stable suspensions representing two to three phase system consisting of liquid and/or solid particles and a gaseous

\* Corresponding author. Tel.: +91-8574-49962; fax: +91-8574-48499/49111.  
E-mail address: jreddy\_s@yahoo.com (S. Jayarama Reddy).

<sup>1</sup> DAAD Visiting Professor, University of Greifswald, Greifswald, Germany.

medium in which the particles are suspended. Aerosols provide reaction sites for pollutant gases, influence and play a fundamental role in cloud formation and modifies precipitation by functioning as condensation nuclei besides acting as carriers for pollutant transport. Also they have great influence on metrology and atmospheric chemistry as well as atmospheric radiation budget. The characteristics and distribution of atmospheric aerosols are highly variable, changing spatially, temporally and with altitude and source. These can vary greatly in size, chemical composition, amount distribution in space and time, and how long they survive in the atmosphere. In addition to their dynamic effect on the Earth's climate, aerosols also have profound impact on the human health and air quality. Atmospheric aerosols influence many atmospheric processes including cloud formation, visibility variation and solar radiation transfer [1–3] and play a major role in acidification of clouds, rain and fog and the transport of pollutants from industrial regions to remote and pristine areas [4,5]. Atmospheric aerosols, as a function of particle size, are classified into three modes: nuclei mode ( $0.02\ \mu\text{m}$ )—primarily particles formed by condensation of gaseous and vapors; accumulation mode ( $0.02\text{--}5\ \mu\text{m}$ )—consists of coagulation of small particles, gas-to-particle conversion (GPC) and condensation vapors onto existing small particles and coarse mode ( $>5\ \mu\text{m}$ )—predominantly generated by bulk-to-particle conversion (BPC). In general, fine particles ( $<2\ \mu\text{m}$ ) arise from anthropogenic sources such as combustion processes including automobile exhaust and partially from gas-to-particle conversions, where as coarse ( $>2\ \mu\text{m}$ ) ones originate mainly from natural processes such as wind action on land and sea surfaces [6–8]. Many of the recent studies have indicated that particulate in accumulation mode ( $0.1\text{--}2.5\ \mu\text{m}$ ) are the most critical with respect to human health, visibility and adverse effects caused by acid precipitation [9–11]. Both the trace gases and aerosols contribute to well known phenomena, such as global climatic changes, photochemical smog formation, acid rain, stratospheric ozone depletion, deterioration of air quality, deforestation, etc. The role of atmospheric aerosols which contribute only about  $10^{-9}$  to  $10^{-7}$  to the mass of the air is manifold [12].

Today, air pollution acquires a great concern world wide due to manifestation of technological and scientific innovations in various fields as well as by the diverse activities of man for his sophistication. Ever increasing concentrations of numerous trace species arising from increasing population, rapid industrialization, transportation activities have negative consequence on the public concern. Recently, urban pollution in developing countries is assuming a very serious dimension. Three mega cities in India (Delhi, Kolkata and Mumbai) are listed among the 10 most polluted cities in the world [13]. Rapid industrial and population growth in certain other areas is leading to a fast deterioration in the total quality of the environment and consequently the public health in Indian cities. Chemical analysis of aerosols in ambient air is important in making clear the sources, transportation and formation mechanism of atmospheric aerosols. In order to understand the sources, behavior and mechanism of formation of the particles and to assess the environmental status of the area, several investigators have reported on the atmospheric particle size distribution and chemical composition for continental, marine background and urban influenced aerosols from various locations throughout the world [14–25]. But in Indian context, little has been done to characterize the aerosols and most of the reported results were focussed on major cities [26–32].

Here, we report the results of the water-soluble major inorganic ions for aerosols collected for the period of 6 months, i.e. from April to September 2001 at an important and rapidly

growing town in southern peninsular India (Tirupati). The principal aim of the present work is to establish base line data on ion composition of atmospheric aerosols at the temple town Tirupati, where proper data is not available on the status of the environment.

## 2. Experimental

### 2.1. Sampling site

Tirupati, a holy pilgrimage town for devotees of Lord Sri Venkateswara is situated in Chittoor district of southern Andhra Pradesh state in India at an altitude of 182.9 m (13.05°N latitude; 79.05°E longitude). Tirupati, as a sampling site, represents an urban area surrounded by major industrial and agricultural activities. Due to inflow of pilgrims, the area has highest impact on the total environment scenario. It has continental type of climate with three distinct seasons: summer, monsoon and winter. The summer season is from April to June, monsoon months are from July to September and winter months are from November to February. The town owes its existence to the sacred temple of Lord Sri Venkateswara situated on the seven hills (Tirumala) adjoining it. The town is considered to be high profile center for education, tourism (mainly due to pilgrimage) and business with a population of 1,89,000 (1991 census). Also the town is affected by a floating population of 60,000 per day (average) in the form of pilgrims. Industrial activities also occupy important aspect in town activity. During summer, the climate is characterized by high daytime temperature ranging between 22 and 43 °C and low relative humidity 29–55% while during the monsoon period, the temperature ranges between 22 and 30 °C and relative humidity varies between 60 and 100%, respectively. The winter months are little bit cool with a temperature ranging between 13 and 32 °C while the relative humidity is 50–90%. The average wind velocity of the town is 7.1 km h<sup>-1</sup> during the study period. The meteorological data (monthly average) for the study period was given in Table 1.

A sampler was installed on the roof (12 m above ground level) of the Physical Sciences Building of Sri Venkateswara University, Tirupati. The sampling site is located in the center of the town (study area) and is about 145 km to northeast from Chennai city and about 120 km east to Bay of Bengal. The sampling site is encompassed with educational institutions

Table 1  
Meteorological conditions of the study area during the study period

Month and year	Maximum temperature (°C)	Minimum temperature (°C)	Relative humidity (%)		Rainfall (mm)	Wind velocity (km h <sup>-1</sup> )
			I	II		
April 2001	36.3	24.9	69	36	107.8	5.4
May 2001	39.9	27.7	55	29	14.0	9.5
June 2001	36.7	27.2	59	37	22.7	12.9
July 2001	35.3	26.4	62	39	114.1	11.7
August 2001	34.1	25.9	63	43	19.6	11.1
September 2001	33.7	24.7	71	48	197.6	5.7

surrounded by areas, exclusively devoted to residential, agricultural, industrial activities and forest wealth. Industrial zones are located in a radius of 15 km on eastern, western and southern side of the town. Traffic density is minimal with maximum traffic during the day, in the immediate vicinity of the site. However, there is dense vehicular traffic on national highway situated about 1 km north of the site. There are foundries and brick kilns situated 5 km west of the site, which are sources of SO<sub>2</sub> and NO<sub>x</sub>, and also chemical and metallurgical industries are situated 15 km east of the site.

## 2.2. Sampling

Sampling was performed on the roof of Physical Sciences Building at a height of about 12 m above ground level using High Volume Sampler (Envirotech. APM 415). Aerosol samples were collected on a glass fiber filter paper for 24 h monitoring. Due to hygroscopic nature of the glass fiber filter which results in the change of weight as a function of humidity, filters were carefully equilibrated in dessicator both before and after sampling to eliminate the effect of humidity and also to obtain accurate particulate measurement. Mass of the aerosol particles collected on each filter was determined by the difference in weights before and after sampling. Sampling was carried out with a frequency, once in a week for a period of 6 months, i.e. from April to September 2001 (15–38th standard week).

## 2.3. Analytical assay

For the analysis of water-soluble fraction, one quarter part of the particulate loaded glass fiber filters was extracted by ultrasonic agitation in 50 ml double distilled water (8–10  $\mu\text{mho cm}^{-1}$ ) for a period of 1 h. These extracts were filtered through a filter paper (Whatman No. 41) into pre-cleaned polypropylene bottles. These were refrigerated at 4 °C and used for the analysis of major inorganic ions. All chemicals used were of analytical reagent grade and solutions were prepared in double distilled water.

Ion chromatography was employed to analyze both inorganic anions (F, Cl, NO<sub>3</sub> and SO<sub>4</sub>), cations (Na, K, Mg and Ca) as well as NH<sub>4</sub>. Chromatography is a fundamental analytical technique, widely used for separation, identification and determination of the chemical components in complex mixtures. No other separation technique is as powerful and greatly applicable as chromatography [33,34]. Ion chromatography provides a simple, cost-effective, fast, accurate and highly sensitive method for the determination of ions at low levels (mg kg<sup>-1</sup>) in environmental samples including atmospheric aerosols [35,36]. Anions analysis was performed by Metrohm Modulor IC: consisting of 709 IC pump, 733 separation center, 732 conductivity detector, 753 suppressor module and 714 IC metro data. For anion analyses, a Metrosep SUPP3 column was employed with a flow rate of 1.0 ml min<sup>-1</sup> with suppressed conductivity mode detection settings at a system pressure of 9.6 MPa. The cations as well as NH<sub>4</sub> were analyzed by Metrohm 761 Compact IC by employing Metrosep cation 1–2 column with a flow rate of 1.0 ml min<sup>-1</sup> with a detection setting in non-suppressed conductivity mode with a system pressure of 4.8 MPa. The details of operating conditions maintained for the analysis of both anions and cations were depicted in Table 2.

Filter blanks were also prepared in the same manner and analyzed for both the inorganic species. Blank values were found to be below detection limits. To test, for complete

Table 2  
Operating conditions employed for the analysis of ions by ion chromatography

Conditions	Anions	Cations
Column	Metrosep SUPP3	Metrosep cation 1–2
Flow rate	1.0 ml min <sup>-1</sup>	1.0 ml min <sup>-1</sup>
Eluent	1.7 mM NaHCO <sub>3</sub> /1.8 mM Na <sub>2</sub> CO <sub>3</sub>	10 mM tartaric acid
Detector setting	Suppressed conductivity detection	Non-suppressed conductivity detection
Loop size	20 μl	10 μl
System pressure	9.6 MPa	4.8 MPa

extraction, filters, which had been extracted in the above manner, were subjected to the same procedures. The values of both the ions were below detection limits in the second extract.

### 3. Results and discussion

#### 3.1. Variation of aerosol ion concentration

Concentrations of water-soluble inorganic ions (Na, NH<sub>4</sub>, K, Mg, Ca, F, Cl, NO<sub>3</sub> and SO<sub>4</sub>) along with statistical results are presented in Table 3. Aerosol mass concentration varied between 79.89 and 24.65 μg m<sup>-3</sup> with an average mass of 55.64 μg m<sup>-3</sup> (Fig. 1) which is higher than the value observed at Silent Valley in the monsoon (30 μg m<sup>-3</sup>) [31] and lower than the value at Pune (73.5 μg m<sup>-3</sup>) [26]. Although air-borne concentrations depend on many processes, including upwind chemical processes, removal by wet and dry deposition and variability in source regions, the wet deposition is an effective mechanism for the removal of aerosols, especially in the size range of 0.1–10 μm [37–39]. It is therefore expected that low concentrations of the atmospheric constituents will occur during and following precipitation events. The similar trend has been observed in our study.

All the water-soluble inorganic ions, in general, show similar temporal variations (Figs. 2 and 3). For comparison, rainfall anomalies are presented in Fig. 4. From the pattern of

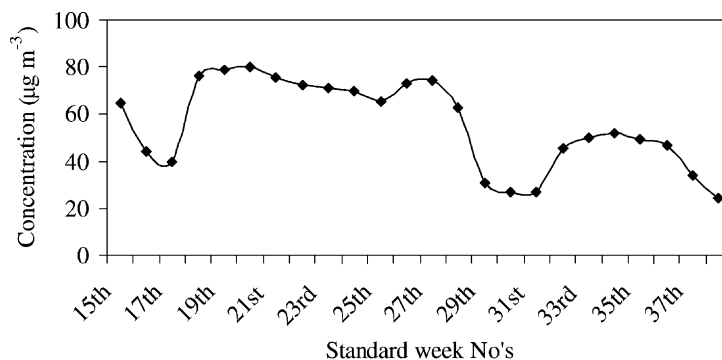


Fig. 1. Variation of aerosol mass during the study period in Tirupati town.

Table 3  
Average concentrations ( $\text{ng m}^{-3}$ ) and statistical results of the aerosol composition

Component	Mean	S.E.	Median	S.D.	Kurtosis	Skewness	Range	Minimum	Maximum
Na	751.4971	48.7764	733.245	238.9546	-1.41653	0.058117	745.37	401.35	1146.72
NH <sub>4</sub>	770.4133	48.90508	726.08	239.585	-1.36158	0.054093	784.49	410.44	1194.93
K	214.5775	12.45899	217.33	61.03633	-1.25445	0.125905	197.96	124.71	322.67
Mg	45.16	4.105117	50.445	20.11088	-1.05563	-0.47756	60.75	11	71.75
Ca	381.6775	20.28226	382.965	99.36236	-0.64356	0.375273	342.22	229.73	571.95
F	20.08917	1.007458	19.04	4.935514	-0.80757	0.521475	16.67	13.07	29.74
Cl	232.1875	10.89328	227.355	53.36595	-0.68116	0.294944	187.35	145.23	332.58
NO <sub>3</sub>	843.4279	88.14747	858.45	431.8326	-1.31361	-0.08407	1315.68	196.59	1512.27
SO <sub>4</sub>	2484.715	155.3782	2588.025	761.1948	-1.5015	-0.13416	2250.24	1321.57	3571.81

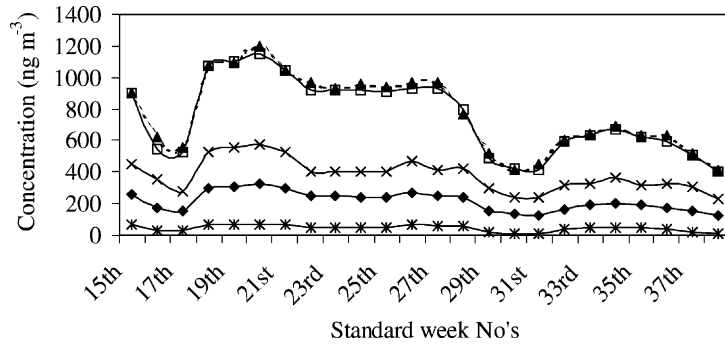


Fig. 2. Variation of cation composition measured during the study period in Tirupati town.

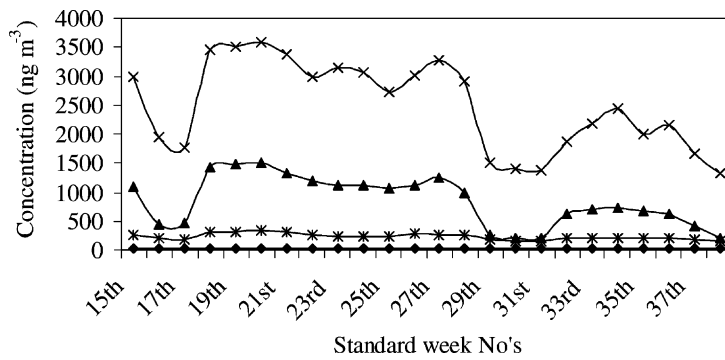


Fig. 3. Variation of anion composition measured during the study period in Tirupati town.

profiles, it can be clearly visualized that the increase and decrease in anion and cation concentrations are in comparison with the increase and decrease in aerosol mass as well as with the rainfall. The concentrations of all the ions, relatively low in the beginning of the sampling period (15th standard week, April 2001) subsequently raised to a maximum in

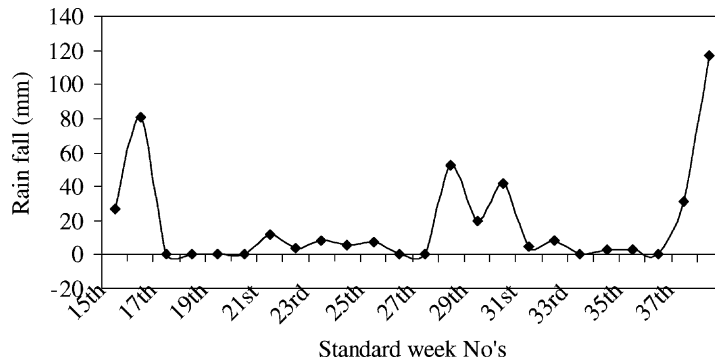


Fig. 4. Rainfall variation of Tirupati town during study period.

the 18th standard week. The temporal variations of cations show three peaks, with greater one in the 20th week (May). After that, the concentrations are gradually decreased, may be due to humidity effect, but peaked again on 27th week (July), while third one on 34th week (August). This may be due to the dry period followed by higher wind velocity (Table 1). Anionic species also display temporal variations similar to those of cations. Concentrations of all the ions were low at the end of the sampling period due to rainfall washout effect. During the sampling period, seasonal distribution of the monitored aerosol mass and the temporal variations in the aerosol ion concentrations show a relationship with meteorological conditions, especially rainfall and presents a clear trend of lowering atmospheric levels during the rainy season due to washout effect. The concomitant increase and decrease in aerosol mass is directly related to the ionic concentration and the aerosol mass in the atmosphere is also dependent on the rainfall.

### 3.2. Ionic composition of aerosols

The average total water-soluble aerosol load (total anion + total cation) was  $5.74 \mu\text{g m}^{-3}$ . Among the ionic components  $\text{SO}_4$ , contributed maximum to the water-soluble aerosol mass (43.26%) followed by  $\text{NO}_3$  (14.68%) and  $\text{NH}_4$  (13.41%). The cations Na, K, Mg and Ca accounted 24.25% to the total water-soluble mass. The ionic balance of the aerosol samples showed a trend  $\text{SO}_4 > \text{NO}_3 > \text{Cl} > \text{F}$  for anions and  $\text{NH}_4 > \text{Na} > \text{Ca} > \text{K} > \text{Mg}$  for cations. The lower contributions of Ca and Mg suggest that they occur mainly as insoluble carbonates, bicarbonates and silicates. Kurtosis calculations on the data set have given a negative value for all the ions, which characterizes a flatness of the distribution of the species compared with normal distribution. Skewness calculations in a data set characterize the degree of asymmetry of a distribution around its mean. Positive skewness indicates a distribution with an asymmetric tail extending toward values that are more positive. Negative skewness indicates a distribution with an asymmetric tail extending toward values that are more negative. As far as asymmetry in the data set is concerned, our study has shown a wide variability, which is mainly the result of the meteorological effects. Standard deviation calculations on the data set show a lower dispersion of the value around the mean only for fluoride, symbolizing more constant levels of it in the environment unlike others.

### 3.3. Marine influence on the composition of aerosols

In order to determine the marine influence on the composition of aerosols, sea salt ratios were calculated using Na as reference element assuming all Na to be of marine origin. The ratios are given in Table 4. It is evident from the table that the ratios of K/Na, Ca/Na,

Table 4

Ratio values of the water-soluble components of aerosols and the corresponding values for sea water

	Cl/Na	K/Na	Mg/Na	Ca/Na	$\text{SO}_4/\text{Na}$
Aerosol	0.31	0.29	0.06	0.51	3.31
Sea water	1.8	0.037	0.038	0.12	0.25



Mg/Na and  $\text{SO}_4/\text{Na}$  are higher while the Cl/Na ratio is less than the sea water ratio. Higher ratios indicate incorporation of non-marine constituents in aerosols. Cl/Na ratio indicates fractionation of sea salt and modifications by non-marine constituents. As expected, there is practically no influence of marine source; aerosol composition may be affected by local terrestrial sources.

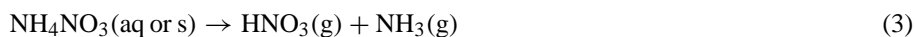
#### 3.4. Acidity of aerosols

Equivalent ratios of  $\text{NH}_4/(\text{NO}_3 + \text{SO}_4)$  were calculated, the ratio value of 1.0 would indicate neutralization of  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  by atmospheric  $\text{NH}_3$ . The observed ratio varied between 0.62 and 0.74. This shows that the aerosol is slightly acidic, the acidity is due to the neutralization of basicity by  $\text{SO}_2$  and  $\text{NO}_x$  derived mainly from brick kilns present in and around Tirupati.

#### 3.5. Assessment of the source of aerosol composition and aerosol chemistry

In general, the size distribution of aerosols through out the world is qualitatively similar, i.e. bimodal with differences only in the percentage contributions of particles present in the two modes [31]. The average concentration of  $\text{SO}_4$  is  $2484.715 \text{ ng m}^{-3}$  (Table 3). Primary emission, gas-phase nucleation or condensation cannot explain the occurrence of  $\text{SO}_4$  particles in fine mode. A possible mechanism could be aqueous-phase oxidation of  $\text{SO}_2$  in cloud droplets [40–42]. The coarse particles may originate from both sea salt and soil particles. Contribution of sea salt sulfate will be insignificant, because this sampling site is an inland site away from the coastal areas. This is further corroborated by high  $\text{SO}_4/\text{Na}$  ratio (Table 4). Hence in this area, sulfate may be soil derived or formed by reactions of gas-phase  $\text{SO}_2$  on the wet surface of basic soil particles. The average concentration of  $\text{NO}_3$  is found to be  $843.4279 \text{ ng m}^{-3}$  (Table 3). Fine particles of  $\text{NO}_3$  may be formed by the homogeneous gas-phase transformation of  $\text{NO}_x$  to  $\text{HNO}_3$ , followed by the reaction with  $\text{NH}_3$  to form  $\text{NH}_4\text{NO}_3$ , which is highly volatile and can remain stable in the particulate phase, if the product of gas-phase concentration of ammonia and nitric acid  $[\text{NH}_3][\text{HNO}_3]$  in the air exceeds the equilibrium product for the reaction (Eq. (1)) [43], or by reaction with pre-existing fine particles (Eq. (2)).  $\text{NH}_4\text{NO}_3$  in the atmosphere may exist in reversible phase equilibrium with gaseous  $\text{HNO}_3$  (Eq. (3)). The phase change corresponds to the transfer of nitrate between the fine particle and gas phase. If atmosphere thermodynamic equilibrium is realized, nitrate may be distributed either as aerosol or gas depending on the respective dissociation equilibrium. Temperature, relative humidity and atmospheric chemical composition may affect the dissociation equilibrium. The coarse particles may be soil derived as well as formed in the atmosphere both during the day and night. During the day, they are formed by the reaction of atmospheric  $\text{HNO}_3$  with air-borne soil [16], that the coarse particles act as a sink for nitric acid. In the night,  $\text{NO}_3$  is formed directly on the soil particles by the reaction (Eqs. (4) and (5)). This sampling site is hardly at a distance of about 1 km from a dairy farm run by the Andhra Pradesh Government Organization, Tirumala Tirupati Devasthanams with a livestock of around 500 herds of cattle. This may act as a major source of  $\text{NH}_3$  gas at the site and suitable humidity and temperature conditions would be favored for the formation of  $\text{NH}_4\text{NO}_3$ . Coarse particles of  $\text{NO}_3$  may be formed by the absorption

and subsequent reaction of NO<sub>2</sub> on the soil aerosol droplet or by the dissolution of gaseous HNO<sub>3</sub>. Hence, it is expected that soil particles readily act as a sink for nitric acid. This has been verified by both field experiments [16] and chamber experiments [44].



Average concentration of the fluoride is seen to be 20.09 ng m<sup>-3</sup> (Table 3). Fluoride may be contributed by emissions from industrial activities like brick kilns and lime pulverization units situated in and around Tirupati. The average concentrations of Cl and Na are found to be 232.1875 and 751.4971 ng m<sup>-3</sup>, respectively (Table 3). The ratio of Cl/Na in aerosols is less than the sea water ratio (Table 4) indicating a deficiency of chloride relative to the Na concentration. Loss of Cl from particulate may be ascribed to reaction of H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> with NaCl to produce HCl (Eqs. (6) and (7)).



The average concentration of NH<sub>4</sub> is seen to be 770.8854 ng m<sup>-3</sup> (Table 3). Fine particulate ammonium may originate by the reaction of NH<sub>3</sub> vapors with acidic gases such as H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub> and HCl or ammonia vapor may react or condense on an acidic particle surface of anthropogenic origin. The stability of the products NH<sub>4</sub>NO<sub>3</sub>, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and NH<sub>4</sub>Cl are different and depend on temperature and relative humidity. Ammonium sulfate is most stable while NH<sub>4</sub>Cl is most volatile; hence NH<sub>3</sub> prefers to react with H<sub>2</sub>SO<sub>4</sub>. Coarse NH<sub>4</sub> particles may be formed, by the reaction of NH<sub>3</sub> gas on sulfate or nitrate enriched sea salt and soil particle when excess NH<sub>3</sub> gas was available. The ideal molar ratio for NH<sub>4</sub>/SO<sub>4</sub>, NH<sub>4</sub>/NO<sub>3</sub> and NH<sub>4</sub>/Cl are 0.37, 0.29 and 0.5, respectively. The observed molar ratio for NH<sub>4</sub> to SO<sub>4</sub>, NO<sub>3</sub> and Cl are 0.83, 0.79 and 1.63, respectively. It is indicative of the fact that an appreciable amount of NH<sub>4</sub> ions are contributed from salts of carbonic acid such as (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> and NH<sub>4</sub>HCO<sub>3</sub> and salts of organic acids viz. CH<sub>3</sub>COONH<sub>4</sub> and HCOONH<sub>4</sub>. These may be formed by the reaction of NH<sub>3</sub> gas with aqueous aerosols. The average concentration of K is found to be 214.5775 ng m<sup>-3</sup> (Table 3). Normally, soil is considered to be the main source of K. The fine particles of K may be released into the atmosphere by burning of plant material [45]; however, many researchers have attributed vegetation as another source of K particles [46]. Plants emit sub-micron K through respiration mechanism. It is believed that guttation is the cause of this emission which occurs by the transport of K from roots to leaves and is released through stomata. This phenomenon takes place under hot and humid conditions and is likely to be favored at this site also.

The average concentrations of Mg and Ca are found to be 45.16 and 381.6775 ng m<sup>-3</sup> (Table 3). Generally soil is considered to be the main source of both Mg and Ca. Fine

particles may be of anthropogenic origin. Higher concentrations of Ca reveal that, it may be contributed by the emissions of industrial activities like ferrous and non-ferrous foundries.

#### 4. Conclusions

Since no ionic composition data on the aerosol composition in Tirupati were reported previously, the results of this work represent first contribution to the knowledge of aerosol composition in an urban area. The results obtained reveal the ionic composition of the aerosol mass and its variation during 6 months of study period. The aerosol ionic composition is found to be dependant on the aerosol mass, meteorological conditions of the area and the atmospheric concentrations are significantly lower in monsoon than in summer. As the site is away from the sea, influence of marine sources are negligible in aerosol composition. Major constituents of the atmospheric aerosols might have been contributed from natural sources, mainly soil, but it was slightly affected by anthropogenic activities.  $\text{SO}_4$  composition is found to be relatively higher which may be due to the emissions of  $\text{SO}_2$  from brick kilns situated in and around Tirupati. Skewness values indicate asymmetric distribution of the components signifying the pronounced effects of meteorological and source strength effects.

#### References

- [1] B.A. Bodhaine, J. Geophys. Res. 88 (1983) 10753.
- [2] R.F. Pueschel, C.C. Van Valin, R.C. Castillo, R.C. Kandlech, E. Ganor, J. Clim. Appl. Meteor. 25 (1986) 1908.
- [3] R.W. Shaw, Sci. Environ. 255 (1987) 96.
- [4] G.T. Wolf, S.R.M.S. Ruthkosky, D.P. Stroup, P.E. Korsog, F.A. Ferman, G.J. Wendel, D.H. Steadman, Atmos. Environ. 20 (1986) 1229.
- [5] E. Swietlicki, S. Puri, H.C. Hansson, H. Edner, Atmos. Environ. 30 (1996) 2795.
- [6] S. Kadowaki, Environ. Sci. Tech. 13 (1979) 1130.
- [7] T. Reichhardt, Environ. Sci. Tech. 29A (1995) 360.
- [8] L.B. Jonathan, L.R. Neil, L. Xuezh, Atmos. Environ. 31 (1997) 171.
- [9] R.F. Phalen, Inhalation Studies: Foundations and Techniques, CRC Press, Boca Raton, FL, 1984.
- [10] L. Cheng, H.S. Sandhu, R.P. Angle, R.H. Myric, Atmos. Environ. 32 (1988) 3835.
- [11] C.A. Pope, M. Thun, J. Namboodira, D.W. Dockery, J.S. Evans, F.W. Speizer, C.W. Heath Jr., Am. J. Respir. Crit. Care Med. 151 (1995) 669.
- [12] H. Horvath, J. Aerosol Sci. 27 (3) (1996) 355.
- [13] P.K. Pandey, K.S. Patel, P. Subrt, Sci. Total Environ. 215 (1998) 123.
- [14] R.L. Lantzy, F.T. Mackenzie, Geochim. Cosmochim. Acta 43 (1979) 511.
- [15] F. Adams, P.V. Espen, W. Maenhaut, Atmos. Environ. 17 (1983) 1521.
- [16] G.T. Wolf, Atmos. Environ. 18 (1984) 977.
- [17] S. Ohta, T. Okita, Atmos. Environ. 24A (1990) 815.
- [18] C.A. Pio, T.V. Nunes, I.M. Santos, J. Aerosol Sci. 23 (Suppl. 1) (1992) S711.
- [19] C.P. Wake, J.E. Dibb, P.A. Mayewski, L. Zhongqin, X. Zichu, Atmos. Environ. 28 (1994) 695.
- [20] Y. Serpil Karakas, G. Semra Tuncel, Atmos. Environ. 31 (18) (1997) 2933.
- [21] H. Zhuang, C.K. Chan, M. Fang, A.S. Waxler, Atmos. Environ. 33 (1999) 843.
- [22] A.G. Clarke, G.A. Azadi-Booger, G.E. Andrews, Sci. Total Environ. 235 (1–3) (1999) 15.
- [23] L. Roger Tanner, J. William Parkhurst, J. Air Waste Manag. Assoc. 50 (8) (2000) 1299.
- [24] Z.L. Cheng, K.S. Lam, L.Y. Chan, T. Wang, K.K. Cheng, Atmos. Environ. 34 (17) (2000) 2771.
- [25] Y.C. Chan, P.D. Voveles, G.H. Mc Tainsh, R.W. Simpson, D.D. Cohen, G.M. Bailay, G.D. McOrist, Sci. Total Environ. 262 (1/2) (2000) 5.

- [26] L.T. Khemani, G.A. Momin, M.S. Naik, R. Vijay Kumar, B.H.V. Ramana Murthy, *Tellus* 34 (1982) 151.
- [27] V.P. Sharma, H.C. Arora, R.K. Gupta, *Atmos. Environ.* 17 (1983) 1307.
- [28] B.S. Negi, S. Sadasivan, U.C. Mishra, *Atmos. Environ.* 21 (1987) 1259.
- [29] U.C. Mishra, *J. Aerosol. Sci.* 19 (1988) 1165.
- [30] V.K. Sharma, R.S. Patil, *Atmos. Environ.* 26 (1992) 135.
- [31] P.D. Safai, L.T. Khemani, G.A. Momin, P.S.P. Rao, A.G. Pillai, *Indian J. Radio Space Phys.* 22 (1993) 56.
- [32] M.K. Reddy, K.G. Rama Rao, P. Murahari Rao, *Indian J. Environ. Health* 41 (3) (1999) 200.
- [33] E. Heftmann (Ed.), *Chromatography: Fundamentals and Applications of Chromatography and Electrophoretic Methods: Part A, Fundamentals: Part B, Applications*, Elsevier, New York, 1983.
- [34] J.A. Jonsson (Ed.), *Chromatographic Theory and Basic Principles*, Marcel Dekker, New York, 1987.
- [35] A. Haider Khwaja, R. Adil Khan, S. Qureshi, *Int. J. Environ. Anal. Chem.* 75 (3) (1999) 285.
- [36] A.Y. Ali-Mohamed, A.H. Jaffer, *Chemos.: Global Change Sci.* 2 (1) (2000) 85.
- [37] L.A. Barrie, *Ann. Glaciol.* 7 (1985) 100.
- [38] P. Warneck, *Chemistry of Natural Atmosphere*, Academic Press, San Diego, 1988.
- [39] B.T. McGann, S.G. Jennings, *Atmos. Environ.* 25A (1991) 791.
- [40] D.A. Hegg, P.V. Hobbs, *Atmos. Environ.* 16 (1982) 2647.
- [41] C. Seigneur, P. Saxena, *Atmos. Environ.* 22 (1988) 105.
- [42] S.N. Pandis, J.H. Seinfeld, C. Pilinis, *Atmos. Environ.* 26A (1992) 2509.
- [43] J.H. Seinfeld, *Atmospheric Chemistry and Physics of Air Pollution*, Wiley, New York, 1986, p. 378.
- [44] Y. Mamane, J. Gottlieb, *Atmos. Environ.* 26A (1992) 1763.
- [45] J.A. Cooper, *J. Air Pollut. Control Assoc.* 8 (1980) 855.
- [46] M.T. Kleinman, B.P. Leaderer, R.L. Tanner, *Air Ann. N. Y. Acad. Sci.* 322 (1979) 115.