

A study on major inorganic ion composition of atmospheric aerosols

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Abstract: Atmospheric aerosol samples were collected from Akola and Buldana region covering around 40 sqkm area during October-November 2002 and were analyzed for ten major inorganic ions namely F⁻, Cl⁻, NO₃⁻, SO₄²⁻, PO₄²⁻, Na⁺, K⁺, Ca²⁺, Mg²⁺ and NH₄⁺ using ion chromatographic technique. The average mass of aerosols was found to be 225.81 µg/m³ with standard deviation of 31.29 and average total water soluble load of total cations and anions was found to be 4.32 µg/m³. The concentration of ions in samples showed a general pattern as SO₄²⁻>NO₃⁻>Cl⁻>PO₄²⁻>F⁻ for anions and Na⁺>Ca²⁺>NH₄⁺>Mg²⁺>K⁺ for cations. The overall composition of the aerosols was taken into account to identify the sources. The trend showed higher concentration of sodium followed by calcium, sulfate, nitrate, phosphate and ammonium and found to be influenced by terrestrial sources. The presence of SO₄²⁻ and NO₃⁻ in aerosols may be due to re-suspension of soil particles. Ca²⁺, Mg²⁺ and Cl⁻ are to be derived from soil materials. The presence of NH₄⁺ may be attributed to the reaction of NH₃ vapors with acidic gases may react or condense on an acidic particle surface of anthropogenic origin. The atmospheric aerosol is slightly acidic due to neutralization of basicity by SO₂ and NO_x.

Key words: Aerosol, Inorganic ions, Ion chromatography

Introduction

Considerable air pollution occurs in mega cities throughout the world. It has a great impact on both local and global environment and can influence the surrounding areas. As the air pollution problems are very complex, a small set of compound has been identified as major contributor to the phenomenon. They are serving as indicators of air quality in pollution control policy (De Koning, 1986). Atmospheric aerosols can be characterized from many ways, *i.e.* by number or mass concentration, chemical composition or by their sources types *etc.* This characteristics display a pronounced variability in time and space due to wide variety of information, transportation and removal processes of the aerosols (Reichhardt *et al.*, 1995; Salma *et al.*, 2001). Today, air pollution acquires a great concern globally due to manifestation of technological and scientific innovations in various fields in addition to diverse activities of man for his sophistication. Recently, urban and non-urban pollution problems are developing in a big way and are assuming a very serious dimension. In India, Delhi, Kolkata and Mumbai are highly polluted among 10 most polluted cities in the world. Rapid industrialization and population explosion are the primary sources for the fast deterioration and change in the total quality of the environment, consequently on public health (Pandey *et al.*, 1998). It is essential to study the sources, transportation and formation mechanism of atmospheric aerosols and particles during assessment of the environmental status. Many studies have reported on the atmospheric particle size distribution and chemical nature by marine, urban and rural influenced aerosols in many areas of the world (Adams, 1983; Chan *et al.*, 2000; Wolf, 1984; Karakas and Tuncel, 1997; Khemani *et al.*, 1994; Ohta and Okita, 1990;

Pio *et al.*, 1992; Wake *et al.*, 1994; Zhuang *et al.*, 1999). But in India, most of the studies focused on major cities (Negi *et al.*, 1987; Mishra, 1988; Sharma *et al.*, 1983; Sharma and Patil, 1992). The main objective of the study is to generate the baseline data of ionic composition.

Materials and Methods

The study area is geographically located at latitude of 20°42'N and Longitude of 77°04'E and its covers District-Akola and Buldhana in Vidarbha region, of Maharashtra. During October and November predominant wind spread in SW, W and NW direction. The calm conditions were prevailing about 21.7% and predominant wind speed of 1-5 kmph. Based on meteorological factors, synoptic scale wind pattern, topography, proper crosswind distribution in downwind direction *etc.*, only four locations were selected (Fig. 1). The sampling sites, Gaigaon and Gandhigram lies between east and north-east side and is surrounded by commercial and traffic environment represent Akola, whereas the other two sites Shegaon and Pimprigaoli lies between south-west and west direction attributed by small scale industries and agricultural activities in Buldana region. In the study area the various activities, namely, residential, agricultural and small scale industrial activities were noticed in addition to vehicular traffic on Kolkata-Mumbai national highway (NH-7).

The suspended particulate matter (SPM) was collected by pre-calibrated high volume sampler (HVS) during October-November 2002 using gravimetric method. Due to hygroscopic nature of the glass filter paper which results in the change in the weight as a function of humidity, filters were carefully equilibrated

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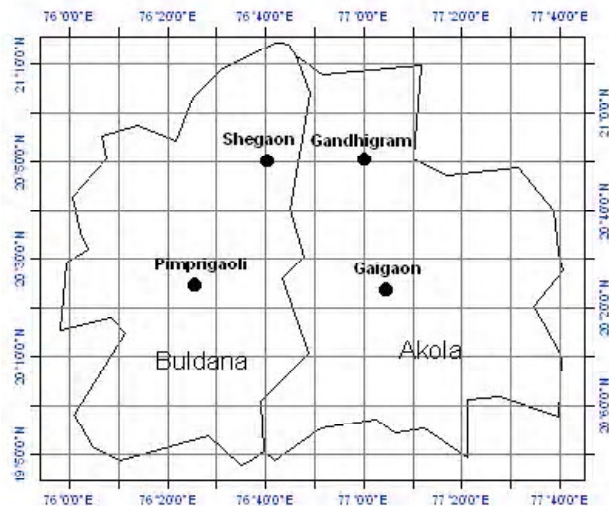


Fig. 1: Study area

in dessicator to maintain accuracy of the samples during the measurement. Mass of aerosol particles collected on glass filter was determined gravimetrically. All samples were collected daily at 24 hrs intervals. Sampling was carried out with a frequency, twice a week during October-November month (2002).

One fourth of each sample and blank was extracted thoroughly ultrasonic agitation in 20 ml of deionized water, the filtrates were analysed for various parameters, pH with a digital pH meter using reference KCl, and glass electrode standardized with pH 4.1 and 9.2 reference buffer. The major inorganic anions and cations were quantitatively determined by Dionex ion chromatograph, a Dionex IonPac AS11 for anions and CS12A for cations, a self-regenerating suppressed conductivity detector and gradient pump. The gradient weak base eluent (1.7 mM sodium carbonate or 1.8 mM sodium bicarbonate) was used for anion detection, while weak acid eluent (2 mM MSA) for cation detection at a flow of 1 ml/min. and air pressure 10 kg/cc. This provides a simple, cost effective, fast accurate and highly sensitive

method for determination of micro level ions present in environmental samples. Accuracy of the analytical data was performed by balancing cations and anions of the individual samples. A significant ionic balance was noticed from experimental data.

Results and Discussion

Average concentrations and standard deviation of inorganic constituents of different locations are presented in Table 1. Average total water soluble inorganic ions (total cations + total anions) are $4.32 \mu\text{g}/\text{m}^3$. Among the ionic constituents sodium contributed maximum to the water-soluble aerosol mass (19.44%) followed by calcium (15.74%), sulphates (12.96%), nitrate (12.73%), chloride (12.50%) and ammonium (10.65%) whereas remaining ions contributed by phosphate (8.56%), magnesium (4.17%) and potassium (2.31), fluoride (0.93%). The ionic balance of the aerosol samples showed a trend of $\text{SO}_4^{2-} > \text{NO}_3^- > \text{Cl}^- > \text{PO}_4^{2-} > \text{F}^-$ for anions and $\text{Na}^+ > \text{Ca}^{2+} > \text{NH}_4^+ > \text{Mg}^{2+} > \text{K}^+$ for cations. The lowest contributions by magnesium and potassium suggest that they occur as insoluble carbonates and silicates.

The pH of aerosols collected from all the locations ranged between 4.55 and 6.14 (average =5.42 and SD =0.48) with a blank value of 5.74 of the aerosol filtrate was a parameter used to denote acidity of aerosols directly. It is well known that low values of aerosols results from acidic matters such as sulfates, nitrates and chloride whereas basic water soluble matters such as ammonium, calcium and magnesium result in the increase in pH values (Mouli *et al.*, 2003). The mean pH of 5.42, slightly lower than blank value indicated that the interaction between the atmospheric gases (SO_2 , NO_x and HCl) or acidic particles (SO_4 , NO_3 and Cl) attributes major route for acidifying processes.

To assess the marine influence on composition of aerosols, sea-salt ratios were calculated using sodium as reference element assuming all sodium to be of marine origin. The ionic ratios of aerosols and corresponding values of sea-

Table - 1: Average concentration and standard deviation of atmospheric aerosol samples of the study area

Aerosols*	Gaigaon		Pimprigaoli		Gandhigram		Shegaon		Total average	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
No	16	-	16	-	16	-	16	-	-	-
Mass	260	43.97	192.75	18.61	308.00	34.29	142.50	17.92	225.81	31.29
pH	5.05	0.47	5.64	0.42	5.25	0.51	5.75	0.26	5.42	0.48
Na^+	0.95	0.21	0.76	0.18	0.83	0.17	0.81	0.03	0.84	0.16
K^+	0.10	0.04	0.18	0.03	0.18	0.08	0.07	0.05	0.10	0.07
Ca^{2+}	0.95	0.05	0.63	0.15	0.73	0.13	0.43	0.04	0.68	0.21
Mg^{2+}	0.18	0.09	0.11	0.02	0.19	0.01	0.25	0.03	0.18	0.07
NH_4^+	0.46	0.05	0.43	0.05	0.47	0.14	0.48	0.05	0.46	0.08
Cl^-	0.79	0.07	0.48	0.08	0.53	0.09	0.37	0.05	0.54	0.17
SO_4^{2-}	0.75	0.17	0.45	0.16	0.64	0.04	0.41	0.04	0.56	0.18
NO_3^-	0.71	0.15	0.39	0.13	0.56	0.13	0.53	0.04	0.55	0.16
PO_4^{2-}	0.37	0.12	0.45	0.13	0.35	0.11	0.31	0.08	0.37	0.11
F^-	0.04	0.01	0.04	0.01	0.04	0.02	0.05	0.01	0.04	0.01

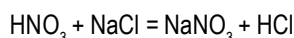
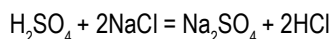
* All units are in $\mu\text{g}/\text{m}^3$ except pH, n = 16

Table - 2: Ionic values of aerosols and the corresponding values of sea water

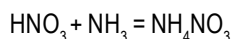
	Cl/Na	K/Na	Mg/Na	Ca/Na	SO ₄ /Na
Aerosol	0.65	0.12	0.22	0.82	0.67
Sea water	1.8	0.037	0.038	0.12	0.25

water are presented in Table 2. It was noticed that the ratios of K⁺/Na⁺, Ca²⁺/Na⁺, Mg²⁺/Na⁺ and SO₄²⁻/Na⁺ are higher while Cl⁻/Na⁺ ratio is less than sea water. This indicated the incorporation of non-marine constituents in aerosols. Cl⁻/Na⁺ ratio indicates fractionation of sea-salt and modifications by non-marine constituents. The contribution of sea-salt is insignificant because the study area is far away from coastal region, the ionic aerosol composition is greatly affected by local terrestrial sources.

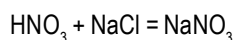
The results of ionic concentration and their various source processes appear to be interfering with the geochemical cycling of ionic constituents. This relationship clearly representing the underlying features of diverse source processes (*i.e.* natural and anthropogenic). In general, size distribution of aerosols throughout the world is similar *i.e.* bimodal with difference only in percentage contributions of particles present in two modes. The average concentration of Cl⁻ and Na⁺ was found to be 0.54 and 0.84 µg/m³ respectively. The ratio of Cl⁻/Na⁺ = 0.65 in aerosols is less than sea-water indicating a deficiency of chloride relative to the sodium concentration. The loss of chloride from aerosol mainly due to reaction of NaCl with H₂SO₄ and HNO₃ to produce HCl (Sienfield, 1986). The reactions are as follow:



The average concentration of SO₄²⁻ was found to be 0.56 µg/m³. The SO₄²⁻/Na⁺ ratio of 0.67 is higher than sea-water indicates that sulfate may be derived from soil or formed by reactions of SO₂ on the wet surface of basic soil particles. The average concentration of NO₃⁻ was found to be 0.55 µg/m³. The fine particles of NO₃⁻ may be formed by the homogenous gas-phase transformation of NO_x to HNO₃, followed by reaction of NH₃ to form NH₄NO₃, which is highly volatile in nature and can remain stable in the particulate phase.



The reaction of nitric acid with pre-existing fine particles gives the product NaNO₃.



The above reaction clearly indicated that coarse particles may be soil derived as well as formed in the atmosphere. It is also noticed that soil particles may act as a sink for nitric acid. The average concentration of ammonium ions was found to be 0.46 µg/m³. The ammonium ions may be formed by the reaction

of ammonia gas on sulfate or nitrate enriched soil particle or sea-salt spray. The observed molar ratio values were higher than ideal. The ideal molar ratio of NH₄⁺/SO₄²⁻, NH₄⁺/NO₃⁻ and NH₄⁺/Cl⁻ are 0.37, 0.29 and 0.50 respectively whereas observed molar ratios of 0.56, 0.55 and 0.84 respectively. This indicates that a significant amount of NH₄⁺ ions are contributed from salt of carbonic acid and salts of organic acid which may be formed by the reactions of NH₃ with aqueous aerosols (Mouli *et al.*, 2003). The origin of aerosols may also from anthropogenic activities. The soil is considered as a main source of calcium, magnesium and potassium. The average concentration of Ca²⁺, Mg²⁺ and K⁺ was found to be 0.68, 0.18 and 0.10 µg/m³ respectively. The higher concentration of calcium indicated that it is also contributed by the emissions of industrial activities in addition to soil. The average concentration of fluoride was found to be 0.04 µg/m³. Fluoride may be contributed by emission from industrial activities like bricks kilns *etc.*

As per the objective of the study the present ionic composition of atmospheric aerosols in the region which elucidate the processes regulating the distribution of aerosol-bound ionic constituents, the monitoring and measurement of inorganic constituents in airborne particulate matter provided an easy method of source identification. The cation and anions in the study area were mostly of natural origin mainly soil, but anthropogenic activities were also contributed to some extent.

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