Water soluble inorganic ions in submicron particulate matter

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Abstract

PM_1 (particles having aerodynamic diameter < 1.0 μm) concentrations were measured at Kerb sampling site in Nagpur, India. Sampling was carried out from December2010 to January 2011. We had collected 36 samples from this site. Sampling was done using a low volume Federal Reference Method Sampler (Partisol Model 2000, Rupprecht & Patashnick Co., Inc., US EPA) operating at a flow rate of 16.7 L per min for a 24 hourly duration. Twenty-four hour samplings were carried out on Whatman PTFE(Teflon) filters of 47mm diameter and 2μm pore size. Kerb site enlightening highest concentration of 97.8 $μg/m^3$ and maximum concentration reached up to 152.4 $μg/m^3$. The highest concentration on kerb site may be due to the New Year celebration, as this highest concentration found on the morning of 1/1/2011. Celebration involves firecrackers for welcoming the New Year. These firecrackers contribute toxic component with fine mass. The chemical speciation data in terms ion concentrations of the collected samples were closely studied. The concentrations of four anions (F^-, Cl^-, NO_3^- and SO_4^{2-}) and five cations (Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}) were determined. Only 16% of water soluble inorganic ions were present in PM_1 near road site, in this 16% sulfate and nitrate were dominating species occupied 78%. This paper reports the atmospheric concentrations of PM_1 mass in kerb sites and its water soluble inorganic components.
Key words PM_1 ,ions

Introduction

The urban area of Nagpur is characterized by residential, commercial, and very high volumes of vehicular traffics; industrial areas are generally outskirt of the city. Urban air is a cocktail of particulates and gaseous pollutants, including nitrogen oxides (NO_X), sulphur dioxide (SO_2), carbon monoxide (CO), benzene, ozone (O_3), a range of polycyclic aromatic hydrocarbons (PAH) and a variety of volatile organic compounds (VOCs), water soluble inorganic and organic compounds. As the major secondary inorganic constitutes of submicron aerosols sulfate, nitrate, ammonium and chloride were intensively studied .[1-2]Human activities do not only emit primary particles but also gaseous precursors of secondary inorganic aerosol and secondary organic aerosol SOx, NOx, and VOC [3]. From previous studies it can also be said that most of the fine particulate SO_4^{2-} and NO_3^- exist as ammonium nitrate (NH_4NO_3) and ammonium sulfate $(NH_4)_2SO_4$ .Ammonium sulfate is the most stable while ammonium chloride is the most volatile, hence ammonia prefers to react with sulfuric acid or sulfate. Ammonium, on the other hand is mainly formed by condensation of ammonia gas on a sulfuric acid particle [4, 5]. Ammonia is commonly emitted by

biological processes and is generally ubiquitous in the environment. Natural and anthropogenic sources, including the fertilizer industry, agricultural fermentation, and farm animal waste, could be sources of NH_3 [6].Calcium and magnesium are commonly associated with dust. Sodium and chloride have multiple sources and include sea-spray, industrial processes, and biomass burning. Fluoride ions mainly originated from phosphate fertilizer generation marine aerosol etc. Since many of these sources were not present in the near vicinity of the current study site, so F^- concentrations was not found in this study. In this study sampling was carried out in winter lower temperature, low wind speed, lower mixing height and poor dispersion conditions. These conditions are responsible for transformation of anions from gas phase to particle phase [7].

Materials and Methods

PM_1 samples were collected from December 2010 to January 2011 for kerb site using a low volume Federal Reference Method Sampler (Partisol Model 2000, Rupprecht & Patashnick Co., Inc., US EPA) operating at a flow rate of 16.7 l min−1 for a 24 hourly duration. The sampler was placed on the roof of building from the surface of 9 m. The samples were collected on Whatman PTFE (Teflon) filters of 47mm diameter and 2μm pore size, ion analysis. During sampling, field blank filters were collected to reduce gravimetric bias due to filter handling during or after sampling. The filters were weighted by using a high-precision five-digit electronic balance (Mettler AE 163). Each filter paper used for sampling was pre-conditioned and post conditioned at $40 \pm 3\%$ relative humidity and in controlled environment at 25˚C for over 24 hour before and after sampling.

Water Soluble Inorganic Ion Analysis

The concentrations of four anions (F^-,Cl^-, NO_3^-,SO_4^{2-}) and five cations (Na^+, NH_4^+, K^+, Mg^{2+}, and $Ca^{2+)}$ were determined in aqueous extracts of the filters prepared in three steps using ultra-pure water. The Teflon filter was placed in a vial with 25 ml of ultra-pure water and sonicated for 60 min. The extracted solution was then shaken for 12 hours and filtered through a syringe filter and stored at 4 ◦C until further analysis.

Analysis of samples for concentration of anions was performed using (Make:Dionex Model: ICS 3000, Germany) ion chromatograph equipped with Dionex Ionpac AG11-HC guard column and AS11-HC separation columns, 25 μL sample loop and conductivity detector. A 30 mM KOH was used as an eluent at a flowr-ate of 1.0 mL min- For analysis of cations in selective samples, the same system was used in combination with AG5 and AS5 cation exchange guard and separation column, respectively. A 6 mM methanosulfonic acid was used as an eluent for cation analysis. The limits of detection for cations and anions were 1 ppb in Dionex ion chromatograph. Dionex five anions standard and Dionex five cations standard were used for the calibration of the ion chromatograph for determination of anions and cations respectively.

Results and discussion

Kerb site varied from 48.4 to 152.4µg/m^3 with an average and standard deviation of 97.8 ± 21.6µg/m^{3}maximum concentration of 152.4µg/m^3 was observed on the morning of 1/1/2011. The highest concentration on near road site may be due to the New Year celebration, as this highest concentration found on the morning of 1/1/2011. Celebration involves firecrackers for welcoming the New Year. These firecrackers contribute toxic component with fine mass. This site chosen as near road site, it is busiest road. Koradi thermal power plant is from 10 km from this site, also very famous temple is away from 9 km from this site.

Table 1

Location	Trend in Water soluble inorganic ions
Kerb site	$SO_4^{2-} > NO_3^- > NH_4^+ > K^+ > Ca^{2+} > Mg^{2+}$

On the basis of literature soil dust and vegetative burning are often the only sources of potassium in many urban environments. It was demonstrated that water-soluble potassium has been commonly used as a marker for biomass burning. SO_4^{2-} commonly represents the stationary pollution sources such as coal combustion, while nitrate represents the mobile sources like vehicle exhaust .Local sanitary wastes could be the sources of NH_4^+ [8].
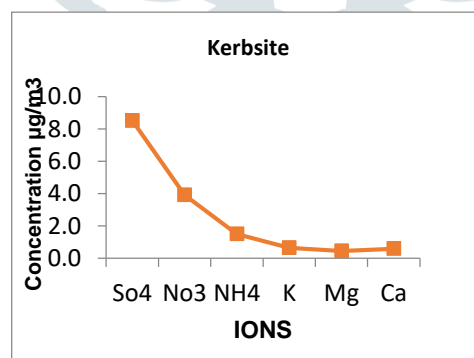
Fig 1

Table 2

Average concentration of ions in µg/m³

Parameter	Near road site
SO_4^{2-}	8.5
NO_3^-	3.9
NH_4^+	1.5
K^+	0.7
Mg^{2+}	0.4
Ca^{2+}	0.6

Results from recent studies have shown that water soluble inorganic ions and carbonaceous aerosol were the major component of PM_1. In submicron fraction, water soluble anions contribute a significant portion to the overall PM_1 mass [9]. Ionic species and carbonaceous aerosol were dominant of PM_1, which attributed 46.0% and 27.5% to the total particle mass [10, 11]. PM_1 and $PM_{2.5}$ measurements at roadside in Hongkong showed that carbonaceous aerosols were major components in fine particles, constituting 45.7% of PM_1 and 44.4% of $PM_{2.5}$ [12]. In India, study carried out in Kanpur, anions contributed to almost 35–40% of overall PM_1 mass and among those anions nitrate and sulfate were the two most predominant species.   As there is no ambient air quality standard for PM_1. There should be standard for PM_1.

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