Time-resolved inorganic chemical composition of fine aerosol and associated precursor gases over an urban environment in western India: Gas-aerosol equilibrium characteristics

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HIGHLIGHTS

- Time-resolved aerosol composition and trace gas concentrations were measured.
- We examine gas-aerosol equilibrium characteristics using ISORROPIA II model.
- $NH_3-NH_4^+$ are in equilibrium with measured particulate and gas composition.
- HCl and HNO_3 deviate from thermodynamic equilibrium possibly due to uptake by dust.

ARTICLE INFO

ABSTRACT

Inorganic ionic constituents (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^- and SO_4^{2-}) of $PM_{2.5}$ and associated trace gases (NH_3, HNO_3 and HCl) were measured simultaneously by Ambient Ion Monitor − Ion Chromatograph (AIM-IC) system with a time resolution of one hour at an urban location in semi-arid region of western India during summer and winter. The average NH_3, HNO_3 and HCl concentrations were 11.6 ± 5.0, 2.9 ± 0.8 and 0.15 μg m^{-3}, respectively, during winter. During summer, NH_3 and HNO_3 concentrations were of similar magnitude, whereas HCl concentration was less than ~0.03 μg m^{-3}. NH_3 concentration exhibited a distinct diurnal variation during both seasons. However, HNO_3 did not show a specific diurnal trend during the observation period in both seasons. The data obtained were used to study gas-aerosol equilibrium characteristics using a thermodynamic equilibrium model, ISORROPIA II. The results suggest that NH_3 exists in equilibrium between measured fine-mode particle and gas phase with a systematic bias of ~14%, whereas HCl and HNO_3 deviate significantly from the modelled data. These observations have implications on thermodynamic equilibrium assumptions used for estimating various aerosol parameters such as liquid water content, pH, etc., thus causing significant bias in chemical transport model results over the study region.

1. Introduction

Atmospheric particulate matter with aerodynamic diameter less than 2.5 μm ($PM_{2.5}$) has the potential to alter the radiative balance of the Earth by scattering or absorbing radiation and influence cloud microphysics. Furthermore, fine aerosols reduce visibility, provide surface for heterogeneous chemical reactions, affect human health and impact ecosystems through deposition of various trace constituents (Finlayson-Pitts and Pitts, 2000; Poschl, 2005; Seinfeld and Pandis, 2006; Mannucci, 2010). For a better understanding of climate forcing, air quality and for taking mitigating measures, knowledge of chemical constituents and their phases in atmospheric $PM_{2.5}$ is essential. The bulk of dry, fine-particle mass is inorganic (typically 25−75%; Heitzenberg, 1989), with NH_4^+, SO_4^{2-} and NO_3^- as main components. In addition, Na^+, Cl^-, Ca^{2+}, Mg^{2+} and K^+ may also be present, associated with crustal and sea-salt sources depending on the location. These species exist in aqueous phase or solid form depending on ambient temperature and relative humidity, and some can get partially volatilized as NH_3, HNO_3 and HCl vapours. Hence, the gas and the particle phases of these semi-volatile constituents are related through thermodynamic equilibrium partitioning. Consequently, many aerosol thermodynamic

equilibrium models such as EQUIL, MARS, AIM, E-AIM, SCAPE, EQUISOLV, ISORROPIA have been developed to simulate the process of aerosol dissolving in water, forming ions and equilibrating with gas phase (Bassett and Seinfeld, 1983; Saxena et al., 1986; Wexler and Seinfeld, 1991; Kim et al., 1993; Jacobson et al., 1996; Nenes et al., 1998; Wexler and Clegg, 2002).

Studies from various geographical locations of the Indian subcontinent have revealed that particulate NH_4^+, SO_4^{2-}, and NO_3^- constitute as much as 25–40 % of $PM_{2.5}$ mass (Kumar and Sarin, 2010; Deshmukh et al., 2011; Rengarajan et al., 2011). The rest of the mass consists of generally organic matter, elemental carbon and mineral dust. An important aspect is to verify whether equilibrium models can adequately predict the equilibrium partitioning of semi-volatile inorganic species over a representative region with reasonable confidence level. Though several studies have documented inorganic constituents of aerosol over the region of western India, data on simultaneous measurement of precursor gases and assessment of gas-aerosol equilibrium are not available. Most of the available information from various locations in India regarding gas phase constituents and aerosol ionic species is based on off-line analytical techniques with extended integration time up to a few days, thereby making impossible to elucidate the changes occurring on time scales of hours. If measurements are made by averaging for long duration, significant changes in temperature, relative humidity (RH) and precursor gases can occur during sampling and the data would be inappropriate for equilibrium calculations. In particular, northern region of the Indian subcontinent is a perennial source of both natural and anthropogenic aerosol and witnesses seasonal wind reversal, transporting marine air masses towards the continental regions during summer. Studies to characterize the influence of high dust and anthropogenic emissions on equilibrium partitioning of semi-volatile species are not reported from this region.

In this paper, results of simultaneous on-line measurement of water-soluble ionic constituents of $PM_{2.5}$ and associated gaseous species over an urban environment in western India along with an analysis of gas-aerosol partitioning of HNO_3, NH_3 and HCl using ISORROPIA II are presented. ISORROPIA II is a computationally efficient model and widely used in global chemical transport models as well as regional climate models (Fountoukis and Nenes, 2007; Knote and Brunner, 2013; Heald et al., 2014). The temporal and average diurnal variations of particulate ionic constituents during the two sampling campaigns in summer and winter are reported in our earlier publication (Sudheer et al., 2014).

2. Experimental

2.1. Measurement site and general meteorology

The measurement site is located at Physical Research Laboratory building at Ahmedabad, India. Ahmedabad is an urban location situated in western India (23.03°N, 72.54°E) with a population of more than 6 million. The sampling location is surrounded by various emission sources both anthropogenic and natural. This region witnesses seasonal reversal of trade winds on annual scale. Typically, during December–February winds are north-easterly, whereas during June–August south-westerly. A detailed description of sampling site and meteorological characteristics is available in Sudheer et al. (2014).

2.2. Measurement of $PM_{2.5}$ ionic constituents and related gaseous species

The inorganic constituents of $PM_{2.5}$ (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, SO_4^{2-}) and associated precursor gases (HCl, HNO_3 and

NH_3) were measured by the Ambient Ion Monitor − Ion Chromatograph (AIM-IC, URG 9000D). The AIM-IC system provides a continuous, near-real-time, hourly online measurement of the water-soluble inorganic constituents of $PM_{2.5}$ and precursor gases. A detailed description of technique and performance evaluation of AIM-IC system is reported in our earlier publication as well as by various other groups (Markovic et al., 2012; Sudheer et al., 2014; Markovic et al., 2014). Briefly, ambient air was taken at a flow rate of 3 L min^{-1} and inlet was connected to a cyclone for 2.5 μm particle size cut off. Water extraction was performed with a modified steam jet collector (Khlystov et al., 1995) after gaseous components were removed from the sampled air with a continuously regenerated parallel plate wet denuder. 5 mM H_2O_2 in deionised water was used as denuder solution. The water extract accumulated in steam jet collector as well as denuder solution were analysed for major cations and anions with two ion-chromatographs (DIONEX 1100) with a time resolution of one hour. For analysis of anions, Dionex AS-14A and AG-14A columns were used and for cations, CS-12A and CG12A were used along with the appropriate electrolytic suppressors. Ambient concentrations of particulate constituents were ascertained from analysis of water extract from steam jet collector. NH_4^+, NO_3^- and Cl^- content in denuder solution were used to calculate NH_3, HNO_3 and HCl concentrations. AIM system was operated during winter from December 22, 2011 to January 16, 2012 and during summer from June 5 to July 4, 2012.

$PM_{2.5}$ samples were collected on quartz filters using a high volume air sampler and subsequent analysis revealed that the AIM-IC generated data are in good agreement with filter based measurements. Balance between the sum of cations and anions suggested that the measurements are consistent with respect to charge neutrality (Sudheer et al., 2014). To verify the collection efficiency of gaseous NH_3, HCl and HNO_3 by the parallel plate denuder, a filter was fixed at the inlet and the solution from steam jet collector was analysed for both cations and anions. Cl^- and NO_3^- in anion channel were not detected and NH_4^+ signal was less than two orders of magnitude compared to that observed during sampling, confirming that the measured gaseous species were removed from the sampled air almost quantitatively. In order to minimize the loss, a short aluminium inlet (1 m length) was used for sampling the ambient air. The ion chromatographs were calibrated before and after the observation period. Standard solutions were injected intermittently to verify consistency of ion chromatograph performance. Markovic et al. (2014) described the comparison of analysis of gaseous species NH_3, HNO_3 and SO_2 with independent measurement techniques, demonstrating that the AIM−IC system yields measured parameters with an uncertainty ranging from 10 to 20%.

The limit of detection (LOD) of NH_3 was determined as 0.02 μg m^{-3} based on reproducibility of cation blank runs on ion chromatograph (3σ). Minimum peak areas of Cl^- and NO_3^- identified by ion chromatography software (Chromeleon®) correspond to 0.02 μg m^{-3} and 0.03 μg m^{-3} of HCl and HNO_3 in ambient air, respectively, based on calibration with standards. LOD for particulate constituents were also estimated from minimum peak areas

Table 1
Limit of detection (LOD) for the measured aerosol ionic constituents and trace gas species. All concentrations are in μg m^{-3}.

Gas species	HCl	HNO_3	NH_3				
LOD	0.02	0.03	0.02				

Particle component	Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	Mg^{2+}	K^+	Ca^{2+}
LOD	0.02	0.03	0.05	0.02	0.02	0.02	0.02	0.02