Environmental Radionuclides and Chemical Constituents in Rain and Aerosols: Biogeochemical Sources and Temporal Variations

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By

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UDAIPUR

Year of submission: 2005

DECLARATION

I hereby declare that the work incorporated in the present thesis entitled “Environmental Radionuclides and Chemical Constituents in Rain and Aerosols: Biogeochemical Sources and Temporal Variations” is my own work and is original. This work (in part or in full) has not been submitted to any University for the award of a Degree or a Diploma.

(Neeraj Rastogi)

CERTIFICATE

I feel great pleasure in certifying that the thesis entitled "Environmental Radionuclides and Chemical Constituents in Rain and Aerosols: Biogeochemical Sources and Temporal Variations" embodies a record of the results of investigations carried out by Neeraj Rastogi under my guidance.

I am satisfied with the analysis of data, interpretation of results and conclusions drawn.

He has completed the residential requirement as per rules.

I recommend the submission of thesis.

Date: 18 April 2005

S. Krishnaswami,
Senior Professor
Physical Research Laboratory

Dedicated to my

“Mummy and Papa”

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Chapter 1

INTRODUCTION

1.1 INTRODUCTION

The study of the atmospheric cycle of chemical constituents involves understanding of their sources, transport, physico-chemical transformation and removal by precipitation scavenging and dry deposition. These atmospheric processes are critical to every major environmental issue related to climate change including radiative forcing, ozone depletion, aerosols and human health, hydrological cycle and acid rain (Prospero et al., 1983; Charlson et al., 1987; Charlson et al., 1992; Ramanathan, et al., 2001a; Huebert et al., 2003; Bates et al., 2004). In this context, the role of aerosols as active constituents of climate system models is increasingly recognized. The anthropogenic component of sulphate and carbonaceous aerosols has substantially increased from pre-industrial time to the present-day and can, thus, influence the climate in different ways. The central question being addressed is: “What is the role of aerosol composition (both inorganic and organic) in determining the indirect radiative forcing of aerosols”. Rainfall patterns can also be affected directly through the influence of aerosols on cloud micro-physical properties. The long-term continuous measurements are, thus, important to evaluate the seasonal variations in aerosol concentrations and properties. Some of the key aspects of aerosol properties are summarized in this chapter.

1.1.1 Effect of aerosols on Earth’s radiation budget:

The increasing concentrations of greenhouse gases in the atmosphere, such as CO_2, CH_4, N_2O absorb upwelling infrared radiation (IR, also referred as long wave) and reduce the intensity of outgoing long-wave (> 4 μm) radiation at the top-of-the atmosphere (TOA). The TOA radiative forcing (i.e. change in the outgoing long-wave radiation), due to the observed increase in greenhouse gases (GHGs) since the early 20th century, is about 2.4 W m^{-2} (IPCC, 2001). Aerosols, on the other hand, may scatter or absorb the incoming solar radiation depending upon their chemical, physical and optical properties. For example, both black carbon (BC) and mineral dust particles absorb ultraviolet radiation in addition to their scattering property. The absorption of radiation lead to heating of the atmosphere, which in turn has the potential to modify atmospheric dynamics and changes in the rainfall intensity and amount (Rosenfeld et al., 2000; Ramanathan et al., 2001a, 2001b; Menon et al., 2002). Global estimates of the TOA radiative forcing (i.e. change in the absorbed solar radiation) due to anthropogenic aerosols range from -0.5 to -2.5 W m^{-2} (IPCC, 2001). The magnitude and negative sign indicate that the atmospheric heating due to greenhouse gases is somewhat counter balanced by cooling effect due to aerosols.

1.1.2 Aerosols and hydrological cycle:

Aerosols also act as cloud condensation nuclei (CCN) i.e. they provide active surface area for the condensation of ambient water vapour to form rain droplets. Because of increase in anthropogenic activities, there is a parallel increase in the number of aerosol particles and hence CCN. For a given amount of water vapour, increase in CCN would reduce the cloud droplet size, and increase the droplet number and, thus, enhance lifetime of the cloud. These micro-physical properties could alter the cloud albedo. The indirect aerosol radiative forcing, in which aerosols affect cloud reflectivity and lifetime, could cause substantial but poorly quantified additional cooling (IPCC, 2001). Roeckner et al (1999) concluded that the hydrological cycle would be weaker in the period (2030-50) as compared to the present day climate when the direct and indirect effects of aerosols are considered. However, because of their relatively short residence time, the warming or cooling effects due to aerosols are largely governed by the regional distribution. The effect of aerosol (acting as CCN) composition on rainfall pattern is growing as a subject of scientific importance in recent years.

1.1.3 Role of aerosols in atmospheric chemistry:

Aerosols also provide surface for in-situ atmospheric chemical transformation processes (Prospero et al., 1983). For example, fine mineral dust can be transported long distances in the atmosphere and thus have the potential to undergo a variety of heterogeneous reactions with atmospheric gases. In principle, it is possible that heterogeneous chemistry of atmospheric aerosols can change both gas-phase chemical balance of the atmosphere and the physico-chemical properties of individual particles. Changes in the properties of individual particles, such as size, shape, composition and hygroscopicity, will alter aerosol optical properties and may have an impact on the Earth’s climate (Krueger et al., 2003). It has been estimated that 1000-3000 Tg (10^{12} g) of mineral aerosols are injected into the atmosphere on an annual basis from wind-blown soils (Dentener et al., 1996; Seinfeld and Pandis, 1998). Thus, radiative effects of mineral aerosols are important (in comparison to other types of aerosols) as they modify both short- and long-wave radiation by scattering in the visible and absorbing in the infrared part of the spectrum (Andreae, 1996; (Sokolik and Toon, 1996). Globally, significant atmospheric burden of mineral aerosols originate from desert regions, ascend to high altitudes and are transported over long distances (Prospero et al., 1989). Mineral aerosols can influence global atmospheric chemistry, cloud properties, and precipitation development (Levin et al., 1996). Their deposition over the world oceans has also been found to be a major source of iron and host of nutrients controlling the surface primary productivity (Duce et al., 1991; Bergametti, 1998).

In recent years, there has been considerable interest on the emissions from Asian region, largely because of the strength and diversity of sources for both natural and pollution-derived aerosols (Prospero et al., 2003; Arimoto et al., 2004). During late winter and early spring (Feb-Apr), mineral dust from the Asian deserts is ubiquitous in the atmosphere, more often a dominant component of aerosols over large parts of Asia. These mineral aerosols (mainly $CaCO_3$) interact with O_3, SO_2, HNO_3 and NO_x, which can significantly influence the chemistry of troposphere (Dentener et al., 1996; Tabazadeh et al., 1998; Underwood et al., 2001; Tang et al., 2004). Many of theses gases, SO_2 and NO_x are released by coal burning and industrial processes into the atmosphere and it is essential to quantify the processes that control their transport, evolution, and subsequent deposition. In regions where dust related alkalinity is balanced by NO_x and SO_2, any additional abundance of NO_x and SO_2 are expected to undergo a very different removal mechanism (Kline et al., 2004).

A large degree of uncertainty in the quantitative estimates of aerosol effects on climate arises due to the lack of data on real-time changes in atmospheric composition of aerosols on regional scales. Changes in emissions of mineral dust, soot, inorganic anions and cations, sea-salts, and a variety of industrial aerosols can all contribute to variability in the chemical composition of aerosols. Furthermore, because of their relatively short lifetime, concentrations and composition of aerosols vary widely on a regional scale. The mixing state of various components in aerosols has a pronounced effect on absorption of UV radiation, cloud-nucleating capacity and atmospheric removal rates (Huebert et al., 2003). Long-term regional scale studies of aerosol composition are, therefore, essential and observational campaigns provide the most direct information about aerosol characteristics and regional scale changes.

1.1.4 Rainwater composition and deposition fluxes of chemical species:

Precipitation is a major removal pathway of selected atmospheric species (aerosols and trace gases) over several regions of the world. Thus, a systematic study of the chemical composition of precipitation helps to probe the chemical state of the atmosphere in which rain-bearing clouds have formed. Further, the chemistry of precipitation determines the deposition fluxes of chemical species over land and oceans. Such estimates of deposition are fundamental in many studies of terrestrial and marine ecology (Norman et al., 2001; Mphepya et al., 2004). The concentrations of chemical species in precipitation are highly variable, which makes it difficult to quantify their fluxes without long-term campaigns. Chemical constituents in rainfall are derived from aerosols and/or gas phase, either incorporated directly in clouds (in-cloud scavenging) or washed-out by precipitation (below-cloud scavenging). A better understanding of the chemical composition of rainwater, therefore, can be achieved by studying the composition and relationship between the two phases (Jaffrezo and Colin, 1988). A major component of variability in rainwater composition is variation in aerosol chemistry resulting from composition of source and modification enroute to site of removal. The coupling between rain and aerosols is expressed by the "scavenging ratio (SR)". It is the ratio of the concentration of an element in precipitation to that in the aerosols. The SR is dimensionless and in conjunction with aerosol data, is the only means for quantitative evaluation of concentrations of various constituents in precipitation especially over remote regions (in absence of chemical data). Furthermore, the scavenging ratios can also be used to investigate the relative importance of aerosol sizes and phases of species (gas and/or particulate) involved in the transfer mechanism (Barrie, 1985; Jaffrezo and Colin, 1988; Rastogi and Sarin, 2003a).

The concentrations of chemical substances in the atmosphere depend on their source strengths, transport and removal (Lacaux and Artaxo, 2003). The biogeochemical cycle of several chemical species in the atmosphere has been perturbed by anthropogenic activities in the regions (Lacaux and Artaxo, 2003). For example, increase in deposition of acidifying sulphur and nitrogen compounds has led to widespread damage to terrestrial ecosystems in several regions of the world. Galloway (1995) had reported that NH_3 emission and subsequent nitrogen accumulation in terrestrial ecosystems has the potential to generate significant acidification in terrestrial and aquatic ecosystems. Input of sulphur and nitrogen oxides in the atmosphere and their deposition in environmental reservoirs will not only result in significant and extensive acidification but also affect the earth's radiation balance, tropospheric oxidizing capacity, ecosystem nutrient balance and ground water quality (Galloway, 1995). Fixed nitrogen (NO_3^-, NH_4^+) is a limiting nutrient in many ecosystems. The increased nitrogen deposition in and around many industrial parts of the world has consequently caused eutrophication (increased primary production caused by the enrichment of an ecosystem with nutrients) of fresh water and marine ecosystems; with consequence of affecting the atmospheric carbon balance (Brasseur et al., 2003). Regional scale studies of both dry and wet deposition fluxes of chemical species are therefore, essential in estimating global budgets of the atmospheric constituents.

1.1.5 Usefulness of environmental radionuclides (^{7}Be and ^{210}Pb):

^{7}Be and ^{210}Pb are the natural radionuclides present in the atmosphere. Several studies (Turekian et al., 1977; Feely et al., 1989; Brost et al., 1991; Feichter et al., 1991; Balkanski et al., 1993; Koch et al., 1996; McNeary and Baskaran, 2003; Duenas et al., 2004; Gaffney et al., 2004; Rengarajan and Sarin, 2004) have shown that useful information about washout, transport and residence time of aerosols in the atmosphere can be obtained from the measurements of ^{7}Be and ^{210}Pb. However, several issues and challenges involving the use of natural radionuclides as tracers are yet to be resolved (Lee et al., 2004). ^{7}Be (half-life = 53.3 days) is produced by cosmic ray spallation of nitrogen and oxygen primarily in lower stratosphere and upper troposphere (Lal and Peters, 1967). Due to its short mean life (~77 days) compared to residence time of stratospheric aerosols (~year), most of the ^{7}Be produced in the stratosphere do not reach troposphere except during spring and summer when tropopause becomes thinner and relatively intense convective mixing takes place (Duenas et al., 2004). Since the production of ^{7}Be in the troposphere is nearly uniform, its flux to the earth's surface remains nearly independent of latitude (Lal and Peters, 1967). Therefore, ^{7}Be can be used as a tracer of stratospheric or high tropospheric sources such as ozone, stratospheric bomb fallout debris, stratospherically injected volcanic components (Viezee and Singh, 1980; Turekian et al., 1983; Graustein and Turekian, 1996).

^{210}Pb (half-life = 22.3 years) is a progeny of ^{238}U. The source of ^{210}Pb is radioactive decay of ^{222}Rn (half-life = 3.8 days) in the atmosphere. ^{222}Rn, being a noble gas, is continuously emitted from soils to the atmosphere. Thus, ^{210}Pb is a tracer of continental air as more than 99% ^{222}Rn is emanating from the surface of continents (Turekian et al., 1977; Turekian et al., 1989; Sarin et al., 1999). Half-life of both the radionuclides are long enough with respect to their residence time in the lower atmosphere, therefore the principal removal pathway of the ^{7}Be and ^{210}Pb is via dry and wet deposition rather than radioactive decay. Since the sources of ^{7}Be and ^{210}Pb are well established and different in terms of altitude, their simultaneous study can provide information of vertical mixing of the atmosphere as a function of time at a given site.

It is turned out from preceding discussions that long-term regional studies of chemical and isotopic composition of aerosols are essential to assess their impact on climate change and air quality, and to understand atmospheric transport, transformation and removal processes. The transformation processes resulting from interactions of natural (mineral dust and sea-salt) and anthropogenically derived chemical species (SO_2, NO_x and their derivatives) are especially important over arid, semi-arid and marine regions as they influence radiative properties. An extensive study on radiative properties of aerosols over northern Indian Ocean during Indian Ocean Experiment (INDOEX) program suggested the need of studying chemical composition of aerosols over Indian region (Ramanathan et al., 2001b). These considerations, motivated by scientific importance of regional scale aerosol study, led to the initiation of a long-term systematic study of aerosol and rainwater chemical composition over selected regions in and around India.

1.2 OBJECTIVES OF PRESENT STUDY

Present study is aimed to determine the chemical and isotopic composition of aerosols and rainwater over selected regions in and around India, their temporal variations, the relation between aerosols and rainwater chemistry, their wet and dry deposition fluxes, and the role of mineral dust as a neutralizing component in these regions. More specifically, main goals of the thesis are:

1. **To characterize the temporal variations in the chemical and isotopic composition of aerosols over an urban site (Ahmedabad), a high-altitude site (Mt Abu), and in the marine boundary layer (over the Bay of Bengal, Indian Ocean and the Arabian Sea),**

2. **To assess the relative source strengths (sea-salt, mineral dust and anthropogenic inputs) contributing to aerosol composition in the regions,**
3. **To infer the interactions of anthropogenic species (sulphate and nitrate) with mineral dust and marine components of aerosols and their impact on aerosol chemistry,**
4. **To assess the factors controlling the chemical characteristics of individual precipitation events and inter-annual variability over a semi-arid region (Ahmedabad),**
5. **To determine scavenging ratios (SRs) of chemical species based on aerosol and precipitation data,**
6. **To quantify the dry and wet deposition fluxes of chemical species at the atmosphere-ecosystem interface.**

Such regional scale studies of chemical and isotopic composition of rain and aerosols are vital in assessing the effects of aerosols on climate and to better understand various atmospheric processes such as lateral and vertical air mass transport and physico-chemical transformations of atmospheric chemical species. Present study also provides a long-term systematic data set on chemical and isotopic composition of aerosols and rainwater over Ahmedabad and Mt Abu; in addition to data on the marine boundary layer of the Bay of Bengal, Indian Ocean and the Arabian Sea. Such studies provide inputs to various global and regional scale climate models. The objectives of the present study overlap with those of several international programs such as International Global Atmospheric Chemistry (IGAC), Deposition of Biogeochemically Important Trace Species (DEBITS), Composition and Acidity of Asian Precipitation (CAAP), Surface Ocean Lower Atmosphere Study (SOLAS) and Global Atmospheric Watch (GAW).

The study on aerosol chemical composition over India is scanty and have gained importance subsequent to the INDOEX program. Most of the available data are based on short-term collections over few sites in India, Agra (Kulshrestha et al., 1998), Pune (Momin et al., 1999), Delhi (Parashar et al., 2001) and Mumbai (Venkataraman et al., 2002). These studies are done during winter-spring periods, under the influence of northeasterly winds. The aerosol chemistry over India during southwest monsoon has not yet been reported. In contrast, there are number of studies on precipitation chemistry (Khemani et al., 1989; Mahadevan et al, 1989; Parashar et al., 1996; Jain et al., 2000; Pillai et al., 2001; Kumar et al., 2002; Kulshreshtha et al., 2003; Safai et al. 2004) for several sites in India, but rainwater composition over western India (Gujarat) is not available in literature. To fill this gap, as well as to obtain comparative data on aerosol chemistry and transformation processes for different locations in India and in the marine boundary layer during the same period, this study was undertaken. It is also important to add here that this study is based on 2-3 year continuous sampling, unlike the earlier reported studies, which are based on seasonal sampling and short-term collection.

1.3 THESIS OUTLINE

The organization of the thesis contents is as under: **Chapter 1** consists introduction of the subject, importance of aerosol study and the specific objectives of this study. **Chapter 2** describes sampling protocol and analytical procedures adopted for chemical and isotopic analyses of rain and aerosols. **Chapter 3** deals with results and discussions on aerosol chemical composition (water-soluble and acid-soluble), their temporal variations, relationship among various aerosol constituents, physico-chemical transformation and comparative characteristics of aerosol data with some of the reported studies. **Chapter 4** is on the results and discussions on rainwater composition, intra-seasonal and inter-annual variations in concentrations of chemical species and the factors controlling these variations. **Chapter 5** provides a coupling between aerosol and rainwater composition by using scavenging ratios and quantification of deposition fluxes for selected species via wet and dry scavenging. **Chapter 6** discusses the radioisotopes data, results and comparison with the reported studies in literature. **Chapter 7** summarizes the important findings of the study and their implications in assessing the impacts of aerosols on climate and scope for future research.

Chapter 2

MATERIALS AND METHODS

2.1 INTRODUCTION

A systematic sampling strategy was designed for the collection of aerosol samples from selected sites on seasonal and spatial scale to achieve the specified objectives (Chapter 1). The sites experience diverse meteorological conditions and hence are expected to have different source strength of aerosols. A well conceived analytical scheme was an integral part of this study wherein bulk-aerosol samples were collected onto tissuquartz filters using high-volume air samplers installed at two sites: a) Ahmedabad, representing a typical urban city located in a semi-arid region of western India; and b) Mt Abu, a high altitude site located at 1680 m (asl) in the Aravali range of mountains characterized by semi-arid climate. Their geographic locations are expected to make an ideal setting for the characterization of sea-salts, mineral aerosols as well as chemical species derived from biogenic and anthropogenic emission sources. The studies were also made in regions such as the marine boundary layer (MBL) where substantial gradient in aerosol constituents, such as urban plume advecting into a relatively non-polluted region is expected. Of specific interest is to understand chemical interactions between marine and continental aerosols. For this, sampling was carried out during a cruise undertaken in the Bay of Bengal, north Indian Ocean and the Arabian Sea. Relevant details of the selected sites, sampling protocols for rain and aerosols and analytical procedures developed for the measurements of chemical species and ^{7}Be and ^{210}Pb in rainwater and aerosol samples are described in the following sections:

2.2 SITE DESCRIPTION

2.2.1 Ahmedabad:

Ahmedabad (23.0^{o}N, 72.6^{o}E, 49 m asl) is one of major cities of India with a population of about 5.6 million. It is located in western India, ~500 km southeast of the Thar Desert (Fig. 2.1). The nearest distance to the Arabian Sea, in the southwest direction, is ~100 km. The local climate is typical of semi-arid type. Monthly average temperature and relative humidity (RH) for the year 2002 are shown in Fig. 2.2a; representing the general pattern of temperature and RH variation over an annual period (Fig. 2.2a). In addition, monthly rainfall during the study period (2000-2002) is also shown in Fig. 2.2b. The annual average rainfall for the city is ~700 mm. It is important to emphasize that at Ahmedabad, the precipitation events seldom occur outside the SW-monsoon period (Jun-Sept).

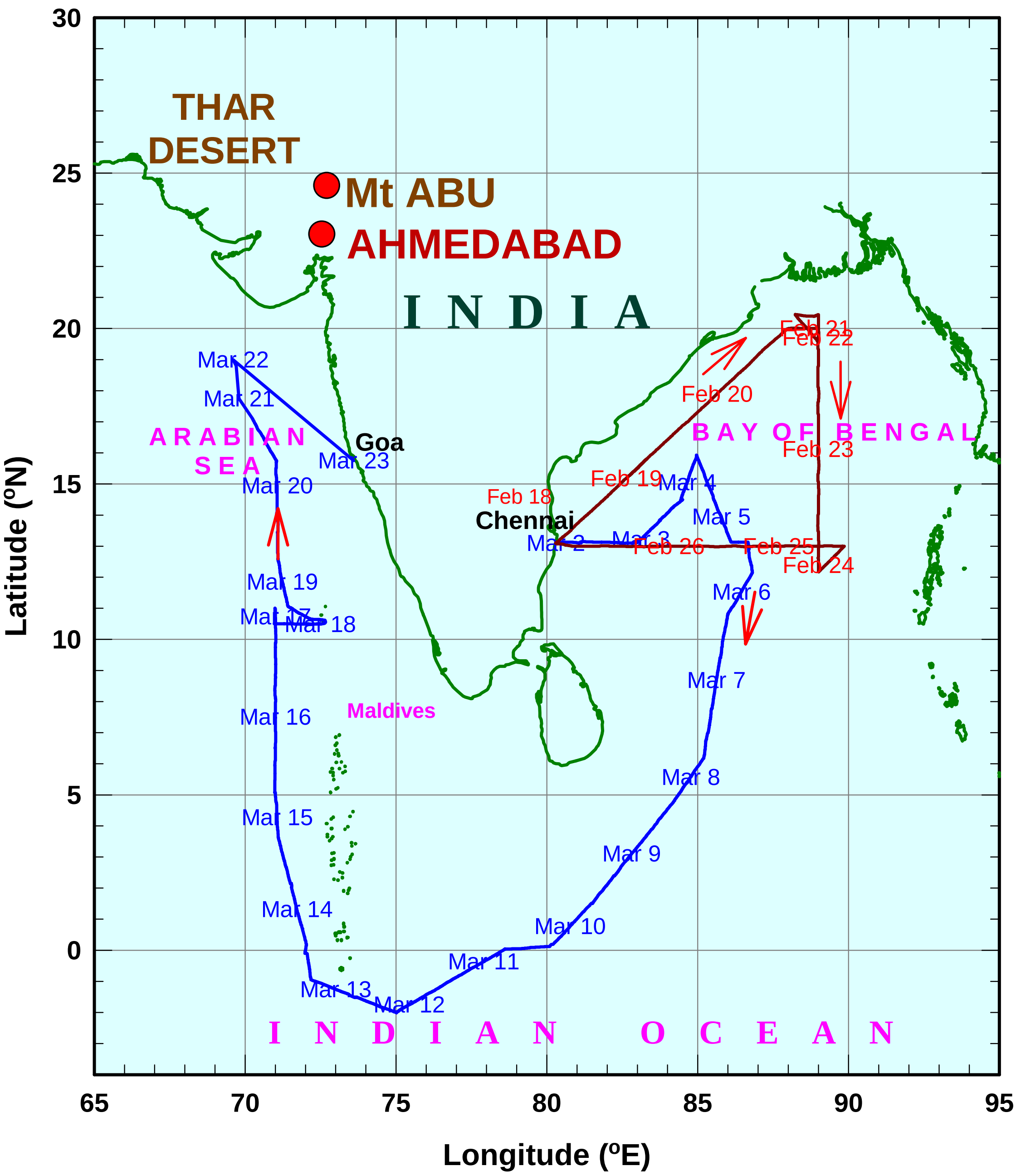

Figure 2.1. Map of India showing the two sampling sites: Ahmedabad and Mt Abu. These sites are located in a semi-arid region of western India. The cruise track onboard ORV Sagar Kanya in the Bay of Bengal, Indian Ocean and the Arabian Sea during Feb-Mar 2001 is also shown along with the sampling dates.

The monthly average temperature over Ahmedabad during Jan-Dec varies between 21 to 34 °C with relatively high temperatures (32 to 34 °C) during summer months (Apr-Jun) and low (21 to 23 °C) during winter months (Dec-Feb). The monthly average RH varies from 26 to 83% with higher RH during SW-monsoon period (Jun-Sept), for rest of the year RH remains less than 40% (Fig. 2.2b).

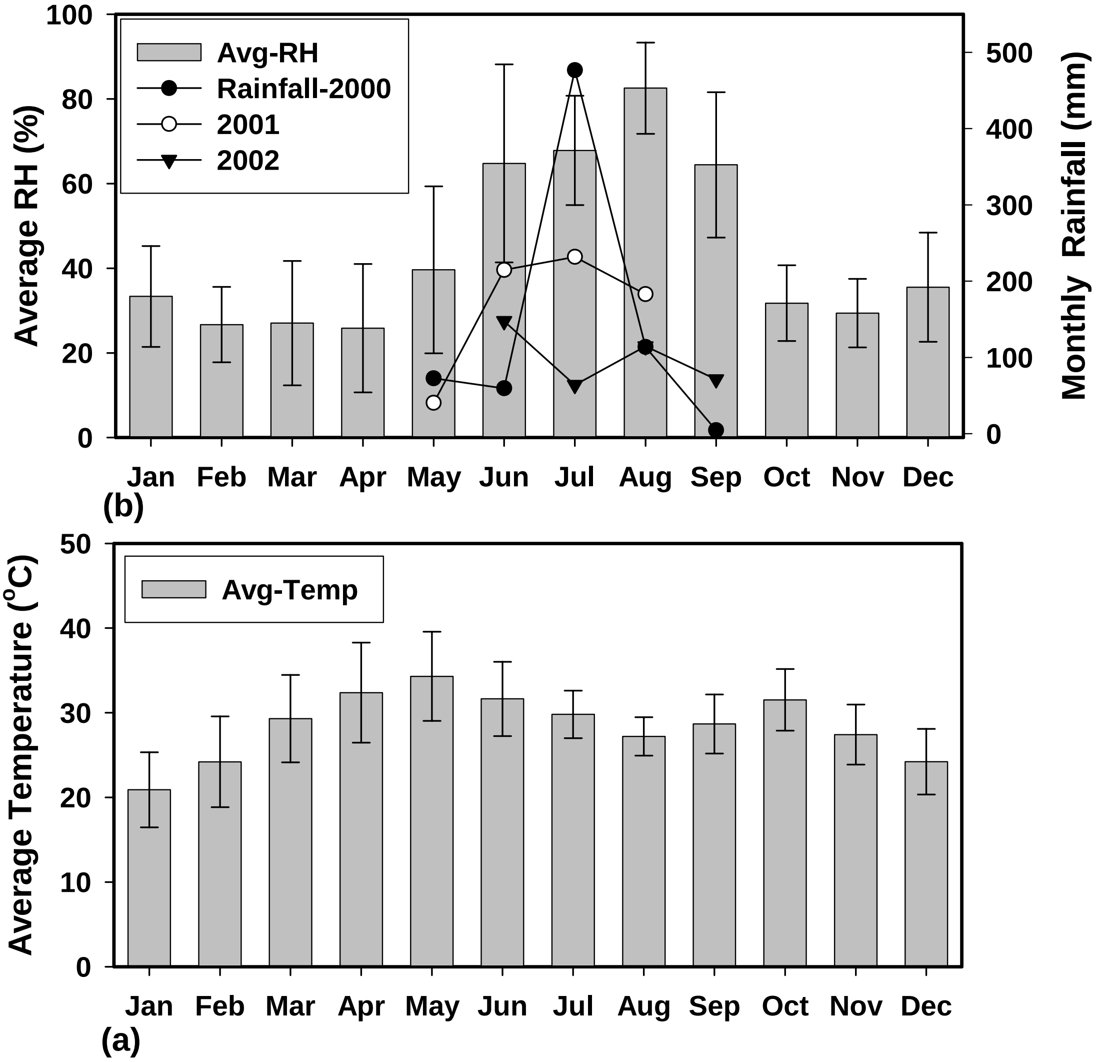

Figure 2.2. Monthly average temperature, RH and rainfall during 2000-2002 over Ahmedabad. Error bar represents the standard deviation of the average values.

The representative average wind patterns from Jan-Dec are shown in Fig. 2.3. The period of May-Aug is dominated by southwesterly winds and that of Nov-Feb by the northeasterly winds (Fig. 2.3). The transition period, between the two major wind patterns, is represented by Mar-Apr and Sept-Oct. During the month of September, the atmospheric transport over study sites has been considered a part of SW-monsoon.

During first-half of September, the predominance of southwesterly winds gradually diminishes.

The sampling set-up for the collection of rainwater and aerosol samples was located on the terrace of an eight-storey building (~40 m above the ground level) in the premises of Physical Research Laboratory, Ahmedabad. The surrounding areas, within a radius of 10 km, are occupied by residential and institutional complexes with overall movement of vehicular traffic. Small-scale industrial complexes are located about 20 km southeast of the site. The emissions from two coal-based thermal power plants, situated in the northeast at a distance of about 10 km (Sabarmati: ~350 MW per day) and 25 km (Gandhi Nagar: 700 MW per day), is an important source of airborne particles.

2.2.2 Mt Abu:

Another sampling site for aerosol study was selected at Guru Shikhar, Mt Abu (24.6°N, 72.7°E, 1680 m asl). Guru Shikhar is a highest mountain peak in the southern end of Aravali range of mountains in western India (Fig. 2.1). The annual rainfall at Mt Abu averages around 600-700 mm and occurs only during SW-monsoon. The site at Guru Shikhar represents free-troposphere characteristics during winter months (Nov-Feb) and lies within the boundary layer during summer months. The proximity of the site to Thar Desert (~300 km), provides an opportunity to assess the role of mineral dust aerosols over the region. The main town of Mt Abu is situated about 10 km from sampling site at an altitude of 1220 m with a population of about 40,000. Therefore, the Guru Shikhar site provides an ideal setting for sampling a relatively clean environment in a semi-arid region. A number of small scale marble quarries are located in the plain region.

2.2.3 Marine boundary layer:

Aerosol sampling was carried out in the MBL of the Bay of Bengal, Indian Ocean and the Arabian Sea during Feb-Mar (2001) period when general wind direction are from continents to ocean (Fig. 2.3). Bulk-aerosol samples were collected onboard ORV Sagar Kanya during the cruises SK-161-A and SK-161-B. The cruise SK-161-A was conducted over the Bay of Bengal (from Feb 18th to 27th 2001, Fig. 2.1); whereas cruise SK-161-B was undertaken through the Bay of Bengal, north Indian Ocean and the Arabian Sea (from Mar 2nd to 23rd 2001, Fig. 2.1).

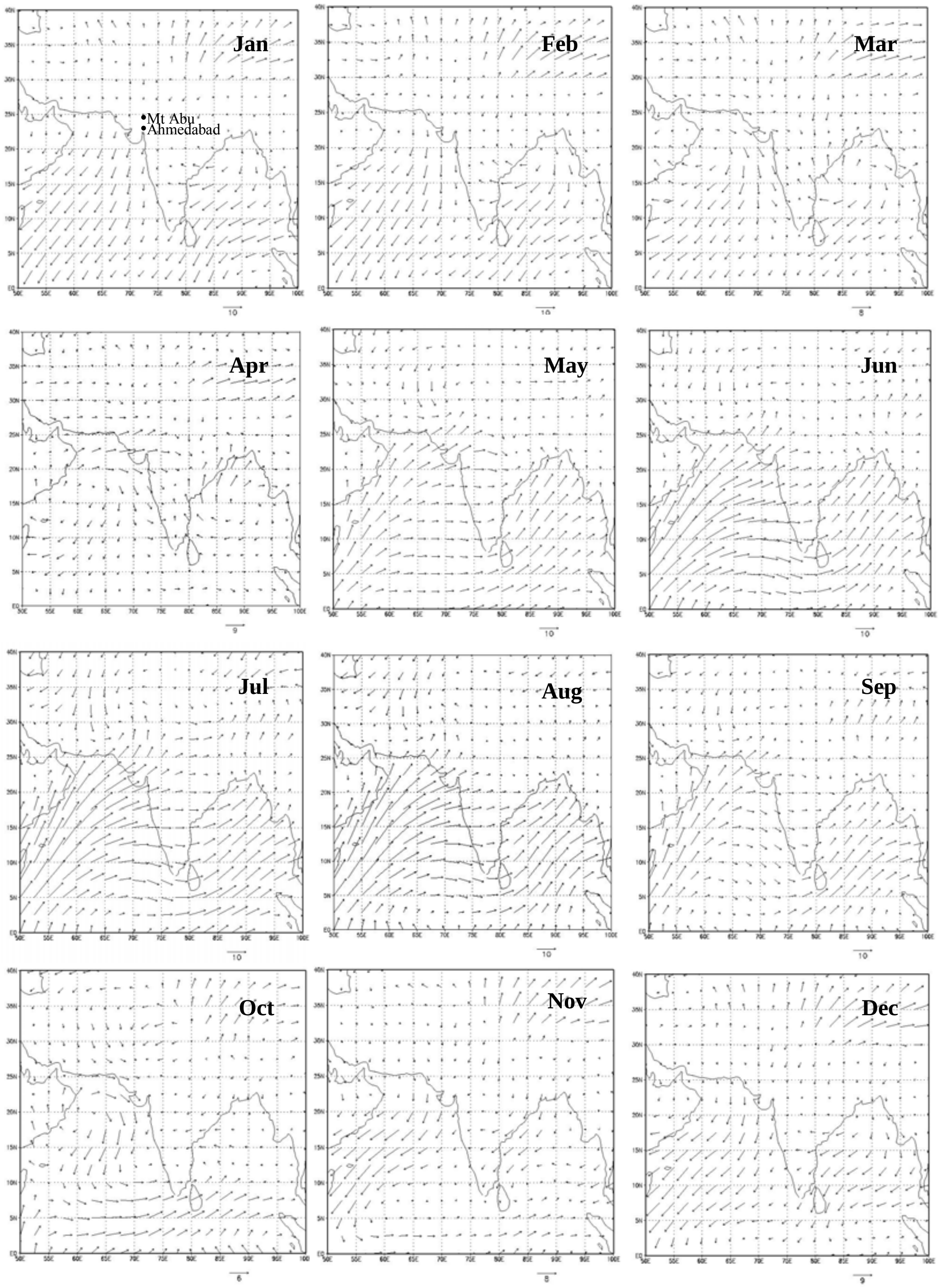

Figure 2.3. Monthly average wind patterns for the study sites at Ahmedabad and Mt Abu. Southwesterly winds dominate during May-Aug while northeasterly winds prevail during Nov-Feb. During Mar-Apr and Sept-Oct, transition between the major wind patterns takes place. The length of arrows represents the magnitude (m s^{-1}) of wind speed (Data adopted from http://www.arl.noaa.gov/ready).

During the cruise period (Feb-Mar 2001), temperature varied between 25 to 32 °C while %RH ranged between 50 to 90% over MBL. Sea condition was generally calm (Force 1 to Force 4) and virtually there was no rainfall over the MBL during the study period.

2.3 SAMPLING

2.3.1 Rainwater sampling:

Rainwater samples were collected from individual rain events, over Ahmedabad, during the period of SW-monsoon (Jun-Sept) for three consecutive years (2000-2002). The total rainfall during 2000 and 2001 was 730 and 680 mm (similar to the average precipitation) while that during 2002, it was only 400 mm, significantly below the normal (data from India Meteorological Department, Ahmedabad). In 2000, almost 65% of the season's rainfall occurred within short duration of ~72 hours (Fig. 2.4). The wet-only precipitation events (ranging from 0.4 to 102 mm) were collected manually using a large diameter PVC funnel (d = 50 cm) fitted to a 5 L polyethylene container. The complete sampling unit (funnel and container) was cleaned with Milli-Q water after each sample collection and was uncovered only during precipitation events, thereby avoiding contribution from dry-fallout. Soon after collection, samples were transferred to the laboratory in pre-cleaned high density polyethylene (HDPE) bottles and filtered using 0.4 μm pore size (47 mm diameter) Nuclepore filters to remove suspended matter, if any. Prior to their use, all HDPE bottles were cleaned repeatedly with distilled water and kept soaked in Milli-Q water (18.2 MΩ resistivity) for atleast 72 hours. In all, 91 samples were collected spread over three years (2000: n = 17; 2001: n = 48; 2002: n = 26). These samples represent individual precipitation either occurring as a single event or successive multiple events in a day (but collected separately). All samples were analyzed for major cations and anions, as discussed in the following section. Whenever the precipitation event exceeded 4 mm, a sample split was drawn for the analysis of ^{210}Pb. These sample aliquots (for ^{210}Pb) were acidified (pH <2) with Quartz distilled HCl (Q-HCl) and stored until analysis. A total of 42 rainwater samples were collected for the assay of ^{210}Pb.

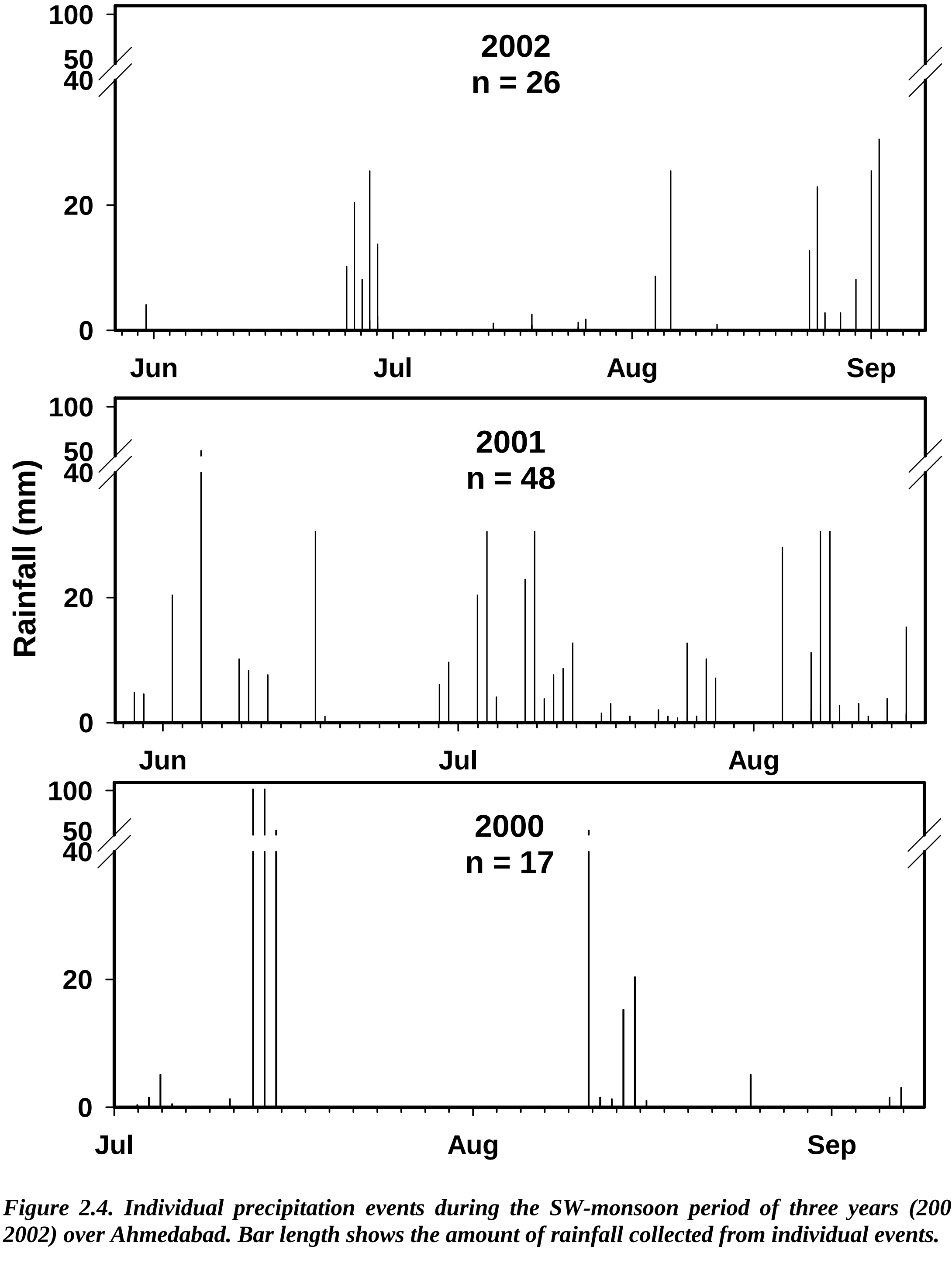

Figure 2.4. Individual precipitation events during the SW-monsoon period of three years (2000-2002) over Ahmedabad. Bar length shows the amount of rainfall collected from individual events.

2.3.2 Aerosol sampling:

Similar to rainwater collection, the sampling site for aerosol collection was also set-up on the terrace of the PRL eight-storey building (~40 m above ground level). Bulk-aerosol samples were collected onto pre-combusted tissuquartz filters (20 x 25 cm, PALLFLEX^{TM}) using high volume air sampler (ENVIROTECH APM 430, flow rate ~1.2 m^3 min^{-1}). The tissuquartz filter has 99.9% collection efficiency for the particle size of 0.3 μm. A uniform sampling frequency was maintained throughout by collecting a sample every tenth day (10th, 20th and 30th of every month). On average, for each sample, ~2000 m^3 of air was filtered by continuous operation of the HV sampler for ~30 hours. A total of 91 samples were collected during June 2000 to January 2003 over Ahmedabad. For a comparative study, 28 samples were collected from Mt Abu during June 2001 to January 2003. A HV sampler was set-up at the terrace of Aeronomy laboratory (1680 m asl) in the campus of Infra-Red Observatory, at Gurushikhar (Mt Abu). A total of 39 samples were collected onboard ORV-Sagar Kanya in cruises SK-161-A and SK-161-B over the marine boundary layer of the Bay of Bengal, Indian Ocean and the Arabian Sea during Feb-Mar, 2001. Sampler was set-up on the upper deck (in front of navigation room, 16 m asl) of the ship. During cruise SK-161-A (Feb 18th to 27th 2001), 18 samples were collected (two samples per day) while during SK-161-B (Mar 2nd to Mar 23rd 2001), 21 samples were collected (one sample per day). All aerosol sampling onboard Sagar Kanya was carried out while cruising at 8-10 knots, thus avoiding the contamination from ship exhaust.

2.4 ANALYTICAL TECHNIQUES

2.4.1 Rainwater analysis:

All rainwater samples were analyzed for pH, electrical conductivity (EC), major chemical species (NH_4^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, $SO_4^=$ and HCO_3^-) and ^{210}Pb (in 42 samples). The pH and EC were measured immediately after sample collection while the chemical analyses were completed within two to three weeks of sampling. A schematic diagram for rainwater sampling and analyses is shown in Fig. 2.5.

(1) pH and Electrical conductivity (EC) measurement:

The pH of rainwater samples were measured using glass electrode attached to a Auto-titrator system (Metrohm 702 SM Titrino) with the precision of ±0.01 pH unit.

Prior to measurement, the system was calibrated with buffer solutions of pH 4.00 ± 0.05, 7.00 ± 0.05 and 9.20 ± 0.05 (freshly prepared from capsules procured from (Merck®). EC was measured by a conductivity probe (Multiline F/Set-3) after calibrating the probe with 0.01 M KCl solution.

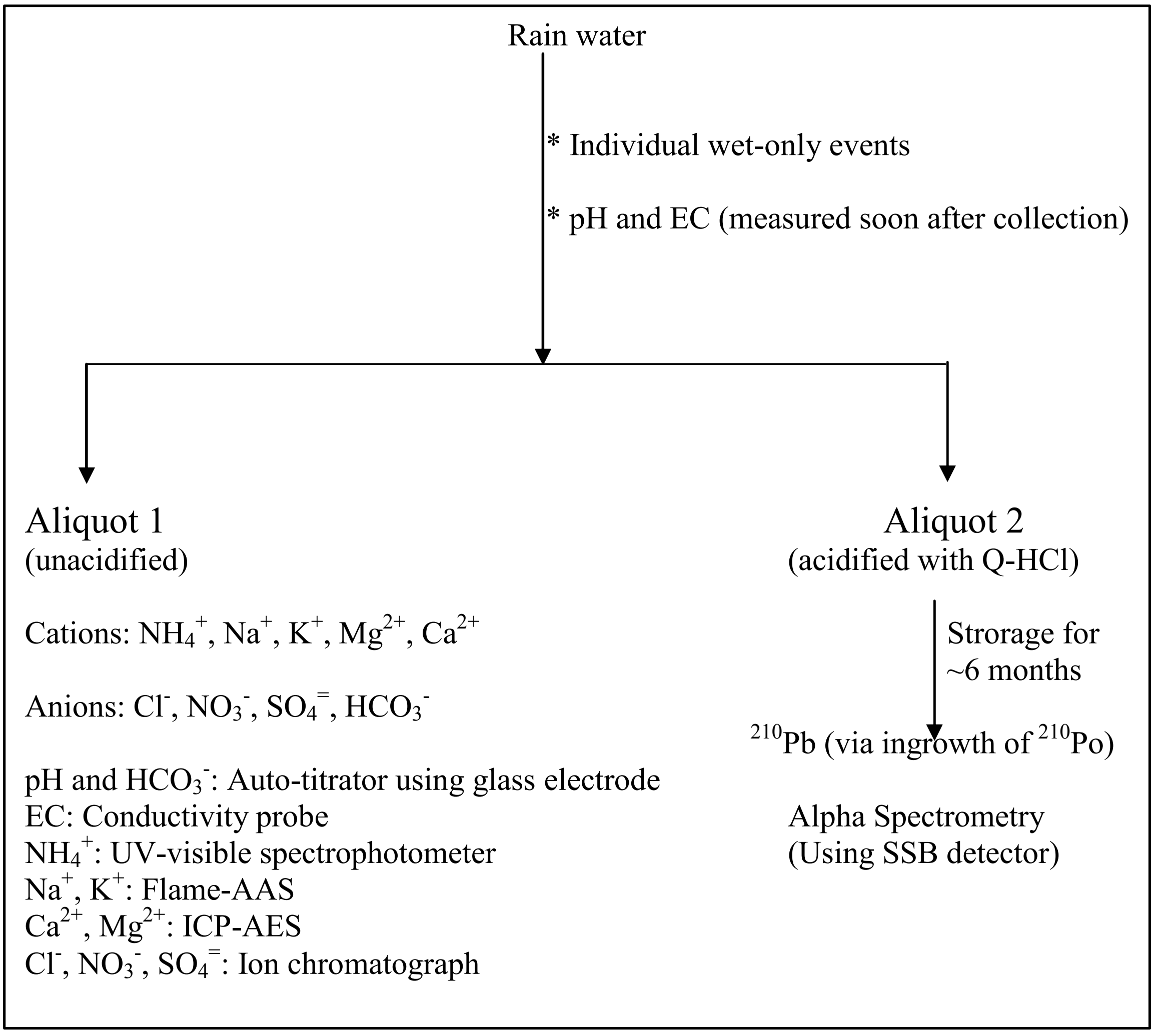

Figure 2.5. Analytical scheme adopted for sampling and analyses of wet-only individual precipitation events.

(2) Major ions:

The abundance of NH_4^+ in all samples was measured by indo-phenol blue method (Weatherburn, 1967) on a UV-Visible spectrophotometer (Beckman, Model 26). Repeat measurements of standards and samples show that precision was better than 2% for NH_4^+. Na^+ and K^+ concentrations were measured on Atomic absorption spectrophotometer (Flame-AAS, Perkin Elmer Model, 4000) using air-acetylene flame and measuring absorbance at wavelengths of 589 nm (Na) and 766.5 nm (K).

Based on the replicate analysis, the precision of the measurements was determined to be better than 2%. The concentrations of Ca^{2+} and Mg^{2+} were measured by Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES, Jobin Yvon, Model 38S) by sequential scanning of the emission lines at 422.673 and 279.806 nm respectively.

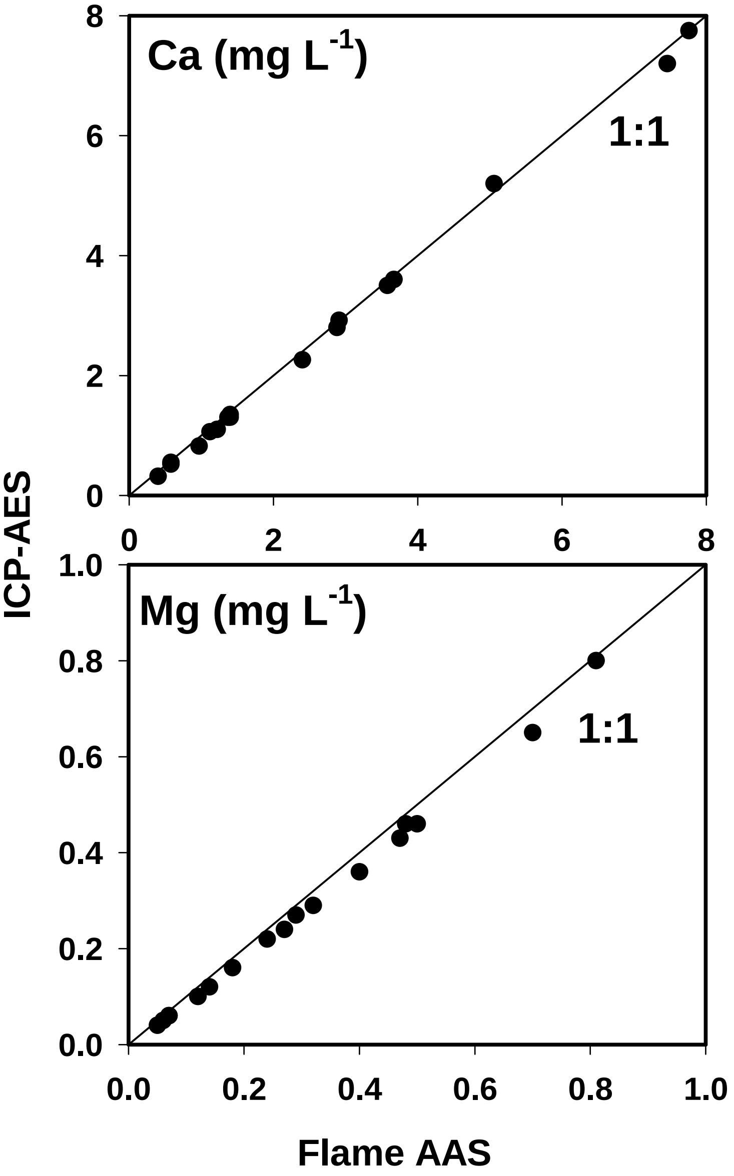

Figure 2.6. Comparison of Mg^{2+} and Ca^{2+} measured in samples using Flame-AAS and ICP-AES. The data exhibits the good agreement between the two techniques.

The ICP-AES was equipped with a Czerny-Turner monochromator of 1 m focal length and 3600 grooves/mm holographic grating. The optical resolution, measured with respect to Cobalt (Co) emission line at 228.616 nm, was found to be 0.006 nm. In case of rainwater samples collected during year the 2000, Ca^{2+} and Mg^{2+} were also measured on Flame-AAS to check the accuracy of analytical measurements with those of ICP-AES. To minimize the effect of chemical and ionization interference on Ca^{2+} measurements on Flame-AAS, lanthanum and potassium were added (at 2000 μg/mL) to all standards and samples. A comparison of the results obtained using the two techniques is shown in Fig. 2.6. A systematic offset of the flame-AAS Mg^{2+} data from the 1:1 line is within 2%. The flame-AAS was usually preferred for low concentrations of Mg^{2+} (< 0.5 mg L^{-1}) and the ICP-AES for higher concentrations (> 0.5 mg L^{-1}) in rain samples. The EC measurement was used as a guide to assess the relative abundances of major constituents in rainwater. Based on the replicate analyses of standards and samples, the precision was determined to be better than 5% for Ca^{2+} and Mg^{2+} on ICP-AES.

The Cl^-, NO_3^- and $SO_4^=$ were measured by Ion Chromatograph (Dionex series 2000i/SP). The analytical separation was achieved on AG4/AS4 columns coupled to an anion-self-regenerating-suppressor (ASRS) in recycle mode and detected by conductivity detector. The samples were injected through 50 μl loop and a combination of Na_2CO_3 (1.8 mM) and $NaHCO_3$ (1.7 mM) was used as an eluent maintained at a flow rate of 1.8 mL min^{-1}. Depending upon the concentrations of individual ions, samples were run at 3 μS, 10 μS and 30 μS scales. The precision, estimated from the standard deviation of repeat measurements of standards and samples, was better than 4% for Cl^-, NO_3^- and $SO_4^=$. Bicarbonate (HCO_3^-) was measured by acid (~0.001 N HCl) titration using Auto-titrator system (Metrohm 702 SM Titrino) in combination with a glass electrode and fixed pH (4.3) end point method. Based on repeat analysis of a number of samples and standards, the reproducibility of bicarbonate measurements is ~2%. In addition, field blanks (Milli-Q water handled along with the precipitation samples) were also analyzed and concentrations of all ions were found to be below their detection limits, as given in Table 2.1.

For all major ions, calibration curve was established using standard solutions prepared in the laboratory by dissolving analytical grade NH_4Cl (for NH_4^+), Na_2CO_3 (for HCO_3^-), NaCl (for Na^+ and Cl^-), KNO_3 (for NO_3^-), KCl (for K^+), Na_2SO_4 (for $SO_4^=$) and $CaCO_3$ (for Ca^{2+}). Pure Mg metal was dissolved in HCl to prepare stock solution for Mg^{2+}. The stock solutions (1000 mg L^{-1}) were suitably diluted for the analysis so that concentration/absorbance was in the linear analytical range. Along with the laboratory standards, commercial standards (Merck® and Calmix-7) were also analyzed to ascertain the accuracy of the measurements. The results showed that accuracy was better than 5% for all measured elements.

Table 2.1 Detection limits (DL) of major ions.

	NH_4^+	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	NO_3^-	$SO_4^=$	HCO_3^-
DL (μg/mL)	0.016	0.01	0.02	0.005	0.04	0.05	0.05	0.10	0.37
DL (μeq/L)	0.9	0.4	0.5	0.4	2.0	1.4	0.8	2.1	6.0
Precision (%)	2	2	2	5	5	4	4	4	2

(3) ^{210}Pb in rainwater:

The analytical procedure adopted for ^{210}Pb analysis in rainwater is summarized in Fig. 2.7. In brief, samples splits from precipitation events exceeding 4 mm were acidified with Q-HCl to pH <1. Subsequently Pb was precipitated as $PbCrO_4$ (at pH ~ 4), scavenged with $Fe(OH)_3$ (at pH ~ 7) and cleaned on 1.5 M HCl column (Fig.2.7). After radiochemical separation, purified Pb fraction was stored for 6 months to allow ingrowth of ^{210}Po and ^{210}Pb. The ingrown ^{210}Po was auto-plated on Ag-disc in presence of a spike solution (^{209}Po) of known strength. The activities of Po isotopes (^{209}Po and ^{210}Po) were assessed on alpha spectrometer according to the procedure described by Sarin et al (1992). Detectors had background counts of <5 counts per day in the energy region of 4.9 and 5.3 MeV, corresponding to the α energies of ^{209}Po and ^{210}Po, respectively. On average, samples were counted for 3-5 days in order to get the counting statistics better than 5%. The ^{210}Pb activity in the rainwater samples was calculated from the ingrown activity of ^{210}Po, corrected for the Pb yield and decay between date of collection and the date of 1.5 M HCl column separation. Procedural blanks starting with distilled water were also prepared along with the samples. The blank level of ^{210}Pb arising mainly from the reagents and Pb carrier are presented in Table 2.2.

Table 2.2 Procedure blanks for ^{210}Pb in rainwater samples.

Code	^{210}Pb	
	dpm	Error
BLK-1	0.039	0.008
BLK-2	0.041	0.005
BLK-3	0.048	0.004
BLK-4	0.022	0.003

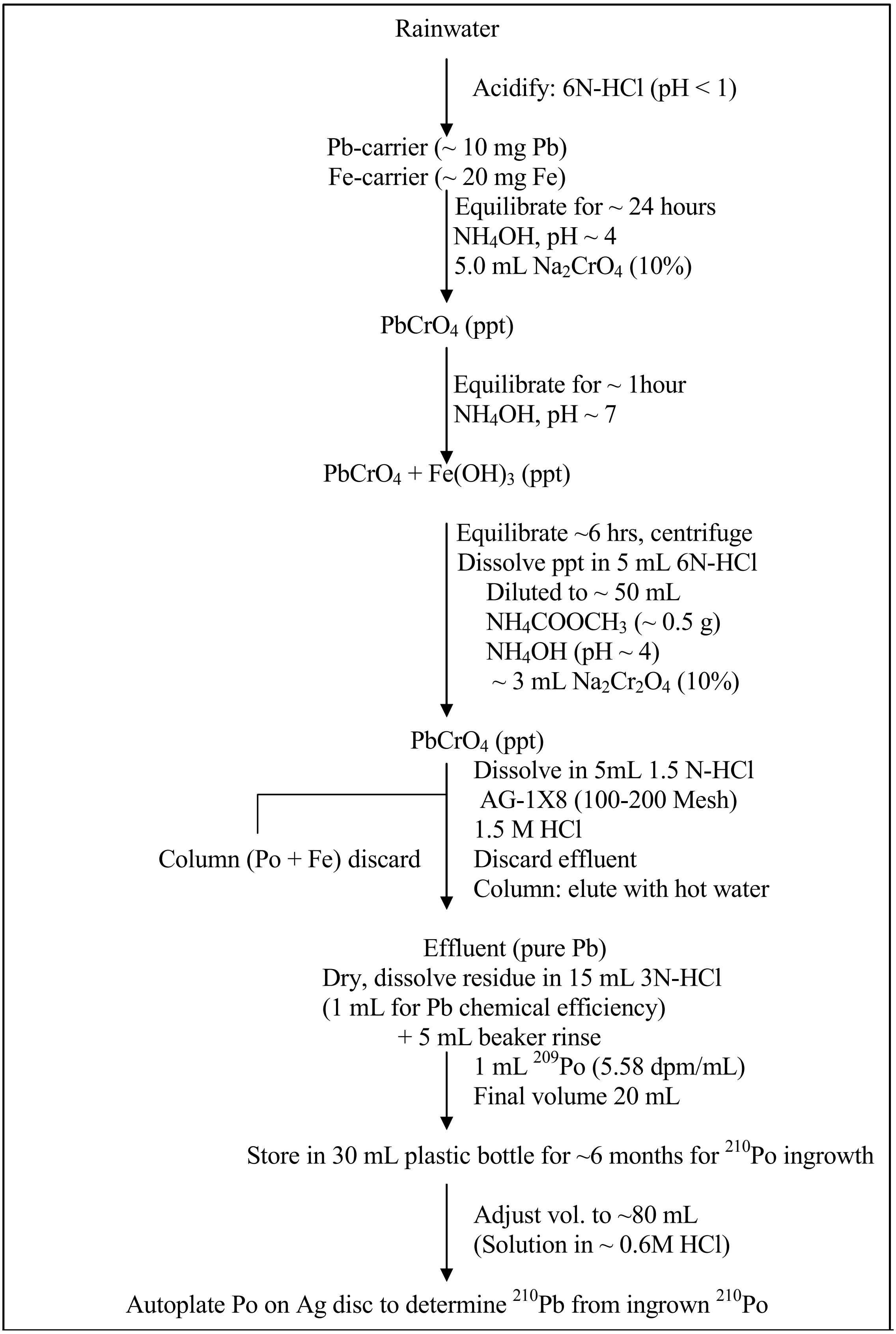

Figure 2.7. Analytical procedure for ^{210}Pb analysis (via ^{210}Po) in rainwater by alpha spectrometry, for details reference is made to Sarin et al (1992).

2.4.2 Aerosols analysis:

All aerosol samples collected from Ahmedabad, Mt Abu and marine boundary layer were analyzed for water-soluble chemical species (NH_4^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, $SO_4^=$ and HCO_3^-), acid-soluble constituents (Al, Fe, Mn, Ca, Mg, Na, K, Zn and Pb) and for radioisotopes (^{7}Be and ^{210}Pb). The sampling and analytical scheme adopted for aerosol study is outlined in Fig. 2.8.

(1) Sample preparation for aerosols:

One-half portion of the filter was cut with the help of a clean stainless steel scalp blade, placed in a Teflon vial, soaked in 15 mL of Milli-Q water (18.2 MΩ resisitivity) for ~30 minutes and ultrasonicated for 10 minutes. The water-extract was centrifuged and transferred to a pre-cleaned 125 mL HDPE bottle. The filter was successively leached with Milli-Q water (15 mL x 5), the leaches were centrifuged, combined and total volume was made-up to 100 mL for the analyses of water-soluble ionic species. The entire handling of the filter was done under a clean laminar flow bench. After the water extraction, the filter was treated with 10 mL of 6N-Q-HCl in a 100 mL Teflon beaker. The extract was separated and the filter was successively leached with acid followed by Milli-Q water. The leaches were combined and total volume was made-up to 50 mL, and solution was stored in a pre-cleaned 60 mL HDPE bottles for the analyses of acid-soluble constituents. All teflonwares were cleaned with concentrated HNO_3 during the course of sample preparation. HDPE bottles were kept soaked in acidified ($pH < 2$) water for atleast 72 hours. Several ($n = 13$) blank filters (one-half portion) were also leached with Milli-Q water and Q-HCl alongwith several batches of sample filters in order to assess the filter and procedural blank contribution to aerosol chemical data.

(2) Chemical analysis of aerosols:

Water extracts of aerosol samples were analyzed for major ions by following the analytical procedures described for the analysis of rainwater in section 2.4.1. Samples were suitably diluted to bring the concentrations in the linear analytical range. The precision of measurements for all major ions analyzed in rainwater and aerosol samples was assessed and the results are shown in Fig. 2.9.

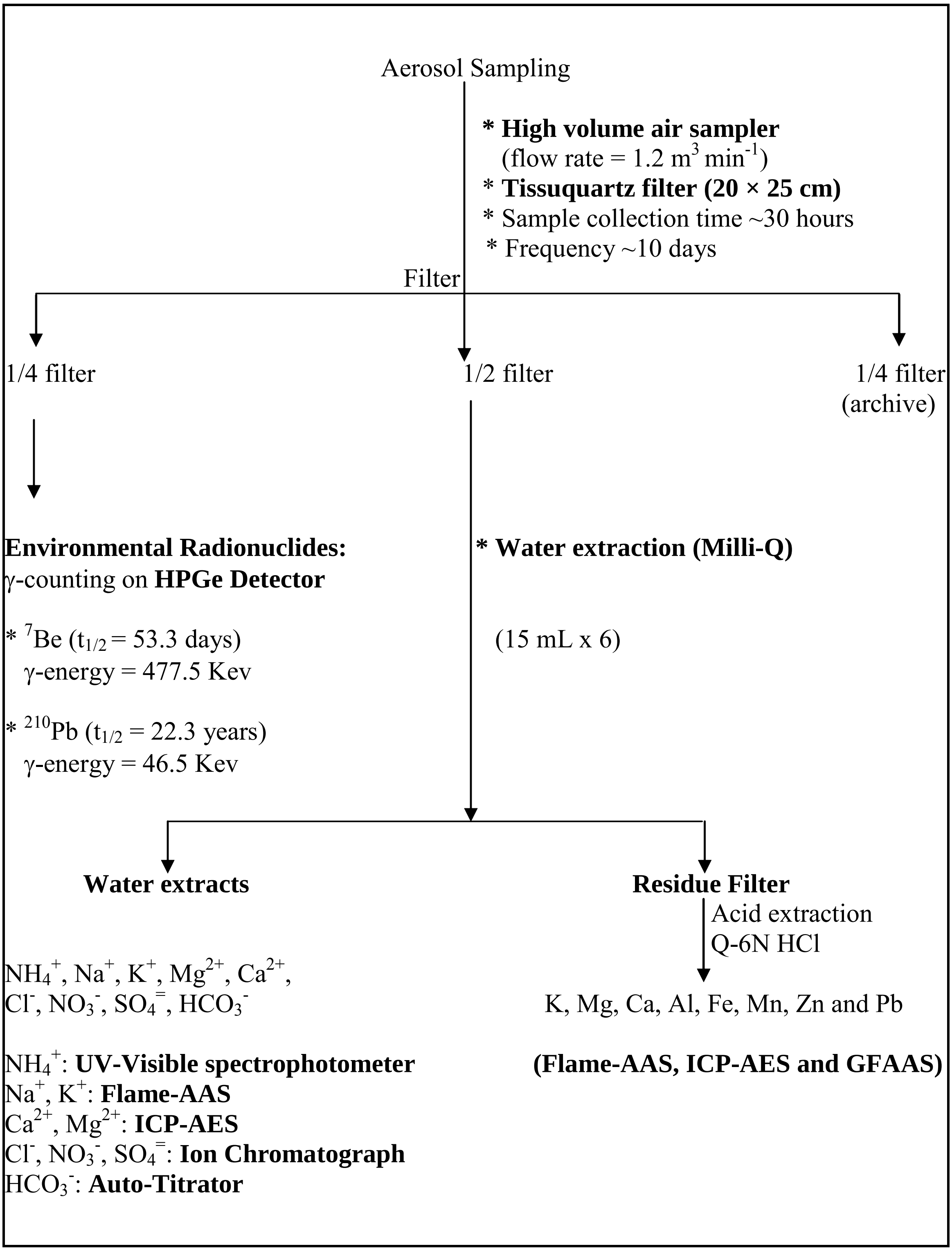

Figure 2.8. Analytical scheme for the sampling and analysis for bulk-aerosol samples collected over Ahmedabad, Mt Abu and marine regions.

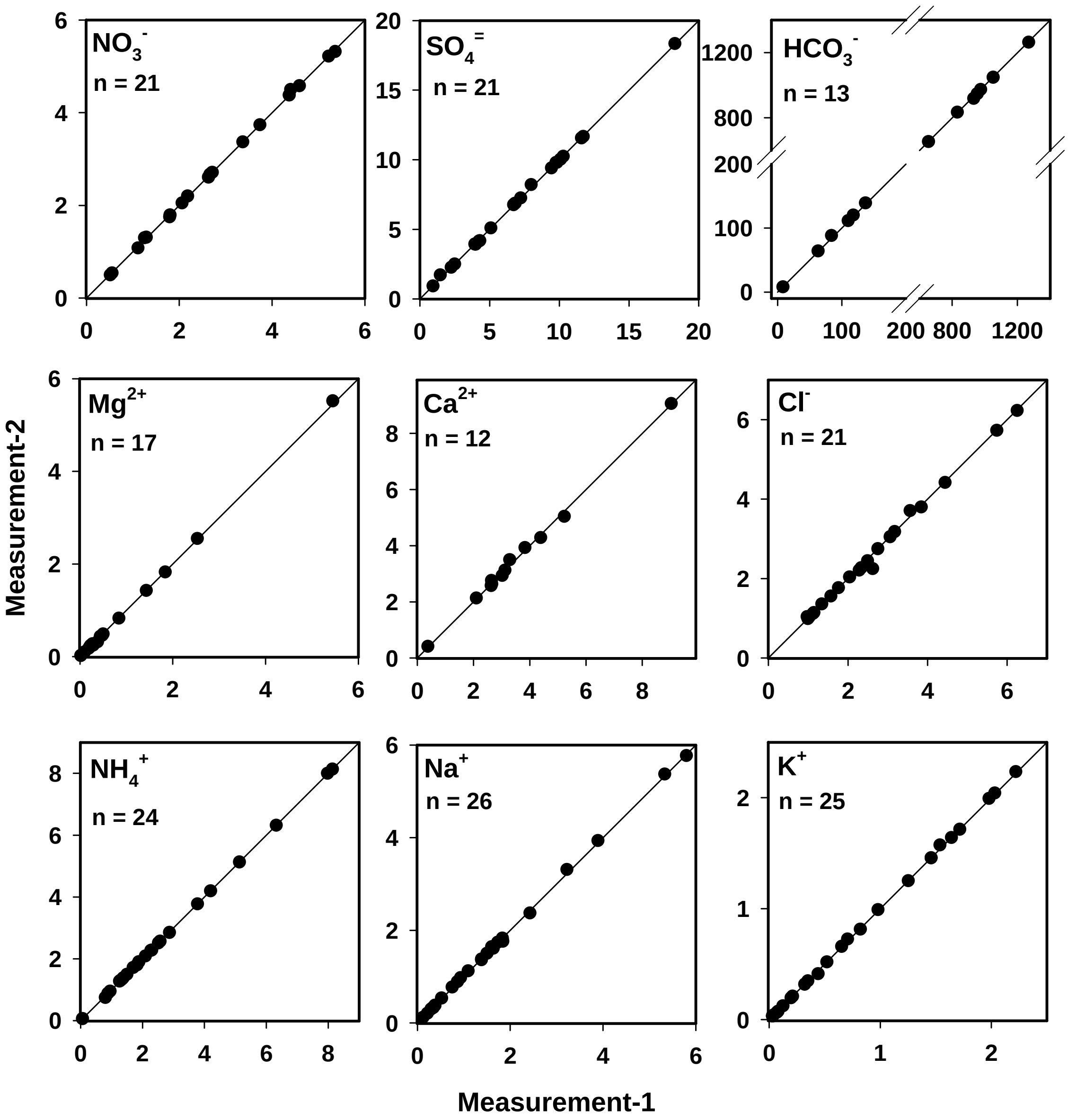

Figure 2.9. Repeat measurements of the chemical species (mg L^{-1}) in rainwater and aerosol samples. Solid lines represent 1:1 correspondence between the data. An equal number of rainwater and aerosol samples were analyzed for repeat measurement.

The procedural blanks were less than 25% of the minimum concentration for Na^+ (0.03 μg m^{-3}) and Cl^- (0.05 μg m^{-3}) observed over Mt Abu and less than 10 % for the remaining ionic species. Accordingly, concentrations of ionic species were corrected for procedure blank. The filter blanks (including procedure blanks) measured for all major ions are given in Table 2.3. Based on the blank concentrations in tissuquartz filters and average volume of air filtered (~2000 m^3), the detection limits for the water-soluble ionic species in aerosols are 1.6 , 12 ± 5, 1.5 ± 0.8, 1.2 ± 0.9, 3.0 ± 1.9, 10 ± 6, 5.0 , 9.0 ± 0.8, and 37 ng m^{-3} for NH_4^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, $SO_4^=$

and HCO_3^-, respectively. Detection limits for NH_4^+, NO_3^- and HCO_3^- in aerosols were calculated based on their instrumental detection limit; 16, 50 and 370 ng mL^{-1}, respectively.

Table 2.3 Average concentration and standard deviation (sd) of ionic species in blank tissuquartz filter (for n = 13) including procedure blank, and their detection limits in aerosols.

	NH_4^+	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	NO_3^-	$SO_4^=$	HCO_3^-
Avg (μg/filter)	3.2	23	3.1	2.5	5.9	21	10	18	73
sd (μg/filter)	-	9	1.6	1.7	3.8	11	-	4	-
Avg (ng m^{-3})	1.6	12	1.5	1.2	3.0	10	5.0	9.0	37
sd (ng m^{-3})	-	5	0.8	0.9	1.9	6	-	1.8	-

Among acid-soluble constituents, Mg, Ca and Al were analyzed by ICP-AES; Fe, Mn, Zn and K by Flame-AAS; Pb by ICP-AES and Graphite Furnace Atomic Absorption Spectrophotometer (GFAAS, Perkin-Elmer AAS, AAnalyst 100 coupled to a Graphite Furnace, HGA 800). In all cases, recommended analytical and instrument settings were used. Commercial standards (Merck®, 23 elements) were used for calibration of Fe, Mn, Zn and Pb. Based on repeated analyses of number of samples and standards, reproducibility of Al, Fe, Mn, Zn and Pb are 5, 2, 2, 2 and 5%, respectively. To further ascertain the accuracy of the measurements for the acid-soluble species, a standard addition method was adopted for the determination of Al and Ca on ICP-AES and for Pb on GFAAS and ICP-AES. The difference between the expected and measured concentrations of Al, Ca and Pb were found to be within the analytical uncertainty limits as shown in Fig. 2.10 and Fig. 2.11. Such a comparison also reveals that the matrix effects arising from water- and acid-leaching of the tissuquartz filters have not affected the analytical measurements.

Filter blanks (inclusive of procedure blanks) were also ascertained for the acid-soluble species as tabulated in Table 2.4.

Table 2.4 Filter blanks (including procedure blanks) for acid-soluble species.

	Al	Fe	Ca	Mg	K	Mn	Zn	Pb
Avg (μg/filter)	26	33	33	2.3	5.5	0.4	3.1	0.4
sd (μg/filter)	15	16	23	2.1	4.0	0.1	2.1	0.4

These values are less than 5% of the minimum concentration collected on filters for all species except for Zn, for which a few samples have shown concentrations close to filter blank. Pb concentrations in filter blank were very low (~10 ng mL^{-1}) or below detection limit (5 ng mL^{-1}).

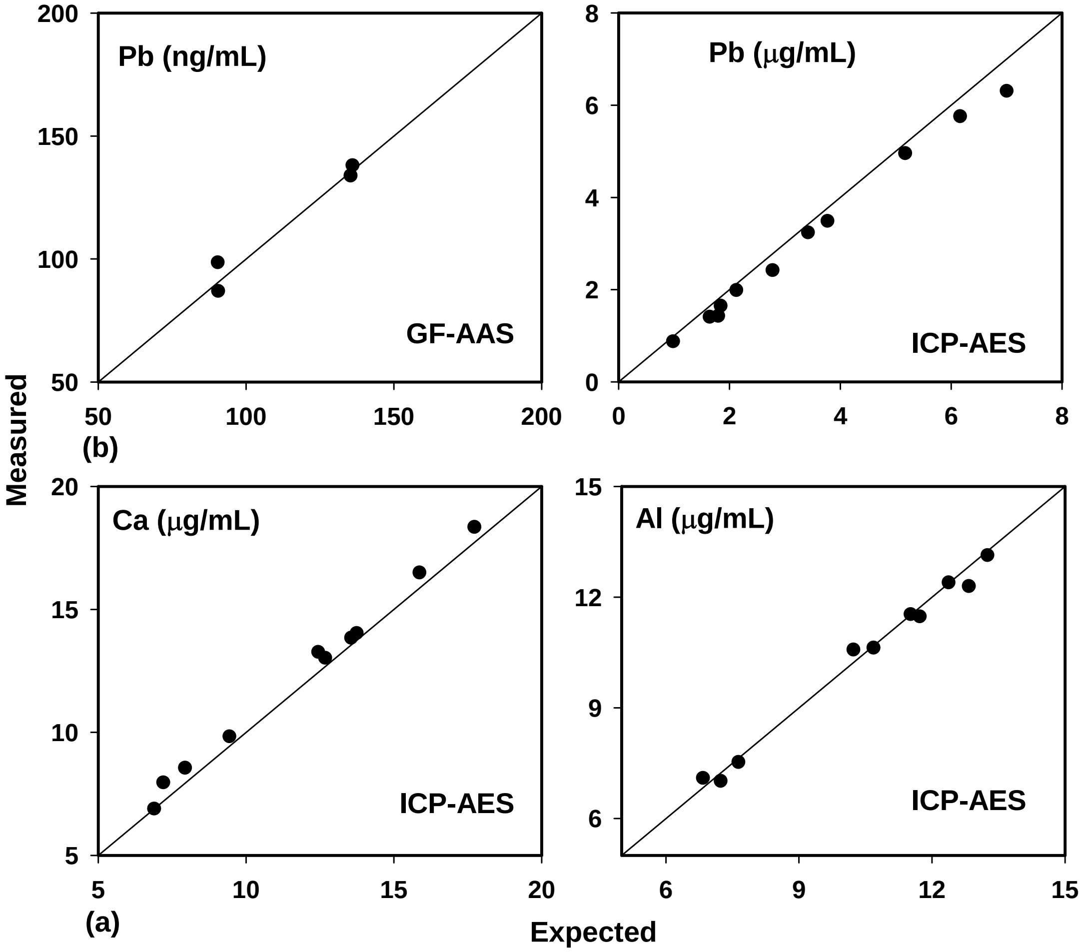

Figure 2.10 (a). Standard addition method to check the matrix effect on the concentrations of Al and Ca on ICP-AES. (b) The accuracy of Pb analysis on ICP-AES and GFAAS. The concentrations measured on GFAAS were 2 to 3 orders of magnitude lower than those analyzed by ICP-AES.

2.4.3 Environmental radionuclides:

For ^{7}Be and ^{210}Pb, one-fourth portion of the sample filter was cut into several strips and packed in a plastic vial (height 5 cm, diameter 2 cm) with a clean Teflon rod and analyzed for ^{7}Be and ^{210}Pb on a high-purity-Germanium (HPGe) well detector (Canberra Model GCW 2523) coupled to Canberra series 35 multi channel analyzer (MCA) (Canberra Series 35+). The detector had active volume of 120.3 cm^{3}, well depth and diameter of 35 and 20.5 mm, respectively. A 15 cm thick lead shielding was used to reduce the background of the detector. MCA was calibrated with respect to 1173 and 1332 keV energy peaks of ^{60}Co point source. The sample counts under the gamma energies at 46.5 keV (intensity = 4.05%) and 477.5 keV (intensity = 10.4%) for ^{210}Pb and ^{7}Be, respectively were used to calculate their activities. The counting efficiency of the detector for ^{7}Be was determines using a ^{238}U standard source, in equilibrium with its daughters.

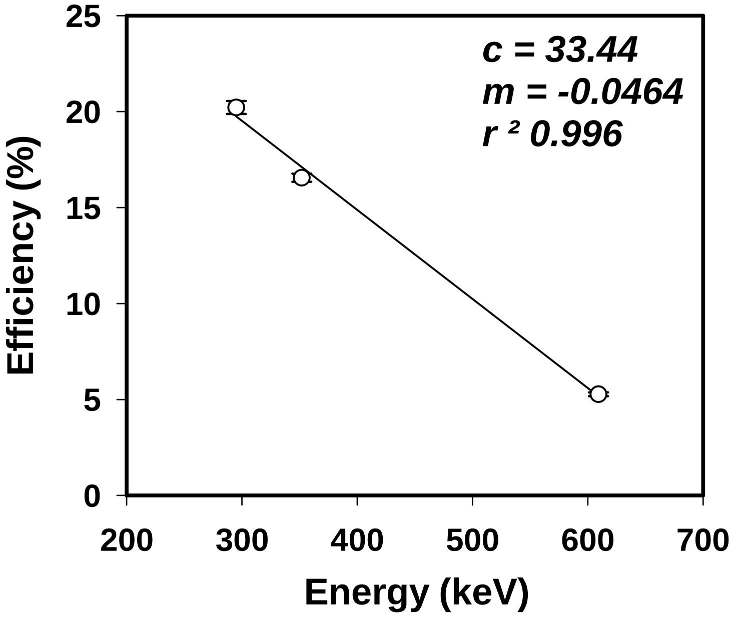

Figure 2.11. Regression plot between the energy of gamma photons of ^{214}Pb (295 and 352 keV) and ^{214}Bi (609 keV) and their detection efficiency. This relation was used to calculate the detection efficiency of ^{7}Be on HPGe detector (Rengarajan and Sarin, 2004).

The efficiency was obtained from the linear interpolation of counting efficiencies for ^{214}Pb (295 and 352 keV) and ^{214}Bi (609 keV) as shown in Fig. 2.11, the counting efficiency for ^{7}Be (477.5 keV) was 11.32 ± 0.52%. ^{7}Be activities were corrected for the decay from time of collection to date of counting. For ^{210}Pb, the detector efficiency was determined from the above standard source, in which the ^{210}Pb activity was precisely measured by alpha spectrometry, via ^{210}Po. For further details reference is made to Rengarajan and Sarin (2004). The propagated errors (errors arising from detector calibration and sample counting) were less than 5% for ^{7}Be and 12% for ^{210}Pb. The activities of ^{210}Pb in several aerosol samples collected during SW-monsoon period were found to be below detection limit (0.10 mBq m^{-3}). A few blank filters equivalent to quarter filter were packed in a plastic vial and counted as samples for ^{7}Be and ^{210}Pb. The gross counts were similar to the background counts in the adjacent channels. Therefore, no blank corrections were made while calculating ^{7}Be and ^{210}Pb concentrations in aerosols.

Chapter 3

CHEMICAL CHARACTERISTICS OF AEROSOLS

3.1 INTRODUCTION

The composition of aerosols is highly variable in space and time and depends upon the relative contribution from diverse sources (sea-salts, mineral dust and anthropogenic emissions). In this context, mineral aerosols produced from windblown soils are an important component of the atmosphere especially over arid and semi-arid regions (Dentener et al., 1996; Song and Carmichael, 2001). On the other hand, rapid industrial development in Asia is responsible for increasingly high concentrations of a variety of air pollutants (like SO_2 and NO_x) (Galloway, 1995; Arimoto et al., 1996; Streets et al., 2003). The ionic composition of aerosols determines to a large extent its acidic or alkaline nature. NH_4^+ and $CaCO_3$ are the major neutralizing species of aerosols and their relative importance over a particular region can be ascertained by comparing their levels in precipitation (Clarke and Karani, 1992).

This thesis study deals with aerosol composition and their temporal variations over the two study sites, Ahmedabad (23.0^{o}N, 72.6^{o}E) and Mt Abu (24.6^{o}N, 72.7^{o}E), and addresses to the issue of uptake of acidic species (NO_3^- and $SO_4^=$) by the mineral aerosols ($CaCO_3$). In addition, the long-range transport of continental aerosols to the Bay of Bengal, Indian Ocean and the Arabian Sea during the late NE-monsoon (Feb-Mar) is also discussed.

3.2 RESULTS AND DISCUSSION

The long-term aerosol data collected over Ahmedabad and Mt Abu has been sub-divided into two groups based on the seasonal wind fields. Monthly average wind patterns over India are presented in Fig. 2.3. The sampling period of May-Aug, when southwesterly winds prevail accompanied by SW-monsoonal precipitation, is referred as WET phase. The remainder time period of the year (Jan-Apr and Sept-Dec), is referred to as DRY period, when atmospheric transport over the study sites is dominated by northeasterly flow. These distinctly different wind fields impart extreme temporal variability in the aerosol characteristics.

3.2.1 Water-soluble ions in aerosols:

The range, arithmetic mean and standard deviation of the abundances of water-soluble inorganic ions (NH_4^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, $SO_4^=$ and HCO_3^-) in the aerosols and their non-sea-salt (nss) components during the WET and DRY periods are summarized in Table 3.1. The ionic concentrations in aerosols are higher over Ahmedabad than those over Mt Abu because of the difference in their altitude above sea level (Ahmedabad being closer to sea level). Abundances of all species, except Ca^{2+}, $SO_4^{=}$ and HCO_3^-, show large seasonal variations at both the sites (Table 3.1). These differences arise due to varying source strength of aerosols, meteorological parameters and physico-chemical transformation processes in the atmosphere.

For comparison, aerosol data reported over a few Indian cities (Mumbai: 19.4°N, 72.8°E, Pune: 18.5°N, 73.8°E and Agra: 27.2°N, 78.1°E) are also given in Table 3.1. The data over Ahmedabad and Mt Abu are based on the long-term average of the two different seasons (WET and DRY) while those from other sites represent short-term collection of aerosols during Nov-March. The concentrations of almost all species are highest over Agra (characterized by large scale industrial pollution) and lowest over Mt Abu; while comparable levels are observed over Pune and Ahmedabad (Table 3.1). The concentration of NH_4^+ is 5-10 times higher over Agra and Pune than that over Ahmedabad and Mt Abu while K^+, NO_3^- and $SO_4^{=}$ are several times higher over Mumbai and Agra than those over other sites (Table 3.1). These regional differences in ionic composition arise due to varying contribution of chemical species from natural and anthropogenic sources and their relative source strengths. Sources of ionic species in aerosols over Ahmedabad and Mt Abu are discussed in the later sections.

3.2.1.1 Charge balance:

The charge balance between total cations (Σ^+) and total anions (Σ^-) measured in the water extracts of aerosols is shown in Fig. 3.1. The Σ^+/Σ^- ratio varies from 0.80 to 1.14 (Av: 1.02, sd: 0.08) over Ahmedabad and 0.86 to 1.19 (Av: 0.96, sd: 0.07) over Mt Abu. However, few of the samples collected during Nov-Feb show noticeable anion deficit over Ahmedabad (urban site) in comparison to those from Mt Abu (high-altitude site) (Fig. 3.1). The departure of data from equiline could possibly arise due to contribution of organic ions during drier months (Nov-Feb). The earlier studies from the Indian region (Kulshrestha et al., 1998; Momin et al., 1999; Venkataraman et al., 2002) had reported on the cation excess in the ion balance of water extracts, which is largely attributed to the lack of bicarbonate measurements.

Table 3.1 Ionic composition of aerosols over Ahmedabad and Mt Abu. All concentrations are in μg m^{-3}.

	Ahmedabad (n = 99)								Mt Abu (n = 25)								Mumbai[a]	Pune[b]	Agra[c]
	WET*				DRY[#]				WET				DRY				DRY	DRY	DRY
Component	Min	Max	AM[d]	SD[e]	Min	Max	AM	SD	Min	Max	AM	SD	Min	Max	AM	SD	AM	AM	AM
NH_4^+	0.004	0.18	0.05	0.06	0.02	1.31	0.48	0.34	bd	bd	-	-	0.023	1.41	0.37	0.38	-	2.14	6.52
Na^+	0.71	4.78	2.42	1.08	0.39	1.75	0.81	0.23	0.56	2.38	1.46	0.74	0.03	0.59	0.28	0.19	2.2	0.48	2.97
K^+	0.09	0.54	0.23	0.09	0.23	1.84	0.76	0.32	0.04	0.22	0.13	0.06	0.06	0.43	0.2	0.09	8.9	0.43	2.50
nss-K^+	0.03	0.41	0.14	0.08	0.20	1.80	0.73	0.32	0.02	0.14	0.08	0.04	0.04	0.42	0.19	0.09	-	-	-
Mg^{2+}	0.15	0.66	0.37	0.15	0.08	0.41	0.25	0.07	0.13	0.6	0.33	0.15	0.04	0.16	0.09	0.04	2.2	0.23	1.24
nss-Mg^{2+}	0.00	0.32	0.08	0.09	0.00	0.29	0.15	0.06	0.06	0.35	0.15	0.09	0.02	0.1	0.06	0.02	-	-	-
Ca^{2+}	1.12	5.41	2.54	0.97	1.55	6.83	2.96	0.86	1.32	2.89	2.39	0.58	0.59	3.32	1.67	0.74	6.2	2.50	3.02
nss-Ca^{2+}	1.06	5.34	2.45	0.96	1.51	6.79	2.93	0.86	1.30	2.80	2.33	0.56	0.59	3.31	1.66	0.74	-	-	-
Cl^-	1.06	8.20	3.96	1.92	0.27	2.02	0.99	0.35	0.84	4.38	2.76	1.53	0.05	0.74	0.31	0.23	2.6	1.81	6.78
NO_3^-	0.09	4.44	0.94	0.76	0.38	4.03	2.07	0.76	0.24	0.69	0.43	0.15	0.12	1.60	0.74	0.44	6.0	2.91	8.37
$SO_4^=$	1.78	6.4	3.71	1.17	2.57	7.73	4.57	1.22	2.09	4.10	3.08	0.79	1.25	4.97	2.71	1.04	6.2	2.98	14.7
nss-$SO_4^=$	1.43	5.52	3.10	1.00	2.39	7.50	4.36	1.19	1.93	3.72	2.71	0.64	1.24	4.94	2.64	1.04	5.5	-	-
HCO_3^-	1.52	13.8	4.19	2.75	1.76	13.1	4.95	2.07	2.63	5.45	4.37	0.88	0.41	8.22	3.50	2.00	-	-	-

*(May-Aug); [#](Jan-Apr, Sept-Dec); [a]Venkataraman et al., 2002; [b]Momin et al., 1999; [c]Kulshrestha et al., 1998; [d]Arithmetic mean; [e]Standard deviation
bd: below detection limit

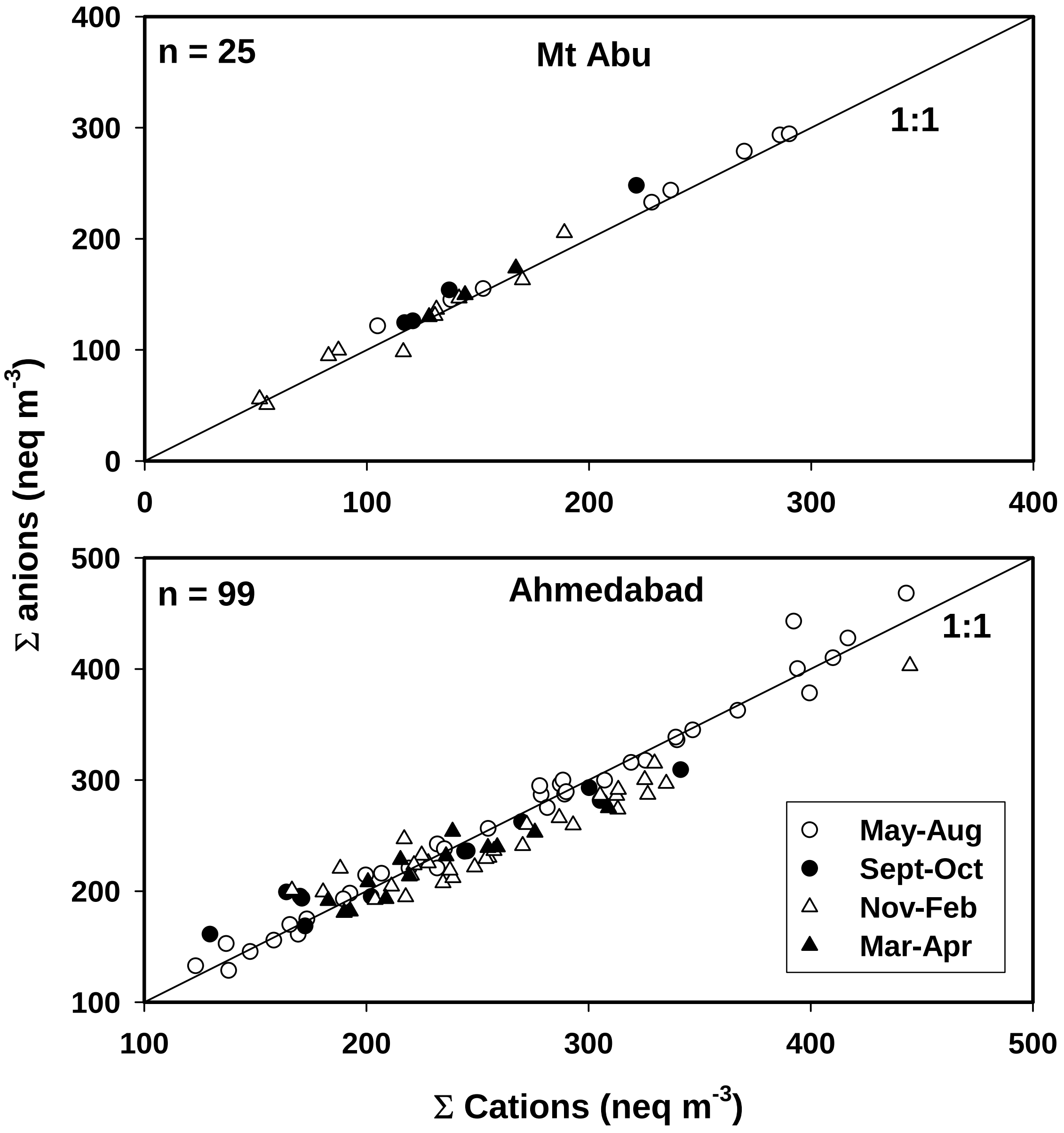

Figure 3.1. Ion balance between Σcations and Σanions in water-soluble fraction of aerosols. Beyond the experimental uncertainties, departure of the data points from equiline could be attributed to minor contribution of organic anions during drier months (Nov-Apr).

The direct measurement of HCO_3^- in aerosols provides a better insight into the chemical transformation processes (as neutralization by $CaCO_3$ will result in reduced concentration of bicarbonate as compared to calcium). Such processes are relatively important over the arid and semi-arid regions contributing large amount of mineral dust to the atmosphere. A major limitation of such studies, involving neutralization processes, is reflected in the use of calcium as a surrogate parameter for $CaCO_3$. Thus, an independent measurement of bicarbonate is an important aspect of the aerosols studies for assessing the total abundance of inorganic carbon in the atmosphere. A comparison of NH_3 and HCO_3^- concentrations with acidic species ($SO_4^=$, NO_3^-) provides information on the neutralizing capacity of the atmosphere over a particular region.

3.2.1.2 Relationships among major ions:

The scatter plots (Figs.3.2a and b) among water soluble ionic species in the aerosols over Ahmedabad and Mt Abu have been used to assess their major sources. The abundances of Na^+, Mg^{2+} and Cl^- at Ahmedabad, during May-Aug (WET phase), are relatively high (Av: 2.42, 0.37 and 3.96 $\mu g\ m^{-3}$, respectively). Na^+ and Cl^- closely follow sea-salt proportion with a marginal excess of Na^+ (Fig. 3.2a). Similarly, Mg^{2+} and Na^+ also follow the sea-water trend with excess of Mg^{2+}. These suggest that the dominant source of Cl^-, Na^+ and Mg^{2+} is sea-salts. The Na^+ excess over Cl^- and Mg^{2+} excess over Na^+ (Fig. 3.2a) suggest the need for additional source, from local dust. Using Na^+ as a reference element for sea-salts correction, non-sea-salt (nss) component of K^+, Mg^{2+}, Ca^{2+} and $SO_4^=$ has been calculated as follows:

$$\text{Non-sea-salt-X} = X_{total} - \{[Na^+] * (X/Na)_{seawater}\}$$

Where, $X = K^+$, Mg^{2+}, Ca^{2+} and $SO_4^=$; X_{total} and $[Na^+]$ are the concentrations of X and Na^+ measured in water-extracts of aerosols; $(X/Na)_{seawater}$ is X to Na^+ ratio in seawater. If Na^+ contribution from dust sources is significant then it would imply that nss-components, as calculated, are of lower limit. The weight ratios of K^+/Na^+, Mg^{2+}/Na^+, Ca^{2+}/Na^+ and $SO_4^=/Na^+$ in seawater are 0.037, 0.120, 0.038 and 0.253, respectively (Keene et al., 1986). On average, the calculated percentage of nss-component for K^+:

60%, Mg^{2+}: 30%, Ca^{2+}: 96% and $SO_4^{=}$: 85% represents the WET phase. During drier months (Jan-Apr, Sept-Dec), average concentrations of Na^+, Mg^{2+} and Cl^- decreases to 0.81, 0.25 and 0.99 µg m^{-3}, respectively. The nss-components of K^+, Mg^{2+}, Ca^{2+} and $SO_4^{=}$ are 95, 60, 99 and 95%, respectively, during DRY months. This suggest negligible contribution of sea-salts to Ca^{2+}, K^+ and $SO_4^{=}$ during DRY period. However, sea-salt contribution is significant to Mg^{2+} and K^+ and minor contribution to $SO_4^{=}$ during WET phase.

A linear correlation is observed between nss-Ca^{2+} and HCO_3^- at both the sites throughout the annual seasonal cycle ($r^2 = 0.63$ at Ahmedabad and $r^2 = 0.87$ at Mt Abu, Fig. 3.2a); suggesting their principal source from mineral dust ($CaCO_3$). It is noteworthy that the slope of the linear regression lines at both the sites are quite similar; but relatively large scatter in the data over Ahmedabad (Fig. 3.2a) is attributed to greater influence of anthropogenically derived components (NO_3^- and $SO_4^{=}$) which in turn can interact with the mineral aerosols. The negative intercepts (c = -0.92 at Ahmedabad and -0.32 at Mt Abu) implies that a significant fraction of HCO_3^- is neutralized at both sites. Alternatively, contribution of Ca^{2+} from sources like gypsum ($CaSO_4$) could be significant, causing greater scatter and temporal variability in the slope of nss-Ca^{2+} vs HCO_3^- (as discussed in later section).

The major sources of NO_3^- and $SO_4^{=}$ in the atmosphere are the oxidation of their gaseous precursors NO_x and SO_2 respectively, emitted from various anthropogenic sources. Both NO_3^- and nss-$SO_4^{=}$ are largely produced as secondary aerosols during the process of coal combustion, biomass burning and vehicular emissions (Seinfeld and Pandis, 1998). Therefore, depending on the relative dominance of gaseous vis-à-vis particulate phase, scatter in the nss-$SO_4^{=}$ and NO_3^- data is not unexpected (Fig. 3.2b), especially during warmer and humid season (Apr-Jun). The nss-$SO_4^{=}/NO_3^-$ weight ratio varies from 1.2 to 4.4 (average: 2.2, sd: 0.8) in DRY period (Jan-May, Sept-Dec) over Ahmedabad. Garg et al (2001) had reported that emission ratio of SO_2/NO_x from all pollutant sources over India averages around 1.3 and that over Ahmedabad is ~2.0 (varying from 1.9 (1990) to 2.0 (1995)).

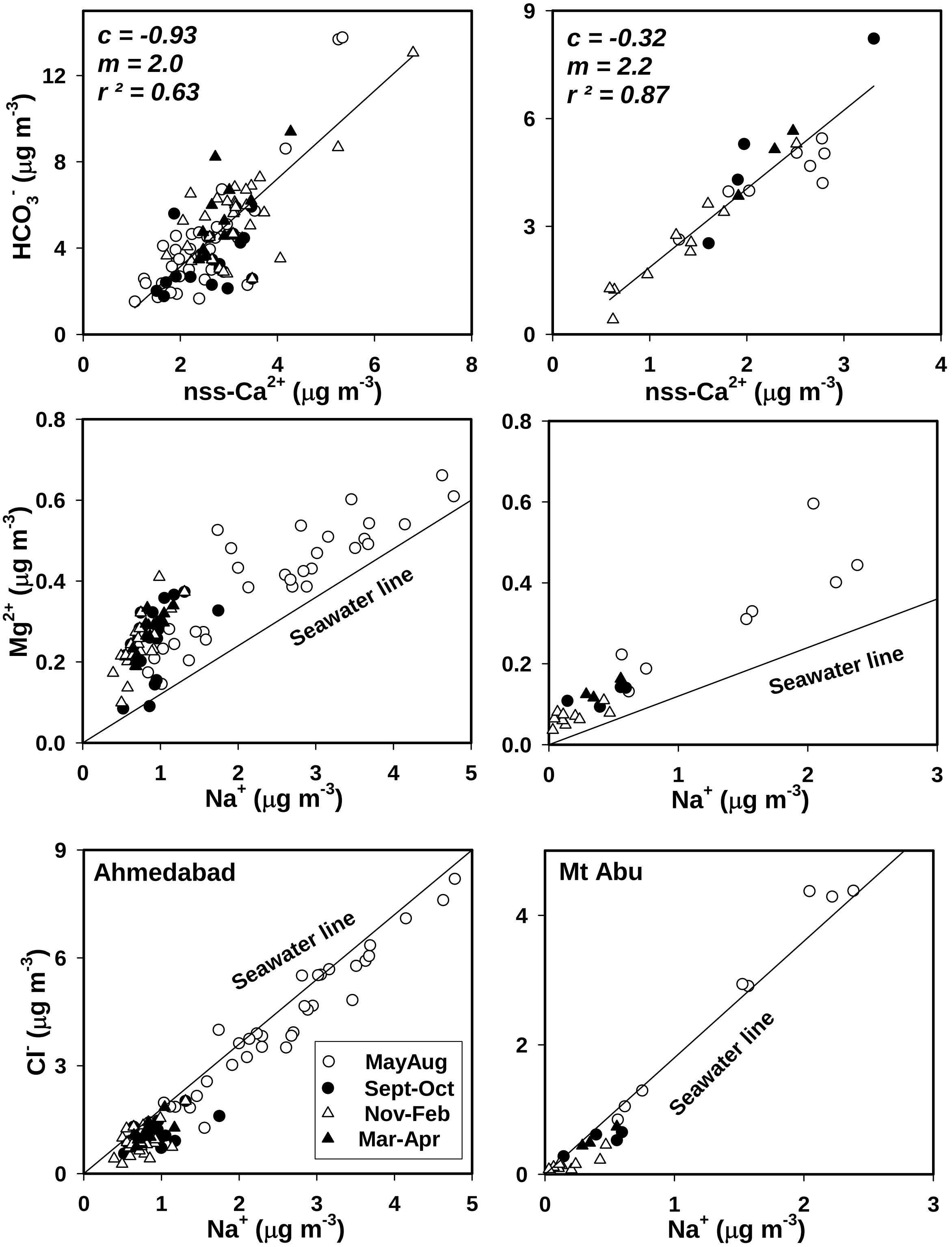

Figure 3.2a. Scatter plots between Cl^- and Mg^{2+} vs Na^+. The scatter of points in Na^+ vs Cl^- and Na^+ vs Mg^{2+} around seawater line suggest that dominant source of these ions is sea-salts. Linear regression plot of non-sea-salt-Ca^{2+} and HCO_3^- indicate their major source from mineral dust. Relatively large scatter and higher intercept in the nss-Ca^{2+} vs HCO_3^- plot (over Ahmedabad) could arise due to the neutralization of HCO_3^- by acidic constituents derived from anthropogenic sources.

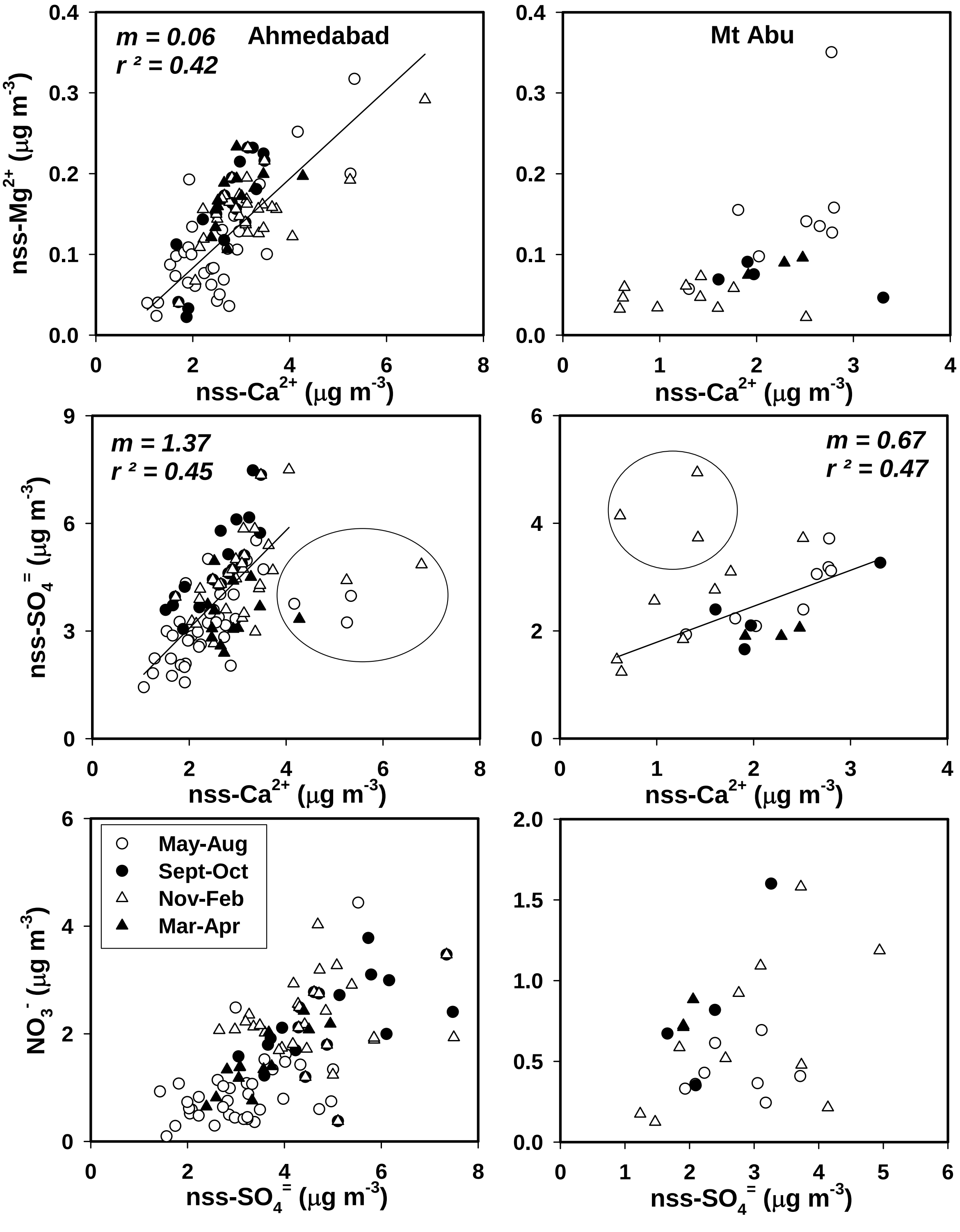

Figure 3.2b. Scatter plots for the source apportionment of nss-$SO_4^=$ and NO_3^-. A large scatter in the nss-$SO_4^=$ vs NO_3^- and nss-Ca^{2+} vs nss-$SO_4^=$ suggest their multiple sources and/or significance of chemical transformation processes. Encircled data points are not included in regression analysis.

This is nearly identical to the average nss-$SO_4^=$/NO_3^- ratio of 2.2 measured in the aerosols over Ahmedabad. Such an observation suggests that the concentration of nss-$SO_4^=$ and NO_3^- in the aerosols are dominated by anthropogenic emissions of SO_2 and NO_x (assuming their conversion efficiency from gaseous to particulate phase is same) and that contribution of nss-$SO_4^=$ from gypsiferrous soils is insignificant.

At Mt Abu, nss-$SO_4^=$/NO_3^- ratios show large variations, 2.0-19.4 (average: 5.6, sd: 4.0), throughout the year. Relatively higher nss-$SO_4^=$/NO_3^- ratios at Mt Abu than those over Ahmedabad could arise due to the differences in regional pollution sources and more importantly due to the altitude difference between the two sites. Several studies (Venkataraman et al., 2002; Tang et al., 2004; Ooki and Uematsu, 2005) have shown that NO_3^- exists largely in coarser particles while $SO_4^=$ follows a bimodal (fine and coarse mode) distribution in aerosols. Winds can transport finer particles to higher altitude, causing relatively higher abundance of $SO_4^=$ than that of NO_3^- over Mt Abu and therefore higher nss-$SO_4^=$/NO_3^- ratios.

In order to place constraints on the contribution of nss-$SO_4^=$ from regional dust sources, its relationship with nss-Ca^{2+} has been investigated for the two sites. The linear regression parameters of the data reveal slope = 1.37, r^2 = 0.45 for the samples over Ahmedabad and for samples from Mt Abu: slope = 0.67, r^2 = 0.47 (Fig. 3.2b). These correlation can be either due to their co-genetic source (such as gypsum) or as in-situ formation of $CaSO_4$ at the surface of mineral aerosols ($CaCO_3$) during atmospheric transport (Wu and Okada, 1994; Zhuang et al., 1999; Jordan et al., 2003; Krueger et al., 2003). In the former case, one would expect a relatively tight correlation among nss-Ca^{2+} and nss-$SO_4^=$; while the dominance of latter process could cause larger scatter (Fig. 3.2b) depending upon the source strength and atmospheric transport of mineral dust ($CaCO_3$) and anthropogenic $SO_4^=$. It is noteworthy that the observed slope of 1.37, over Ahmedabad, is about a factor of two higher than that over Mt Abu (Fig. 3.2b); further attesting that in-situ formation of $CaSO_4$ on aerosol surface is a plausible mechanism. However, based on chemical data alone it is difficult to quantify the relative contribution of nss-$SO_4^=$ from gypsiferrous soils vis-à-vis in-situ formed $CaSO_4$.

Arimoto et al (1996) had reported that the differences in the nss-$SO_4^=$/NO_3^- ratios at different sites could arise from the regional differences in the pollution component of aerosols. Yao et al (2002) had used $SO_4^{=}/NO_3^{-}$ ratios as an indicator of the relative dominance of stationary (coal combustion, biomass burning) versus mobile (vehicular emissions) sources of sulphur and nitrogen in the atmosphere and attributed higher ratios to the dominance of stationary pollutant sources and lower ratios to that of mobile sources. In this study, the dominance of stationary polluting sources over vehicular emissions is the most likely cause for the higher $SO_4^{=}/NO_3^{-}$ ratios observed at both the sites.

The nss-Mg^{2+}/nss-Ca^{2+} ratio, at Ahmedabad, ranges from 0.013 to 0.100 (average: 0.043, sd: 0.018) during WET phase and 0.012 to 0.080 (average: 0.053, sd: 0.015) during DRY period. In comparison, nss-Mg^{2+}/nss-Ca^{2+} ratio over Mt Abu varies from 0.044 to 0.126 (average: 0.064, sd: 0.028) during WET and 0.009 to 0.093 (average: 0.042, sd: 0.020) during DRY period. A large scatter in the nss-Mg^{2+} vs nss-Ca^{2+} data (Fig. 3.2b) suggest that contribution of water-soluble nss-Mg^{2+} from dust sources (unlike nss-Ca^{2+}) is relatively insignificant over Mt Abu.

3.2.1.3 Temporal variations in ionic concentrations:

The inter-annual and seasonal variations in the concentrations of Na^{+}, nss-Ca^{2+}, nss-$SO_4^{=}$, NO_3^{-}, NH_4^{+} and nss-K^{+} over Ahmedabad and Mt Abu are depicted in Figs. 3.3a and 3.3b. The abundance of Na^{+} is considered as a proxy of sea-salts and that of nss-Ca^{2+} as contribution from mineral dust. The major sources of NH_4^{+} are animal and human excreta and biomass burning, and for nss-K^{+} is biomass burning (Andreae et al., 1998; Seinfeld and Pandis, 1998; Venkataraman et al., 2002; Maxwell-Meier et al., 2004). The major sources of nss-$SO_4^{=}$ and NO_3^{-} are fossil fuel, biomass burning and vehicular emissions (Seinfeld and Pandis, 1998). Therefore, temporal variations in the concentrations of Na^{+}, nss-Ca^{2+}, nss-$SO_4^{=}$, NO_3^{-}, NH_4^{+} and nss-K^{+} would reflect on their variable source strength (Figs.3.3a and b). In general, lowest concentrations of water soluble ionic species (except for Na^{+}, Cl^{-} and Mg^{2+}) are observed during WET period (Table 3.1). Samples collected immediately after rain events correspond to low aerosol mass loading in the atmosphere and hence concentrations of all species are relatively low.

The concentrations of Na^{+}, Cl^{-}, and Mg^{2+} (representing sea-salts) increases significantly during WET period under the influence of southwesterly winds (originating from the Arabian Sea) in comparison to those during DRY period (dominated by northeasterly winds) (Table 3.1, Fig. 3.3a). However, inter-annual variability in the observed temporal pattern is insignificant, during the course of this study (2000-2002). Wang and Shooter (2001) had reported that the average concentrations of Na^+, Cl^-, and Mg^{2+} were closely related to the average wind pattern and rainfall over New Zealand. Among all the ions, concentration of nss-Ca^{2+} exhibits least temporal variability (Fig. 3.3a); suggesting a fairly uniform source strength of mineral dust ($CaCO_3$).

The temporal variability of nss-$SO_4^=$ is not significantly pronounced (Fig. 3.3a); suggesting that the aerosol abundance of nss-$SO_4^=$ is dominated by local pollution sources. In contrast, aerosol NO_3^- concentration exhibits strong seasonal variability with relatively large decrease during the warm and humid period (from April to August, Fig. 3.3b). Matsumoto and Okita (1998) had reported that the volatile loss of NH_3, HNO_3 and HCl from NH_4NO_3 and NH_4Cl are significantly pronounced during summer months. The relatively low NO_3^- concentration in the aerosols during the warmer period (Fig. 3.3b) is attributed to preferential partitioning of NO_3^- in gaseous phase and/or due to the predominance of oceanic air mass (southwesterly winds). Relatively high NO_3^- concentrations during winter months (Dec-Feb) is attributed to the enhanced downwind transport of pollutants (Fig. 3.3 b). In the absence of strong local sources, the abundances of chemical species at a high altitude site in Mt Abu (1680 m asl) are expected to be dominated by their long-range transport.

During the DRY period, water-soluble NH_4^+ concentration ranges from 0.004 to 1.3 $\mu g\ m^{-3}$ (average: 0.53 sd: 0.36) over Ahmedabad and from 0.02 to 1.4 $\mu g\ m^{-3}$ (average: 0.41 sd: 0.47) at Mt Abu; whereas concentration is often below detection limit (0.001 $\mu g\ m^{-3}$), at both the sites, during the WET phase (Table 3.1, Fig. 3.3b). The observed concentrations are significantly lower than those reported over other parts of India and few global sites (Kulshrestha et al., 1998; Momin et al., 1999; Kerminen et al., 2001; Fang et al., 2002; Kocak et al., 2004; Takeuchi et al., 2004).

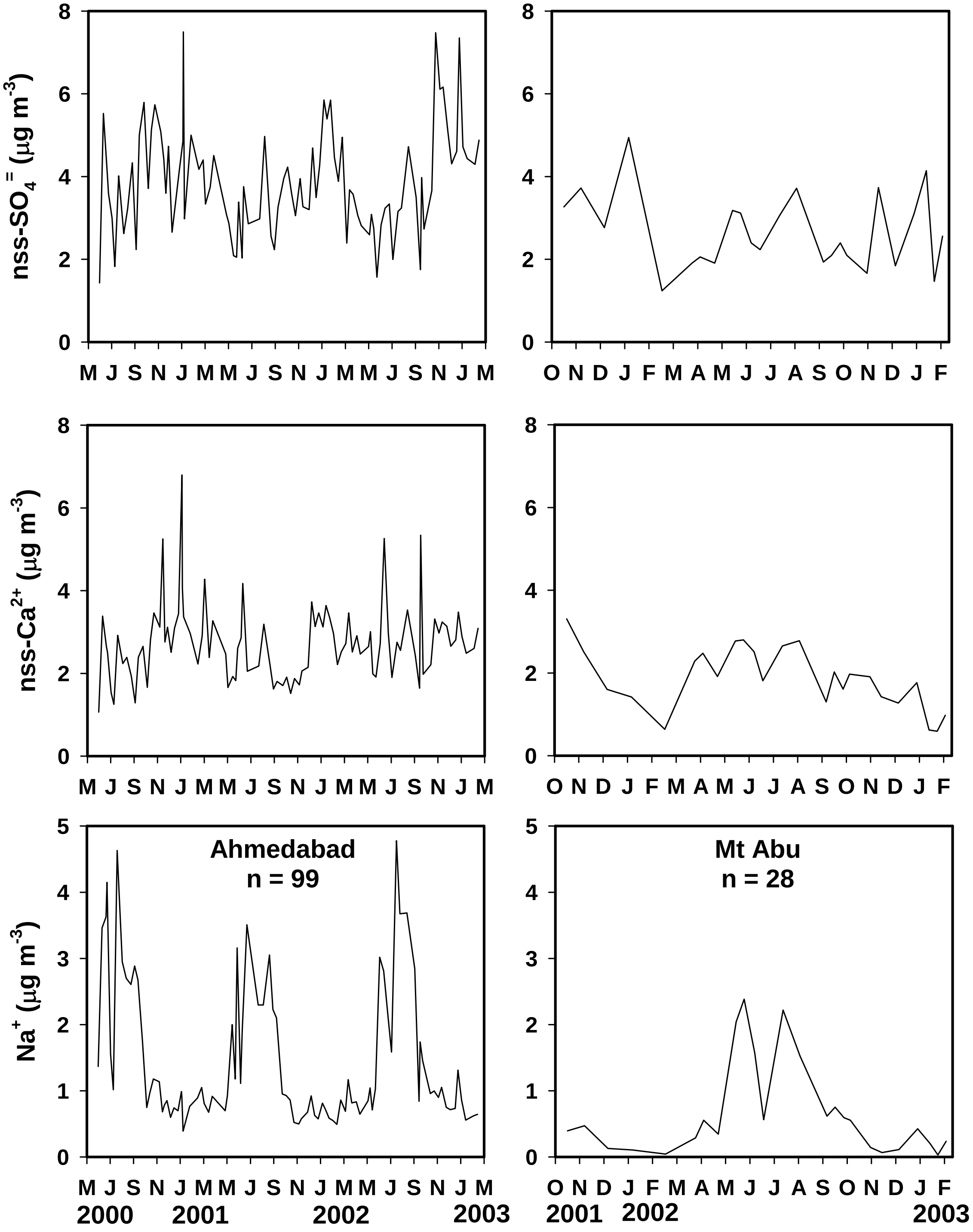

Figure 3.3a. Temporal variations in Na$^+$, nss-Ca^{2+} and nss-SO$_4^=$ at Ahmedabad and Mt Abu. High Na$^+$ concentrations during May-Aug imply that the sea-salt contribution to the ionic composition of aerosols peaks during during this period (when southwesterly winds bring oceanic air mass). Seasonal variation in nss-Ca^{2+} is relatively less pronounced; suggesting predominance and uniform contribution of dust sources to the ionic composition. Variation trend of nss-SO$_4^=$ is similar to those of other anthropogenic species (Fig. 3.3b) but its absolute concentration does not change significantly, suggesting that it is largely originated from local pollution sources.

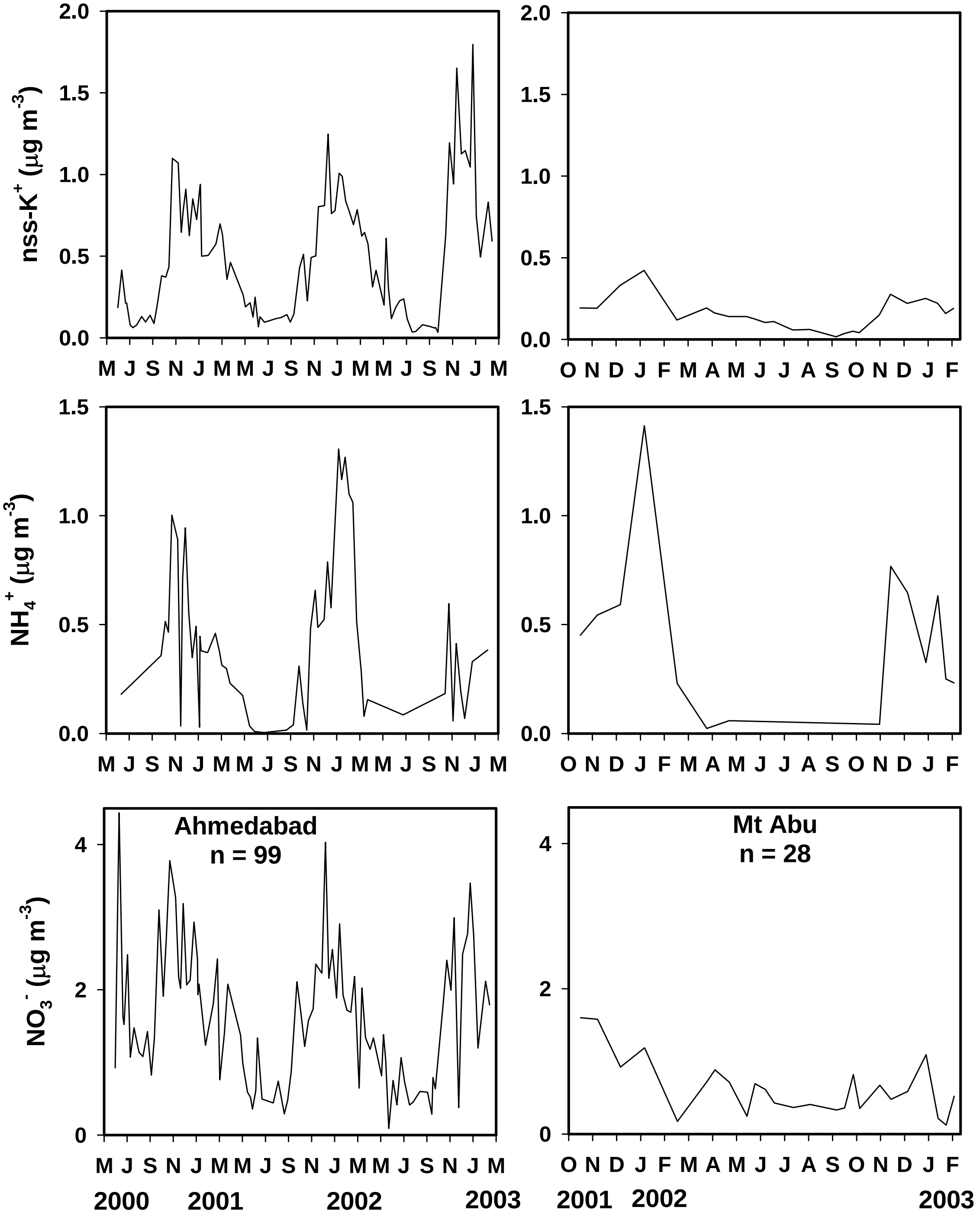

Figure 3.3b. Temporal variations in anthropogenically derived constituents. These constituents (NO_3^-, NH_4^+ and nss-K^+) derived primarily from anthropogenic and biogenic emissions peak during winter months (dominated by northeasterly winds) with minimum during SW-monsoon. These seasonal changes are more pronounced in samples from Ahmedabad.

Relatively low concentration, during the WET period, is attributed to the predominance of southwesterly winds (low in NH_4^+) and rapid removal of aerosols (via wet deposition). The volatilization loss of NH_4^+ (if any) as NH_4NO_3 or NH_4Cl aerosols could also be significant (Matsumoto and Okita, 1998) as monthly average ambient temperature is relatively high (32 to 34 ^oC) during Apr-June before the onset of SW-monsoon. The elevated levels of NH_4^+ in precipitation events, studied for a three-year period over Ahmedabad (Rastogi and Sarin, 2005), suggest dominant occurrence of NH_4^+ in gaseous phase. During winter months (Nov-Feb), NH_4^+ concentration in aerosols is relatively high under the influence of northwesterly winds transporting large-scale pollutants (Fig. 3.3b).

Similar to NH_4^+, nss-K^+ also shows large temporal variability with significantly higher concentrations during DRY period (Table 3.1, Fig. 3.3b); suggesting its variable source from continental emissions (biomass burning). In absence of a meaningful relationship with nss-Ca^{2+}, contribution of nss-K^+ from dust sources is expected to be relatively insignificant. The large variability in the NH_4^+/NO_3^- (range: 0.01 to 0.69) and nss-K^+/NO_3^- ratios (range: 0.12 to 3.0) observed over Ahmedabad, during DRY period, is attributed to variable anthropogenic sources.

The average contribution (on weight basis) of measured ions (NH_4^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, $SO_4^=$ and HCO_3^-) to the total water-soluble salts (Σ salts) is shown in Fig. 3.4. Among cations, Ca^{2+} is the most dominant, contributing 15-20% to Σ salts, at both the sites, with relatively high contribution during DRY period. The contribution of Na^+ varies by factor of ~3 between the DRY (2-4%) and WET period (10-12%). The contributions of K^+ and Mg^{2+} do not exceed 5% to Σ salts (Fig. 3.4). Among anions, NO_3^- and HCO_3^- contribute about 5 and 25%, respectively to the Σ salts during the WET period (Fig. 3.4); and nearly equal contribution (~20%) arise from Cl^- and $SO_4^=$. Similar to Na^+, the contribution of Cl^- decreases by a factor of ~3 from WET to DRY period at both sites (Fig. 3.4). Based on the HCO_3^- contribution to the ionic composition, it is evident that the ambient aerosols, at both the sites, have significant neutralizing capacity. As NH_4^+ concentration is relatively small in comparison to HCO_3^- (Fig. 3.4), neutralization of acidic species (NO_3^-, $SO_4^=$) is dominated by mineral dust.

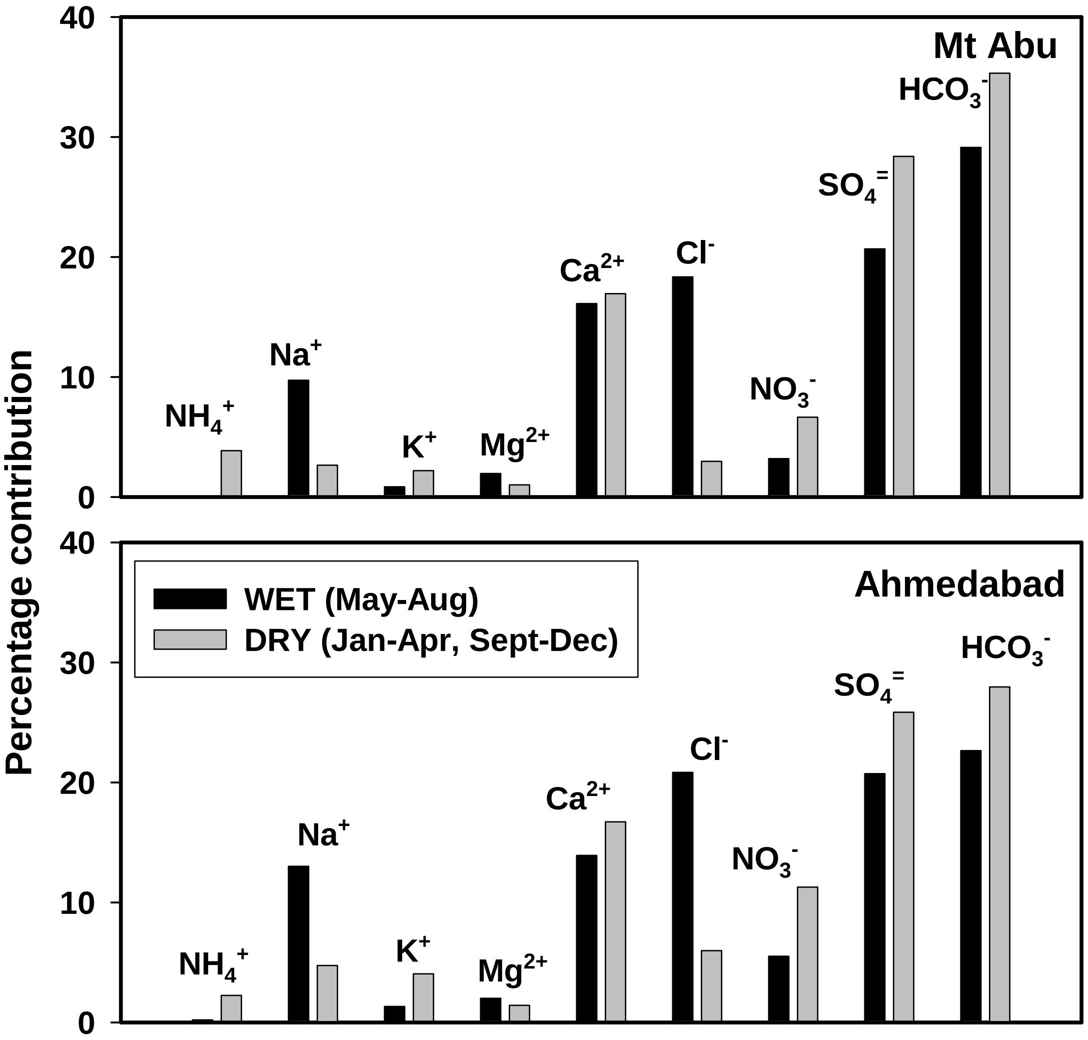

Figure 3.4. Percentage contribution of different ions (on weight basis) to the total water-soluble components of aerosols in different seasons over Ahmedabad and Mt Abu; indicating significant seasonality in aerosol ionic composition and the relative dominance of mineral dust in all season at both sites.

3.2.1.4 Acid uptake by mineral dust:

The relationship among ionic species (nss-Ca^{2+} vs nss-$SO_4^=$, Fig. 3.2b) provides evidence for the neutralization of nss-$SO_4^=$ by mineral dust ($CaCO_3$). Neutralization reaction can also occur with NO_3^-. In addition, NH_4^+ and nss-K^+ are potential constituents for the neutralization of acidic species. Maxwell-Meier et al (2004) used ion balance among (K^+ + NH_4^+) vs (NO_3^- + $SO_4^=$) and (Ca^{2+} + Mg^{2+}) vs $CO_3^=$ to investigate the extent of chemical interactions. Their interpretation was based on the observation that whenever complete neutralization of (NO_3^- + $SO_4^=$) is balanced by (K^+ + NH_4^+), the data plotted on (Ca^{2+} + Mg^{2+}) vs $CO_3^=$ tends to closely follow the equiline. The data set plotted in Fig. 3.5a suggest that (nss-K^+ + NH_4^+) are not sufficient for the complete neutralization of the total acidity (NO_3^- + nss-$SO_4^=$) and that their contribution is minimum during summer months (May-Aug).

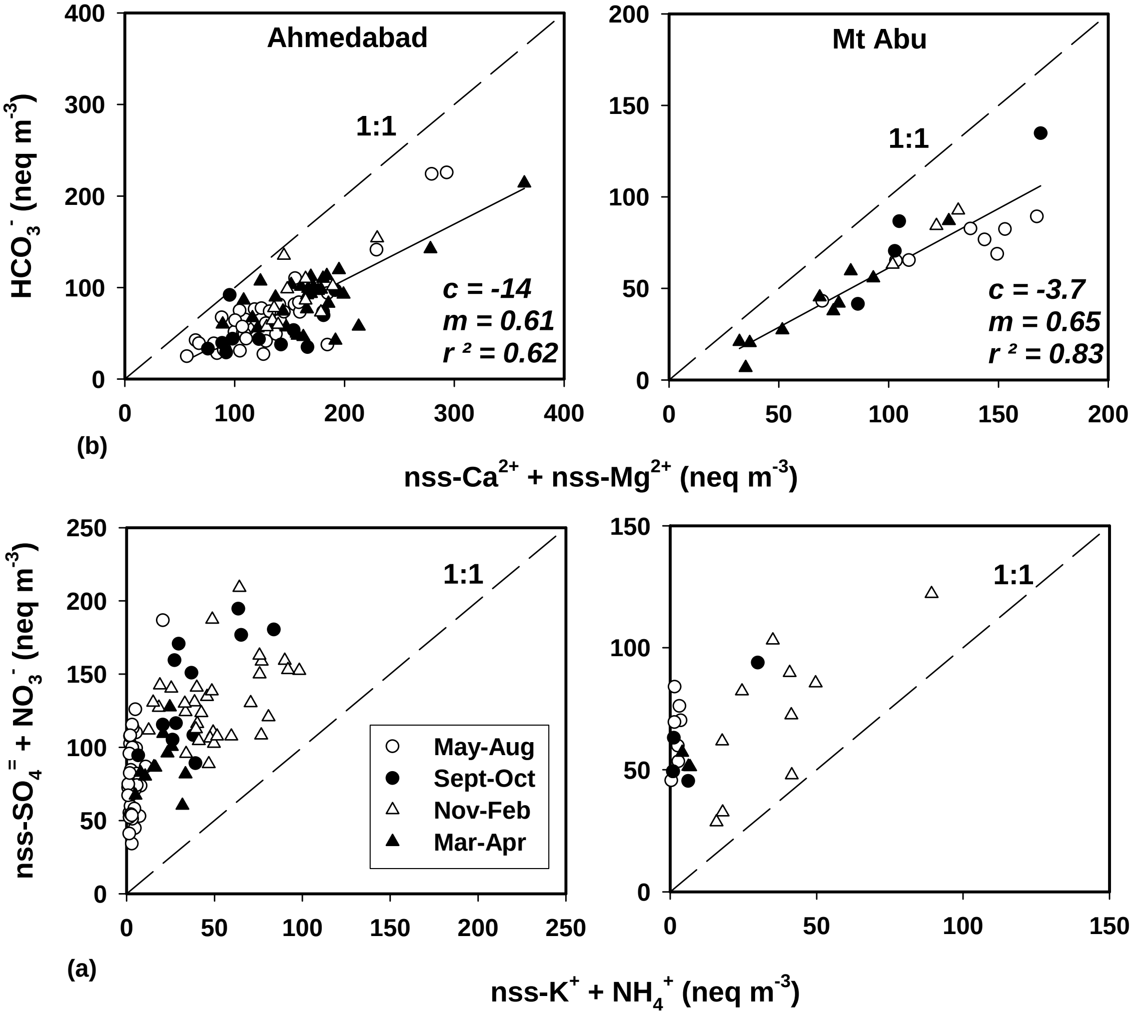

Figure 3.5. (a) The lack of significant relationship between (nss-K^++ NH_4^+) and (nss-$SO_4^=$+ NO_3^-) suggests that nss-K^+ and NH_4^+ in aerosols are not sufficient to neutralize the total acidity (nss-$SO_4^=$ + NO_3^-). (b) Deviation of data points towards (nss-Ca^{2+}+ nss-Mg^{2+}) suggest uptake of acidic species by mineral aerosols and subsequent neutralization of HCO_3^-.

The (nss-Ca^{2+} + nss-Mg^{2+}) exhibit significant correlation with HCO_3^- over Ahmedabad (slope = 0.61, r^2 = 0.62) and Mt Abu (slope = 0.65, r^2 = 0.83) with almost all data points lying below the equiline (Fig. 3.5b). The slopes of the linear regression lines significantly less than one suggest that the uptake of excess acid by mineral dust is predominant over the study region (Rastogi and Sarin, 2004). The excess acid (EA) is (in equivalent units) defined as:

$$\text{Excess acid (EA)} = (NO_3^- + \text{nss-}SO_4^=) – (NH_4^+ + \text{nss-}K^+)$$

Percentage EA of the total acid vary as 29 to 93% (average: 67%, sd: 16) over Ahmedabad and 13 to 98% (average: 66%, sd: 26) over Mt Abu in DRY period. In contrast, EA constitutes for more than 90% during the WET period over both sites. This suggests that significant fraction of total acid is available for neutralization with mineral dust in all seasons. The carbonates of Ca^{2+} and Mg^{2+} in aerosols would react with EA as follows:

$$CaCO_3 + H_2SO_4 \Rightarrow CaSO_4 + CO_2 + H_2O \quad (1)$$

$$CaCO_3 + 2HNO_3 \Rightarrow Ca(NO_3)_2 + CO_2 + H_2O \quad (2)$$

$$MgCO_3 + H_2SO_4 \Rightarrow MgSO_4 + CO_2 + H_2O \quad (3)$$

$$MgCO_3 + 2HNO_3 \Rightarrow Mg(NO_3)_2 + CO_2 + H_2O \quad (4)$$

The average nss-Mg^{2+}/nss-Ca^{2+} ratio in the aerosols is < 0.05 at Ahmedabad and < 0.07 at Mt Abu; suggesting dominant abundance of $CaCO_3$, though contribution from $MgCO_3$ has also been included in calculation of acid uptake by mineral dust. The neutralization of excess acid by mineral dust, occurring as a dominant reaction, is expected to yield a negative decreasing trend between EA/(nss-Ca^{2+} + nss-Mg^{2+}) and HCO_3^-/(nss-Ca^{2+} + nss-Mg^{2+}) as observed in Fig. 3.6 ($r^2 = 0.50$ at Ahmedabad and $r^2 = 0.53$ at Mt Abu). Thus, percentage uptake of EA by mineral dust can be calculated from the amount of HCO_3^- neutralized (defined as nss-Ca^{2+} + nss-Mg^{2+} - HCO_3^-) and total EA. It is implicit in these calculations that their measured concentrations in the water-soluble extracts are derived from dust sources.

$$\text{EA uptake (\%)} = [(\text{nss-}Ca^{2+} + \text{nss-}Mg^{2+} - HCO_3^-) / \text{Total EA}] * 100$$

Such an approach suggests that, on average, mineral aerosols in a semi-arid region can account for as much as 80% of the uptake of excess acid. Such documentation of large uptake of acidic species by mineral dust, observed over the two sites located in a semi-arid region of India, is an important aspect of this study. These chemical reactions could significantly alter the size distribution of sulphate and nitrate aerosols (from fine to coarse mode) as well as surface properties of mineral dust (from hydrophobic to hydrophilic).

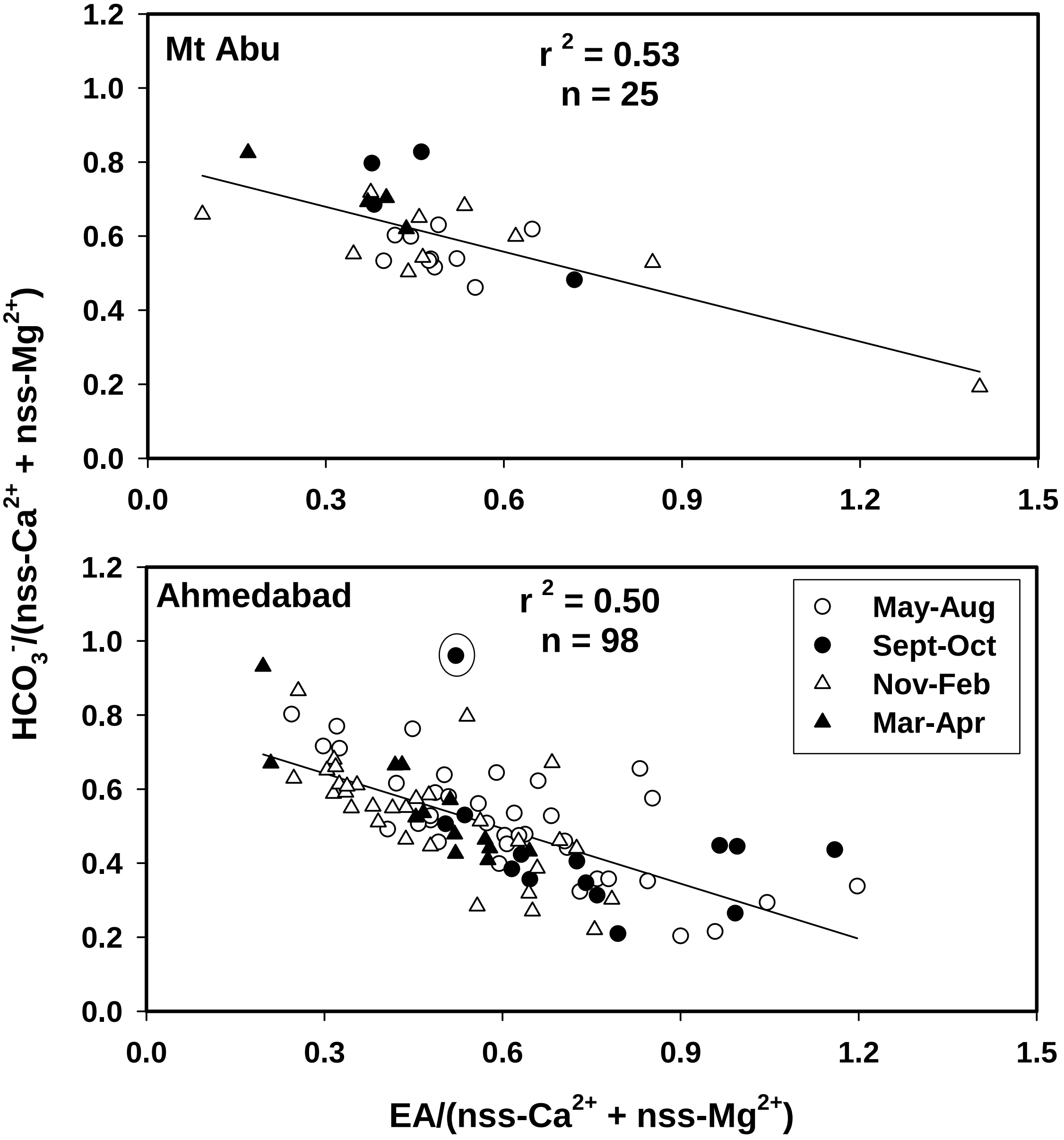

Figure 3.6. Scatter plot of HCO_3^- and EA with respect to (nss-Ca^{2+} + nss-Mg^{2+}). The anti correlation between the two variables is an evidence of excess acid (EA, defined in text) uptake by carbonate content in aerosols. Encircled data point has not been included in regression analysis.

Furthermore, this may affect the ability of mineral dust to act as CCN. Changes in size distribution may also have implication in estimating the impact of SO_2 emissions on climate cooling in several regions, such as India and China where major industrial developments are expected (Andreae and Crutzen, 1997; Song and Carmichael, 2001).

3.2.2 Acid-soluble species in aerosols:

The concentrations of selected constituents (Al, Fe, Ca, Mg, K, Mn, Zn and Pb), measured in acid extracts of aerosols collected during the WET and DRY periods from the two sites at Ahmedabad and Mt Abu, are summarized in Table 3.2. This Table also includes arithmetic mean and standard deviation of their concentrations. For comparison, the data reported from other regions in India: Mumbai (Venkataraman et al., 2002) and Pune (Momin et al., 1999) and a site from China (Arimoto et al., 2004) are also presented in Table 3.2. The acid-soluble species in aerosols follow the sequence Ca > Fe > Al > Mg > K > Zn > Mn > Pb over Ahmedabad and Mt Abu (Table 3.2). In general, during the DRY period, concentrations of Al, Fe, Ca, Mg and K are about 2x higher while Mn, Zn and Pb are nearly four times higher than those in WET period over Ahmedabad (Table 3.2). In contrast, aerosol samples collected from Mt Abu exhibit an opposite trend; concentrations of all elements except those of Zn and Pb in the WET period are higher by factors of 2-3 than those in DRY period (Table 3.2). These observations have been discussed further in later sections.

3.2.2.1 Relationships among acid-soluble elements:

Regression analysis among Al and other elements (Fe, K, Mn, Ca and Mg) has been investigated to assess their major sources in aerosols (Figs. 3.7 and 3.8). Al is commonly used as a reference element for mineral dust (Duce et al., 1991; Arimoto et al., 1996; Arimoto et al., 2004). The abundances of Al and Fe in aerosols are strongly correlated over Ahmedabad (r^2 = 0.91, slope = 1.24) and Mt Abu (r^2 = 0.99, slope = 1.34) as shown in (Fig. 3.7a). The higher slopes of the linear regression lines (assuming that Al and Fe are leached by acid in proportion to their abundance in aerosols) suggests that aerosols are significantly enriched in Fe compared to the Fe/Al ratio in upper continental crust (UCC). Furthermore, the close similarity in the slopes of the regression lines for Fe, Al data from the two sites (Fig. 3.7a) indicates uniformity in the composition of mineral aerosols (derived from local dust sources) and their atmospheric transport.

Table 3.2 Concentrations (μg m^{-3}) of elements in acid-soluble fraction of aerosols over Ahmedabad and Mt Abu.

	Ahmedabad								Mt Abu								Mumbai[1] India	Pune[2] India	ZBT[3] China	
	WET[$]				DRY[#]				WET				DRY							
	Min	**Max**	**AM[a]**	**SD[b]**	**Min**	**Max**	**AM**	**SD**	**Min**	**Max**	**AM**	**SD**	**Min**	**Max**	**AM**	**SD**	**AM**	**AM**	**AM**	**UCC[c]**
Al	0.48	4.57	**1.79**	0.89	0.78	6.22	**2.98**	1.09	0.97	6.30	**2.90**	1.75	0.30	3.36	**1.33**	0.77	1.89	2.81	4.3	8.04[d]
Fe	0.57	6.43	**2.36**	1.23	1.15	7.34	**4.07**	1.30	0.74	8.72	**3.55**	2.55	0.35	4.15	**1.58**	0.95	2.32	3.34	2.5	3.50d
Ca	0.57	6.32	**2.94**	1.48	0.89	12.5	**5.17**	2.10	0.24	9.21	**4.16**	3.38	0.10	6.13	**1.20**	1.52	-	-	5.2	3.00[d]
Mg	0.19	2.66	**1.01**	0.56	0.38	3.41	**1.31**	0.58	0.28	4.93	**2.04**	1.52	0.08	2.26	**0.69**	0.55	-	-	1.5	1.5[d]
K	0.12	0.83	**0.34**	0.17	0.17	1.21	**0.58**	0.21	0.21	1.31	**0.58**	0.35	0.07	0.71	**0.29**	0.17	-	-	1.5	1.5[d]
Mn*	10	100	**42**	23	15	443	**115**	93	10	146	**57**	44	4	63	**22**	15	150	53	62	600[e]
Zn*	3	290	**43**	50	28	1076	**189**	162	5	19	**11**	5	1	31	**14**	10	350	45	48	71[e]
Pb*	2	163	**32**	42	5	1406	**136**	216	2	4	**3**	1	3	22	**8**	5	-	-	23	17[e]
Fe/Al	1.07	1.62	**1.32**	0.12	1.07	2.12	**1.39**	0.19	0.77	1.39	**1.20**	0.18	1.00	1.34	**1.17**	0.09	1.23	1.19	0.58	0.44
Ca/Al	0.64	2.61	**1.68**	0.47	0.76	2.67	**1.76**	0.48	0.25	2.16	**1.33**	0.60	0.26	1.83	**0.67**	0.44	-	-	1.21	0.38
Mg/Al	0.22	0.75	**0.56**	0.12	0.30	0.71	**0.44**	0.09	0.29	0.87	**0.69**	0.18	0.22	0.70	**0.46**	0.14	-	-	0.35	0.17
K/Al	0.15	0.30	**0.20**	0.03	0.16	0.25	**0.20**	0.02	0.16	0.23	**0.20**	0.02	0.17	0.27	**0.22**	0.03	-	-	0.35	0.35
Mn/Al	0.015	0.049	**0.024**	0.008	0.018	0.174	**0.042**	0.038	0.010	0.026	**0.019**	0.005	0.012	0.024	**0.016**	0.003	0.079	0.019	0.014	0.007
Zn/Al	0.004	0.136	**0.029**	0.030	0.011	0.624	**0.075**	0.091	0.002	0.010	**0.005**	0.003	0.001	0.026	**0.012**	0.008	0.185	0.016	0.011	8.9E-04
Pb/Al	0.001	0.180	**0.025**	0.042	0.002	0.478	**0.056**	0.088	0.000	0.003	**0.001**	0.001	0.001	0.021	**0.008**	0.007	-	-	0.005	2.1E-04

[$](May-Aug); [#](Jan-Apr, Sept-Dec); *ng m^{-3}; [1]Venkataraman et al., 2002; [2]Momin et al., 1999; [3]Arimoto et al., 2004

[a]Arithmetic mean; [b]Standard deviation; [c]UCC: Upper continental crust, from McLennan, 2001; [d](%); [e](ppm)

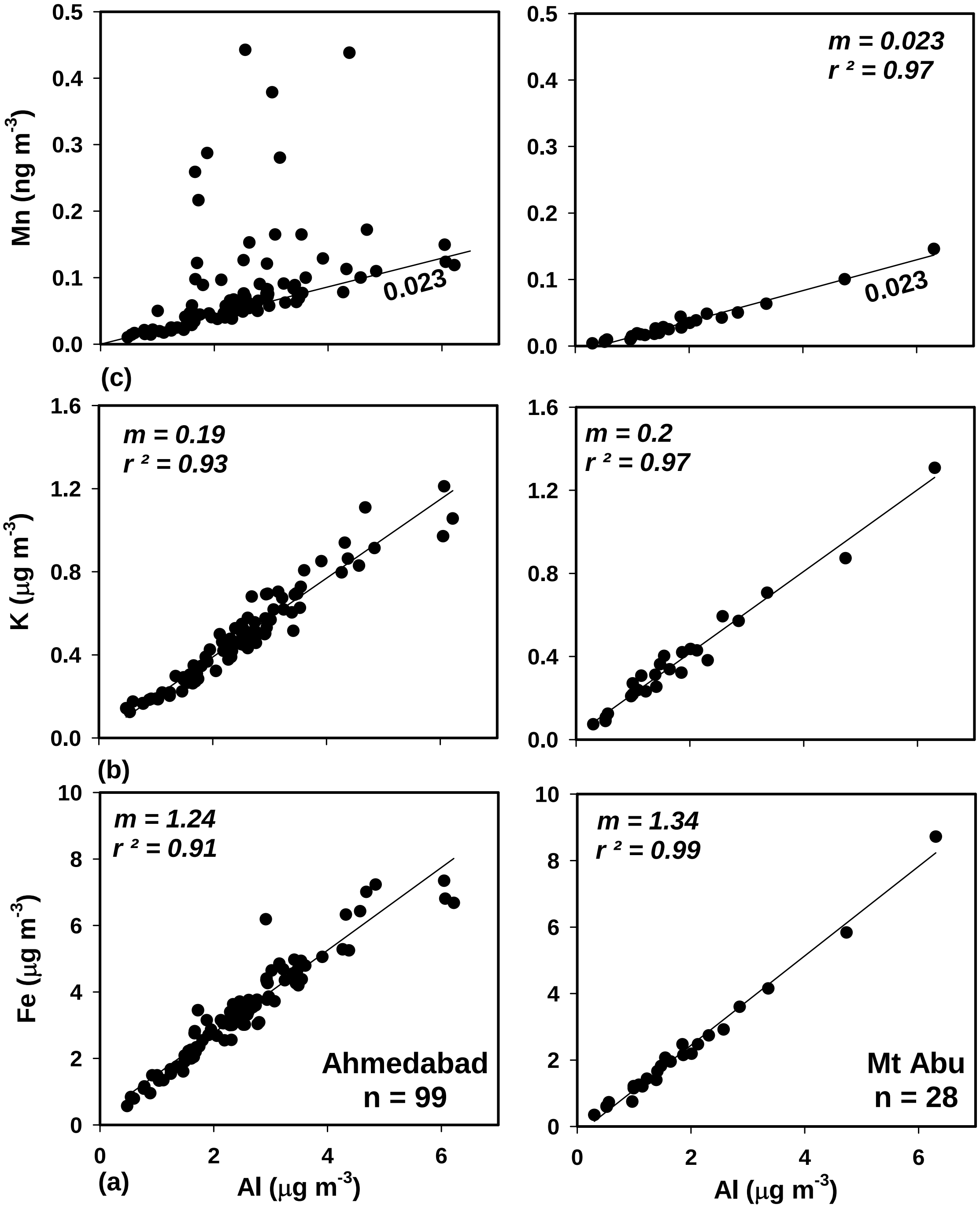

Figure 3.7. Regression plots among Al (a proxy of mineral dust) and Fe, K and Mn. The data show a strong linear trend except w.r.t. Al-Mn at Ahmedabad. This trend suggests their dominant sources from mineral dust. A significant contribution of Mn from anthropogenic sources is reflected in the aerosol data from an urban site (Ahmedabad) in comparison to the slope (m = 0.023) of linear regression data at Mt Abu.

It is noteworthy that similar Fe/Al ratios centering around 1.2 were reported from other Indian sites (Venkataraman et al., 2002; Momin et al., 1999). Likewise, K and Al show a strong positive correlation; with nearly identical slopes over Ahmedabad (r^2 = 0.93, slope = 0.19) and Mt Abu (r^2 = 0.97, slope = 0.20) (Fig. 3.7b) attesting to the earlier contention of uniformity in composition of mineral dust on a large continental scale. The relationship among Mn and Al exhibits contrasting features for the data from the two sites (Fig. 3.7c). For the aerosol composition over Ahmedabad, data points falling above the linear regression line with a slope of 0.023 (same as observed over Mt Abu), suggests significance of anthropogenic sources for an urban site (Pacyna et al., 1984). It is relevant to state that average Mn concentration in aerosols over Ahmedabad is nearly 5 times higher than that observed at Mt Abu (Table 3.2).

The linear regression plots among Al, Ca and Mg are depicted in Fig. 3.8. Ca and Al show statistically significant correlation over Ahmedabad (r^2 = 0.69, slope = 1.54) and Mt Abu (r^2 = 0.90, slope = 1.40) (Fig. 3.8a), suggesting their source from mineral dust. However, Mg abundance in aerosols when normalized to Al exhibits regional differences with varying Mg/Al and Mg/Ca ratios at the two sites (Figs. 3.8b and 3.8c) influenced by the relative dominance of different minerals (calcite/dolomite). Several studies have reported high carbonate content in soils from Asian region (Dentener et al., 1996; Song and Carmichael, 2001; Jordan et al., 2003). Overall, Fe/Al, Ca/Al and Mg/Al ratios in the aerosols are 2-3 times higher than those in UCC (McLennan, 2001); suggesting characteristic enrichment of Fe, Ca and Mg in the aerosols derived from local dust sources (Table 3.2).

Similar to Fe/Al ratios, K/Al ratios are also quite consistent (~0.20) in different season at both sites. However, the abundance ratio of K/Al is lower than that reported at Zhenbeitai, China (Arimoto et al., 2004), and in UCC (McLennan, 2001). Such comparison of data suggests regional differences in the composition of mineral dust. The Ca, Mg and K were measured in water-soluble as well as in acid-soluble fractions of aerosols collected over Ahmedabad and Mt Abu. In general, a poor relationship is observable among their abundances in the two fractions: water vis-à-vis acid. This is attributed to the leaching of different phases of aerosols by water and acid.

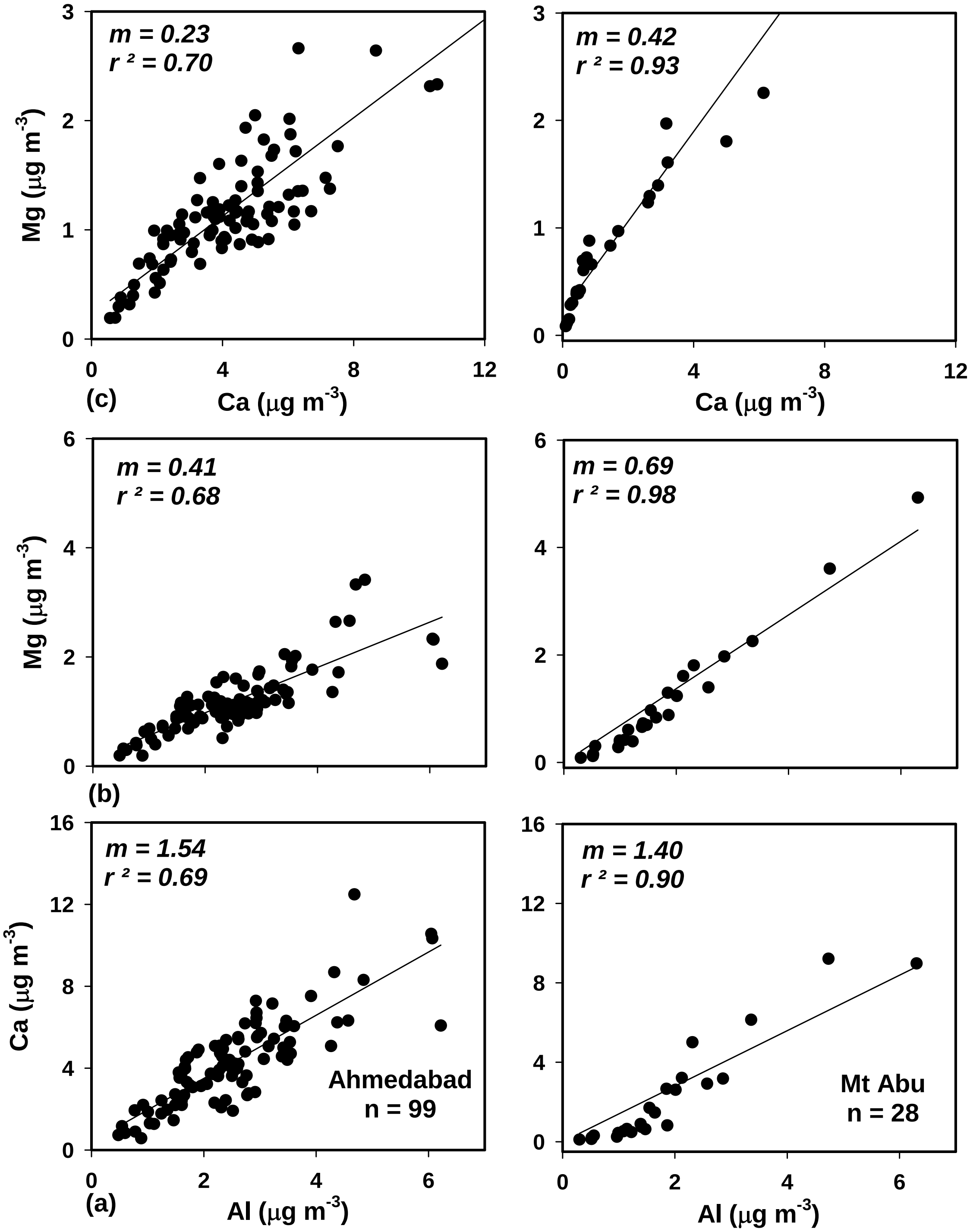

Figure 3.8. Regression plots among Al, Ca and Mg. The data exhibit linear correlation with comparable slopes for Al vs Ca plots but different for Al vs Mg and Ca vs Mg plots. The results suggest relative enrichment of Mg in samples at Mt Abu.

In case of Ca and Mg, poor correlation between the two fractions could arise due to their presence as water-soluble soil salts and acid leachable silicate phase; whereas in case of K, its dominant occurrence from biogenic sources could contribute to water-soluble fraction and acid-soluble K from mineral dust sources. The ratios of trace elements normalized to Al (Mn/Al, Zn/Al and Pb/Al) have been used for deriving the enrichment factors (EFs), as discussed in the later section.

3.2.2.2 Temporal variations of acid-soluble species:

The temporal variations of Al, Fe, Ca, Mg, K, and Mn measured in acid-soluble fraction are shown in Fig. 3.9a and b. The temporal trends of Al, Fe, Ca, Mg and K over the two sites (and of Mn with others over Mt Abu) are quite similar; suggesting their dominant source from mineral dust which in turn dictates the aerosol mass loading. The seasonal data in Figs. 3.9a and b also documents relatively higher concentration of acid-soluble constituents over Ahmedabad during November to May. The temporal variation of Mn, presumably dominated by anthropogenic sources during the DRY period, over Ahmedabad are distinctly different than those derived from local dust sources. In contrast, average concentrations of all acid-soluble species (except Zn and Pb) are lower in DRY period than those during WET period over Mt Abu. These observations are attributed to the decrease in boundary layer (BL) height during winter months (Oct-Feb) representing free tropospheric (FT) conditions at Guru Shikhar (Mt Abu). The concentrations of dust derived trace metals (e.g. Al and Fe) are comparable over both sites during relatively warmer months (Mar-Sept) when the site at Guru Shikhar is within the BL. The concentration of Mg is somewhat higher over Mt Abu than that over Ahmedabad during high dust events. Its likely source could be attributed to local desert soils with higher Mg/Al ratios.

Out of 127 samples collected over Ahmedabad (n = 99) and Mt Abu (n = 28), 40 samples were weighed on a semi-micro balance to determine total suspended particulate (TSP) concentrations. The measured concentration of Fe in aerosols exhibits a strong linear positive correlation with the TSP (Fig. 3.10); thus indicating that mineral aerosols make dominant contribution to TSP on a seasonal and spatial scale.

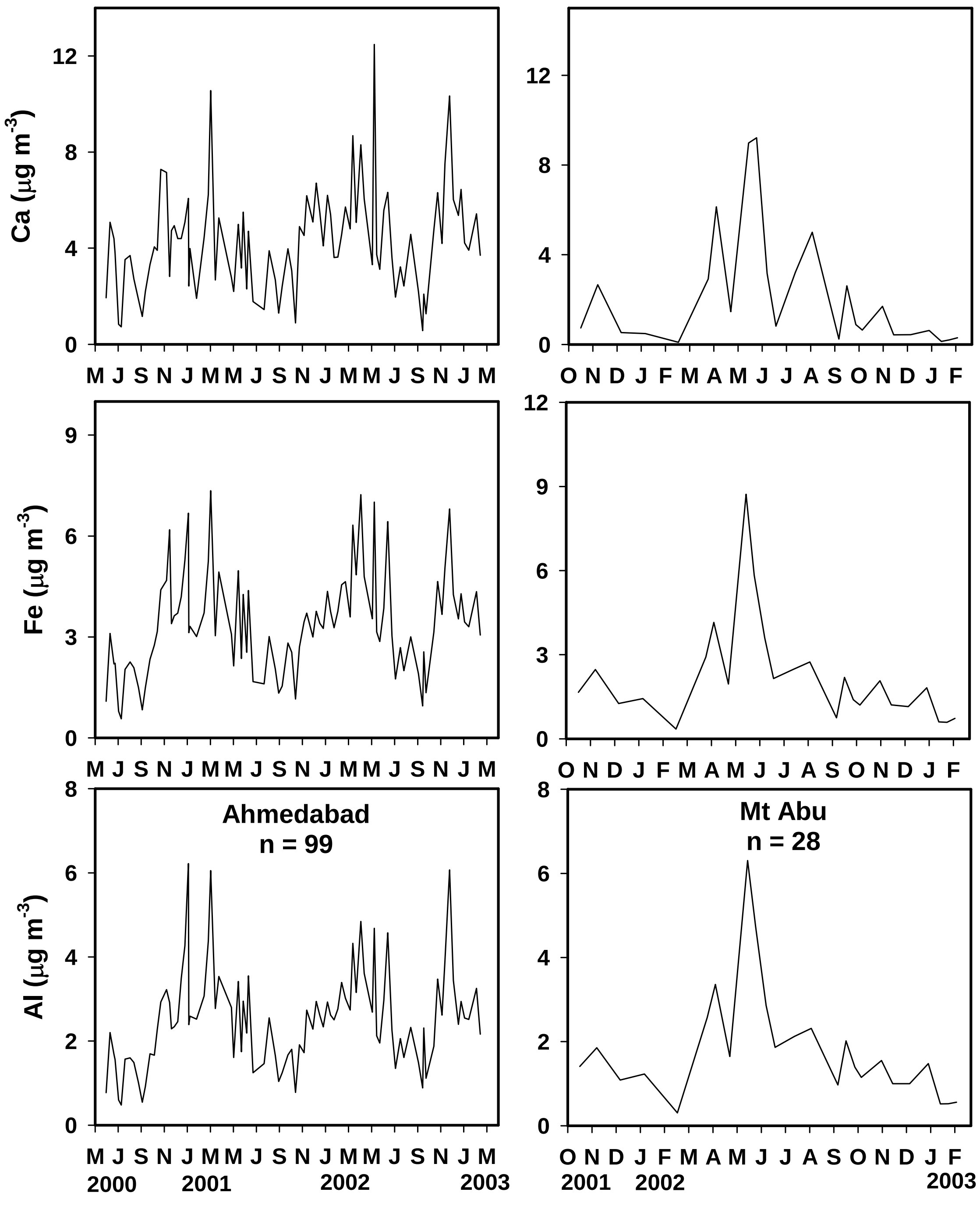

Figure 3.9a. A close similarity in the temporal variations of Al, Fe and Ca concentrations suggest their principal source from local dust.

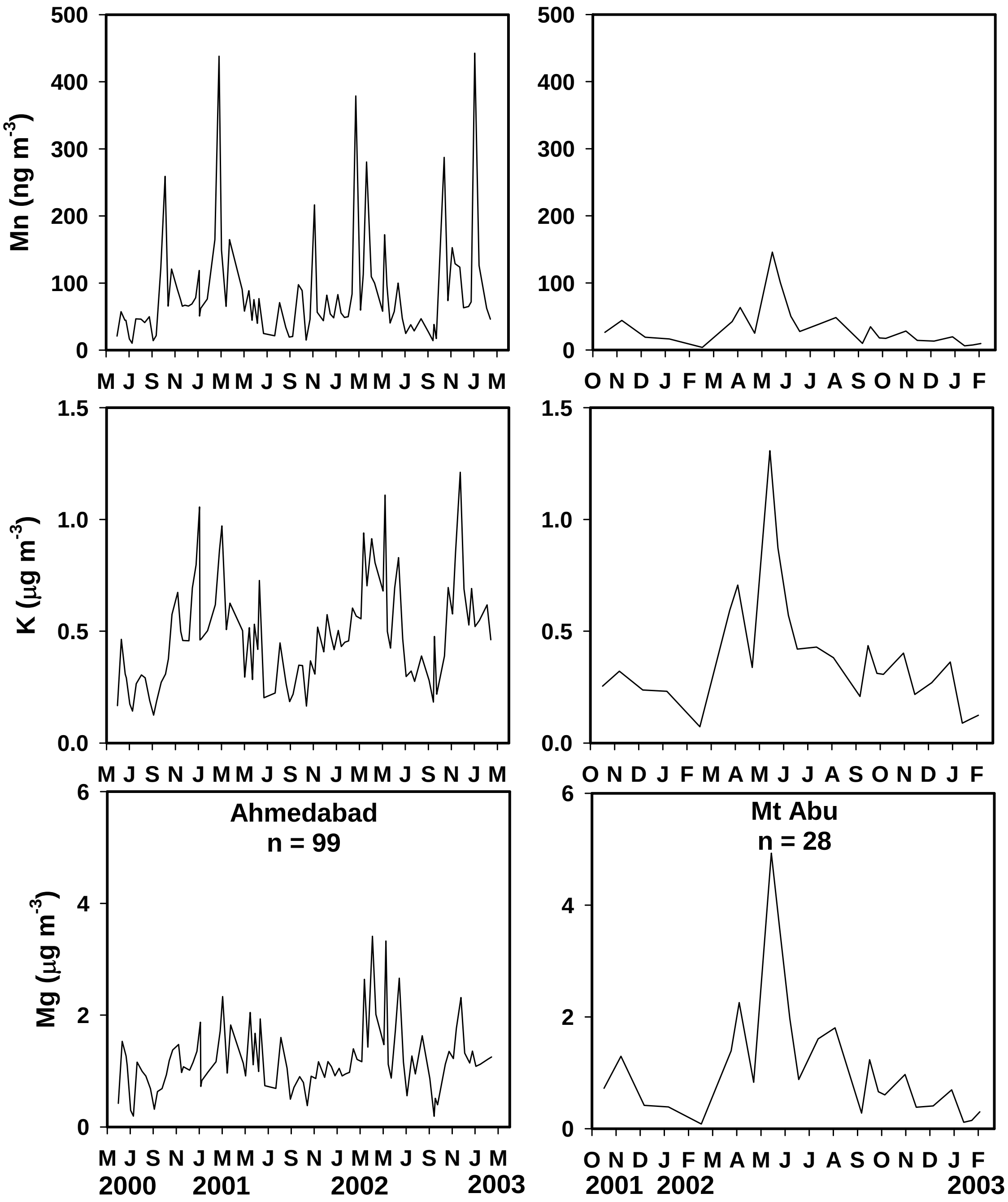

Figure 3.9b. Temporal variations of Mn during DRY period over Ahmedabad is different when compared to those of other soil derived components (Mg and K), suggesting significant additional source (anthropogenic activities) of Mn over Ahmedabad (urban city).

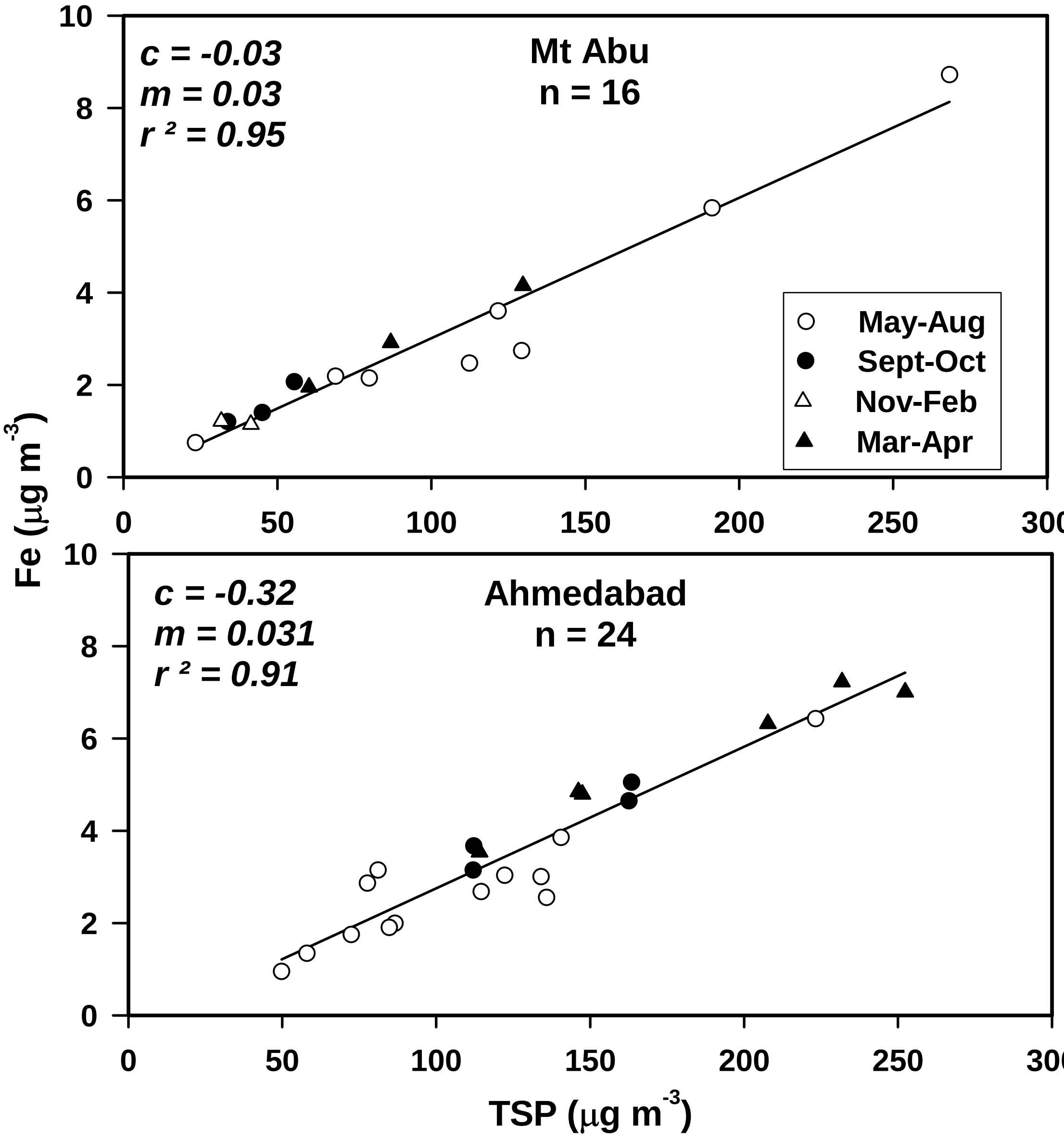

Figure 3.10. Scatter diagram between TSP and acid-soluble Fe abundance in aerosols. The strong positive correlation allows one to estimate the TSP from the measured content of Fe.

Sources of Zn and Pb in the atmosphere are non-ferrous metal production, iron and steel manufacturing, coal and wood combustions (Pacyna et al., 1984; Nriagu and Pacyna, 1988). Until a decade ago, one of major the source of Pb to atmosphere was vehicular emission (gasoline combustion) but now because of ban on leaded petrol, this source is not expected to contribute significantly to Pb abundance in the atmosphere.

Concentrations of Zn and Pb are about an order of magnitude higher over Ahmedabad than that over Mt Abu (Table 3.2), indicating the influence of anthropogenic emissions on air quality over an urban city. As a result of various anthropogenic emissions, Zn and Pb exist in finer mode. The temporal variability of these species, over both the sites, are similar to those of NH_4^+, nss-K^+ and nss-$SO_4^=$ in aerosols. Because of the absence of local industrial pollutants in and around Mt Abu, the observed concentrations of Zn and Pb are expected to be influenced by long-range transport. Concentrations of these species are significantly lower in WET period than those in the DRY period because of the rapid removal of aerosols in the former period and prevailing wind fields during these seasons. Atmospheric concentration of Pb over Ahmedabad is higher than those reported over several sites in literature (Pacyna et al., 1984; Arimoto et al., 2004) but significantly lower than that reported over two heavily polluted cities (Mumbai and Moradabad) in India (Tripathi et al., 1989).

3.2.2.3 Enrichment Factors of trace elements:

The sources of trace elements are frequently investigated through the analysis of elemental concentration ratios. One approach for this is to compare ratios in the samples with those in a likely source material by calculating enrichment factors (EFs) (Rahn, 1976). EFs relative to UCC are used to understand the relative dominance of dust and anthropogenic sources for any element (X) in aerosols, it is calculated as follows:

$$EF_X = (X/Al)_{aerosols}/(X/Al)_{ucc}$$

If EF is close to unity, it indicates that the element X is primarily derived from crustal dust; EF >> 1 suggests that the abundance of X in aerosols is controlled by input from multiple sources. Temporal variations in EFs estimated for Mn, Zn and Pb in each aerosol sample have been plotted in Fig. 3.11. EFs for any trace element in aerosols with a value of < 5 is considered as mainly derived from mineral aerosols (Arimoto et al., 1989). EF of Mn is fairly constant (~5) over Mt Abu in all seasons, suggesting it is largely derived from mineral aerosols but over Ahmedabad, many samples exhibit higher EFs, indicating significant anthropogenic source of Mn over this urban site. EFs of Zn and Pb are about an order of magnitude higher during DRY than those in WET period, indicating the level of increase in the contribution of pollution sources to ambient aerosols in DRY period.

Comparison of EFs of Zn and Pb over Ahmedabad and Mt Abu reflects the relative air quality over these sites. At Mt Abu, high EFs of Zn and Pb during DRY period are attributed to the long-range transport of pollutants by northeasterly winds while low EFs during WET period, could be because of rapid removal of aerosols and dominant oceanic air-mass (free of pollutants).

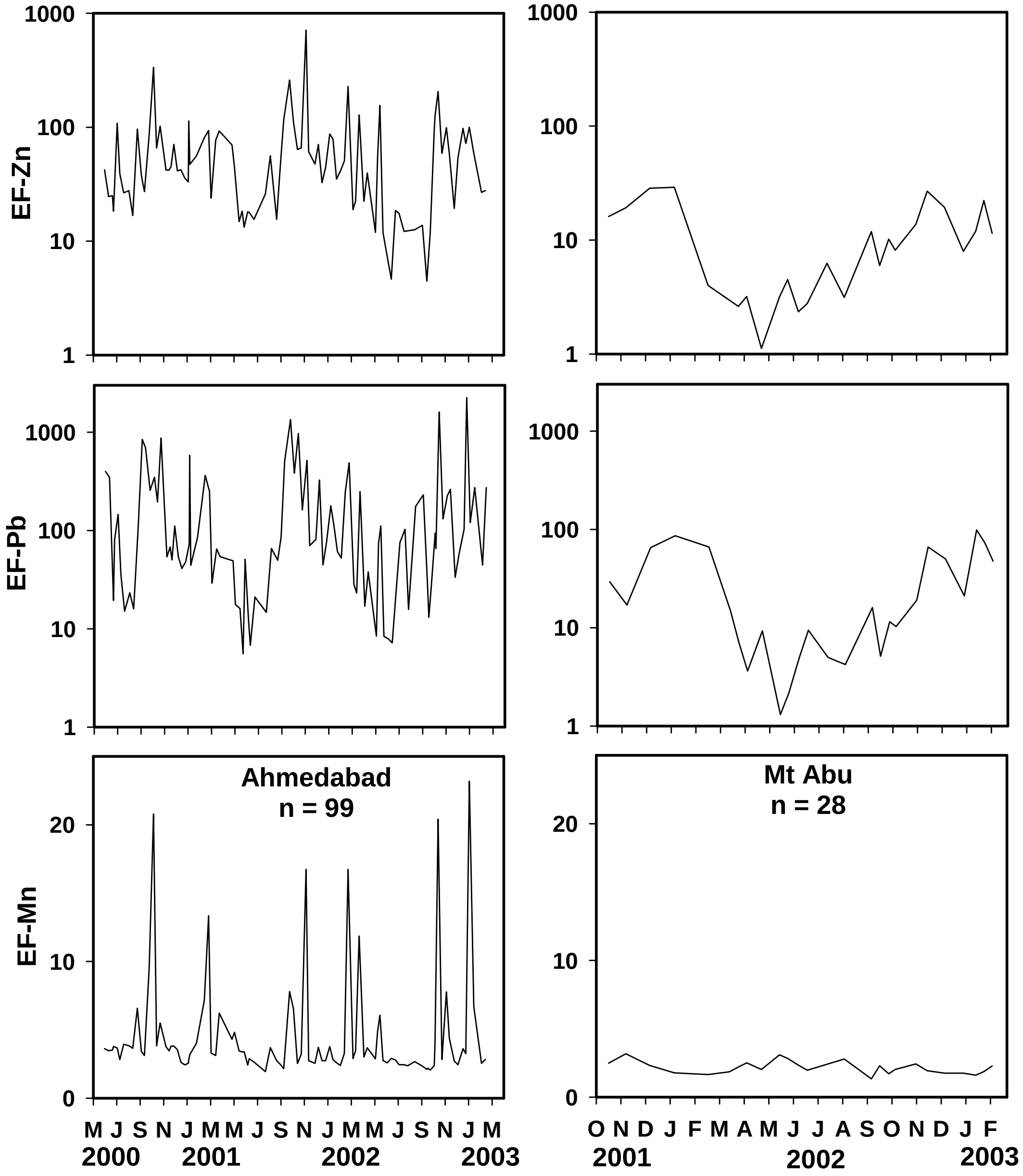

Figure 3.11 Time-series plots of enrichment factors (EFs) of Mn, Zn and Pb. The EF of Mn over Ahmedabad and Zn and Pb at both sites are quite high (>5) and indicate that they are largely derived from anthropogenic sources. Contrbution of anthropogenic sources is significantly higher during DRY period.

3.2.3 Aerosol studies in the MBL:

Bulk-aerosol samples were collected from the MBL of the Bay of Bengal (BOB), Indian Ocean (IO) and the Arabian Sea (AS) during Feb-Mar 2001 motivated by the perspective of understanding the transport pattern and chemical characteristics of aerosols in these regions. During the sampling period, the MBL is under the influence of NE-winds from continent to ocean (Fig. 2.3). The samples were analyzed for water-soluble ions, acid-soluble species and environmental radionuclides (^{7}Be, ^{210}Pb). The range, arithmetic mean and standard deviation of water-soluble ionic species and their non-sea-salt components are given in Table 3.3.

Table 3.3 Concentrations (μg m^{-3}) of water-soluble ionic species in aerosols over MBL.

	Bay of Bengal				**Indian Ocean**				**Arabian Sea**			
Constituent	**Min**	**Max**	**AM***	**SD[#]**	**Min**	**Max**	**AM**	**SD**	**Min**	**Max**	**AM**	**SD**
NH_4^+	0.13	1.04	**0.55**	0.28	0.18	0.77	**0.58**	0.20	<0.03	0.17	**0.17**	-
Na^+	0.15	4.73	**1.33**	1.25	0.38	0.85	**0.62**	0.16	0.62	2.11	**1.33**	0.61
K^+	0.07	0.56	**0.37**	0.10	0.17	0.35	**0.27**	0.06	0.04	0.18	**0.11**	0.04
nss-K^+	0.07	0.44	**0.32**	0.10	0.16	0.32	**0.25**	0.05	0.02	0.15	**0.06**	0.05
Mg^{2+}	0.05	0.59	**0.21**	0.16	0.10	0.14	**0.12**	0.02	0.17	0.38	**0.27**	0.08
nss-Mg^{2+}	0.00	0.11	**0.05**	0.03	0.03	0.06	**0.04**	0.01	0.06	0.13	**0.11**	0.03
Ca^{2+}	0.09	1.00	**0.45**	0.26	0.19	0.38	**0.29**	0.07	0.56	3.33	**1.76**	0.97
nss-Ca^{2+}	0.08	0.93	**0.39**	0.26	0.17	0.35	**0.26**	0.07	0.53	3.25	**1.71**	0.97
Cl^-	0.01	4.69	**0.78**	1.46	0.02	0.07	**0.04**	0.02	0.09	3.45	**1.61**	1.16
NO_3^-	0.01	1.05	**0.21**	0.33	0.01	0.07	**0.03**	0.02	0.08	0.83	**0.41**	0.26
$SO_4^{=}$	2.42	7.73	**4.97**	1.69	4.10	5.43	**4.78**	0.49	3.70	5.55	**4.47**	0.60
nss-$SO_4^{=}$	2.26	7.38	**4.64**	1.70	3.95	5.26	**4.62**	0.47	3.33	5.01	**4.13**	0.55

[*] Arithmetic mean; [#] Standard deviation. The non-sea-salt (nss) component of ionic species is derived based on their ratio with Na^+ in sea-salts.

The pronounced non-sea-salt components of K^+ (60-99%), Ca^{2+} (36-99%), Mg^{2+} (5-80%) and $SO_4^{=}$ (73-99%) indicate that meteorological conditions, favouring the transport of continental emissions (anthropogenic and mineral), dominate the aerosol composition in the MBL of BOB, IO and AS (Fig. 3.12). Fig. 3.13 shows the average percentage contribution of ionic species to the total water-soluble salts in aerosols over marine region. On average, $SO_4^{=}$ is the most dominant and accounts for ~60% of the ionic composition. Na^+ and NH_4^+ are the major cations over BOB and IO while Ca^{2+} dominates over AS.

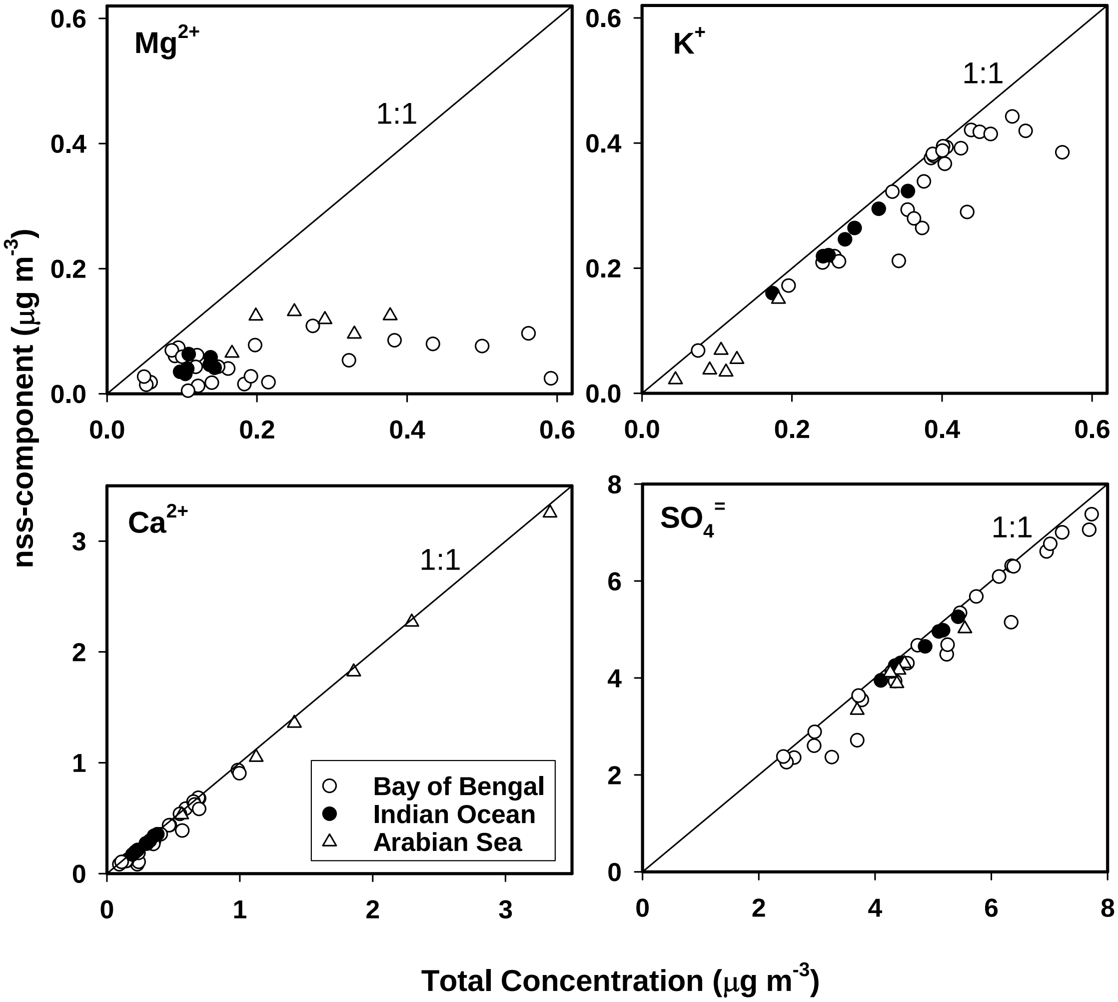

Figure 3.12. The non-sea-salt (nss) components of K^{+}, Ca^{2+}, Mg^{2+} and SO$_4^{=}$ plotted as a function of their total concentrations. For, Ca^{2+}, K^{+} and SO$_4^{=}$, the nss-components account for almost all of their abundance, suggesting the dominance of anthropogenic sources on the chemical characteristics of aerosols. However, Mg^{2+} abundance is largely influenced by sea-salts.

Relatively higher abundance of Ca^{2+} over AS is attributed to the transport of mineral aerosols originating from large expanse of Arabian Desert. The observed slope of 5.2 for the regression line between nss-Ca^{2+} and nss-SO$_4^{=}$ in the MBL of BOB and IO is nearly 4 times higher than that for the site at Ahmedabad (slope ~1.4) (Fig. 3.2b). This is attributed to the long-range transport of finer aerosols (enriched in sulphate derived from anthropogenic sources) than that of coarser particles (Ca^{2+} from mineral dust) to the MBL.

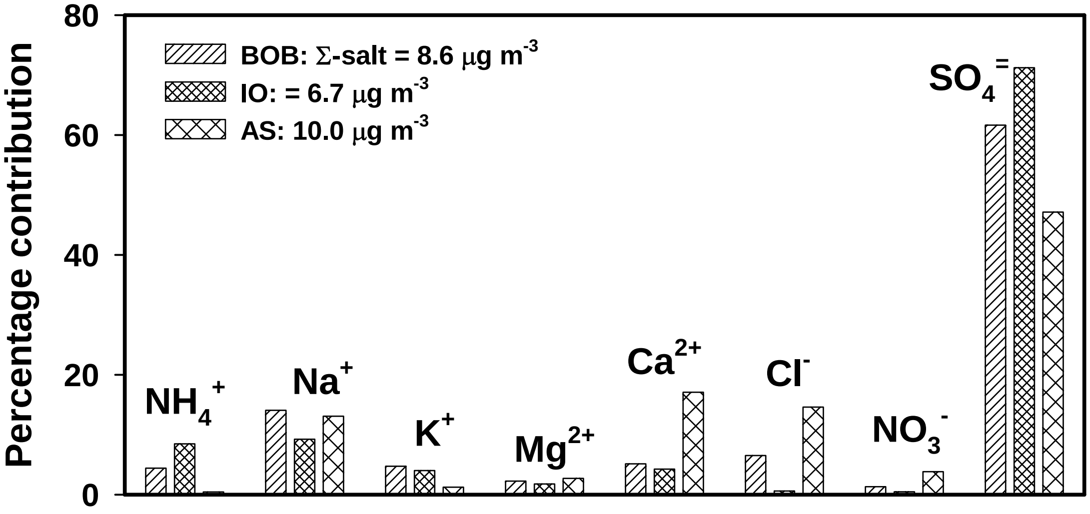

Figure 3.13. Percentage contribution of ionic species to Σ salts in aerosols over MBL suggest dominance of anthropogenic sources (using $SO_4^=$ as proxy) to aerosol composition.

The impact of higher abundance of nss-$SO_4^=$ found in all samples (ranged from 2.3 to 7.4 μg m^{-3}) is conspicuously reflected in the widespread depletion of chloride (55-98%) from sea-salt particles. The biogenic source (DMS i.e. dimethyl sulphide) contributes no more than ~1 μg m^{-3} of $SO_4^=$ (Lelieveld et al., 2001). The depletion of Cl^- has been calculated as follows:

$$\text{Cl-deficit (\%)} = \{[(Na^+ * 1.8) - Cl_{measured}] / (Na^+ * 1.8)\} * 100$$

where (Na^+ * 1.8) is expected Cl^- concentration from sea-salts, if there is no loss of Cl^- by any process and all Na^+ is originating from sea-salts. Spatial variability in Cl^-/Na^+ ratio in aerosols, and percentage Cl-deficit varying as a function of nss-$SO_4^=$ are shown in Fig. 3.14. High Cl-deficit is strongly correlated with high nss-$SO_4^=$ (Fig. 3.14), suggesting that sea-salts are a potential sink for anthropogenic SO_2 over marine regions. Johansen and Hoffmann (2004) have recently reported on large Cl-deficit over the Arabian Sea due to nss-$SO_4^=$. It is noteworthy that when contribution of mineral aerosols to the ionic composition (using Ca^{2+} as an index) is comparable to sea-salt contribution, depletion of Cl^- by nss-$SO_4^=$ is relatively less predominant as observed over the Arabian Sea (Fig.

3.14). The transect covered in the Indian Ocean exhibits near quantitative depletion of Cl^- from sea-salts (Fig. 3.14). This could arise as a result of competition between mineral and sea-salt aerosols for acid uptake. Zhuang et al (1999) reported that in low RH (<50%) and high Ca^{2+} (with respect to Na^+) condition, neutralization of acidic species is preferred by mineral aerosols than by sea-salts. In the present study, Cl^-/Na^+ ratio in aerosols over Ahmedabad and Mt Abu during WET period are quite close to seawater ratio (Fig. 3.2a), where mineral dust contribution is predominant. These observations strongly suggest that both mineral dust and sea-salts could act as a potential sink for acidic species ($SO_4^=$ and NO_3^-).

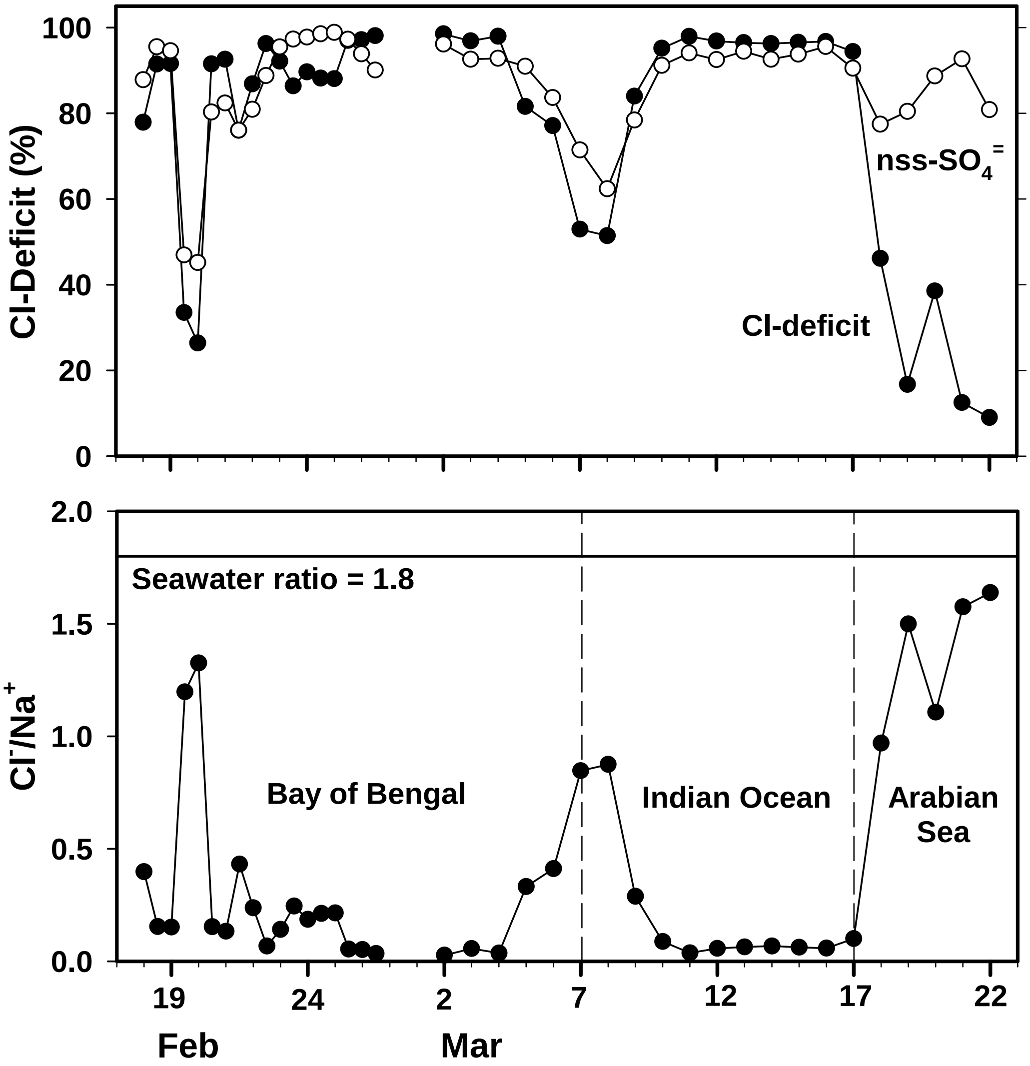

Figure 3.14. Spatial variability in Cl^-/Na^+ ratio and %Cl-deplteion and %nss-$SO_4^=$. Calendar dates correspond to the cruise track given in Fig.2.1. In most of the samples, Cl^- is highly depleted and %Cl-depletion is closely associated with %nss-$SO_4^=$, suggesting sea-salts are the major sink of nss-$SO_4^=$ over marine regions.

The concentrations range, arithmetic mean, standard deviation and enrichment factors of species (Al, Fe, Mn, Zn and Pb) measured in acid-soluble fraction of aerosols in the MBL are given in Table 3.4.

Table 3.4 Concentrations (ng m^{-3}) of trace elements and their enrichment factors (EFs) measured in acid-soluble fraction of aerosols in the MBL.

Element	Min	Max	AM*	SD[#]	EF	Min	Max	AM	SD	EF	Min	Max	AM	SD	EF
Al	40	645	**291**	188	-	141	263	**187**	44	-	309	1865	**762**	584	-
Fe	40	807	**309**	222	2.3	123	291	**193**	55	2.3	326	2488	**953**	822	2.7
Mn	0.8	7.2	**3.2**	1.7	1.2	0.9	1.3	**1.1**	0.2	1.0	1.9	38	**13**	14	1.8
Zn	2.1	21	**6.5**	4.4	40	<2	<2	**-**	-		3.1	35	**13**	13	16
Pb	3.7	17	**8.5**	3.4	214	4.8	7.6	**6.5**	0.9	171	2.7	5.5	**4.2**	1.1	37

*Arithmetic mean; [#]Standard deviation

The concentrations of Fe (40-2488 ng m^{-3}) and Al (40-1865 ng m^{-3}) exhibit large spatial variations during Feb-March over marine region of BOB, IO and AS, and their scatterplot shows a very strong correlation (r^2 = 0.99) (Fig. 3.15); suggesting coherency in their source (from mineral dust) and transport processes.

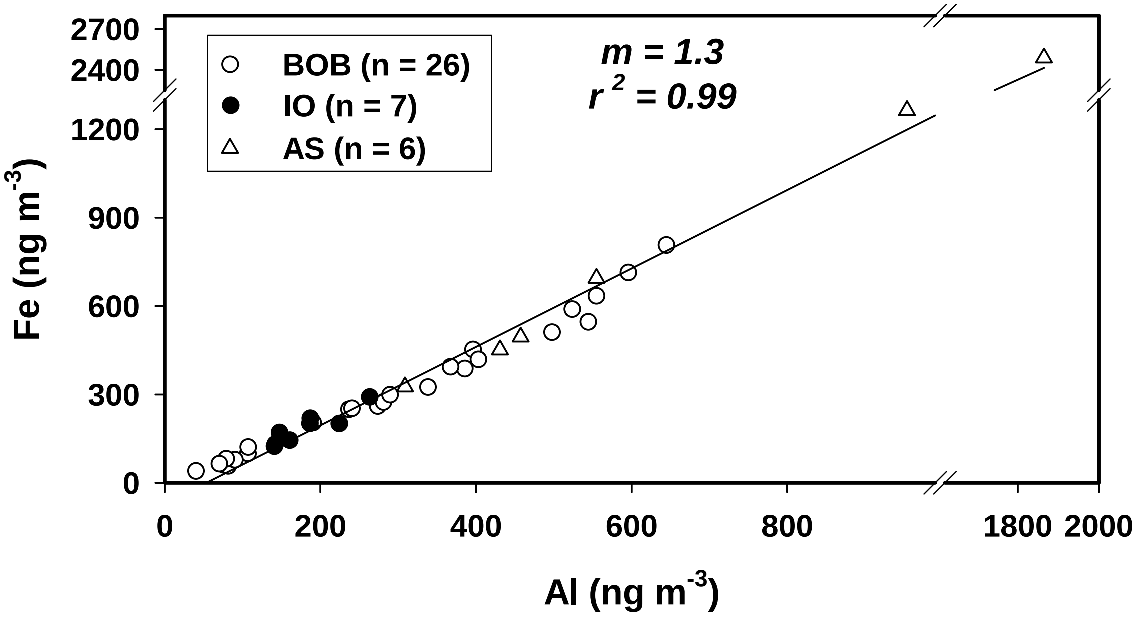

Figure 3.15. Linear regression plot between Al and Fe shows strong correlation with slope similar to that observed over Ahmedabad and Mt Abu, suggesting large scale enrichment of Fe in aerosols derived from dust emission sources.

The average Fe/Al mass ratio observed over marine regions is ~1.3, significantly higher than that in UCC (0.44) but similar to those observed over Ahmedabad and Mt Abu; further supports a characteristic and wide-spread feature of Fe enrichment in aerosols over Indian region. The impact of anthropogenic sources on trace metal concentrations is evident over the marine region with concentrations of Zn and Pb varying as 2.1-35 and 2.7-17 ng m^{-3} respectively (Table 3.4). Average EFs for Zn and Pb are the highest over BOB, (Table 3.4), suggesting relatively large scale contribution from anthropogenic emissions.

3.2.3.1 Deposition fluxes of trace elements over MBL:

Dry deposition fluxes of trace elements (Al, Fe, Mn, Zn and Pb) during study period (Feb-Mar), over the MBL of the Bay of Bengal, Indian Ocean and the Arabian Sea, have been calculated as follows:

$$\text{Dry deposition flux} = C * V_d$$

Where, C is the concentration of trace element (μg m^{-3}); V_d is deposition velocity (m d^{-1}). For Al, Fe and Mn, deposition velocity was considered as 1.0 cm s^{-1} and that for Zn and Pb as 0.1 cm s^{-1} (Duce et al., 1991). Average dry deposition fluxes (μg m^{-2} d^{-1}) of trace elements during study period over MBL are given in Table 3.5. For comparison, trace elements fluxes over two islands (Enewetak and Samoa, Arimoto et al., 1989) and world oceans (Duce et al., 1991) are also presented in Table 3.5. However, reported fluxes over MBL (in this study) are the average of February and March months while those over other sites are annual average. Fluxes of all trace elements, except Pb, are highest over the Arabian Sea and lowest over the Indian Ocean. This is attributed to relatively large input of mineral dust to the Arabian Sea from vast expanse of desert areas. The deposition flux of Fe, a very important micro nutrient for surface ocean primary productivity, is significantly higher over the MBL of study region than those over world oceans (Table 3.5). It has major implications to surface ocean biogeochemistry of northern Indian Ocean.

Table 3.5 Dry deposition fluxes (μg m^{-2} d^{-1}) of trace elements over MBL of the Bay of Bengal (BOB), Indian Ocean (IO) and the Arabian Sea (AS), and world oceans.

	BOB	IO	AS	Enewetak[#]	Samoa[#]	N. Pacific[$]	S. Pacific[$]	N. Atlantic[$]	S. Atlantic[$]	N. Indian[$]	S. Indian[$]	GLOBAL[$]
Al	193	158	541	33	3.7-49	231	17	179	19	300	38	110
Fe	194	161	636	16	1.3-9.2	104	8	77	8	132	16	48
Mn	2.3	0.9	6.6	0.2-0.3	0.06-0.14	-	-	-	-	-	-	-
Zn*	476	-	802	550	380-1600	329	36	1694	130	511	79	405
Pb*	681	558	353	190	60-110	82	8	49	55	164	27	110

[#]Arimoto et al., 1989; [$]Duce et al., 1991; *ng m^{-2} d^{-1}

3.3 SUMMARY AND CONCLUSIONS

The major observations and conclusions drawn from the results reported in this chapter are:

- The concentrations of water-soluble and acid-soluble constituents in aerosols over Ahmedabad and Mt Abu suggest pronounced seasonal variability in composition arising due to changes in meteorological conditions (wind regimes) and source strengths of aerosols but inter-annual variability is insignificant.
- On average, mineral dust contribution to the aerosol ionic composition is dominant and remains more or less uniform during all seasons. The sea-salt contribution increases significantly (by factor of ~3) in WET period and that of anthropogenic sources in DRY period.
- Sea-salt contribution is insignificant to Ca^{2+} (<2%) and $SO_4^=$ (<10%), minor to K^+ (<20%) and significant to Mg^{2+} (~60%) abundances in aerosols over Ahmedabad and Mt Abu.
- Acidic species (nss-$SO_4^=$ and NO_3^-) are largely neutralized by $CaCO_3$ rather than NH_4^+ at both sites, unlike several other studies reported over India and world. On average, calcium and magnesium carbonates uptake ~80% of the excess acid over both study sites.
- Significant amount of NH_4^+ and NO_3^- is present in gaseous phase over study regions during summer months (Apr-Jun).
- Large chloride depletion (upto 90%) was observed over MBL of the Bay of Bengal and Indian Ocean due to neutralization reaction between sea-salts and anthropogenic $SO_4^=$.
- In the presence of comparable contribution from sea-salts and mineral dust to ionic composition, acid uptake is preferred by mineral dust.
- Fe/Al ratios over Ahmedabad, Mt Abu and MBL of the Bay of Bengal, Indian ocean and the Arabian Sea are remarkably similar (~1.3), suggesting wide-spread feature of Fe enrichment (with respect to UCC) in aerosols over the Indian region.
- EFs of Mn, Zn and Pb over study sites suggest that Zn and Pb are predominantly contributed by anthropogenic activities over all study sites with relatively large contribution over Ahmedabad and marine regions. Mn is largely derived from

mineral dust over Mt Abu and MBL but at Ahmedabad, it is significantly contributed by anthropogenic sources also.

- Dry deposition fluxes of Fe (160-640 μg m^{-2} d^{-1}) and Pb (350-680 ng m^{-2} d^{-1}) are significantly higher over MBL of the Bay of Bengal, Indian Ocean and the Arabian Sea than those reported over world oceans.

Chapter 4

RAINWATER CHEMICAL COMPOSITION

4.1 INTRODUCTION

The aerosols and gases from natural and anthropogenic sources are incorporated into raindrops through in-cloud and below-cloud scavenging processes. Therefore, study of the chemical composition of precipitation is important for understanding these processes. Over the past two decades, several studies have been carried out on the chemical composition of rainwater over large parts of India mainly to characterize the acidic/alkaline nature of precipitation events (Khemani et al., 1989; Ravichandran and Padmanabhamurty, 1994; Parashar et al., 1996; Saxena et al., 1996; Jain et al., 2000; Norman et al., 2001; Kumar et al., 2002; Naik et al., 2002; Kulshreshtha et al., 2003; Safai et al., 2004). The acid rain is reported only from a few industrial pockets (Ravichandran and Padmanabhamurty, 1994; Naik et al., 2002). Despite large anthropogenic emissions of acidifying oxides of sulphur and nitrogen, alkaline pH of rainwater is common over India. This indicates the presence of neutralizing compounds such as calcium carbonate and ammonia (Norman et al., 2001). Dust is a major component of atmospheric aerosols especially over the arid and semi-arid regions of India. Thus, it is also likely to influence the chemical characteristics of rainwater in addition to the growing influence of anthropogenic emissions from urban areas. Ahmedabad, one of the major urban cities of India and situated in a semi-arid region at the periphery of Thar Desert, is an ideal site to study the relative influence of natural and anthropogenic sources to the rainwater composition. In this study, chemical analysis of individual wet-only events (n = 91) collected over Ahmedabad during the SW-monsoon (Jun-Sept) for a three-year period (2000-2002) has been carried out. Complete precipitation data is given in Appendix 3.

4.2 RESULTS AND DISCUSSION

4.2.1 Data quality assessment:

The charge balance between cations (NH_4^+, Na^+, K^+, Mg^{2+} and Ca^{2+}) and anions (Cl^-, NO_3^-, $SO_4^=$ and HCO_3^-) was assessed through regression analyses of the data (Fig. 4.1). The results yield a value of 0.997 for the slope (m), 0.997 for correlation coefficient (r^2) and an intercept not significantly different than zero (c = 5.8 μeq L^{-1}). All these suggest that the measured ions by and large account for almost all solutes in the rainwater and that the contribution from organic ions is negligible. The acceptable range, as per United State Environmental Protection Agency (USEPA) protocol, for ion difference in rainwater samples is 30-60% (for sum of ions 50-100 μeq L^{-1}) and 15-30% for the samples having ion sum >100 μeq L^{-1}. In this study, the anions to cations ratio ranged from 0.83 to 1.43, with 70% of the samples having charge balance within 5% of the equivalent ratio (1.0). The maximum deviation in the ion balance are in rainwater samples having total dissolved solids (TDS) < 4.0 mg L^{-1}, wherein the abundance of HCO_3^- is below detection limit (<6 μeq L^{-1}).

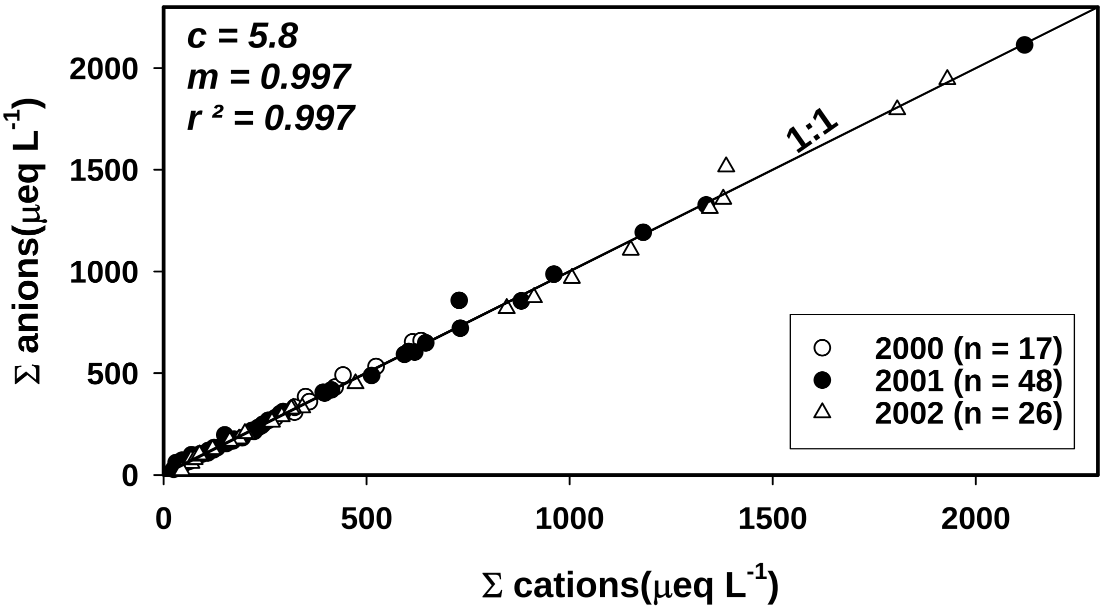

Figure 4.1. Charge balance between Σcations (NH_4^+, Na^+, K^+, Mg^{2+} and Ca^{2+}) and Σanions (Cl^-, NO_3^-, $SO_4^=$ and HCO_3^-) for individual precipitation events. Almost all data points lie on the equilibrium line attesting the high quality of data and suggesting that the contribution of organic acids is insignificant at the study site.

It is important to state that in this study HCO_3^- content is based on its measurement in all rain samples unlike most of the reported studies over the Indian region, wherein HCO_3^- is calculated as the difference between Σ cations and Σ (Cl^- + NO_3^- + $SO_4^=$) or based on the empirical relationship between pH and HCO_3^- (Parashar et al., 1996; Jain et al., 2000; Pillai et al., 2001; Kumar et al., 2002; Kulshreshtha et al., 2003; Safai et al., 2004).

4.2.2 Chemical characteristics of rainwater:

The minimum and maximum concentrations (μeq L^{-1}) of measured cations and anions in precipitation events and their volume-weighted mean (VWM) are summarized in Table 4.1. The VWM concentration for all chemical species is computed from their ionic concentration C_n (μeq L^{-1}) and precipitation volume P_n (mm) of the events as:

$$VWM = \Sigma C_n P_n / \Sigma P_n$$

On average, the ion abundance in precipitation samples follows the sequence $Ca^{2+} > HCO_3^- > Cl^- > Na^+ > SO_4^= > NH_4^+ > NO_3^- > Mg^{2+} > K^+$ (Table 4.1). The VWM concentrations of all species were quite similar for the year 2000 and 2001 but relatively higher in year 2002. This trend follows somewhat inverse relation to the rainfall amount during these three years (2000: 728 mm; 2001: 681 mm and 2002: 398 mm). These concentrations have been compared with the reported data from other parts of India (Table 4.1). The VWM concentrations of measured ions in rain events over Ahmedabad (this study) are significantly higher when compared to the rainwater composition over Pune (Pillai et al., 2001).

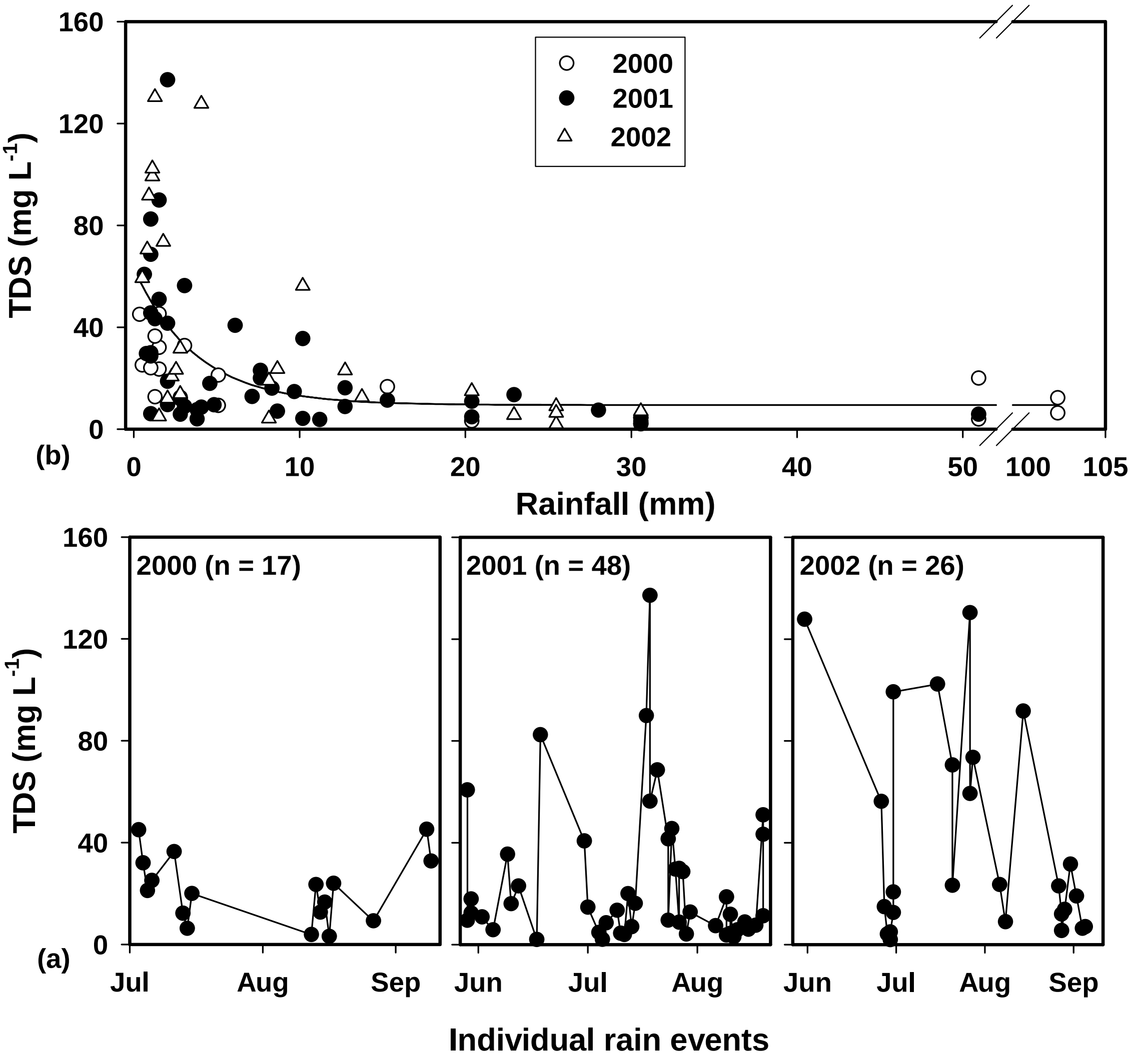

Figure 4.2. Seasonal and inter-annual variations of Total Dissolved Solids (TDS) (a) for individual rain events during 2000-2002 and (b) with rainfall. The rain events with high TDS are those occurring after an antecedent dry period.

Table 4.1: Range and volume-weighted-mean concentrations (μeq L^{-1}) in precipitation over Ahmedabad during SW-monsoon of the three-year (2000-2002) period

	Ahmedabad										Agra^a	Delhi^b	Pune^c
	2000 (n = 17)			2001 (n = 48)			2002 (n = 26)			3 years (n = 91)	7 years		6 years
Parameter	Min	Max	VWM	Min	Max	VWM	Min	Max	VWM	VWM	AM	AM	VWM
Rainfall (mm)	0.4	102	-	0.6	51	-	0.5	31	-	-	-	-	-
pH	6.1	7.4	6.7*	5.2	8.2	6.7*	5.6	7.9	6.7*	6.7*	7.0	5.4	6.1
EC (μS cm^{-1})	9	77	19	4	242	19	6	204	29	21	-	-	-
NH_4^+	1.7	220	27.8	2.0	107	26.7	2.3	153	41.4	30	40	26	10
Na^+	7.0	176	28.6	1.3	1030	40.1	3.0	750	61.7	41	18	82	24
K^+	0.8	31.2	3.1	0.6	38.4	2.9	0.6	53.0	4.6	3.4	7.6	44	1
nss-K^+	0.6	30.1	2.5	0.3	16	2.1	0.4	41.8	3.2	2.5	-	-	-
Mg^{2+}	4.1	66.7	15.1	1.5	251	12.5	1.9	173	19.2	15	46	70	12
nss-Mg^{2+}	1.4	35.7	8.6	0.0	34.0	3.4	0.5	55.9	5.3	5.6	-	-	-
Ca^{2+}	20.0	387	72.8	6.5	739	63.7	5.5	1057	114	78	56	134	52
nss-Ca^{2+}	19.3	381	71.6	6.4	694	61.9	5.2	1035	111	76	-	-	-
Cl^-	12.4	242	38.2	3.1	1190	46.3	8.5	983	75.3	50	32	140	26
NO_3^-	1.0	61.3	8.7	1.3	85.2	13.5	5.0	115	19.7	13	23	67	11
$SO_4^=$	6.7	219	30.4	4.8	431	36.2	7.9	318	49.2	37	36	90	23
nss-$SO_4^=$	5.6	214	26.9	4.6	306	31.3	7.2	256	41.8	32	-	-	-
HCO_3^-	25	253	75	8	482	56	12	836	93	71	-	-	14
TDS (mg l^{-1})	3.2	45.2	10.9	2.0	137	10.6	1.9	130	16.8	12.0	-	-	-

[a] Kumar et al., 2002; [b]Ravichandran and Padmanabhamurty, 1994; [c]Pillai et al., 2001; [*]calculated based on average [H$^+$]

Total dissolved salts (TDS) for each rain event have been calculated by summing up the concentrations (mg L^{-1}) of all measured ions. In general, variations in TDS reflect the variations in concentrations of individual chemical species except for constituents those are predominantly derived from gaseous phase scavenging (e.g. NH_4^+, NO_3^- and $SO_4^=$). The temporal and inter-annual variations in the TDS (varying from 1.9 to 137 mg L^{-1}) of individual precipitation events are depicted in Fig. 4.2a. These data demonstrate that the abundances of chemical constituents in individual rain events are controlled largely by precipitation amount and below-cloud scavenging (Fig. 4.2b). It is also observed that there is a large scatter in TDS at low rainfall (<5 mm), rain events occurring after an extended period of dry phase generally have relatively high TDS in contrast to those in multiple frequent events spread over 2-3days (low in TDS, Figs.4.2a and 4.2b).

4.2.2.1 Rainwater pH:

The pH of individual precipitation events collected over a period of three years varied from 5.2 to 8.2. The frequency diagram of measured pH shows that ~90% of rainwater samples fall in the pH range of 6.0 to 7.5 with a mean of 6.7 (Fig. 4.3). The pH of rainwater in equilibrium with atmospheric CO_2 is expected to be 5.6 (Charlson and Rodhe, 1982). Rainwater having pH lower than 5.6, is defined as acidic and greater than 5.6 as alkaline. Based on this scale, majority of precipitation over Ahmedabad is alkaline.

The pH of an individual precipitation event depends upon the relative contributions of acidic (e.g. $SO_4^=$, NO_3^-) and alkaline (NH_3 and $CaCO_3$) components. Alkaline rainwater pH suggests dominance of neutralizing rather than acidifying constituents over Ahmedabad. In the sample having lowest pH (5.2) NO_3^- and $SO_4^=$ accounts for 17% and 53%, respectively, to the anion balance (HCO_3^- was less than a percent); whereas NH_4^+ and Ca^{2+} contribute 20 and 34% respectively to the total cations (Table 4.2). The difference in free acidity between the “lowest” sample (pH 5.2, $[H^+]$ = 6.31 μeq L^{-1}) and natural rainwater in equilibrium with atmospheric CO_2 (pH 5.6, $[H^+]$ = 2.51 μeq L^{-1}) is only 3.8 μeq L^{-1}. This would suggest that most of the $SO_4^=$ and NO_3^- are present as neutral salts ($(NH_4)_2SO_4$, NH_4NO_3) and not as dissociated acids. In the sample with highest pH (8.2), contribution of Ca^{2+} accounts for 52% of the total cations (NH_4^+

was less than a percent) and HCO_3^- represents 40% of the total anions; while NO_3^- and $SO_4^=$ contribute only 4 and 15%, respectively to the anion balance.

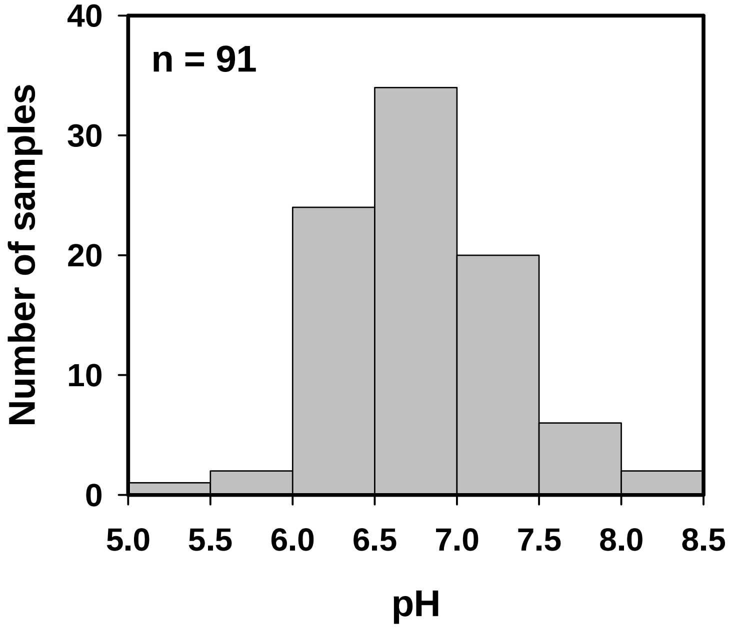

Figure 4.3. Frequency distribution of pH measured in precipitation events, collected during SW-monsoon period of three years. The pH ranged from 5.2 to 8.2 (average: 6.7), suggesting the alkaline nature of rainwater over Ahmedabad.

In a recent study, Al-Momani (2003) had reported alkaline pH (6.4 ± 0.9) of rainwater (even though concentrations of NO_3^- and $SO_4^=$ were high) over Jordan because of the neutralization of acidity by calcite rich local dust. Table 4.2 summarizes the average percentage contribution of individual cations to Σ cations and individual anions to Σ anions for the different pH range of samples (Fig. 4.3). It is noteworthy that pH is increasing with increasing percentage contribution of alkaline species (HCO_3^-) while contribution of acidic species (NO_3^- and $SO_4^=$) is higher in low pH-range samples. These observations ascertain that the pH of rainwater is controlled by the relative contribution of acidic (NO_3^-, $SO_4^=$) and alkaline (mainly HCO_3^-) components.

Table 4.2: Relative contribution of ionic species (on equivalent basis) in different pH-range of samples.

pH-range	n	NH_4^+	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	NO_3^-	$SO_4^=$	HCO_3^-
		…………% of Σ cations…….....					……% of Σ anions………			
5.0-5.5	1	20	34	3	9	34	30	17	53	0
5.5-6.0	2	16	24	2	8	49	28	11	42	20
6.0-6.5	24	38	19	2	6	36	22	13	30	35
6.5-7.0	34	24	22	2	8	44	27	11	27	34
7.0-7.5	20	10	32	2	9	46	38	6	19	37
7.5-8.0	6	3	31	1	9	55	36	6	17	42
8.0-8.5	2	1	32	1	10	55	35	4	17	44

4.2.2.2 Sources of major ions in rainwater:

The Na^+ and Cl^- concentrations for all rain events exhibit a linear positive relationship with Cl^-/Na^+ ratio nearly identical to that in sea salts (Fig. 4.4). In a few of the samples (collected during the year 2000) excess Cl^- could arise due to gaseous chloride from industrial sources and/or as a manifestation of Cl^--displacement from sea-salts (NaCl) by HNO_3/H_2SO_4 (Keene et al., 1999).

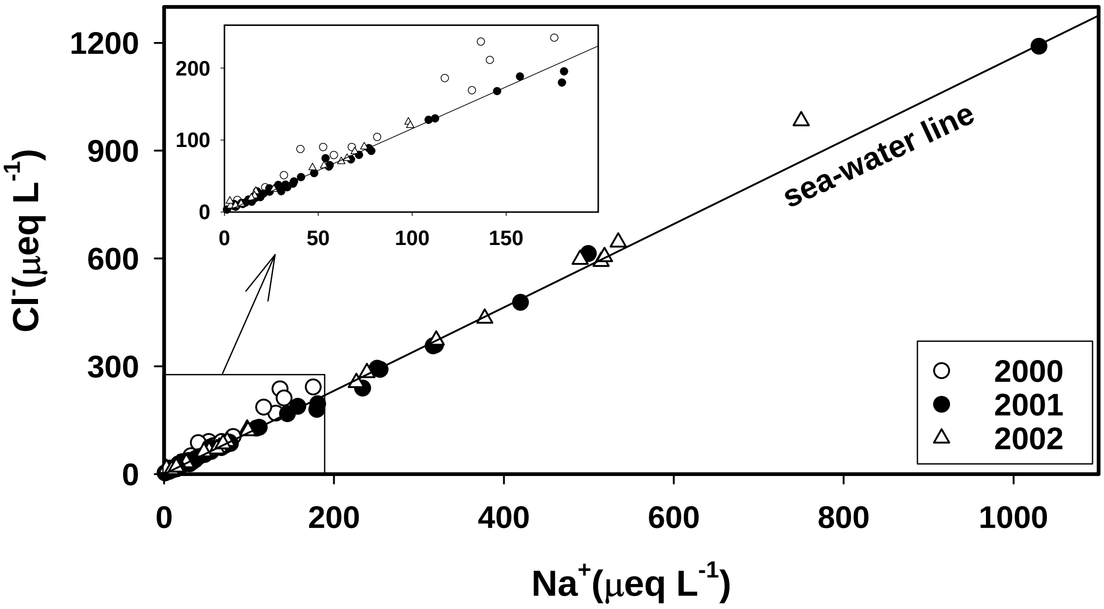

Figure 4.4. Scatter plot of Na^+ and Cl^-; most of the data points fall on the seawater line. This indicates their principal source from sea-salts and they are not fractionated during inland transport. This also suggests that contribution of soil dust to Na^+ is negligible.

This is relevant as the sampling period (Jun-Sept) during the year 2000 was marked by an episodic heavier precipitation event (~500 mm on 12-14 July) spread over 72 hours; while rest of the season had few isolated showers (<5 mm) with extended periods of dry phase (Fig. 2.4). Under these meteorological conditions, contribution of gaseous chloride could influence rainwater composition.

Based on the relationship in Fig. 4.4 and using Na^+ as a reference element for sea-salts (Keene et al., 1986), the non-sea-salt (nss) components of Ca^{2+}, $SO_4^=$, K^+ and Mg^{2+} are presented in Table 4.1. In all precipitation events, contribution of nss-Ca^{2+} varied from 94 to 99% and that of nss-$SO_4^=$ as 67 to 99%; suggesting that their abundances are dominated by crustal and anthropogenic sources (Fig. 4.5).

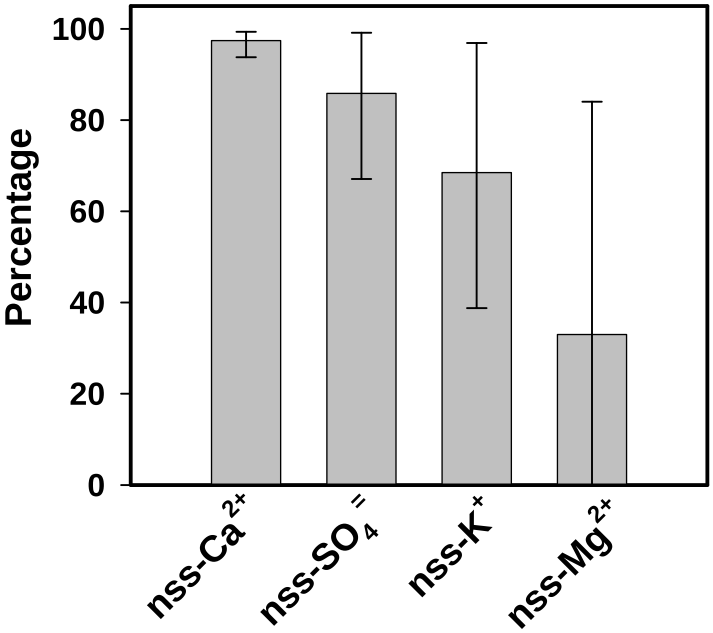

Figure 4.5. Average non-sea-salt content of Ca^{2+}, $SO_4^=$, K^+ and Mg^{2+} in rainwater. Error bar shows the minimum and maximum values of nss-content. The high nss-Ca^{2+} and nss-$SO_4^=$ suggest that contribution of sea-salts is insignificant their abundances. In contrast, for K^+ and Mg^{2+}, it is quite significant.

In contrast, nss-Mg^{2+} and nss-K^+ varies from 0 to 84% and 39 to 97%, respectively; suggesting that the sources contributing these constituents vary widely with individual precipitation events and overall there is a significant contribution of sea-salts to K^+ and Mg^{2+} in rainwater. The rain events occurring after extended period of dry phase generally had higher contribution of nss-Mg^{2+} and nss-K^+ to the cation balance, reflecting their dominant source from soil dust.

Several studies (Galloway, 1995; Kaya and Tuncel, 1997; Tuncer et al., 2001, Mphepya, et al., 2004) have reported that the NO_3^- and nss-$SO_4^=$ contents in rainwater are dictated by dissolution of HNO_3 (aq, g) and H_2SO_4 (aq, g) derived from various anthropogenic sources of NO_x and SO_2, and their secondary aerosols. To check on this, regression analysis between NO_3^- and nss-$SO_4^=$ abundances was carried out, which show a linear trend between them ($r^2 = 0.67$, Fig. 4.6). This trend indicates that these species are derived from same anthropogenic inputs. The nss-$SO_4^=/NO_3^-$ equivalent ratio in the individual events ranges from 0.8 to 6.7 but for most of the samples it is in a narrow range of 2 to 3. Also, the VWM ratio for the three year data centers around 2 to 3; suggesting that the nss-$SO_4^=$ is the dominant acidifying component in rainwater. Recently, Tuncer et al (2001) have reported an average $SO_4^=/NO_3^-$ equivalent ratio of 2.4 ± 1.2 over Anatolia, Turkey; concluding that the acidity transported to the study region is primarily in the form H_2SO_4 rather than HNO_3. The concentration of NH_4^+ varies considerably (range: 1.7-220 μeql^{-1}; VWM: 26.7-41.4 μeq L^{-1}, Table 4.1) independent of precipitation volume; and on average it accounts for 17-19% of the total cations (on equivalent basis).

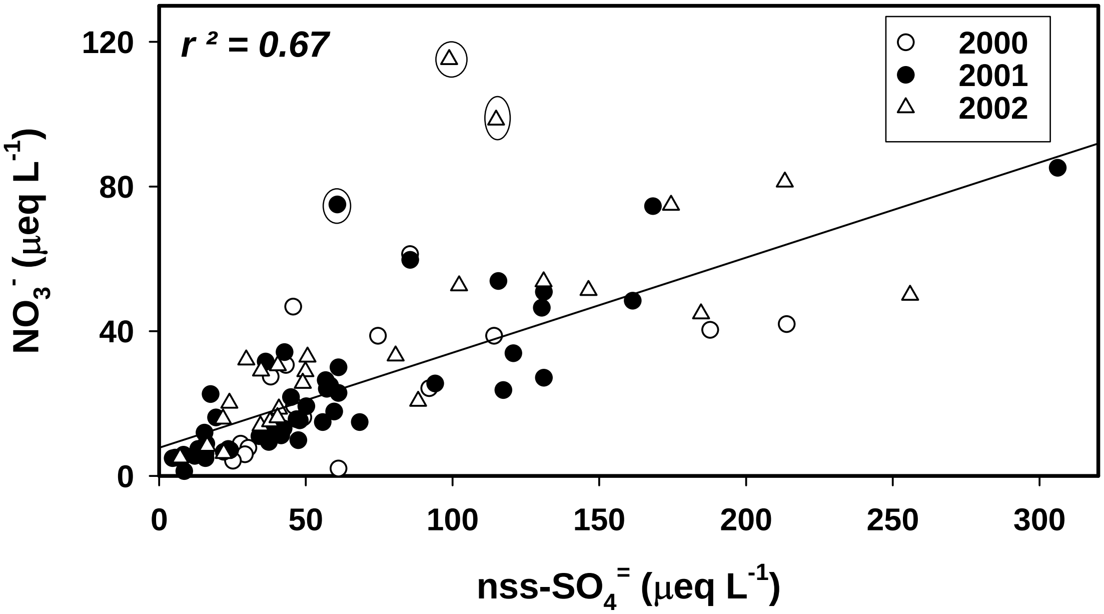

Figure 4.6. Scatter plot of nss-$SO_4^=$ and NO_3^-. The significant linear trend suggests their anthropogenic origin in precipitation. Encircled data points are excluded from regression analysis.

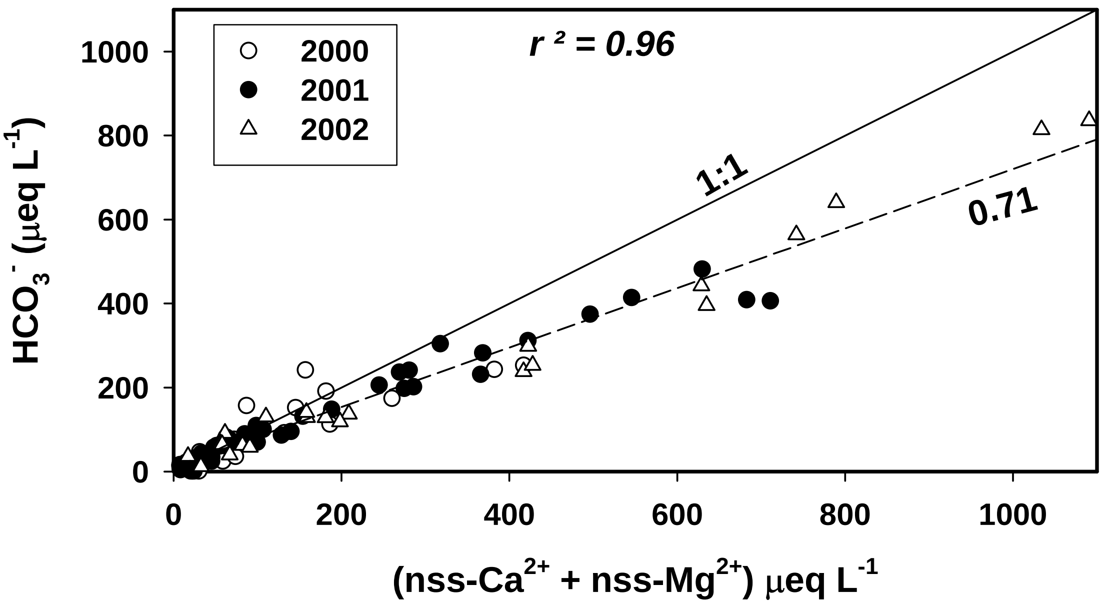

Figure 4.7. Scatter-plot between (nss-Ca^{2+} + nss-Mg^{2+}) and HCO_3^-; the solid line represents the equivalent ratio of 1.0 and the best-fit line through the data is shown by dotted line (slope = 0.71). The major source of these ions is crustal dust and a significant fraction of HCO_3^- is neutralized by acidic components (NO_3^- and $SO_4^=$).

The sources of nss-Ca^{2+}, nss-Mg^{2+} and HCO_3^- have been investigated based on the inter-relationship shown in Fig. 4.7. The regression parameters for the linear relation in Fig. 4.7, $r^2 = 0.96$, slope = 0.71, suggest that their abundances in the precipitation events are dominated by local dust sources. The nss-Mg^{2+}/nss-Ca^{2+} equivalent ratio (VWM) for all rainwater samples is 0.07; suggesting that almost all HCO_3^- is associated with nss-Ca^{2+}. The slope of regression line less than unity (Fig. 4.7) provides an evidence that significant fraction of HCO_3^- is either neutralized by acidic components $SO_4^=$ and NO_3^- (Equation 1) and/or there is an additional source for nss-Ca^{2+} such as gypsum ($CaSO_4$). It is noteworthy that the statistical correlation between nss-Ca^{2+} and nss-$SO_4^=$ exhibits a linear positive trend ($r^2 = 0.85$) with slope of the regression line as 0.24 (Fig. 4.8). Thus, the significant contribution of nss-Ca^{2+} from gypsum seems unlikely in the rain events collected in this study. The observed relationship between nss-Ca^{2+} and nss-$SO_4^=$ (Fig. 4.8) could arise due to following reaction:

$$Ca^{2+}(aq) + 2HCO_3^-(aq) + 2H^+(aq) + SO_4^=(aq)$$
$$\Rightarrow Ca^{2+}(aq) + SO_4^=(aq) + 2H_2O + 2CO_2(g) \qquad (1)$$

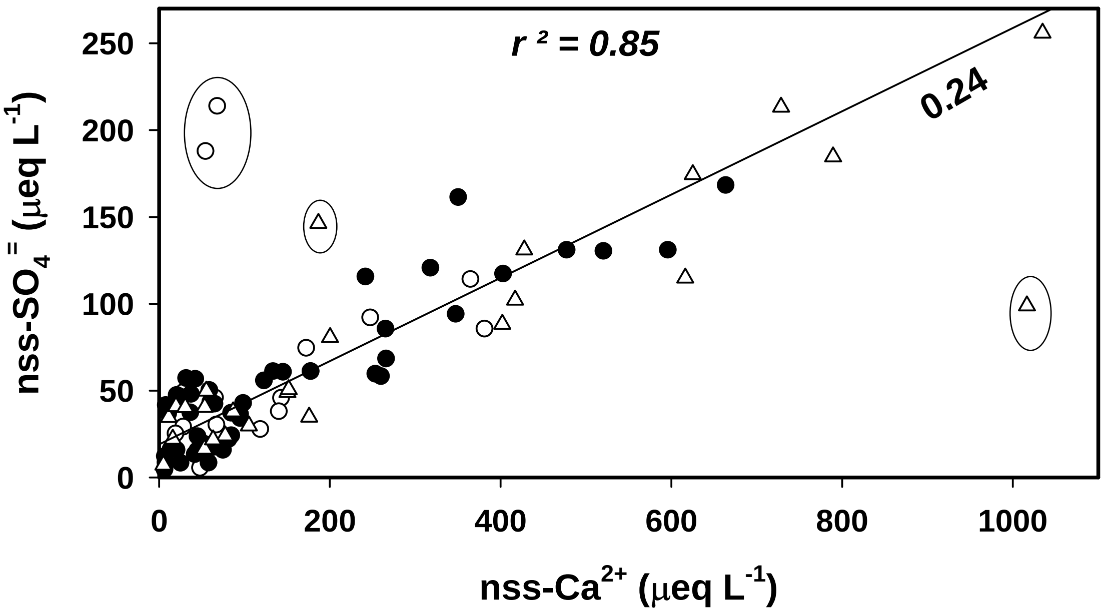

Figure 4.8. Plot of nss-Ca^{2+} vs nss-SO$_4^=$. Regression analysis of data yields a slope of 0.24 and correlation coefficient (r^2 = 0.85). This study proposes that the significant correlation between nss-Ca^{2+} and nss-SO$_4^=$ is due to neutralization reaction between $CaCO_3$ and H_2SO_4 in the atmosphere. Encircled data points are excluded from regression analysis.

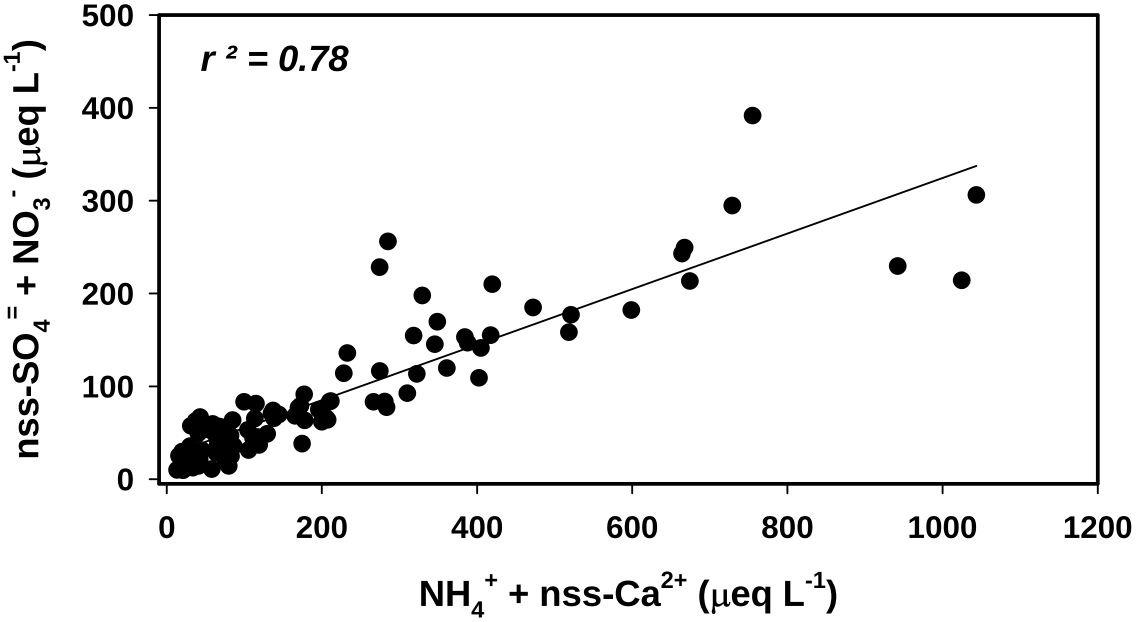

Figure 4.9. Relationship between ([NH$_4^+$] + [nss-Ca^{2+}]) and ([nss-SO$_4^=$] + [NO$_3^-$]) suggests that acidity in rainwater is mainly neutralized by NH$_4^+$ and $CaCO_3$.

The dominance of the neutralization reaction (Equation 1) during low precipitation rain events (<5 mm) and higher abundances of both $SO_4^{=}$ and TDS, is evident from the departure of data from 1:1 line (Fig. 4.7). However, from the composite chemical composition of rainwater, it is difficult to assess the relative contribution of gypsum vis-a-vis anthropogenic sources for the abundance of nss-$SO_4^{=}$. In order to gain further insight, regression analysis between ([nss-Ca^{2+}] + [NH_4^+]) and ([nss-$SO_4^{=}$] + [NO_3^-]) was carried out. The results show a linear trend with $r^2 = 0.78$ for $n = 91$. This would imply that acidic characteristic of $SO_4^{=}$ and NO_3^- is neutralized by NH_4^+ and $CaCO_3$ (Fig. 4.9).

4.2.3 Relationship between rainfall and ionic concentrations:

The concentrations of various ions exhibit large variations in individual precipitation events. The interrelation between precipitation amount and concentrations of Na^+, Cl^-, NO_3^-, Ca^{2+}, HCO_3^- and $SO_4^{=}$ has been examined in terms of the log-log plots (Fig. 4.10). These plots show an overall decreasing trend in concentration with increasing precipitation amount that can be described as

$$C = C_o P^{-m}$$

Or

$$\log C = \log C_o - m \log P$$

where C is the concentration of a chemical constituent, P refers to precipitation volume, C_o and m are constants (Takeda et al., 2000). The magnitude of the slope m can provide information on the role of precipitation in controlling the constituent concentration (C). If m is close to unity, it would indicate that the concentration (C) of a particular constituent is inversely proportional to precipitation volume i.e. it is removed by “below-cloud” scavenging (wash-out) at an early stage of the precipitation event and its concentration decreases successively with precipitation amount. If the m is far less than unity, it implies that the concentration of a chemical species in rain is mainly governed by “in-cloud” scavenging and/or increase in its atmospheric concentration (between the antecedent dry phase) from gaseous and/or particulate phase. In addition, variations in the source strength (dust and anthropogenic) could also influence the concentrations of chemical species in rainwater.

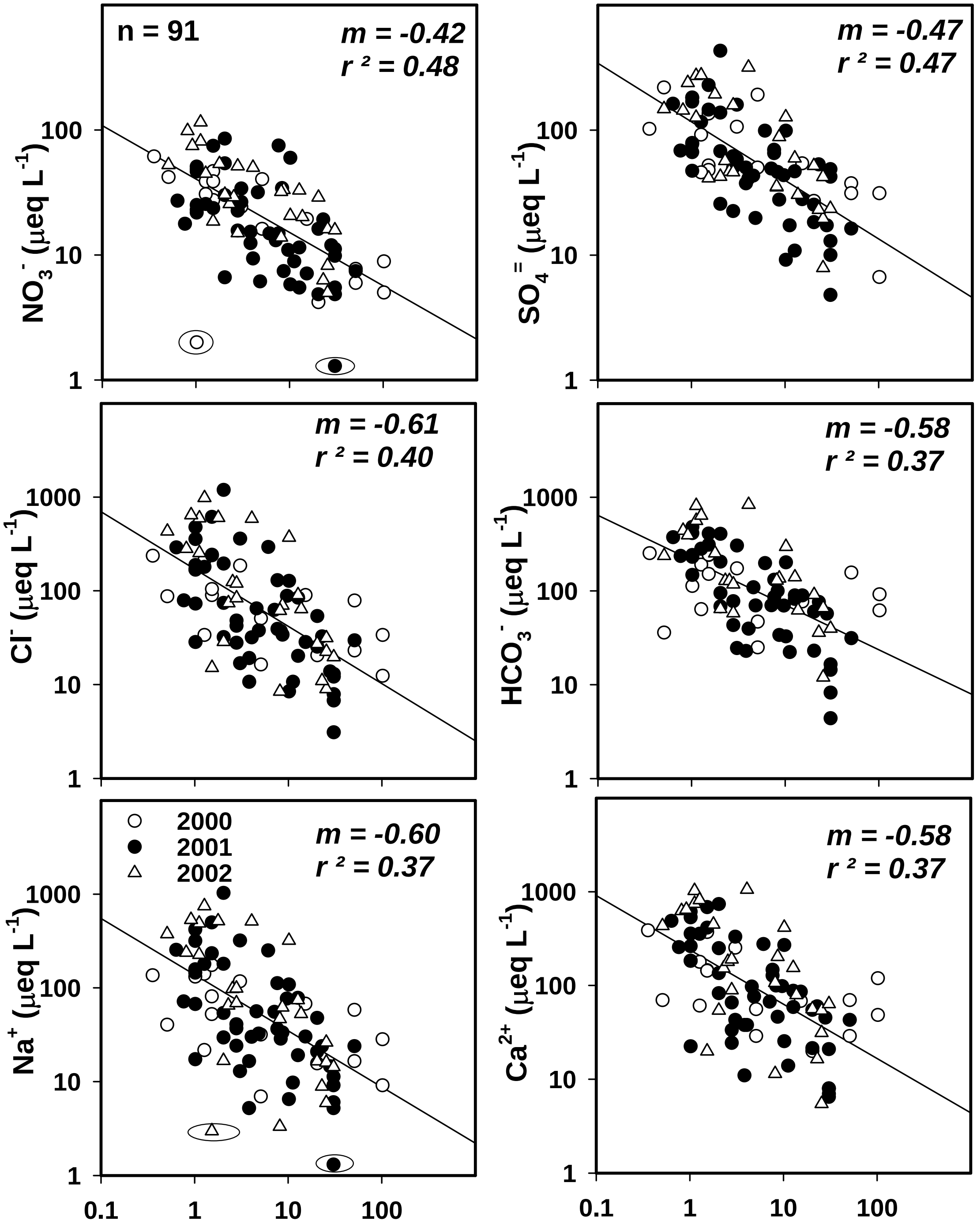

Figure 4.10. Log-log plots between precipitation amount and concentrations of major constituents. Encircled data points are not included in regression analyses. Relatively steeper slope of the regression line (for Na^+, Cl^-, Ca^{2+} and HCO_3^-) suggest that the concentration of these species is largely controlled by successive dilution effect with increasing precipitation.

It is important to emphasize that in this study individual rain events were collected spread over the entire SW-monsoon (Jun-Sept); therefore data in Fig. 4.10 are not strictly representative of successive precipitation from a single rain event. As a result, none of the major ions plotted in Fig. 4.10 show slope close to unity. The slope coefficients for Na^+, Cl^-, Ca^{2+}, HCO_3^- (0.58-0.61) are higher than those for NO_3^- and $SO_4^=$ (Fig. 4.10). This is an indication that source strengths for the latter two species are more variable in space and time. The relatively steeper slope (Fig. 4.10) for Na^+, Cl^-, Ca^{2+} and HCO_3^-, derived from particulate phase (sea-salts and crustal dust), could largely result from their efficient wash-out during early stage of precipitation. The concentration of NH_4^+ shows very poor correlation with precipitation amount; indicating that it is largely derived from gaseous phase. Rastogi and Sarin (2003a) have documented that NH_4^+ is primarily scavenged from gaseous phase based on its relatively high scavenging ratio and low concentration in aerosols during the SW-monsoon period over the study site.

4.2.4 Seasonal variability in rainwater composition:

To understand the variability in rainwater characteristics from event to event, percentage contribution of major ions to the TDS for individual rain event has been calculated and plotted for NH_4^+, NO_3^-, $SO_4^=$, Na^+, Ca^{2+} and Mg^{2+} as a function of TDS (Fig .4.11). For low TDS samples, percentage contribution of ionic species derived from anthropogenic sources (mainly gas phase emissions contribute to NH_4^+, NO_3^- and $SO_4^=$) varies in a different fashion than those derived from natural sources (Na^+, Ca^{2+} and Mg^{2+}). In samples characterized by high TDS, contribution of all ions remains uniform from event to event (Fig. 4.11). Samples with low TDS are generally associated with heavy rainfall and/or multiple events occurring in a short time period; whereas high TDS samples are those occurred after extended period of dry phase prior to the rain events (Figs. 4.2a and Fig. 4.2b). Therefore, it is expected that low TDS samples would be dominated by in-cloud scavenging process and high TDS samples by below-cloud scavenging. The contribution of anthropogenically derived components (NH_4^+, NO_3^- and $SO_4^=$) is relatively high in low TDS samples.

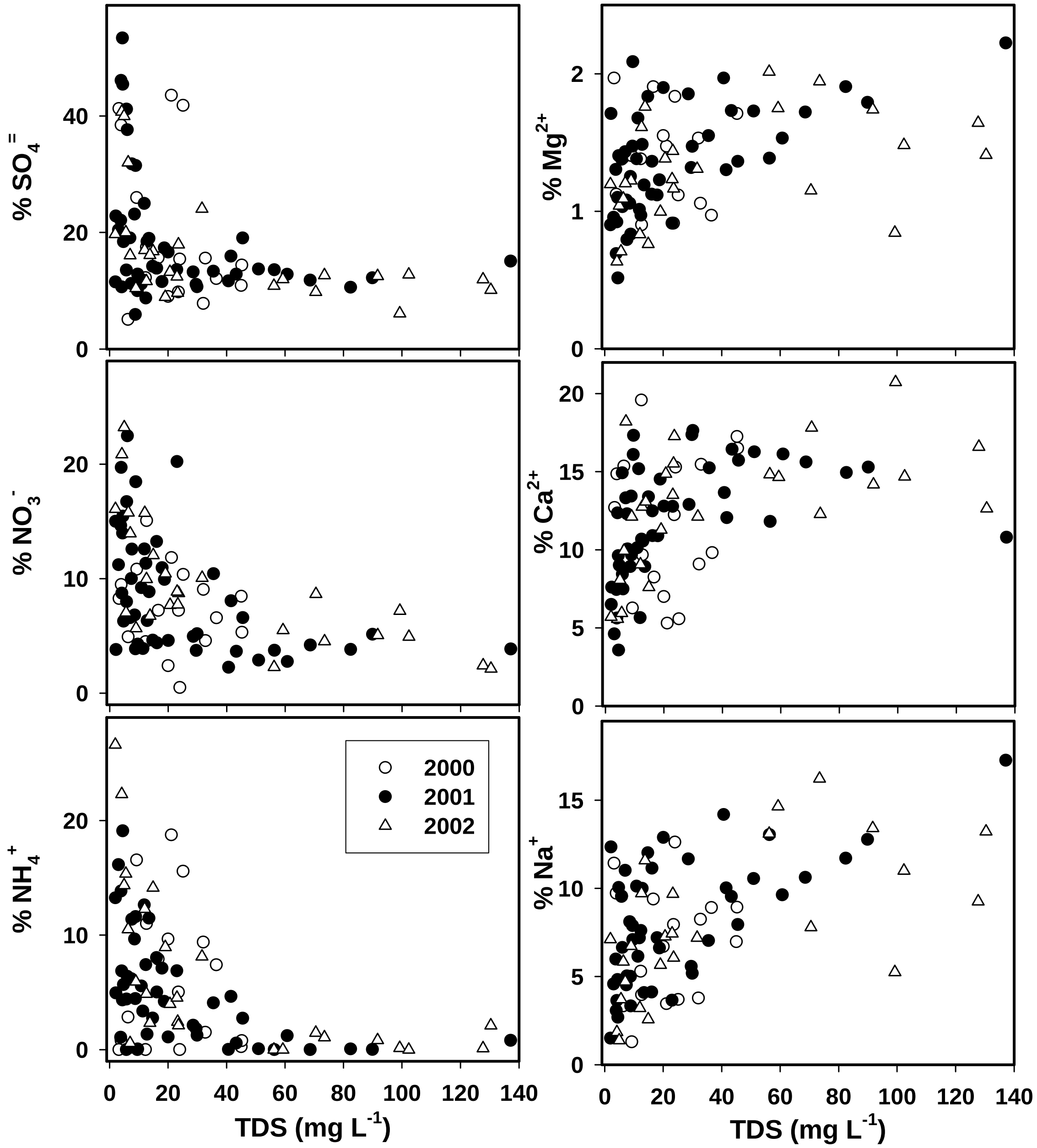

Figure 4.11. Variations in anthropogenically derived constituents (NH_4^+, NO_3^- and $SO_4^=$) contribution to TDS in individual precipitation events. The results show relatively large contribution in low TDS (heavy precipitation) events while contribution of Na^+, Ca^{2+}, Mg^{2+} derived from natural sources (sea-salts and soil dust), is larger in high TDS (low precipitation events) samples.

This observation is clearly evident for NH_4^+ and NO_3^-; suggesting that these two components are largely present in gaseous phase and therefore, they are scavenged more efficiently by heavier precipitation event in comparison to that by low rainfall event.

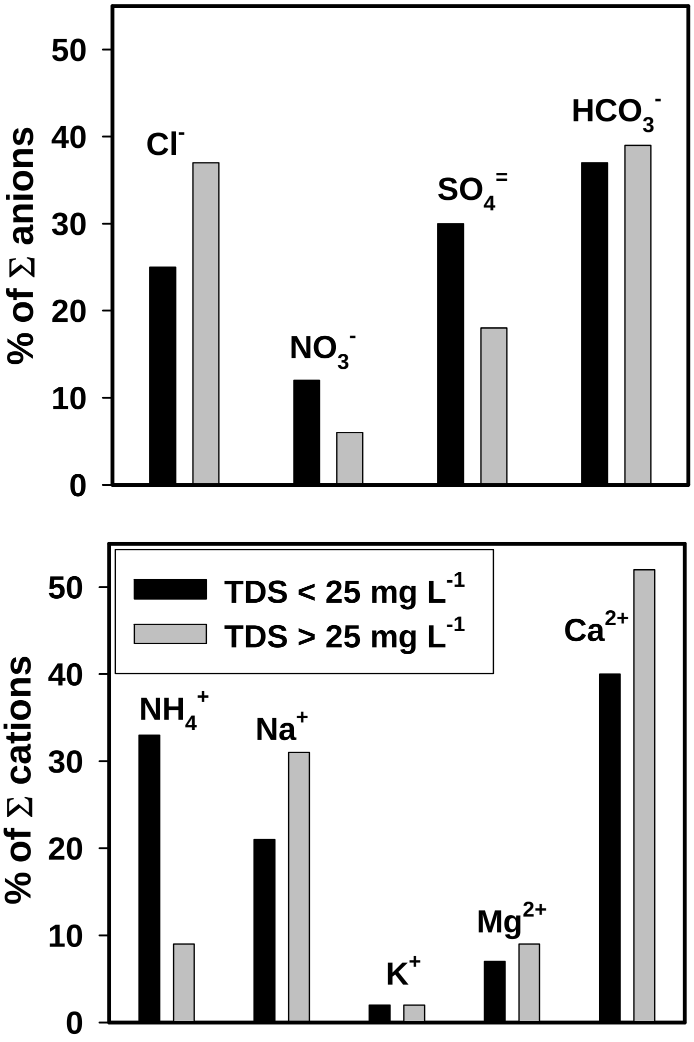

Figure 4.12. Contribution of various cations and anions to Σ cations and Σ anions as a function of TDS. It is seen that high and low TDS samples (i.e. low and high rainfall events) exhibit different chemical composition; with relatively large contribution of anthropogenic sources to low TDS and natural sources to high TDS rains.

The abundance of Na^+, Ca^{2+} and Mg^{2+}, from natural sources (sea-salts, soil dust) which exist in particulate form in the atmosphere contribute significantly to high TDS samples. Based on Fig. 4.11, rainwater data have been sub-divided into two groups: samples with TDS < 25 mg L^{-1} and > 25 mg L^{-1}. Contribution of different cations to Σ cations and anions to Σ anions for these two groups is shown in Fig. 4.12. It is clear that the contribution of anthropogenic constituents to rainwater composition is higher in low TDS rain events; whereas components from natural sources are relatively more dominant in high TDS events. However, contribution of HCO_3^- is quite uniform in both cases.

4.2.5 Inter-annual variability in rainwater composition:

It is seen from data that the concentration of individual constituents and therefore, TDS has varied significantly from event to event (Fig. 4.2, Fig. 4.11); however, volume-weighted-mean ionic composition of annual rains do not show significant variability (Fig. 4.13).

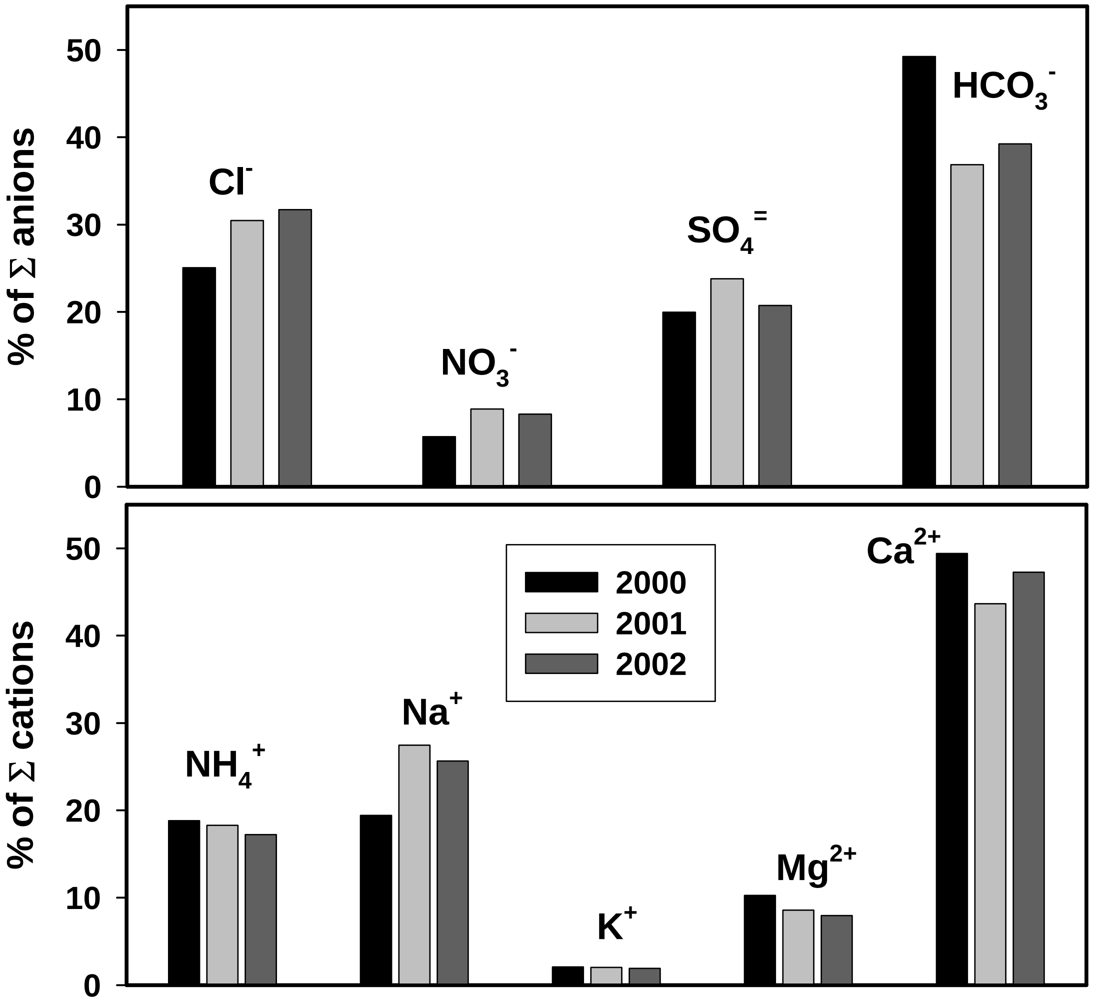

Figure 4.13. Volume-weighted-average cationic and anionic composition of rainwater over the period of three years (2000-2002), suggests insignificant inter-annual variability in precipitation composition over Ahmedabad. Contribution of Ca^{2+} and HCO_3^- suggests that the dust sources dominate the rainwater composition.

The annual average composition of 2000, 2001 and 2002 are roughly the same, within ±20% of each other. Therefore, the data reported in this study can be considered as a representative of the rainwater composition for this semi-arid region. Calcium is the dominant cation (45%) followed by Na^+ (~25%), NH_4^+ (~20%), Mg^{2+} (~10%) and K^+ (2%). Among anions, contribution of HCO_3^- (~40%) dominates; while Cl^- (~30%) and $SO_4^=$ (25%) are comparable and that of NO_3^- is ~10% (Fig. 4.13).

4.2.6 Neutralization factors

Neutralization factors (NFs) of NH_4^+, Ca^{2+} and Mg^{2+} have been calculated for the three year data based on the following empirical relation and tabulated in Table 4.3.

$$(NF)_X = [X]/\{[NO_3^-] + [nss\text{-}SO_4^=]\}$$

where X = NH_4^+, nss-Ca^{2+} and nss-Mg^{2+}

Table 4.3: Neutralization Factors*

		NH_4^+	Ca^{2+}	Mg^{2+}	References
A'bad	Min	0.01	0.15	0.00	This study
	Max	2.81	4.75	0.50	"
	AM#	0.73	1.77	0.11	"
	s.d.$	0.60	1.13	0.09	"
Delhi	AM	0.91	0.25	0.02	Parashar et al., 1996
Pune	AM	0.66	1.64	0.43	Parashar et al., 1996

*Calculated as per emperical formula given in the text

#Arithmetic Mean (AM); $standard deviation (s.d.)

The NFs of NH_4^+, Ca^{2+} and Mg^{2+} vary as 0.01-2.8, 0.2-4.8 and 0-0.5 with the average value of 0.7 ± 0.6, 1.8 ± 1.1 and 0.1 ± 0.1, respectively (Table 4.3); thus suggesting that the main neutralizing components in rainwater are nss-Ca^{2+} and NH_4^+ over Ahmedabad. The contribution of Mg^{2+} to the neutralization of rainwater acidity is negligible (Table 4.3). The NF of NH_4^+ and Ca^{2+} are quite similar for the precipitation events over Ahmedabad and Pune; but the NF of Mg^{2+} over Pune is higher than that over Ahmedabad (Table 4.3). The NF of NH_4^+ is higher while that of Ca^{2+} is 6-7 times lower over Delhi than at Pune and Ahmedabad (Table 4.3); suggesting that pollution sources over Delhi region overwhelm the abundances of NH_4^+, NO_3^- and $SO_4^=$.

4.3 SUMMARY AND CONCLUSIONS

The individual precipitation (wet-only) events, collected during SW-monsoon for three-year period (2000-2002) from an urban, semi-arid site, Ahmedabad, India, are analyzed for pH, EC, major cations and anions to identify their sources, processes of in-cloud/below-cloud scavenging and to establish "representative" chemical composition of rainwater over this region. The major observations and conclusions of this study are

- The pH of rainwater is alkaline (average pH: 6.7) because of neutralization of rain with dust from regional alkaline soils. These dust supply plays an important role in controlling the composition of rainwater.
- The major source of Na^+ and Cl^- is sea-salts, Ca^{2+} and HCO_3^- is mineral dust, NH_4^+, NO_3^- and $SO_4^=$ is from anthropogenic emissions. K^+ and Mg^{2+} are contributed by both sea-salts and mineral dust.
- The acidity in the rainwater is largely neutralized by nss-Ca^{2+} whereas NH_4^+ plays minor and nss-Mg^{2+} insignificant roles. This is unlike in rainwater over temperate regions where NH_4^+ is reported as the dominant neutralizing component.
- Among acidic constituents, nss-$SO_4^=$ dominates over NO_3^-; the VWM equivalent ratios of nss-$SO_4^=$ to NO_3^- vary between 2 to 3 during the three-year period.
- The concentrations of chemical species in individual precipitation events are largely controlled by precipitation volume and their abundances in gaseous and/or particulate phases in the atmosphere. Large fraction of NH_4^+ and NO_3^- and significant fraction of $SO_4^=$ is scavenged from gaseous phase over Ahmedabad.
- Rainwater composition is different for low and high TDS precipitation events with relatively large contribution of anthropogenic constituents in low TDS events and naturally occurring species in high TDS events.
- The volume-weighted "average" annual ionic composition for three years do not show significant variations (within ±20%). Their relative contributions from dust (~50%), anthropogenic (~25%) and sea-salts (~25%) sources provide a representative characterization of rain events in this region.

Chapter 5

SCAVENGING RATIOS AND DEPOSITION FLUXES OF MAJOR IONIC SPECIES

5.1 INTRODUCTION

Precipitation plays an important role in determining the deposition fluxes of chemical species at the atmosphere-ecosystem interface through two dominant processes termed as in-cloud scavenging and below-cloud scavenging (Harrison and Pio, 1983; Barrie, 1985; Jaffrezo and Colin, 1988). In the latter process, concentration of a particular constituent is dictated by precipitation amount but more importantly by its scavenging efficiency. This led to the development of the concept of scavenging ratio, which is based on the simplified assumption that the concentration of a constituent in precipitation is related to its concentration in air (Engelmann, 1971). It also assumes that chemical composition of air column, from earth's surface to cloud height, is uniform. The scavenging ratio (SR) is defined as the dimensionless ratio of the concentrations of a species in precipitation and in aerosols:

$$SR = (C_{rain} / C_{air})* \rho$$

where, C_{rain} is the concentration in rainwater (μg g^{-1}), C_{air} is the concentration in aerosols (μg m^{-3}) for a particular species and ρ is the density of air (~1200 g m^{-3}). The SRs constitutes a potential tool for estimating the wet deposition of species in remote areas from their concentrations in aerosols those are measurable with relative ease and convenience (Arimoto et al., 1985; Duce et al., 1991). SRs are also useful for investigating the mechanism of transfer between aerosols and precipitation apart from their predictive ability (Jaffrezo and Colin, 1988). However, SRs vary greatly in time and space, even for a specific constituent as its scavenging efficiency is dictated by the phase in which it occurs (gaseous/particulate) (Barrie, 1985; Rastogi and Sarin, 2003a); particle size and hygroscopic nature of aerosols (Buat-Menard and Duce, 1986; Jaffrezo and Colin, 1988) and their vertical distribution (Harrison and Allen, 1991). In spite of the several complexities, some elucidation of the wet deposition processes has been achieved. For instance, Jaffrezo and Colin (1988) had reported the dependence of SR on particle size; Harrison and Pio (1983) had used relative differences in the composition of aerosols and rainwater to infer the incorporation height of the species in the atmosphere; whereas Barrie (1985) had inferred the percentage of incorporation of $SO_4^{=}$ and NO_3^- by the in-cloud oxidation of SO_2 and NO_2, respectively. A simultaneous and long-term study on the chemical composition of rainwater and aerosols from an urban site (Ahmedabad) has led to a logical assessment of SRs for major ions. Such studies are poorly documented in the literature especially for a semi-arid region.

5.2 RESULTS AND DISCUSSION

5.2.1 Scavenging Ratios:

The SRs of major chemical species (NH_4^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, $SO_4^=$ and HCO_3^-) have been calculated for twenty-six aerosol-rain pairs (defined as the sampled aerosols followed by precipitation event within less than ~2-3 days interval between aerosol and rainwater collection) collected over a three year period (2000-2002) during SW-monsoon. The minimum, maximum and geometric mean of SRs for all measured chemical species in aerosol-rain pair are given in Table 5.1.

Table 5.1: Scavenging ratios of ionic species for an urban site (Ahmedabad).

	1			2	3	4	5
	Min	Max	G.M.*	G.M.	G.M.	G.M.	G.M.
NH_4^+	3084	1900800	185506	-	-	-	-
Na^+	55	5055	725	444	360	2100	836-1328
K^+	170	7531	1220	951	300	2000	-
Mg^{2+}	111	4691	809	596	400	-	-
Ca^{2+}	156	6413	1346	1048	320	1100	-
Cl^-	100	8509	1021	2941	350	1400	-
NO_3^-	727	16234	2791	-	-	-	618-1124
$SO_4^=$	272	4645	1047	743	-	-	407-752
HCO_3^-	541	10722	2397	-	-	-	-

1. Ahmedabad (this study). 2. Paris [*Jaffrezo and Colin*, 1988]. 3. Enewetak [*Arimoto et al*., 1985].
4. Florida Key [*Buat-Menard and Duce*, 1986].
5. Ranges for Bermuda, Barbados and Ireland [*Galloway et al.*, 1993], *Geometric mean

The SRs for all components varied over one to two orders of magnitude from event to event except for NH_4^+ for which variation was over three orders of magnitudes. The order of geometric mean of SRs for major chemical species is $NH_4^+ >> NO_3^- > HCO_3^- > Ca^{2+} \approx K^+ > SO_4^= \approx Cl^- > Mg^{2+} \approx Na^+$ (Table 5.1).

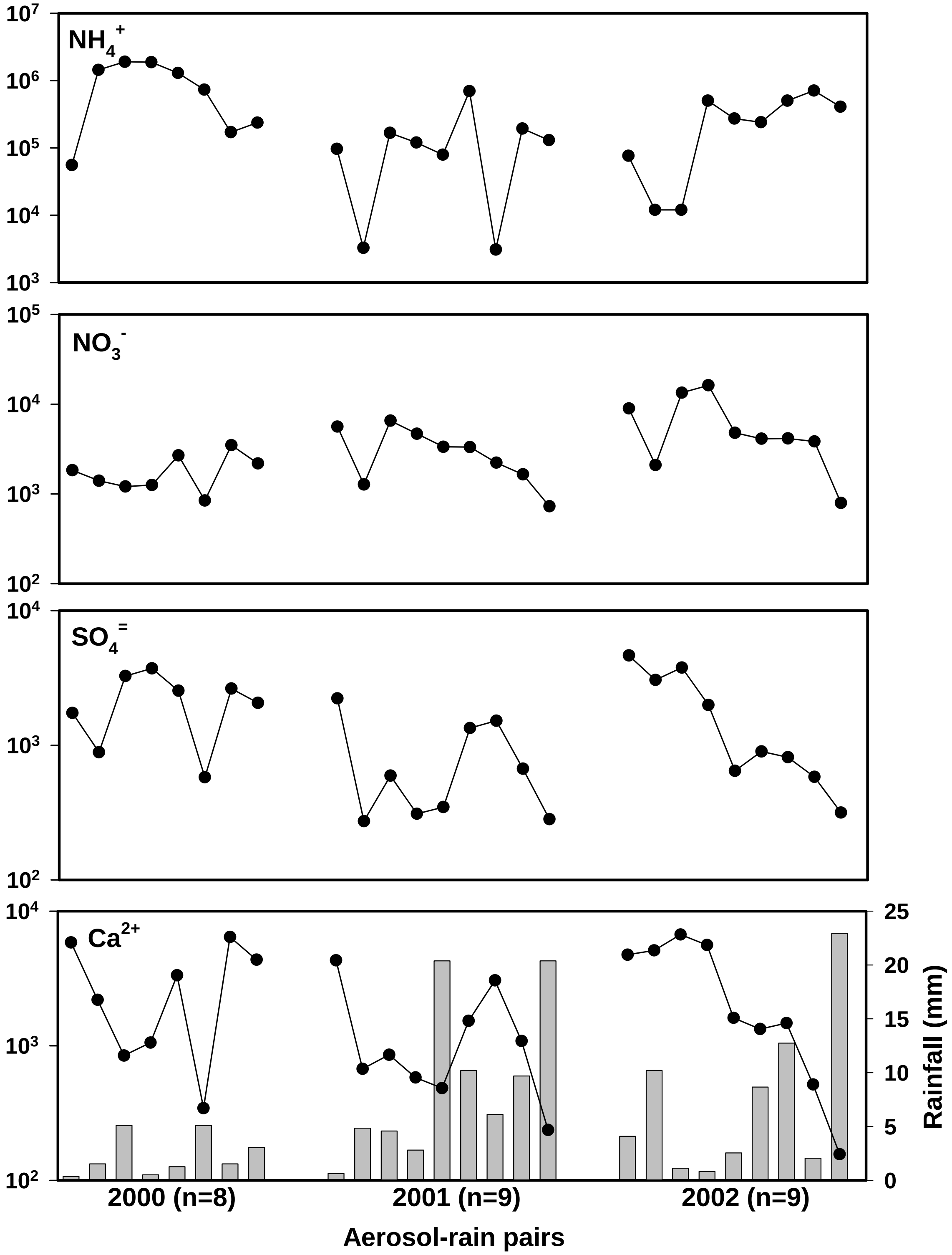

Figure 5.1. Variability in the scavenging ratios of Ca^{2+}, $SO_4^{=}$, NO_3^- and NH_4^+ for each aerosol-rain pair collected during the SW-monsoon period. Bar length represents rainfall amount for the corresponding rain event.

The variations in SRs of Ca^{2+}, $SO_4^{=}$, NO_3^- and NH_4^+ from one aerosol-rain pair to another, along with the precipitation amount of corresponding rain event, are plotted in Fig. 5.1. In general, there is an anti-correlation between the two, high SR of a species is associated with low precipitation. The antecedent dry period and gaseous/particulate phase are also important in determining the concentration of a species in rain (as discussed in Chapter 4) which in turn dictate the SRs. The SRs of Ca^{2+} vary in conjunction with that of $SO_4^{=}$ for several aerosol-rain pairs (Fig. 5.1); suggesting that $SO_4^{=}$ is present in particulate phase similar to Ca^{2+}. The relatively high and uniform SR for NO_3^- in different aerosol-rain pairs are attributable to its predominant scavenging from gaseous phase and uniformity of its source strength (mainly vehicular emissions). The SR of NH_4^+ varies independent of precipitation volume (Fig. 5.1); indicating its scavenging from gaseous phase with variable source strength. In general, variable source strength refers to variable wind speed and frequency of precipitation which in turn affects the abundances of primary aerosols in the atmosphere, or change in emission flux of various pollutants (like SO_2, NO_x and NH_3). A general decrease in the SRs of all ions is associated with relatively high rainfall; suggestive of the role of precipitation in controlling SRs in these events (Fig. 5.1).

The observed variations in the SRs from one species to another mainly reflect the differences in the partitioning of the constituents between the gas and particulate phases, particle size and their solubility (Rastogi and Sarin, 2003a). The highest SR is associated with NH_4^+ as its concentration is often below detection limit (<0.001 $\mu g\ m^{-3}$) in aerosols during the SW-monsoon; suggesting that the occurrence of NH_4^+ in rain is dominated by gas phase scavenging. Although, the abundances of Na^+, Mg^{2+} and Cl^- are dominated by soluble sea-salts, the lowest SRs associated with these species are primarily due to their comparable abundances in aerosols. The intermediate range of SRs observed for Ca^{2+}, K^+, $SO_4^{=}$ and HCO_3^- indicate their scavenging from particulate phase. However, several constituents derived from particulate phase exhibit variable scavenging efficiency which is attributed to their size distribution (Buat-Menard and Duce, 1986; Jaffrezo and Colin, 1988). These characteristics of aerosols could explain relatively high SRs for HCO_3^- and Ca^{2+} ions, predominantly derived from dust sources (coarser particles). The SR of $SO_4^{=}$ is close to that of Ca^{2+} and HCO_3^-; suggesting that it is also largely present in coarse mode.

However, anthropogenically derived $SO_4^{=}$ is expected to be present in fine mode but its presence in coarse mode over the study region could either be due to its source from gypsum or neutralization reaction of anthropogenic $SO_4^{=}$ with $CaCO_3$ (as discussed in Chapter 3 and Chapter 4).

For comparison, reported geometric mean values of SRs for paired samples over Paris (Jaffrezo and Colin, 1988), Enewetak (Arimoto et al., 1985), Florida Key (Buat-Menard and Duce, 1986) and Bermuda, Barbados and Ireland (Galloway et al. 1993) have also been given in Table 5.1. The geometric mean of SRs of almost all species at Ahmedabad appears quite similar (within a factor of two) to those at Paris and Florida Key (Table 5.1). Kane et al (1994) reported that SRs values from urban sites to remote islands are broadly consistent (with a total range of a factor of ten) and we observed the SRs values consistent within a factor of five for urban area (Ahmedabad) to remote areas over ocean at different parts of world (Table 5.1). The reported SRs values of major ions at Ahmedabad can be used for estimating their wet deposition fluxes over and around Indian region.

5.2.2 Relationship between scavenging ratio and rainfall:

As discussed in Chapter 4, the concentration of a chemical species generally decreases with the increasing amount of rainfall because of dilution effect. For all constituents, an overall decreasing trend in SRs with increasing precipitation amount has been observed for individual aerosol-rain pairs. This relationship has been discussed by some of the studies reported in literature (Barrie, 1985; Savoie et al., 1987; Jaffrezo et al., 1990) and is represented by the following regression line:

$$\log SR = \log a - b^{*} \log R \qquad (1)$$

Where SR is scavenging ratio, R is rainfall amount (mm), a is intercept and b is slope of regression line. The slope of regression line would depend on the type of scavenging processes (in-cloud/below-cloud) while intercept (value of SR for 1 mm precipitation) is influenced by the meteorological parameters and concentration of species in the atmosphere over a particular region. For all constituents, b and r (correlation coefficient) values are given in Table 5.2 and compared with the reported data from different sites in Paris (Jaffrezo et al., 1990), Miami and American Samoa (Savoie et al., 1987). All r

values are significant at 0.05 level, except for NH_4^+. However, SRs for particular species depend upon several factors as discussed in earlier section. Slope of the regression line in equation (1) would reflect the extent of in-cloud/below-cloud scavenging for Na^+, K^+, Mg^{2+} and Ca^{2+}; whereas for the remaining species (NH_4^+, Cl^-, NO_3^-, $SO_4^=$ and HCO_3^-), slope is likely to be dependent not only on the above processes but also on their relative abundance in particulate and/or gaseous phase. The slope closer to unity suggest the dominance of below-cloud scavenging largely from the particulate phase while slope far less than unity indicates the dominance of either in-cloud scavenging process or below-cloud gaseous phase scavenging or both.

Table 5.2: Relation between scavenging ratios and rainfall.

	Ahmedabad[a] n = 26		Paris[b] n= 82		Miami[c] n= 78		Samoa[c] n= 72	
	b*	r[#]	b	r	b	r	b	r
NH_4^+	0.18	0.12	-	-	-	-	-	-
Na^+	0.44	0.42	0.34	0.33	0.29	0.59	0.56	0.83
K^+	0.62	0.64	0.31	0.42	-	-	-	-
Mg^{2+}	0.48	0.50	0.41	0.51	-	-	-	-
Ca^{2+}	0.55	0.58	0.34	0.41	-	-	-	-
Cl^-	0.63	0.59	0.63	0.45	-	-	-	-
NO_3^-	0.23	0.33	-	-	0.28	0.52		
$SO_4^=$	0.41	0.53	0.12	0.19	0.26[$]	0.50	0.51[$]	0.74
HCO_3^-	0.48	0.65	-	-	-	-	-	-

[a]This study; [b]*Jaffrezo et al.*, 1990; [c]*Savoie et al.*, 1987; *slope; [#]correlation coefficient; [$]for nss-$SO_4^=$

In the present study, slope of the line based on equation (1) ranges from 0.41 to 0.63 for Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^- and $SO_4^=$; whereas the slopes for NO_3^- (0.23) and NH_4^+ (0.18) are significantly lower (Table 5.2). The nature of scavenging process, though is difficult to assess based only on the relation between SRs and rainfall, the results indicate that the latter two species seem to be removed by in-cloud scavenging or below-cloud gaseous phase scavenging. Alternatively, a comparison of ionic ratios in rain and aerosols can be attempted to understand these processes.

5.2.3 Comparison of ionic ratios in rain and aerosols:

The ionic ratios of major constituents in rain have been compared with those in aerosols and plotted for each aerosol-rain pair for which individual SRs have been calculated. This comparison avoids the bias due to precipitation volume and mass loading on the concentration of species in rain and aerosols, respectively. The Cl^-/Na^+ ratio in rain and aerosols resemble close to the seawater value of 1.8 for the data during year 2001 and 2002 (Fig. 5.2a); suggesting that both are scavenged by rain from particulate phase. During the sampling period of 2000, significant scavenging of Cl^- from the gaseous phase is discernible based on the relatively high Cl^-/Na^+ ratios in rain than in aerosols. The HCO_3^-/Ca^{2+} (Fig. 5.2b) and $SO_4^=/Ca^{2+}$ (Fig. 5.2c) ratios in aerosols appear to be the mirror image of each other; whereas in rain these ratios do not follow any definite trend. This can be understood in terms of uptake of anthropogenically derived H_2SO_4 by mineral aerosols and subsequent neutralization reaction as discussed in Chapter 3. The relatively high abundance of $SO_4^=$ in the aerosols leads to enhanced neutralization of $CaCO_3$ and hence decrease in HCO_3^-/Ca^{2+} ratio. Whenever NH_4^+/Ca^{2+} ratio is high in rain than that in aerosols, neutralization of $SO_4^=$ is preferred by NH_4^+ and hence, HCO_3^-/Ca^{2+} and $SO_4^=/Ca^{2+}$ ratios in rain do not show any relation (Fig. 5.2b, c and d). In contrast, when NH_4^+/Ca^{2+} ratios in rain and aerosols were low and similar, HCO_3^-/Ca^{2+} and $SO_4^=/Ca^{2+}$ ratios are anti-correlated; indicating the neutralization of $SO_4^=$ by $CaCO_3$ in those rain events. Although, HCO_3^-/Ca^{2+} ratios in rain and aerosols are not always identical (because of neutralization of $CaCO_3$ by H_2SO_4), both Ca^{2+} and HCO_3^- in rain are derived from particulate phase only. In most of the rain-aerosol pairs, $SO_4^=/Ca^{2+}$ ratio in rain was lower than that in aerosols, in few cases, it was similar and in some cases, it was higher (Fig. 5.2c).

These observations re-emphasizes dominance of $SO_4^=$ by anthropogenic sources and that of Ca^{2+} by regional dust emissions. The comparison of NH_4^+/Ca^{2+} ratios in rain and aerosols clearly indicates that the large fraction of NH_4^+ is scavenged from gaseous phase (Fig. 5.2d). Remote source of dust particles in rain is further confirmed by comparing nss-Mg^{2+}/nss-Ca^{2+} ratios in rain and aerosols (Fig. 5.2e). In most of the events, this ratio was lower in rain than that in aerosols; suggesting significant amount of dust (with different nss-Mg^{2+}/nss-Ca^{2+} ratio) is scavenged by clouds before reaching and precipitating over study site. Alternatively, differences in nss-Mg^{2+}/nss-Ca^{2+} ratio in rain and aerosol could also arise due to the differences in the solubility of $CaCO_3$ and $MgCO_3$.

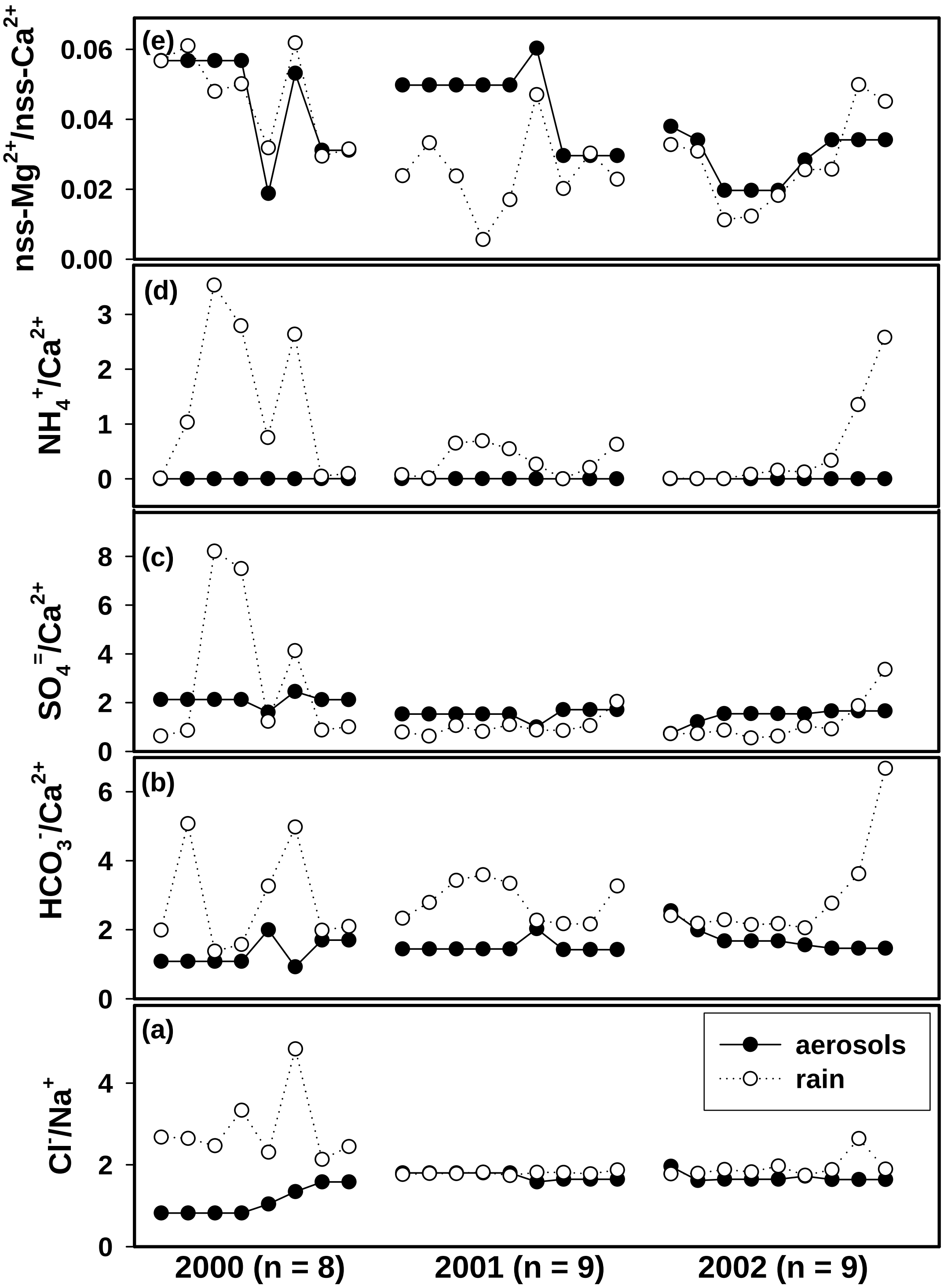

Figure 5.2. Comparison of ionic ratios in aerosols and subsequent rain event suggests the phase (particulate/gaseous) and type of scavenging (in-cloud/below-cloud) dominant for the species e.g. similar Cl^-/Na^+ ratios in aerosols and rain during 2001 and 2002 would indicate that Na^+ and Cl^- in rain are derived from ambient aerosols.

5.2.4 Dry and wet deposition fluxes of ionic species:

Wet and dry depositions are the removal pathways of chemical species from the atmosphere. Over study site, wet removal is dominant during SW-monsoon (Jun-Sept) because most of the rainfall occurs in this period. Remaining part of the year is dominated by dry deposition. To assess the relative dominance of dry and wet deposition processes for major ionic species over Ahmedabad, attempts are made using rainwater and aerosol chemical composition data.

Annual dry and wet deposition fluxes of major ionic species (NH_4^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, $SO_4^=$ and HCO_3^-) have been calculated based on their concentrations in aerosols and volume-weighted-mean concentrations in precipitation using following equations:

$$\text{Dry deposition flux} = [X]_{aerosol} * V_d \qquad (1)$$

$$\text{Wet deposition flux} = [X]_{rain} * P \qquad (2)$$

Where,

$[X]_{aerosol}$: Concentration (mg m^{-3}) of ionic species X in individual aerosol samples,

V_d: Deposition velocity (m d^{-1}),

$[X]_{rain}$: Volume weighted mean (VWM) concentration (mg m^{-3}) of ionic species,

P: Precipitation (m y^{-1}).

For dry fallout, deposition velocity is considered as 0.1 cm s^{-1} (86.4 m d^{-1}) for fine particles (NH_4^+ and K^+), 0.3 cm s^{-1} (259.2 m d^{-1}) for NO_3^- and 1.0 cm s^{-1} (864 m d^{-1}) for coarse particles (Na^+, Mg^{2+}, Ca^{2+}, Cl^-, $SO_4^=$ and HCO_3^-) as per Duce et al. (1991). Here, $SO_4^=$ has been considered as coarse particle based on its SR similar to that of Ca^{2+} and its proposed reaction with mineral dust as discussed in Chapter 3. The annual average dry deposition fluxes of species have been calculated by multiplying the daily average dry deposition fluxes with 365. In order to calculate the wet deposition flux, VWM of ionic species for particular year has been multiplied by annual precipitation for that year. As mentioned in Chapter 2 that annual precipitation for the years 2000, 2001 and 2002 are 728, 681 and 398 mm, respectively and those occurred during SW-monsoon only (Jun-Sept). Annual dry and wet deposition fluxes of major ionic species over Ahmedabad for three-year (2000-2002) period are given in Table 5.3.

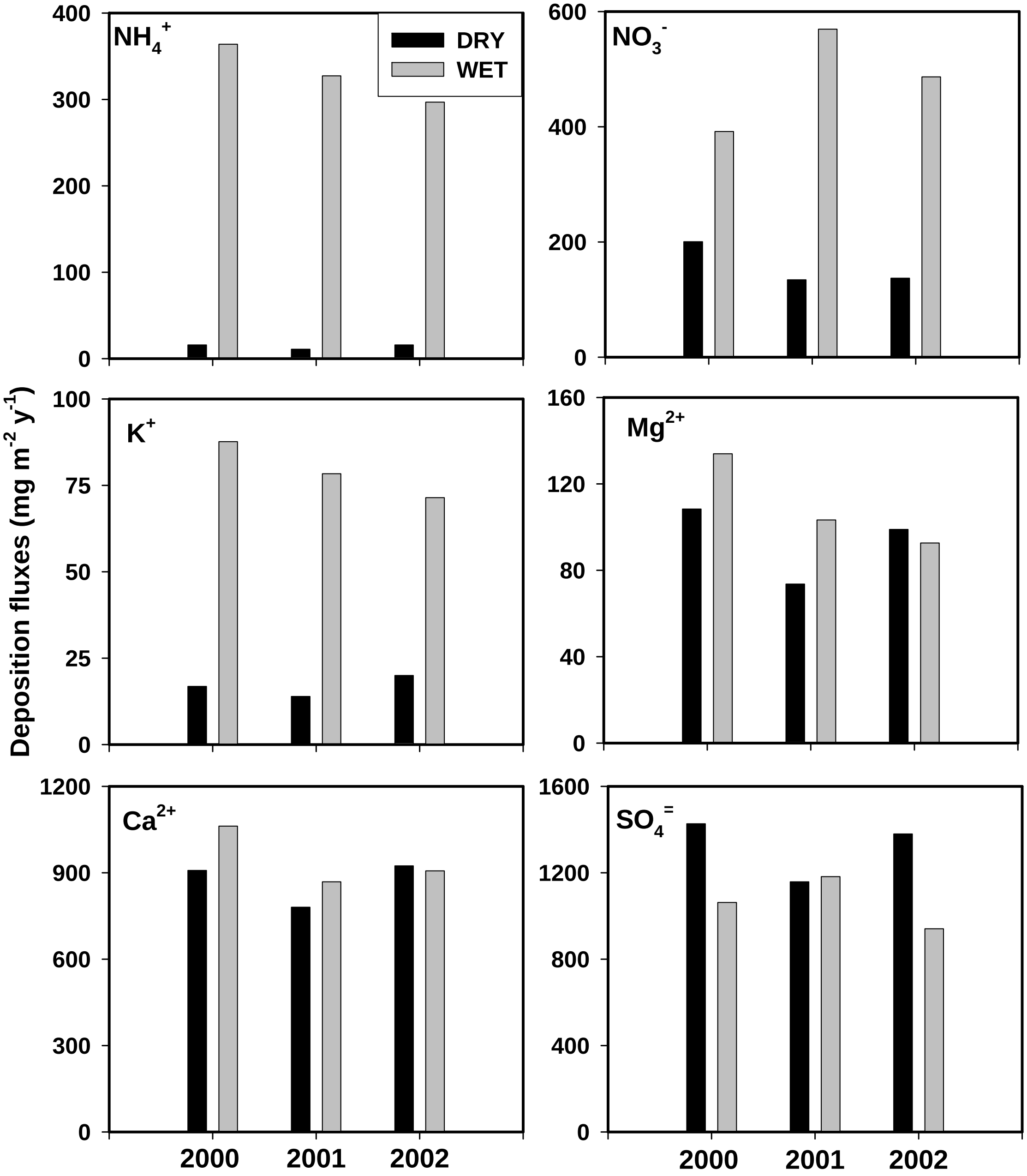

Figure 5.3. Comparison of dry and wet deposition fluxes of major ionic species for three years over Ahmedabad suggests that wet deposition is major removal pathway for NH_4^+, K^+ and NO_3^- and similar to dry deposition for remaining ionic species. Inter-annual variability in deposition fluxes is insignificant.

For comparison, dry and wet deposition fluxes over Pune, wet deposition flux over Hyderabad, dry deposition flux over Delhi (India) and dry and wet deposition fluxes over Ankara (Turkey) are also given in Table 5.3. It is noteworthy that in spite of large seasonal variability in the absolute concentrations of ionic species, their annual dry and wet deposition fluxes are not significantly different (within 20%) during the study period of three years (2000-2002) over Ahmedabad (Table 5.3, Fig. 5.3). The ratios of dry to wet deposition fluxes for individual species are also given in Table 5.3 to assess the relative contribution of the type of atmospheric removal processes (dry and wet) for different ionic species over different sites. Dry/Wet flux ratios for NH_4^+ (0.04-0.07), K^+ (0.18-0.28) and NO_3^- (0.24-0.51) suggest that the wet deposition is the major removal pathway for these ions while for remaining ions, wet and dry depositions are comparable (Table 5.3, Fig. 5.3). Dry deposition largely depends upon the size of the particles. For example, dry deposition of fine particles would be low because of their low deposition velocity but wet deposition can efficiently scavenge fine and coarse particles as well as species from gaseous phase. However, if same species is present in the form of fine and coarse particle as well as in gas phase then low precipitation event may not be able to scavenge it as efficiently as heavy precipitation can scavenge it from all the forms.

Annual dry and wet deposition fluxes of major ionic species over Ahmedabad (three year average) and Pune (three year average) are shown in Fig. 5.4. Wet deposition is the major removal pathway for NH_4^+, Na^+, Cl^- and $SO_4^=$ while dry deposition is also significant for remaining ions over Pune (Table 5.3, Fig. 5.4). Wet and dry deposition fluxes for NO_3^- are significantly higher over Pune than that over Ahmedabad while for Ca^{2+}, Na^+ and Cl^-, fluxes are somewhat lower (Fig. 5.4). Reported wet deposition fluxes of all major ions (except K^+) are lower over Hyderabad (Kulshreshtha et al., 2003) than those observed over Ahmedabad. Dry deposition fluxes of NH_4^+ is ~4 times higher and K^+ is ~20 times higher while Na^+, Ca^{2+}, Cl^- and $SO_4^=$ are significantly lower over Delhi (Kulshreshtha et al., 1996) than that over Ahmedabad (Table 5.3). This suggest that aerosol composition over Delhi is dominated by biomass burning derived species (NH_4^+ and K^+) while over Ahmedabad, contributions of crustal dust and sea-salts are relatively more. Kaya and Tuncel (1997) reported that the dry deposition is dominant or comparable to wet deposition for all ionic species over Ankara, Turkey (Table 5.3).

Table 5.3: Annual dry and wet deposition fluxes (mg m^{-2} y^{-1}) and dry/wet deposition ratios for major ionic species

	Ahmedabad[a]									**Pune**[b]			**Hyderabad**[c]	**Delhi**[d]	**Ankara, Turkey**[e]		
	2000			**2001**			**2002**			**1992-94**			**1999-2001**	**1994**	**1992-1994**		
	Dry	Wet	D/W	Dry	Wet	D/W	Dry	Wet	D/W	Dry	Wet	D/W	Wet	Dry	Dry	Wet	D/W
NH_4^+	16	364	0.04	11	327	0.03	16	297	0.05	22	310	0.07	90	69	162	175	0.93
Na^+	576	479	1.20	398	627	0.63	419	564	0.74	62	288	0.22	115	69	118	44	2.69
K^+	17	88	0.19	14	78	0.18	20	71	0.28	70	102	0.69	117	336	51	13	3.92
Mg^{2+}	108	134	0.81	74	103	0.71	99	93	1.07	67	117	0.57	36	179	80	14	5.71
Ca^{2+}	908	1062	0.85	780	869	0.90	924	907	1.02	590	786	0.75	280	661	3886	254	15.30
Cl^-	775	986	0.79	607	1119	0.54	670	1063	0.63	231	493	0.47	426	387	200	216	0.93
NO_3^-	201	392	0.51	134	569	0.24	137	487	0.28	732	1128	0.65	248	234	270	345	0.78
$SO_4^=$	1427	1062	1.34	1158	1182	0.98	1379	940	1.47	350	1061	0.33	336	562	718	883	0.81
HCO_3^-	1344	3338	0.40	1310	2328	0.56	1633	2260	0.72	-	-		-	-	-	-	

[a]This study; [b]Pillai et al., 2001; [c]Kulshrestha et al., 2003; [d]Kulshrestha et al., 1996; [e]Kaya and Tuncel, 1997

Observations in this study and their comparison with other sites suggest that dry and wet deposition fluxes of ionic species depend upon the composition of aerosol and rainwater which in turns depend upon source strengths and meteorological parameters over a particular region.

5.3 SUMMARY AND CONCLUSIONS

Study of aerosol-rain coupling and deposition fluxes of major ionic species over Ahmedabad have brought out following important observations and conclusions:

- The order of SRs for major chemical species is $NH_4^+ >> NO_3^- > HCO_3^- > Ca^{2+} \approx K^+ > SO_4^= \approx Cl^- > Mg^{2+} \approx Na^+$.
- The scavenging ratios for individual species depend upon rainfall amount, dry period between the rain events, phase (gaseous/particulate) of the component in the atmosphere and source strengths, in addition to their size and solubility.
- NH_4^+ and NO_3^- are predominantly scavenged from gaseous phase and hence associated with relatively high SRs. In contrast, relatively low SRs are the characteristics of ionic species that occur in particulate phase. Major ions (except NH_4^+ and NO_3^-) including large fractions of Cl^- and $SO_4^=$ are scavenged from particulate phase by both in-cloud and below-cloud scavenging processes.
- Wet deposition is the major removal pathway of NH_4^+, K^+ and NO_3^- over study site while for other ionic species, dry and wet depositions are comparable.
- Inter-annual variability in the dry and wet deposition fluxes of ionic species is not significant during 2000-2002.

Chapter 6

ENVIRONMENTAL RADIONUCLIDES

6.1 INTRODUCTION

The naturally occurring radionuclides, ^{7}Be and ^{210}Pb, have proven as useful tracers to study the vertical and lateral transport of air masses and residence time of aerosols (Lal and Peters, 1967; Bhandari et al., 1970; Turekian et al., 1977; Feely et al., 1989). The source functions of both these nuclides are well known, as discussed in Chapter 1. ^{7}Be ($t_{1/2}$ = 53.3 days) is produced by the interaction of cosmic rays with N and O atoms in the atmosphere, its maximum production (~170 mBq m^{-3}) occurs in the lower stratosphere (Lal et al., 1958). It has been established that ^{7}Be concentration exhibits spatial and temporal variations in surface air (Lal and Peters, 1967; Feely et al., 1989; Dibb et al., 1994). The source of ^{210}Pb ($t_{1/2}$ = 22.3 years) is the radioactive decay of ^{222}Rn ($t_{1/2}$ = 3.8 days) emanating from surface soils to the atmosphere. Anthropogenic sources, such as coal combustion and nuclear explosions, contribute less than 1% for ^{222}Rn and ^{210}Pb in the atmosphere (Duenas et al., 2004 and references therein). Several studies (Turekian et al., 1977; Balkanski et al., 1993) have reported a uniform ^{222}Rn flux of 1.0 atom cm^{-2} s^{-1} from land to the atmosphere under non-freezing conditions while emission from oceans and lakes are negligible (<1%). However, ^{222}Rn flux shows large spatial and temporal variabilities depending upon ^{226}Ra content of the soils, their porosity and meteorological conditions in a particular region (Feichter et al., 1991).

Soon after their production, both these radionuclides quickly attach to ambient aerosol particles. Thereafter their behavior is similar to those of aerosol particles with respect to their transport and removal (Turekian et al., 1977). As these nuclides contribute only atomic amounts to aerosols, they do not affect the physical and chemical properties of aerosols (Brost et al., 1991). Half-life of both these nuclides are long enough with respect to their residence time (same as that of aerosols, ~a week) in the lower atmosphere, therefore most of ^{7}Be and almost all of ^{210}Pb in the troposphere are removed by dry and wet deposition rather than by radioactive decay.

A limited number of studies have reported the concentrations of ^{7}Be and ^{210}Pb from the sites over the Indian region (Bhandari, 1965; Lal and Peters, 1967; Rangarajan et al., 1968; Joshi et al., 1969; Bhandari et al., 1970; Rangarajan and Gopalkrishnan, 1970; Anand and Rangarajan, 1990). In this thesis, a long-term study on the concentrations of these two nuclides in aerosols sampled for a period of 31 months (Jun

2000 to Jan 2003) over Ahmedabad (49 m asl) and for 15 months (Oct 2001 to Jan 2003) at a site in Mount Abu (1680m asl) has been carried out. The measured activities of ^{7}Be and ^{210}Pb in aerosols are given in Appendix 2.

6.2 RESULTS AND DISCUSSION

6.2.1. Temporal variability in ^{7}Be and ^{210}Pb concentrations:

The range and average activities of ^{7}Be and ^{210}Pb and ^{7}Be/^{210}Pb ratios during WET (May-Aug) and DRY period (Jan-Apr, Sept-Dec) over Ahmedabad and Mt Abu are given in Table 6.1. For comparison, their activities over Bombay (Rangarajan and Gopalkrishnan, 1970; Joshi et al., 1969), Malaga (Duenas et al., 2004), and Detroit (McNeary and Baskaran, 2003) are also given in Table 6.1. The ^{7}Be activity ranges from 0.82 ± 0.05 to 6.0 ± 0.3 mBq m^{-3} (average: 3.6 mBq m^{-3}, sd: 1.2) over Ahmedabad and that at Mount Abu from 1.5 ± 0.1 to 7.6 ± 0.3 (average: 4.4, sd: 1.4). The ^{210}Pb activity varies from 0.10 ± 0.01 to 1.9 ± 0.2 mBq m^{-3} (average: 0.73, sd: 0.44) over Ahmedabad while from 0.25 ± 0.04 to 1.8 ± 0.2 (average: 0.68, sd: 0.38) over Mt Abu (Fig. 6.1). These activities are comparable to those reported in literature (Joshi et al., 1969; Rangarajan and Gopalkrishnan, 1970; Feely et al., 1989; Winkler et al., 1998; McNeary and Baskaran, 2003; Duenas et al., 2004; Gaffney et al., 2004). However, significant differences in the concentrations of ^{7}Be and ^{210}Pb are observed during WET and DRY period over Ahmedabad and Mt Abu (Table 6.1). These seasonal variations are discussed in the following sections.

The temporal variability of ^{7}Be and ^{210}Pb during May 2000 to Jan 2003 over Ahmedabad, and during Oct 2001 to Jan 2003 over Mt Abu are shown in Fig. 6.1. The average concentration of ^{7}Be is ~20% higher over Mt Abu (~1700 m asl) than that over Ahmedabad (~50 m asl) because of the altitude difference of 1650 m between these two sites; but the seasonal variations are quite similar for the two sites. Furthermore, no significant inter-annual variability is observed for ^{7}Be activity. The surface air ^{7}Be concentration depends on four processes: (1) removal by dry and wet scavenging, (2) stratosphere-troposphere exchange (STE), (3) downwind transfer in the troposphere, and (4) lateral transfer from middle and subtropical latitudes to higher and lower latitude (Feely et al., 1989).

Table 6.1: ^{7}Be and ^{210}Pb concentrations (mBq m^{-3}) and ^{7}Be/^{210}Pb ratio in aerosols.

	^{7}Be				^{210}Pb				^{7}Be/^{210}Pb			
	Min	Max	**Avg**	sd	Min	Max	**Avg**	sd	Min	Max	**Avg**	sd
Ahmedabad (23.0°N, 72.6°E, 49 m asl)												
WET	0.8	4.0	2.5	0.8	0.1	0.6	0.3	0.1	2.8	14.0	7.7	2.3
DRY	1.9	6.0	4.2	0.8	0.3	1.9	0.9	0.4	2.1	12.5	5.6	2.6
All data	0.8	6.0	**3.6**	1.2	0.1	1.9	**0.7**	0.4	2.1	14.0	**6.3**	2.7
Mt Abu (24.6°N, 72.7°E, 1680 m asl)												
WET	1.5	5.2	3.1	1.3	0.3	0.6	0.4	0.1	5.9	10.3	7.8	1.4
DRY	3.8	7.6	5.0	1.0	0.4	1.8	0.8	0.4	2.7	12.4	7.1	2.7
All data	1.5	7.6	**4.4**	1.4	0.3	1.8	**0.7**	0.4	2.7	12.4	**7.4**	2.3
Bombay (19.0°N,72.9°E, sea-level)*												
	2.1	5.3	**3.4**	-	0.2	1.5	**0.7**	-	-	-	-	-
Malaga (36.7°N, 4.9°W, sea-level)#												
	1.3	11.9	**4.6**	1.6	0.1	1.6	**0.6**	0.3	8.4	11.0	-	-
Detroit (42.4°N, 83.2°W, 175 m asl)$												
	1.5	9.8	**4.8**	-	0.3	4.2	**1.2**	-	1.4	18.9	**6.1**	-

*Rangarajan and Gopalkrishnan, 1970; Joshi et al., 1969; #Duenas et al., 2004; $McNeary and Baskaran, 2003

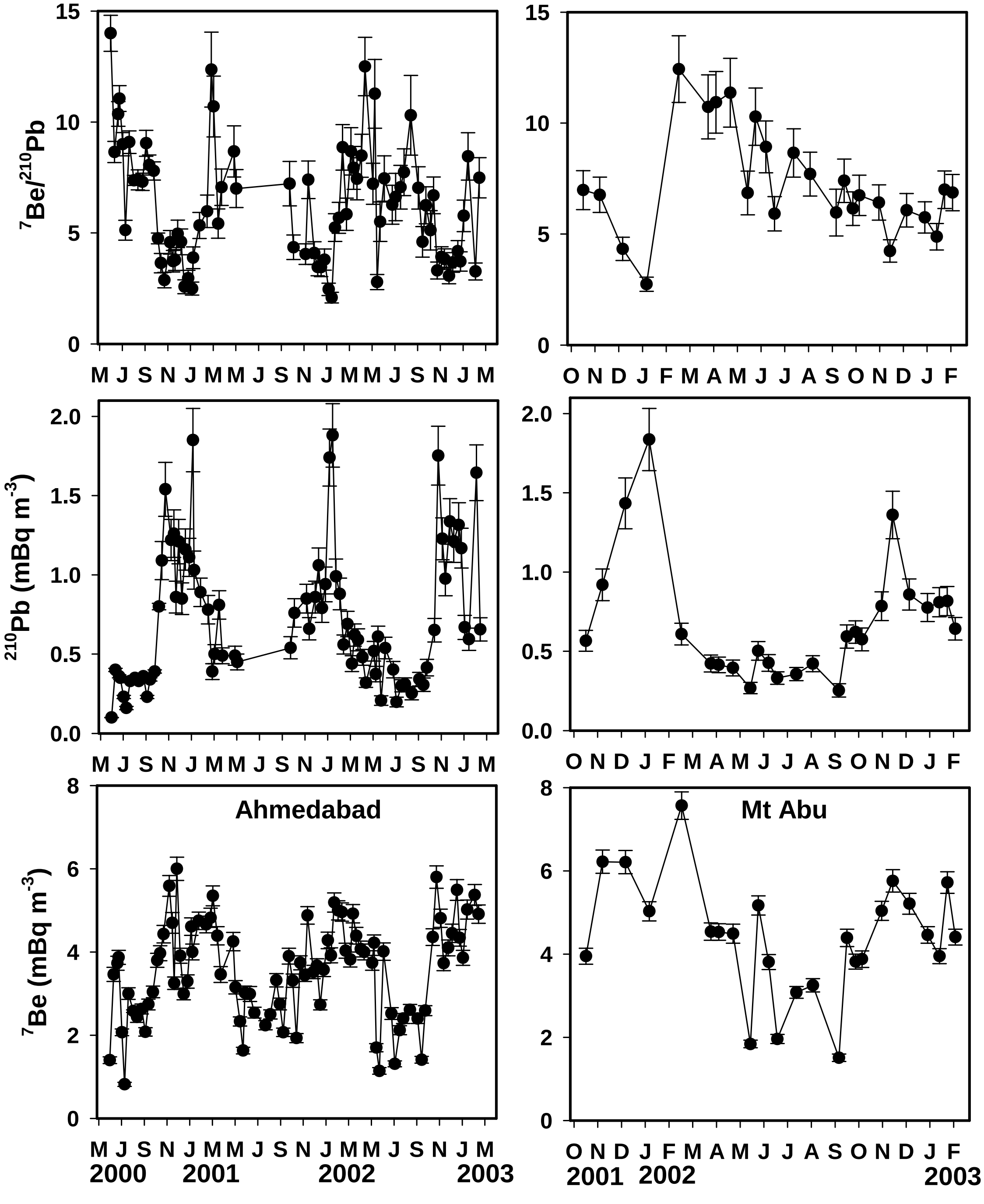

Figure 6.1. Temporal variability in ^{7}Be and ^{210}Pb activities and ^{7}Be/^{210}Pb ratio over Ahmedabad and Mt Abu. Both radionuclides show significant seasonal variability but inter-annual variability is insignificant. Variations in ^{7}Be/^{210}Pb ratios suggest that vertical mixing of air masses is most intense during spring and summer (Mar-Aug) while lateral transport is dominant during winter months (Nov-Feb).

All these four processes are subject to seasonal variation; as a result surface concentration of ^{7}Be is a complicated function of these processes. For example, stratosphere-troposphere exchange is maximum during spring and summer when troposphere is less stable with enhanced downward transfer from the stratosphere due to convective mixing (Brost et al., 1991). In this study, ^{7}Be concentrations are found to be minimum during rainy season (Jun-Aug) over both the sites; suggesting wet scavenging to be dominant process in controlling the concentrations of ^{7}Be during this period. The relatively high concentrations during winter months (Nov-Feb) are attributed to lateral transport (northeasterly winds) from mid- to low-latitudes; whereas enhanced tropospheric exchange dominates during spring (Mar-Apr). Also, there is virtually no removal via wet precipitation during this period, which may contribute to higher residence time for aerosols during this season.

The temporal variability of ^{210}Pb is also shown in Fig. 6.1. The seasonal trends are nearly uniform at both sites and are also similar to those reported over geographically different sites (Bombay, Srinagar, Delhi, Nagpur and Calcutta) in India (Joshi et al., 1969). A shift in surface winds from continental to maritime and vice-versa results in seasonal variations of ^{210}Pb activities (Joshi et al., 1969). Relatively low ^{210}Pb activities during May-Aug are due to the dominance of wet scavenging and prevailing wind fields which bring Rn poor maritime winds to study sites (Rastogi and Sarin, 2003b). The higher ^{210}Pb activities, during Nov-Feb, can be attributed to NE-winds which cover large continental area; coupled with near absence of wet removal during this period.

In addition to meteorological factors, activities of ^{7}Be and ^{210}Pb in aerosols are affected by the abundance of total suspended particulates (TSP) in the atmosphere. In general, their concentrations per cubic meter of air should vary in proportion to aerosol abundance. Duenas et al (2004) have reported statistically significant correlation among these radionuclides and aerosol mass loading. On the other hand, El-Hussein et al (2001) and McNeary and Baskaran (2003) do not observe any meaningful relationship between aerosol mass and ^{7}Be and ^{210}Pb activities. Winkler et al (1998) had reported that distribution of ^{7}Be and ^{210}Pb are unimodal (log-normal) and associated with submicron aerosols of about 0.5-0.6 μm aerodynamic diameter. In the present study, their relationship with aerosol mass (TSP) has been investigated. The results show that though a linear increasing trend is observable among TSP, ^{7}Be and ^{210}Pb concentrations over Ahmedabad, relative differences in their seasonal trends are dominant for its poor statistical significance. The relatively high abundance of mineral aerosols (coarser size particles) during summer months (Apr-May) is one of the regional factors controlling the aerosol ^{7}Be and ^{210}Pb inter-relation; whereas at Mt Abu, seasonal changes in the height of boundary layer is a dominant factor.

The use of ^{7}Be/^{210}Pb ratio cancels the effect of wet removal (Koch et al., 1996) and aerosol mass in understanding the atmospheric mixing processes. For the data reported in this study, ^{7}Be/^{210}Pb ratio varies from 2.1 ± 0.2 to 14.0 ± 1.8 (average: 6.3, sd: 2.7) over Ahmedabad and from 2.7 ± 0.3 to 12.4 ± 1.6 (average: 7.4, sd: 2.3) over Mt Abu (Table 6.1, Fig. 6.1). At both the sites, ^{7}Be/^{210}Pb ratios are higher during spring and summer and lower during winter months. The higher ratios during spring (Mar-Apr) are attributed to the stratosphere-troposphere (S-T) mixing which supplies ^{7}Be rich stratospheric air to lower altitudes. In summer, convective currents transport ^{222}Rn (^{210}Pb) and ^{7}Be across the S-T boundary, leading to the higher ^{7}Be/^{210}Pb ratios (Koch et al., 1996; McNeary and Baskaran, 2003). This also explains the observed lower ^{210}Pb concentrations during Mar-Apr over the two sites. The lower ^{7}Be/^{210}Pb ratios during winter months suggest that atmosphere is relatively stagnant with respect to vertical mixing and ^{210}Pb activity is affected by advective transport from large northern continental area.

6.2.2 Use of ^{7}Be and ^{210}Pb as independent tracers of air mass and chemical species:

A linear regression analysis was performed between ^{7}Be and ^{210}Pb for the data during WET and DRY period (Fig. 6.2). The relationship between the concentrations of ^{7}Be and ^{210}Pb is expected to provide information on the atmospheric removal process for these nuclides and their use as independent atmospheric tracers (Todd et al., 1989; Baskaran et al., 1993; Baskaran and Shaw, 2001; McNeary and Baskaran, 2003; Duenas et al., 2004). These studies have observed significant correlation attributable to their similar removal mechanisms, and have concluded that these two nuclides cannot be used as the independent air mass tracers. In this study, ^{7}Be and ^{210}Pb are found to be linearly related during WET period (Fig. 6.2), when wet deposition is the dominant removal process for atmospheric constituents. However, during DRY period, activity of ^{210}Pb varies independent of ^{7}Be (Fig. 6.2). Among several factors, regional sources of mineral aerosols (from surface soils) enriched in ^{210}Pb is a likely cause. This observation would imply that at the sites characterized by year-round precipitation activities, these environmental nuclides cannot be used as independent air mass tracer but the sites where rainfall is limited to few months such as in the arid, semi-arid regions, ^{7}Be and ^{210}Pb can be used as independent atmospheric tracers during DRY period. Several studies have reported that ^{7}Be and ^{210}Pb can be used as a tracer of aerosols transport but only few of them documented meaningful relation between chemical species and these two environmental nuclides.

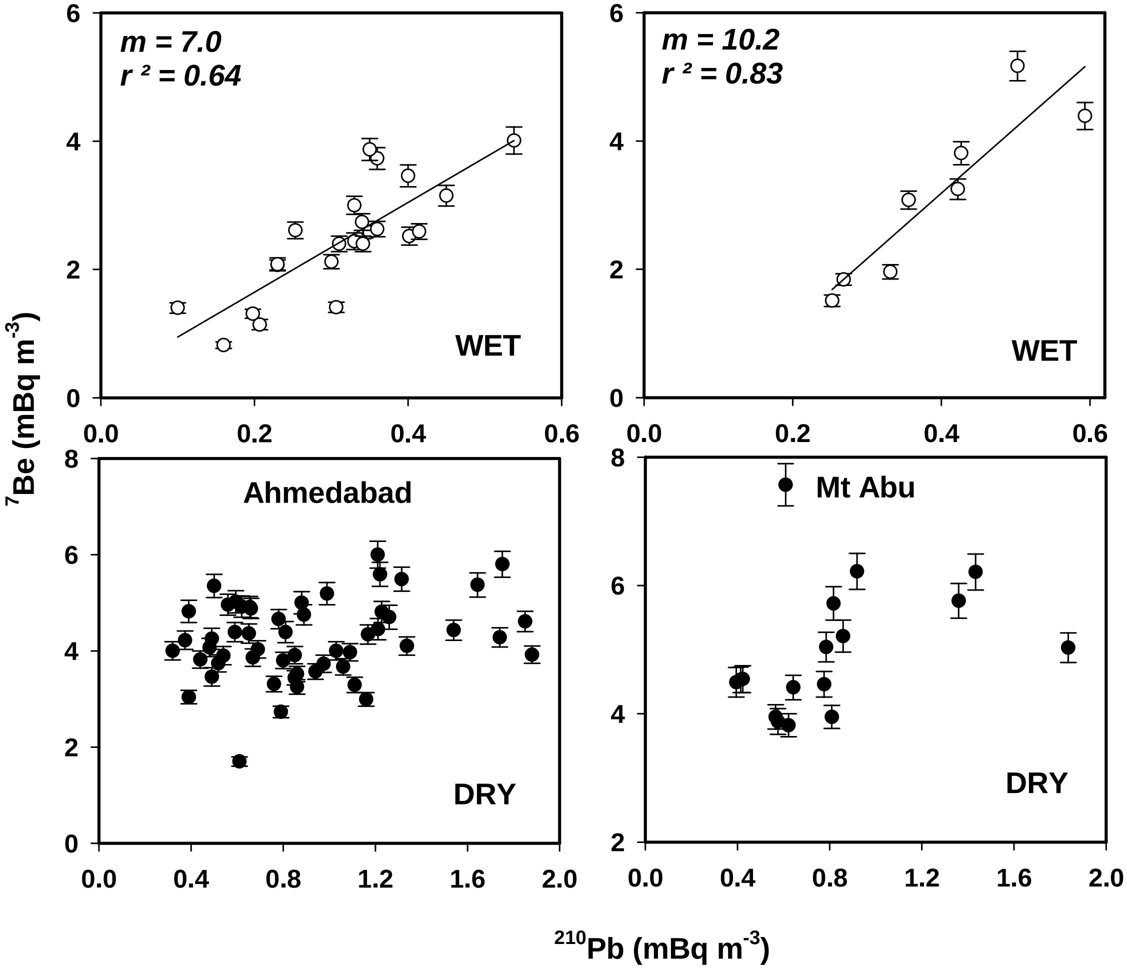

Figure 6.2. The relationship between ^{210}Pb and ^{7}Be activities in surface air during WET and DRY phases over Ahmedabad and Mt Abu. A significant correlation is observed between these nuclides during WET period because of similar removal mechanism (wet deposition).

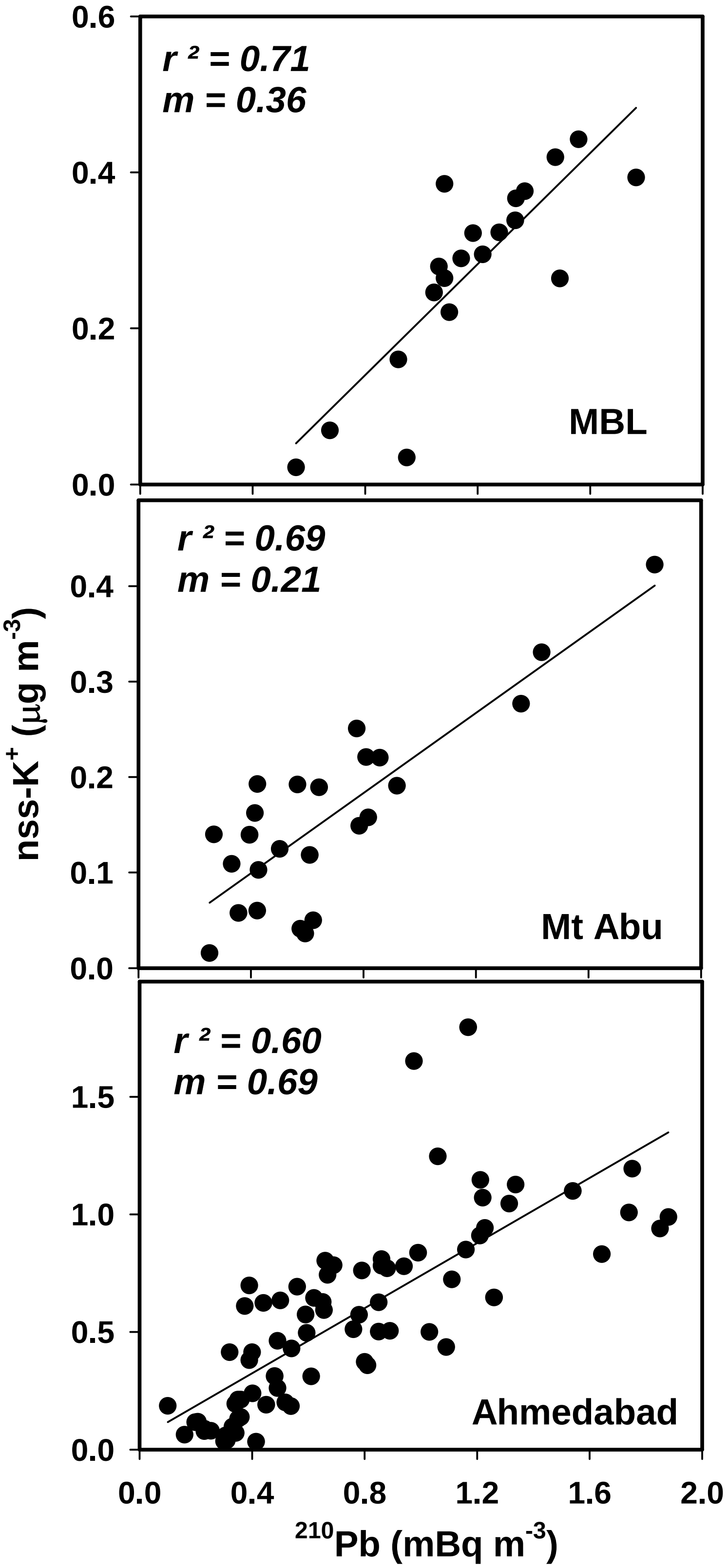

Figure6.3a. Relation between ^{210}Pb and nss-K$^+$ measured in aerosols over Ahmedabad, Mt Abu and MBL. The strong correlation among all these species suggests their common transport in finer aerosols.

For example, Turekian et al (1989) reported a linear positive correlation between ^{210}Pb and Al measured in aerosols over Oahu Island in the North Pacific Ocean whereas Sarin et al (1999) reported a linear relationship between ^{210}Pb and NO_3^- in aerosols measured over Arabian Sea. On similar lines, Uematsu et al (1994) observed relationship between ^{7}Be and NO_3^- over Oahu Island; and Graustein and Turekian (1996) reported linear relation between ^{7}Be and O_3 over Izana Island. These correlations have been often explained in terms of transport processes of chemical species in the atmosphere. In the present study, ^{210}Pb shows linear relationship with nss-K^+ over Ahmedabad (r^2 = 0.60) and Mt Abu (r^2 = 0.69) (Fig. 6.3a). At Mt Abu, the relationship with Pb (r^2 = 0.88) is also statistically significant (Figs. 6.3b).

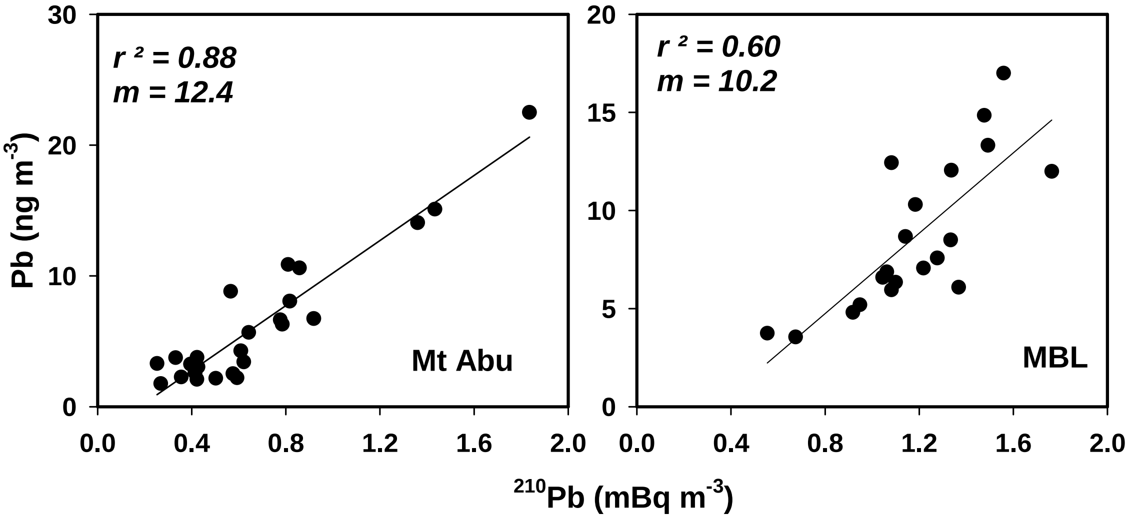

Figure 6.3b. Relation between ^{210}Pb and Pb in aerosols over Mt Abu and marine boundary layer (MBL). The linear trend suggests their similar transport mechanism over these sites.

In contrast, ^{7}Be does not show significant correlation with any of the measured chemical species either at Ahmedabad or at Mt Abu. The relation between ^{210}Pb and chemical species is attributed to the dominance of horizontal transport process for finer aerosols; whereas for other species local/regional sources would be predominant. Linear relation between ^{210}Pb and nss-K^+ and higher abundance of nss-K^+ over Ahmedabad during winter months suggest long-range transport of biomass burning derived aerosols. This is also evident from temporal variation plots of nss-K^+ and ^{210}Pb in aerosols (Fig. 3.3b, Fig. 6.1), with higher concentrations during Nov-Feb associated with NE-winds and lower during May-Aug (SW-winds). These observations further supports the contention that ^{210}Pb, nss-K$^+$ and Pb are primarily transported as finer aerosols, though they are derived from diverse emission sources. It is noteworthy that stable Pb does not show significant correlation with ^{210}Pb over Ahmedabad (unlike data from Mt Abu); suggesting that relatively high aerosol loading with high ^{210}Pb overwhelms the statistical relationship, otherwise expected, with Pb derived from local anthropogenic sources.

6.2.3 ^{7}Be and ^{210}Pb in the marine boundary layer:

The concentrations of ^{7}Be and ^{210}Pb were also measured in aerosols samples collected from the marine boundary layer (MBL) of the Bay of Bengal, Indian Ocean and the Arabian Sea during Feb-March 2001. Their activities over the MBL are given in Appendix 2. The temporal and spatial variabilities (along the cruise track in Fig. 2.1) of ^{7}Be, ^{210}Pb and ^{7}Be/^{210}Pb activity ratios are depicted in Fig. 6.4. The activity of ^{7}Be varies from 2.6 ± 0.2 to 7.4 ± 0.4 mBq m^{-3} (average: 5.4, sd: 1.3) while that of ^{210}Pb ranges from 0.55 ± 0.07 to 1.8 ± 0.2 mBq m^{-3} (average: 1.2, sd: 0.3) (Fig. 6.4). ^{7}Be shows significant variability over the Bay of Bengal in first phase of the cruise (18-24 Feb). Later its concentration increases to as high as 7.4 mBq m^{-3} (2 to 7 March) and remains more or less uniform over the Indian Ocean and Arabian Sea (Fig. 6.4, Fig. 2.1). This is the period (early spring) when maximum vertical mixing is expected (Feely et al., 1989). The observations over Ahmedabad and Mt Abu also show a parallel increase in ^{7}Be due to enhanced tropospheric exchange. The signatures of enhanced transport of continentally derived chemical species to the MBL are evident from relatively high ^{210}Pb concentrations (~1.4 mBq m^{-3}) during 18 Feb to 7 March. The relatively low concentrations of ^{210}Pb over the Arabian Sea are a manifestation of changes in the wind fields (Fig. 2.3) and/or transport of coarser size mineral aerosols. Over the Arabian Sea, the observed ^{210}Pb concentrations (~0.7 mBq m^{-3}) are similar to those reported by Sarin et al (1999) during the same period (Feb-Mar). The observed uniformity in the concentration of ^{7}Be in the MBL and the variations in the ^{7}Be/^{210}Pb ratio over the Bay of Bengal and the Arabian Sea are largely dominated by variations in the ^{210}Pb concentration associated with significant transport of continental material during the late NE-monsoon.

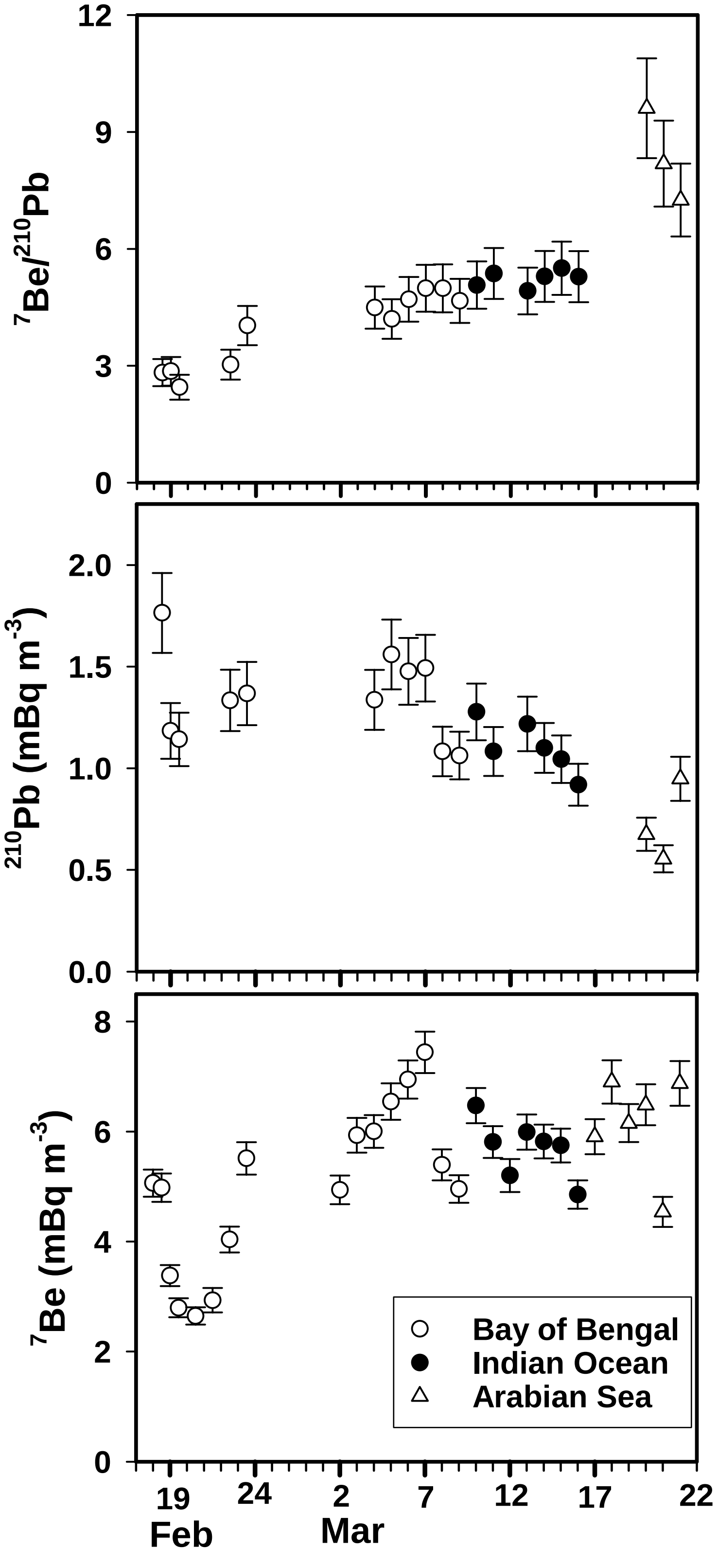

Figure 6.4. ***Temporal and spatial variability in ^{7}Be and ^{210}Pb concentrations and ^{7}Be/^{210}Pb ratio over marine boundary layer.***

Similar to the observations over Mt Abu, ^{210}Pb is significantly correlated with nss-K^{+} (r^2 = 0.71) and Pb (r^2 = 0.60) in the MBL (Fig. 6.3a and b); an observation attesting to the dominant role of continental pollutants.

6.2.4 ^{210}Pb in precipitation:

The ^{210}Pb activity has been measured in precipitation samples (n = 42) collected during the period of SW-monsoon for three consecutive years (2000-2002), which is an important aspect of this study. The measured ^{210}Pb activity in an individual precipitation event and the rainfall amount are given in Appendix 3.

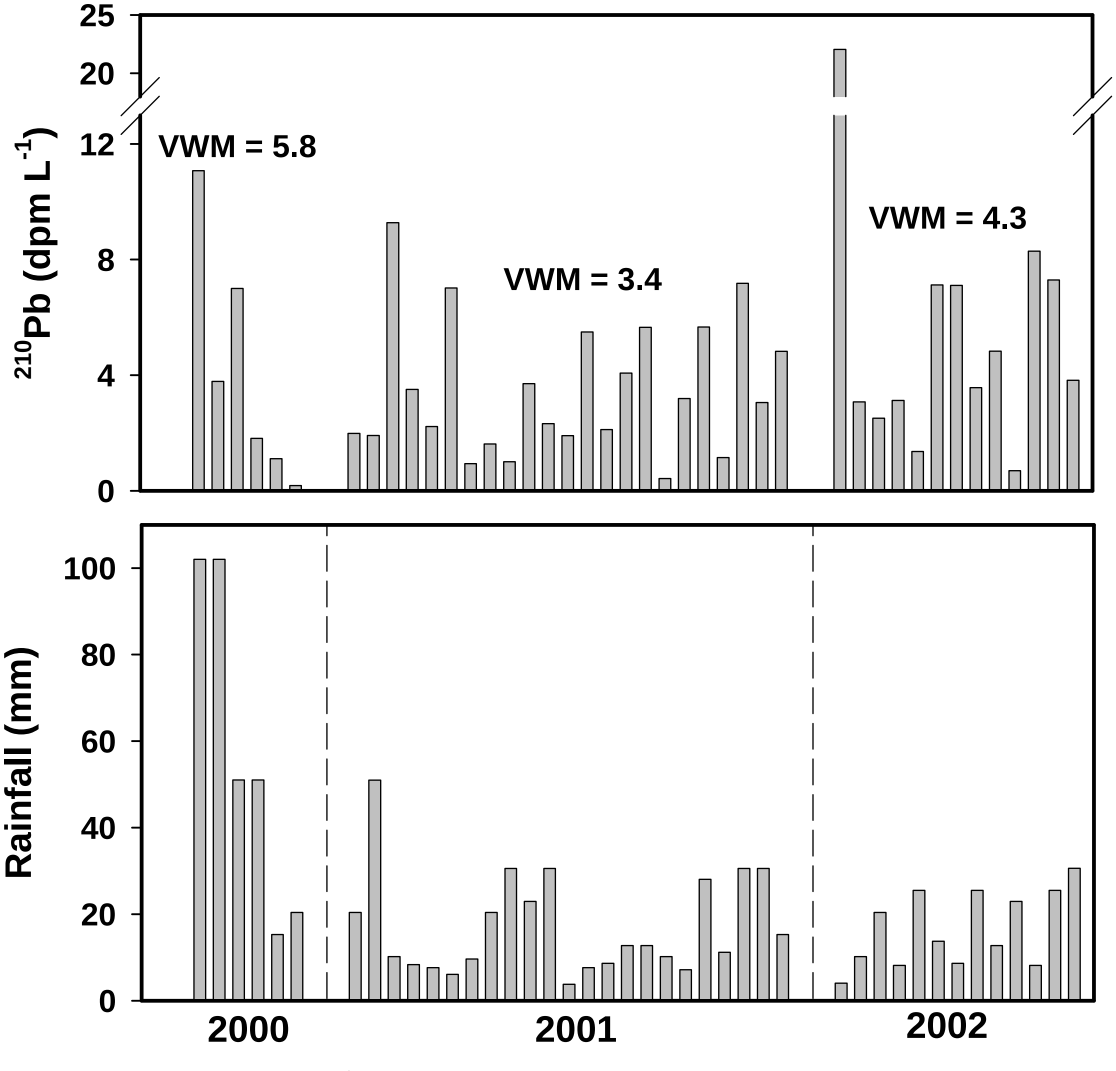

Figure 6.5. Concentration of ^{210}Pb and rainfall amount for individual rain event (n = 42) during SW-monsoon (2000-2002). In general, higher concentration of ^{210}Pb is associated with relatively low precipitation amount.

Numerous factors including the amount and duration of rainfall, the antecedent dry phase between the two successive rain events and cloud height affect the concentration of ^{210}Pb in precipitation. The measured ^{210}Pb activity in wet-only individual precipitation events ranges from 0.2 to 22 dpm L^{-1} (average: 4.3, sd: 3.8), comparable to the range (2.2 to 22 dpm L^{-1}) reported by Joshi et al (1969) and average concentration (5.9 dpm L^{-1}) by Lal et al. (1979) over Mumbai. The variabilities in ^{210}Pb activity and precipitation amount for individual events are shown in Fig. 6.5. In general, relatively high ^{210}Pb concentrations are associated with lower precipitation amount after antecedent dry period. Similar to the relation between rainfall amount and concentration of chemical species (discussed in Chapter 4), a log-log plot has been constructed between rainfall and ^{210}Pb concentration. The statistical parameters (r^2 = 0.004, slope = 0.07) suggest that abundance of ^{210}Pb in rain is dominated by in-cloud scavenging.

Table 6.2: Volume-weighted-mean concentration (dpm L^{-1}) of ^{210}Pb in rainwater

Site	Latitude	Longitude	^{210}Pb	Reference
Ahmedabad	23.0^{o}N	72.6^{o}E		This study
2000			5.8	
2001			3.4	
2002			4.3	
Mumbai	19.0^{o}N	72.9^{o}E		Lal et al., 1979
1970			5.9	
New Haven	41.0^{o}N	73.0^{o}W		Turekian et al., 1983
1977			8.0	
Bermuda	33.0^{o}N	64.0^{o}W		Turekian et al., 1983
1977			4.1	
Norfolk	36.9^{o}N	76.3^{o}W		Todd et al., 1989
1983			5.9	
1984			6.6	
Galveston	29.3^{o}N	94.8^{o}W		Baskaran, et al., 1993
1989			6.8	
1990			7.0	
1991			11.4	
Detroit	42.4^{o}N	83.2^{o}W		McNeary and Baskaran, 2003
1999-2001			21.2	

The volume-weighted-mean (VWM) ^{210}Pb concentration over Ahmedabad is 4.5 dpm L^{-1} for all rainwater samples collected over a period of three years; whereas for an individual year 2000, 2001 and 2002, VWM are 5.8, 3.4 and 4.3 dpm L^{-1}, respectively (Table 6.2). McNeary and Baskaran (2003) had reported that frequency of precipitation plays a significant role on the VWM concentration of ^{210}Pb, rather than the amount of precipitation. A similar conclusion is derived based on results obtained in this study as the total number of precipitation events were minimum during the year 2000 and maximum in 2001 (Fig. 2.4). The calculated VWM of ^{210}Pb shows inverse trend (Table 6.2); suggesting that increase in number of rain events results in decrease of VWM of ^{210}Pb and it is independent of the total precipitation amount for the full season. These VWM values are comparable to some of the reported studies in the literature (Turekian et al., 1983; Todd et al., 1989; Baskaran et al., 1993); and significantly lower than that reported by McNeary and Baskaran (2003), as given in Table 6.2.

As discussed earlier (Chapter 5), scavenging ratio (SR) relates the average concentration of a chemical species in precipitation to its average concentration in the air. A similar approach has been used for ^{210}Pb based on the following relationship:

$$SR = C_{rain}/C_{air} * \rho$$

Where, C_{rain} is VWM concentration of ^{210}Pb (4.5 dpm kg^{-1}) for all precipitation events collected during the SW-monsoon period of three years, C_{air} is the average ^{210}Pb concentration in aerosols (0.33 mBq m^{-3} or 0.02 dpm m^{-3}) collected during the same WET period and ρ is density of air (1.2 kg m^{-3}). This calculation is based on the assumption that the ^{210}Pb content of the air at the height of precipitation cloud is same as that measured in aerosols at the surface level. The calculated SR of ^{210}Pb over Ahmedabad is 271 which is comparable with the values of 217 and 637 reported by Todd et al (1989) and McNeary and Baskaran (2003), respectively. The SR of ^{210}Pb is useful for calculating the deposition rates of other elements that have similar scavenging characteristics (Arimoto et al., 1985).

The wet deposition fluxes (dpm cm^{-2} d^{-1}) of ^{210}Pb for individual wet-only precipitation events have been calculated as:

$$\text{Wet deposition Flux} = [C] * P$$

Where, [C] is ^{210}Pb concentration (dpm cm^{-3}) and P is precipitation amount (cm) for individual events. A significant positive correlation (r^2 = 0.57) has been observed between precipitation amount and deposition flux of ^{210}Pb (Fig. 6.6); indicating the importance of rainfall in the removal of ^{210}Pb from the atmosphere. A poor correlation between rainfall amount and ^{210}Pb concentration and significant positive correlation between rainfall amount and ^{210}Pb deposition flux also suggests the fast replenishment rate of ^{210}Pb in the atmosphere. Annual wet deposition fluxes of ^{210}Pb for the years 2000, 2001 and 2002, calculated based on the VWM concentration of ^{210}Pb and annual precipitation in corresponding years, are 0.42, 0.23 and 0.17 dpm cm^{-2} y^{-1}, respectively.

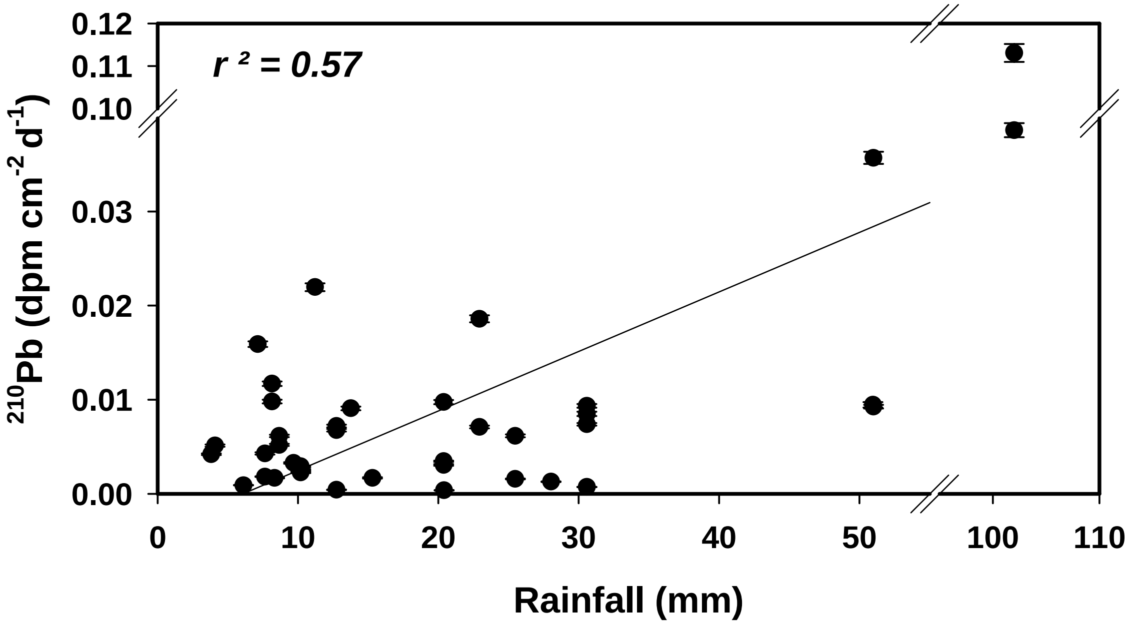

Figure 6.6. Relationship between ^{210}Pb flux and precipitation amount suggests that wet deposition flux of ^{210}Pb is significantly dependent on the rainfall amount.

6.3 SUMMARY AND CONCLUSIONS

The study of radioinuclides (^{7}Be and ^{210}Pb) in aerosols over Ahmedabad, Mt Abu and MBL of the Bay of Bengal, Indian Ocean and the Arabian Sea, and ^{210}Pb in rainwater over Ahmedabad brought out following major observations and conclusions:

- ^{7}Be and ^{210}Pb activities over Ahmedabad and Mt Abu show significant seasonality but their inter-annual variations are not pronounced. The seasonal variability in their concentrations is attributed to the prevailing wind fields (northeasterly/southwesterly), mixing of atmosphere (vertical/lateral) and precipitation.

- The observed relationship between ^{7}Be and ^{210}Pb over Ahmedabad, Mt Abu and MBL, and as reported in few other studies, suggests that during DRY period (in near absence of their atmospheric removal via wet deposition), they can be used as independent tracers of air mass.
- A strong linear positive correlation is observed between ^{210}Pb and nss-K^{+} over Ahmedabad, and among ^{210}Pb, nss-K^{+} and Pb over Mt Abu and MBL. It is inferred in terms of their similar transport mechanism and co-existence in finer aerosols.
- The comparable ^{210}Pb activities over MBL and continental stations (Ahmedabad and Mt Abu) ascertain that air mass over MBL during study period is largely dominated by continental air.
- Volume-weighted-mean concentrations of ^{210}Pb in precipitation over Ahmedabad for the year 2000, 2001 and 2002 are 5.8, 3.4 and 4.3 dpm L^{-1}, respectively, and corresponding wet deposition fluxes are 0.42, 0.23 and 0.17 dpm cm^{-2} y^{-1}, respectively.

Chapter 7

SYNTHESIS AND SCOPE OF FUTURE RESEARCH

7.1 SYNTHESIS

Seasonal and regional scale studies on chemical composition of aerosols are important to understand and assess their impact on climate and environmental change. Observational campaigns provide the most direct information about aerosol characteristics. Towards this, bulk-aerosol samples were collected over Ahmedabad (Jun 2000 to Jan 2003), Mt Abu (May 2001 to Jan 2003) and MBL of the Bay of Bengal, Indian Ocean and the Arabian Sea (Feb-Mar 2001). In addition, individual wet-only precipitation events were collected over Ahmedabad during the SW-monsoon period of three years (2000-2002). Aerosol samples were analyzed for water-soluble ionic species (NH_4^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, $SO_4^=$ and HCO_3^-), acid-soluble constituents (Al, Fe, Mn, Ca, Mg, K, Zn and Pb) and radionulides (^{7}Be and ^{210}Pb) while individual precipitation events for major ionic species and ^{210}Pb.

The study on aerosol chemical composition over Ahmedabad and Mt Abu suggests that chemical species derived from sea-salts (Na^+ and Cl^-) and anthropogenic sources (NH_4^+, K^+, NO_3^-, Zn and Pb) exhibit large seasonal variability depending on meteorological parameters and source strengths of the species. Aerosol chemical composition is dominated by mineral dust component throughout the year with relative increase in contribution from sea-salts during May-Aug (southwesterly winds) and anthropogenic sources during Nov-Feb (northeasterly winds). Dominant abundance of mineral dust in the atmosphere is also supported by the alkaline nature of rainwater (average pH = 6.7) studied over Ahmedabad. The chemical composition of rainwater is determined by dissolution of mineral dust (~50%) followed by contributions from sea-salts and anthropogenic sources of similar magnitude. In precipitation samples, the concentrations of all chemical species (except NH_4^+) are found to be largely controlled by precipitation volume and the time period between the rain events, source strength and phase (gaseous/particulate) of species. The comparison of NH_4^+/Ca^{2+} in rain and aerosols suggests that large fraction of NH_4^+ is scavenged by rain from the gaseous phase. The inter-annual variability of any species is not significantly pronounced in aerosols and rainwater and therefore, their average composition provides representative characteristics of aerosols and rain over study region.

Ca^{2+} is found to be the major neutralizing constituent in aerosols and rain rather than NH_4^+ (unlike temperate regions). As a result, mineral aerosols (mainly $CaCO_3$) are found to be major sink for atmospheric acidic species ($SO_4^=$ and NO_3^-)

over semi-arid study sites. In contrast, the ionic composition of aerosols over MBL is dominated by anthropogenic sources (~60% $SO_4^=$ over Bay of Bengal) over sea-salts and mineral dust. The comparison of nss-$SO_4^=$/nss-Ca^{2+} ratio over MBL (5.2) and Ahmedabad (~1.4) further suggests the dominance of long-range transport of polluted air mass over MBL. A large chloride depletion (upto ~90%) from sea-salts observed over MBL (maximum over Bay of Bengal), is attributed to the neutralization reaction between sea-salts and anthropogenic acidic species (mainly sulphate). This indicates that sea-salts act as a potential sink for sulphate aerosols over MBL. The observations over Arabian Sea suggest that wherever mineral dust and sea-salts contributions to aerosol ionic composition are comparable, neutralization of acidic species is preferred by mineral dust. The observed chemical interactions among natural (mineral dust and sea-salts) and anthropogenic species (sulphate and nitrate) could significantly alter the size distribution of sulphate and nitrate aerosols (from fine to coarse mode) as well as surface properties of mineral dust (from hydrophobic to hydrophilic). Such observations, if not considered, can introduce significant uncertainties in global and regional scale climate models.

In acid-soluble fraction of aerosols, the Fe/Al ratios are found to be remarkably similar (~1.3) over Ahmedabad, Mt Abu and MBL and comparable to those reported by some other studies over Mumbai and Pune; suggesting a wide-spread feature of Fe enrichment in aerosols with respect to upper continental crust over Indian region. The dry deposition fluxes of Al, Fe, Mn, Pb and Zn were estimated over MBL of the Bay of Bengal, Indian Ocean and the Arabian Sea. Fe (160-640 $\mu g\ m^{-2}\ d^{-1}$) and Pb (350-680 $ng\ m^{-2}\ d^{-1}$) fluxes were found to be significantly higher than those reported over world oceans. High deposition flux of Fe over northern Indian Ocean can significantly affect the surface ocean biogeochemistry which in turn may influence the regional as well as global climate.

The coupling between rain and aerosols was studied in terms of scavenging ratios (SRs: defined as the ratio of the concentration of a species in rain to that in aerosols), calculated for individual species. This study suggests that SRs depend on precipitation volume during an event, abundance of species in the gaseous vis-a-vis particulate phase, and the source strength of species in addition to their particle size and solubility. SRs of ionic species exhibit large variability from one event to another. The order of geometric mean values of SRs for major chemical species is NH_4^+ >>

NO_3^- > HCO_3^- > Ca^{2+} ≈ K^+ > $SO_4^=$ ≈ Cl^- > Mg^{2+} ≈ Na^+ over Ahmedabad. In the absence of actual precipitation data, these SRs are the only means of estimating wet deposition fluxes of species based on their measured concentration in aerosols. Using rain and aerosol chemical data, wet and dry deposition fluxes of ionic species have been calculated. Wet deposition is found to be the major removal pathway for NH_4^+ (95%), K^+ (80%) and NO_3^- (75%) over Ahmedabad while for remaining ionic species, dry and wet depositions are comparable.

^{7}Be and ^{210}Pb activities over Ahmedabad and Mt Abu show significant seasonality which is attributed to the prevailing wind directions (northeasterly/southwesterly), mixing of atmosphere (vertical/lateral) and precipitation over study sites. The strong linear positive correlation is observed between ^{210}Pb and a few chemical species (nss-K^+ and Pb) over Mt Abu and MBL. It is inferred in terms of their long-range transport from large continental area to these study sites. The measured ^{210}Pb activities over MBL are comparable to those observed over continental stations (Ahmedabad and Mt Abu). This certifies that air mass over MBL is largely dominated by continental air during study period. Wet deposition fluxes of ^{210}Pb over Ahmedabad for the consecutive year 2000, 2001 and 2002 are 0.42, 0.23 and 0.17 dpm cm^{-2} y^{-1}, respectively.

7.2 Scope of future research

The present study though provides significant amount of data on chemical and isotopic composition of aerosols and rainwater over a semi-arid region in India and sources contributing to them, more comprehensive studies are needed to better understand various atmospheric processes particularly those pertaining to aerosols and their impact on environmental change. A few of them are as follows:

(a) Size-segregated aerosol study:

Chemical composition of bulk-aerosols as measured in this study provides data on elemental/species abundances in an integrated sample of particles present in the atmosphere. Studies based on size-segregated aerosol chemical characteristics would provide information not only about the distribution of different chemical species in various sizes, but also to better understand the sources of species and the physico-chemical transformation processes among them.

Scanning Electron Microscope (SEM) surface chemical studies of these size-segregated aerosols is advisable to get physical evidences of chemical transformation processes between mineral dust/sea-salts and acidic species (as reported in this study).

(b) Gaseous pollutants:

The major sources of sulphate and nitrate aerosols in the atmosphere is the oxidation of their gaseous precursors (SO_2 and NO_x) while that of ammonium aerosol is the neutralization of gaseous NH_3 by acidic species. To gain better understanding of the partitioning of these species between gaseous and particulate phase in the atmosphere and the factors/processes control this partitioning, simultaneous measurements of SO_2, NO_x and NH_3, along with the aerosol and rainwater chemical composition, are essential.

(c) Diurnal variation in aerosol characteristics:

The results of present study have suggested that meteorological parameters (wind direction, temperature, relative humidity and rainfall) play significant role in controlling the concentrations of chemical and isotopic constituents in the atmosphere. In contrast to wind direction, the RH and temperature show large diurnal variations. Anthropogenic emissions also exhibit diurnal variations. These variations are expected to affect concentration of gaseous and aerosol components in the atmosphere. The study of diurnal variation in concentrations of size-segregated aerosols and gaseous components would be helpful in addressing the issue that how the change in meteorological parameters and emission source strengths influences the atmospheric abundances of chemical species.

(d) Organic and Black carbon contents of aerosols:

Aerosol studies over several parts of the world have reported that organic and black carbon contributes significantly to the total aerosol mass and directly/indirectly affect the regional/global radiative forcing and hydrological cycle. Three-year rainwater study over Ahmedabad, during SW-monsoon, suggests that contribution of organic ions to rainwater composition is insignificant. In contrast, water-soluble aerosol characteristics during Nov-Feb (a period dominated by northeasterly winds) over Ahmedabad indicate that there may be minor contribution of organic ions in this period over this urban site. However, water-insoluble organic compounds might be present in aerosols over study region. Direct measurements of organic and black carbon would provide the data on their contribution to the total aerosol loading.

REFERENCES

Al-Momani, I.F., 2003. Trace elements in atmospheric precipitation at northern Jordan measured by ICP-MS: acidity and possible sources. Atmospheric Environment 37, 4507-4515.

Anand, S.J., Rangarajan, C., 1990. Studies on the activity ratios of polonium-210 to lead-210 and their dry-deposition velocities at Bombay in India. Journal of Environmental Radioactivity 11, 235–250.

Andreae, M. O. 1996. Raising dust in the greenhouse. Nature 380, 340–389.

Andreae, M. O., Andreae, T. W., Annegarn, H, Beer, J., Cachier, H., Canut, P., Elbert, W., Maenhaut, W., Salma, I., Wienhold, F. G., Zenker, T., 1998. Airborne studies of aerosol emissions from savanna fires in southern Africa: 2. Aerosol chemical composition. Journal of Geophysical Research 103, 32,119-32,128.

Andreae, M. O., Crutzen P. J., 1997. Atmospheric aerosols: biogeochemical sources and role in atmospheric chemistry. Science 276, 1052-1058.

Arimoto, R., Duce, R. A., Ray, B. J., 1989. Concentrations, sources and Air-Sea exchange of trace elements in the atmosphere over Pacific Ocean. Chemical Oceanography Vol. 10 edited by Riley J P and Chester R (Academic press, New York), 107-149.

Arimoto, R., Duce, R. A., Savoi, D. L., Prospero, J. M., Talbot, R., Cullen, J. D., Tomza, U., Lewis, N. F., Ray, B. J., 1996. Relationships among aerosol constituents from Asia and North Pacific during PEM-West A. Journal of Geophysical Research 101, 2011-2023.

Arimoto, R., Duce, R.A., Ray, B.J., Unni, C.K., 1985. Atmospheric trace elements at Enewetak atoll: Transport to the ocean by wet and dry deposition. Journal of Geophysical Research 90, 2391-2408.

Arimoto, R., Zhang, X. Y., Huebert, B. J., Kang, C. H., Savoie, D. L., Prospero, J. M., Sage, S. K., Schloesslin, C. A., Khaing, H. M., Oh, S. N., 2004. Chemical composition of atmospheric aerosols from Zhenbeiitai, China, and Gosan, South Korea, during ACE-Asia. Journal of Geophysical Research 109, D19S04, doi: 10.1029/2003JD004323.

Balkanski, Y.J., Jacob, D.J., Gardner, G.M., 1993. Transport and residence times of tropospheric aerosols inferred from a global three-dimensional simulation of ^{210}Pb. Journal of Geophysical Research 98, 20573–20586.

Barrie, L. A., 1985. Scavenging ratios, wet deposition, and in-cloud oxidation: an application to the oxides of sulphur and nitrogen, Journal of Geophysical Research 90, 5789-5799.

Baskaran, M., Coleman, C.H., Santschi, P.H., 1993. Atmospheric deposition and fluxes of ^{7}Be and ^{210}Pb at Galveston and College Station, Texas. Journal of Geophysical Research 98, 20555–20571.

Baskaran, M., Shaw, G.E., 2001. Residence time of arctic haze aerosols using the concentrations and activity ratios of ^{210}Po, ^{210}Pb and ^{7}Be. Journal of Aerosol Science 32, 443–452.

Bates, T. S., et al., 2004, Marine boundary layer dust and pollutant transport associated with the passage of a frontal system over eastern Asia. Journal of Geophysical Research 109 D19S19, doi:10.1029/2003JD004094.

Bergametti, G. 1998. Mineral aerosols: Renewed interest for climatic forcing and tropospheric chemistry studies. IGACtivities Newsl., 1, 13–17.

Bhandari, N., 1965. Studies of some physical processes occurring in the atmosphere based on radionuclides of natural and artificial origin. Ph D. Thesis, University of Bombay.

Bhandari, N., Lal, D., Rama, T., 1970. Vertical structure of the troposphere as revealed by radioactive tracer studies. Journal of Geophysical Research 75, 2974-2980.

Brasseur, G.P., Prinn, R.G., Pszenny, A.P., (Eds) 2003. Atmospheric Chemistry in a Changing World. Springer, Germany.

Brost, R. A., Feichter, J., Heimann, M., 1991. Three-dimensional modeling of the concentration and deposition of ^{210}Pb aerosols. Journal of Geophysical Research 96, 22,423– 22,445.

Buat-Menard, P., Duce, R.A., 1986. Precipitation scavenging of aerosol particles over remote marine regions, Nature 321, 508–510.

Charlson, R. J., Lovelock, J. E., Andrea, M. O., Warren, S. G., 1987. Oceanic phytoplankton, atmospheric sulfur, cloud albedo and climate. Nature 326, 655– 661.

Charlson, R.J., Rodhe, H., 1982, Factors controlling the acidity of natural rainwater. Nature, 295, 683-685.

Charlson, R.J., Schwartz, J., Hales, J. M., Cess, R. D., Coakley, J. A., Hansen, J. E., Hoffman, D. J., 1992. Climate forcing by anthropogenic aerosols. Science 255, 423-430.

Clarke, A.G., Karani, G. N., 1992. Characterization of the carbonate content of atmospheric aerosols. Journal of Atmospheric Chemistry 14, 119-128.

Dentener, F.J., Carmichael, G. R., Zhang, Y., Lelieveld, J., Crutzen, P. J., 1996, Role of mineral aerosol as a reactive surface in the global troposphere. Journal of Geophysical Research 101, 22869-22889.

Dibb, J. E., Meeker, L. D., Finkel, R. C., Southon, J. R., Caffee, M. W., Barrie, L. A., 1994. Estimation of stratospheric input to the Arctic troposphere: ^{7}Be and ^{10}Be in aerosols at Alert, Canada. Journal of Geophysical Research 99, 12855-12864.

Duce, R.A., Liss, P.S., Merrill, J.T., Atlas, E.L., Buat-Menard, P., Hicks, B.B., Miller, J.M., Prospero, J.M., Arimoto, R., Church, T.M., Ellis, W., Galloway, J.N., Hansen, L., Jickells, T.D., Knap, AH., Reinhardt, K.H., Schneider, B., Soudine, A., Tokos, J.J., Tsunogai, S., Wollast, R., Zhou, M., 1991. The atmospheric input of trace species to the world ocean. Global Biogeochemical Cycles 5, 193-259.

Duenas, C., Fernandez, M. C., Carretero, J., Liger, E., Canete, S., 2004. Long-term variation of the concentrations of long-lived Rn descendants and cosmogenic ^{7}Be and determination of the MRT of aerosols. Atmospheric Environment 38, 1291-1301.

El-Hussein, A., Mohamemed, A., El-Hady, M.A., Ahmed, A.A., Ali, A.E., Barakat, A., 2001. Diurnal and seasonal variation of short-lived radon progeny concentration and atmospheric temporal variations of ^{210}Pb and ^{7}Be in Egypt. Atmospheric Environment 35, 4305–4313.

Engelmann, R.J., 1971. Scavenging prediction using ratios of concentrations in air and precipitation. Journal of Applied Meteorology 10, 493-497.

Fang, G.C., Chang, C.N., Wu, Y.S., Fu, P.C., Yang, C.J., Chen, C.D., Chang, S.C., 2002. Ambient suspended particulate matters and related chemical species study in central Taiwan, Taichung during 1998-2001. Atmospheric Environment 36, 1921-1928.

Feely, H.W., Larsen, R.J., Sanderson, C.G., 1989. Factors that cause seasonal variability in Be-7 concentrations in surface air. Journal of Environmental Radioactivity 9, 223-249.

Feichter, J., Brost, R. A., Heimann, M., 1991. Three-dimensional modeling of the concentration and deposition of ^{210}Pb aerosols. Journal of Geophysical Research 96, 22,447– 22,460.

Gaffney, J. S., Marley, N. A., Cunningham, M. M., 2004. Natural radionuclides in fine aerosols in the Pittsburgh area. Atmospheric Environment 38, 3191-3200.

Galloway, J.N., 1995. Acid deposition: Perspectives in time and space. Water, Soil and Air Pollution 85, 15-24.

Galloway, J.N., Savoie, D.L., Keene, W.C., Prospero, J.M., 1993. The temporal and spatial variability of scavenging ratios for nss sulfate, nitrate, methanesulfonate and sodium in the atmosphere over the North Atlantic Ocean. Atmospheric Environment 27, 235-250.

Garg, A., Shukla, P. R., Bhattacharya, S., Dadhwal, V. K., 2001. Sub-region (district) and sector level SO_2 and NO_x emissions for India: assessment of inventories and mitigation flexibility. Atmospheric Environment 35, 703-713.

Graustein, W. C., Turekian, K. K., 1996. ^{7}Be and ^{210}Pb indicate an upper troposphere source for elevated ozone in the summertime subtropical free troposphere of the eastern North Atlantic. Geophysical Research Letters 23, 539-542.

Harrison, R.M., Allen, A.G., 1991. Scavenging ratios and deposition of sulphur, nitrogen and chlorine species in eastern England. Atmospheric Environment 25, 1719-1723.

Harrison, R.M., Pio, C.A., 1983. A comparative study of the ionic composition of rainwater and atmospheric aerosols: implications for the mechanism of acidification of rainwater. Atmospheric Environment 17, 2539–2543.

Huebert, B. J., Bates, T., Russell, P. B., Shi, G., Kim, Y. J., Kawamura, K., Carmichael, G., Nakajima, T., 2003. An overview of ACE-Asia: Strategies for quantifying the relationships between Asian aerosols and their climatic impacts. Journal of Geophysical Research 108, 8633, doi:10.1029/ 2003JD003550.

IPCC, 2001. Intergovernmental Panel on Climae Change, Third Assessment Report. Cambridge University Press, Cambridge.

Jaffrezo, J.L., Colin, J.L., 1988. Rain-aerosol coupling in urban area: scavenging ratio measurement and identification of some transfer processes. Atmospheric Environment 22, 929-935.

Jaffrezo, J.L., Colin, J.L., Gros, J.M., 1990. Some physical factors influencing scavenging ratios. Atmospheric Environment 24, 3073-3083.

Jain, M., Kulshrestha, U.C., Sarkar, A.K., Parashar, D.C., 2000. Influence of crustal aerosols on wet deposition at urban and rural sites in India. Atmospheric Environment 34, 5129-5137.

Johansen, A. M., Hoffmann, M. R., 2004. Chemical characterization of ambient aerosol collected during the northeast monsoon season over the Arabian Sea: Anions and cations. Journal of Geophysical Research 109, doi:10.1029/2003JD004111.

Jordan, C.E., Dibb, J. E., Anderson, B. E., Fuelberg, H. E., 2003. Uptake of nitrate and sulfate on dust aerosols during TRACE-P. Journal of Geophysical Research 108, 8817, doi: 10.1029/2002JD003101.

Joshi, L. U., Rangarajan, C., Gopalakrishnan, S., 1969. Measurement of lead-210 in surface air and precipitation. Tellus 21, 107-112.

Kane, M.M., Rendell, A.R., Jickells, T.D., 1994. Atmospheric scavenging processes over the North Sea. Atmospheric Environment 28, 2523-2530.

Kaya, G., Tuncel, G., 1997. Trace element and major ion composition of wet and dry deposition in Ankara, Turkey. Atmospheric Environment 23, 3985-3998.

Keene, W.C., McCulloch, A., Graedel, T.E., Lobert, J.M., Aucott, M.L., Gong, S.L., Harper, D.B., Kleiman, G., Midgley, P., Moore, R.M., Seuzaret, C., Sturges, W.T., Benkovitz, C.M., Koropalov, V., Barrie, L.A., Li, Y.F., 1999. Composite global emissions of reactive chlorine from anthropogenic and natural sources: Reactive Chlorine Emissions Inventory. Journal of Geophysical Research 104, 8429-8440.

Keene, W.C., Pszenny, A. P., Gallloway, J. N., Hawley, M. E., 1986. Sea salt correction and interpretation of constituent ratios in marine precipitation. Journal of Geophysical Research 91, 6647-6658.

Kerminen, V.M, Hillamo, R., Teinila, K., Pakkanen, T., Allegrint, I., Sparapani, R., 2001. Ion balances of size-resolved tropospheric aerosol samples: implications for the acidity and atmospheric processing of aerosols. Atmospheric Environment 35, 5255-5265.

Khemani, L.T., Momin, G.A., Prakash Rao, P.S., Safai, P.D., Singh, G., Chatterjee, R.N., Prakash, P., 1989. Long-term effects of pollutants on pH of rainwater in north India. Atmospheric Environment 23, 753-756.

Kline, J., Huebert, B. , Howell, S., Blomquist, B., Zhuang, J., Bertram, T., Carrillo, J., 2004. Aerosol composition and size versus altitude measured from the C-130 during ACE-Asia. Journal of Geophysical Research 109, D19S08, doi:10.1029/2004JD004540.

Kocak, M., Kubilay, N., Mihalopoulos, N., 2004. Ionic composition of lower tropospheric aerosols at a Northeastern Mediterranean site: implications regarding sources and long-range transport. Atmospheric Environment 38, 2067-2077.

Koch, D.M., Jacob, D.J., Graustein, W.C., 1996. Vertical transport of tropospheric aerosols as indicated by ^{7}Be and ^{210}Pb in a chemical tracer model. Journal of Geophysical Research 101, 18151–18666.

Krueger, B.J., Grassian, V.H., Laskin, A., Cowin, J.P., 2003. The transformation of solid atmospheric particles into liquid droplets through heterogeneous chemistry: Laboratory insight into the processing of calcium containing mineral dust aerosol in the troposphere. Geophysical Research Letter 30, 1148, doi: 10.1029/2002GL016563.

Kulshrestha, U.C., Kulshrestha, M.J., Sekar, R., Sastry, G.S.R., Vairamani, M., 2003. Chemical characteristics of rainwater at an urban site of south-central India. Atmospheric Environment 37, 3019-3026**.**

Kulshrestha, U.C., Sarkar, A.K., Srivastava, S.S., Parashar, D.C., 1996. Investigation into atmospheric deposition through precipitation studies at New Delhi (India). Atmospheric Environment 30, 4149-4154.

Kulshrestha, U.C., Saxena, A., Kumar, N., Kumari, K. M., Srivastava, S. S., 1998. Chemical composition and association of size differentiated aerosols at a suburban site in a semi-arid tract of India. Journal of Atmospheric Chemistry 29, 109-118.

Kumar, R., Rani, A., Singh, S.P., Kumari, K.M., Srivastava, S.S., 2002. A long term study on chemical composition of rainwater at Dayalbagh, a suburban site of semi-arid region. Journal of Atmospheric Chemistry 41, 265-279.

Lacaux, J.P., Artaxo, P., 2003. DEBITS: Past, Present and Future. IGACtivities Newsletter Issue No. 27, 1-5.

Lal, D., Malhotra, P. K., Peters, B., 1958. On the production of radioisotopes in the atmosphere by cosmic radiation and their application to meteorology. Journal of Atmospheric and Terrestrial Physics 12, 306-328.

Lal, D., Nijampurkar, V. N., Rajagopalan, G., Somayajulu, B. L. K., 1979. Annual fallout of ^{32}Si, ^{210}Pb, ^{22}Na, ^{35}S and ^{7}Be in rains in India. Proceedings Indian Academy of Science 88, 29-40.

Lal, D., Peters, D., 1967. Cosmic ray produced radioactivity on the earth. Handbook of Physics 46, 551-612.

Lee, H. N., Wan, G., Zheng, X., Sanderson, C. G., Josse, B., Wang, S., Yang, W., Tang, J., Wang, C., 2004. Measurements of ^{210}Pb and ^{7}Be in China and their analysis accompanied with global model calculations of ^{210}Pb. Journal of Geophysical Research 109, doi:10.1029/2004JD005061.

Lelieveld et al., 2001. The Indian Ocean Experiment: widespread air pollution from south and southeast Asia. Science 291, 1031-1036.

Levin, Z., Ganor, E., Gladstein, V., 1996. The effects of desert particles coated with sulfate on rain formation in the eastern Mediterranean. Journal of Applied Meteorology 35, 1511– 1523.

Mahadevan, T.N., Negi, B.S., Meenakshy, V., 1989. Measurements of elemental composition of aerosol matter and precipitation from a remote background site in India. Atmospheric Environment 23, 869–874.

Matsumoto, M., Okita, T., 1998. Long term measurements of atmospheric gaseous and aerosol species using an annular denuder system in Nara, Japan. Atmospheric Environment 32, 1419-1425.

Maxwell-Meier, K., Weber, R., Song, C., Orsini, D., Ma, Y., Carmichael, G. R., Streets, D.G., 2004. Inorganic composition of fine particles in mixed mineral dust-pollution plumes observed from airborne measurements during ACE-Asia. Journal of Geophysical Research 109, D19S07, doi: 10.1029/2003JD004464.

McLennan, S., 2001. Relationships between the trace element composition of sedimentary rocks and upper continental crust. Geochemistry Geophysics Geosystems 2 (4), doi:10.1029/2000GC000109.

McNeary, D., Baskaran, M., 2003. Depositional characteristics of ^{7}Be and ^{210}Pb in southeastern Michigan. Journal of Geophysical Research 108 (D7), 4210.

Menon, S., Hansen, J., Nazarenko, L., Luo, Y., 2002. Black carbon contributes to droughts and floods in China. Science 297, 2250-2253.

Momin, G.A., Rao, P. S. P., Safai, P. D., Ali, K., Naik, M. S., Pillai, A. G., 1999. Atmospheric aerosol characteristics studies at Pune and Thiruvananthpuram during INDOEX programme-1998. Current Science 76, 985-989.

Mphepya, J.N., Pienaar, J.J., Galy-Lacaux, C., Held, G., Turner, C.R., 2004. Precipitation chemistry in semi-arid areas of Southern Africa: a case study of a rural and an industrial site. Journal of Atmospheric Chemistry 47, 1-24.

Naik, M. S., Momin, G. A., Rao, P. S. P., Safai, P. D., Ali, K., 2002. Chemical composition of rainwater around an industrial region in Mumbai. Current Science 82, 1131-1137.

Norman, M., Das, S.N., Pillai, A.G., Granat, L., Rodhe, H., 2001. Influence of air mass trajectories on the chemical composition of precipitation in India. Atmospheric Environment 35, 4223-4235.

Nriagu, J. O., Pacyna, J. M., 1988. Quantitative assessment of worldwide contamination of air, water and soils by trace metals. Nature 333, 134-139.

Ooki, A., Uematsu, M., 2005. Chemical interactions between mineral dust particles and acid gases during Asian dust events. Journal of Geophysical Research 110, D03201, doi:10.1029/2004JD004737.

Pacyna, J. M., Semb, A., Hanssen, J. E., 1984. Emission and long-range transport of trace elements in Europe. Tellus 36B, 163-178.

Parashar, D.C., Granat, L., Kulshrestha, U.C., Pillai, A.G., Naik, M.S., Momin, G.A., Prakash Rao, P.S., Safai, P.D., Khemani, L.T., Naqvi, S.W.A., Narverkar, P.V., Thapa, K.B., Rodhe, H., 1996. Chemical composition of precipitation in India and Nepal. A preliminary report on an Indo-Swedish Project on Atmospheric Chemistry, Report CM-90, Department of Meteorology, Stockholm University.

Parashar, D.C., Kulshrestha, U.C., Jain, M., 2001, Precipitation and aerosol studies in India. Environmental Monitoring and Assessment 66, 47-61.

Pillai, A.G., Naik, M.S., Momin, G.A., Rao, P.S.P., Safai, P.D., Ali, K., Rodhe, H., Granat, L., 2001. Studies of wet deposition and dustfall at Pune, India. Water Air and Soil Pollution 130, 475-480.

Prospero J.M., Savoie, D.J., Arimoto, R., 2003. Long-term record of nss-sulfate and nitrate in aerosols on Midway Island, 1981-2000: Evidence of increased (now decreasing?) anthropgenic emissions from Asia. Journal of Geophysical Research 108, 4019, doi: 10.1029/2001JD001524.

Prospero, J. M., Uematsu, M., Savoie, D. L., 1989. Mineral aerosol transport to the pacific Ocean. Chemical Oceanography, vol. 10, edited by J. P. Riley, R. Chester, and R. A. Duce, 188– 218, Academic, San Diego, California.

Prospero, J.M., Charlson, R.J., Mohnen, V., Jaenicke, R., Delany, A.C., Moyers, J., Zoller, W., Rahn, K., 1983. The atmospheric aerosol system: an overview. Reviews of Geophysics and Space Physics 21, 1607-1629.

Rahn, K.A., 1976a. The chemical composition of the atmospheric aerosol. Technical Report, University of Rhode Island, 1 July 1976.

Ramanathan, V., Crutzen, P. J., Kiehl, J. T., Rosenfeld, D., 2001a. Aerosols, climate, and the hydrological cycle. Science 294, 2119-2124.

Ramanathan, V., et al., 2001b. Indian Ocean Experiment: An integrated analysis of the climate forcing and effects of the great Indo-Asian haze. Journal of Geophysical Research 106, 28,371– 28,398.

Rangarajan, C., Gopalakrishnan, S., 1970. Seasonal variation of Be-7 relative to Cs-137 in surface air at tropical and sub-tropical latitudes. Tellus 22, 115-121.

Rangarajan, C., Gopalakrishnan, S., Sadasivan, S., 1968. Atmospheric and precipitation radioactivity in India. Tellus 20, 269-283.

Rastogi, N, Sarin, M.M., 2005. Chemical characteristics of individual rain events from a semi-arid region in India: three-year study. Atmospheric Environment (In press).

Rastogi, N., Sarin, M.M., 2003a, Rain-aerosol coupling over Ahmedabad: Scavenging ratios of chemical species. In proceedings: National symposium on Biochemical sciences: health and environmental aspects, Dayalbagh Educational Institute, Agra, India. 2-4 October, 98-100.

Rastogi, N., Sarin, M.M., 2003b. Seasonal variations of ^{7}Be and ^{210}Pb concentrations in aerosols: Implications to atmospheric transport of trace species. In proceedings:

National symposium on Biochemical sciences: health and environmental aspects, Dayalbagh Educational Institute, Agra, India. 2-4 October, 98-100.

Rastogi, N., Sarin, M.M., 2004. Chemical uptake of acidic species by mineral aerosols over a semi-arid region. IASTA-Bulletin, Vol-16, 186-189.

Ravichandran, C., Padmanabhamurty, B., 1994. Acid precipitation in Delhi, India. Atmospheric Environment 28, 2291-2297.

Rengarajan, R., Sarin, M. M., 2004. Atmospheirc deposition fluxes of ^{7}Be, ^{210}Pb and chemical species to the Arabian Sea and Bay of Bengal. Indian Journal of Marine Sciences 33, 56-64.

Roeckner, E., Bengtsson, L., Feichter, J., Lelieveld, J., Rodhe, H., 1999. Transient climate change simulation with a coupled atmosphere-ocean GCM including the tropospheric sulfur cycle, Journal of Climate 12, 3004-3032.

Rosenfeld, D., 2000. Suppression of rain and snow by urban and industrial air pollution. Science 287, 1793–1796.

Safai, P.D., Rao, P.S.P., Momin, G.A., Ali, K., Chate, D.M., Praveen, P.S., 2004. Chemical composition of precipitation during 1984–2002 at Pune, India. Atmospheric Environment 38, 1705-1714.

Sarin, M. M., Bhushan, R., Rengarajan, R., Yadav, D. N., 1992. Simultaneous determination of ^{238}U series nuclides in waters of Arabian Sea and Bay of Bengal. Indian Journal of Marine Sciences 21, 121-127.

Sarin, M. M., Rengarajan, R., Krishnaswami, S., 1999. Aerosol NO_3^- and ^{210}Pb distribution over the central-eastern Arabian Sea and their air-sea deposition fluxes. Tellus 51B, 749-758.

Savoie, D.L., Prospero, J.M., Nees, R.T., 1987. Washout ratios of nitrate, non-sea-sulfate and sea salt on Virginia Key, Florida and on American Samoa. Atmospheric Environment 21, 103–112.

Saxena, A., Kulshrestha, U.C., Kumar, N., Kumari, K.M., Srivastava, S.S., 1996. Characterization of precipitation at Agra. Atmospheric Environment 30, 3405-3412.

Seinfeld, J.H., Pandis, S.N., 1998. Atmospheric Chemistry and Physics. First Edition, John Wiley, New York.

Sokolik, I. N., Toon, O. B., 1996. Direct radiative forcing by anthropogenic airborne mineral aerosols. Nature 381, 681– 683.

Song, C. H., Carmichael, G. R., 2001. A three-dimensional modeling investigation of the evolution processes of dust and sea-salts particles in east Asia. Journal of Geophysical Research 106, 18131-18154.

Streets, D. G., et al., 2003. An inventory of gaseous and primary aerosol emissions in Asia in the year 2000. Journal of Geophysical Research 108, 8809, doi:10.1029/2002JD003093.

Tabazadeh, A., Jacobson, M. Z., Singh, H. B., Toon, O. B., Lin, J. S., Chatfield, R. B., Thakur, A. N., Talbot, T. W., Dibb, J. E., 1998. Nitric acid scavenging by mineral and biomass burning aerosols. Geophysical Research Letter 25, 4185–4188.

Takeda, K., Marumoto, K., Minamikawa, T., Sakugama, H., Fujiwara, K., 2000. Three-year determination of trace metals and the lead isotope ratio in rain and snow depositions collected in Higashi-Hiroshima, Japan. Atmospheric Environment 34, 4525-4535.

Takeuchi, M., Okochi, H., Igawa, M., 2004. Characteristics of water-soluble components of atmospheric aerosols in Yokohama and Mt Oyama, Japan from 1990 to 2001. Atmospheric Environment 38, 4701-4708.

Tang, Y., et al., 2004. Three-dimensional simulations of inorganic aerosol distribution in east Asia during spring 2001, Journal of Geophysical Research 109, D19S23, doi:10.1029/2003JD004201.

Todd, J.F., Wong, G.T.F., Olsen, C.R., Larsen, I.L., 1989. Atmospheric depositional characteristics of beryllium-7 and lead-210 along the southeastern Virginia coast. Journal of Geophysical Research 94, 11106–11116.

Tripathi, R. M., Khandekar, R. N., Raghunath, R., Mishra, U. C., 1989. Assessment of atmospheric pollution from toxic heavy metals in two cities in India. Atmospheric Environment 23, 879-883.

Tuncer, B., Bayar, B., Yesilyurt, C., Tuncel, G., 2001. Ionic composition of precipitation at the Central Anatolia (Turkey). Atmospheric Environment 35, 5989-6002.

Turekian, K. K., Graustein, W. C., Cochran, J. K., 1989. Lead-210 in the SEAREX program: an aerosol tracer across the Pacific. Chemical Oceanography Vol. 10 edited by Riley J P and Chester R (Academic press, New York), 51-81.

Turekian, K.K., Benniger, L.K., Dion, E.P., 1983. Beryllium-7 and 210Pb total depositional fluxes at New Haven, Conneticut and Bermuda. Journal of Geophysical Research 88, 5411–5415.

Turekian, K.K., Nozaki, Y., Benninger, L.K., 1977. Geochemistry of atmospheric Radon and Radon products. Annual Review, Earth Planetary Sciences, 5, 227-255.

Uematsu, M., Duce, R. A., Prospero, J. M., 1994. Atmospheric beryllium-7 concentrations over Pacific Ocean. Geophysical Research Letters 21, 561-564.

Underwood, G. M., Song, C. H., Phadnis, M., Carmichael, G. R., Grassian, V. H., 2001. Heterogeneous reactions of NO_2 and HNO_3 on oxides and mineral dust: A combined laboratory and modeling study. Journal of Geophysical Research 106, 18,055–18,066.

Venkataraman, C., Reddy, C. K., Josson, S., Reddy, M. S., 2002. Aerosol size and chemical characteristics at Mumbai, India, during the INDOEX-IFP (1999). Atmospheric Environment 36, 1979-1991.

Viezee, W., Singh, H.B., 1980. The distribution of Be-7 in the troposphere: implications on stratosphere/troposphere air exchange. Geophysical Research Letter, 7, 805-808.

Wang, H., Shooter, D., 2001. Water soluble ions of atmospheric aerosols in three New Zealand cities: seasonal changes and sources. Atmospheric Environment 35, 6031-6040.

Weatherburn, M.W., 1967. Phenol hypochlorite reaction for determination of ammonia, Analytical Chemistry 39, 971-974.

Winkler, R., Dietl, F., Frank, G., Tschiersch, J., 1998. Temporal variation of ^{7}Be and ^{210}Pb size distributions in ambient aerosol. Atmospheric Environment 32, 983–991.

Wu, P.M., Okada, K., 1994. Nature of coarse nitrate particles in the atmosphere-a single particle approach, Atmospheric Environment 28, 2053-2060.

Yao, X., Chan, C. K., Fang, M., Cadle, S., Chan, T., Mulawa, P., He, K., Ye, B., 2002. The water-soluble ionic composition of PM 2.5 in Shanghai and Beijing, China. Atmospheric Environment 36, 4223-4234.

Zhuang, H., Chan, C. K., Fang, M., Wexler, A. S., 1999. Formation of nitrate and non-sea-salt sulfate on coarse particles. Atmospheric Environment 33, 4223-4233.

LIST OF PUBLICATIONS

Papers:

1. **N. Rastogi** and M.M. Sarin, 2005. Chemical characteristics of individual rain events from a semi-arid region in India: Three-year study. *Atmospheric Environment* (In press).

2. **Neeraj Rastogi** and M.M. Sarin, 2004. Chemical uptake of acidic species by mineral aerosols over a semi-arid region, IASTA-Bulletin, Vol-16, 186-189.

3. **Neeraj Rastogi** and M.M. Sarin, 2003. Seasonal variations of ^{7}Be and ^{210}Pb concentrations in aerosols: Implications to atmospheric transport of trace species. In proceedings: National symposium on Biochemical Sciences: Health and Environmental Aspects, Dayalbagh Educational Institute, Agra, India. 2-4 October, 109-110.

4. **Neeraj Rastogi** and M.M. Sarin, 2003. Rain-aerosol coupling over Ahmedabad: Scavenging ratios of chemical species. In proceedings: National symposium on Biochemical Sciences: Health and Environmental Aspects, Dayalbagh Educational Institute, Agra, India. 2-4 October, 98-100.

Communicated:

1. **N. Rastogi** and M.M. Sarin, 2005. Chemical characteristics of ambient aerosols from urban and high altitude sites in western India: Role of mineral dust and anthropogenic sources. (*Atmospheric Environment*, under review).

2. Dutta, K., Bhushan, R., Somayajulu, B. L. K., **Rastogi, N.**, 2005. Interannual variation of atmospheric Δ^{14}C over the northern Indian Ocean. (*Journal of Geophysical Research-Atmosphere*, under review).

Abstracts:

1. **N. Rastogi** and M.M. Sarin, Temporal variation of dry and wet deposition of atmospheric nitrogen at an urban site of a semi-arid region in India, abstract in 8th International Global Atmospheric Chemistry (IGAC) conference held at Christchurch, New Zealand during 4th – 9th Septemeber, 2004.

2. **Neeraj Rastogi** and M.M. Sarin, Comparative chemical characteristics of atmospheric aerosols at Ahmedabad and Mount Abu, abstract in National Space Science Symposium-2004 held at Mahatma Gandhi University, Kottayam, Kerala, February, 2004.

3. **Neeraj Rastogi** and M.M. Sarin, Three-year characterization of chemical composition of individual precipitation events over a semi-arid region, abstract in National Space Science Symposium-2004 held at Mahatma Gandhi University, Kottayam, Kerala, February, 2004.

4. A.K. Sudheer, M.M. Sarin and **N. Rastogi,** Anthropogenic sulphate-rich aerosols in the marine boundary layer over Bay of Bengal, abstract in National Space Science Symposium-2004 held at Mahatma Gandhi University, Kottayam, Kerala, February, 2004.

5. M.M. Sarin, A.K. Sudheer, **N. Rastogi**, Chemical characteristics of aerosols in the MBL of Bay of Bengal: Implications to transport of pollutants, XXIII General Assembly of the International Union of Geodesy and Geophysics IUGG-2003 held at Sapporo, Japan, June - July, 2003.

6. M.M. Sarin, A.K. Sudheer, **N. Rastogi**, Mineral dust and anthropogenic trace element inputs to the tropical Bay of Bengal, Geophysical Research Abstract, Vol. 5, 14677, 2003.

7. **Neeraj Rastogi**, M.M.Sarin, Temporal variability in chemical and isotopic composition of aerosols in an urban atmosphere, abstract in National Space Science Symposium-2002 held at Barkatullah University, Bhopal, February, 2002.

8. A.K.Sudheer, **Neeraj Rastogi**, M.M.Sarin, Atmospheric Be-7 and Pb-210 concentrations over Bay of Bengal: Implications to transport of pollutants, abstract in National Space Science Symposium-2002 held at Barkatullah University, Bhopal, February, 2002.

9. M.M. Sarin, A.K. Sudheer, **N. Rastogi**, Sulphate-rich aerosols and enhanced chloride depletion in the MBL of Bay of Bengal, abstract in international conference on "Atmospheric chemistry in the earth system: From regional pollution to global change", held at Crete, Greece, September, 2002.

Manuscripts under preparations:

1. **N. Rastogi** and M.M. Sarin, Rain-aerosol coupling over a semi-arid urban site in India: Scavenging ratios of chemical species.

2. **N. Rastogi** and M.M. Sarin, Temporal variations in surface air concentrations of ^{7}Be and ^{210}Pb over a low and high altitude sites in India.

3. **N. Rastogi** and M.M. Sarin, Trace metals in aerosols over a semi-arid region in India.