

Spatial and temporal variability in concentration and characteristics of aerosols at Visakhapatnam (east) and Goa (west) coasts of India

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Abstract

Knowledge on the variability in quantity and compositions of various size groups of aerosols is important to understand their sources and their role in biogeochemical and climate processes. Here, we studied total suspended particles (TSP), PM₁₀ and PM_{2.5} for their quantitative and water soluble compositional (F⁻, Cl⁻, SO₄²⁻, NO₃⁻, NH₄⁺, Na⁺, K⁺, Ca²⁺ and Mg²⁺) distributions, and to understand their nature and potential sources at Goa and Visakhapatnam on the west and east coasts, respectively, of India. While the mean concentrations of TSP were found to be 117±44 and 85±51 µg/m³ its maximal levels occurred in spring intermonsoon (SIM; 141±52) and winter monsoon (WM; 155±145 µg/m³) seasons at Goa and Visakhapatnam, respectively. PM₁₀ and PM_{2.5} exhibited higher ranges at Visakhapatnam than Goa. The increase in PM_{2.5} abundance from WM to SIM at Visakhapatnam seems to occur in coincidence with decrease in TSP favoured by topography and ambient meteorological conditions. Locally released and seasonally transported (from land and sea) constituents contributed to the observed variability in aerosol compositions. Sulphate dominated the aerosol composition at both Goa (57-64%) and Visakhapatnam (43-55%) followed by NO₃⁻ (5-16% and 6-18%, respectively) where the former component was higher in PM₁₀ and PM_{2.5}. The NO₃⁻ was more in TSP. Relations between SO₄²⁻ and NH₄⁺ suggested possible presence of NH₄HSO₄. Examination of ionic ratios and balance suggested near neutrality in PM₁₀ and PM_{2.5} while TSP were acidic at the both locations. Notable relations between Ca²⁺ and NO₃⁻, particularly in PM₁₀ at Goa, indicated their release from mining related activities.

Keywords

Aerosols, TSP, PM₁₀, PM_{2.5}, water soluble ionic species, Goa, Visakhapatnam, India

1. Introduction

The atmosphere has been recognized as a significant source of nutrient and pollutants to oceans (Mahowald et al, 2010; Ito et al, 2019; Jickells et al., 2005). Atmospheric particles (aerosols) emitted from continents are transported over considerable distances before being deposited. Wet deposition is an important removal mechanism, although dry deposition assumes significance in regions where the concentration of larger size fraction of aerosols is high and rainfall is less. Aerosols deposition depends on a few factors which include emission strengths and distances of the sources (natural and anthropogenic) and meteorological conditions (mainly wind direction and speed). These factors govern the variability of aerosols on spatial and temporal scales at any location. Apart from contributing to global cycles of materials the transport of aerosol substances have assumed significance in promoting biological productivity of the oceans but for the current concerns of acidifying the ocean waters. The nature of aerosols is of great importance for their potential impact on regional biogeochemistry, climate, and hydrological cycles.

The land-ocean system of South Asia is one of the most important in the world climate regions that experience reversal of wind directions annually associated with summer (SM) and winter (WM) monsoons.. In view of the intense anthropogenic activities and the dynamic monsoon associated wind systems it is important to understand the temporal and spatial variability in aerosol composition in this region. Unless such variability is understood it is hard to estimate or visualize the nature of impacts of aerosol transports and deposition on the neighboring oceans. In recent decades, India ranks as the second largest, emitter of anthropogenic aerosols in Asia (Ohara et al., 2007), which will have an impact on the climate of South Asia (Ji et al., 2011). Studies on the composition of aerosols, reported from the Indian region are mainly from urban/semi-urban locations (Kulshrestha et al., 1998, Momin et al., 1999), whereas, those from the rural or remote regions are few (Khemani et al., 1985; Mahadevan et al., 1989). The importance of atmospheric transports to Indian Ocean and global climate has been highlighted with the detection of polluted air transport from South Asia in winter causing a haze over the Indian Ocean (Ramanathan et al., 2002). The concerns came about export of anthropogenic black carbon and sulphate aerosols that can potentially influence regional hydrological cycles.

The tropical North Indian Ocean consists of the Bay of Bengal in the east and the Arabian Sea in the west, together with their marginal seas. Both these ocean basins, land locked in the north, are separated by the Indian Subcontinent and experience seasonally reversing monsoons (Wyrski, 1973). Consequently, the surface circulation in both the basins undergoes seasonal reversals (Shetye and Shenoi, 1988). The Arabian Sea is known to be biologically more productive than the Bay of Bengal

mainly due to the presence of strong seasonal upwelling regimes in the former basin (Qasim, 1977). The significance of atmospheric dust supply to biological production has been recognized in this region (Srinivas and Sarin, 2013; Yadav et al., 2016; Ramswamy et al., 2017). Transport of pollutant aerosols to the Bay of Bengal in northeast or winter (WM) and spring intermonsoon (SIM) seasons from the Indian Subcontinent (Kumar et al., 2008; Srinivas et al., 2011) and natural dust to the Arabian Sea (Ramswamy et al., 2017) in southwest or summer monsoon (SM) from West Asia highlight the differences in long-range sources and nature of aerosols between the two basins. The west coast of India receives heavy rainfall in SM whereas east coast receives meagre precipitation in the late WM. A few investigations (Kulshreshta et al., 1998) have dealt with the inorganic chemical composition of size-distributed aerosols in coastal cities of India whereas many attempts focused on the characterisation of TSP and are short-term studies (Joseph et al., 2012; Agnihotri et al., 2011; Hegde et al., 2016)

Here we hypothesize that differences in sources along with local (anthropogenic, biogenic and meteorological) conditions, topography and long range transports effect differences in size groups and chemical characteristics of aerosols between Goa (west) and Visakhapatnam (east) coastal locations of India, which will have implications to biogeochemical processes in the adjoining seas. Keeping the strong seasonal variability in wind directions our study covered WM, SIM, SM and fall inter-monsoon (FIM) periods. We present data obtained on seasonal distributions of aerosol mass concentrations and their water-soluble inorganic ions concentrations in TSP (0.1-100 μm), PM_{10} (<10 μm) and $\text{PM}_{2.5}$ (<2.5 μm) groups of aerosols at these two coastal stations. To our knowledge this study is the first attempt to studying variability in TSP, PM_{10} and $\text{PM}_{2.5}$ distributions and their respective water soluble inorganic chemical compositions simultaneously in the coastal regions of India.

2. Material and Methods

The study locations Visakhapatnam (17.62°N and 83.22°E) and Goa (15.50°N and 73.83°E) are mining related activity hubs. Otherwise Goa is less industrialized in comparison to Visakhapatnam, which houses many heavy industries. At Visakhapatnam attempts have been made to study air pollution in relation to meteorological conditions (Rao, 2014) and mitigation measures (Kumar, 2013; Rao, 2014). Chemical characterization of aerosols over Goa has been carried out by Agnihotri et al. (2011, 2015).

We conducted experiments on variability in TSP, PM_{10} and $\text{PM}_{2.5}$ mass concentrations and their compositions in Goa (from October 2011 to May 2012 and from February to May 2013) and at

Visakhapatnam (from September 2013 to May 2014) covering SM, WM, SIM and FIM seasons. Figure 1 shows the topography of the study locations. Sampling was carried out at the top of the Institute buildings' (CSIR-National Institute of Oceanography) at both the locations at heights of ~56m (Goa) and 20m (Visakhapatnam) above mean sea level. Meteorological data were obtained using Automatic Weather Stations (AWS) installed on the respective buildings rooftops. Air mass back trajectories (AMBTs) were prepared to trace the possible distant source regions and routes of aerosols transported to the two sampling sites. The back trajectories were computed using Global Data Assimilation System (GDAS) database of the National Oceanic and Atmospheric Administration (NOAA) Air Resources Laboratory and the Hybrid Single-Particle Lagrangian Integrated Trajectory model (HYSPLIT program, version- 4.0, <http://ready.arl.noaa.gov/HYSPLIT.php>), at arrival heights of 100, 500 and 1000 m (Draxler, 1999). The HYSPLIT Model is developed by NOAA and is a computer model that is being widely used to compute air parcel trajectories and deposition or dispersion of atmospheric pollutants. It is basically a hybrid between the Lagrangian approach and the Eulerian methodology. We have prepared AMBTs for the week preceding sampling date.

TSP and PM₁₀ aerosols were collected on pre-combusted quartz (PALLFLEX, 8"x10") and PM_{2.5} on PTFE (47 mm) filters. The amounts of aerosols collected on the filters were determined gravimetrically using electronic balances with 1 mg (Sartorius MF 5 for TSP and PM₁₀) and 1 µg (Sartorius BSA 2245-CW for PM_{2.5}) sensitivities. The aerosol samples (47 mm hole punches for TSP and PM₁₀, and PTFE filters of PM_{2.5}) were treated with 50 ml of Milli-Q water using an ultrasonicator for 30 minutes and the water soluble inorganic ions were analysed following Kumar et al. (2010). The water extracts were transferred to clean Teflon tubes and subjected for Ion Chromatographic analysis. The ions (F⁻, Cl⁻, SO₄²⁻, NO₃⁻, NH₄⁺, Na⁺, K⁺, Ca²⁺ and Mg²⁺) were analyzed using Ion Chromatograph (850 Professional IC) with a cation exchange column (Metrosep C4-150/4.0) and an anion exchange column (Metrosep A Supp 5 250/4.0) and a conductivity detector. The eluents used were a mixture of 3.2 mM l Na₂CO₃, 1 mM l NaHCO₃ and 100 mM l H₂SO₄ at a flow rate of 0.7 ml/min for anions, and 2 mM l HNO₃ at a flow rate of 0.9 ml/min for cations. Along with the samples, two filter blanks were also analysed and used for corrections. Results were corrected for procedural blanks: Cl⁻ = 0.84, NO₃⁻ = 0.058, SO₄²⁻ = 3.9, Na⁺ = 0.12, NH₄⁺ = 0.012, K⁺ = 0.026, Mg²⁺ = 0.015 and Ca²⁺ = 0.12 µg/m³. The extracts were introduced into the chromatograph through a 20 µl loop. Calibrations were done by sets of standards containing either anions or cations. The overall precision in these measurements was <10%. Non-sea salt (nss)

components were estimated following the formulae, given below, and information given in Kumar et al. (2008), Keene et al., 1986) and Sarin et al. (2010), respectively.

$$\text{nss- K}^+ = \text{K}^+ - 0.037 * \text{Na}^+ \quad (1)$$

$$\text{nss-Ca}^{2+} = \text{Ca}^{2+} - 0.038 * \text{Na}^+ \quad (2)$$

$$\text{nss- Mg}^{2+} = \text{Mg}^{2+} - 0.12 * \text{Na}^+ \quad (3)$$

$$\text{nss-SO}_4^{2-} = \text{SO}_4^{2-} - 0.25 * \text{Na}^+ \quad (4)$$

in which 0.037, 0.038, 0.12, 0.25 were weight ratios of K^+ , Ca^{2+} , Mg^{2+} and SO_4^{2-} to Na^+ in seawater. K^+ , Ca^{2+} , Mg^{2+} and SO_4^{2-} in eqs (1) to (4) represent their observed concentrations in aerosols.

3. Results

3.1. Meteorological conditions

Average air temperatures in WM and SIM show Goa was marginally warmer than Visakhapatnam whereas it was nearly the same in FIM (Table 1). Both locations experience low temperatures in WM, than in other seasons due to the inflow of cold dry air from north India. Seasonal means indicate that Goa was less humid (67 to 74%) than Visakhapatnam (70 to 83%). Wind speed was lower in Goa (average of $\sim 1.3 \pm 0.4$ m/s, Table 1) than at Visakhapatnam ($\sim 5 \pm 0.2$ m/s in general). Higher wind speed at Visakhapatnam seems to have been caused by the existence of an upper air Jet stream that blows in the easterly direction. This tropical easterly jet stream blows roughly along the Kolkata-Bangalore axis (Hussain, 2012).

3.1.1. Comparison between AWS and AMBT winds

Goa

The AMBTs in FIM, SIM and WM are shown in Figure 2. In SIM winds arrived from the northwest after originating in northwest or southern parts of the Arabian Sea. During WM, the monsoon wind brings dry, cool, and dense north Indian and central Asian air masses to the study site though local wind (AWS) blew from northeast (December 2011) or south (February 2013) directions (Table 1). During FIM the sampling site received air parcels from the east as the wind blew from East Asia and reached Goa after passing over the Bay of Bengal and peninsular terrain. This period marks the transition from wet to dry atmospheric conditions over the Indian subcontinent. During WM and FIM the site received air masses from or through Indian landmass but along the coastline in SIM season.

The measured AWS wind speeds at the site varied between FIM (0.98 ± 0.6 m/s) and SIM (1.7 ± 0.4 m/s). Wind directions showed remarkable temporal variability both in AWS (Table 1) and AMBT (Figure. 2) records. It is to be noted that while AWS and AMBT wind direction results agreed in FIM, in WM and SIM the disagreements are striking. In winter AWS results (Table 1) show winds blowing from west-southwest or south-southeast whereas AMBT (Figure. 2) depicts that it reaches the site from the northeast. On the other hand, in SIM, Table 1 suggests, AWS winds blew from the southwest but AMBT results show that it comes from northwest. Despite these differences, which are to be expected since AWS observations were carried out near the ground level and the AMBT analyses refer to higher altitudes, these two modes of results together facilitate a broad understanding of winds/air masses directions and the expected sources/nature of aerosols transported to the study site.

Visakhapatnam

The AMBT results (Figure 2) suggest the dominant source of air-masses to be north India during WM. The western source of air masses is striking for SM when the local winds changed from west to east (September; Table 1). However, in FIM and SIM air-masses mostly originated from east, southeast Asia and northeast. The air masses originating in the west and arriving in Visakhapatnam can transport natural dust aerosols from Gulf region or from Thar Desert (Madhavan et al., 2008), marine aerosols released by the Arabian Sea and anthropogenic aerosols from the subcontinent. Aerosols transported from east may have marine (Bay of Bengal) or polluted southeast Asia sources. Comparison between AWS wind directions (Table 1) and AMBT (Figure 2) revealed consistent trends between the two in SIM and SM (from southwest) and FIM (blew from northeast) but were different in WM as AMBT showed winds reaching the site from northeast when the local winds (AWS) blew from southwest. In general, both Goa and Visakhapatnam sites received winds originated from east in FIM, north in WM, and from respective neighbouring seas in SIM and SM seasons.

3.2. Variability in mass concentrations of TSP, PM₁₀ and PM_{2.5}

TSP

Concentrations of TSP (n=70) varied from 15 to 225 $\mu\text{g}/\text{m}^3$ (Supplementary Figure 1) with an average of 117 ± 44 $\mu\text{g}/\text{m}^3$ (Table 2), which agrees with the annual average aerosol concentration (109 ± 37 $\mu\text{g}/\text{m}^3$) observed by the Goa State Pollution Control Board at the nearby Mormugoa Port during April 2010 - March 2011 (<http://goaspcb.gov.in/wpcontent/uploads/2012/06/Ambient-Air-Quality.pdf>). The highest average concentration of TSP of 141 ± 52 $\mu\text{g}/\text{m}^3$ occurred in SIM followed

by WM ($113 \pm 34 \mu\text{g}/\text{m}^3$) and the lowest ($51 \pm 36 \mu\text{g}/\text{m}^3$) in FIM season. Table 2 suggests in general that nearly half of the TSP is comprised of PM_{10} whereas 50% of the latter was by $\text{PM}_{2.5}$, particularly in WM. An increasing trend in TSP concentrations but a decreasing one in PM_{10} can be seen from WM to SIM season (Supplementary Figure 1).

TSP concentrations varied from 19 to $188 \mu\text{g}/\text{m}^3$ (Supplementary Figure 1) with an average of $85 \pm 51 \mu\text{g}/\text{m}^3$ during this study (Table 2). Its concentrations showed strong seasonal variation with the highest of $155 \pm 145 \mu\text{g}/\text{m}^3$ in WM followed by that in SM ($131 \pm 48 \mu\text{g}/\text{m}^3$), FIM ($92 \pm 35 \mu\text{g}/\text{m}^3$) and SIM ($40 \pm 17 \mu\text{g}/\text{m}^3$). TSP concentrations in WM, SM and FIM were ~ 4 , 3 and 2 times higher than that in SIM, respectively. The maximal concentrations during WM may be attributed to low air temperature of about 24°C that keeps air column stable at the ground level and reduces mixing height due to inversion. The increased stability at the ground facilitates stagnation and hence the build-up of the particles.

PM_{10} and $\text{PM}_{2.5}$

The PM_{10} varied from 6 to $256 \mu\text{g}/\text{m}^3$ (Supplementary Figure 1). Its annual average was $69 \pm 60 \mu\text{g}/\text{m}^3$ at Visakhapatnam (Table 2). Concentrations of PM_{10} during WM and SM were ~ 3 times and during FIM ~ 2 times higher than that in SIM. On the other hand, the average concentration of $\text{PM}_{2.5}$ in WM ($93 \pm 26 \mu\text{g}/\text{m}^3$) was nearly equivalent to that ($98 \pm 24 \mu\text{g}/\text{m}^3$) in SIM (Table 2). Higher mass concentrations of $\text{PM}_{2.5}$ in SIM seem to be a result of orography in which Visakhapatnam sampling site is located and higher temperature and humidity. The wind blew from southwest at the sampling site in SIM. Mountainous terrain on three sides of the study site at Visakhapatnam seems to restrict the dispersion of particles, resulting in their accumulation in the city. Average concentrations of TSP, PM_{10} and $\text{PM}_{2.5}$ observed in this study are in excess of the NAAQS levels (National Ambient Air Quality Standards), which are 60, 60 and $40 \mu\text{g}/\text{m}^3$, respectively, at Visakhapatnam. TSP was higher but PM_{10} and $\text{PM}_{2.5}$ were lower than NAAQS levels in Goa.

While seasonal TSP concentrations exhibited wide variability in concentrations both in Goa and Visakhapatnam that of PM_{10} exhibited at the latter site. On the other hand average $\text{PM}_{2.5}$ seem to be steady in all seasons studied in Goa ($30 \pm 10 \mu\text{g}/\text{m}^3$) and Visakhapatnam ($94 \pm 24 \mu\text{g}/\text{m}^3$) with three times higher concentration at the latter site than in the former. Thus, PM_{10} and $\text{PM}_{2.5}$ were more abundant in Visakhapatnam than in Goa whereas the TSP at these places was nearly the same despite varied seasonal trends (Table 2, Supplementary Figure 1).

3.3. Variability in water soluble ionic compositions of TSP, PM₁₀ and PM_{2.5}

Goa

Average mass concentrations of water-soluble inorganic components in Goa and at Visakhapatnam are presented in Table 3. In TSP, SO₄²⁻ (20.35 µg/m³) was found to be in maximal abundance followed by NO₃⁻, Cl⁻, Na⁺, NH₄⁺, Ca²⁺, K⁺ and Mg²⁺. While SO₄²⁻ (16.24 µg/m³) was again the most abundant in PM₁₀ the second and third abundant were Na⁺ and Ca²⁺. These were followed by NO₃⁻, NH₄⁺, Cl⁻, Mg²⁺ and K⁺. In PM_{2.5} maximal SO₄²⁻ (7.89 µg/m³) was followed by Na⁺, NH₄⁺, Cl⁻, NO₃⁻, Ca²⁺, K⁺ and Mg²⁺. Concentrations of SO₄²⁻, NO₃⁻ and NH₄⁺ were higher in TSP than in PM₁₀ and PM_{2.5} (Table 3).

Variability of SO₄²⁻, NH₄⁺ and K⁺ in TSP exhibited higher concentrations in SIM and early WM with general lows during peak WM (Figure 3). On the other hand, NO₃⁻, Na⁺, Ca²⁺ and Cl⁻ showed maximal values in WM while Mg²⁺ exhibited no clear trend. Table 4 shows average SO₄²⁻ concentration (28.86 µg/m³) to be the highest during SIM followed by WM and FIM seasons. The second most abundant NO₃⁻ exhibited an increase from FIM (1.35 µg/m³) to WM (6.73 µg/m³) but decreased again in SIM. Similar to NO₃⁻, Ca²⁺, Na⁺ and Cl⁻ ions were found to be higher in WM in TSP. Seasonal distributions of ionic species in PM₁₀ showed higher concentrations for SO₄²⁻, NH₄⁺ and K⁺ in WM (Table 4; Supplementary Figure 2). On the other hand, NO₃⁻, Mg²⁺, Ca²⁺ and Cl⁻ were higher in SIM and exhibited consistent increase. The ionic abundance in PM_{2.5} (µg/m³), on an average, showed the general trend for inorganic ions as SO₄²⁻ > NH₄⁺ > Na⁺ > NO₃⁻ ≈ Cl⁻ > Ca²⁺ > K⁺ > Mg²⁺ in SIM (Table 3). In WM these were in the order: SO₄²⁻ > Na⁺ > Cl⁻ > NH₄⁺ ≈ Ca²⁺ > NO₃⁻ > K⁺ ≈ Mg²⁺ (Table 4; Supplementary Figure 3). NO₃⁻ and K⁺ showed close similarity in their concentrations in SIM and WM seasons. However, NH₄⁺ concentration in SIM was at times double to that in WM. The SO₄²⁻ was more in WM than in SIM in PM_{2.5} (Table 4), which is opposite to that in TSP that showed maximal concentration in SIM (Table 4).

Visakhapatnam

The SO₄²⁻ was present in TSP at the highest concentration of 16.77 µg/m³, followed by NO₃⁻, Cl⁻, Ca²⁺, Na⁺, NH₄⁺, Mg²⁺ and K⁺. In PM₁₀ SO₄²⁻ was at the maximal concentration of 18.70 µg/m³ followed by nearly equal levels of Ca²⁺, Na⁺ and NO₃⁻, which were followed by NH₄⁺, Cl⁻, Mg²⁺ and K⁺. The ionic abundances in PM_{2.5}, on an average, showed that SO₄²⁻ was the highest (18.4 µg/m³) followed by Ca²⁺, Na⁺, NO₃⁻, Cl⁻, NH₄⁺, Mg²⁺ and K⁺. The SO₄²⁻ dominated the composition in all sizes groups of aerosols and showed marginal enrichment in PM₁₀ and PM_{2.5} than in TSP aerosols. Ca²⁺ assumed second most abundance in PM₁₀ and PM_{2.5} whereas it was fourth in TSP. The second

most abundant NO_3^- in TSP became fourth in PM_{10} and $\text{PM}_{2.5}$. The Cl^- was the third most abundant in TSP but became the sixth in PM_{10} and fifth in $\text{PM}_{2.5}$. The pattern and levels of abundances in PM_{10} and $\text{PM}_{2.5}$ were almost similar and were different from that in TSP.

Variabilities in TSP water soluble components in Table 4 and Figure 3 exhibit more conspicuous seasonal changes at Visakhapatnam than in Goa. All components showed minimal values in SIM period. Anthropogenically influenced components NH_4^+ , SO_4^{2-} , K^+ and NO_3^- exhibited maximal levels in WM. The increase in levels of these components began in December (Figure 3) when significant changes in meteorological conditions occurred associated with strong cold winds (Table 1, Figure 2). On the other hand, the dust and sea salt associated components (Na^+ , Ca^{2+} , Cl^- and Mg^{2+}) showed maximal values in SM followed by FIM and WM with minimal levels in SIM season. The SO_4^{2-} , NO_3^- , Cl^- , Ca^{2+} and Na^+ were found at higher concentrations ($>1 \mu\text{g}/\text{m}^3$) in TSP. The contributions of cations to average aerosols composition were found in this study to be in the order $\text{Ca}^{2+} > \text{Na}^+ > \text{NH}_4^+ > \text{Mg}^{2+} > \text{K}^+$. On an average, SO_4^{2-} and NO_3^- contributed 42% and 18%, respectively, of the total water soluble composition in TSP (Figure 4). The seasonal and total study averages in ionic chemical components of PM_{10} aerosols are given in Tables 4 and 3, respectively. In PM_{10} , all the ions (Supplementary Figure 2) showed high concentration in WM. Levels of SO_4^{2-} , NO_3^- and NH_4^+ , were higher in WM as these species transform through gas to particle conversion processes from their respective precursor gases [SO_2 , and NO_x get oxidized and react with moisture in atmosphere. NH_4^+ forms from reduction of its precursor ammonia gas (NH_3)]. Seasonal variability in water soluble components in $\text{PM}_{2.5}$ (Supplementary Figure 3) show gradual increases in NO_3^- , Ca^{2+} and Mg^{2+} from WM to SIM (Table 4). The NO_3^- , Ca^{2+} and Mg^{2+} seasonal variabilities at Visakhapatnam contradict that at Goa for $\text{PM}_{2.5}$ and TSP but agree with that for PM_{10} . The percent contributions of ions in three size groups of aerosols are shown in Figure 4. The SO_4^{2-} contributed more than 50% of the total water soluble ionic composition in all size groups at both places except for its 43% in TSP at Visakhapatnam. While Ca^{2+} contribution increased with decreasing particle size at Visakhapatnam that of NO_3^- decreased at both places. The contribution of Cl^- was the highest in TSP whereas that of Na^+ was in PM_{10} . Percentage contribution of NH_4^+ was 4% in TSP but with marginally increased contributions in PM_{10} and $\text{PM}_{2.5}$.

4. Discussion

4.1. Variability in mass concentrations of TSP, PM_{10} and $\text{PM}_{2.5}$

The major drivers of the differences in concentrations of particles in various seasons are source strengths together with the Indian monsoon system and the associated forcings. The mass concentrations of TSP were nearly in the same range at both study locations (Supplementary Figure

1). PM_{10} concentration range at Goa is nearly equal to that of lower levels of seasons except WM-SIM at Visakhapatnam. The PM_{10} ranges were comparable during WM and SIM. But occasional peaks at Visakhapatnam far exceeded the normal range at the same location. $PM_{2.5}$ was significantly higher at Visakhapatnam than in Goa wherein its concentrations at the latter site were nearly below its minimal abundances at the former. The TSP gradually increased from FIM to the following SIM at Goa but that at Visakhapatnam decreased from FIM, WM to SIM (Supplementary Figure 1). The highest seasonal average of $155 \pm 145 \mu\text{g}/\text{m}^3$ for TSP occurred in WM at Visakhapatnam but it ($141 \pm 52 \mu\text{g}/\text{m}^3$) occurred in SIM at Goa. During monsoons (WM and SM) air over these locations seemed to contain more TSP and PM_{10} (Table 2). At both locations PM_{10} concentrations decreased from FIM to SIM whereas $PM_{2.5}$ showed no clear trend (Supplementary Figure 1). In fact, $PM_{2.5}$ was more abundant in SIM than the other two size groups at Visakhapatnam (Table 2). While a clear particle size distributions pattern ($PM_{2.5}$ abundance seems half of that of PM_{10} and the latter being half of that of TSP) could be noticed at Goa no such trend was observed at Visakhapatnam (Table 2). Visakhapatnam is bounded by hill ranges on three sides (Figure 1) that limited the dispersion of air. The orography of Visakhapatnam together with warm humid conditions and the changed wind direction appears to favour $PM_{2.5}$ accumulation in SIM as TSP and PM_{10} decreased. A major portion of the city comes under this specific orographic region where most of the industrial and commercial activities take place. Wind movement is either western or eastern and is limited to area within the hill ranges (Figure 1). Hence, accumulation of atmospheric particles is facilitated in the city due to continuous anthropogenic releases and their poor dispersion. Temperature inversion, in winter, further slows air circulation and aids aerosol accumulation. Higher mixing heights are observed during winter than in summer, except during morning and evening hours, due to development of internal boundary layer influenced by sea breeze during daytime and orography (Krishna et al., 2006). Goa orography (Figure 1) is different from that of Visakhapatnam with Western Ghats lined up in the east of the sampling location whereas the Arabian Sea lies on its west (Figure 1). Industrial activity is less in Goa than in Visakhapatnam. The distance between Western Ghats and sampling site is far enough for easy dispersion of air masses and particles. Low anthropogenic activity and reduced hindrance from orography resulted in low concentrations of PM_{10} and $PM_{2.5}$ at Goa than at Visakhapatnam. In general, our observed mass concentrations of TSP and PM_{10} are lower at Visakhapatnam compared to that reported in earlier studies for the Indo-Gangetic plain and some coastal areas, except for $PM_{2.5}$, (Supplementary Table 1).

4.2. Variability in water soluble ionic concentrations in aerosols

TSP

The nss- SO_4^{2-} appears to nearly constitute total SO_4^{2-} in aerosols at both locations (Figures 3 and 5). The nss components of SO_4^{2-} , Ca^{2+} and K^+ simply mimicked their total concentration distributions and confirmed their dominant anthropogenic (SO_4^{2-} and K^+ in early WM and SIM, and Ca^{2+} in late WM at Goa and at peak WM at Visakhapatnam) and natural (marine emissions for SO_4^{2-} in SIM at Goa and dust minerals for Ca^{2+} in SM at Visakhapatnam) sources. The dust may originate in the far west and transported to Visakhapatnam (Madhavan et al., 2008). Ranges of seasonal averages in SO_4^{2-} concentration were comparable at both regions (10 ± 8 to 29 ± 11 $\mu\text{g}/\text{m}^3$ at Goa, and 4.4 ± 2 to 27 ± 16 $\mu\text{g}/\text{m}^3$ at Visakhapatnam) but the seasons of its maximal values differed (Figure 3). These differences seem to have been caused largely by local pollution and that transported by winds from the north in WM at Visakhapatnam. Both anthropogenic and marine emissions account for that in SIM in Goa. The marine originated SO_4^{2-} might include that formed from oxidation of dimethyl sulphide (DMS) emitted from phytoplankton activities in the Arabian Sea associated with southwest wind driven upwelling processes. The higher concentration of NO_3^- in WM can be ascribed to emissions from biomass/biofuel burning that were carried by winds from the north and northeast India. Observed average concentrations in our study indicate that SO_4^{2-} and Cl^- are higher (Supplementary Table 2) than at other sites in India, Nepal and China perhaps due to combined marine and continental sources both Goa and Visakhapatnam experience.

PM₁₀

The SO_4^{2-} , NH_4^+ and K^+ showed decreasing trends from WM to SIM both at Goa and Visakhapatnam (Supplementary Figure 2). However, NO_3^- and dust/sea salt proxies' concentrations progressively increased as the SIM advanced in Goa but that was not the case at Visakhapatnam. Episodic increases in all constituents occurred at Visakhapatnam with maximal values in WM and SIM. Sulphate was the most dominant at Goa (66%) and Visakhapatnam (55%) followed by Na^+ and Ca^{2+} at the former but by nearly equal levels of these two cations and NO_3^- at the latter station (Figures 4). In comparison to those from adjacent regions our study shows higher enrichments because of the continental influence, but Allahabad city seems obviously more polluted with NH_4^+ and NO_3^- (Supplementary Table 3).

PM_{2.5}

Peaks in water soluble components occurred in late WM for SO_4^{2-} , NH_4^+ , K^+ , Cl^- and Ca^{2+} in Goa (Supplementary Figure 3). Increases in SO_4^{2-} , NO_3^- , Mg^{2+} and Ca^{2+} were obvious towards late WM

at Visakhapatnam. Dominant SO_4^{2-} contribution (78%) in WM was reduced to 39% in SIM since NH_4^+ , Na^+ , Cl^- , NO_3^- and Ca^{2+} contributions increased in the latter season in Goa (Table 4). Sulphate contribution was nearly the same (~55%) in WM and SIM followed by Ca^{2+} (~13%) at Visakhapatnam. In general, SO_4^{2-} contribution was reduced at Visakhapatnam due to higher percentages of Ca^{2+} , Cl^- , NO_3^- and Na^+ than in Goa (Figure 4). A comparison with studies over North Bay of Bengal and Hyderabad revealed that the present study areas are more polluted than the land locked city, which seem even less polluted with SO_4^{2-} and NO_3^- than the North Bay that comes under the influence of South East Asian transports (Supplementary Table 4).

4.3. Associations among water soluble ions in aerosols

Goa

The relations between NO_3^- and NH_4^+ , and NO_3^- and SO_4^{2-} are poor although these three ions primarily are of anthropogenic origin. The main reason appears to be differences in variations in their sources and their strengths as exemplified by their temporal trends in Table 4 and Figures 3. The variability of nss-SO_4^{2-} (Figure 5) essentially reflects that of total SO_4^{2-} since the former contributes majorly. Satsangi et al. (2013) and Rengarajan et al. (2007) obtained significant positive correlations $r^2=0.7$, ($p>0.001$) and $r^2 = 0.82$, ($p > 0.001$), respectively, between $\text{NH}_4^+/\text{SO}_4^{2-}$ molar ratios and NO_3^- concentrations at Agra and Hisar (both land stations) but our coastal data did yield highly scattered relations (Supplementary Figure 4a). Further, a plot between NO_3^- and NH_4^+ did not suggest 1:1 stoichiometry and hence does not support NH_4NO_3 presence; and if does it would be a very minor component of NO_3^- .

The NH_4^+ and SO_4^{2-} may form ammonium sulphate compounds (NH_4HSO_4 and/or $(\text{NH}_4)_2\text{SO}_4$) in aerosols. Figure 6 exhibits good positive linear relationships between NH_4^+ and nss-SO_4^{2-} in TSP, PM_{10} and $\text{PM}_{2.5}$ that agree well with their temporal co-variability in aerosols (Table 4) and suggests near similar processes and sources governing their abundances. Slope of the observed relationship in Figure 6 for TSP is only 0.16 advocating that at best the ammonium sulphate form could be NH_4HSO_4 as a minor form of SO_4^{2-} . The same is applicable to PM_{10} and $\text{PM}_{2.5}$ too though fairly consistent positive linear relations were found. (Figure 5).

Visakhapatnam

The correlation between NH_4^+ and NO_3^- ($r^2 = 0.7$, $p<0.01$) was good but the main linear relation actually represents WM data (Supplementary Figure 4b). This relation in WM suggests that proportional and/or common sources are responsible for their observed levels in aerosols in WM. Unlike a single season (WM) setting up the positive relationship between NH_4^+ and NO_3^- all seasons

data accounted for the observed positive linear relation between NO_3^- and SO_4^{2-} . A poor but linear trend was found in the relation between NO_3^- and $\text{NH}_4^+/\text{SO}_4^{2-}$ ($r^2 = 0.3$; Supplementary Figure 4b). A good correlation ($r^2=0.7$, $p<0.01$) between Mg^{2+} and Ca^{2+} suggests their common origin from dust particles. The Ca^{2+} abundance has been used as a reference material for crustal matter (Satsangi et al., 1998; Singh et al., 2001; Satsangi et al., 2002, Satsangi et al., 2013). The ratios of $\text{Na}^+/\text{Ca}^{2+}$, $\text{Mg}^{2+}/\text{Ca}^{2+}$ and $\text{Cl}^-/\text{Ca}^{2+}$ in Visakhapatnam aerosols are close to those in soils and hence indicate their common source in the crustal materials. Very different ratios for K^+ , NO_3^- and SO_4^{2-} against Ca^{2+} clearly suggest that the first three ions primarily added from non-crustal sources. The NH_4^+ relation with nss-SO_4^{2-} , in equivalents, for TSP is significant ($r^2= 0.6$; $p<0.01$) with a slope of 0.37 (Figure 5) suggesting that NH_4HSO_4 might contribute majorly to total NH_4^+ . The formation of NH_4NO_3 by chemical neutralization at the present site is supported by a weak positive correlation (Supplementary Figure 4b) between $\text{NH}_4^+/\text{SO}_4^{2-}$ and NO_3^- ($r^2=0.30$, $p > 0.01$). Satsangi et al (2013) and Rengarajan et al.(2007) also found significant positive correlation between $\text{NH}_4^+/\text{SO}_4^{2-}$ and NO_3^- . Thus NH_4^+ possibly exists in the forms of NH_4HSO_4 and NH_4NO_3 in the aerosols at Visakhapatnam.

4.4. Ionic balance and aerosol acidity

The NO_3^- and SO_4^{2-} constitute the major fraction of secondary inorganic aerosol formed from the oxidation of NO_x and SO_2 , respectively. Their subsequent reactions with ambient gaseous ammonia together with Ca^{2+} and Mg^{2+} ions may neutralize the acidity of aerosols to some extent (Seinfeld et al., 1998). The range of $\sum(\text{Ca}^{2+}+\text{Mg}^{2+}+\text{NH}_4^+)$ was nearly double at Visakhapatnam than that at Goa, while $\sum(\text{SO}_4^{2-}+\text{NO}_3^-)$ was in the same range (Supplementary Figure 5). Slopes of relations in equivalent units between these two (0.18 at Goa and 0.44 at Visakhapatnam) indicate excess $\sum(\text{SO}_4^{2-}+\text{NO}_3^-)$ than required to neutralize $\sum(\text{Ca}^{2+}+\text{Mg}^{2+}+\text{NH}_4^+)$.

Degree of neutralization in aerosols depends on the balance between available total anions and cations. Wu et al. (2017) defined neutralization Factor (NF) and Total Acidity ($[\text{H}^+]_{\text{T}}$) as below in view of the significant contributions of the ions considered to the total water soluble salts..

$$\text{NF} = ([\text{NH}_4^+] + [\text{Na}^+]) / (2*[\text{SO}_4^{2-}] + [\text{NO}_3^-] + [\text{Cl}^-]) \quad (5)$$

and

$$[\text{H}^+]_{\text{T}} = 2*[\text{SO}_4^{2-}] + [\text{NO}_3^-] + [\text{Cl}^-] - [\text{NH}_4^+] - [\text{Na}^+] \quad (6)$$

As our present study found significant contributions also from Ca^{2+} , Mg^{2+} and K^+ ions we have revised the above equations as

$$NF = ([NH_4^+] + [Na^+] + 2*[Ca^{2+}] + 2*[Mg^{2+}] + [K^+]) / (2*[SO_4^{2-}] + [NO_3^-] + [Cl^-]) \quad (7)$$

and

$$[H^+]_T = 2*[SO_4^{2-}] + [NO_3^-] + [Cl^-] - [NH_4^+] - [Na^+] - 2*[Ca^{2+}] - 2*[Mg^{2+}] - [K^+] \quad (8)$$

Here concentrations are in $\mu\text{eq}/\text{m}^3$. We computed NF and $[H^+]_T$ using Eqs. (5) to (8) and the results are shown in Table 5. When considered only Na^+ and NH_4^+ as cations responsible to neutralize SO_4^{2-} , NO_3^- and Cl^- ions (Eqs. (5); Wu et al., 2017) the NFs were <1 for all size groups at both Goa and Visakhapatnam. Consideration of eq. (7) changed the factors to >1 for PM_{10} and $PM_{2.5}$ at Visakhapatnam and for $PM_{2.5}$ in Goa. On the other hand NF of PM_{10} at Goa and TSP at both locations remained <1 . Wu et al. (2017) formulation revealed average $[H^+]_T$ to range from 0.11 ± 0.27 $\mu\text{eq}/\text{m}^3$ for $PM_{2.5}$ in Goa to 0.43 ± 0.3 for TSP at Visakhapatnam (Table 5). On the other hand, the average total acidity was same (0.23 ± 0.2) for PM_{10} at both locations. But eq. (8) revealed near neutrality in PM_{10} and $PM_{2.5}$ while TSP remained acidic at both Goa and Visakhapatnam (Table 5). Therefore, our results suggest acidic nature for TSP but near neutrality for PM_{10} and $PM_{2.5}$ at both locations. Near neutrality in PM_{10} and $PM_{2.5}$ is facilitated by significant presence of alkaline ions from crustal materials.

4.5. Sources of aerosols

The $[NO_3^-] / [SO_4^{2-}]$ ratio may provide an idea about the contribution of different major anthropogenic activities. If this ratio is > 1 , it indicates greater contribution of NO_3^- emissions from mobile sources (vehicular emissions) and when < 1 , it indicates greater contribution of SO_4^{2-} from stationary industrial emissions (Arimoto et al., 1996). The average ratio of NO_3^-/SO_4^{2-} over this entire study period was found to be 0.4 ± 0.36 , which suggests stationary (local) sources to be dominant in Goa. No significant correlation ($r^2=0.12$, $p>0.05$) was found between Mg^{2+} and Ca^{2+} (Supplementary Figure 4a) suggesting that they originated from different sources. Possibly Ca^{2+} might have originated from local soil particles (result of mining emissions) and Mg^{2+} from sea-salt emissions. Calcium and NO_3^- in TSP are better related in Goa ($r^2=0.4$) than at Visakhapatnam ($r^2=0.2$). Positive relation between Ca^{2+} and NO_3^- in PM_{10} was stronger at Goa ($r^2=0.9$; $p < 0.05$) than at Visakhapatnam ($r^2=0.4$; $p < 0.05$), which is also the case with PM_2 ; stronger correlation at Goa ($r^2 = 0.7$; $p < 0.05$) than at Visakhapatnam ($r^2 = 0.2$; $p > 0.05$). Stronger relations at Goa for PM_{10} and $PM_{2.5}$ reveal the significant emissions of mining particles in these size groups. Late winter peaks in Ca^{2+} and NO_3^- indicated increased dust emissions from local mining industry in which nitrogenous compounds are used as detonators in blasting the mines in Goa.

The Mg^{2+}/Na^+ values in our aerosol samples differed, at both locations in all size groups of particles with both lower and higher ratios, from their expected average seawater ratio of 0.11. The average ratio was much less in TSP in Goa whereas it was higher than 0.11 in TSP at Visakhapatnam and in PM_{10} and $PM_{2.5}$ particles at both places (Table 5). Deviations in Mg^{2+}/Na^+ in aerosols from the seawater ratio can be attributed to differences in mineralogical compositions (Keene et al., 1986). Temporal variability in SO_4^{2-} and K^+ ions (Figure 3) and their nss-fractions (Figure 5) did show higher concentrations during early and late WM at Goa but during WM at Visakhapatnam. The nss- SO_4^{2-} is a significant indicator of industrial emissions (Keene et al, 1986; Sarin et al,2010), particularly fossil fuels burning, when air masses originate over land masses. However, reduced sulphur emissions can be a source when air flows from the sea. Figures 3 and 5 depict higher SO_4^{2-} , NH_4^+ and nss- SO_4^{2-} at Goa and their minimal values at Visakhapatnam suggesting contrasting sources during SIM season. Figure 2 reveals that air masses originated over the respective neighboring seas in SIM. Higher values of SO_4^{2-} , NH_4^+ and nss- SO_4^{2-} at Goa seem to have resulted from the emissions from the coastal Arabian Sea since winds from southwest began to increase before the SM season. On the other hand, nss- K^+ is an indicator of biomass (Li et al., 2003; Guieu et al., 2005) and coal (Yu et al., 2018) burning. Aerosols seem to have originated from Southeast Asia in FIM and over India during WM and SIM observations in Goa (Figure 2) and are laden with pollutants such as SO_4^{2-} and K^+ . The available information for SM season at Visakhapatnam suggests relatively high levels of SO_4^{2-} and NO_3^- (than those in SIM at this location) and also that of mineral dust associated ions Ca^{2+} and Mg^{2+} . So also high are Na^+ and Cl^- . While the NO_3^- enrichment compared to SIM could be ascribed to industrial releases those of the remaining ions seem related to natural emissions. Figure 2 depicts the flow of air masses to Visakhapatnam to have originated in the west and it is known that the desert dust is carried in this direction during SM season (Ramaswamy et al., 2017).

5. Conclusions

We have carried out experiments to find the differences in concentrations of water soluble cations (NH_4^+ , Ca^{2+} , Mg^{2+} , Na^+ , K^+) and anions (SO_4^{2-} , NO_3^- , Cl^-) in TSP, PM_{10} and $PM_{2.5}$ to understand their sources and nature through associations among the components at Goa and Visakhapatnam. $PM_{2.5}$ was more abundant facilitated by orography and warm humid air at Visakhapatnam than in Goa. The composition of all size groups of aerosols was dominated by SO_4^{2-} to which its nss-component contributed nearly to the total followed by NO_3^- . Relations among SO_4^{2-} , NO_3^- and NH_4^+ are weak and their ratios suggest the forms of NH_4HSO_4 and NH_4NO_3 to be minor components of respective anions. Ratio of NO_3^- to SO_4^{2-} suggested the aerosols composition to be dominantly

contributed by local stationary sources. Ionic balance suggested TSP to be acidic whereas PM₁₀ and PM_{2.5} were near neutral at both locations. Strong positive relation between Ca²⁺ and NO₃⁻ in PM₁₀ indicates dust releases from mining related activities, particularly in Goa.

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Illustrations

Main Tables titles

Table 1. Number of TSP, PM₁₀ and PM_{2.5} samples collected along with averaged meteorological data (with mean deviations) at Goa and Visakhapatnam. SM refers to Summer monsoon, FIM to Fall Intermonsoon, WM to Winter monsoon and SIM to Spring Intermonsoon.

Table 2. Variations in mean mass concentrations ($\mu\text{g}/\text{m}^3$) of TSP, PM₁₀ and PM_{2.5} with standard deviations (SD) at Goa and Visakhapatnam in various seasons and total study period.

Table 3. Average concentrations ($\mu\text{g}/\text{m}^3$) with standard deviations of water-soluble ions in TSP, PM₁₀ and PM_{2.5} at Goa and Visakhapatnam observed in this study.

Table 4. Seasonal variations in average concentrations ($\mu\text{g}/\text{m}^3$) with standard deviations of water-soluble ions in TSP, PM₁₀ and PM_{2.5} at Goa and Visakhapatnam.

Table 5. Neutralization factors, Total acidity ($\mu\text{eq}/\text{m}^3$) and $\text{Mg}^{2+}/\text{Na}^{2+}$ ratios in TSP, PM₁₀ and PM_{2.5} at Goa and Visakhapatnam.

Main Figure Titles

Figure 1. Google earth topography maps for study locations in Goa and Visakhapatnam. Areas bordered by dark lines are hills pertaining to Western Ghats in Goa and Eastern Ghats in Visakhapatnam. Ghat refers to a Mountain range.

Figure 2. Air mass back trajectories (AMBT) showing long-range pathways of aerosols during SM, FIM, WM and SIM seasons at Goa and Visakhapatnam along with their orography (see text).

Figure 3. Temporal variations in water soluble NH_4^+ , SO_4^{2-} , NO_3^- , Cl^- , K^+ , Na^+ , Ca^{2+} and Mg^{2+} ($\mu\text{g}/\text{m}^3$) in TSP at Goa and Visakhapatnam.

Figure 4. Percent contributions of water-soluble ionic components at (a) Visakhapatnam and (b) Goa for the entire study period in TSP, PM₁₀ and PM_{2.5}.

Figure 5. Temporal variability in nss- Ca^{2+} , nss- SO_4^{2-} and nss- K^+ concentrations ($\mu\text{g}/\text{m}^3$) in TSP at Goa and Visakhapatnam.

Figure 6. Relations between nss- SO_4^{2-} and NH_4^+ in (a) TSP (b) PM₁₀ and (c) PM_{2.5} for the entire study period at Goa and Visakhapatnam. Units are in $\mu\text{eq}/\text{m}^3$. Symbols \square - for SM, Δ for SIM, \bullet - for WM and \star for FIM.

Supplementary Table titles

Supplementary Table 1. Comparison of mass concentrations of three size groups of aerosols at Goa and Visakhapatnam with those at other Indian cities

Supplementary Table 2. Comparison of water soluble ionic composition of TSP of Goa and Visakhapatnam with that over some Indian and world cities.

Supplementary Table 3. Comparison of water soluble ionic composition of PM₁₀ of Goa and Visakhapatnam with that over Indian Ocean basins and Allahabad city. BoB= Bay of Bengal and AS= Arabian Sea.

Supplementary Table 4. Comparison of water soluble ionic composition of PM_{2.5} at Goa and Visakhapatnam with N-BoB basins and Hyderabad city. BoB= Bay of Bengal

Supplementary Figure titles

Supplementary Figure 1. Temporal variability in TSP, PM₁₀ and PM_{2.5} concentrations ($\mu\text{g}/\text{m}^3$) at Goa and Visakhapatnam.

Supplementary Figure 2. Temporal variations of water-soluble ionic concentrations ($\mu\text{g}/\text{m}^3$) in PM₁₀ at Goa and Visakhapatnam.

Supplementary Figure 3. Temporal variations of water-soluble ionic concentrations ($\mu\text{g}/\text{m}^3$) in PM_{2.5} at Goa and Visakhapatnam.

Supplementary Figure 4(a). Relations between various ionic components ($\mu\text{g}/\text{m}^3$) in TSP at Goa: (a) NO_3^- and NH_4^+ , (b) SO_4^{2-} and NO_3^- , (c) $\text{NH}_4^+/\text{SO}_4^{2-}$ and NO_3^- and (d) Mg^{2+} and Ca^{2+} .

Supplementary Figure 4(b). Relations between various ionic components ($\mu\text{g}/\text{m}^3$) in TSP at Visakhapatnam: (a) NO_3^- and NH_4^+ , (b) SO_4^{2-} and NO_3^- , (c) $\text{NH}_4^+/\text{SO}_4^{2-}$ and NO_3^- and (d) Mg^{2+} and Ca^{2+} . Symbols : □- for SM, Δ- for SIM, ●- for WM and * for FIM.

Supplementary Figure 5. Relations between $\sum(\text{Ca}^{2+}, \text{Mg}^{2+} \text{ and } \text{NH}_4^+)$ and $\sum(\text{NO}_3^- \text{ and } \text{SO}_4^{2-})$ (units in $\mu\text{eq}/\text{m}^3$) in TSP at Goa and Visakhapatnam during the entire study period.

Table 1. Number of TSP, PM₁₀ and PM_{2.5} samples collected along with averaged meteorological data (with mean deviations) at Goa and Visakhapatnam. SM refers to Summer monsoon, FIM to Fall Intermonsoon, WM to Winter monsoon and SIM to Spring Intermonsoon.

Season	Number of Samples (TSP)	Number of Samples (PM ₁₀)	Number of Samples (PM _{2.5})	Temperature (°C)	Relative Humidity (%)	Wind speed (m/s)	Wind direction (°)
Goa (2011-12)							
FIM (October-November)	6	Nil	Nil	28±0.8	67±11	0.98±0.6	93±31
WM (December-February)	47	Nil	Nil	25±1.2	68.2±8.23	1±0.45	258±116
SIM (March-May)	17	Nil	Nil	28±1.5	74±5.6	1.7±0.40	212±33
Goa (2013)							
WM (February)	Nil	7	7	26.4±1.5	68±7.8	1.4±0.17	154±48
SIM (March-May)	Nil	8	9	28.3±0.3	72.6±5	1.5±0.7	243±48
Visakhapatnam (2013-2014)							
FIM (October-November)	3	6	Nil	28.0±0.6	82.0±5	4.65±2	45±16
WM (December-February)	8	10	11	24.3±0.8	70±12	4.6±1.6	207±70
SIM (March-May)	8	11	5	27.4±1.7	81.8±5.6	5±1.8	192±64
SM (September)	4	8	Nil	28±0.7	83.4±5.02	5±2.3	223±35

Table 2. Variations in mean mass concentrations ($\mu\text{g}/\text{m}^3$) of TSP, PM_{10} and $\text{PM}_{2.5}$ with standard deviations at Goa and Visakhapatnam in various seasons and total study period.

Aerosol Size Group	Total Study period	SM	FIM	WM	SIM
Goa					
TSP	117±44	-	51±36	113±34	141±52
PM_{10}	55±9	-	-	60±6	50±9
$\text{PM}_{2.5}$	30±10	-	-	32±10	28±9
Visakhapatnam					
TSP	85±51	131±48	92±35	155±145	40±17
PM_{10}	69±60	93±82	66±17	92±68	32±14
$\text{PM}_{2.5}$	94±24	-	-	93±26	98±24

Table 3. Average concentrations ($\mu\text{g}/\text{m}^3$) with standard deviations of water-soluble ions in TSP, PM_{10} and $\text{PM}_{2.5}$ at Goa and Visakhapatnam observed in this study.

Goa			
Species	TSP	PM_{10}	$\text{PM}_{2.5}$
Cl^-	3.7±4.7	0.8±1.5	0.7±1
NO_3^-	5.7±3.7	1.5±1.3	0.6±0.5
SO_4^{2-}	20.3±10.9	16.2±5.5	7.9±13.5
Na^+	2.6±1.4	2.4±1	1±0.5
NH_4^+	1.3±0.8	1±0.9	0.9±0.9
K^+	0.5±0.2	0.3±0.2	0.3±0.2
Mg^{2+}	0.1±0.1	0.4±0.4	0.2±0.3
Ca^{2+}	1.2±0.8	2.2±1.8	0.6±0.6
Visakhapatnam			
	TSP	PM_{10}	$\text{PM}_{2.5}$
Cl^-	6.1±7.6	1.6±2.3	2.4±2.7
NO_3^-	7±5.6	3.5±2.8	2.5±1.4
SO_4^{2-}	16.7±13.6	18.7±11.7	18.4±9.2
Na^+	3±2.2	3.5±1.4	2.8±1.5
NH_4^+	1.6±2.4	2±1.6	1.7±1.7
K^+	0.4±0.3	0.5±0.2	0.5±0.2
Mg^{2+}	0.5±0.4	0.5±0.4	0.5±0.4
Ca^{2+}	3.5±2	3.6±3	4.4±2.3

	Goa						Visakhapatnam							
TSP														
Species	FIM (n=6)		WM (n=47)		SIM (n=17)		SM (n=4)		FIM (n=3)		WM (n=8)		SIM (n=8)	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Cl ⁻	0.45	0.65	4.88	5.35	1.57	1.56	20.53	7.42	2.47	0.54	3.31	2.82	3.07	2.51
NO ₃ ⁻	1.35	0.51	6.74	3.70	4.30	2.77	9.20	2.93	7.13	3.85	10.64	6.48	2.32	2.10
SO ₄ ²⁻	9.99	7.95	18.60	9.33	28.86	10.55	20.16	4.67	17.86	5.33	27.05	15.65	4.40	2.03
Na ⁺	1.28	0.38	3.05	1.46	1.94	0.62	6.93	2.04	3.07	0.76	2.62	1.35	1.59	0.69
NH ₄ ⁺	0.51	0.52	1.25	0.72	1.78	0.82	0.46	0.28	1.28	0.31	3.64	3.30	0.35	0.56
K ⁺	0.20	0.14	0.48	0.13	0.54	0.17	0.40	0.02	0.47	0.20	0.57	0.41	0.10	0.06
Mg ²⁺	0.07	0.04	0.10	0.10	0.11	0.07	1.20	0.23	0.55	0.21	0.46	0.23	0.31	0.13
Ca ²⁺	0.55	0.26	1.41	0.93	0.94	0.30	6.88	0.86	3.79	1.52	3.19	1.64	2.08	0.57

Table 4. Seasonal variations in average concentrations ($\mu\text{g}/\text{m}^3$) with standard deviations of water-soluble ions in TSP, PM₁₀ and PM_{2.5} at Goa and Visakhapatnam.

	Goa				Visakhapatnam							
PM ₁₀												
Species	WM (n=7)		SIM (n=8)		SM (n=8)		FIM (n=4)		WM (n=10)		SIM (n=11)	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Cl ⁻	0.45	0.24	1.24	2.02	1.48	1.49	0.76	0.52	2.21	3.24	1.49	2.30
NO ₃ ⁻	0.90	0.56	1.99	1.57	3.73	1.74	2.36	0.55	4.34	3.42	3.03	3.39
SO ₄ ²⁻	18.47	7.55	14.29	1.83	16.69	11.38	19.68	14.32	25.74	13.26	13.41	6.72
Na ⁺	2.36	0.96	2.44	1.16	4.08	2.44	2.83	0.22	3.57	1.04	3.36	0.89
NH ₄ ⁺	1.55	1.07	0.45	0.32	0.92	0.91	1.99	1.47	3.45	1.82	1.43	0.95
K ⁺	0.39	0.23	0.18	0.09	0.34	0.17	0.48	0.18	0.63	0.14	0.37	0.12
Mg ²⁺	0.22	0.11	0.50	0.53	0.56	0.25	0.33	0.08	0.65	0.44	0.52	0.49
Ca ²⁺	1.45	0.57	2.79	2.22	4.64	3.87	2.56	0.50	4.41	4.02	2.55	1.05

	Goa				Visakhapatnam			
	PM _{2.5}							
Species	WM (n=7)		SIM (n=9)		WM (n=11)		SIM (n=5)	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Cl ⁻	0.67	0.91	0.71	1.06	1.48	1.45	4.41	3.75
NO ₃ ⁻	0.54	0.54	0.69	0.51	2.19	1.54	3.30	0.88
SO ₄ ²⁻	13.91	19.2 4	3.20	2.53	15.75	7.35	24.24	11.03
Na ⁺	0.88	0.61	1.05	0.32	2.37	0.84	3.98	2.12
NH ₄ ⁺	0.60	0.74	1.22	1.04	2.22	1.87	0.59	0.19
K ⁺	0.32	0.22	0.34	0.20	0.49	0.27	0.43	0.15
Mg ²⁺	0.33	0.39	0.13	0.11	0.36	0.25	0.91	0.36
Ca ²⁺	0.60	0.60	0.56	0.54	3.52	1.78	6.19	2.31

Table 5. Neutralization factors, Total acidity ($\mu\text{eq}/\text{m}^3$) and $\text{Mg}^{2+}/\text{Na}^{2+}$ ratios in TSP, PM₁₀ and PM_{2.5} at Goa and Visakhapatnam.

Place	Aerosol	Neutralization Factor Average \pm Std Dev (Range)		Total Acidity Average \pm Std Dev (Range)		$\text{Mg}^{2+}/\text{Na}^{2+}$ Average \pm Std Dev (Range)
		Wu (2017) Eq (5)	This Study Eq (7)	Wu (2017) Eq (6)	This Study Eq (8)	
Goa	TSP	0.37 \pm 0.44 (0.21-3.86)	0.54 \pm 0.64 (0.3-5.63)	0.43 \pm 0.20 (0.06-0.92)	0.35 \pm 0.19 (0.1-0.83)	0.04 \pm 0.03 (0-0.12)
	PM ₁₀	0.42 \pm 0.19 (0.03-0.7)	0.56 \pm 0.23 (0.05-0.83)	0.23 \pm 0.11 (0.07-0.4)	0.08 \pm 0.14 (-0.13-0.35)	0.16 \pm 0.13 (0.05-0.5)
	PM _{2.5}	0.76 \pm 0.80 (0.15-3.20)	1.51 \pm 1.38 (0.18-5.40)	0.11 \pm 0.27 (-0.15-1.02)	0.05 \pm 0.28 (-0.18-0.99)	0.16 \pm 0.10 (0.01-0.35)
Visakhapatnam	TSP	0.38 \pm 0.12 (0.03-0.65)	0.86 \pm 0.31 (0.06-1.45)	0.41 \pm 0.30 (0.03-0.87)	0.18 \pm 0.23 (-0.06-0.72)	0.18 \pm 0.03 (0.12-0.21)
	PM ₁₀	0.59 \pm 0.19 (0.32-0.92)	1.14 \pm 0.37 (0.50-1.96)	0.23 \pm 0.19 (0.02-0.75)	-0.01 \pm 0.20 (-0.42-0.59)	0.14 \pm 0.06 (0.05-0.36)
	PM _{2.5}	0.54 \pm 0.55 (0.11-2.55)	1.15 \pm 0.91 (0.05-4.43)	0.27 \pm 0.25 (-0.26-0.99)	- 0.001 \pm 0.20 (-0.59-0.35)	0.14 \pm 0.11 (-0.21-0.28)

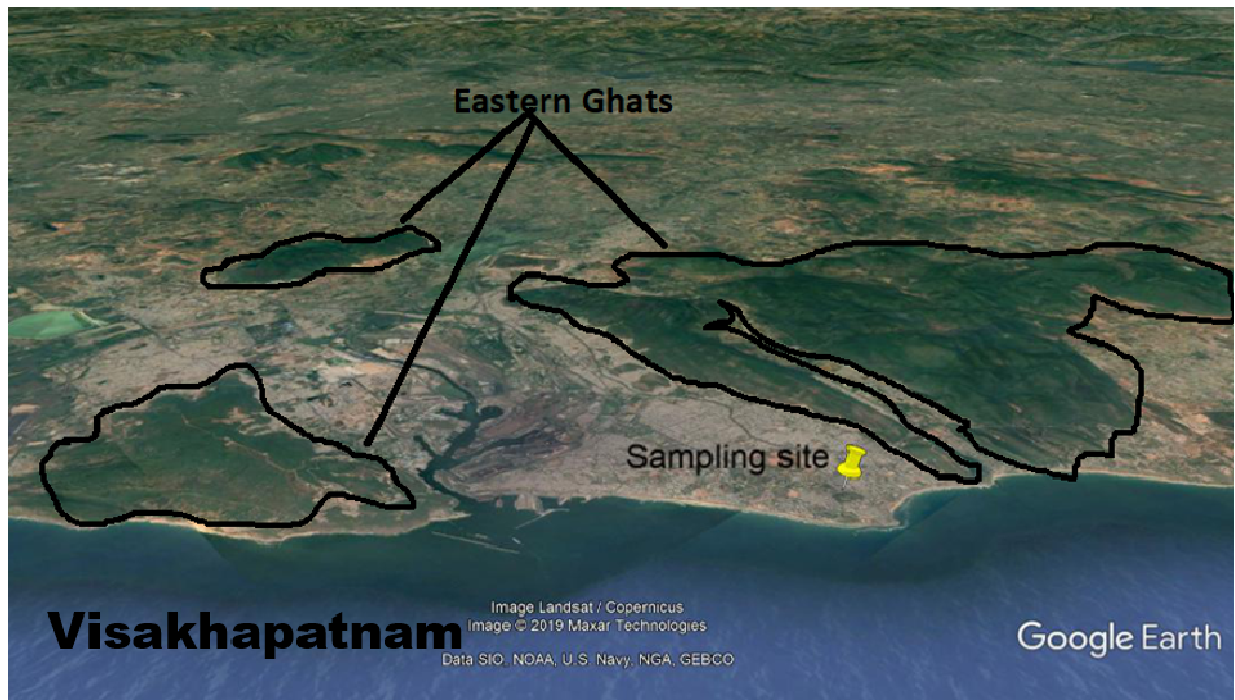
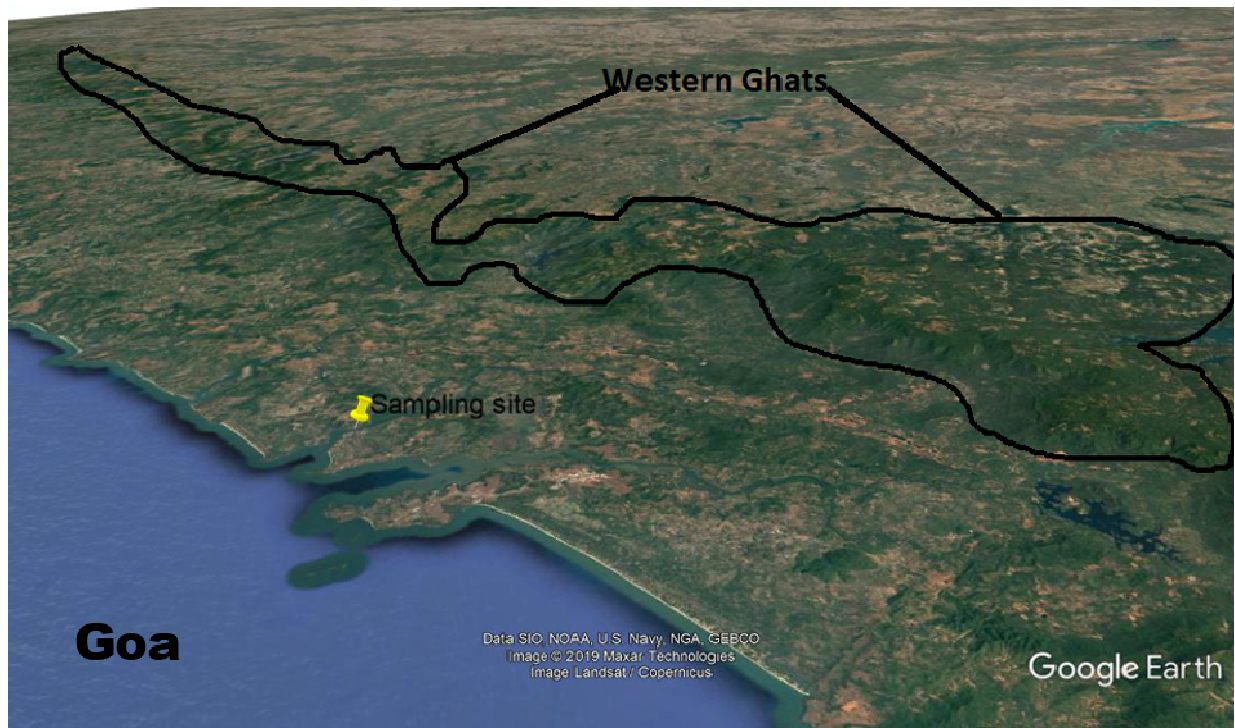


Figure 1. Google earth topography maps for study locations in Goa and Visakhapatnam. Areas bordered by dark lines are hills pertaining to Western Ghats in Goa and Eastern Ghats in Visakhapatnam. Ghat refers to a Mountain range.

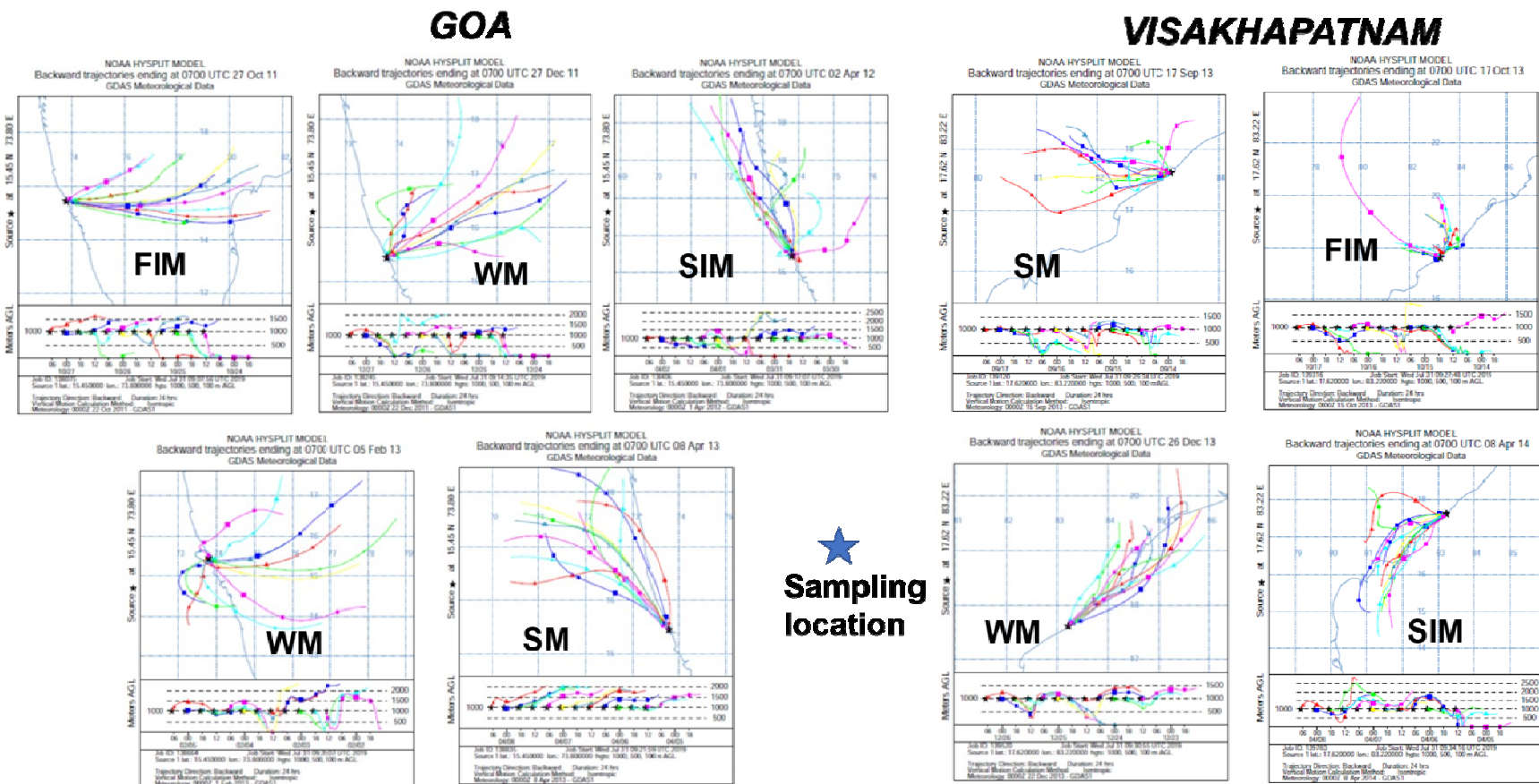


Figure 2. Air mass back trajectories (AMBT) showing possible long-range pathways of aerosols during SM, FIM, WM and SIM seasons at Goa and Visakhapatnam along with their orography (see text)

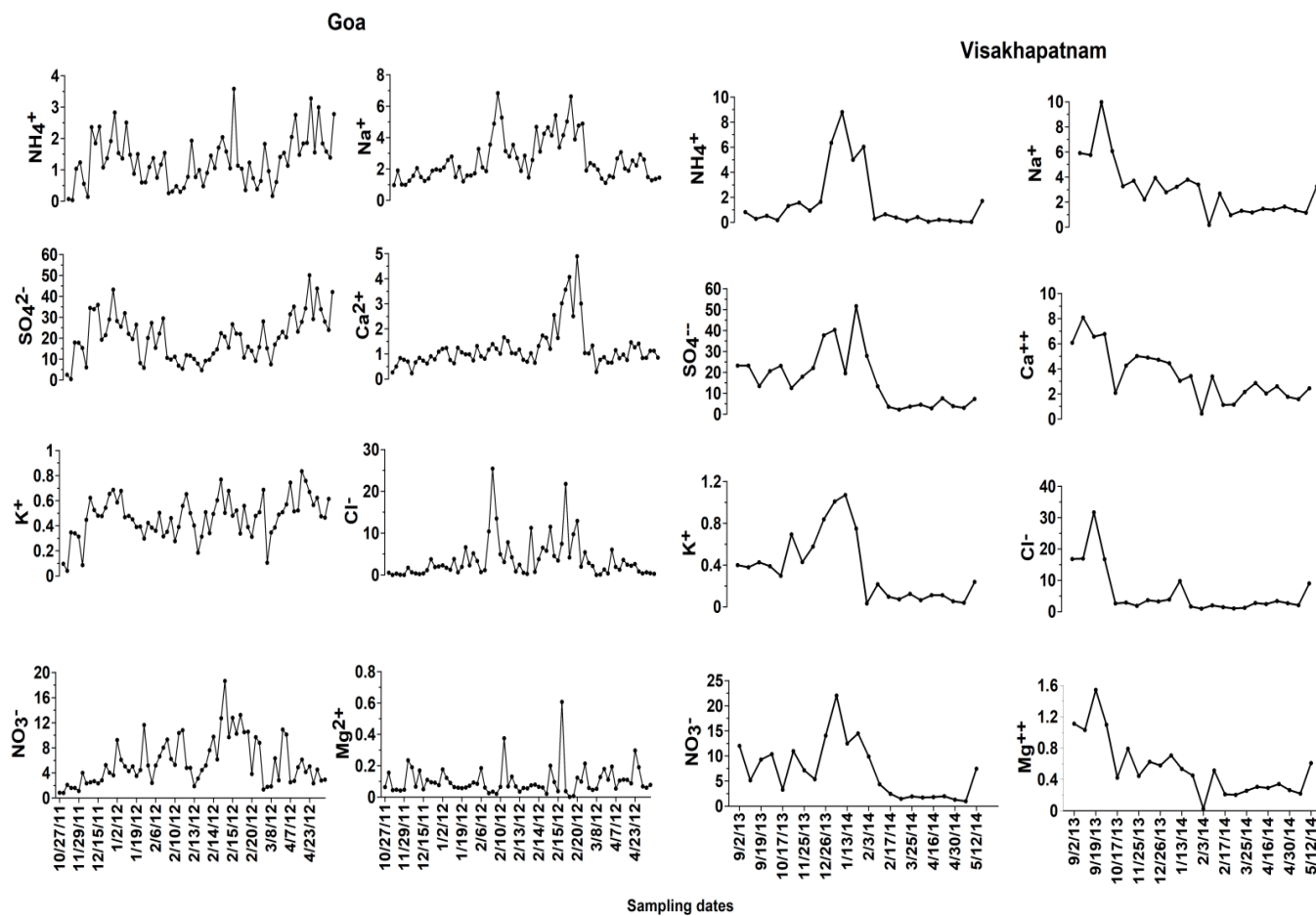


Figure 3. Temporal variations in water soluble NH_4^+ , SO_4^{2-} , NO_3^- , Cl^- , K^+ , Na^+ , Ca^{2+} and Mg^{2+} ($\mu\text{g}/\text{m}^3$) in TSP at Goa and Visakhapatnam.

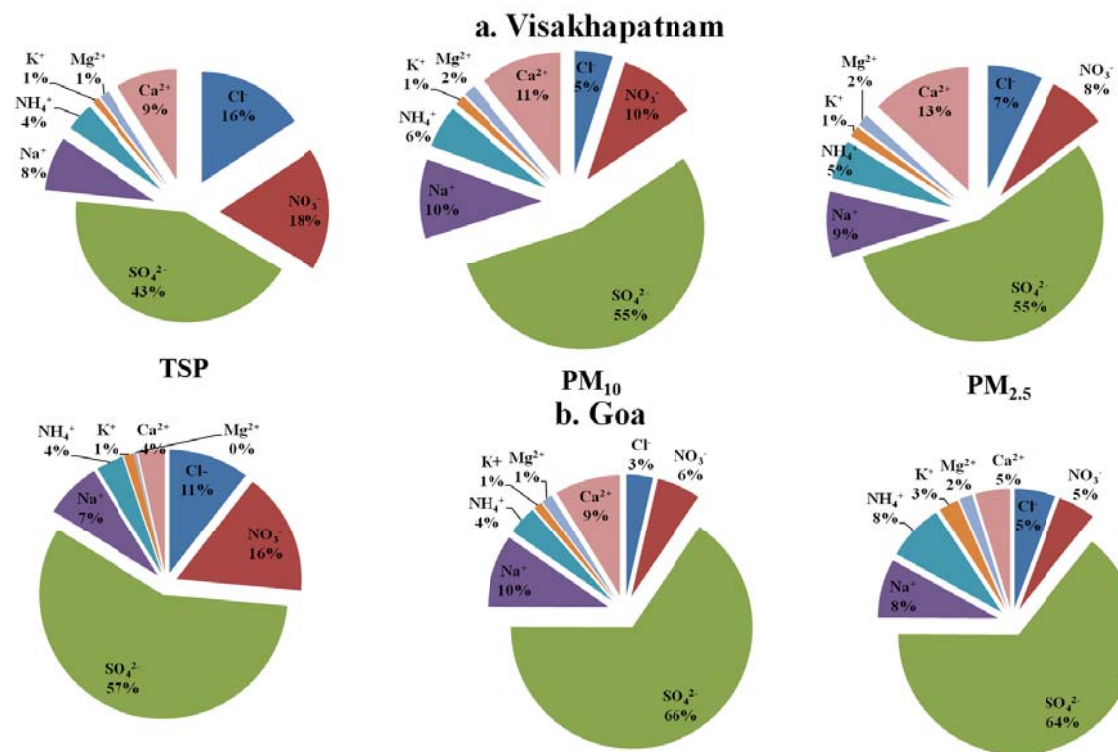


Figure 4. Percent contributions of water-soluble ionic components at (a) Visakhapatnam and (b) Goa for the entire studyperiod in TSP, PM₁₀ and PM_{2.5}.

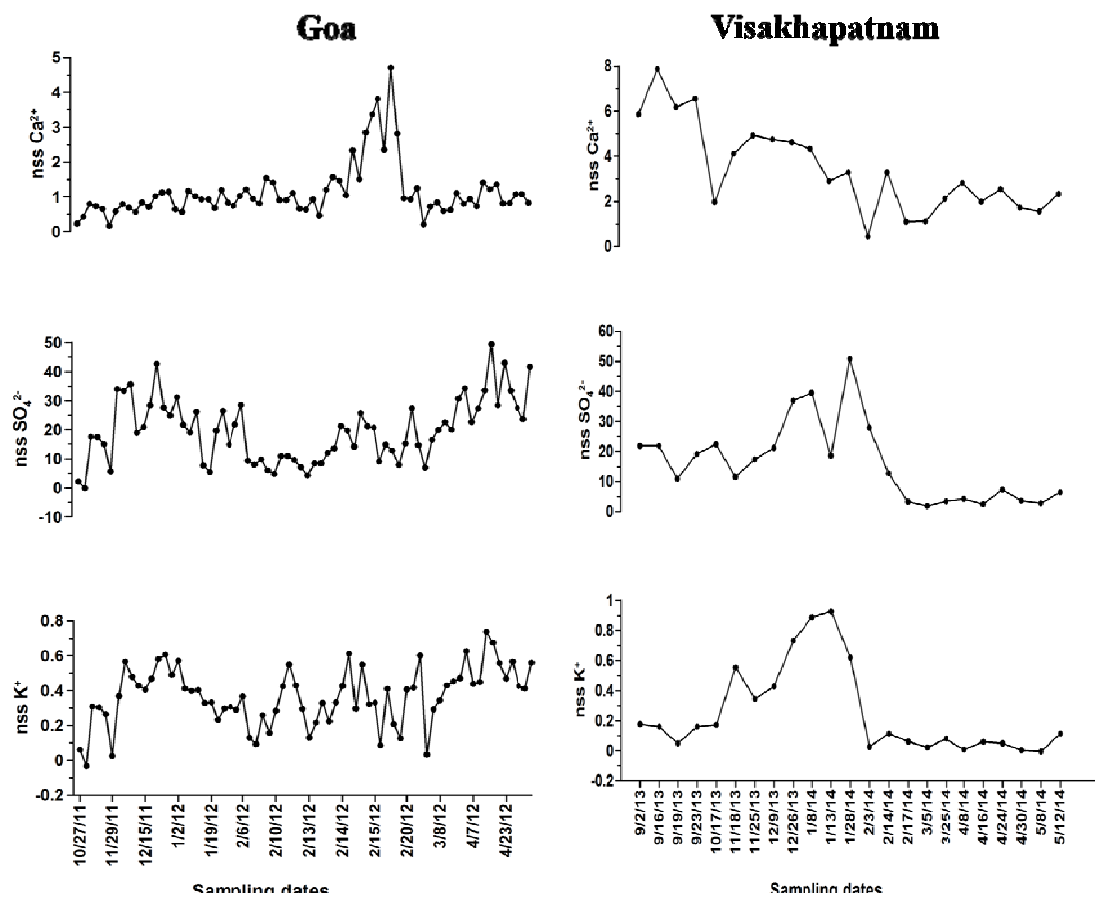


Figure 5. Temporal variability in nss-Ca²⁺, nss-SO₄²⁻ and nss-K⁺ concentrations (μg/m³) in TSP at Goa and Visakhapatnam.

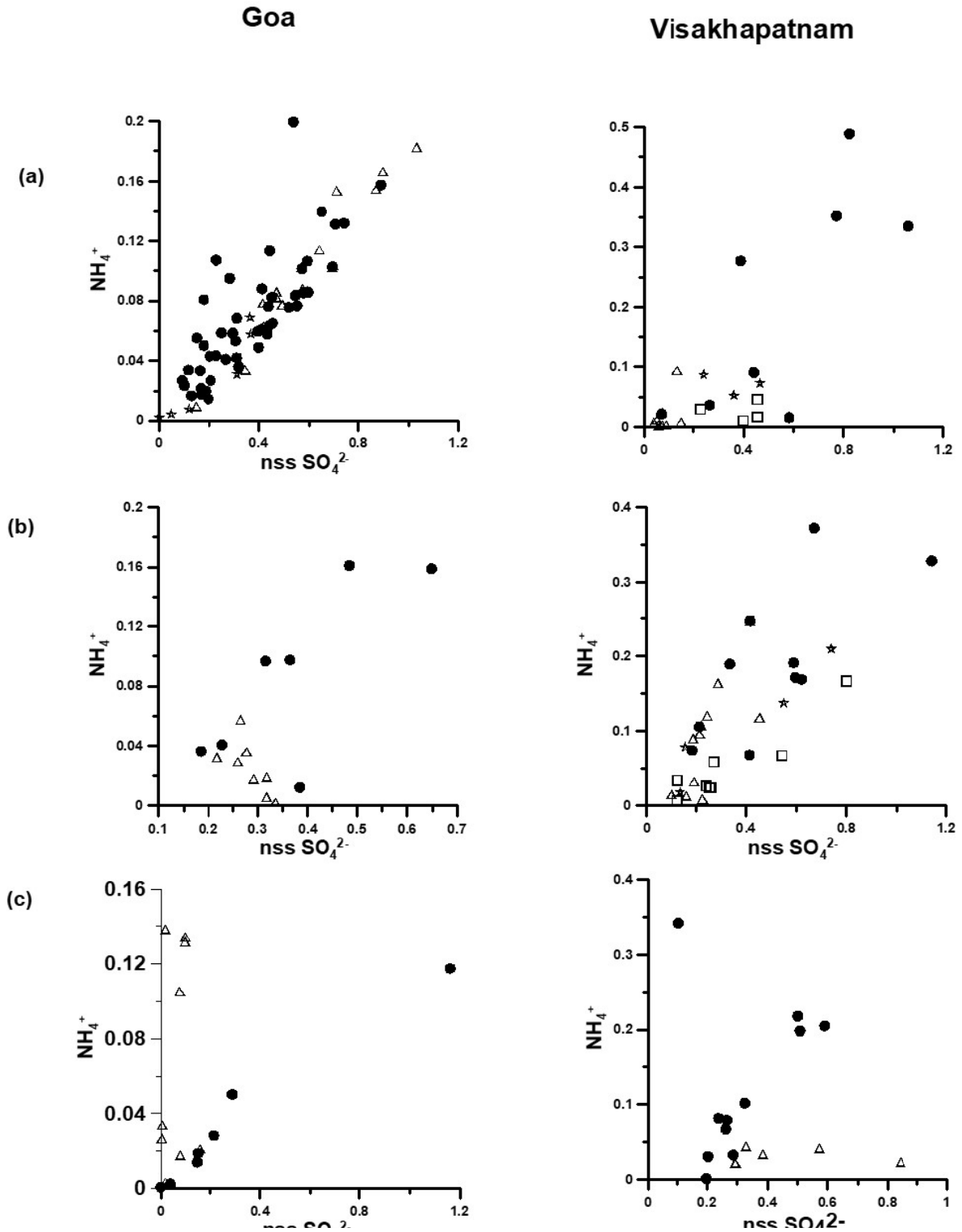


Figure 6. Relations between nss-SO_4^{2-} and NH_4^+ in (a) TSP (b) PM_{10} and (c) $\text{PM}_{2.5}$ for the entire study period at Goa and Visakhapatnam. Units are in $\mu\text{eq./m}^3$. Symbols \square - for SM, Δ for SIM, \bullet - for WM and \star for FIM.

Supplementary Material

Spatial and temporal variability in concentration and characteristics of aerosols at Visakhapatnam(east) and Goa (west) coasts of India

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Supplementary Information: 4Tables and 5 Figures

Supplementary Table 1. Comparison of mass concentrations of three size groups of aerosols at Goa and Visakhapatnam with those at other Indian cities

	TSP	PM₁₀	PM_{2.5}	References
Goa	117	55	30	This study
Visakhapatnam	85	69	94	This study
Delhi		113	99	Tiwari et al (2008)
Mumbai		83	52	Kumar et al (2003)
Chennai		135	73	Srimuruganandam and Nagendra (2010)
Hyderabad		135	50	Gummeneni et al (2011)
Agra	213	163	98	Satsangi et al (2011,2013)
Calcutta		445	313	Das et al (2015)
Hisar	177			Rengarajan (2007)
Jaduguda	194			Ram and Sarin (2010)

Supplementary Table 2. Comparison of water soluble ionic composition of TSP of Goa and Visakhapatnam with that over some Indian and world cities.

Place	Study period	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺	References
Visakhapatnam, India	September 2013- May 2014	6.11	7.04	16.7	3.07	1.63	0.37	0.55	3.52	This Study
Pokhara, Nepal	April 2013- April 2014	0.51	1.94	4.23	1.87	1.17	1.06	0.33	8.39	Tripathee et al (2016)
Agra, India	January 2009- December 2010	4.6	6.7	5.9	4	2.7	3.5	1.4	6.7	Satsangi et al (2013)
Xian , China	October 2006- September 2007	4.6	16.1	34	1.4	8.3	2.3	0.9	11.4	Shen et al (2009)
Ahmedabad, India	May 2000- January 2003	0.99	2.07	4.57	0.81	0.48	0.76	0.25	2.96	Rastogi and Sarin (2005)
Goa, India	October 2011-May 2012	3.70	5.69	20.35	2.63	1.31	0.47	0.25	2.96	This study

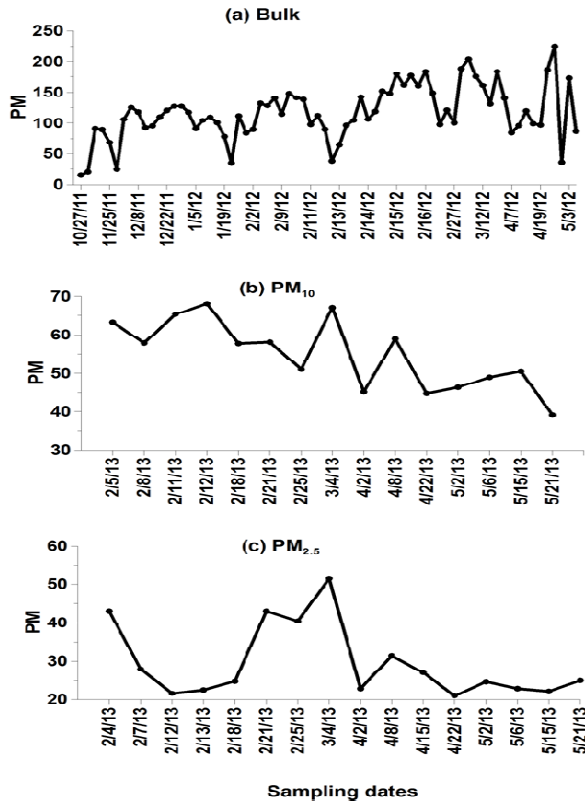
Supplementary Table 3. Comparison of water soluble ionic composition of PM₁₀ of Goa and Visakhapatnam with that over Indian Ocean basins and Allahabad city. BoB= Bay of Bengal and AS= Arabian Sea.

Ion	Goa (This study)	Visakhapatnam (This study)	N-BoB (Srinivas et al.,2011)	BoB (Reddy et al., 2008)	AS (Reddy et al., 2008)	Allahabad (Reddy et al., 2008)
Cl ⁻	0.87	1.62	-	2.3	1.5	2.9
NO ₃ ⁻	1.48	3.52	0.1	1.1	0.5	25.0
SO ₄ ²⁻	16.24	18.70	2.6	8.6	4.5	15.8
Na ⁺	2.40	3.53	0.12	1.7	0.4	1.4
NH ₄ ⁺	0.97	1.99	0.25	1.5	1.3	13.8
K ⁺	0.28	0.45	0.33	2.2	0.02	2.0
Mg ²⁺	0.37	0.55	0.04	0.2	0.04	.01
Ca ²⁺	2.17	3.62	0.11	1.2	0.30	1.9

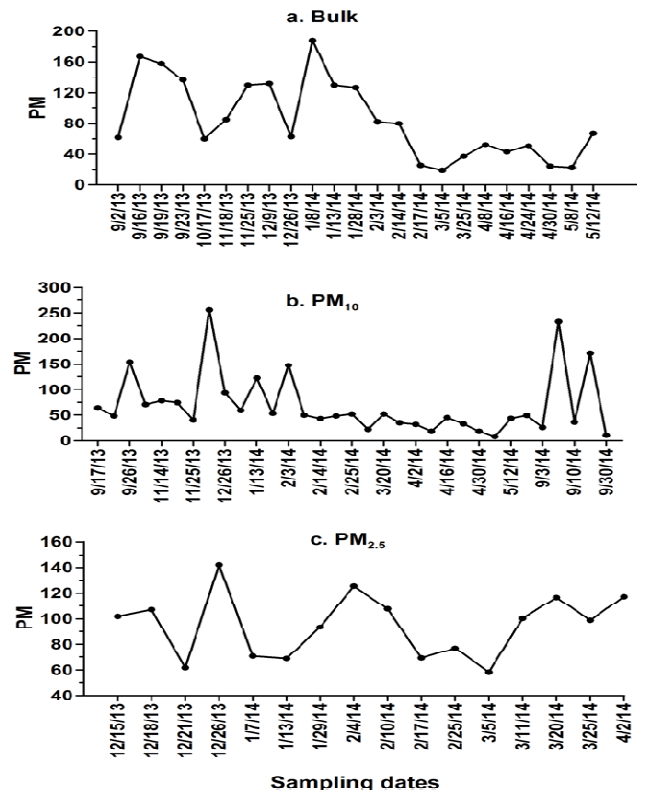
Supplementary Table 4. Comparison of water soluble ionic composition of PM_{2.5} at Goa and Visakhapatnam with N-BoB basins and Hyderabad city. BoB= Bay of Bengal

	Goa (This study)	Visakhapatnam (This study)	N-BoB (Srinivas et al.,2011)	Hyderabad (Reddy et al., 2008)
Cl ⁻	0.67	2.4	0.06	0.3
NO ₃ ⁻	0.54	2.54	0.37	0.5
SO ₄ ²⁻	13.91	18.4	11.9	0.8
Na ⁺	0.88	2.87	0.37	0.1
NH ₄ ⁺	0.60	1.71	4.4	0.1
K ⁺	0.32	0.47	0.6	0.09
Mg ²⁺	0.33	0.53	0.03	0.1
Ca ²⁺	0.60	4.36	0.07	0.8

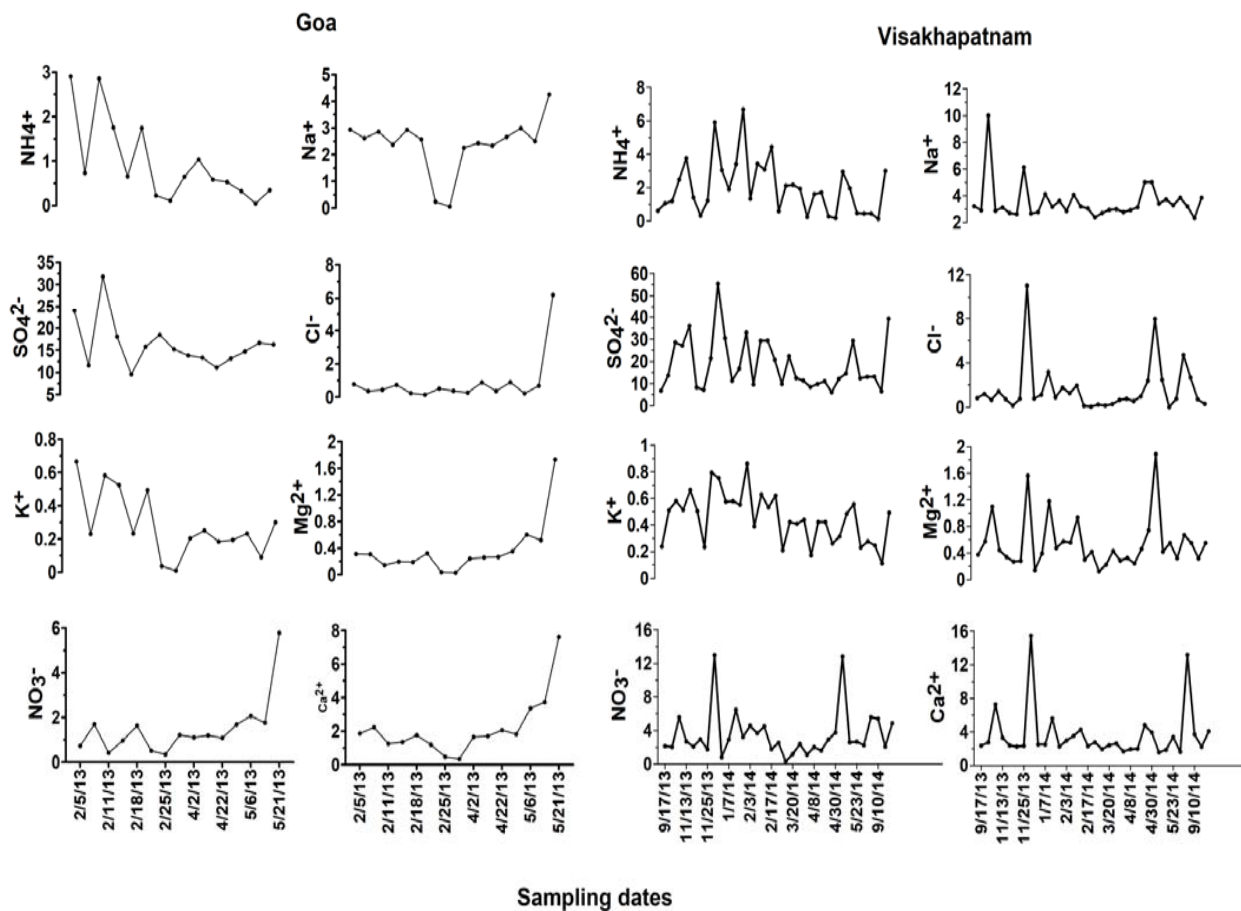
Goa



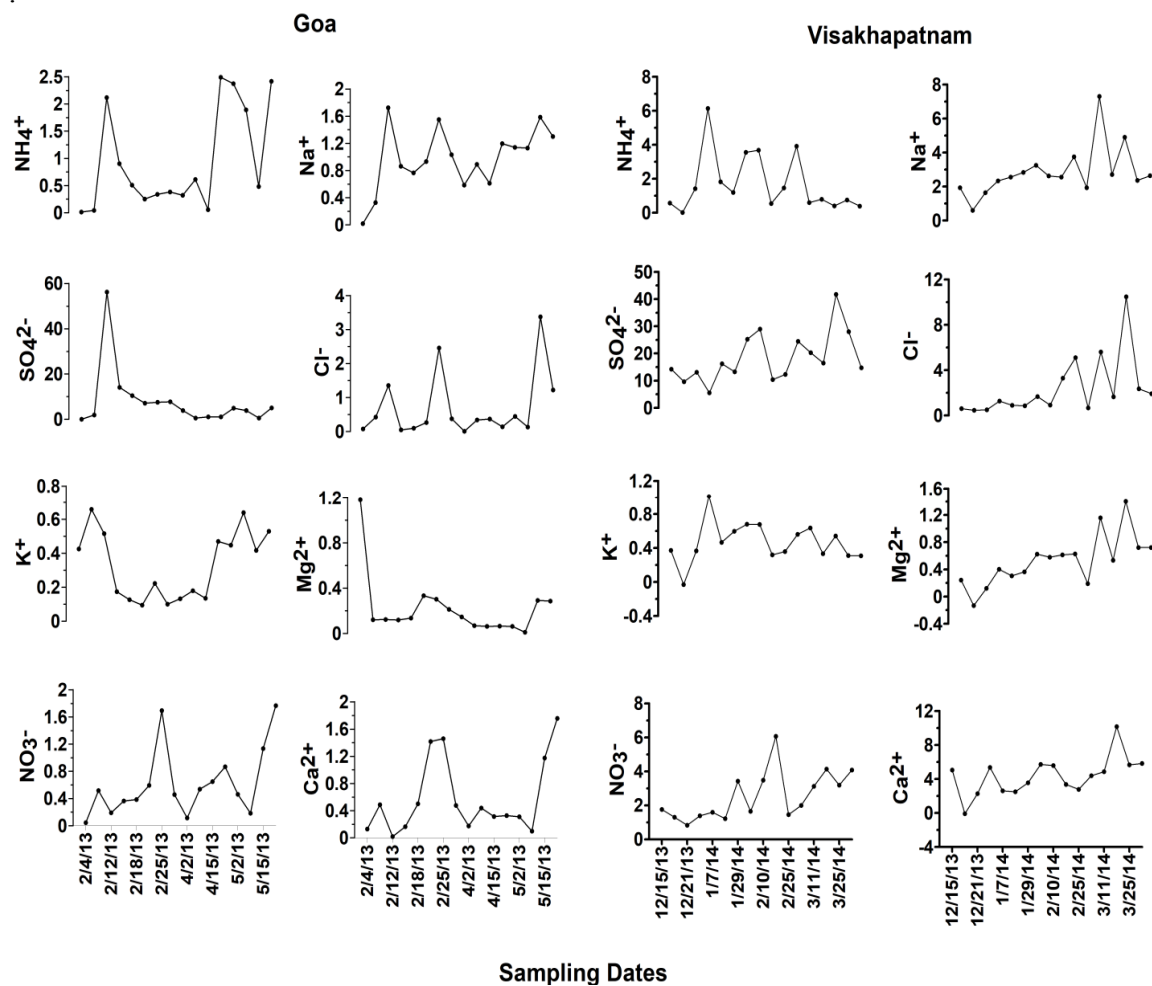
Visakhapatnam



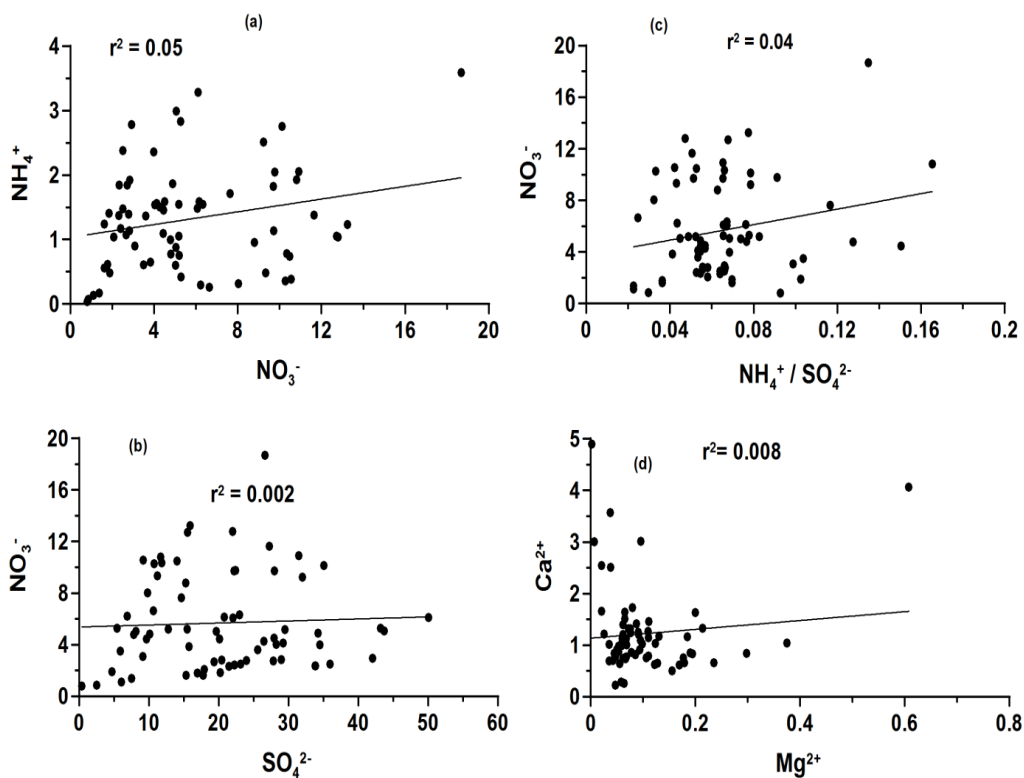
Supplementary Figure 1. Temporal variability in TSP, PM₁₀ and PM_{2.5} concentrations ($\mu\text{g}/\text{m}^3$) at Goa and Visakhapatnam.



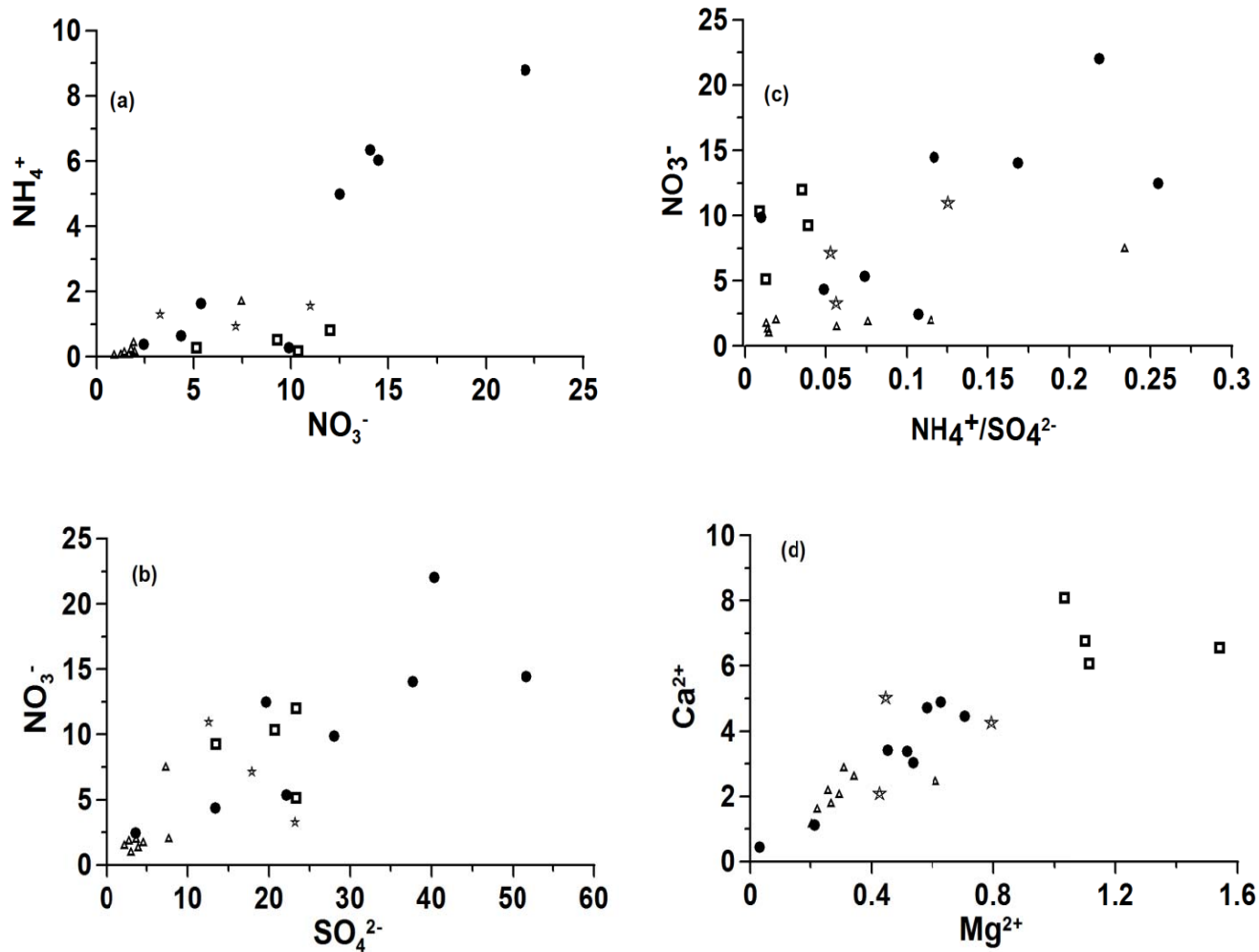
SupplementaryFigure 2. Temporal variations of water-soluble ionic concentrations ($\mu\text{g}/\text{m}^3$) in PM_{10} at Goa and Visakhapatnam.



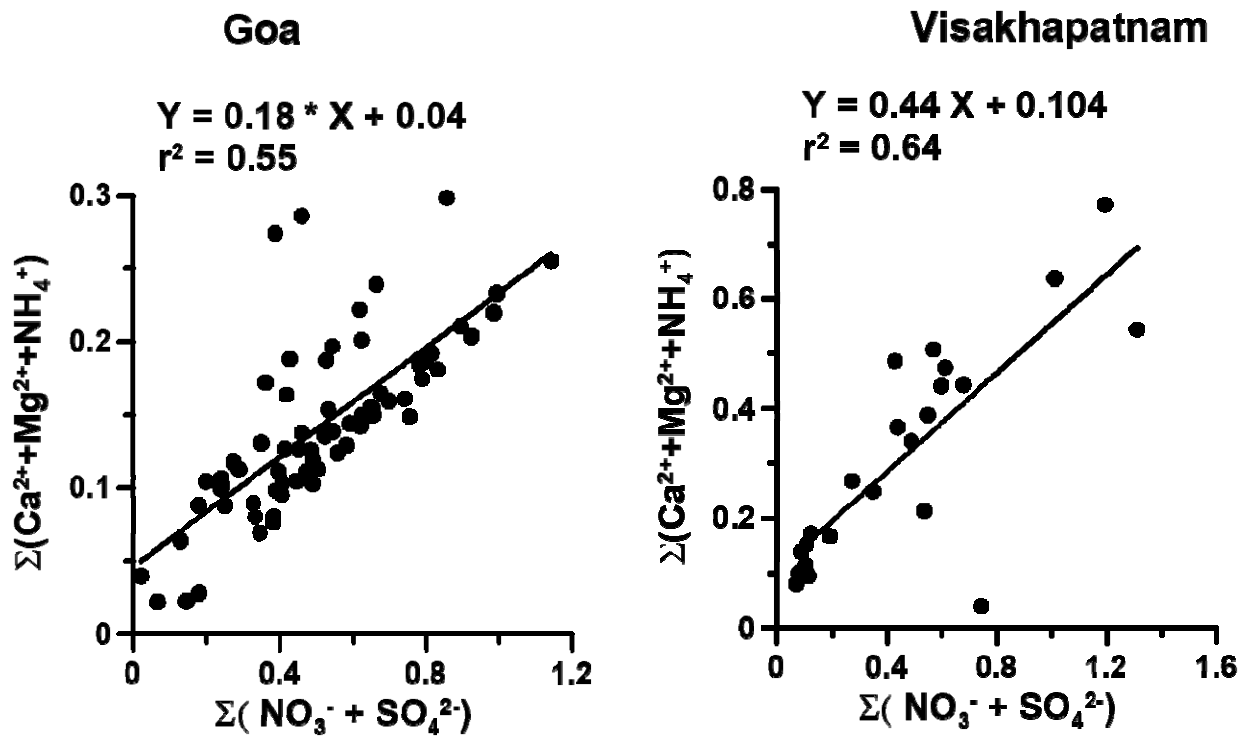
Supplementary Figure 3. Temporal variations of water-soluble ionic concentrations ($\mu\text{g}/\text{m}^3$) in $\text{PM}_{2.5}$ at Goa and Visakhapatnam.



Supplementary Figure 4(a). Relations between various ionic components ($\mu\text{g}/\text{m}^3$) in TSP at Goa: (a) NO_3^- and NH_4^+ , (b) SO_4^{2-} and NO_3^- , (c) $\text{NH}_4^+ / \text{SO}_4^{2-}$ and NO_3^- and (d) Mg^{2+} and Ca^{2+} .



Supplementary Figure 4(b). Relations between various ionic components ($\mu\text{g}/\text{m}^3$) in TSP at Visakhapatnam: (a) NO_3^- and NH_4^+ , (b) SO_4^{2-} and NO_3^- , (c) $\text{NH}_4^+/\text{SO}_4^{2-}$ and NO_3^- and (d) Mg^{2+} and Ca^{2+} . Symbols : \square - for SM , Δ - for SIM, \bullet - for WM and \star for FIM.



Supplementary Figure5. Relations between $\Sigma(\text{Ca}^{2+}, \text{Mg}^{2+}$ and $\text{NH}_4^+)$ and $\Sigma(\text{NO}_3^-$ and $\text{SO}_4^{2-})$ (units in $\mu\text{eq}/\text{m}^3$) in TSP at Goa and Visakhapatnam during the entire study period.