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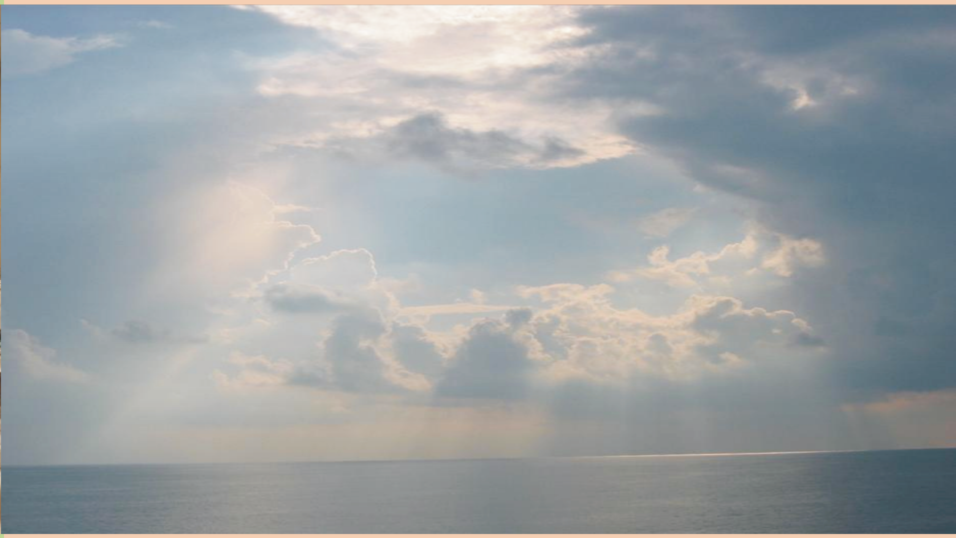

The Chemistry of Rain: Long -Term Observations and Insights from Indian GAW Stations

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Meteorological Monograph

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PREFACE

India Meteorological Department (IMD) monitors precipitation chemistry at 11 stations across India. These stations are part of the Global Atmosphere Watch (GAW), is a program established by the World Meteorological Organization (WMO) to monitor and understand the atmospheric composition and its change. IMD’s Precipitation Chemistry laboratory in Pune analysed the rainwater samples collected from these stations for the period 1987 to 2021.

The rapid growth of urban areas and industries contributes to heightened air pollution, subsequently impacting the chemical composition of rainfall. Analysing the composition of rain aids in determining the relative significance of many sources of particulate matter and gases. Assessment of the chemical composition of rainwater allows for the evaluation of the influence of local pollutants as well as pollutants transported from distant sources. Changes in precipitation chemistry have become an important environmental issue in many parts of the world because of the disastrous impacts on the ecosystem due to acid deposition. Over the past few decades, the international community has increasingly focused on the problem of acid precipitation due to its significant direct impacts on aquatic and terrestrial ecosystems and indirect effects on human health.

The present study analyzed the precipitation chemistry at ten GAW stations in India from 1987 to 2021. Rainwater pH at these locations varied from slightly acidic to mildly alkaline

I would like to appreciate the commendable efforts by Scientists from IMD and Dr. P. D. Safai to bring out this important publication. It is hoped that the information it contains will be useful for the public and research community.

(Dr. M. Mohapatra)

Director General of Meteorology

1. Introduction

Rapid industrialization, urbanization, and increased anthropogenic activities have resulted in increased concentrations of pollutants in the atmosphere, existing in both particulate and gaseous forms. Over time, the atmosphere removes these pollutants through wet and dry deposition processes (Rao, 1997). Recent concerns about escalating air pollution have led to increased attention on wet deposition, which is in the form of precipitation or rainwater. Rainwater plays a crucial role in purifying the atmosphere by scavenging atmospheric gases and aerosols (Andreae and Merlet, 2001), which can transfer the pollutants and nutrients from the atmosphere to soil and aquatic ecosystems. The chemistry of rainwater changes in accordance with the air pollutants. Precipitation chemistry has become an important environmental issue in many parts of the world because of the disastrous impacts on the ecosystem due to acid deposition. The presence of CO2 in the atmosphere makes normal rainwater slightly acidic due to the formation of carbonic acid that leads to pH of 5.65 which is regarded as CO2 equilibrated neutral pH. The normal acidity of rainwater is below this value. If the rainfall is more acidic due to the presence of SO4 and NO3 that originate from their gaseous precursors then is referred to as the acid rain.

Over the past few decades, the international community has increasingly focused on the problem of acid precipitation due to its significant direct impacts on the aquatic and terrestrial ecosystems and indirect effects on the human health. Wet deposition composition mirrors the atmospheric composition it traverses. The acidity levels of rainfall have been progressively increasing over recent years in many parts of the world due to increased industrialization and heightened reliance on fossil fuels. Many regions across the northern hemisphere, such as Europe, East Asia, and North America (Singh and Agrawal 2007), have documented instances of acid rain impact. Acid deposition events are occurring more frequently in China as well (Zhou et al. 2019) due to rapid industrialization. In India, even though acidic rainwater has been reported at certain industrial locations, overall the pH has been residing in the alkaline range (Khemani, 1989).

Analysing the composition of rain aids in determining the relative significance of many sources of particulate matter and gases. Assessment of the chemical composition of rainwater allows for the evaluation of the influence of local pollutants as well as pollutants transported from distant sources upwind(Roy et al., 2016). The composition of rainwater fluctuates both spatially and temporally, influenced by factors such as climate, sources of natural and human-made pollutants, precipitation amount, topography, etc. (Bhaskar and Rao 2017). The different types of contaminants present have an impact on the acidity or alkalinity of precipitation. Atmospheric emissions of acidic compounds like SO4 and NO3 are the main drivers behind the acidification of rainfall. NOx and SOx serve as precursors to major acids, undergoing transformation into HNO3 and H2SO4 upon interaction with water in the atmosphere (Hu et al., 2003; Kulshrestha et al., 2003;Roy et al.,2016). The acidity of precipitation can also be impacted by changes in climate and the accumulation of sea salts (Wright and Jenkins, 2010). According to Khan and Sarwar (2014) and Roy et al. (2016), species originating from soil have significant concentrations of basic cations, which along with gaseous ammonia, can neutralize acidic elements in rainwater and affect the acidity of the atmosphere.

The rapid growth of urban areas and industries contributes to heightened air pollution, subsequently impacting the chemical composition of rainfall. Industrialization and urbanization on a global scale have heightened energy consumption from diverse sources. In India, a rapidly developing country with diverse geographical features and industrial activities, the phenomenon of acid rain may be a future environmental concern. Increased concentrations of particulate and gaseous matter, which in turn exacerbate air pollution, have resulted from the use of fossil fuels, particularly coal for electricity generation, oil for transportation, and the consequences of industrialization (Singh and Agrawal 2005). The World Energy Outlook 2019 states that India's annual consumption of fossil fuels increased from 208 million tonnes in 2000 to 708 million tonnes in 2017.The combustion of fossil fuels primarily generates sulfur dioxide (SO2) and nitrogen oxides (NOx), which are major contributors to the formation of acid rain. Additionally, emissions from agricultural activities, such as the burning of crop residues and the use of fertilizers, contribute to atmospheric acidity in India.

The local sources influence the chemical composition of rainwater. Both anthropogenic and natural activities can affect sources behind the variation in rainwater acidity. Anthropogenic activities contribute acidic gases such as sulfur dioxide (SO2) and nitrogen oxides (NOx), as well as basic gases like ammonia (NH3), leading to increased acidity in rainwater. Dust particles are an important source of base cations like Ca, which can neutralize the acidity of rainwater in some parts of the country (Khemani, 1989; Kulshrestha et al., 2003). Therefore, the understanding of the major cations and anions which contribute to the neutralization of rainwater is necessary.

Rainwater chemistry has been extensively studied at various locations across India. (Khemani, 1989; Mukhopadhyay et al., 1992; Kulshrestha et al., 2003; Safai et al., 2004; Soni and Sarkar, 2005; Momin et al., 2005; Budhavant et al., 2011; Soni et.al.,2012; Tiwari et al., 2016; Vizaya Bhaskar and Rao, 2017; Bhaskar et al., 2022). Many studies are conducted over short durations and focus on specific locations for analysis. While high pH values are reported for numerous locations, there is a documented decreasing trend in the pH of rainwater across India (Soni et.al.,2012; Vizaya Bhaskar and Rao, 2017).

Analysis of the chemical composition of rainfall helps to provide an insight into the chemical status of the atmosphere and the possible sources of air pollutants that contribute to acid precipitation. Furthermore, the study of rainwater chemistry is crucial for quantifying and characterizing atmospheric contaminants. This aids in protecting natural ecosystems by minimizing air quality degradation, acidification of water bodies and soils, and ecosystem disruption.

A proper understanding of rain chemistry is very essential for assessment of the possibility of acid rain. The aim of this report is to evaluate the long-term trends in the acidity of rainwater samples as well as the understanding of various major ionic components and their sources, which contribute to the acidification/neutralization of precipitation in India.

2. Data and Methodology

The Global Atmosphere Watch (GAW) is a program established by the World Meteorological Organization (WMO) to monitor and understand the atmospheric composition and its change. GAW stations are set up worldwide to monitor various parameters, including precipitation chemistry. GAW supplies data for scientific evaluations and early warnings for changes in the chemical composition and associated physical properties of the atmosphere that could negatively impact our environment.In India, there are 10 GAW precipitation chemistry stations scattered across the country,asshown in Fig.1

Rainwater samples were obtained on an event basis by fitting a polyethylene funnel into a polyethylene bottle housed within a thermally insulated wooden box to shield it from sunlight.The funnel is cleaned daily with deionized water. Minor dry deposition may have occurred due to the manual operation of the collector.Whatman-41 papers were used to filter samples as soon as they were collected in order to remove insoluble particulate matter. After every precipitation event, pH and electrical conductivity measurements were made at the station. The event samples are then mixed to form daily or monthly samples. For daily sampling frequency periods, samples are stored in 100 ml High-Density Polyethylene bottles, pre-cleaned with deionized water on a daily basis. Samples are then transported to the analytical laboratory in Pune for chemical analysis. Before being analyzed for major anions and cations, samples were refrigerated at temperatures below 4°C without the use of preservatives. Nevertheless, samples can undergo chemical degradation between the time of collection and the laboratory analysis, which can result in the loss of organic acids and ammonium (Kulshrestha et al., 2005). This error could have an impact on the data used in this study.

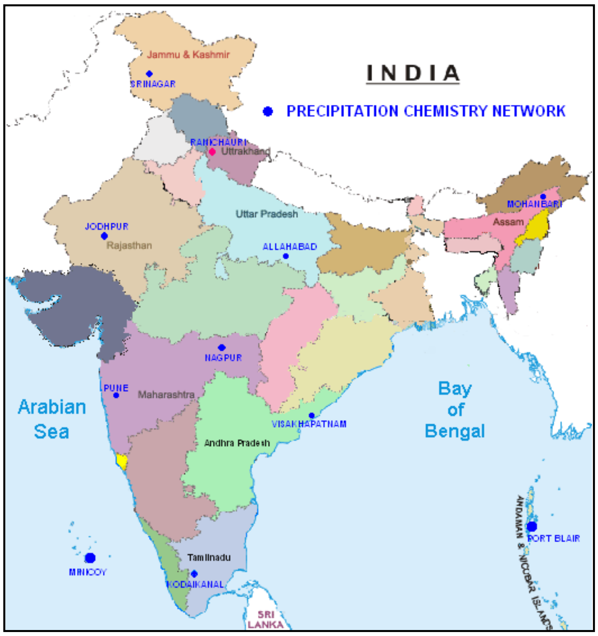

Fig.1. Locations of IMD GAW stations of Precipitation Chemistry Network

2.1 Analytical Methodology

Chemical analyses of precipitation samples were conducted at the Central Laboratory in CR&S Pune, focusing on major anions (SO_4^{2-}, Cl^-, and NO_3^-), major cations (Mg^{2+}, NH_4^+, K^+, Na^+, and Ca^{2+}), pH, and Specific Conductivity. It should be noted that the ionic balance within the prescribed limits (WMO TD No. 1251) was achieved after the computation of bicarbonate ion (HCO_3^-) from pH of rain water for all the chemical analyses. However, the observed small imbalance in the computations arises from the fact that some of the weak organic acids were not analyzed. Before determining the pH, standardization was carried out using reference buffers with pH values of 4.0, 7.0, and 9.2 and measured using a digital pH meter with glass electrodes. Conductivity measurements followed standard methods, employing a conductivity bridge calibrated with 0.01N KCl solution.

UV-V is Spectrophotometric methods were used to determine SO_4^-, NO_3^-, Cl^-, and NH_4^+andan atomic absorption spectrophotometer (PerkinElmer AAaalyst300) was used to measure the concentrations of Na^+, K^+, Ca^{2+}, and Mg^{2+} till 2002. After 2002, the Ion chromatographic method is used to determine SO_4^-, NO_3^-, Cl^-, and NH_4^+. The system used was a Dionex DX-600 ion chromatograph, and the IC columns for cations and anions were Dionex Ion Pac CS12 and AS11, respectively, with guard columns CG12 and AG11. The eluents were NaOH and Methane Sulphonic Acid (MSA) for anions and cations, respectively. NIST-certified ionic standards were used for IC, AAS, pH meter, and Conductivity meter calibration. All standards are prepared using de-ionized water with a conductivity of 0.054 μS/cm.

2.2 Data Presentation and Quality Control

The amount of rainfall affects the concentration of ionic species in rainwater. The precipitation results are shown as the Precipitation Weighted Mean (Volume Weighted Mean;VWM) to compensate this effect. All the averages used in this study are precipitation volume weighted means; this includes averages of pH also which have been computed from the corresponding H^+ ion concentrations. The precipitation-weighted mean concentrations (PWM) were calculated as follows:

$$PWC = \frac{\sum_i Conc\ X\ RF}{\sum_i RF}$$

Where Conc is the concentration of the analyte (in μeql^{-1}) measured for each sample, and RF is the corresponding rain gauge reading (in mm) for each sample.

The non-sea salt (nss) values of a specific component were determined by calculating the difference between the measured concentrations of the chemical species of interest and the corresponding concentration of sodium ions, under the assumption that all sodium originates from marine sources (Keene et al., 1986; Singh et al., 2007).

Non-sea salt contribution can be computed as:

$$[\, X_i \,]_{nss} = [X_i\,] - [\frac{X}{Na^+}]_{seawater} \times [Na^+]_i$$

where $[X_i]_{nss}$ is the non-sea salt concentration of species X in sample i,

$[X_i]$ is the total measured concentration of chemical species *X* in sample *i,*

$[\frac{X}{Na^+}]_{seawater}$ is the ratio of these species as measured in seawater,

$[Na^+]_i$ is the concentration of Na^+ in sample i (Tiwari et al., 2016).

To verify the reliability of the ion data as well the completeness of measured parameters, the ion balance criteria were examined initially.

$$Ionic\ Balance\ \% = \frac{[CE - AE]}{[CE + AE]} x100$$

AE is the anion sum in μeql^{-1}, and CE is the cation sum in μeql^{-1} (WMO, 2004).

Data points falling outside the range (m-3σ, m+3σ) were considered as extreme outliers and removed, where 'm' is the long-term average and 'σ' is the standard deviation.

Computed the neutralization factors (NF) for the key cations (Ca^{2+} , $NH_4{}^+$) to determine the main dominant neutralizing ion that neutralizes acidic ions such as $SO_4{}^{2-}$ and $NO_3{}^-$, using the following formula.

$$NF(X_i) = \frac{[X_i]}{NO_3^- + SO_4^{2-}}$$

$[X_i]$ is the total measured concentration of chemical species *X* in sample *i,*

The fractional acidity (FA) was calculated to assess the acid neutralization capacity of rainwater using the following equation (Zhou et.al., 2013)

$$FA = \frac{[H^+]}{[SO_4^{2-}] + [NO_3^-]}$$

3. Results & Discussions

3.1 Allahabad

Allahabad, located at the confluence of the Ganges and Yamuna rivers in the Indo-Gangetic Basin near the Tropic of Cancer, experiences unique winter meteorological conditions that often result in significant aerosol and pollutant build up. This densely populated and fertile region is a notable source of sulfur, nitrogen, and carbon pollutants from various human activities, including biomass burning and vehicular emissions. Dust storms frequently occur here from March to June, with dust originating from Oman, southwest Asian basins, and the Thar Desert, often mixed with anthropogenic pollutants during transport. The observatory, originally located at the Civil Aviation Training Centre in Bamrauli, was moved to ChakMundera in 1992 and then to Ghoorpur in 2012. A thermal power plant is located 20 km from the site, and a cement factory is also nearby.A railway track is also in the vicinity of the observatory.

Chemical composition of rainwater samples collected from Allahabad during wet (June - September) and dry seasons (October, November, December, January, February, and March) showed that the pH for the entire period of 1987 to 2021 varied from 4.4 to 8.2 for the wet season and 4.3 to 7.9 for the dry season, with average values of 5.0 and 5.1, respectively indicating slight acidification of rainwater over the three decades. The frequency distribution of pH (Fig2) showed that the maximum frequency (19.7% and 17.9%) was in the range of 5.5-6 and 7-7.5 during the wet and dry seasons, respectively. The acidic nature of most rainwater samples in recent years (with monthly pH values below 5.65) can be attributed to the relocation of the observatory, which is now situated near a thermal power plant and a cement factory.The percentage contribution of measured ionic spices (PCMI) during wet and dry seasons is shown in Fig.2. The maximum fraction was from NO_3^- (22%) and the minimum from NH4 (3%) during the dry season. The total of anions was less than the total of cations. However, some of the organic anions were not measured in the rain. The excess cations accumulated in the atmosphere from local sources during the dry season were washed out by rain during monsoon. So, the maximum fraction was from Ca^{2+} (22%) and the minimum from NH4 (3%) during the wet season. Higher concentrations of NO_3^- than SO_4^{2-}were observed throughout the year over this region. The Indo-Gangetic Basin (IGB) is a major source of various pollutants, particularly those containing sulfur, nitrogen, and carbon compounds (Habib et al. 2006). The acidic nature of rainwater due to rapid urbanization is neutralized by the dissolution of atmospheric dust containing aerosols which are enriched by Ca^{2+}. NO_3^- was dominant among anions, and Ca^{2+} was dominant among the cations during both seasons.

Long-term temporal variations of pH during wet and dry seasons are shown in Fig.3. The pH reflected the combined impact of acidic and alkaline substances, which come from their respective sources. The trend in pH over Allahabad showed a statistically significant (significant at 10% significant level) decreasing trend in both seasons. The wet season showed a higher decreasing trend(-0.74/decade) than the dry season(-0.40/decade). To understand the overall effect of various ions on the rainwater, which gives the acidic or alkaline nature, the temporal variability of acidic components (nssSO_4^{2-} and NO_3^-) and alkaline components (nssCa^{2+} and NH_4^+) is presented in Fig 4-5. It is observed that there was a statistically increasing trend in nssSO_4^{2-} and NH_4^+ during dry (36.97 μeql^{-1}/decade and 11.89 μeql^{-1}/decade, respectively) and wet (26.35 μeql^{-1} /decade and 11.68 μeql^{-1} /decade, respectively) seasons. The trend in nss Ca^{2+} showed a decrease of about -7.41. μeql^{-1} /decade during dry season and -33.64 μeql^{-1}/decade during wet season and the trend was statistically significant at 10% significant level during wet season. A declining trend of -5.91 μeql^{-1} /decade and -34.85 μeql^{-1} /decade was observed for NO3$^-$ during the dry and wet seasons, respectively. The trend was significant during the wet season. However, the combined impact of these four components on rainwater lowers the pH level, indicating that the net acidic effect of $SO_4{}^{2-}$ and $NO_3{}^-$ was not offset by the alkaline effect of Ca^{2+} and NH_4^+.

Neutralization factors are an indicator of identifying the acid-neutralizing capacity of different cations in the rainwater. The fractions of anions or cations originating from the sea do not play any role in deciding the acidity/alkalinity of the rainwater sample. Thus, for Allahabad, neutralization factors were computed for non-sea salt fractions, i.e., nssCa^{2+} and nssSO_4^{2-} and shown in Fig.6. Mostly, Ca^{2+} arises from mineral dust, and NH_4^+ is from both natural and anthropogenic activities. Neutralizing factor from $Ca^{2+}$was higher than NH_4^+ over Allahabad during both seasons. However, in recent years, NF for Ca^{2+} showed a significant (at 10% significant level) decreasing trend in both dry (-0.12/decade) and wet (-0.15/decade) seasons, which indicateda reduced neutralizing capacity due to decreased calcium sources or changes in atmospheric conditions. NF for NH_4^+ showed a significant increasing trend of about 0.06/decade (dry season) and 0.08/decade (wet season). However, the decreasing trend in nss $Ca^{2+}$was not compensated by the increasing trend in NH_4^+, resulting in a lowering of pH.

The time series of the ratio of nss $SO_4{}^{2-}$ and $NO_3{}^-$ is given in Fig 7. The trend in this ratio showed a significant increase during both wet (0.87/decade) and dry (0.55/decade) seasons inferring a greater prevalence of sulfate from non-sea-salt sources compared to nitrate, which indicated more dominance of stationary (industrial emissions) sources over the mobile (vehicular emissions) sources in the recent years.

The acidity of rainfall is determined by the balance between acid-forming substances like sulfate and nitrate and alkaline compounds that neutralize them. Fractional acidity (FA) is an indicator often used to quantify the acid neutralization capacity of rainwater. FA of rainwater at Allahabad is shown in Fig.7. The average FA values were 0.04 during the dry season and 0.06 during the wet season, suggesting that approximately 96% and 94% of the acidity in the dry and wet seasons, respectively, was neutralized by alkaline constituents. The time series analysis of fractional acidity (FA) revealed a significant increasing trend of 0.05 per decade during the wet season, while the dry season showed an insignificant trend of 0.01 per decade. The increasing trend in fractional acidity (FA) suggests that a larger proportion of alkaline components in rainwater have been neutralized by acidic substances. As a result, thecapacity of rainwater to buffer against acidity decreases, which leads to a decrease in the pH.

3.2. Jodhpur

Jodhpur district has numerous industries involved in cement, industrial gases, textiles, and various other sectors. However, there are no major polluting industries immediately near the observatory. The district is rich in non-metallic minerals like Sandstone, Gypsum, Rhyolite, Dolomite, Limestone, Jasper, and Granite. There is significant aerosol and dust deposition from frequent summer dust storms, which contribute to increased chemical concentrations in rainfall. The urban development around the station has also increased significantly.

Analysis has been carried out for the dry and wet seasons separately for the period 1987-2021 and is given in Fig 7. In the wet season, 24.0% of the samples fall within the pH range of 6.5 to 7, while in the dry season, 37.5% fall within the range of 7 to 7.5. The pH range spaned from 5.6 to 8.5 during the dry season and from 5.7 to 8.3 during the wet season, with average values of 6.8 and 6.5, respectively. The alkaline nature of the rainwater samples may be attributed to dust particles from the nearby Thar Desert (Soni et al. 2012). The percentage contribution of measured ionic species (PCMI), as shown in Figure 8, indicatedthat Ca^{2+} contributedthe most (32% in the dry season and 26% in the wet season), while NH_4^+ contributedthe least (≤1% in both seasons). The higher concentration of Ca^{2+} and NO_3^-, which were the predominant measured cation and anion respectively, indicated the influence of dust aerosols and anthropogenic activities in this region.Also, it is noticed that the contribution from the calculated HCO_3^- was higher over Jodhpur during both seasons. HCO_3^- and Ca^{2+} primarily originate from windblown dust and terrestrial sources, such as the dissolution of regional limestone or alluvial carbonated sediments (Avila et al.,1997).

Figure 9 illustrated the time series analysis of pH from 1987 to 2021.The trend in pH over Jodhpur showed a significant (significant at 10% significant level) decline in both seasons, with a more pronounced decrease in the wet season (-0.33/decade) compared to the dry season (-0.21/decade).The temporal variability of acidic components (nssSO_4^{2-} and NO^{3-}) is shown in Fig.10. During the dry season, there was an increase in nssSO_4^{2-} by approximately 14.87μeql^{-1}/decade, though this trend was not statistically significant. Conversely, in the wet season, nssSO_4^{2-} decreased at a rate of -4.59 μeql^{-1}/decade. Figure 11 shows the temporal variability of alkaline components (nssCa^{2+} and NH_4^+). The trend in nssCa^{2+} indicated a decrease of about -83.88μeql^{-1}/decade in the dry season and a decrease of -23.07μeql^{-1}/decade in the wet season, with statistically significant trend only during dry season. NH_4^+ showed an increasing trend in both seasons, with an increase of about 2.33 μeql^{-1}/decade (not significant) for the dry season and 5.73 μeql^{-1} /decade (significant at 10% level) for the wet season.

The neutralization factors were computed for non-sea salt fractions, i.e. Nss Ca^{2+} and Nss SO_4^{2-} and shown in Fig.12. During both seasons, the neutralization factor (NF) from nss Ca^{2+} was higher than that from NH_4^+. In recent years, however, the NF for Ca^{2+} showed a significant decreasing trend in both the dry (-1.30 per decade) and wet (-1.07 per decade) seasons. Conversely, the NF for NH_4^+ has exhibited an insignificant increasing trend of approximately 0.01 per decade in the dry season and 0.03 per decade in the wet season. Despite this increase in NH_4^+, it did not offset the decline in nss Ca^{2+}, leading to a reduction in pH.

Figure 13 presents the time series of the ratio of nss SO_4^{2-} to NO_3^- and FA. The trend in the ratio of nss SO_4^{2-} to NO_3^- showed a significant decrease of -1.19/ decade during the wet season (at the 10% significance level) and an, insignificant decrease of -1.91/ decade during the dry season. This trend suggested that nitrate is becoming more dominant than nss SO_4^{2-}, likely due to the recent increase in combustion activities related to agriculture along with increasing vehicular emissions.

At Jodhpur, the average FAvalues were 0.001 in the dry season and 0.002 in the wet season. No trends in FA were observed during either season from 1987 to 2021.

3.3. Kodaikanal

The observatory is situated on the campus of the Indian Institute of Astrophysics, approximately 250 km from the southern tip of India, 145 km from the west coast, and 200 km from the east coast. Industrial activity in the area is limited, with only a small thermometer factory located 6 km away. The region is influenced by a combination of marine air from the Arabian Sea and the Bay of Bengal, as well as local biomass burning, and the soil is primarily acidic.

The frequency distribution of pH at Kodaikanal, is shown in Figure 14, indicated that the highest frequencies (38.2% and 31%) were in the ranges of 5-5.5 and 5.5-6 during the dry and wet seasons, respectively. The pH at Kodaikanal fluctuated between 4.7 and 7.8 in the dry season and between 4.9 and 7.3 in the wet season, with average values of 5.4 and 5.6, respectively. These pH values were close to typical rainwater, which generally has a pH of about 5.65 due to the natural presence of carbon dioxide (CO_2) in the atmosphere, dissolving into rainwater to form mild carbonic acid. Fig.14 illustrated the PCMI during both the wet and dry seasons. During the dry season, the largest fractions were from NO_3^- and Cl^- (12% and 14% respectively), with the smallest from Mg^{2+} and K^+ (4%). In the wet season, the highest fractions were from $Cl^-$and Ca^{2+} (15%), while the lowest came from Mg^{2+} and K^+ (5%). Cl^- was the dominant anion which could be product of natural processes such as weathering of rocks and minerals in the surrounding areas or from agricultural Practices, while Ca^{2+} was the dominant cation in both seasons indicating impact of the dust which could be originating from certain construction activities over this high altitude tourist destination. Mixed influence of natural (Cl & Na; dust-Ca & HCO_3) and anthropogenic (SO_4 & NO_3) sources at Kodaikanal maintaining pH around CO_2-equilibrated neutral value of 5.65 in both wet & dry seasons.

The trend in pH at Kodaikanal (Fig.15) showed a significant (significant at 10% significant level) decrease in both seasons, with a more pronounced decrease in the wet season (-0.33/decade) compared to the dry season (-0.19/decade).The temporal variability of acidic components (nssSO_4^{2-} and NO_3^- , as shown in Fig.16) indicated an increasing trend in both the dry and wet seasons. During the dry season, nssSO_4^{2-} showed a significant increase of 2.83 μeql^{-1}/decade, and NO_3^- increased by 3.65μeql^{-1}/decade. In the wet season, nssSO_4^{2-} increased by approximately 0.88μeql^{-1}/decade, while NO_3^- increased by 5.67μeql^{-1}/decade.

Figure 17shows the temporal variability of alkaline components (nssCa^{2+} and NH_4^+). The nssCa^{2+} exhibited a significant increase of approximately1.62μeql^{-1}/decade during thedry season and an1.93μeql^{-1} /decade in the wet season.NH_4^+ showed an upward trend in both seasons, with an increase of about 1.47 μeql^{-1}/decade in the dry season and 0.36 μeql^{-1} /decade in the wet season; however, neither trend wasstatistically significant.

The neutralization factor (NF) from nss Ca^{2+} and NH_4^+ showed a minimal variation (Fig.18). Specifically, the NF for Ca^{2+} exhibited a slight decreasing trend of -0.03per decade during the dry season, though this change was not significant. Conversely, in the wet season, it showed a slight increasing trend of 0.03 per decade. The NF for NH_4^+ , demonstrated a slight decreasing trend of approximately -0.05 per decade in the dry season and -0.03 per decade in the wet season. The time series of the ratio of nssSO_4^{2-} and NO_3^- is given in Fig 19.The trend showed the balance between sulfate and nitrate in rainwater was changing with the seasons, increasing slightly in the dry season (0.15per decade), and decreasing slightly in the wet season(-0.02per decade).Figure 18 presents the time series of fractional acidity (FA), which shows a higher average value of 0.12 during the dry season compared to 0.09 in the wet season. Notably, both seasons exhibited a significant increasing trend of 0.04 per decade.

3.4. Mohanbari

The Brahmaputra River flows near the station and this area is dominated by Oil & Natural Gas and Tea industries. Pollution sources include various oilfields, the Namrup Fertilizer plant, and a thermal power plant, all located 40 to 66 km away. The soil in this area is formed from Brahmaputra River deposits, with older alluvium having higher acidity and lower exchangeable calcium (pH 4.2-5.5), while newer alluvium is less acidic. Paddy is grown in the lowlands, and tea is cultivated in the uplands where rainwater drains quickly.

The frequency distribution of pH analysis for the dry and wet seasons from 1987 to 2021 is presented in Fig.20. During the wet season, 34.7% of the samples had pH levels between 5-5.5, while 26.% of the dry season samples had pH levels ranging 4.5-5. The pH varied from 4 to 7.7 in the dry season and from 4.1 to 7.1 in the wet season, with average values of 4.7 and 5.1, respectively. Organic acids, primarily formic and acetic, can significantly contribute to lowering rainwater pH levels in densely vegetated areas such as Mohanbari (Soni et al. 2012). The percentage contribution of measured ionic species (PCMI) shown in Fig.20 highlighted that NO_3^- was the largest contributor (30% in the dry season and 25% in the wet season), while K^+ had the smallest contribution (5% in both seasons). All cations except Ca^{2+} also showed least contribution of 5% during dry season. The predominant anion at Mohanbari throughout the year was NO_3^-, likely resulting from emissions from nearby oil refineries (Bhaskar & Rao,2017). At Mohanbari, the concentration of individual cation species was generally low, with the exception of Ca^{2+}.

Figure 21 illustrates the long-term temporal variations in pH during the wet and dry seasons. The trend in pH showed a significant decrease in both seasons, with a trend of -0.23/decade during dry seson and -0.15 /decade during wet season Fig. 22 and 23 show the temporal variability of acidic components ($nssSO_4^{2-}$ and NO_3^-) and alkaline components ($nssCa^{2+}$ and NH_4^+) respectively. The $nssSO_4^{2-}$ showed a significant increase of 7.83 μeql^{-1}/decade in the dry season and a slight decrease of -1.17 μeql^{-1}/decade in the wet season. In contrast, NO_3^- exhibited a decrease of -15.12μeql^{-1}/decade in the dry season and an increase of 4.70 μeql^{-1}/decade in the wet season. The trends in NO_3^- for both seasons were not statistically significant. The $nssCa^{2+}$ showed an increase of 5.35 μeql^{-1} /decade during the dry season and 1.68 μeql^{-1} /decade in the wet season. NH_4^+ showed a declining trend in both seasons, with rates of -0.01 μeql^{-1}/decade in the dry season and -3.80 μeql^{-1}/decade in the wet season; however, the trend was not statistically significant only in both the seasons.

The neutralization factor (NF) from nss Ca^{2+} showed minimal change in both seasons, with a slight increase of 0.05/decade in the dry season and a slight decrease of -0.09/decade in the wet season (Fig. 24). The NF for NH_4^+, showed a negligible decreasing trend during the dry season. However, in the wet season, it showed a significant decreasing trend of -0.11 per decade. This suggests that the neutralizing capacity of NH_4^+ and nss Ca^{2+} is diminishing, which might contribute to the continued acidity of rainwater at Mohanbari.

Fig.25 presents the time series of the ratio between $nssSO_4^{2-}$ and NO_3^- as well as FA. The trend indicated a significant increase of 0.14/decade in dry season, and a slight decreasing trend of-0.03/decade in the wet season. This suggests a greater prevalence of sulfate from non-sea-salt sources relative to nitrate, highlighting the increasing influence of industrial emissions and agricultural activities in recent years. At Mohanbari, the average value of FA was 0.17 for both dry and wet seasons, indicating the slightly acidic nature of rainwater compared to other stations. Also, FA showed a significant increasing trend of 0.07 per decade during the dry season and 0.05 per decade during the wet season.

3.5. Minicoy

Minicoy Island, located in the Lakshadweep archipelago, is a small crescent-shaped island mostly covered by coconut trees. Its clean maritime environment, minimal industrial activity, and year-round rainfall make it an ideal location for long-term precipitation chemistry measurements. The surrounding sea significantly contributes to the chemical composition of precipitation, and air masses from Arabia, Iran, and Somalia influence the wind patterns during the monsoon season (Soni et al.2012).

The frequency distribution, along with the measured ionic spices at Minicoy, is shown in Fig.26.The frequency distribution showed that that the highest frequencies (21.8% and 31.2%) werein the ranges of 6.5-7 and 6-6.5 during the dry and wet seasons, respectively. The pH at Minicoy ranged between 4.6 and 8.1 in the dry season and between 4.2 and 7.8in the wet season, with average values of 5.7, for both seasons. These pH values were close to the CO2 equilibrated value of 5.6. The percentage contribution of measured ionic species (PCMI; shown in Fig.26), indicated that Cl^- contributed the most (21% in the dry season and 28% in the wet season), while $NH_4{}^+$ contributed the least (3% in the dry season and 2% in the wet season). The predominant cation and anion observed at Minicoy during both seasons are Na^+ and Cl^- respectively, indicating relatively high oceanic influence in this region. Relative to other ions, Ca2+ also predominated over this region due to the long-range transport of soil dust from the Arabian Peninsula (Soni and Sarkar 2005).

The trend in pH at Minicoy (Fig. 27) indicated a significant decline at the 10% level in both the dry and wet seasons, with a sharper decrease during the dry season (-0.53/decade) compared to the wet season (-0.30/decade). The time series revealed a noticeable drop in pH in recent years. Sea salt components are used instead of non-sea salt ones because they more accurately reflect the environmental conditions of island stations. Sea salt influences various atmospheric and oceanic processes which can impact the chemical composition of rainfall. Since Minicoy is an island station, sea salt fractions of$SO_4{}^{2-}$ and Ca^{2+} are used for the calculations.Temporal variability in acidic components (SS $SO_4{}^{2-}$ and $NO_3{}^-$) is shown in Fig. 28, andSS $SO_4{}^{2-}$ showeda decreasing trend of -0.66μeql^{-1}/decade in the dry season with an insignificant decrease of -0.43μeql^{-1}/decade in the wet season. Acidic component $NO_3{}^-$ also showed a decrease of-0.27μeql^{-1}/decade in the dry season and an increase of 0.04μeql^{-1}/decade in the wet season; these trends were statistically insignificant.

Figure 29 shows the temporal variability of alkaline components (SS Ca^{2+} and NH_4 $^{+}$). The SSCa^{2+} exhibiteda significant decrease of-0.20.μeql−1 /decade during thedry season and an insignificant decrease of -0.13μeql^{-1} /decade in the wet season.NH_4^{+} showed an upward trend of 0.49/decade in the dry season, with a declining trend of -3.82 μeql^{-1}/decade in the wet season; however, none of these trends was statistically significant.

Therewas no observable pattern over time in the neutralizing factor of SSCa^{2+} (Fig.30). It means that the neutralizing capacity of SSCa^{2+} fluctuated without any systematic increase or decrease over the observed period. The NF for NH_4 $^{+}$ showed a slight decreasing trend of -0.09 per decade during the wet season, though this change was insignificant. Conversely, it showed an increasing trend of 0.08 per decade in the dry season. Fig31 presents the time series of the ratio between SS SO_4 $^{2-}$ and NO_3 $^{-}$. There was a decrease in trend in both seasons (-0.24/decade, -1.86/decade in the wet season). Fig30 also presents the time series of FA. The average value of FA during dry and wet seasons was 0.07 and 0.04, respectively. The trend in FA during the dry season was 0.05/decade (significant at10 % significant level), and the wet season was 0.01/decade (statistically not significant)

3.6. Nagpur

The observatory at Nagpur, situated near Dr. Babasaheb Ambedkar International Airport, has been surrounded by extensive urbanization and industrialization since 1981. Several pollution sources near the station, including a thermal power station and various industries within a 75 km radius, potentially contribute to environmental pollution in the area. Additionally, major highways and a railway trunk route pass through the city, further impacting the environment at Nagpur.

The frequency distribution of pH and Percentage contribution of measured ionic species in rainwater at Nagpur are shown in Fig.32. During the dry season,35% of the samples had pH levels between 5-5.5, while 35.1% of the wet season samples had pH levels ranging 5.5-6. The pH varied from 4.5 to 7.9 in the dry season and from 4.4 to 7.4 in the wet season, with average values of 5.3 in both season. pH remained slightly acidic at Nagpur and was attributed to the emissions from the coal-fired power plant located about 10 km to the northwest, along with an increase in vehicular traffic (Soni and Sarkar 2005, Bhaskar & Rao,2017). The PCMI (Fig.32) revealed that Ca^{2+} was the major contributor, accounting for 25 % in the dry season and 22% in the wet season, while K^{+} contributed the least, with 5% and 4% in dry and wet seasons respectively. NO_3^- was the dominant anion in Nagpur, contributing 23% in the dry season and 18% during the wet months. The elevated concentration of NO_3^- in the dry season was attributed to increased contributions from thunderstorms in the pre-monsoon period apart from the vehicular emissions. Ca^{2+} was the dominant cation in Nagpur during both seasons.

The trend in pH at Nagpur (Fig. 33) revealed a notable decrease at the 10% significance level in both the dry and wet seasons, with a trend of -0.30 per decade in the dry season and -0.35 per decade in the wet season. Fig. 34 and 35 showed the temporal variability of acidic components ($nssSO_4^{2-}$ and NO_3^-) and alkaline components ($nssCa^{2+}$ and NH_4^+) respectively. The $nssSO_4^{2-}$ showeda significant increasing trend in both seasons, with a rate of 18.92μeq l^{-1} per decade during the dry season and 7.91μeq l^{-1} per decade in the wet season. NO_3^- showeda significant decrease of -11.36μeq l^{-1} per decade in the dry season and a minor decrease of -0.19μeq l^{-1} per decade in the wet season. The $nssCa^{2+}$ demonstrated a significant decline of -29.27μeq l^{-1} per decade in the dry season and -11.96μeq l^{-1} per decade in the wet season. Conversely, NH_4^+ exhibitedan increasing trend in both seasons, with rates of 0.05μeq l^{-1} per decade (significant at 10 % significant level) in the dry season and 0.04μeq l^{-1} per decade (insignificant) in the wet season.

The neutralization factor (NF) from nss Ca^{2+} showed a t decreasing trend of -0.63/decade in the dry season and a significant decrease of -0.29/decade in the wet season (Fig. 36). The NF for NH_4^+, showed a significant increasing trend of 0.05 per decade during the dry season and an increase of 0.04 per decade during the wet season. Neutralizing factor from Ca2+ was higher than NH4+ over Nagpur during both seasons. However, the decrease in nss Ca^{2+} was not offset by the increase in NH_4^+, leading to a reduction in pH.

Figure 37. presents the time series of the ratio between $nssSO_4^{2-}$ and NO_3^- as well as FA. The trend indicated a significant increase in both seasons, with an increase of 0.41/decade in the dry season and 0.30/decade in the wet season. This indicated a higher concentration of sulfate from non-sea-salt sources compared to nitrate, underscoring the significant pollution in Nagpur due to elevated industrial emissions.The mean FA at Nagpur was 0.12 during the wet season, which is higher than the dry season value of 0.04. Both seasons showed a significant increasing trend, with FA rising by 0.02 per decade in the dry season and 0.09 per decade in the wet season.

3.7. Port Blair

Port Blair, the area is hilly and undulating, with the open sea to the east. The Barren Island volcano, 135 km ENE of Port Blair, is the only active volcano in the Indian subcontinent. No industries are on this island; local pollution sources include ship traffic and a diesel power generator about 10 km away.

The frequency distribution, along with the measured ionic spices at Port Blair, is shown in Fig.38.The frequency distribution showed that that the highest frequencies (35.8% and 40%) are in the ranges of 5-5.5 and 5.5-6 during the dry and wet seasons, respectively. The pH at Port Blair varied between 4.9 and 8.2 in the dry season and between 4.8 and 7.1 in the wet season, with average values of 5.6 in both seasons.These pH values were close to typical CO2 equilibrated value for neutral pH for rainwater, which is ~5.6. The percentage contribution of measured ionic species (PCMI; shown in Fig.37), indicated that Cl^- contributed the most (24% in the dry season and 27% in the wet season), while NH_4^+ and K^+ contributed the least (4% in the dry season and 3% in the wet season). The predominant cation and anion observed at Port Blair during both seasons were Na^+ and Cl^- respectively, indicating relatively strong oceanic influence in this region, similar to Minicoy.

The pH showed (Fig.39) a minimal temporal variation with a slight decreasing trend of -0.02/decade in the dry season and a significant decreasing trend of -0.12 per decade in the wet season. Temporal variability in acidic components (ss SO_4^{2-} and NO_3^-, as seen in Fig. 40) showed a decreasing trend in dry and wet seasons. ss SO_4^{2-} showed an insignificant trend of -0.46 μeql^{-1} /decade in the dry season, with a significant decrease of -0.98µeql−1 /decade in the wet season. However, NO_3^- showed an insignificant decrease of -6.64 μeql^{-1} /decade in the dry season and -3.38 μeql^{-1} /decade in the wet season.

Figure 41 shows the temporal variability of alkaline components (SS Ca^{2+} and NH_4^+). The ssCa^{2+} exhibited a decrease of -0.14 µeql−1 /decade (not significant) during thedry season and -0.30 μeql^{-1} /decade (significant at 10 % significant level) in the wet season. NH_4^+ showed a downward trend of -1.10 /decade in the dry season and -2.19 μeql^{-1}/decade in the wet season; however, neither trend was statistically significant.

The neutralization factor (NF) for ss Ca^{2+} showed aminimal increasing trend of 0.01/decade in the dry and wet seasons (Fig. 42). The NF for NH_4^+ showed an increasing trend of 0.05/ during the dry season and a slight decreasing trend of -0.02/decade during the wet season. Figure 43 presents the time series of the ratio between ss $SO_4{}^{2-}$ and $NO_3{}^{-}$. The trend indicated an insignificant increase of 0.11/decade in the dry season and a decrease of -0.06/decade in the wet season. The time series of FA at Portblair is shown in Fig.43. The mean value of FA during the dry season was 0.14, while in the wet season it was 0.13. FA exhibited a significant upward trend in both seasons, increasing by 0.06 per decade in the dry season and 0.08 per decade in the wet season.

3.8. Pune

Pune is one of the most urbanized, densely populated, and polluted cities in Maharashtra. Pune is a rapidly expanding city located ~100 km from the west coast and on the leeward side of the Western Ghats. The observatory is located on the campus of Agriculture College and is surrounded by agriculture fields. There are no industries in the vicinity of the observatory. Vehicular traffic is the main source of pollution in Pune and is rising tremendously.

The frequency distribution of pH, along with the Percentage contribution of measured ionic species in the rainwater at Pune, is shown in Fig.43. In the wet season, 33.6% of the samples fall within the pH range of 6-6.5, while in the dry season, 29.8% fall within the range of 5.5-6. The pH range spaned from 4.7 to 7.1 during the dry season and from 4.9 to 7.3 during the wet season, with average values of 5.4 and 5.9, respectively.

The percentage contribution of measured ionic species (PCMI), as shown in Fig.43, indicated that Ca^{2+} contributed the most (21% in the dry season and 24% in the wet season), while K^+ contributed the least (3% in the dry season and 2% in the wet season). The higher concentration of Ca^{2+} and $NO_3{}^{-}$, which were the predominant cation and anion respectively, indicated the influence of dust aerosols and anthropogenic activities in this region. Calcium exhibited the highest concentration in both seasons, reflecting the prevalence of soil sources and the impact of increasing construction activities. During the wet season, increased concentration of Na^+ and Cl^- (approximately 15%) was attributed to sea spray carried by onshore winds from the Arabian Sea, especially during the southwest monsoon (Bhaskar et al., 2022).

The pH showed (Fig.45) a minimal declining trend in the dry season(-0.08/decade) and a significant decreasing trend of -0.15 per decade in the wet season. Temporal variability in acidic components nss$SO_4{}^{2-}$ and $NO_3{}^{-}$ is given in Fig. 46. The nss$SO_4{}^{2-}$ showed a significant increase of 12.17 μeql−1 /decade and 5.56μeql−1 /decade in dry and wet seasons respectively.

NO_3^- also showed a rise of 10.55 μeql^{-1} /decade in the dry season and 3.88 μeql^{-1} /decade in the wet season (both trends are insignificant). The alkaline component nssCa^{2+} exhibited an increase of 12.15 μeql−1 /decade during the dry season and 5.27 μeql^{-1} /decade in the wet season (Fig. 47). NH_4^+ showed an upward trend of 0.83 μeql^{-1} /decade in the dry season and a downward trend of -2.43 μeql^{-1}/decade in the wet season (Fig. 47); however, both trends were not statistically significant. The significance of nssSO_4^{2-} and nssCa^{2+} in the acidification of rainwater in Pune was greater compared to NO_3^- and NH_4^+. Nevertheless, the combined impact of these four components led to a decrease in pH, indicating that the net acidic effects of SO_4^{2-} and NO_3^- were not sufficiently counterbalanced by the alkaline effects of Ca^{2+} and NH_4^+ (Bhaskar et al., 2022).

The neutralization factor (NF) from nss Ca^{2+} showed a decreasing trend of -0.03/decade in the dry season and -0.14/decade in the wet season (Fig. 48; both trends are not significant)). The NF for NH_4^+ showed a decreasing trend of -0.02 per decade during the dry season and a significant decrease of -0.08 per decade in the wet season. Figure 49 presents the time series of the ratio between nssSO_4^{2-} and NO_3^-. The trend indicated a significant increase of 0.14/decade in the wet season and an insignificant increase of 0.08/decade in the dry season. It highlights the significant influence of non-sea-salt sulfate (nssSO_4^{2-}) and at the same time emphasizes the major role of vehicular emissions in acidification of rainwater in Pune.No noticeable variation was observed in the time series of FA, as illustrated in Fig. 49. The trend is almost flat in both seasons, with average FA values of 0.04 in the dry season and 0.02 in the wet season.

3.9. Srinagar

Srinagar, situated inan elevated valley with an extra-tropical climate, is influenced by extra-tropical weather systems. Dust carried by western disturbances impacts the chemical composition of precipitation in the region. Srinagar station is surrounded by Chinar trees. Nearby, there are brick kilns, a silk factory, and a cement factory. Other than these, there are no major polluting industries in the area. Since 1981, several residential colonies have been established around the station.

The frequency distribution of pH, along with the Percentage contribution of measured ionic species in the rainwater at Srinagar, is shown in Fig.50. In both dry and wet seasons (30.1% and 34% respectively), most of the samples fell within the pH range of 6.5-7. The pH varied from5.2

to 7.9 during the dry season and from 5.3 to 8.2 during the wet season, with average values of 6.2 and 6.4, respectively. Rainwater at Srinagar showed a predominant alkaline nature which could be attributed to the to the influence of airborne alkaline rich dust particulate matter transported from the Thar Desert (Soni et al., 2012) in association with convective activity/movement of western disturbances (Bhaskar & Rao, 2017).

The analysis of PCMI (shown in Fig.50) indicatedthat Ca^{2+} contributes the most (34% in the dry season and 32% in the wet season), while NH_4^+ contributedthe least (<=1% in the dry season and the wet season) throughout the year at Srinagar.Ca^{2+} and NO_3^- were the abundant cation and anion, respectively, at Srinagar.The increased concentration of Ca^{2+} can be attributed to the long-range transport of soil dust from the Thar Desert as well as dust contributions from the cement factory in Srinagar. The higher levels of NO_3^- are due to emissions from the brick industry and the cement factory located within a 15 km radius.

The pH showed (Fig.51) a significant decreasing trend in both seasons (-0.23/decade in the dry season and -0.18/decade in the wet season). However, the rainwater remains alkaline at Srinagar all these years. Temporal variability in acidic components, $nssSO_4^{2-}$ and NO_3^-, is shown in Fig 52. $nssSO_4^{2-}$ showed an upward trend of 6.96µeql^{-1}/decadein the dry season and a significant upward trend of 11.10 µeql^{-1} /decade in the wet season. However, NO_3^- showedincreaseof11.19µeql^{-1}/decade in the dry season and a decrease of -9.41µeql^{-1}/decade in the wet season.However, neither trend is statistically significant.

Figure 53 showed the temporal variability of alkaline components ($nssCa^{2+}$ and NH_4^+). The $nssCa^{2+}$ exhibitedan increase of12.15µeql^{-1}/decade during the dry season and 5.27µeql$^{-1\,/}$decade in the wet season.NH_4^+ showed an upward trend of -0.83/decade in the dry season and a downward trend of -2.43 µeql^{-1}/decade in the wet season. The trends in the alkaline componentsare not statistically significant.The rising levels of nssSO4 were not completely arrested by buffering ions like nssCa and also the decline in levels of NH_4^+ hadled to a decline in pH.

The neutralization factor (NF) from nss Ca^{2+} and NH_4^+ is given in Fig.54. For nss Ca^{2+}, there is a slight decline of -0.03per decade during the dry season and a significant decline of -0.14 per decade during the wet season. The NF for NH_4^+ showeda modest increase of 0.02per decade in the dry season, with a significant increase of 0.08/decade in the wet season.Figure 55 presents the time series of the ratio between $nssSO_4^{2-}$ and NO_3^-. The trend indicated an increase of 0.08/decade in the dry season and a significant increase of 0.14/decade in the wet season. It highlights the significant impact of $nssSO_4{}^{2-}$, primarily emitted from local sources like brick kilns, which contributes to the reduction in pH levels at Srinagar.Time series analysis of FA indicated (given in Fig.55) an increase of $1.3x10^{-3}$/decade (significant at 10 % level) during the dry season and $6.1\ x10^{-3}$/decade(insignificant) during the wet season.

3.10. Vizag

Visakhapatnam, often called the Steel City of Andhra Pradesh, is home to numerous major sources of pollution, including various industries, refineries, power plants, and fertilizer facilities within a 50 km radius of the observatory. The emissions from these establishments significantly affect the composition of rainfall at Vizag. The Bay of Bengal is located approximately 1 km to the southeast of the siteand the emissions from shipping yards are another source for pollution.

The frequency distribution of pH, along with the Percentage contribution of measured ionic species in the rainwater at Vizag, is shown in Fig.56. The frequency distribution showed that the highest frequencies (27.1% (dry)and 29.3%(wet)) were in the ranges of 4.5-5 and 5-5.5 during the dry and wet seasons, respectively. The pH varied from 4.4 to 8.1 during the dry season and from 4.4 to 7.6 during the wet season, with average values of 5.1 and 5.0, respectively. Rainwater at Vizag showed a predominantly acidic nature, which could be attributed to the influence of numerous surrounding industries and sea spray (Soni and Sarkar 2005).

The analysis of PCMI (shown in Fig.56) indicatedthat NO_3^-,Cl^-, and Na^+contributed the most (18%,17%,16% respectively in the dry season and 16%,19%, and 17% respectively in the wet season), while K^+ contributedthe least (3% in the dry season and the wet season) at Vizag. $NO_3{}^-$ and Cl^- were the abundant cations in the dry and wet seasons, respectively. The most abundant anion was Na^+. The increased concentration of Na^+ and Cl^- can be attributed to the strong oceanic influence in this region. The higher levels of $NO_3{}^-$ were due to large industrial emissions.

The pH showed (Fig.57) a significant decreasing trend of -0.18/decade in the dry season and a significant increase of 0.18/decade in the dry season. However, the long-term mean values of rainwater every month are slightly acidic in nature. Temporal variability in acidic components, $nssSO_4{}^{2-}$ and $NO_3{}^-$, is shown in Fig 58. $nssSO_4{}^{2-}$ showed a significant upward trend of 10.0 μeql^{-1}/decade in the dry season and 17.12 μeql^{-1} /decade in the wet season. However,

NO_3^- shows a non-significant decrease of -16.95μeql^{-1}/decade in the dry season and asignificant decreaseof-40.36μeql^{-1}/decade in the wet season. Figure 59illustratedthe temporal variability of alkaline components (nss Ca^{2+} and NH_4^+). nss Ca^{2+} showed a decline of -9.54μeq l^{-1} per decade in the dry season and -8.03μeq l^{-1} per decade in the wet season. The NH_4^+ also exhibited a decrease of -3.62 μeq l^{-1} per decade in the dry season and a decrease of -0.94 μeq l^{-1} per decade in the wet season. The trends in the acidic components are not statistically significant.

The neutralization factor (NF) from nss Ca^{2+} andNH_4^+ is given in Fig.60. and the changes in NF for these ions were minimal for both seasons. For nss Ca^{2+}, there was a decrease of -0.11 per decade during the dry season and 0.02 per decade during the wet season. The NF for NH_4^+ showed a modest increase of 0.01 per decade in dry season with a significant increase of 0.05 per decade in the wet season. Figure 61 presented the time series of the ratio between nssSO_4^{2-} and NO_3^-. The trend indicated a significant increase of 0.28/decade in the dry season and 0.65/decade in the wet season. The trend in FA at Vizag (illustrated in Fig. 61) indicated a decline of 0.01 per decade during the wet season, while the dry season experienced an increase of 0.01 per decade from 1987 to 2021. The average FA values were 0.06 for the wet season and 0.05 for the dry season.

4. Conclusions

The present study analyzed the precipitation chemistry at ten GAW stations in India from 1987 to 2021. Rainwater pH at these locations varied from slightly acidic to mildly alkaline. Stations such as Vizag , Mohanbari and Allahabad exhibited more acidic mean pH values, while Jodhpur and Srinagar had more alkaline values. For the remaining stations, the pH values were close to the neutral pH of ~5.65.This suggests variability in atmospheric conditions and local sources affecting rainwater chemistry.

The observed acidity of rain water at Vizag can be attributed to the emissions by numerous sources including those from the oil refinery, power plant, fertilizer facility and the shipping yard. At Mohanbari, apart from the acidic nature of local soil, certain weak organic anions originated from surrounding vegetation sources could be the reason behind acidic pH. Conversely, in locations like Jodhpur and Srinagar, dust particles from the nearby Thar Desert likely neutralize acidic components, raising the pH of rainwater.

Seasonal variations in pH indicate that, in most locations, rainwater tends to be slightly more acidic during the dry season than the wet season. This is because the highest concentration of acidic particles is typically removed at the beginning of a rain event, resulting in lower pH values. As the rain event progresses, pH values generally increase. Seasonal pH analysis shows a consistent trend toward slightly acidic to neutral pH levels in rainwater across various locations, regardless of the season.

Trend analysis of pH at the GAW stations revealed a general decrease over time in most locations, influenced by both acidic and alkaline components. Significant reductions in pH were observed at all stations except Port Blair, Vizag, and Pune, irrespective of the season. Allahabad, Jodhpur, and Nagpur experienced notable decreases in pH due to the prevalence of acidic components. In contrast, regions like Srinagar and Pune, while also experiencing pH declines, showed some buffering effects from alkaline ions such as nssCa^{2+} and NH_4^+.

NO_3^- was the dominant among anions reflecting the impact of increased emissions from combustion sources particularly from vehicular, industrial and residential/agricultural burning activities. Ca^{2+} was the predominant cation in many areas, notably Allahabad, Jodhpur, Kodaikanal, Pune, Srinagar, and Nagpur, suggesting a significant influence of dust aerosols and soil particles, likely from long-range transport and local construction activities. Locations such as Minicoy, Port Blair, and Vizag showed high levels of Cl^- and Na^+, indicating strong oceanic influences.

Analysis of neutralization factors across various locations provided critical insights into rainwater's capacity to neutralize acidity. In some regions, the NF for nss Ca^{2+} showed a significant decreasing trend over time, as observed in Allahabad, Jodhpur, and Nagpur. This reduction in NF for Ca^{2+} indicates a diminished capacity to neutralize acidic components, possibly due to reduced calcium sources or changes in atmospheric conditions, contributing to increased rainwater acidity. Conversely, the NF for NH_4^+ generally increased in many stations, including Allahabad, Jodhpur, and Nagpur. However, this increase was not always sufficient to counterbalance the decrease in nss Ca^{2+}. The limited buffering capacity of NH_4^+ in many areas suggests that the overall acid-neutralizing effect remains inadequate to prevent rainwater acidification. In some regions, the NF for nss Ca^{2+} either remained stable or increased, indicating some buffering capacity, though other factors such as changes in acidic components or fluctuating NH_4^+ levels also influence pH trends.

Analysis of the time series data for the ratio of non-sea-salt sulfate (NSS SO_4^{2-}) to nitrate (NO_3^-) across various locations revealed significant trends and seasonal variations in sources. At Allahabad, Nagpur, Srinagar, and Vizag, this ratio increased significantly over time, indicating a rising dominance of sulfate from non-sea-salt sources compared to nitrate. The increased sulfate concentrations are likely associated with industrial emissions and other local sources becoming more prominent relative to nitrate. Seasonal variations in the ratio were also observed in locations such as Port Blair, Kodaikanal, Jodhpur, and Minicoy. In areas like Jodhpur and Minicoy, the ratio significantly decreased, particularly during the wet season, suggesting that nitrate is becoming more dominant, possibly due to increased agricultural activities and vehicular emissions.

The analysis of fractional acidity (FA) across various regions reveals an upward trend. While Kodaikanal, Mohanbari, and Nagpur experienced significant increases in FA, indicating a decline in the buffering capacity of rainwater, Jodhpur and Pune showed minimal changes. A unique feature observed across all these stations is the increase in FA alongside a decrease in pH at nearly all GAW sites.

The analysis of precipitation chemistry across India shows that urbanization and industrialization have a significant impact on the composition of rainwater. Additionally, shifts in combustion sources and agricultural practices also influence chemical wet deposition more than large-scale geographical factors. However, acid rain does not currently pose a major and immediate threat to our region.

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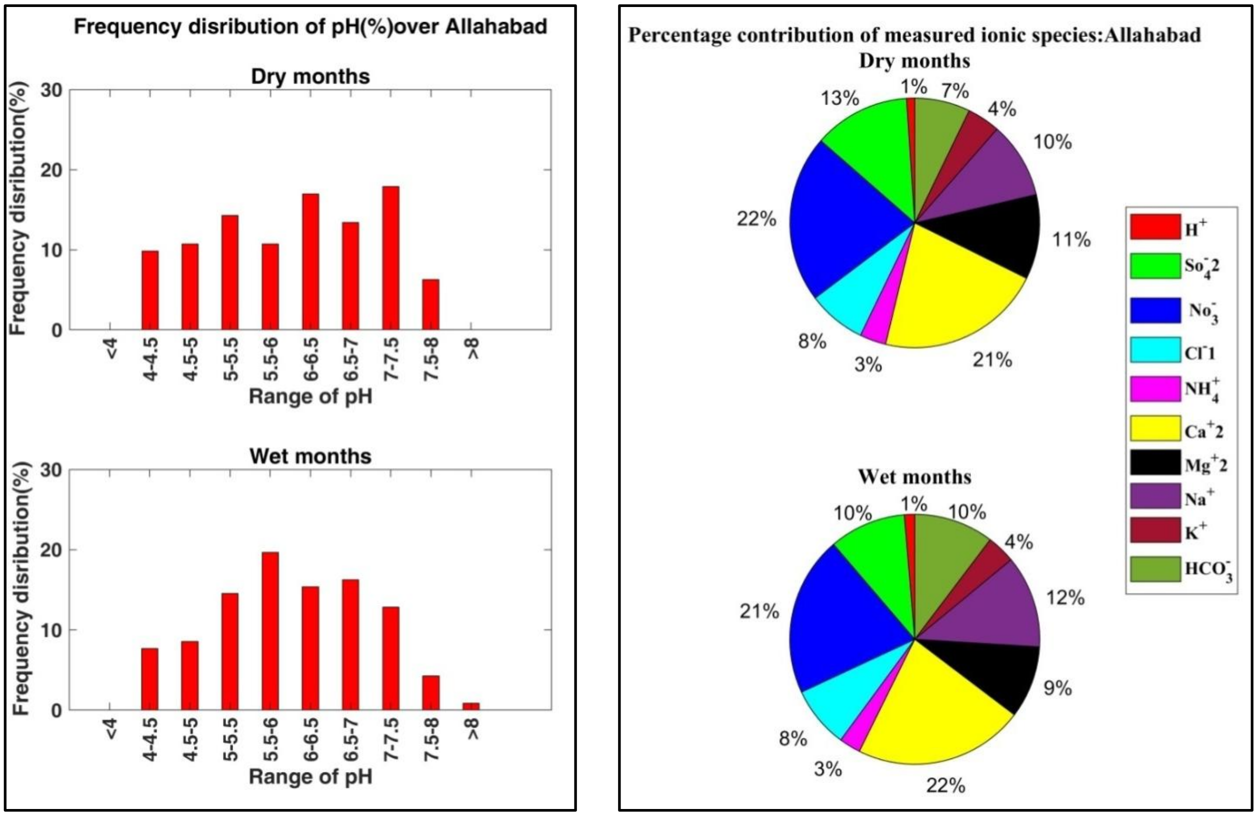

Fig.2. Frequency distribution of pH and Percentage contribution of measured ionic species in Rainwater at Allahabad during 1987-2021

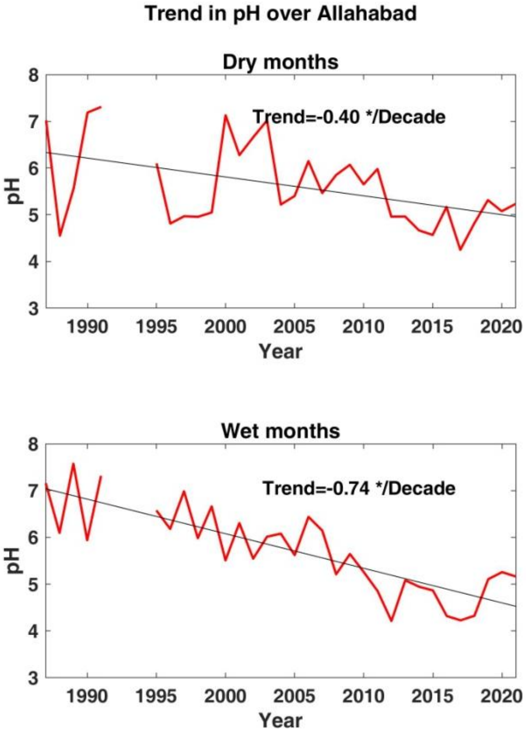

Fig.3. Long-term trend of pH at Allahabad during 1987–2021

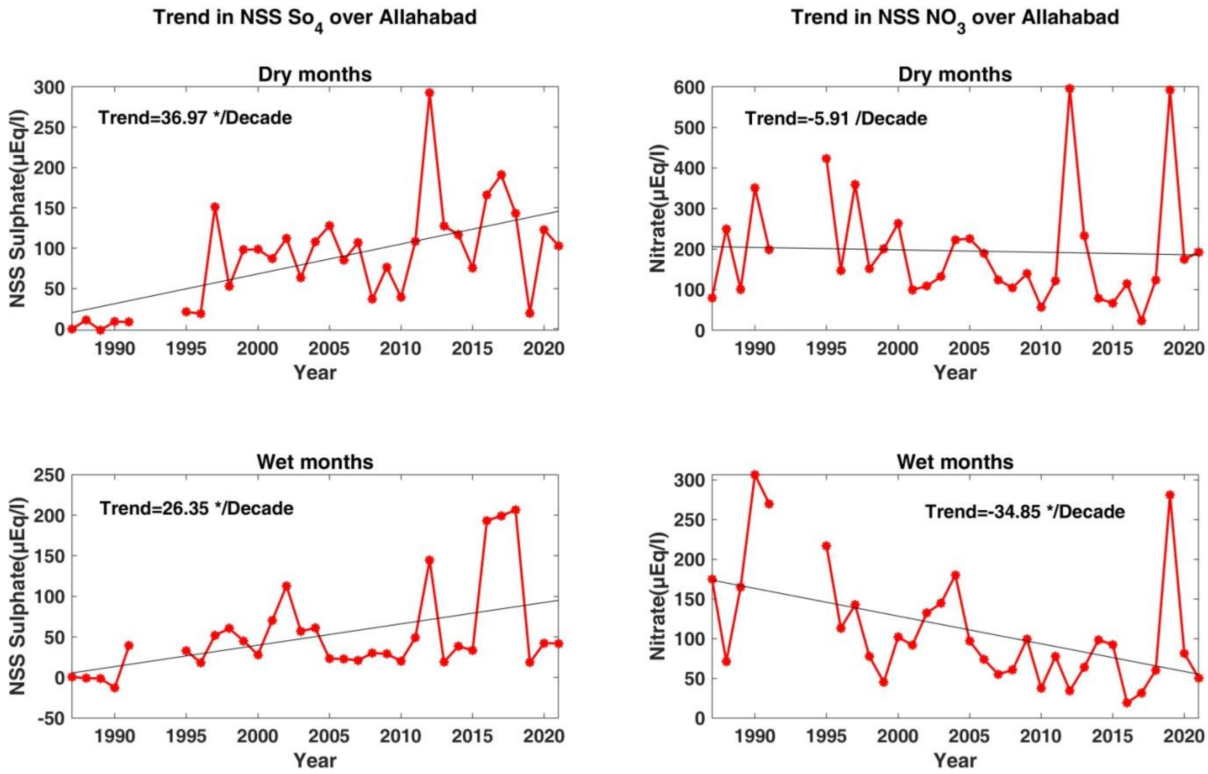

Fig.4. Long term trend of NSS SO_4 and NO_3 at Allahabad during 1987–2021

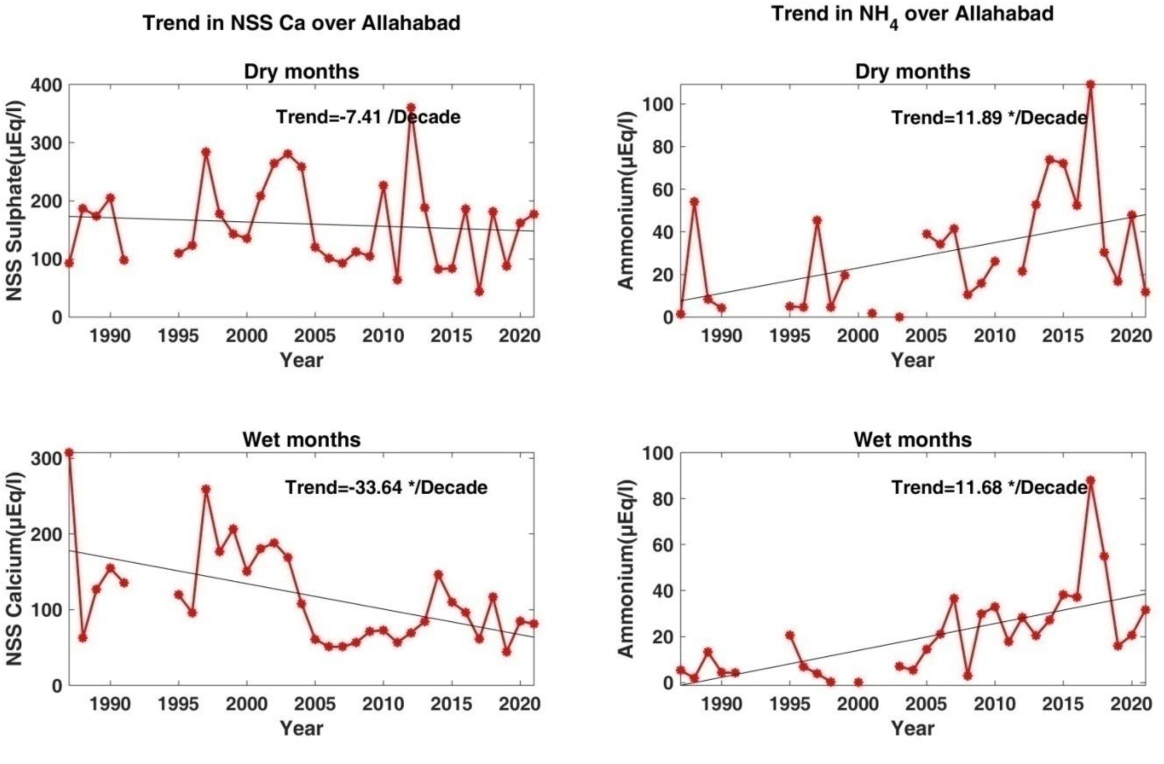

Fig. 5. Long-term trend of NSS Ca and NH_4 at Allahabad during 1987–2021

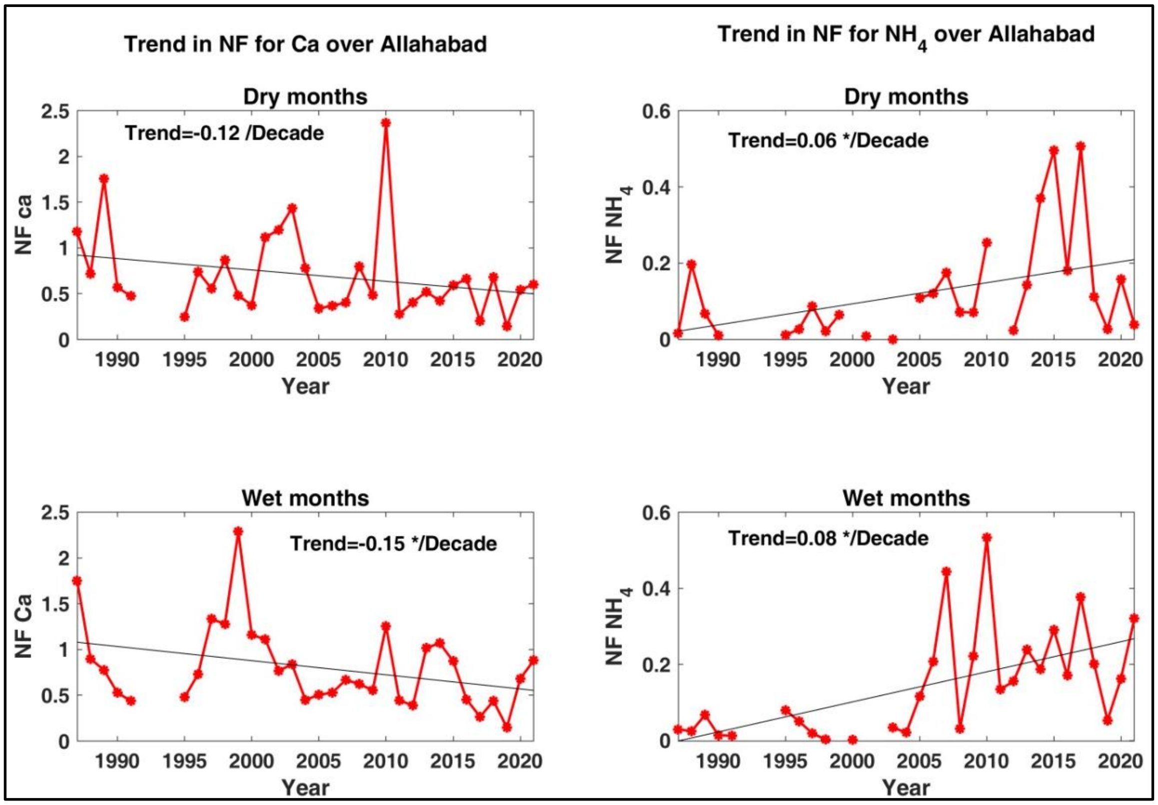

Fig.6. Long-term trend NFof NSS Ca and NH_4 at Allahabad during 1987–2021

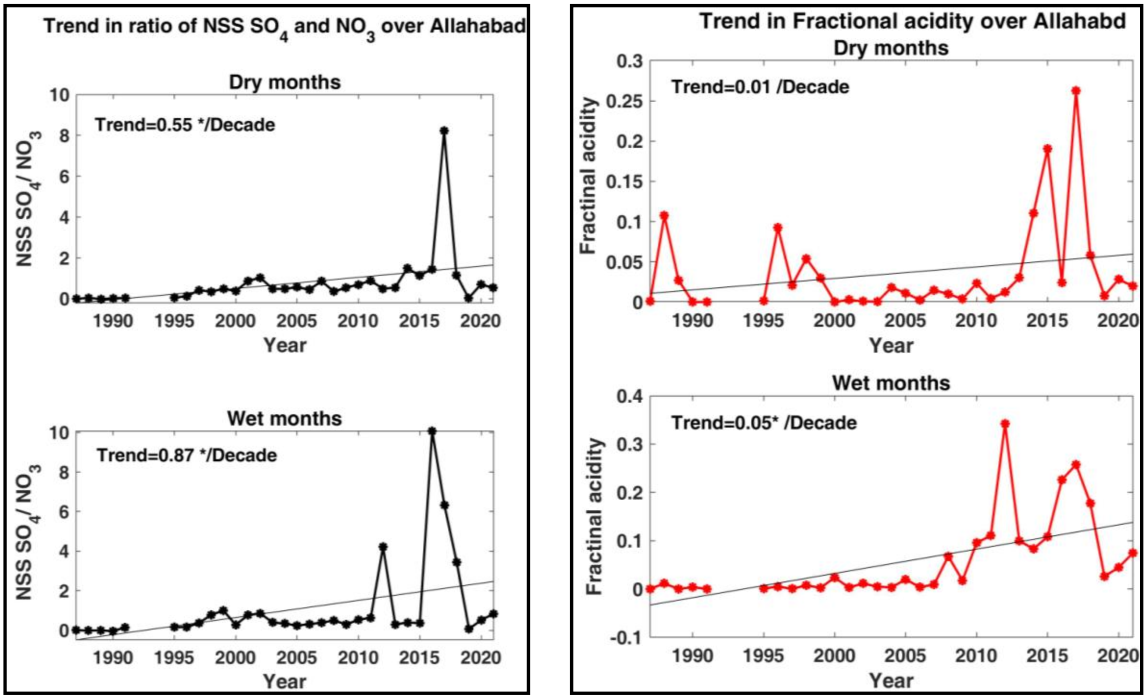

Fig.7. Long-term trend in the ratio of NSS SO_4 and NO_3 and Fractional acidity at Allahabad during 1987–2021

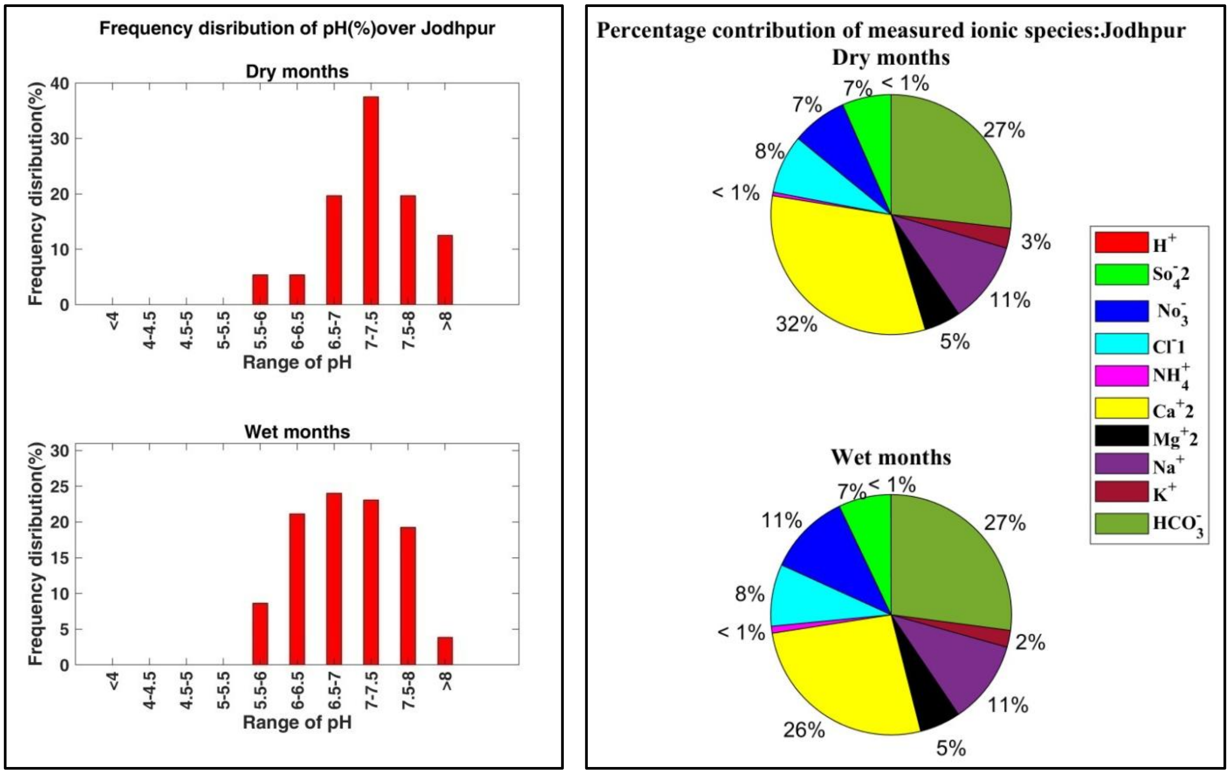

Fig.8. Frequency distribution of pH and Percentage contribution of measured ionic species in Rainwater at Jodhpur during 1987-2021

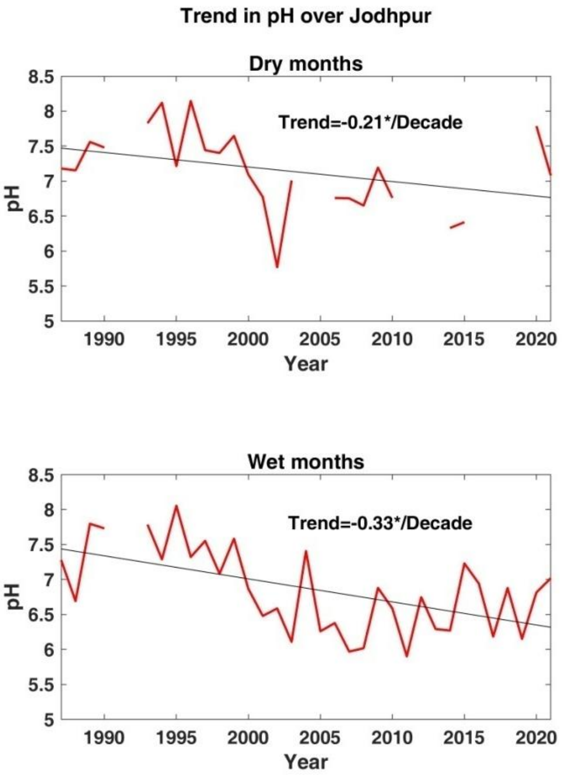

Fig. 9. Long-term trend of pH at Jodhpur during 1987–2021

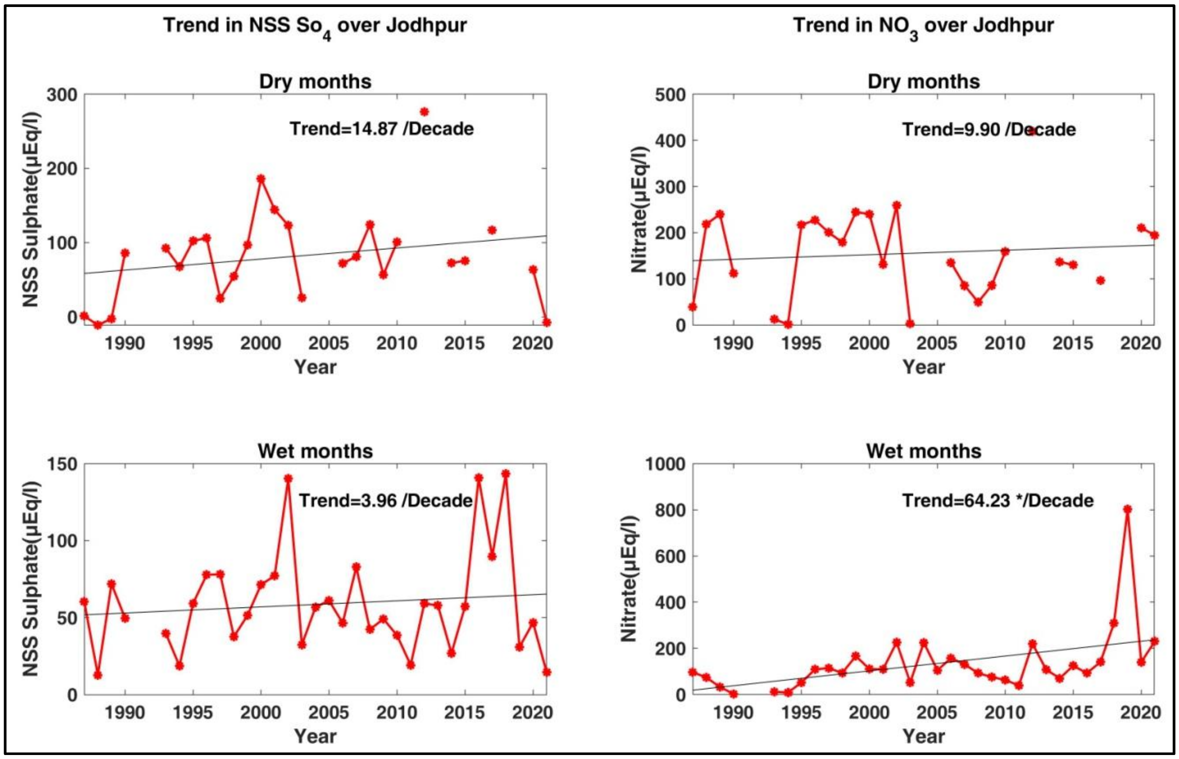

Fig. 10. Long-term trend of NSS SO4 and NO3 at Jodhpur during 1987–2021

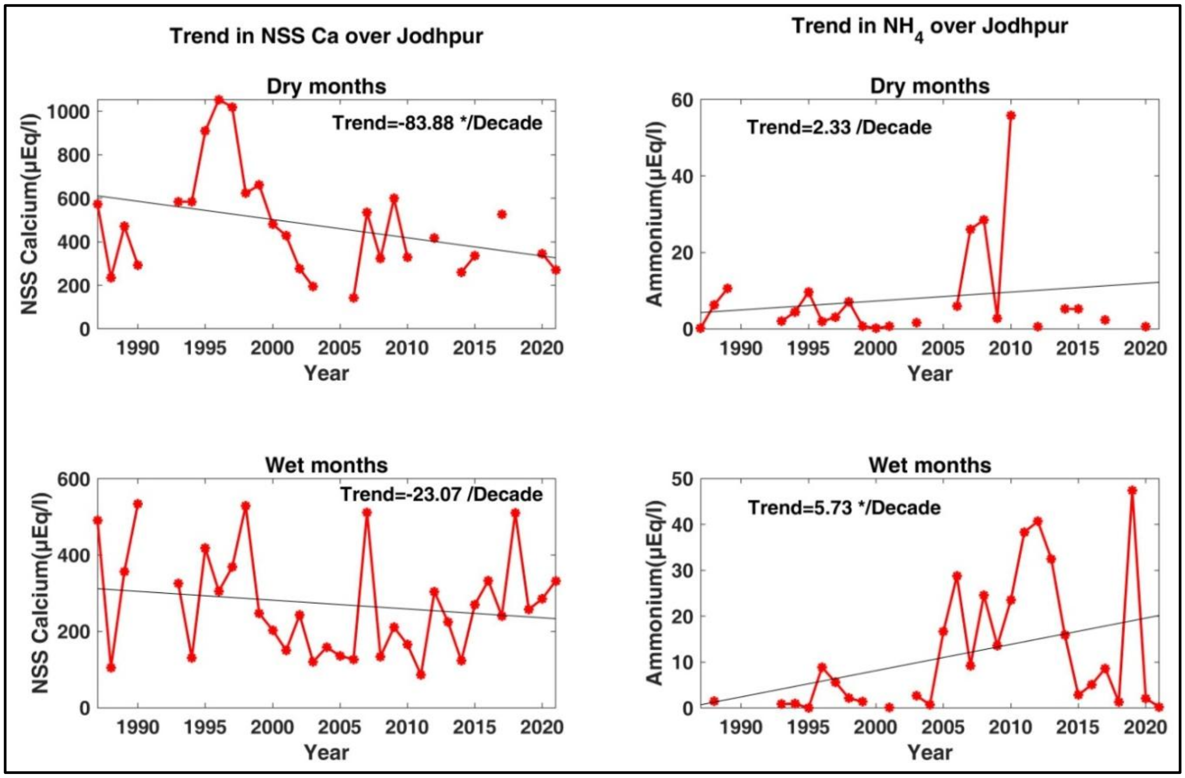

Fig.11 Long-term trend of NSS Ca and NH_4 at Jodhpur during 1987–2021

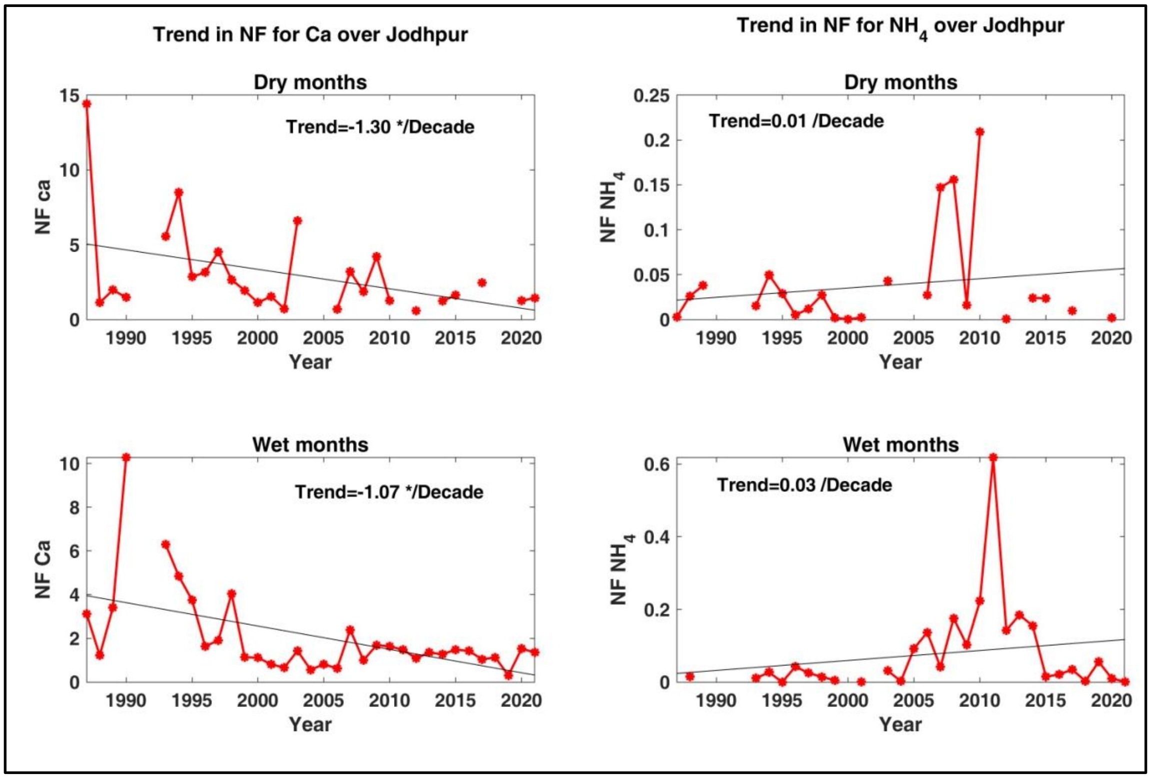

Fig.12. Long-term trend NF of NSS Ca and NH_4 at Jodhpur during 1987–2021

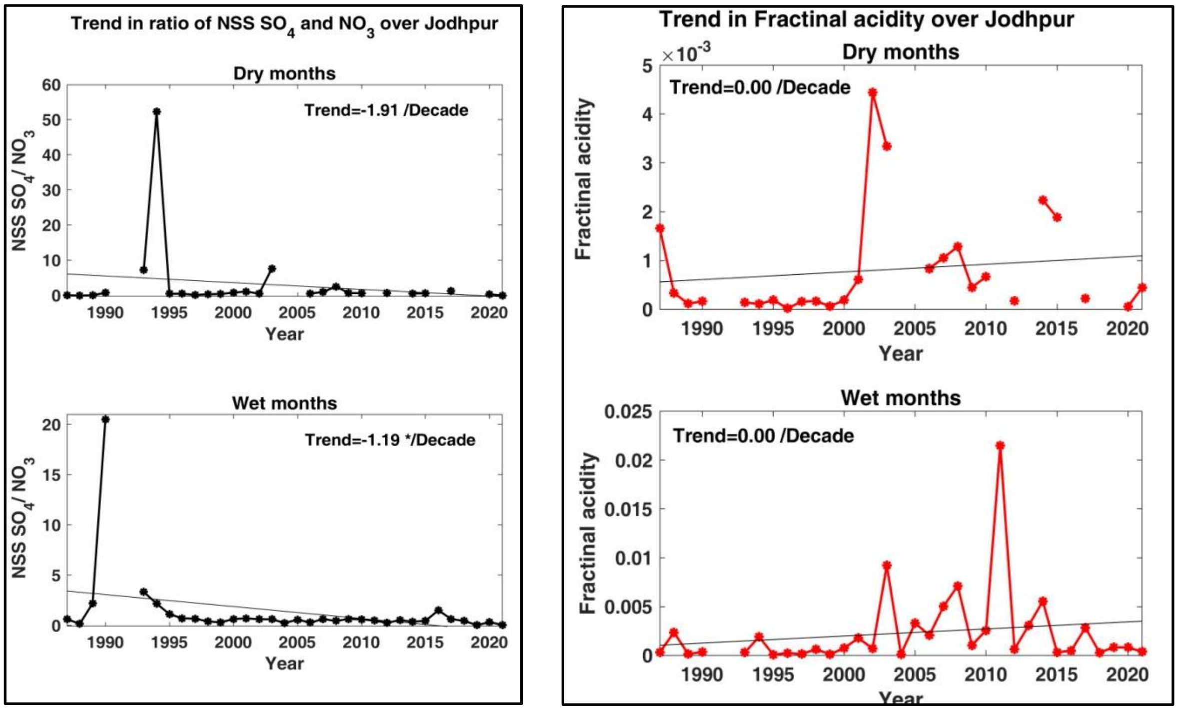

Fig.13. Long-term trend in the ratio of NSS SO_4 and NO_3 and fractional acidity at Jodhpur during 1987–2021

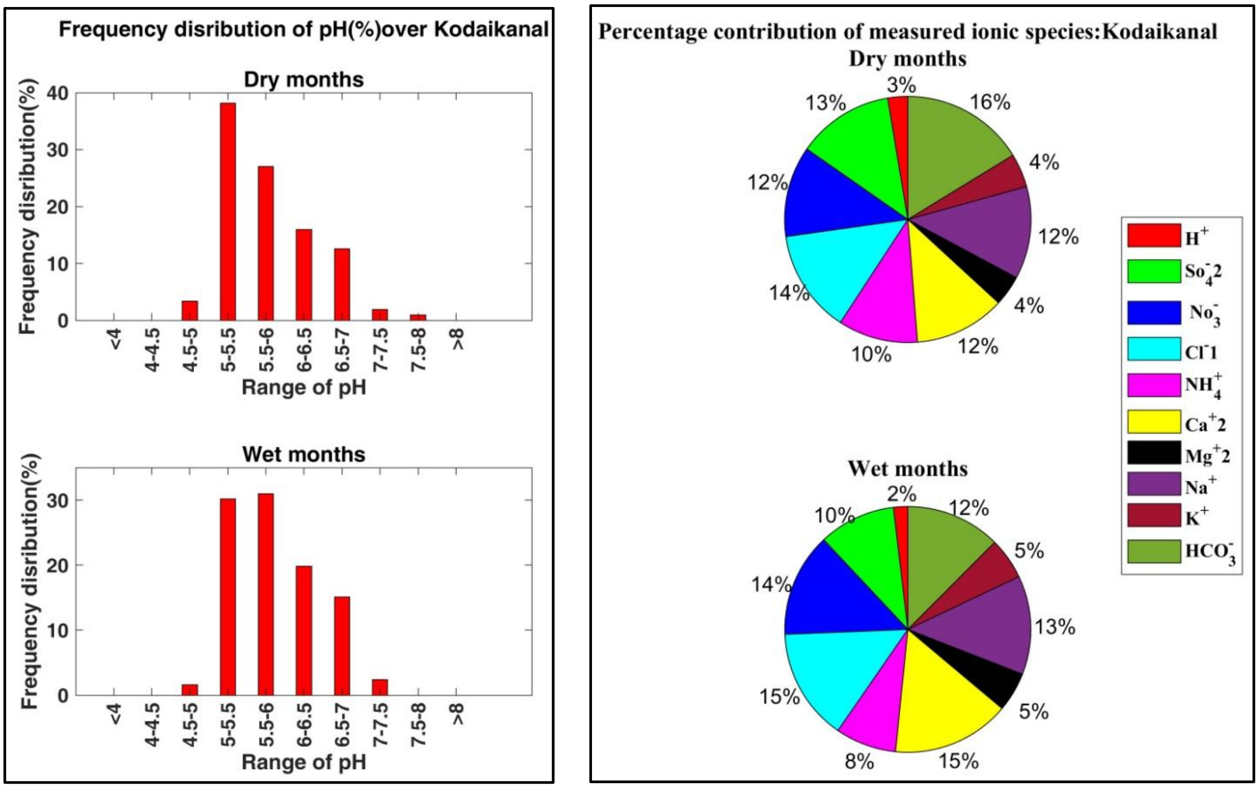

Fig.14. Frequency distribution of pH and Percentage contribution of measured ionic species in Rain water at Kodaikanal during 1987-2021

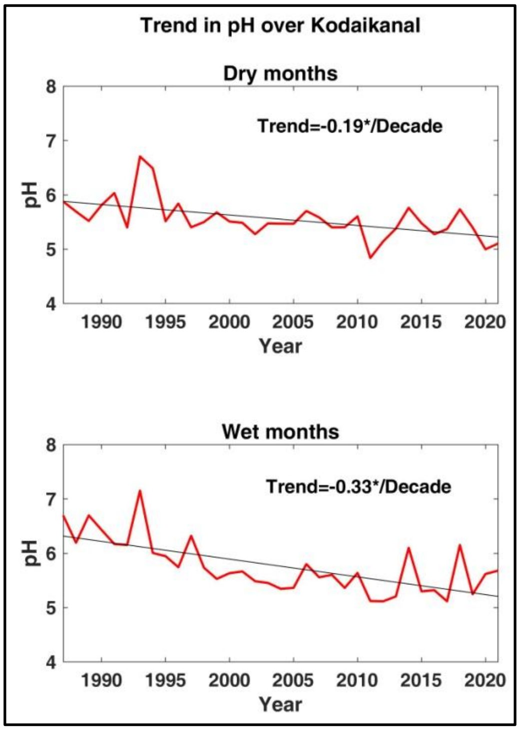

Fig. 15. Long-term trend of pH at Kodaikanal during 1987–2021

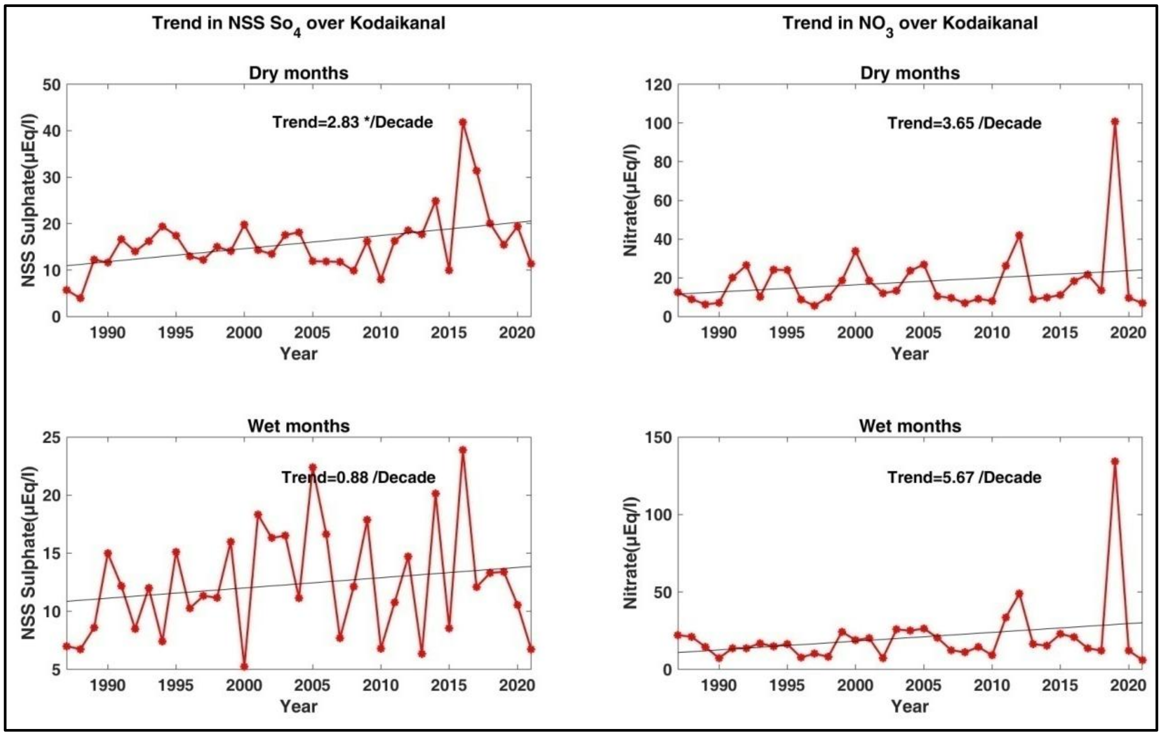

Fig. 16. Long-term trend of NSS SO4 and NO3 at kodaikanal during 1987–2021

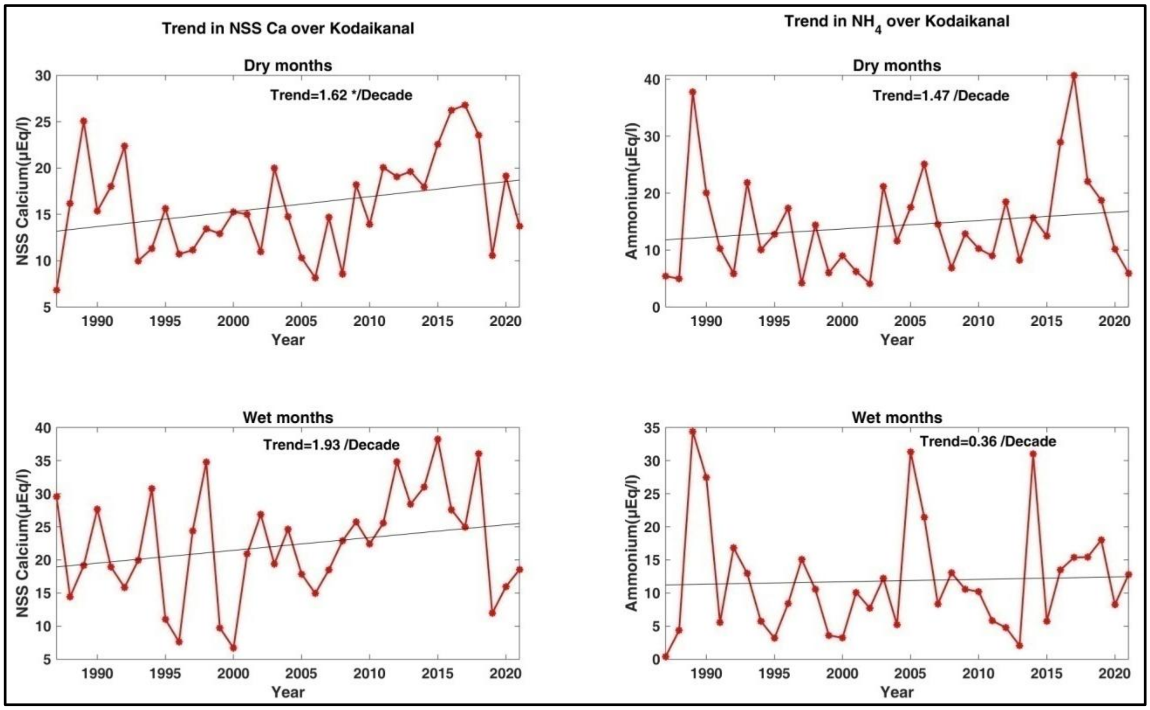

Fig.17. Long-term trend of NSS Ca and NH4 at kodaikanal during 1987–2021

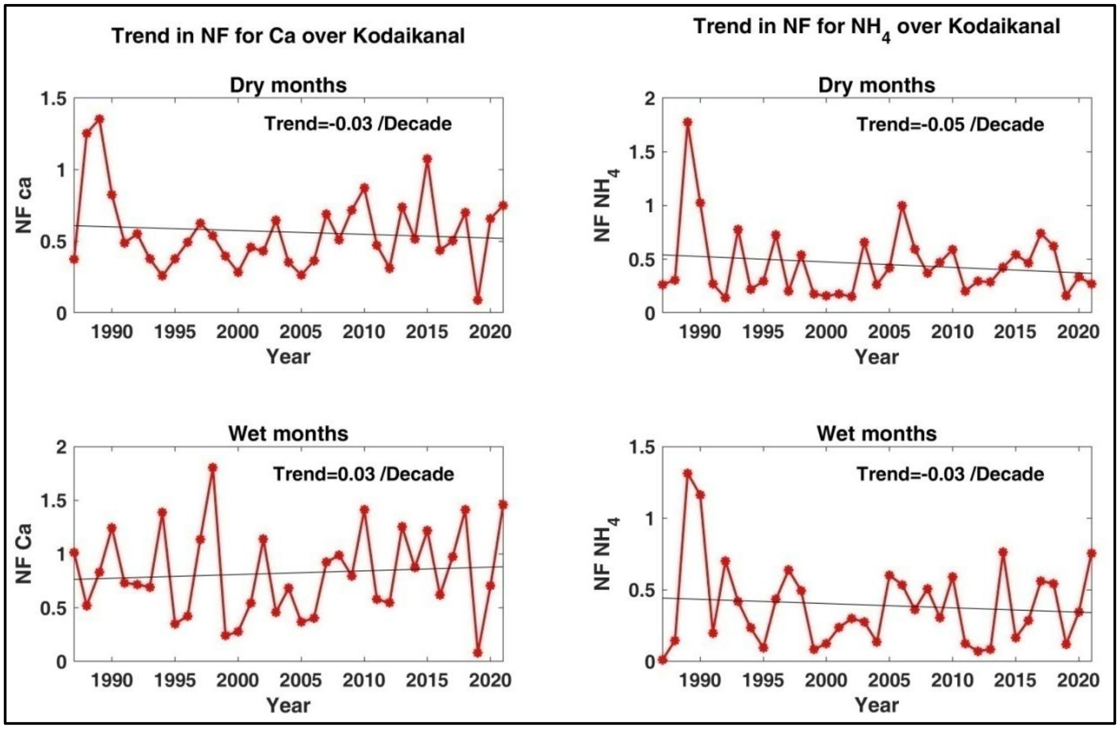

Fig.18. Long-term trend of NF Ca and NH4 at kodaikanal during 1987–2021

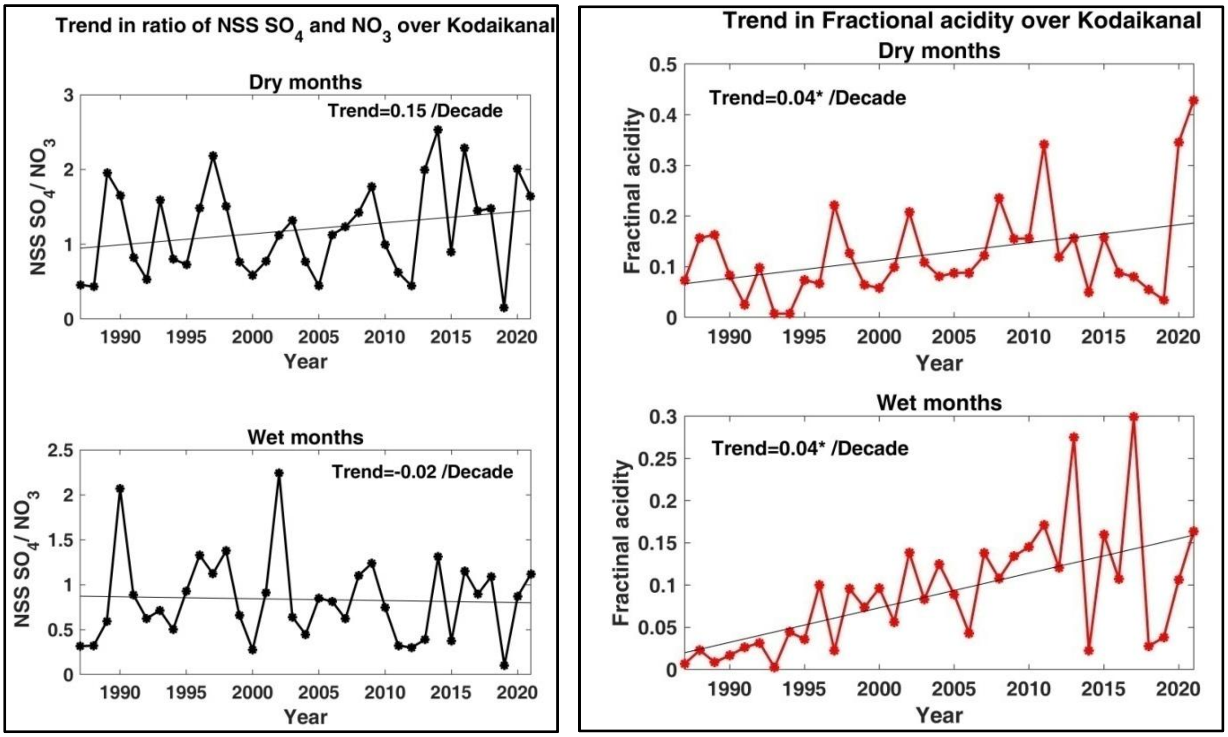

Fig.19. Long-term trend in the ratio of NSS SO_4 and NO_3 and fractional acidity at Kodaikanal during 1987-2021

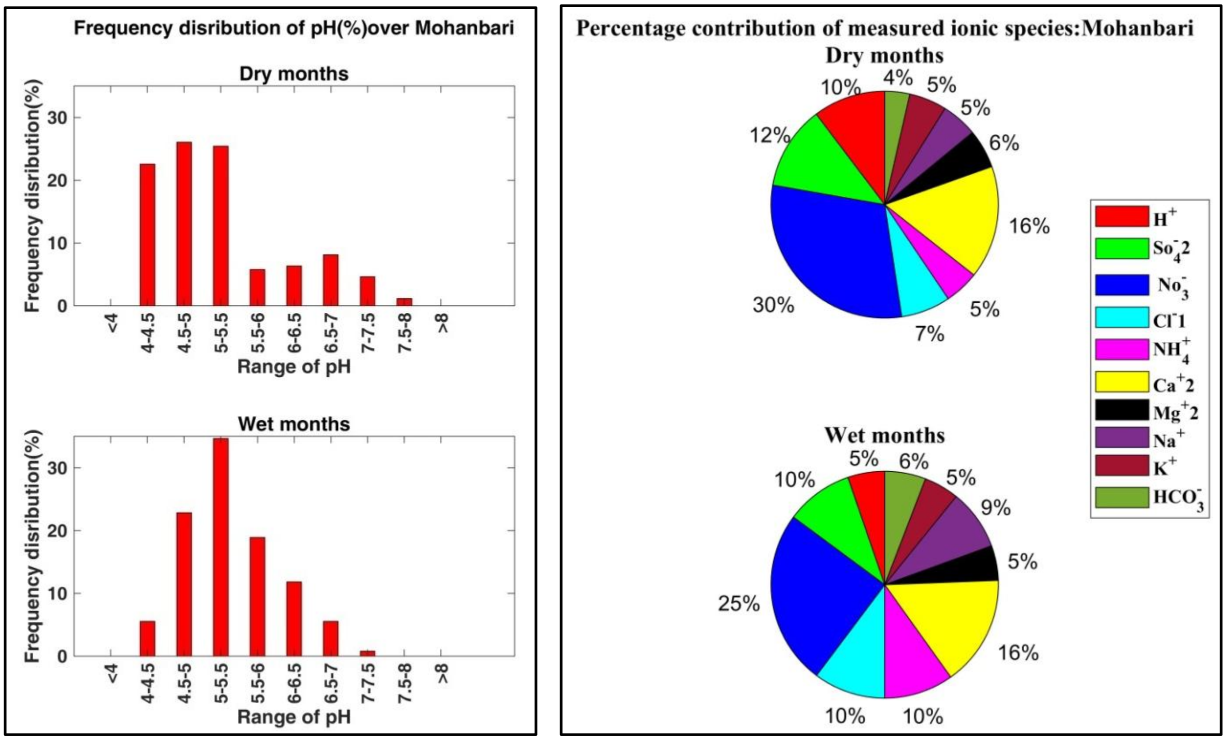

Fig.20. Frequency distribution of pH and Percentage contribution of measured ionic species in Rainwater at Mohanbari during 1987-2021

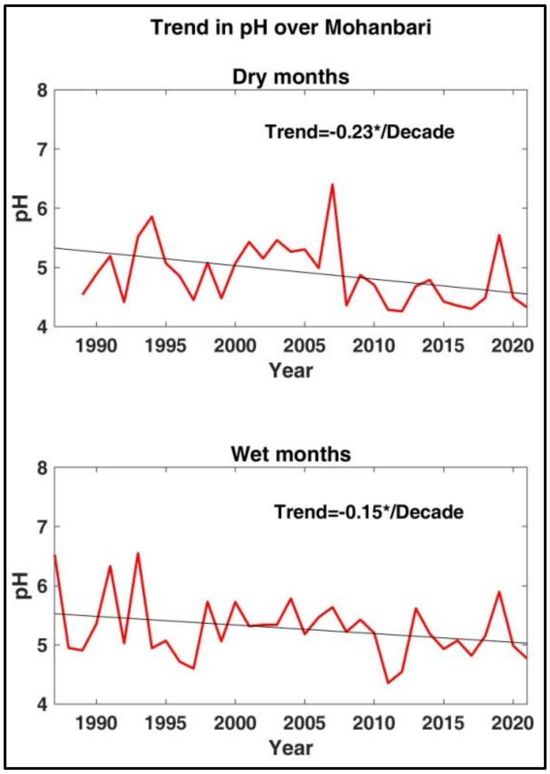

Fig. 21. Long-term trend of pH at Mohanbari during 1987–2021

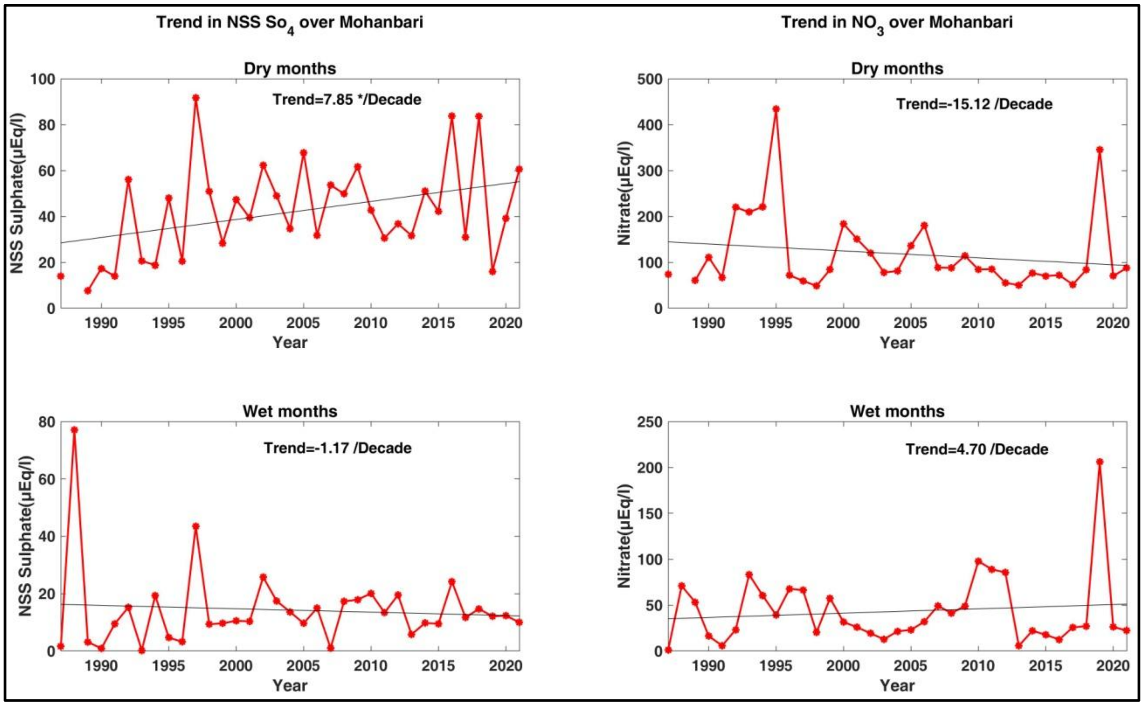

Fig. 22. Long-term trend of NSS SO4 and NO3 at Mohanbari during 1987–2021

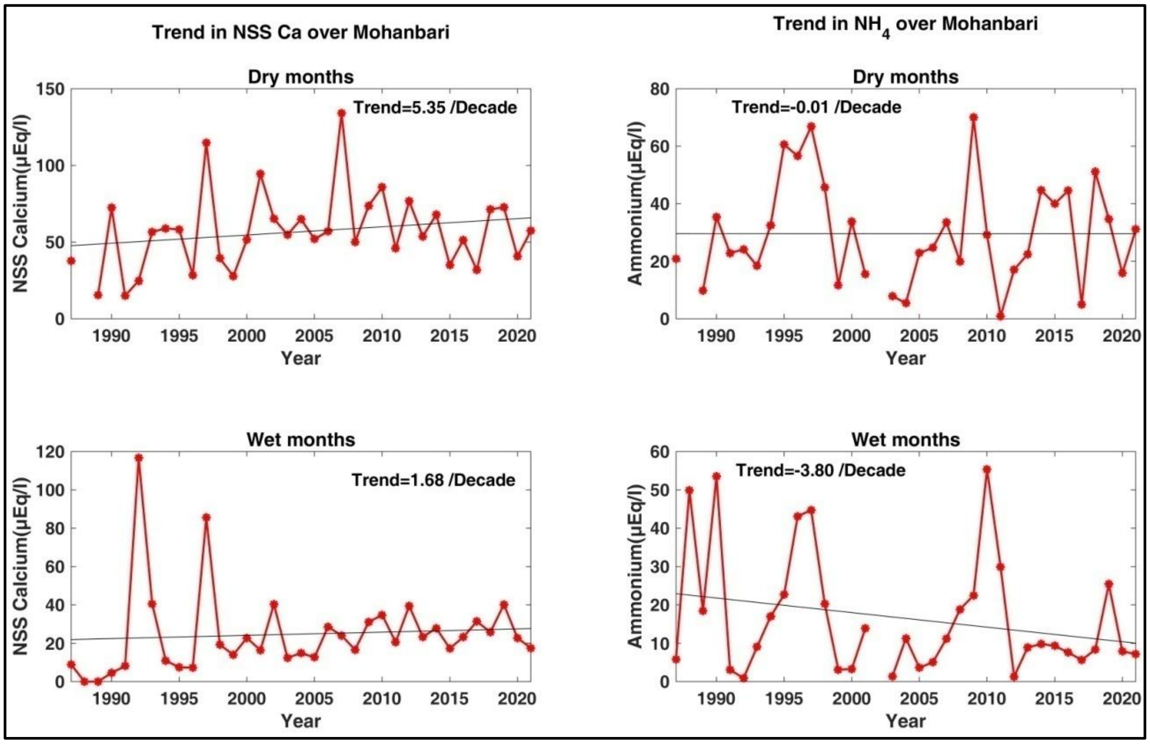

Fig.23. Long-term trend of NSS Ca and NH4 at Mohanbari during 1987–2021

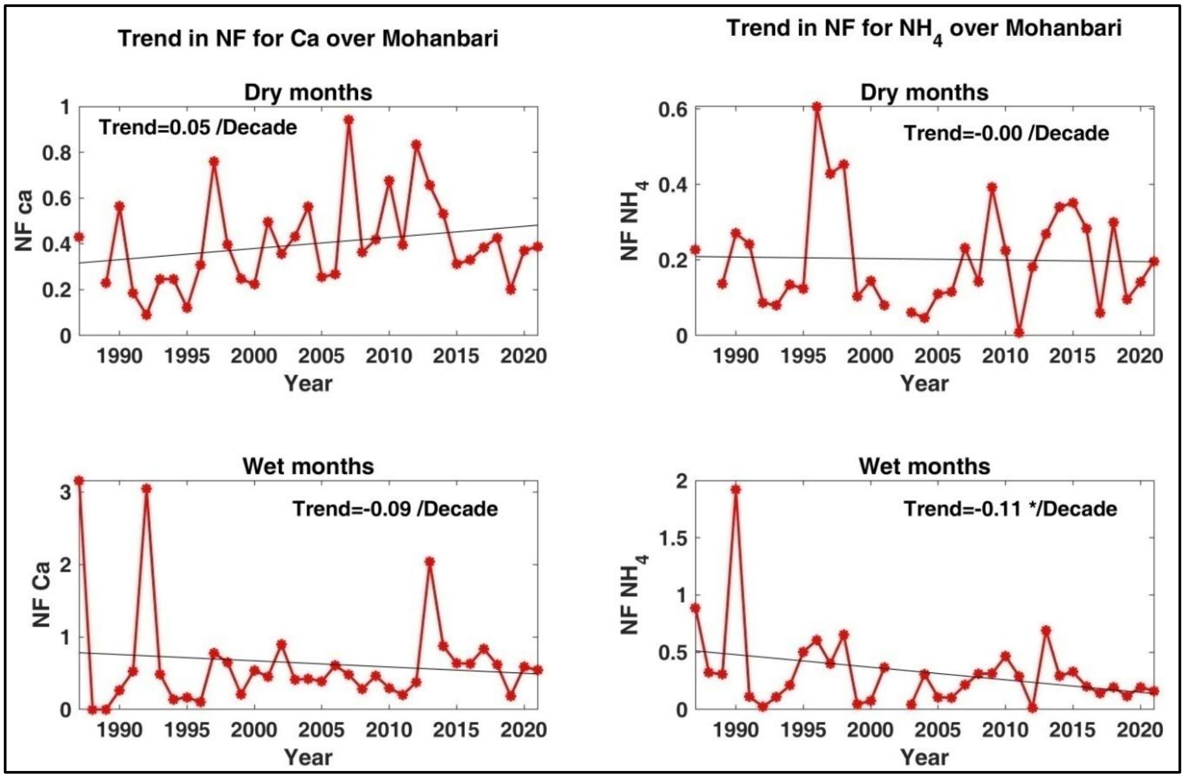

Fig.24. Long-term trend of NF Ca and NH4 at Mohanbari during 1987–2021

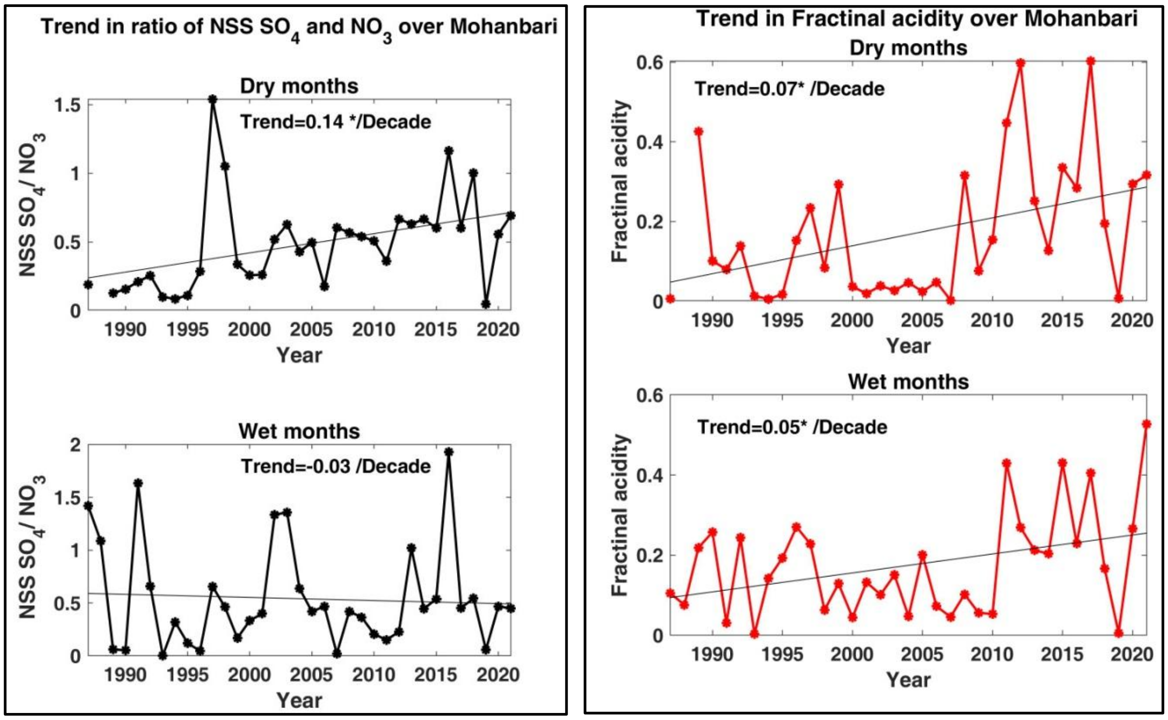

Fig.25. Long-term trend in the ratio of NSS SO_4 and NO_3 at Mohanbari during 1987–2021

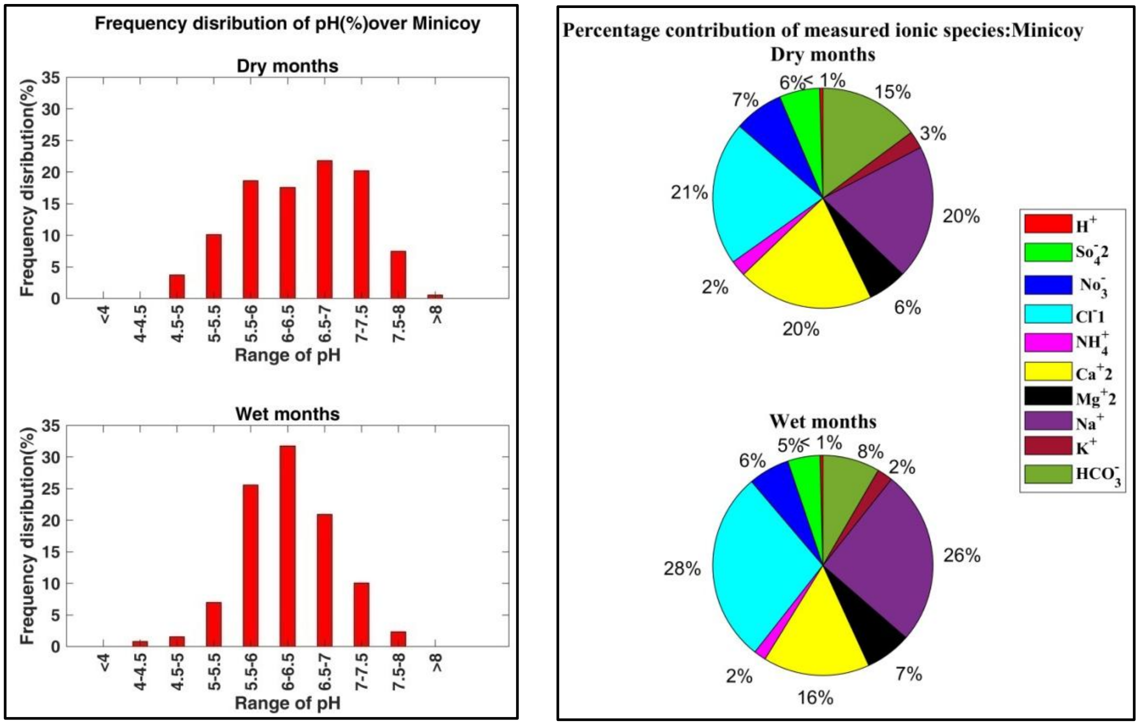

Fig. 26. Frequency distribution of pH and Percentage contribution of measured ionic species in Rain water at Minicoy during 1987-2021

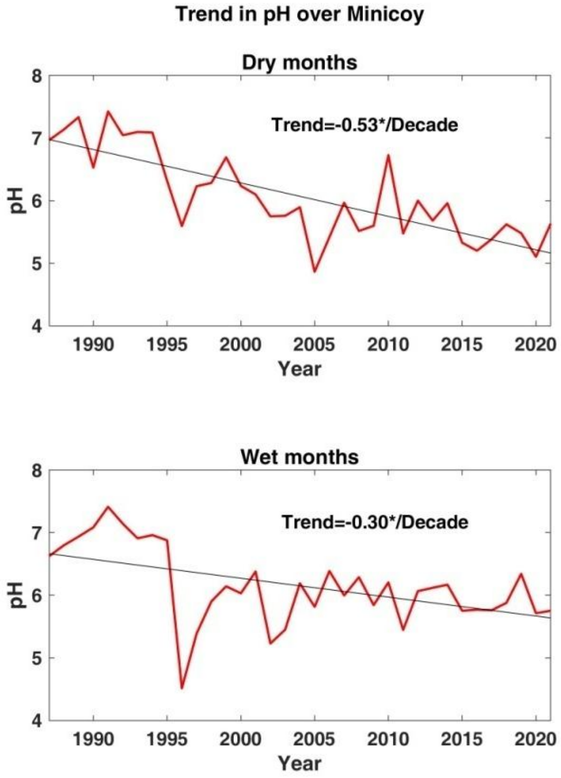

Fig. 27. Long-term trend of pH at Minicoy during 1987–2021

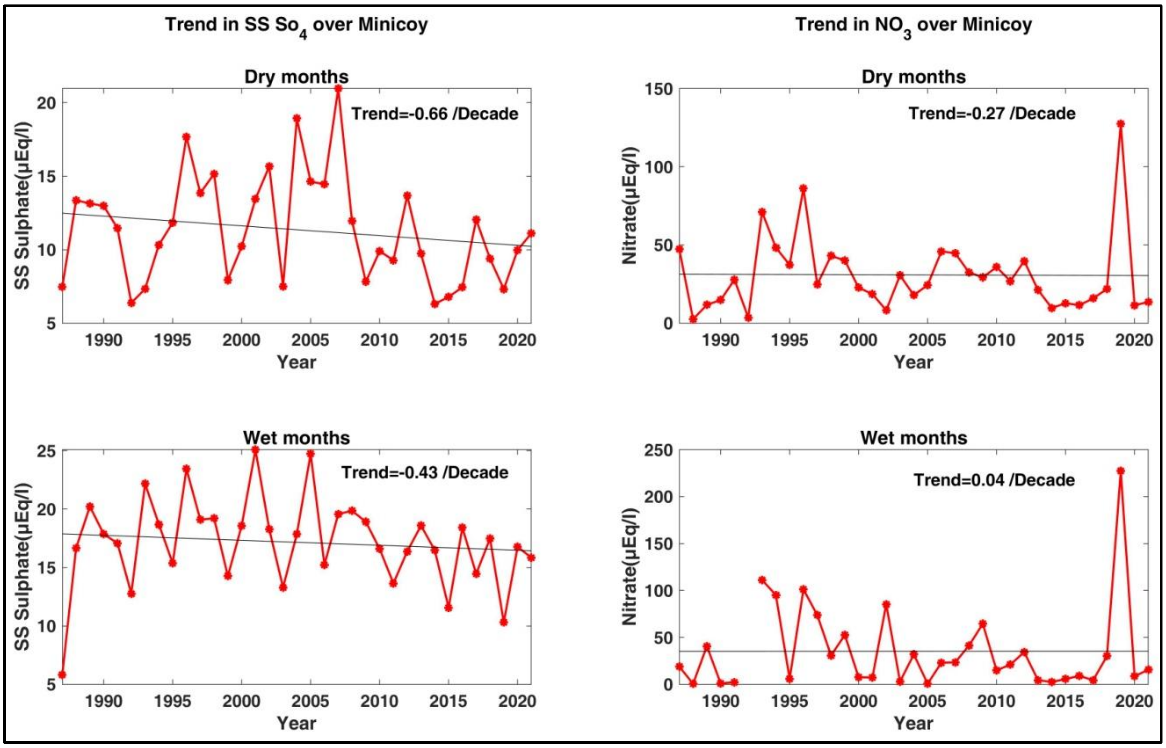

Fig. 28. Long-term trend of SS SO4 and NO3 at Minicoy during 1987–2021

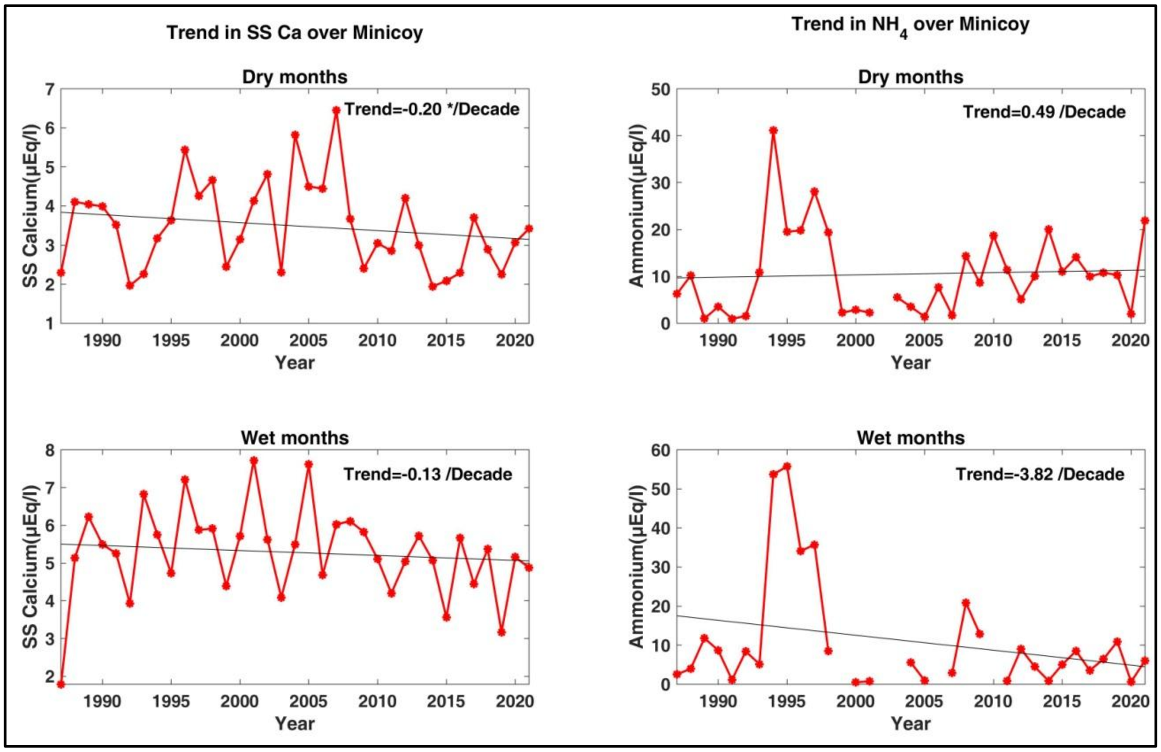

Fig.29. Long-term trend of SS Ca and NH_4 at Minicoy during 1987–2021

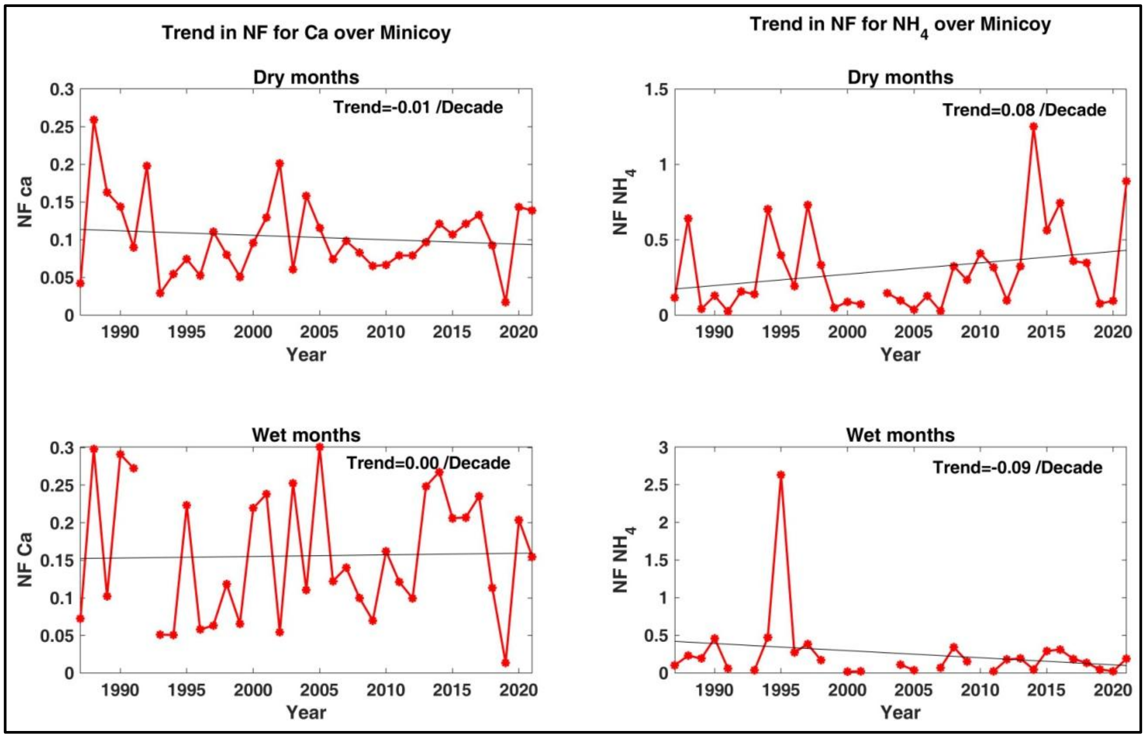

Fig.30. Long-term trend of NF of SS Ca and NH4 at Minicoy during 1987–2021

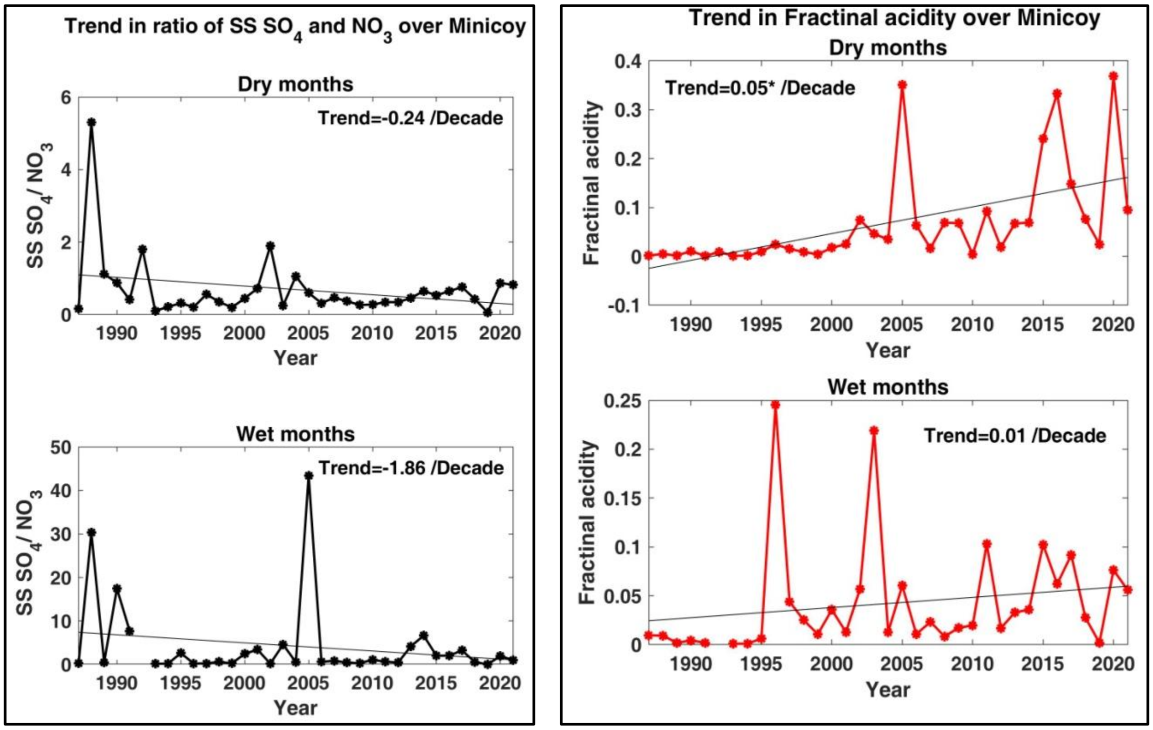

Fig. 31. The long-term trend in the ratio of SS SO_4 and NO_3 and fractional acidity at Minicoy during 1987–2021

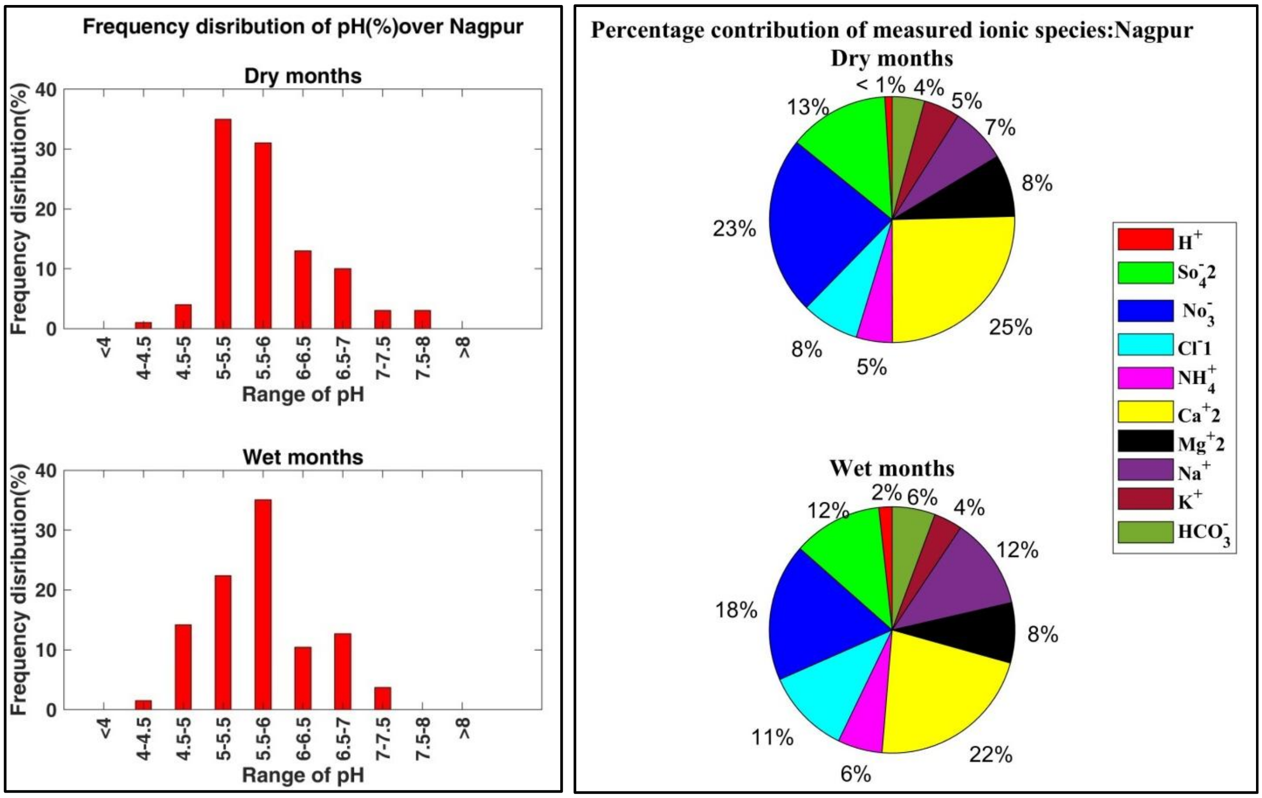

Fig. 32. Frequency distribution of pH and Percentage contribution of measured ionic species in Rainwater at Nagpur during 1987-2021

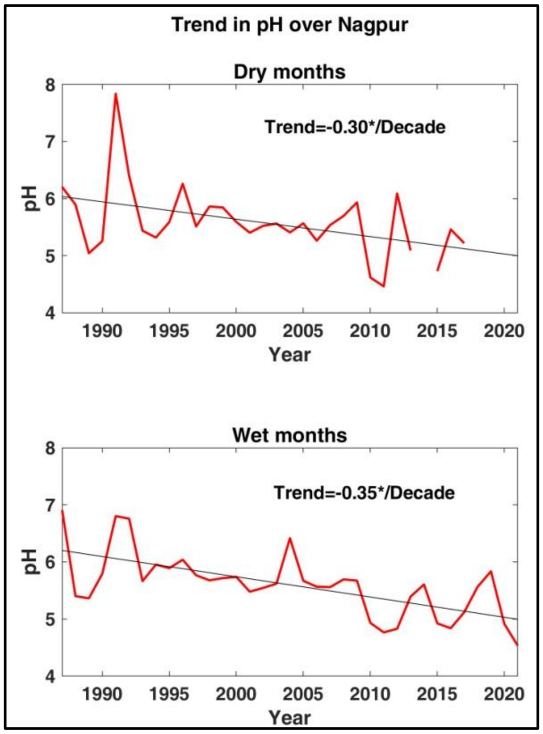

Fig. 33. Long-term trend of pH at Nagpur during 1987–2021

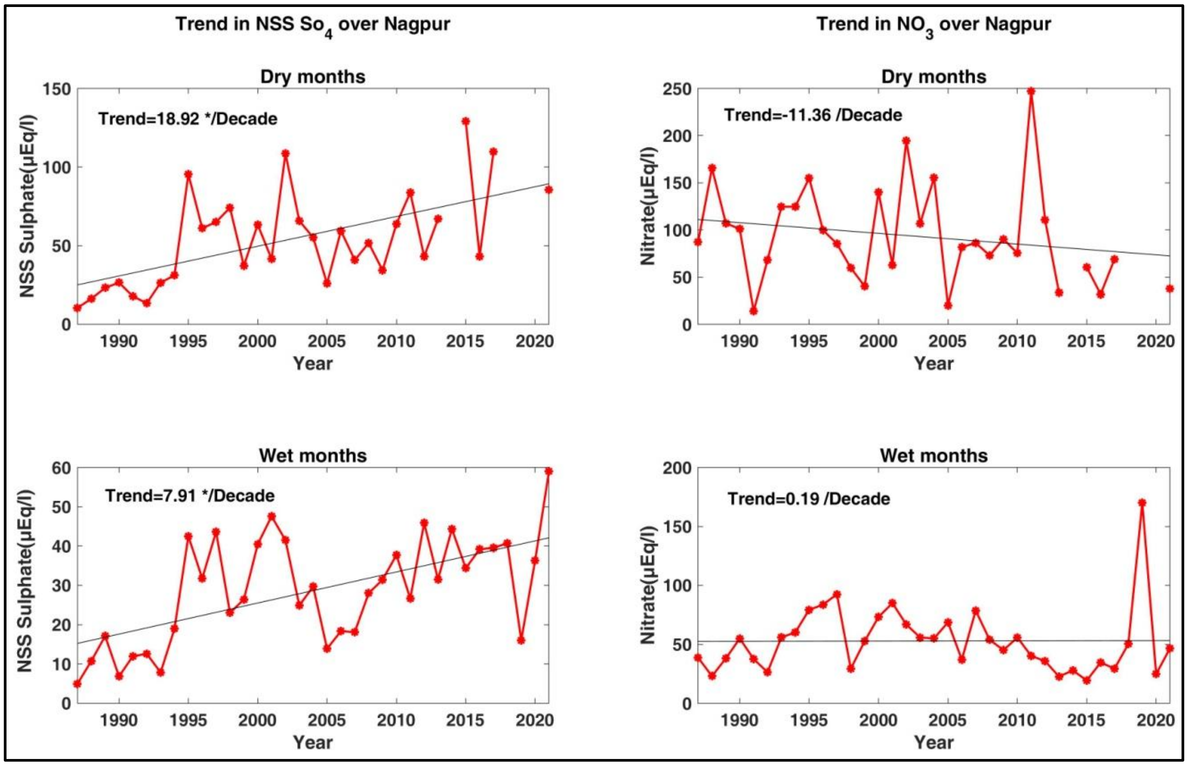

Fig. 34. Long-term trend of NSS SO4 and NO3 at Nagpur during 1987–2021

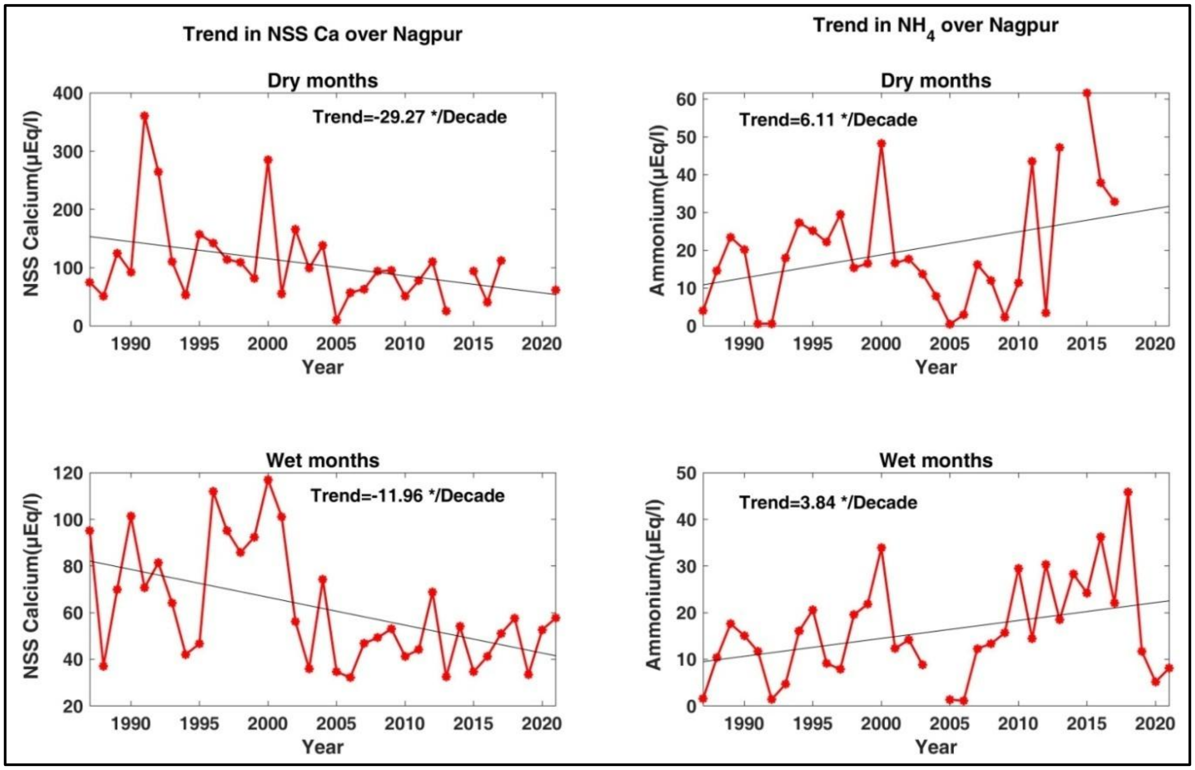

Fig.35. Long-term trend of NSS Ca and NH_4 at Nagpur during 1987–2021

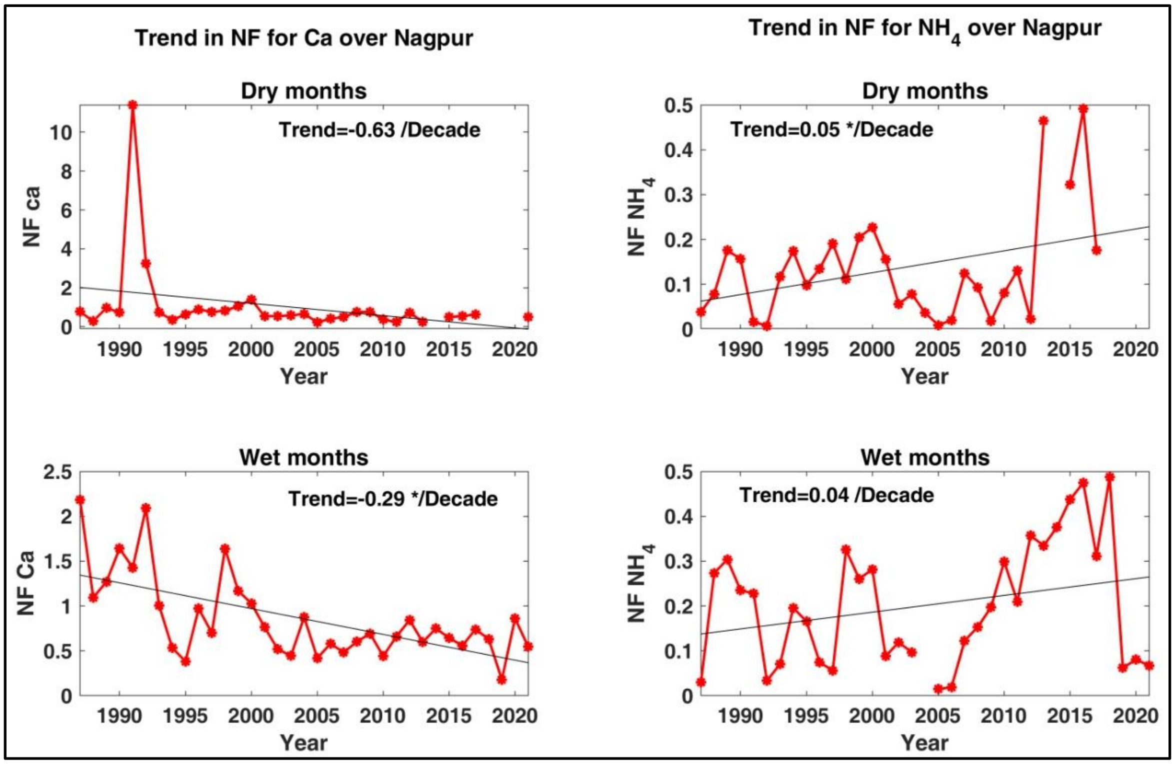

Fig.36. Long-term trend of NF of NSS Ca and NH4 at Nagpur during 1987–2021

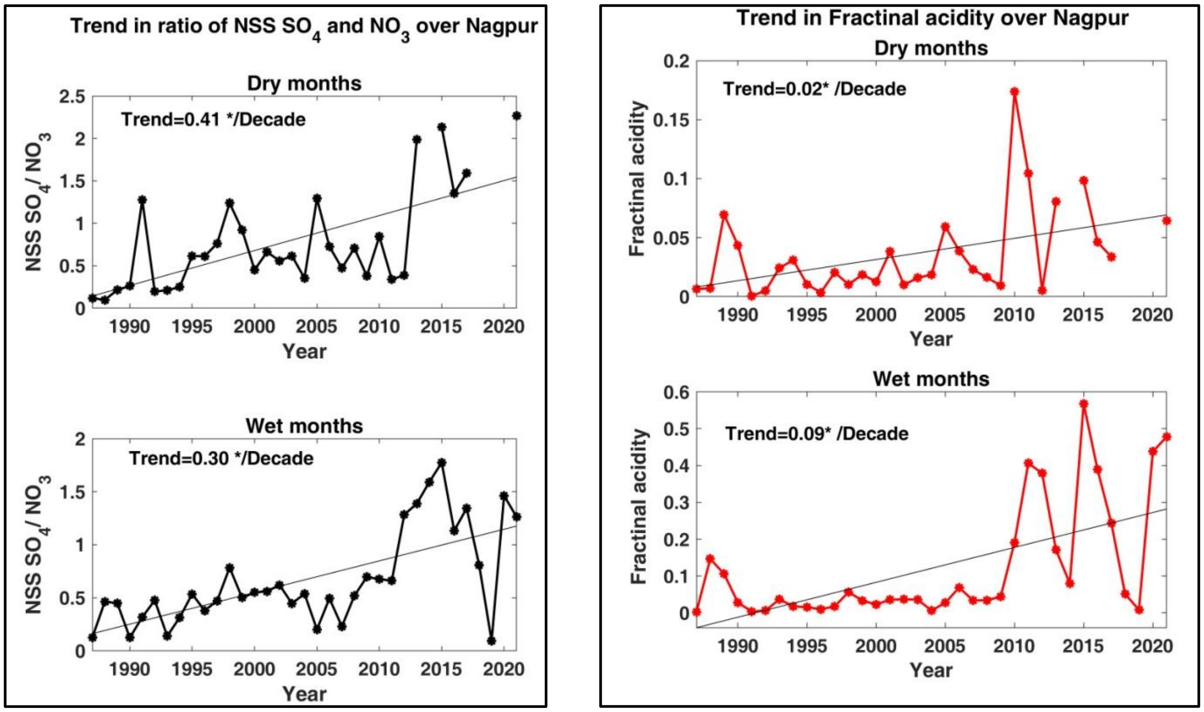

Fig.37. Long-term trend in the ratio of NSS SO_4 and NO_3 and fractional acidity at Nagpur during 1987–2021

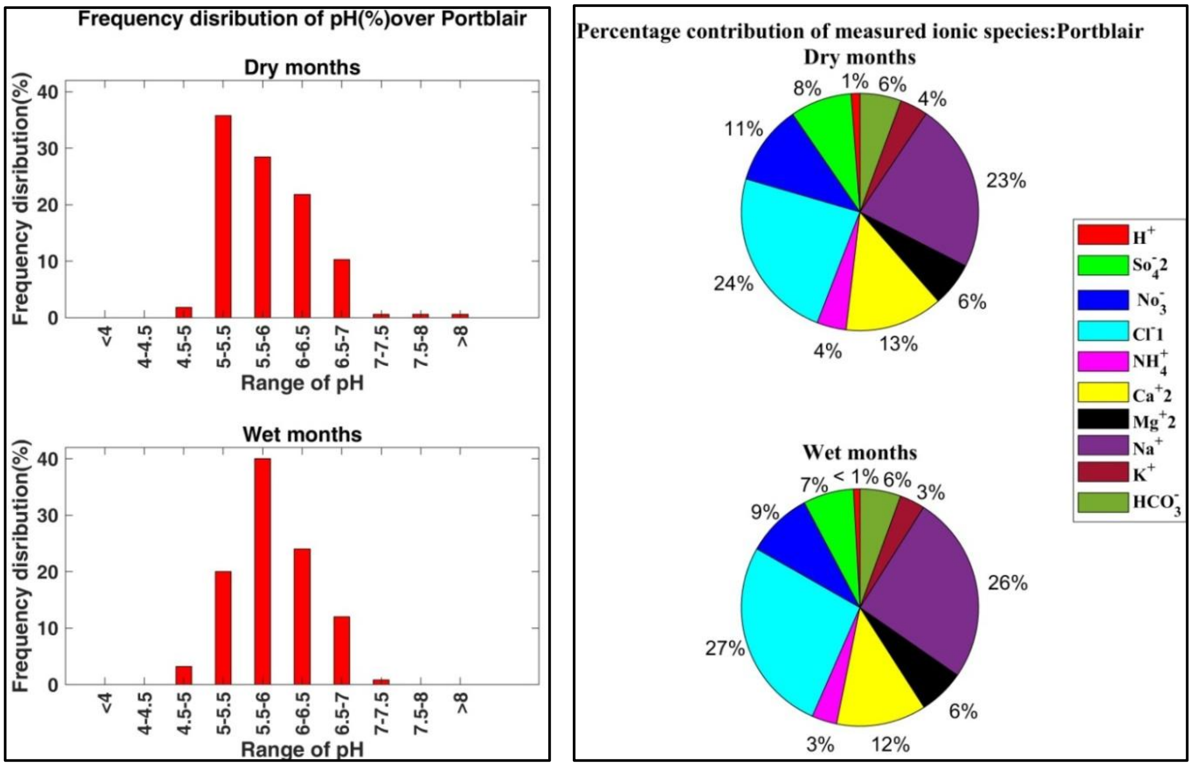

Fig.38. Frequency distribution of pH and Percentage contribution of measured ionic species in RW at Port Blair during 1987-2021

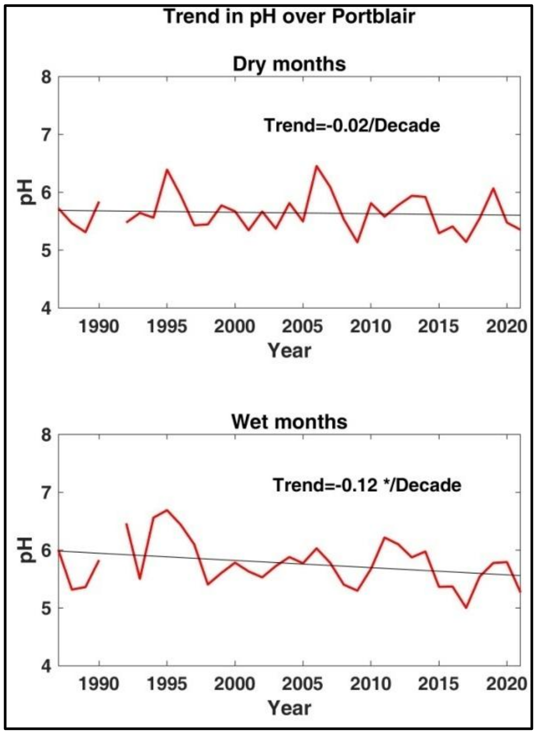

Fig. 39. Long-term trend of pH at Portblair during 1987–2021

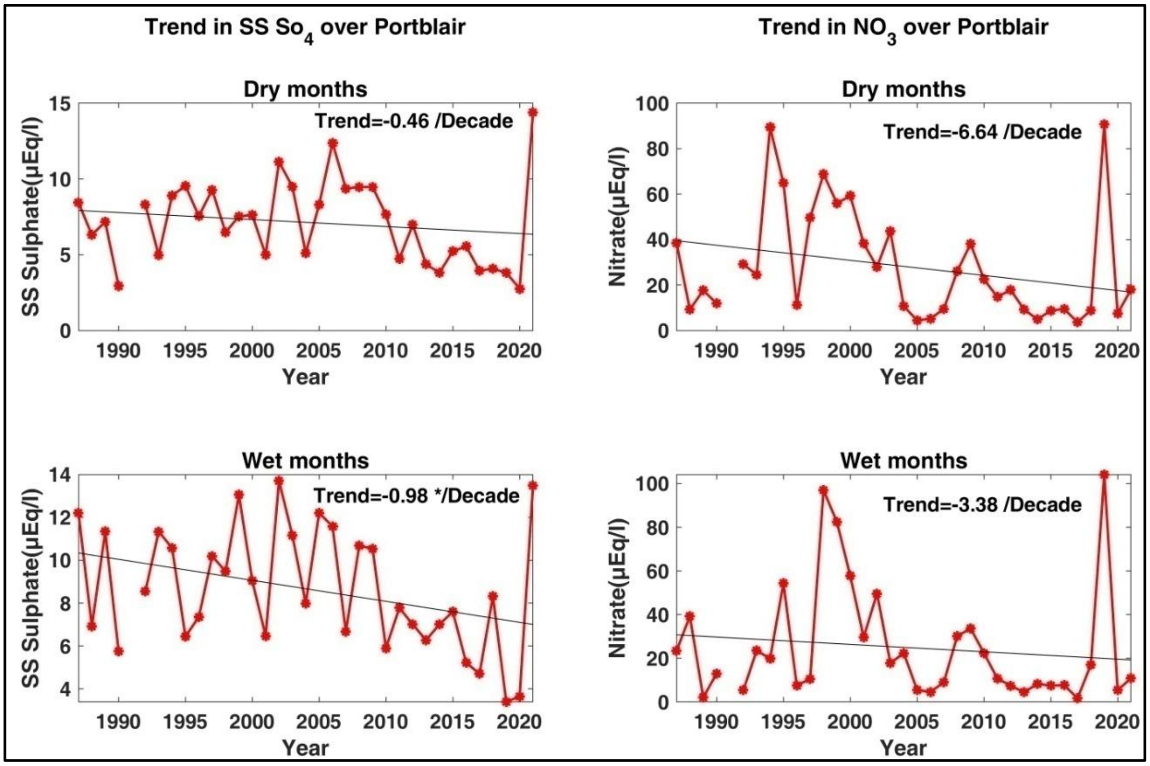

Fig. 40. Long-term trend of SS SO4 and NO3 at Port Blair during 1987–2021

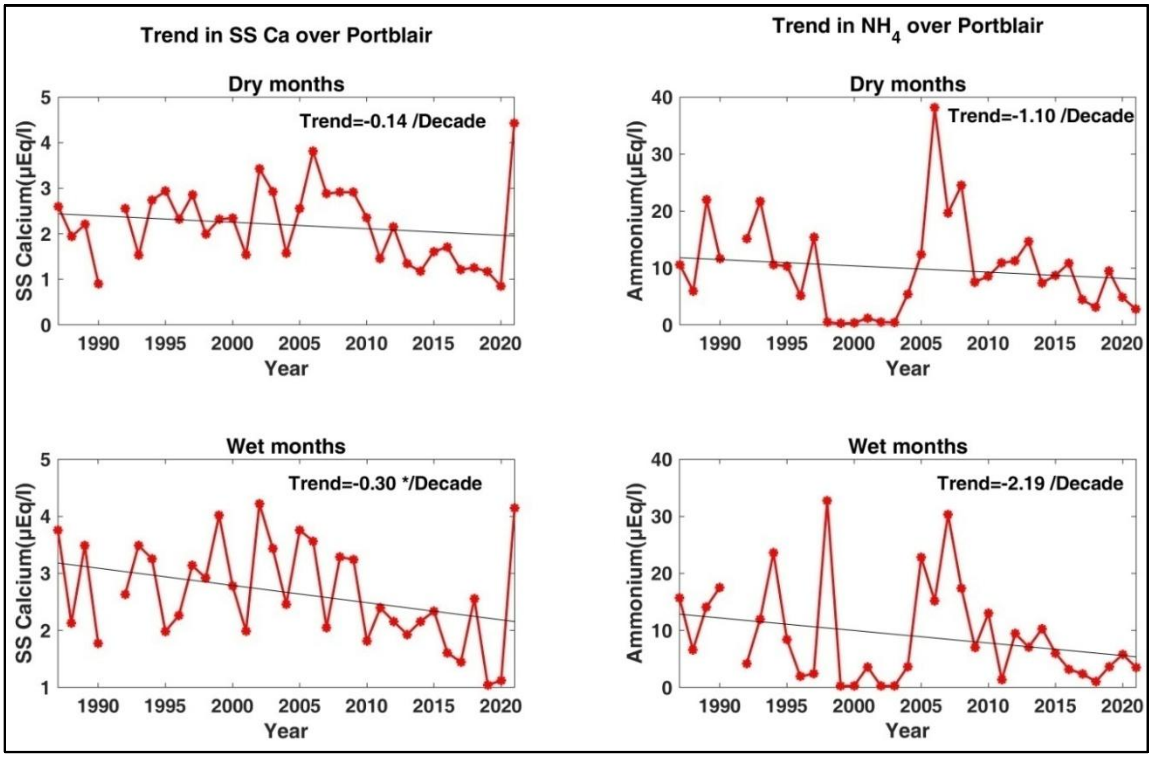

Fig.41. Long-term trend of SS Ca and NH_4 at Port Blair during 1987–2021

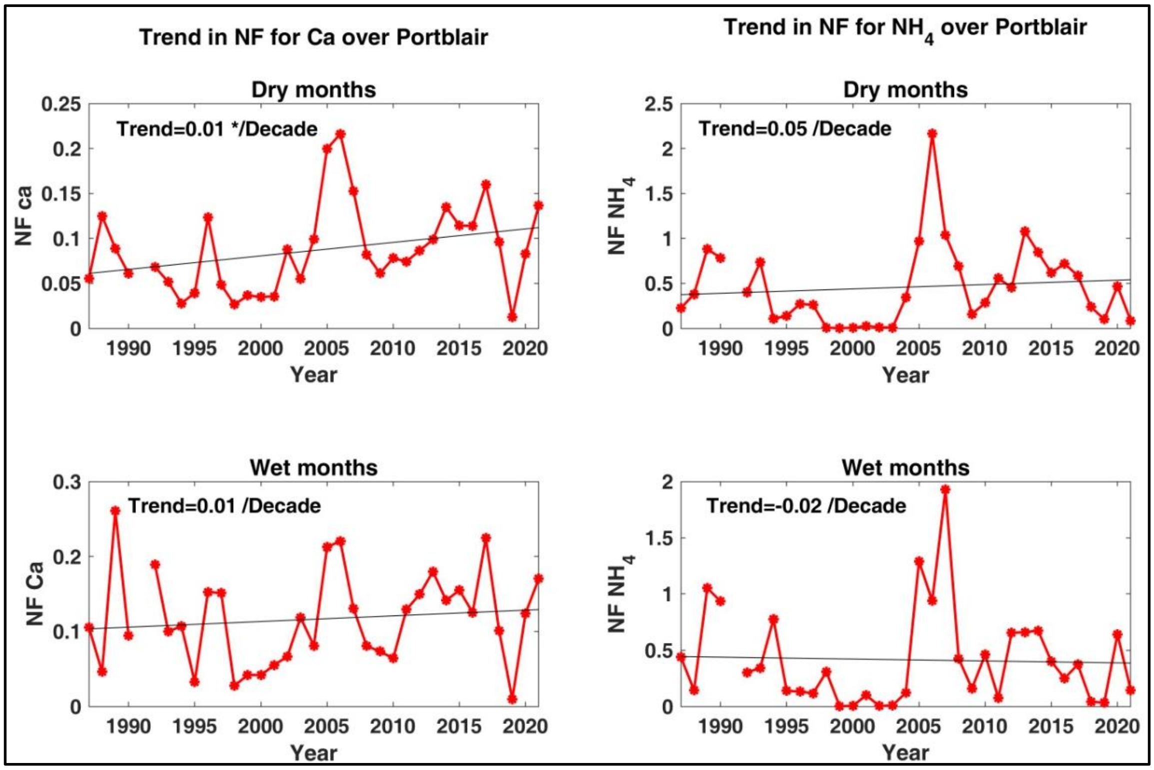

Fig.42. Long-term trend of NF of SS Ca and NH4 at Port Blair during 1987–2021

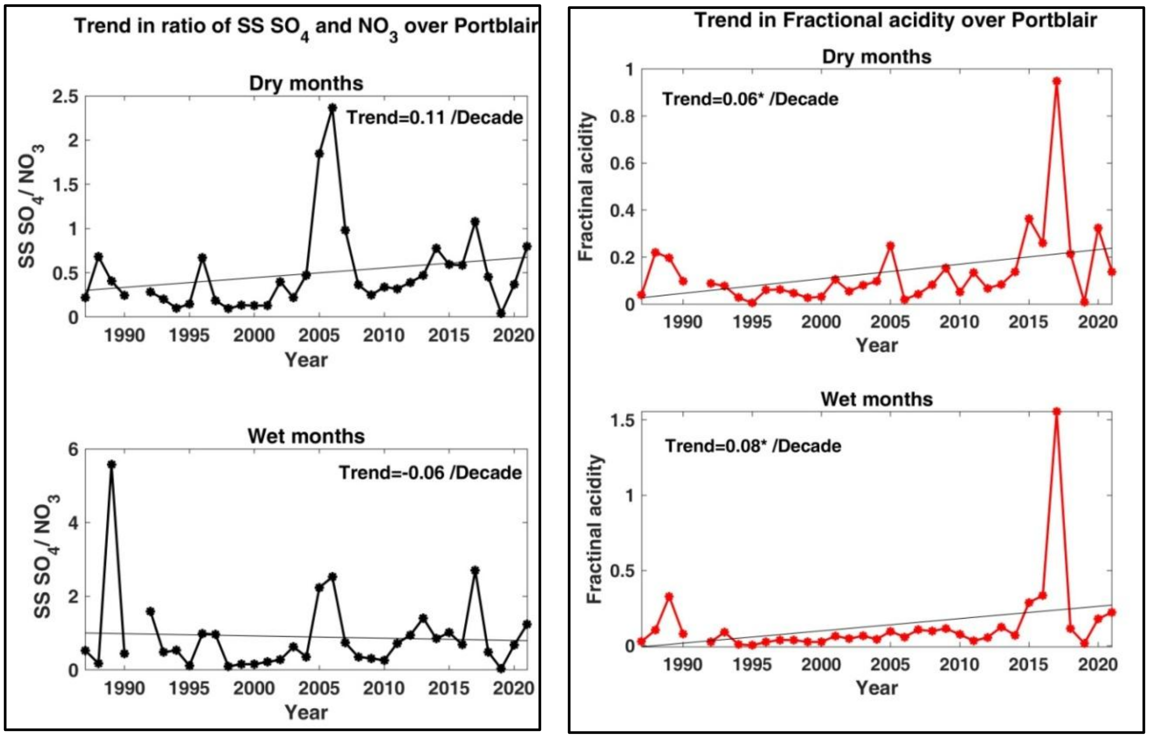

Fig. 43. Long-term trend in the ratio of NSS SO_4 and $NO_3$and fractional acidity at Portblair during 1987–2021

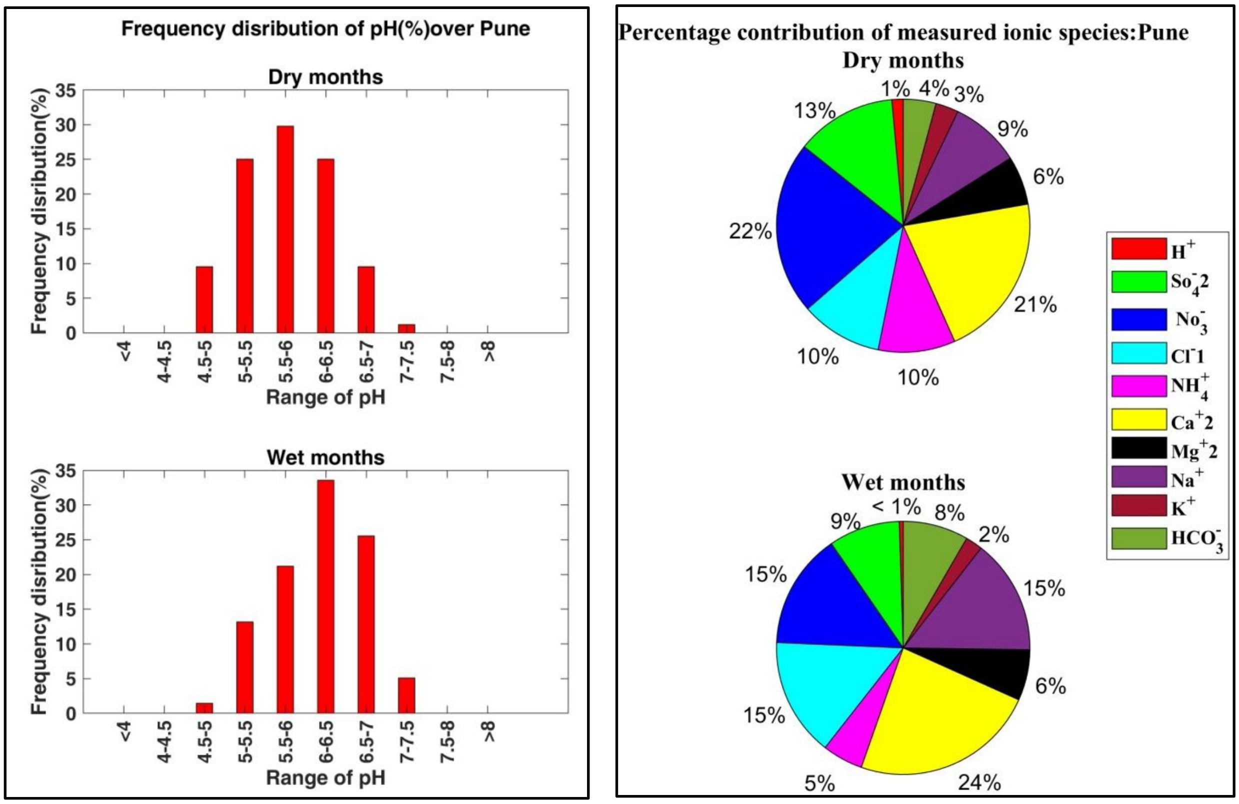

Fig.44. Frequency distribution of pH and Percentage contribution of measured ionic species in Rainwater at Pune during 1987-2021

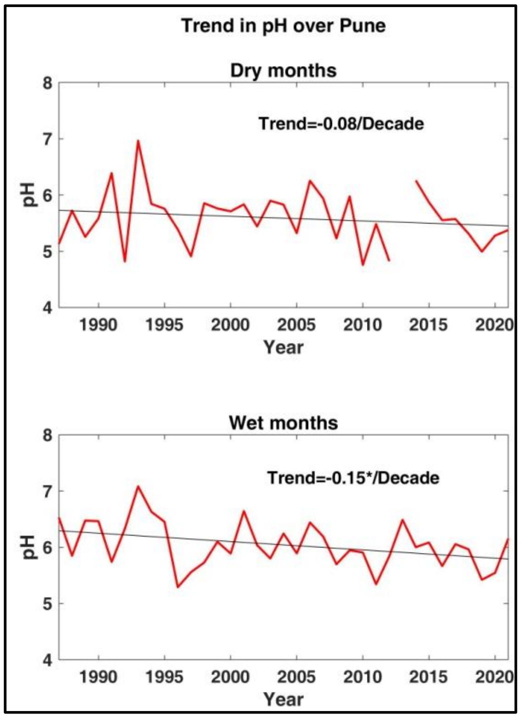

Fig. 45. Long-term trend of pH at Pune during 1987–2021

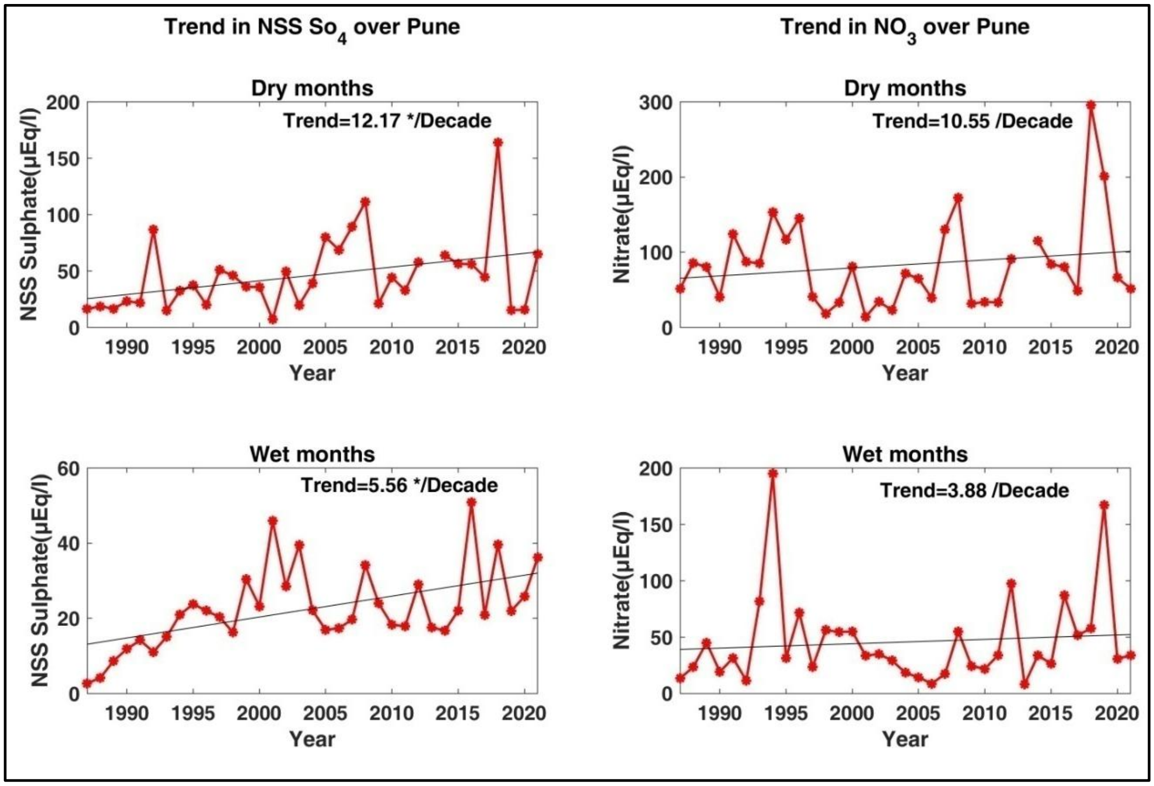

Fig. 46. Long-term trend of NSS SO4 and NO3 at Pune during 1987–2021

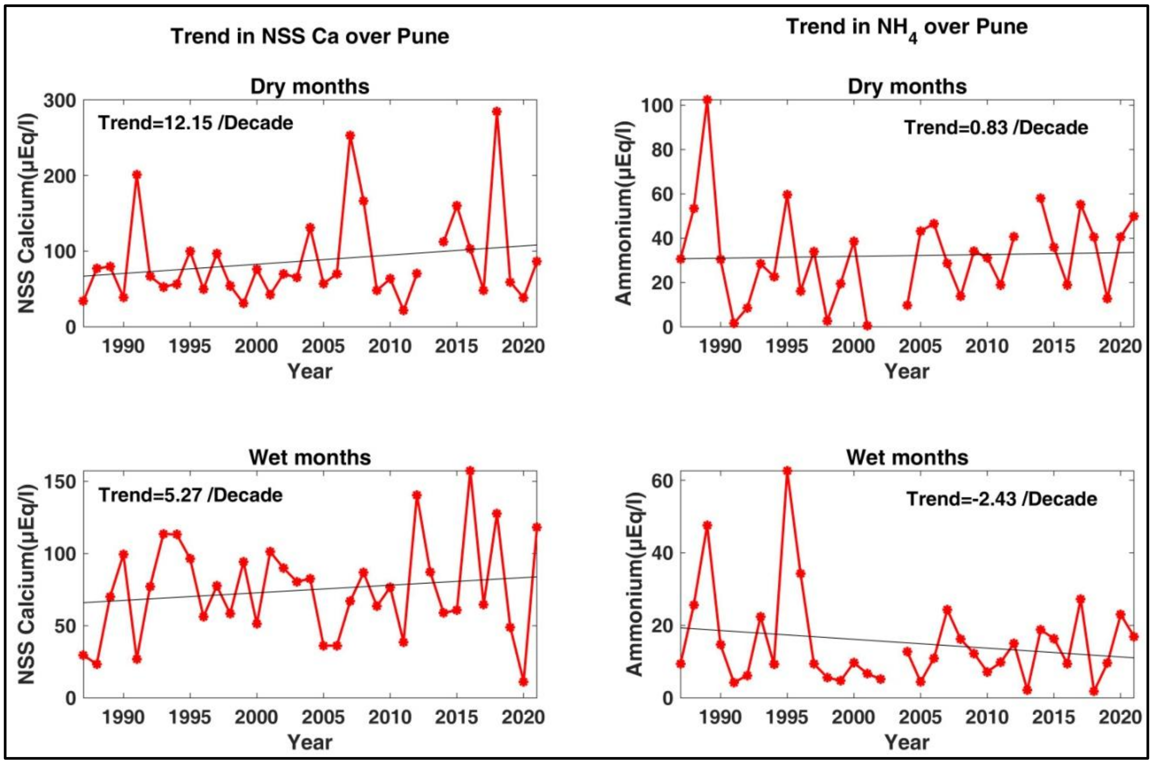

Fig.47. Long-term trend of NSS Ca and NH$_4$ at Pune during 1987–2021

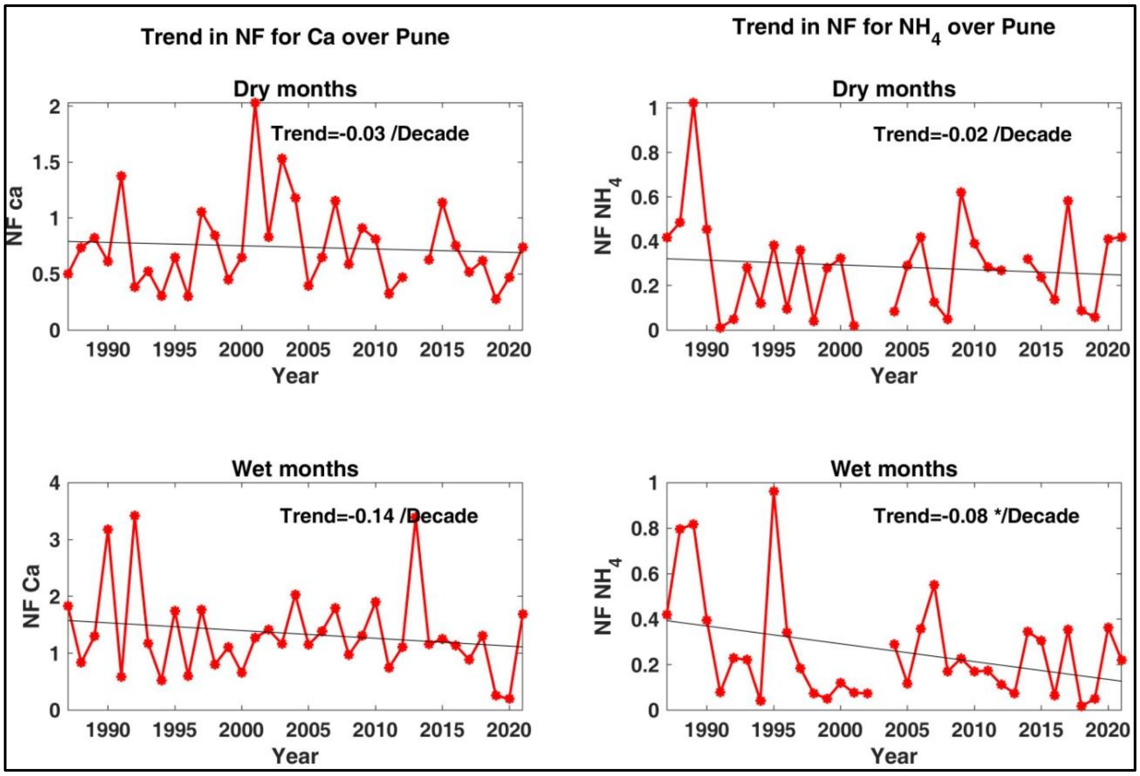

Fig.48. Long-term trend of NF of NSS Ca and NH4 at Pune during 1987–2021

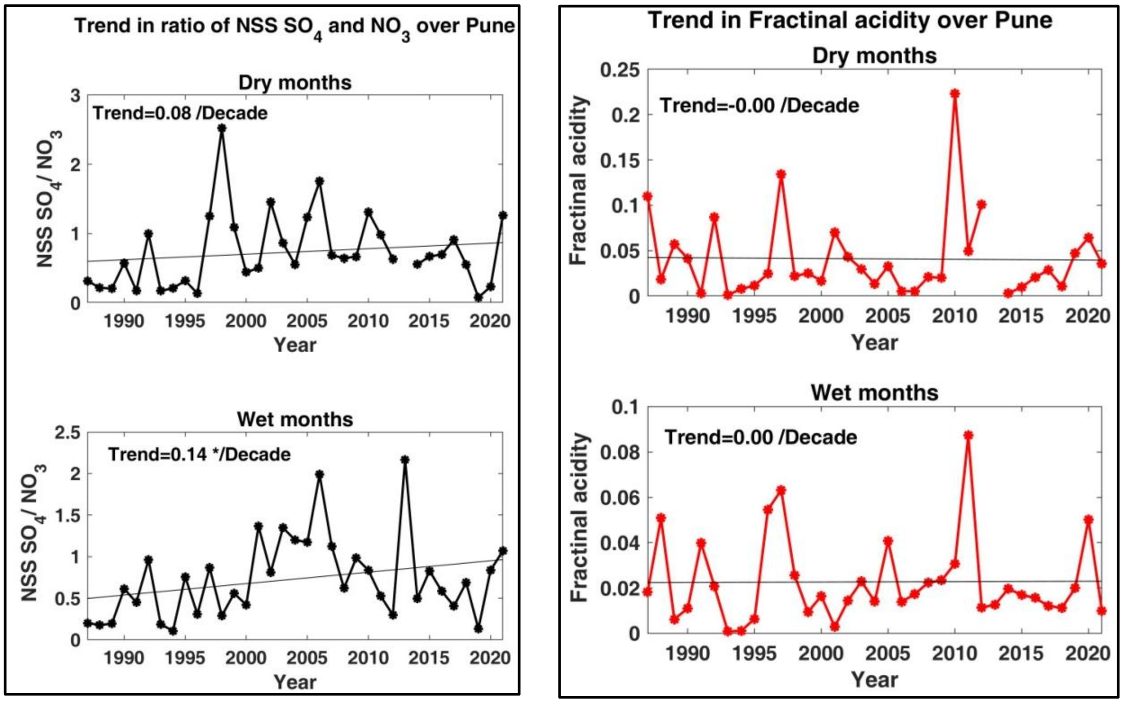

Fig .49. Long-term trend in the ratio of NSS SO_4 and $NO_3$and fractional acidity at Pune during 1987–2021

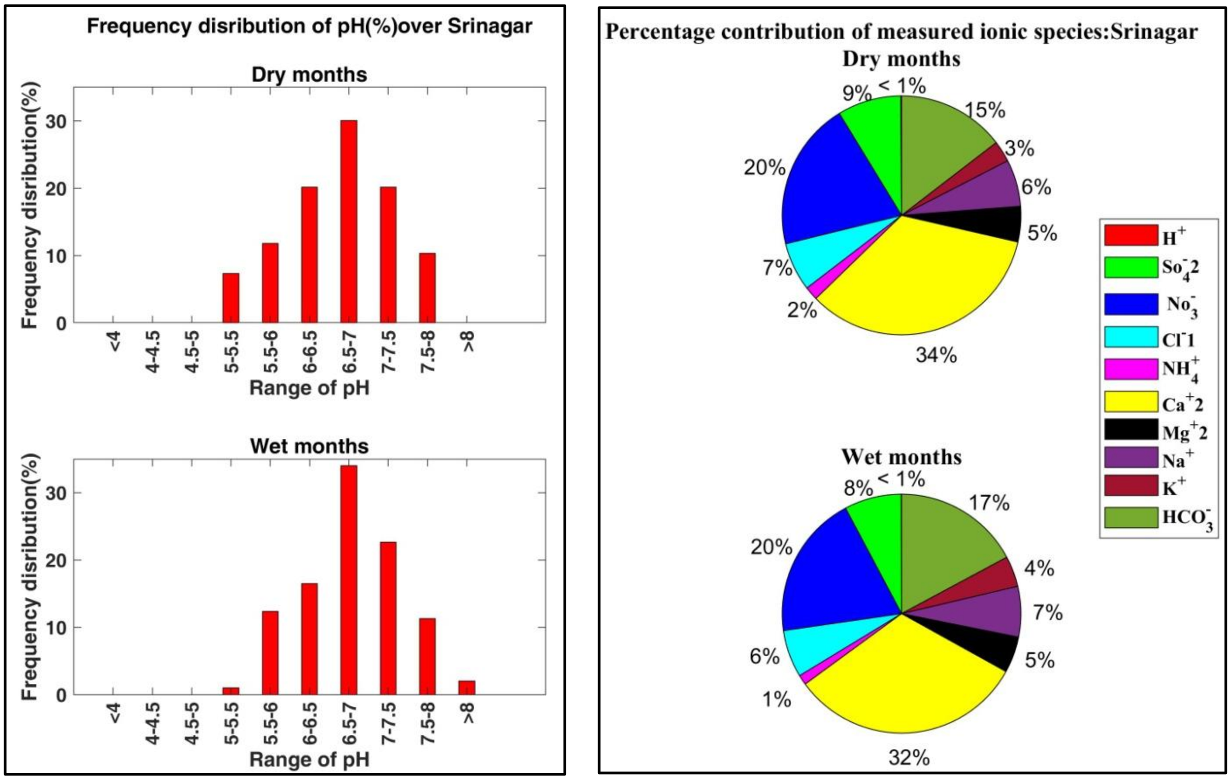

Fig.50. Frequency distribution of pH and Percentage contribution of measured ionic species in RW at Srinagar during 1987-2021

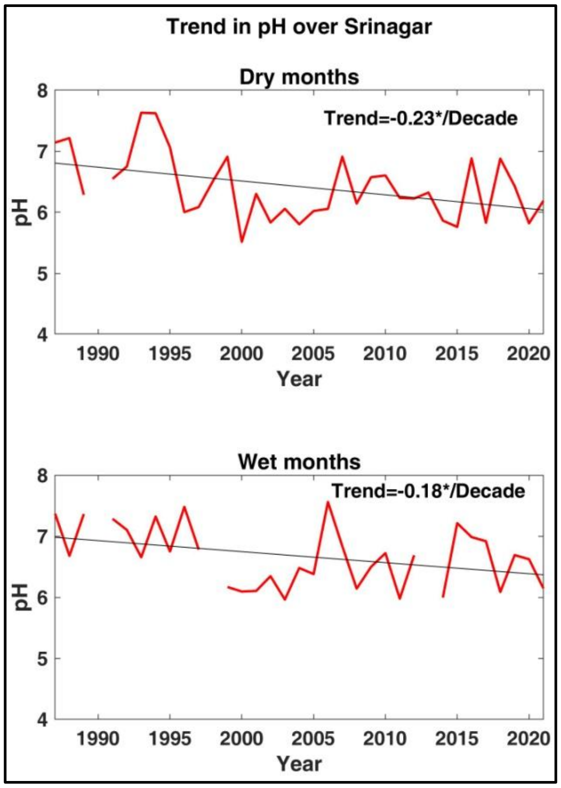

Fig. 51. Long-term trend of pH at Srinagar during 1987–2021

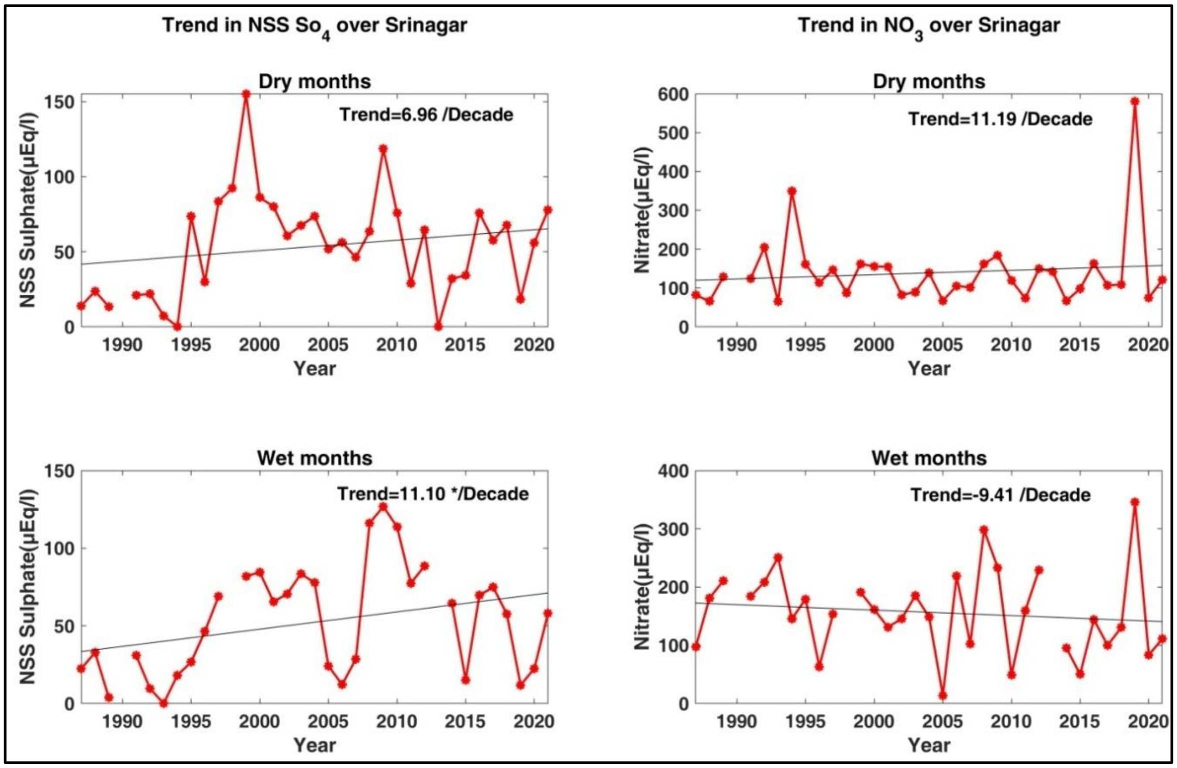

Fig. 52. Long-term trend of NSS SO4 and NO3 at Srinagar during 1987–2021

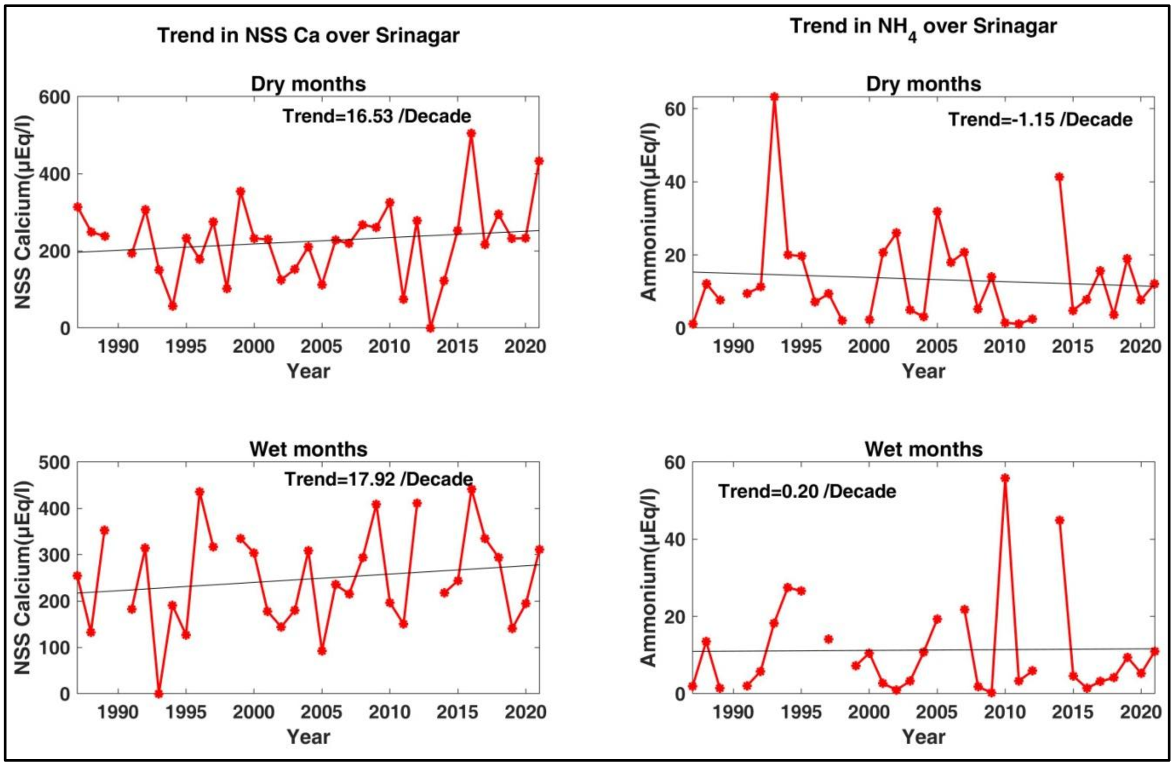

Fig.53. Long-term trend of NSS Ca and NH4 at Srinagar during 1987–2021

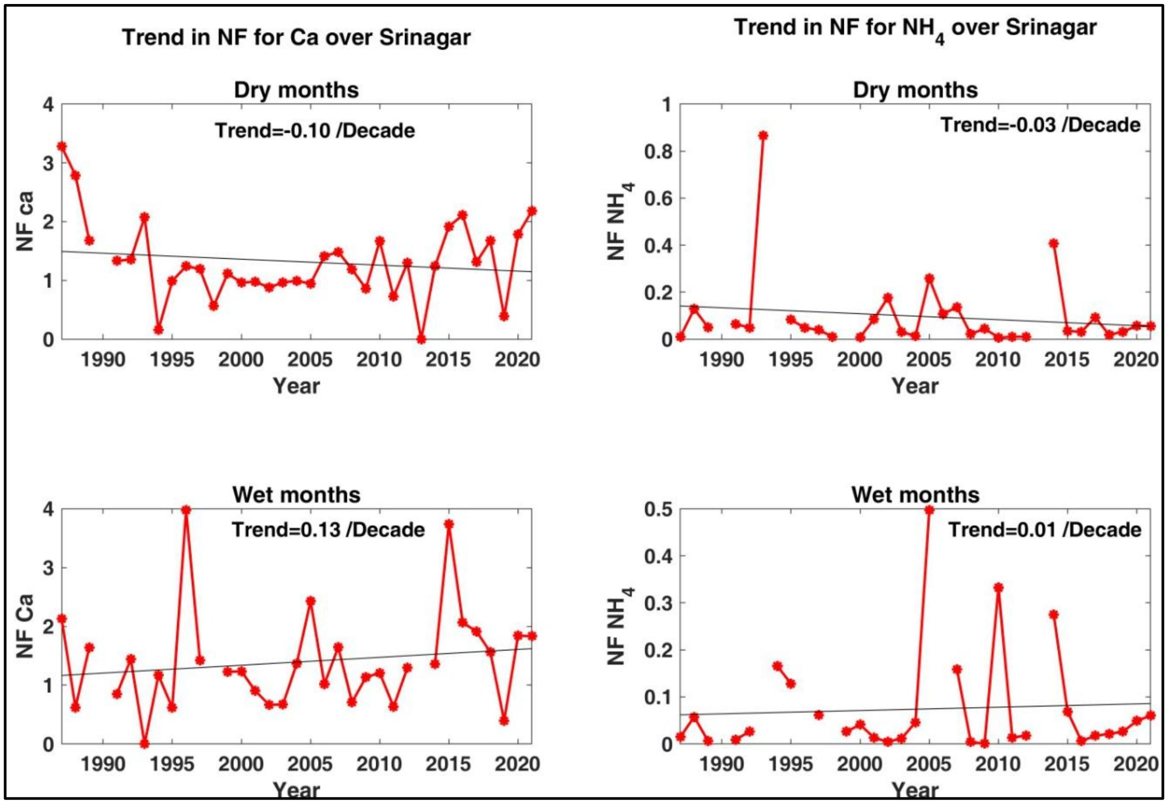

Fig.54. Long-term trend of NF of NSS Ca and NH4 at Srinagar during 1987–2021

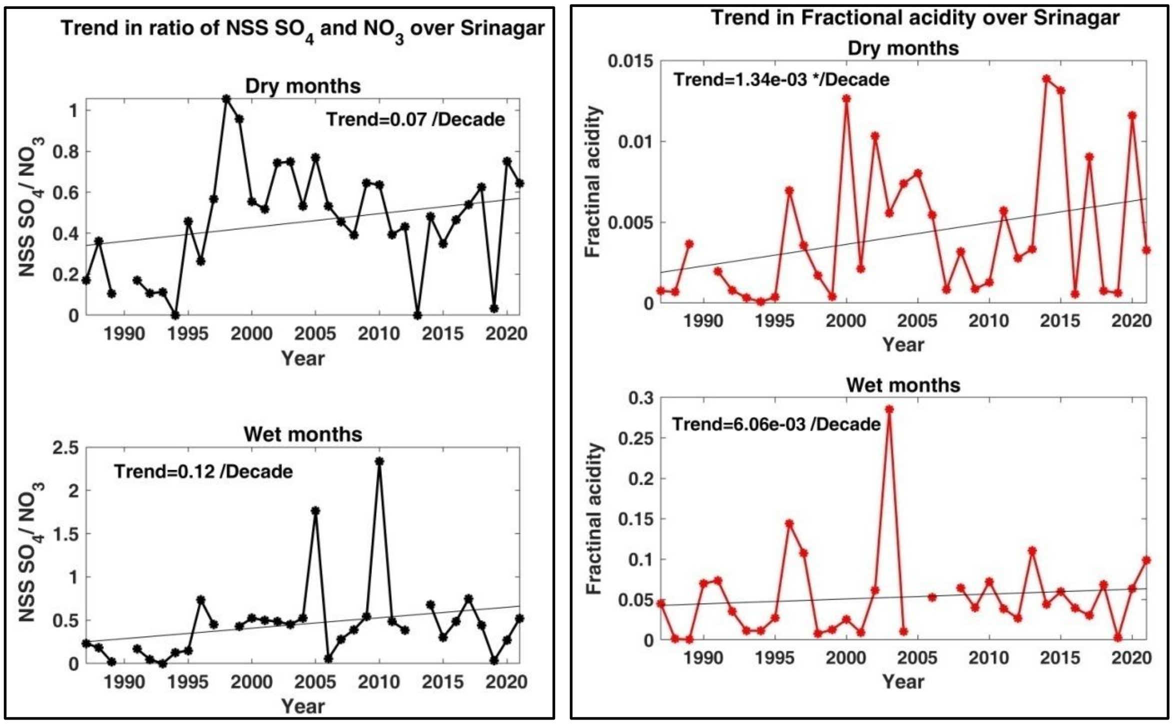

Fig. 55. Long-term trend in the ratio of NSS SO_4 and NO_3 at Srinagar during 1987–2021

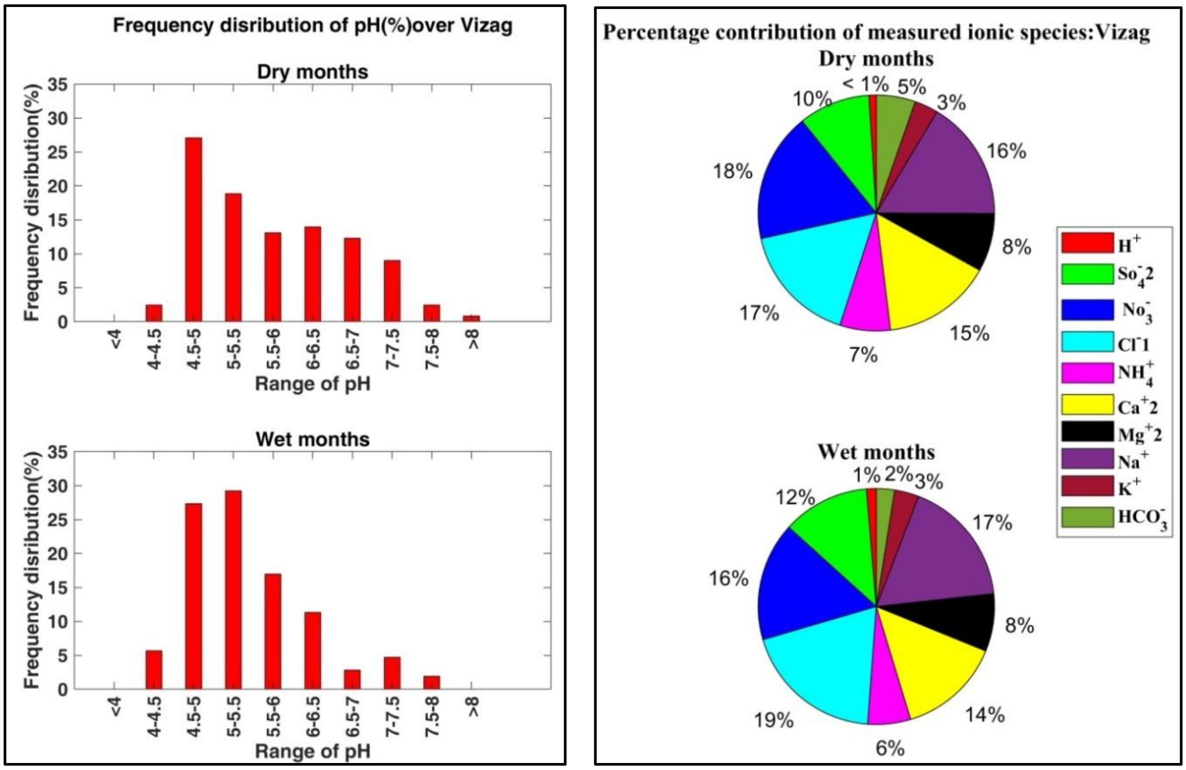

Fig. 56. Frequency distribution of pH and Percentage contribution of measured ionic species in Rainwaterat Vizag during 1987-2021

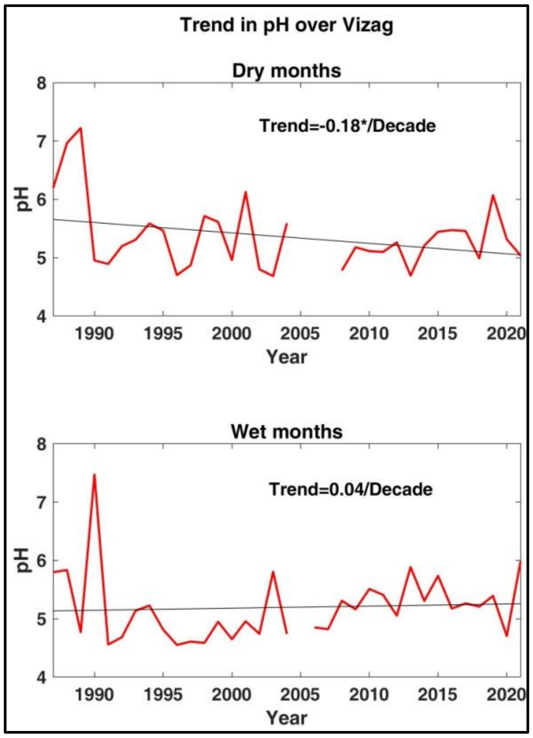

Fig. 57. Long-term trend of pH at Vizag during 1987–2021

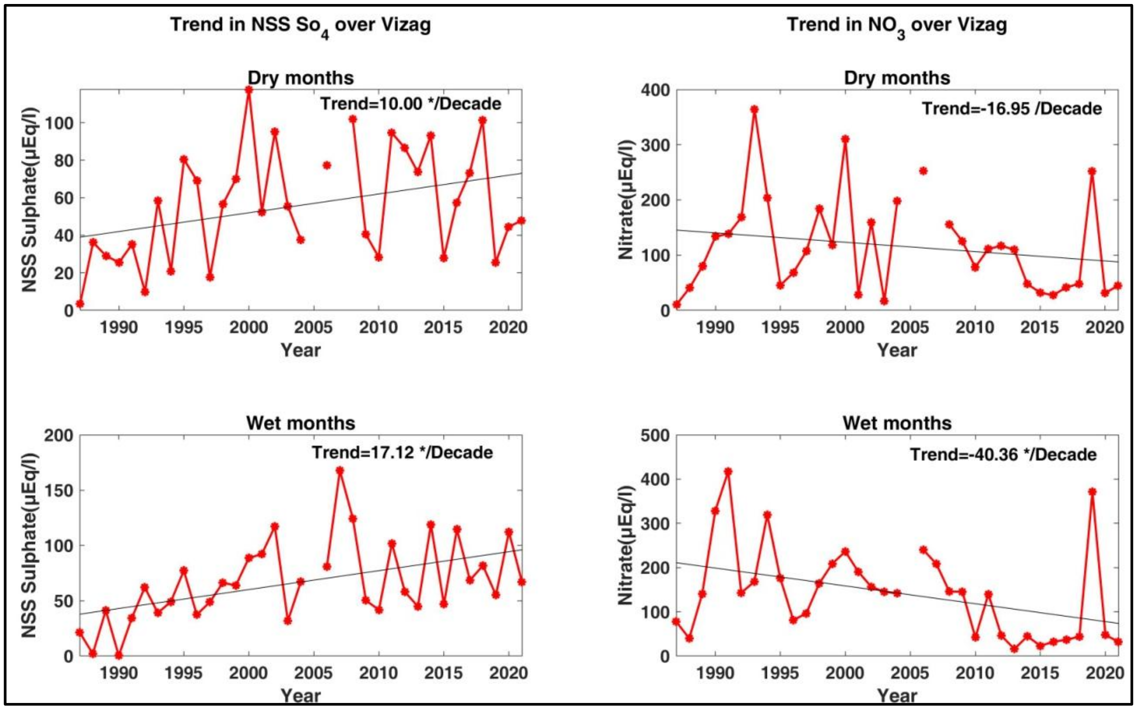

Fig.58. Long-term trend of NSS SO4 and NO3 at Srinagar during 1987–2021

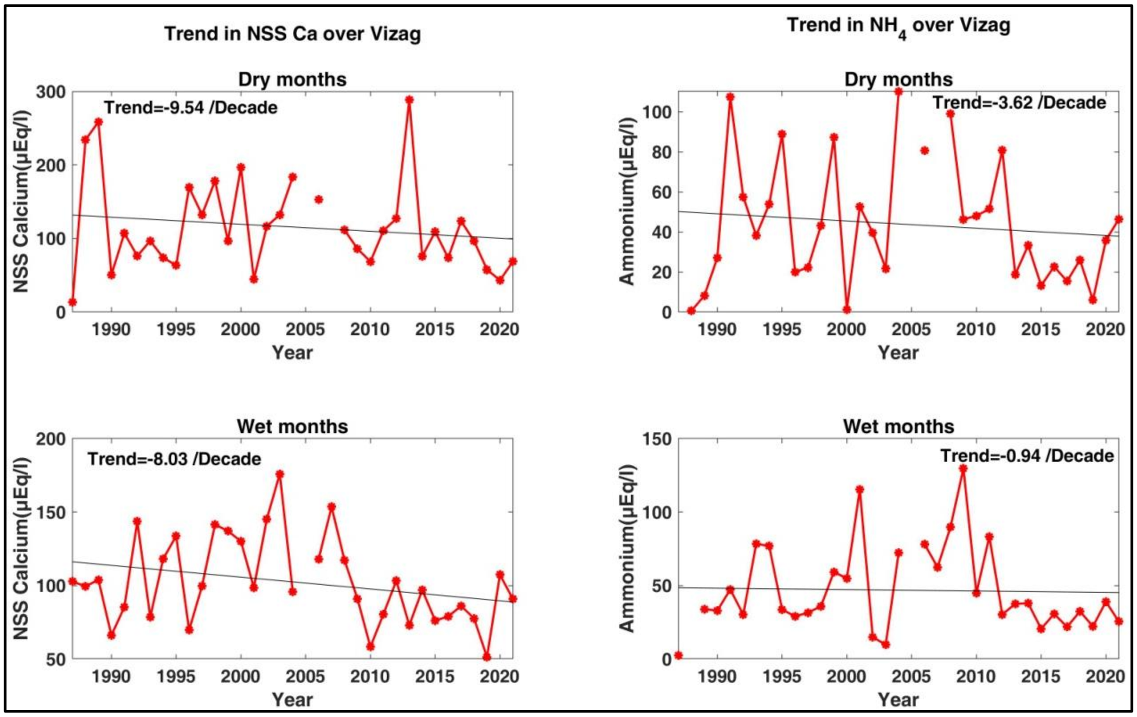

Fig.59. Long-term trend of NSS Ca and NH_4 at Vizag during 1987–2021

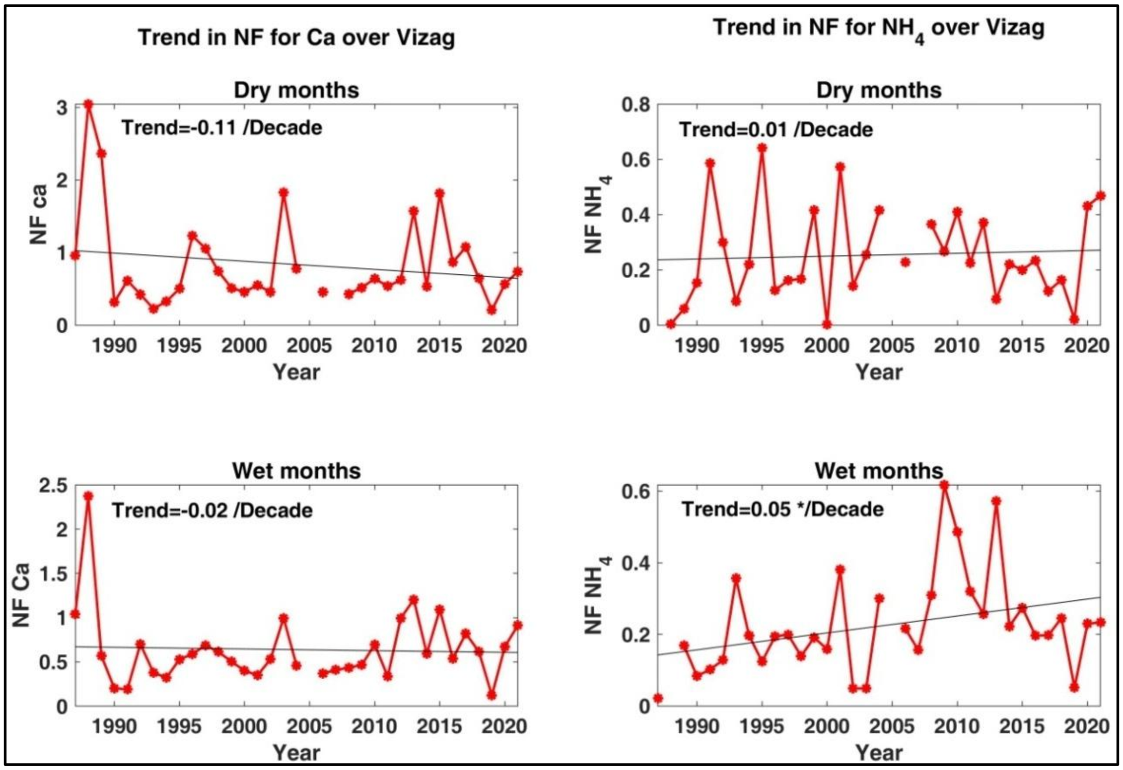

Fig.60. Long-term trend of NF of NSS Ca and NH4 at vizag during 1987–2021

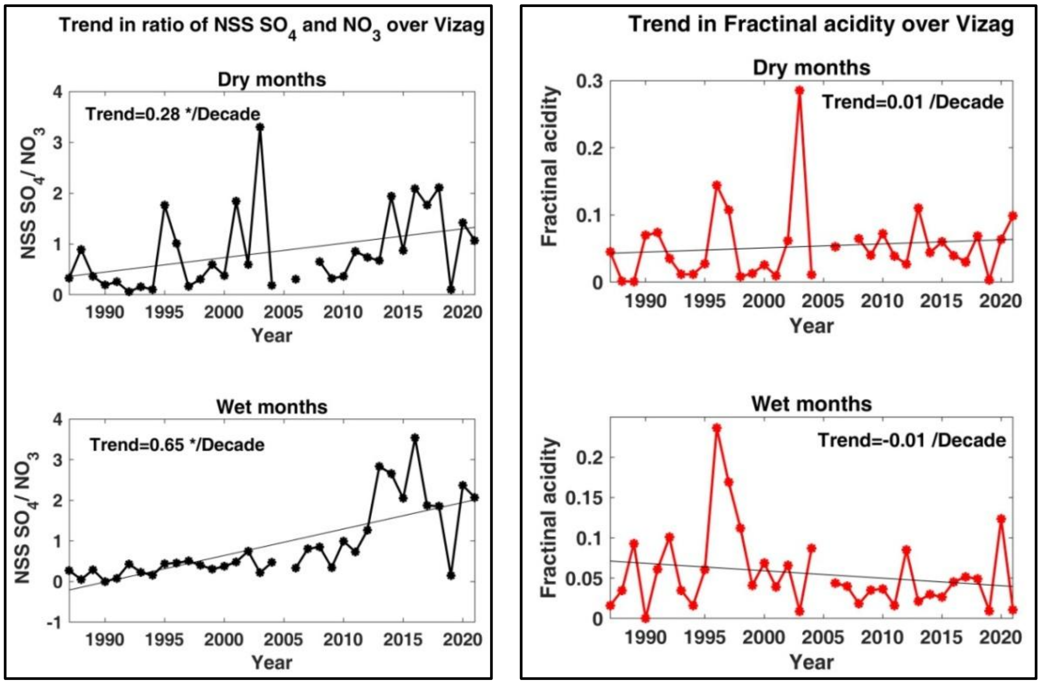

Fig. 61. Long-term trend in the ratio of NSS SO_4 and NO_3 and fractional acidityat Vizag during 1987–2021

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