Assessment of air quality and chemical fingerprints for atmospheric fine aerosols in an Indian smart city

Abhishek Gupta and Amit Dhir

Department of Environmental Science & Engineering, Marwadi University, Rajkot, India; School of Energy & Environment, Thapar Institute of Engineering & Technology, Patiala, India

ABSTRACT
Ambient air quality of Rajkot city is analyzed along with chemical characterization such as anions, cations, metals and non-sea salts (nss) to understand the chemical footprints on a regional scale. Two sites, rural and urban area are selected for sampling of PM$_{10}$,PM$_{2.5}$,SO$_2$ and NO$_2$, but no major differences are found in ambient air quality. The concentration of ions is found to be high during summer and winter, that is, months of May and December. The concentration of anions and cations in chronological order is $\text{Cl}^-$ < $\text{SO}_4^{2-}$ < $\text{NO}_3^-$ < $\text{NO}_2$ < $\text{PO}_4^{3-}$ < $\text{F}^-$ and $\text{NH}_4^+$ < $\text{Ca}^{2+}$ < $\text{K}^+$ < $\text{Na}^+$ < $\text{Mg}^{2+}$. Similarly, the metal concentration follows the order Na$<$Mg$<$Al$<$Fe$<$Cr$<$Zn$<$Pb$<$Cu$<$Mn$<$As. Majority of metal concentration is lowest during the monsoon season and highest during post-monsoon seasons. Non-sea salts component of fine dust is found highest during the summer season, possibly due to westerly winds from the Arabian sea. Relative contribution by anthropogenic dust was maximum during winter and summer season whereas sea-salt dust in Monsoon and post-monsoon.

1. Introduction
With the advancements in the field of science and technology, all developing and developed countries are ushered toward rampant industrialization and urbanization, becoming the leading cause of numerous environmental problems [1,2]. The rising contributions from anthropogenic sources at the global and local levels are causing climatic- and health-related issues [3,4]. As reported by WHO, exposure to fine particulate matter leads to the death of approximately 7 million people every year worldwide [5,6]. Air pollutant’s acute and chronic health effects on humans are mainly determined by two parameters, that is, the concentration of pollutants and time of contact [7]. The primary sources of high pollutant concentrations in urban areas are agricultural burning, vehicular emission, industrial emission and others. Whereas for the agro-economic-based country, the major source is biomass burning [8].

Being a developing country, India’s Economic growth is supported by the agriculture and industrial sectors. Both the sectors are releasing many air pollutants in the ambient air [9]. According to the Indian Ministry of Agriculture, harvesting of crops generates about 500 Mt of crop residues annually, subsequently used as fodder for animals and fuel for domestic and industrial purposes. As per the Ministry of New & Renewable Energy, 92 Mt out of 140 Mt is surplus and is burned on-field each year [10]. The burning of crops generates solid as well as gaseous air pollutants, deteriorating the local air quality status. Study on the effect of biomass burning toward aerosol mass concentration for Patiala city in India was carried out using aerosol optical depth and ion analysis [11]. A similar result has been reported using ion analysis for Indo-Gangetic plain (IGP), India [12,13]. Moreover, this situation gets worse during the winter season due to the reduction in mean mixing depth and poor convection [8,14].

There are different metrics and methods used to measure air quality, related pollutants and their contributions. The quality of local and regional ambient air is being represented by the Air Quality Index (Sub-Indices method), a numerical term that can directly relate to associated health effects. The contribution of vehicular mobility to air pollution can be evaluated by standardizing the concentration of various criteria pollutants like PM$_{10}$, PM$_{2.5}$, NO$_2$, and SO$_2$ [15].

Air quality can also be represented by the chemical characterization of aerosol, which includes ion analysis, metal analysis and OC/EC analysis. The source and process by which aerosols have gone through can be examined by knowing the composition [16,17]. The presence of different water-soluble cations and anions in coarse and fine particulate matter present in the lower atmosphere have been investigated for seasonal and spatial variation [16,18]. In September 2015, 193 countries, developing and developed countries alike, adopted the Sustainable Development Goals (SDG), known officially as the 2030 Agenda for Sustainable
Development [19,20]. Air pollution is recognized as a pressing sustainability concern and is directly mentioned in two SDG targets: SDG 3.9 (substantial reduction of health impacts from hazardous substances) and SDG 11.6 (reduction of adverse impacts of cities on people). Industrial emissions not only affect the SDG directly associated with the environment but also has a close relationship with the SDGs of other dimensions, such as SDG4 (quality education), SDG9 (industrial, innovation and infrastructure), SDG12 (responsible consumption and production) and SDG16 (peace, justice and strong institutions) [20,21].

Rajkot is an urban agglomeration in the western part of Gujarat State, India, which hosts multiple industrial zones and predominant cotton and peanut crops. This study mainly focuses on assessing ambient air quality with the help of chemical characterization of fine aerosol along with calculation of Z score and Air Quality Index (AQI) considering four major air pollutants: fine particulate matter, coarse particulate matter, nitrogen dioxide and sulfur dioxide. The outcome of this study will help us develop a better understanding of chemical composition and potential sources of particulate matter and provide useful information for establishing control strategies of aerosol pollution.

2. Data & methodology

2.1. Study area and air sampling

Rajkot city lies between North latitude 22°10’ and 22°25’ and East longitude 70°40’ and 70°55’ and is an urban station, surrounded by agricultural land of Saurashtra region of the state of Gujarat, India (Figure 1). It is the 22nd fastest growing city globally and the 4th largest city in the state with an approximate population of 2 million, situated at an elevation of ~128 m from sea level. It has a semi-arid climate with summer as hot and dry; monsoon from July to October (~500 to 600 mm) and pleasant winters from November to February. The city is well connected by road and rail, having more than 500 foundry units, industrial parts including diesel engines, automotive parts, bearings, pumps, etc. in three industrial zones named Shapar GIDC, Metoda GIDC and Aji GIDC.

Wind data (speed and direction) were monitored for the period of 1 year, that is, Dec 2016 to Nov 2017, on an hourly basis using a monitoring station (INSTRUMEX WMS-51 Automatic Weather Monitoring Station) installed at Marwadi University (22°22’04.8”N 70°47’51.5”E) Rajkot. Conventional wind roses were plotted considering a calm period as ≤ 1 kmph of wind speed, on a quarterly, half-yearly and annual basis. Windrose pro software is used to generate a diagrammatic presentation of wind rose by considering wind direction and speed as input variables [15].

Based on locations of urban and industrial clusters, land use pattern (Table 2) and wind rose diagrams developed from wind data collected for Dec 2016–Nov 2017, two sampling sites were used for the 24 h averaged sampling of PM_{10}, PM_{2.5}, SO_{2} and NO_{2} for Rajkot city. S1, as a suburban site, is surrounded by commercial markets, schools and residential buildings whereas S2, as a rural site, is surrounded by agricultural land and Rajkot Morbi state highway. Sampling was carried out from Dec 2017 to November 2018. A total of 72 samples of specific pollutants on every sampling site were collected and 36 were analyzed as part as per seasons consideration: Winter (December, January and February); Summer (March, April and May); Monsoon rainy season (June to September) and Post-monsoon period (October to November).

24 h averaged sampling of fine and coarse dust particles has been carried out by using the PM_{10}-PM_{2.5} sampler of Instrumex, model number IPM-FDS-2.5μ/10μ, designed as per United States Environmental Protection Agency and Central Pollution Control Board norms [22]. The sampler was placed at a height of ~15 m above the ground and the sampler was programmed to run at

Figure 1. Sampling Station in Rajkot City.
a flow rate of 16.67 LPM (accuracy ±2%), fitted with a real-time control system having an accuracy of ±2 min/month. Quartz filter paper of 46.2 mm has been used for Coarse dust sampling (PM10) 46.2 mm Quartz filter paper along with silicon oil-dipped 37-mm glass fiber filters in cascade impactor assembly were used for PM2.5 sampling. The mass concentration of PM10 and PM2.5 was determined using the Gravitric method. The sample of the gaseous pollutant was done using dust sampler attachment (IP 117 Model, thermoelectrically cooled gaseous sampler), which can work with a flow rate of 0–2 L/min, with least count of 0.1 L/ min having sampling train of four impinger tubes of 35- ml capacity. NO2 and SO2 were estimated using Indian standard methods [13,14], that is, Modified Jacob & Hochheiser (Na-Arsenite) and Improved West and Gaeke method, respectively. The Sampler’s flow rate was kept to be 1.5 L/min and analysis of NO2 and SO2 was done using a spectrophotometer at wavelengths of 540 and 560 nm, respectively. To collect meteorological data, INSTRUMEX WMS-51 Automatic Weather Monitoring Station is used as a sensor for Wind speed, Direction, Relative humidity, rainfall and Atmospheric pressure. The model has a 3-cup anemometer installed and has an accuracy of ±1 mph and ±3º.

2.2. Z score

Z score is used to standardized concentrations of air pollutants, that is, PM10, PM2.5, SO2 and NO2. Z score greater than 0 represents higher values than the average value, whereas less than 0, represents a low level. Z score for all pollutants was calculated using [15]:

\[ Z = \frac{(X-\mu)}{\sigma} \]

where

\[ Z = \text{Z score of pollutant} \]

\[ X = \text{Average concentration of a pollutant in a specific zone} \]

\[ \mu = \text{Average concentration of pollutant for all the zones} \]

\[ \sigma = \text{The standard deviation of pollutant} \]

Comparison of contribution from vehicular sources and industrial sources can be observed with the help of a ratio of SO2/NO2. It has been observed that NO2 emissions are more from vehicular sources, whereas SO2 is from fossil fuel burning in industrial activity [15,23]. AQL was calculated by sub-indices approached published by Ministry of Environment, Forest and Climate Change (MoEFCC) in 2014. Sub-indices were calculated for four major criteria pollutants and then maximum value becomes the overall AQL and specific pollutant becomes responsible pollutant [24].

2.3. Chemical analysis

Water-soluble ion analysis was carried out with the Dionex ICS-3000 Ion Chromatography System. Water-soluble anions and cations (Na+, NH4+, K+, Ca2+, Mg2+, Cl−, F−, NO3−, PO43−, NO2− and SO42−) were estimated by dissolving filter paper into deionized water (resistivity 18.2MΩ cm) using ultrasonicator for 90 min. The solution was filtered through a syringe filter fitted with an assembly having 0.22-μm nylon membrane filters. Then, the filtrate is transferred to a polypropylene sample bottle treated with 2% HNO3, and deionized water in order to remove impurities. Then, this filtrate is analyzed in triplicates (estimated analytical error – 3 to 5%) by an IC sampler with flow rates ranging from 0.001 to 10.0 mL/min and operating pressures up to 35 MPa (5000 psi). The Conductivity Detector has a signal range up to 15,000 μS. 20 mM sodium hydroxide (50% w/w) is used as an eluent for concentrations of the anions (F−, Cl−, NO3−, PO43−, NO2− and SO42−), whereas MSA (Methane sulfonic acid, 5 mM) is used for cations (Na+, NH4+, K+, Ca2+ and Mg2+). IonPac-AS11-analytical column with a guard column is used along with a CSRS-300 suppressor for cations, whereas an ASRS-300 4-mm anion micro-membrane suppressor for anions. Chromeleon software package is used for processing chromatograms and analyzing chromatography data, which were collected at 5 Hz. Blank filters were analyzed for the removal of positive and negative corrections from anions and cations [25].

Whereas metal analysis for Iron, Zinc, Aluminum, Lead, Sodium, Magnesium Copper, Chromium, Arsenic and Manganese was carried out using an Agilent micro-wave plasma spectrophotometer (4100 MP-AES, Agilent Technologies, Santa Clara, CA, USA). Nitrogen was obtained from the air using a nitrogen generator (Agilent 4107, Agilent Technologies). Analysis was carried out in triplicate with 15 s for uptake time, 20 s for torch stabilization time and 5 sec as reading time.

2.4. Source contribution in ion concentration

Sources for analyzed water-soluble inorganic ions can be summarized as (i) Marine – majorly for Sodium and chloride, in small proportion for calcium, potassium and magnesium [26]; (ii) Crustal – Calcium and Potassium [27]; (iii) Biomass burning – Sulfate, Nitrate, Potassium, Ammonium and non-sea salt potassium and sulfate [28]. Na+ concentration can be used as the reference species for estimation of sea salt concentration, Sea salt concentration = Cl− + 1.47 × Na+ where 1.47 is the mass ratio of summation of Mg2+, Na+, Ca2+, K+, SO42− to the Na+ in seawater. The non-sea salt components of potassium, sulfate, calcium, magnesium and chloride are calculated, considering sodium as a reference species [26,29].

\[ \text{nas})- K^+ = K^+ \text{ measured} – Na^+ \times 0.038(2) \]
Results

The deviation of wind direction to be the North West direction and maximum wind speed during May 2017. Monsoon season during May to August, results into the cleanup of pollutants during this period as represented in Figure 2. The land use pattern for Rajkot city shows that agricultural activities do not play an important role compared to the industrial and urban clusters [30]. Seasonal variation of meteorological parameters has been reflected in Table 1, showing heavy winds along with high humidity level during monsoon season. Least seasonal average value of wind speed is observed during winter season along with very less rainfall during winter and summer season. Whereas no rainfall was observed during post monsoon season.

3. Results & discussion

Wind rose diagrams reflect predominant wind direction to be the North West direction and maximum wind speed during May 2017. Monsoon season during May to August, results into the cleanup of pollutants during this period as represented in Figure 2. The land use pattern for Rajkot city shows that agricultural activities do not play an important role compared to the industrial and urban clusters [30]. Seasonal variation of meteorological parameters has been reflected in Table 1, showing heavy winds along with high humidity level during monsoon season. Least seasonal average value of wind speed is observed during winter season along with very less rainfall during winter and summer season. Whereas no rainfall was observed during post monsoon season.

3.1. Spatial and temporal variation

Spatial distribution of specific pollutants, that is, PM₁₀, PM₂.₅, SO₂ and NO₂ are presented in Figure 3. Results indicate the maximum concentration of PM₁₀ (111.45 μg/m³) and PM₂.₅ (68.9 μg/m³) during January 2018, which can be due to the inversion phenomenon taking place during the winter season. Similarly, concentrations for gaseous pollutants, that is, SO₂ and NO₂ were observed maximum during December–February, whereas minimum during August and September, which can be due to the

Figure 2. A half-yearly and annual wind rose diagram.

Table 1. Seasonal Variation of meteorological parameters for Rajkot city. Range (minimum-maximum), mean and standard deviation (SD).

| Season          | Statistics | Temperature (°C) | Dew Point (°F) | Humidity (%) | Wind Speed (m/sec) | Rainfall (mm) |
|-----------------|------------|------------------|----------------|--------------|-------------------|--------------|
| Dec 2017 to Feb 2018 | Range      | 10.55 – 38.33    | 24 – 68        | 12 – 100     | 0 – 7.15          | 0 – 3        |
|                 | Mean± SD   | 22.46 ± 5.69     | 49.03 ± 8.28   | 47.79 ± 19.89 | 1.66 ± 1.27       | 0 ± 0.11     |
| March 2018 to May 2018 | Range      | 15 – 43.88       | 5 – 98         | 0 – 7.15     | 0 – 9              | 0 – 0.41     |
|                 | Mean± SD   | 30.82 ± 5.86     | 57.98 ± 13.9   | 44.28 ± 24.73 | 2.05 ± 1.13       | 0.02 ± 0.41  |
| June 2018 to Sept 2018 | Range      | 23.88 – 40.55    | 32 – 100       | 0 – 9.38     | 0 – 376           | 9.32 ± 16.9  |
|                 | Mean± SD   | 28.81 ± 3.05     | 75.65 ± 2.15   | 78.12 ± 15.3 | 3.87 ± 1.57       | 9.32 ± 16.9  |
| Oct 2018 to Nov 2018   | Range      | 15.55 – 38.33    | 39 – 78        | 0 – 8.04     | 0 – 0              | 0 ± 0        |
|                 | Mean± SD   | 27.33 ± 5.34     | 59.54 ± 9.57   | 51.72 ± 20.24 | 2.53 ± 1.36       | 0 ± 0        |
washout phenomenon taking place during the monsoon season. The average concentrations for SO₂ and NO₂ are always on the lower side of Indian ambient air quality standards. In contrast, the concentration of PM₁₀ and PM₂.₅ was found to be on the higher side on few occasions during the month of January–February.

The spatial distribution of pollutant concentration is represented in Figure 4 along with their distribution across seasons. No comparative difference in ambient air quality across Site 1 and Site 2 was observed due to Site 2 (Rural site) presence near the state highway having high mobility of heavy vehicles. The concentration of pollutants gets lowed during the Monsoon and Post-monsoon season, which can be associated with the precipitation and heavy wind during those seasons. Significant air pollutant affecting society’s health is fine aerosol particles, that is, PM₂.₅, as they can travel across the respiratory tract, finally reaching the lungs. Therefore, it is better to understand the occurrence and changes across the pathway to predict the associated health by analyzing the ions and metal composition.

Z score is calculated to study the impact of various pollution sources on both locations as shown in Table 3. In urban areas, all Z score values are greater than 0, with minimum values in SO₂ and NO₂, indicating that the metropolitan area can be characterized as PM₁₀/PM₂.₅ pollution zone due to construction and industrial activity. In contrast, the Z score for rural areas is with a negative sign showing a low pollution zone with a minimum value of PM₁₀. Due to this, rural areas can be characterized as PM₂.₅/SO₂/NO₂ with nearly similar values of concentration of sulfur dioxide and nitrogen dioxide as compared to urban areas, which can be due to vehicular movement as S₂ is near to a state highway.

To study the impact of vehicular activity compared to industrial activity ratio of SO₂/NO₂ is calculated and it is observed that the value is nearly 1 showing the equal contribution of SO₂ and NO₂ in lowering the air quality. SO₂ emissions are majorly from industrial activities and agricultural burning, whereas NO₂ emission is majorly from vehicular emission. Similar findings were reported for Indian cities, including Delhi and Mandi Gobindgarh [15,31].

**Table 2.** Land use pattern for Rajkot city.

| Area Type                  | % of land covered |
|----------------------------|-------------------|
| Built Up                   | 58.41             |
| Agricultural               | 14.26             |
| Urban Area                 | 13.83             |
| Urban Green                | 12.51             |
| Water bodies and River     | 1.09              |

**Figure 3.** Temporal Variation of criteria pollutants (a) PM₁₀, (b) PM₂.₅, (c) SO₂ and (d) NO₂.
3.2. Air quality index

Overall, the air quality was also assessed by calculating AQI as per the Indian standard method for Rajkot city on a monthly and seasonal basis (Figure 5). Maximum AQI was found to be in the range of 100–150 (Moderately polluted) during the winter season, specifically in January and March 2017. PM$_{2.5}$ was the responsible pollutant for three significant seasons i.e. winter, summer and post-monsoon, except for monsoon, where the responsible pollutant was PM$_{10}$. The minimum value of AQI was 77.28, and the responsible pollutant was PM$_{10}$ observed in August 2018 due to rainfall activity. In contrast, a peak value of 128.14 was reported in January 2018, associated with low wind speed and lower temperature, resulting in lesser dispersion. AQI data can be used to validate the characterization of PM$_{2.5}$ instead of PM$_{10}$ as the significantly responsible air pollutant found to be is PM$_{2.5}$. They are the very fine dust particles that can reach to respiratory tract causing severe acute and chronic health effects.

3.3. Ion analysis

Ion analysis was carried out of very fine aerosols (PM$_{2.5}$) to determine the composition of various water-soluble cations (Na$^+$, NH$_4^+$, K$^+$, Ca$^{2+}$ and Mg$^{2+}$) and anions (F$^-$, Cl$^-$, NO$_3^-$, PO$_4^{3-}$, NO$_2^-$ and SO$_4^{2-}$) as they can help in determining the source and process through which aerosol had gone through. Monthly and seasonal variability for individual ion concentration was represented in Figure 6 and Figure 7. Among anions, chloride and sulfate ions have maximum contribution in the overall anion concentration in PM$_{2.5}$ collected. Water-soluble anionic concentration was foremost in the winter season and minimum during the monsoon season [29]. During the summer season, a high concentration of water-soluble ions can be associated with an increase in secondary aerosol formation along with high temperature [32].

### Table 3. Z score and SO$_2$/NO$_2$ ratio for sampling stations.

| Zone          | PM$_{10}$ | PM$_{2.5}$ | SO$_2$ | NO$_2$ | SO$_2$/NO$_2$ ratio |
|---------------|-----------|------------|--------|--------|--------------------|
| Semi-Urban Area | 0.37      | 0.22       | 0.09   | 0.1    | 1.06               |
| Rural Area    | –0.37     | –0.22      | –0.09  | –0.1   | 1.09               |

#### 3.3.1. Anion concentration

Monthly and seasonal variations of water-soluble anions present in the fine aerosol are represented as µg/m$^3$ in Figure 6. Cl$^-$ and SO$_4^{2-}$ anions show the highest concentrations of 0.54–5.41 µg/m$^3$ and 0.14–5.29 µg/m$^3$ respectively. The average concentration of anions found during the sampling year is 0.033, 2.201, 1.258, 0.175, 0.103 and 0.066 for F$^-$, Cl$^-$, SO$_4^{2-}$, NO$_3^-$, NO$_2^-$ and PO$_4^{3-}$, respectively. The individual figure of Figure 6 describes mean, median line, 25%-75%, range within 1.5IQR, and outliers. Range 25%–75% represents the range of the dataset between the 25th percentile to 75th percentile. The box formed between 25% and 75% is known as the interquartile range (IQR). Therefore, range within 1.5IQR is defined as the line drawn up to 1.5 times of its IQR. The point outside the IQR is known as outliers. The individual discussion on anions is described below.

Figure 4. Spatial Variation of pollutants concentration.

Figure 5. Monthly and seasonal variation for AQI.
The concentrations of Cl\textsuperscript{-} ions vary in the range of 0.541–5.412 μg/m\textsuperscript{3} with an annual average value of 2.201 μg/m\textsuperscript{3}. The annual variability of chloride ions is found to be 53.97%. Chloride concentration during the summer season is found highest and lowest during the monsoon season. Figure 6a and Figure 6b represent Cl\textsuperscript{-} ions box plots of the monthly and seasonal, respectively. The monsoon season for outliers is because of non-rainy days for extended periods, whereas outliers during winter may be due to temperature variation. Seasonal variation shows during the monsoon season concentration of chloride ions are lower compared to other seasons. The SO\textsubscript{4}\textsuperscript{2-} ions concentration is 0.138–5.288 μg/m\textsuperscript{3} with an annual average value of 1.258 μg/m\textsuperscript{3}. The annual variability of SO\textsubscript{4}\textsuperscript{2-} ions found 77.8%. Figure 6c and Figure 6d show the monthly and seasonal SO\textsubscript{4}\textsuperscript{2-} ions box plot. It is found from Figure 6c that the lowest concentration is found during June, July, and August, whereas the highest concentration variability is found during February and March. The seasonal variation of SO\textsubscript{4}\textsuperscript{2-} ions shows that summer has the highest concentration, whereas winter has the lowest concentrations. Higher Cl\textsuperscript{-} and SO\textsubscript{4}\textsuperscript{2-} ions can be due to high contribution made by vehicular emission [25].

The F\textsuperscript{-} ions concentration is found in 0.000–0.179 μg/m\textsuperscript{3} with an average annual value of 0.033 μg/m\textsuperscript{3}. The annual variability of F\textsuperscript{-} ions concentration is 107.3%. Figure 6e and Figure 6f show the monthly and seasonal variability representing high variability during January and lowest during June and October. Seasonal analysis shows that the F\textsuperscript{-} ions variation is less similar. The NO\textsubscript{2} ions concentrations are 0.025–0.575 μg/m\textsuperscript{3} with an average value of 0.175 μg/m\textsuperscript{3}. The annual variability of NO\textsubscript{2} ions concentrations is found 48.9%. It is found from Figure 6g that the highest concentration of NO\textsubscript{2} ions is found during February and March were lowest in June.

The PO\textsubscript{4}\textsuperscript{3-} ions concentration lies in the range of 0.000–0.686 μg/m\textsuperscript{3} with an annual average value of 0.066 μg/m\textsuperscript{3}. Higher variability of more than 200% is found in PO\textsubscript{4}\textsuperscript{3-} ions concentration. It is found from Figure 6i that the highest concentration...
and higher variability of \( \text{PO}_4^{3-} \) ions are found during December. Similarly, it is seen from Figure 6j that winter \( \text{PO}_4^{3-} \) ions have higher variability highest concentration. It is also found from Figure 6i and Figure 6j that during monsoon season and June–September, there is no or small concentration of \( \text{PO}_4^{3-} \) ions. The \( \text{NO}_3^- \) ions concentration lies in the range of 0.000–2.455 \( \mu\text{g}/\text{m}^3 \) with an average annual value of 0.103 \( \mu\text{g}/\text{m}^3 \). The annual variability of \( \text{NO}_3^- \) ions is found at 317.1%, that is, the highest variation in anion concentrations. Figure 6k and Figure 6l show monthly and seasonal, respectively, variability of \( \text{NO}_3^- \) ions concentrations. The seasonal variability in Figure 6l shows a higher variability in summer and comparatively lower in all other seasons.

### 3.3.2. Cation’s concentration

Figure 7(a-j) shows the concentration of the seasonal and annual cation of water-soluble ions. The chronological order of average cation concentration is \( \text{NH}_4^+ \), \( \text{Ca}^{2+} \), \( \text{K}^+ \), \( \text{Na}^+ \) and \( \text{Mg}^{2+} \) and the annual average concentration is 2.002 \( \mu\text{g}/\text{m}^3 \), 1.274 \( \mu\text{g}/\text{m}^3 \), 0.675 \( \mu\text{g}/\text{m}^3 \), 0.668 \( \mu\text{g}/\text{m}^3 \) and 0.168 \( \mu\text{g}/\text{m}^3 \). Figure 7 representing major contributions made by \( \text{NH}_4^+ \) ion along with \( \text{Ca}^{2+} \) and \( \text{K}^+ \) ion. \( \text{Na}^+ \) ion concentration was found to be maximum during winters and post-monsoon seasons. The legends are the same as described in Figure 6. The individual cations are described below.

The \( \text{NH}_4^+ \) ion concentration varies in the range of 0.028–5.171 \( \mu\text{g}/\text{m}^3 \) with an average value of 2.002 \( \mu\text{g}/\text{m}^3 \). The variability of \( \text{NH}_4^+ \) ion concentration is 71.1%. Figure 7a and 7b show the \( \text{NH}_4^+ \) ion concentration monthly and seasonally, respectively. Figure 7a demonstrates that the \( \text{NH}_4^+ \) ion concentration is highest during December–May, but suddenly after May, it becomes lowest and found lowest during June–November. Similarly, Figure 7b shows the highest concentration in winter and summer, whereas the lowest in monsoon and post-monsoon season. The \( \text{K}^+ \) ions concentration varies in the range of 0.126–3.665 with an annual average value of 0.675. The highest variability in cation concentration is found in \( \text{K}^+ \) ions concentration, that is, 78.8%. Figure 7g and Figure 7h show the \( \text{K}^+ \) ions concentration of monthly and seasonal, respectively. The highest variation in monthly \( \text{K}^+ \) ions concentration is found during February–May,
whereas lower during December–January and June–November. Both K⁺ and NH₄⁺ ions represent contribution made by biomass-based emission [17,25].

The Ca²⁺ ion concentration varies in the range of 0.469–2.905 μg/m³ with an average value of 1.274 μg/m³. The variability of Ca²⁺ ion concentration is found at 43.2%, that is, the second-lowest variability in cation variation. Figure 7c and Figure 7d show the Ca²⁺ ion concentration of monthly and seasonal, respectively. The Mg²⁺ ions concentrations vary in the range of 0.059–0.863 μg/m³ with an average value of 0.168 μg/m³. The variability of Mg²⁺ ions concentrations is found at 66.9%. Figure 7e and 7f show the concentrations of the Mg²⁺ ions of monthly and seasonal, respectively, whereas Figure 7g shows higher variability during February–August whereas lowest during September–January. The highest variability in Ca²⁺ ion concentration is found in May and July, whereas seasonal shows during summer. Monsoon and post-monsoon seasons show the lowest concentration variability of Ca²⁺ ion concentration. Higher concentration of Mg²⁺ and Ca²⁺ ions can be correlated with the presence of metal-based industrial cluster within the study area [33].

The Na⁺ ions concentration varies in the range of 0.235–1.333 μg/m³ with an average value of 0.668 μg/m³. The variability of Na⁺ ions concentration is found at 35.1%, that is, lowest variability in cation variation. Figure 7i and Figure 7j show the Na⁺ ions concentration monthly and seasonally, respectively. The higher variability of Na⁺ ions concentration is found during November, whereas the highest Na⁺ ions concentration is found during January. Seasonal analysis shows that the winter and post-monsoon seasons have higher variability and highest concentration. Similar results were also reported for Kolkata, a city near to Indian coastal line [28,33].

3.4. Metal analysis

Metal analysis was carried out of very fine aerosols (PM₀.₂₅) to determine the presence of various metal constituents in the air. The metals analyzed for this study are Iron (Fe), Zinc (Zn), Aluminium (Al), Lead (Pb), Sodium (Na), Chromium (Cr), Magnesium (Mg), Copper (Cu), Manganese (Mn) and Arsenic (As). Figure 8a-j shows the bar chart of the seasonal average with error (standard deviation) of all these metals. Table 4 shows the coefficient of variance in the percentage of various metals to show the variability during the seasons. Figure 8 shows that all metal concentrations except lead is found higher during post-monsoon season, whereas lead is found highest during the winter season.

Iron is found highest during post-monsoon season, that is, 0.6850 μg/m³ with a standard deviation of 0.2188 μg/m³. The maximum average concentration for Fe (0.6230 ± 0.0625 μg/m³) was observed during Monsoon and Zn (0.1425 ± 0.0478 μg/m³) during post-monsoon season. Increased value can be associated with industrial activities as study area is having more than 500 foundry and other allied industries [33,34]. Aluminium (Al) concentration is also found highest during post-monsoon season, that is, 0.8655 ± 0.2798 μg/m³ and the average, whereas Lead (Pb) concentration is found highest during the winter season, that is, 0.1043 ± 0.0255 μg/m³. The sodium concentration is in chronological order with season (winter – post-monsoon season), that is, 8.6811 ± 2.0159 μg/m³, 7.5057 ± 0.9572 μg/m³, 9.9275 ± 1.6532 μg/m³ and 10.1049 ± 3.1580 μg/m³ respectively. The concentration of chromium, magnesium, copper, manganese and arsenic is found highest during the post-monsoon season, that is, 0.1615 ± 0.0549 μg/m³, 1.9117 ± 0.5939 μg/m³, 0.0988 ± 0.0358 μg/m³, 0.0751 ± 0.0245 μg/m³ and 0.0770 ± 0.0247 μg/m³ respectively.

3.5. Sea salt estimation concerning Na⁺

As the study area is close to India’s western coastal line, the contribution was studied by estimating sea salt concentration (SS). These sea concentrations are Na⁺, sea-salt components of Cl⁻, Ca²⁺, Mg²⁺, K⁺ and SO₄²⁻ by considering Na⁺ concentration as the reference species along with contribution from anthropogenic (AA) aerosols (NH₄⁺, nss- K⁺, F⁻, NO₃⁻, PO₄³⁻, nss-Cl⁻ and nss-SO₄²⁻), and Dust aerosols (DA) (nss-Ca²⁺ and nss-Mg²⁺). Table 5 shows the range (minimum-maximum), mean with standard deviation of various non-sea salts. Highest concentration of nss is found in nss-Cl⁻ where higher variability of nss is found in nss-SO₄²⁻. Figure 9a-c is the box plot distribution of AA, DA and SS. It is found from Figure 9a that anthropogenic aerosol concentration is higher during February–May, whereas December–January and June–November is found lower. Figure 9b,c shows the similar results that dust aerosols and sea salt aerosols are higher during December–May and lower during June–November. Non-sea salt concentration was found high during the summer season, extending from March to June. It can be due to westerly winds from the Arabian sea, as it even reflects that wind direction is from during that period West to East or Southwest to the northeast. Maximum value for non-sea salt – nss-K⁺ was reported during February with the weight of 3.63 μg/m³, and march for nss-SO₄²⁻ with a value of 5.13 μg/m³. Non-sea salt Cl⁻ concentration observed was 4.31 μg/m³ with higher values during the summer season and least values during the monsoon season, which are following other studies carried out for Kolkata [29], Lanzhou [34], Mohal and Kothi [35]. Figure 10 shows the relative contribution of daily anthropogenic aerosols, dust aerosol and sea salt aerosol. Figure 10 demonstrates that anthropogenic aerosols contribution is highest till May where sea salt aerosols is higher during June–November. Dust aerosols contribution was in between 8% and 22%, lower throughout the year compared to sea salt aerosols and anthropogenic aerosols.
Conclusion

Air quality assessment for Rajkot city demonstrates no comparative difference in ambient air quality across the urban and rural sites. The rural site was also observed having urban site air quality due to its presence near the state highway having high mobility of heavy vehicles. AQI represented that the responsible pollutant for three season was PM$_{2.5}$ except monsoon season with maximum value of 117 in March and minimum of 77.28 during August 2018. The concentration of pollutants gets lowered during the Monsoon and Post-monsoon season, which can be associated with precipitation and heavy wind during those seasons. Spatial and temporal, along with variation in AQI across the months

![Figure 8. Seasonal variation of trace metal concentration.](image)

**Table 4. Coefficient of variance (%) of metal found in aerosol particles.**

|       | Fe  | Zn  | Al  | Pb  | Na  | Cr  | Mg  | Cu  | Mn  | As  |
|-------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Winter| 10.06 | 8.43 | 18.31 | 24.52 | 23.22 | 13.58 | 7.90 | 20.37 | 14.09 | 21.04 |
| Summer| 20.28 | 25.89 | 30.91 | 33.31 | 12.75 | 30.48 | 31.58 | 30.97 | 14.96 | 31.15 |
| Monsoon| 16.63 | 27.62 | 44.16 | 27.80 | 16.65 | 35.14 | 31.48 | 25.92 | 16.19 | 19.68 |
| Post Monsoon| 31.95 | 33.57 | 32.34 | 30.39 | 31.25 | 34.04 | 31.07 | 36.21 | 32.61 | 32.14 |

**Table 5. Seasonal variation of the non-sea salt component in major water-soluble ions.**

|       | nss-K$^+$ | nss-SO$_{4}^{2-}$ | nss-Ca$^{2+}$ | nss-Mg$^{2+}$ | nss-Cl$^-$ |
|-------|-----------|------------------|--------------|--------------|------------|
| Annual | 0.10–3.63 0.65 ± 0.53 | 0.03–5.13 1.09 ± 0.97 | 0.44–2.88 1.25 ± 0.55 | 0.00–0.81 0.09 ± 0.12 | 0.01–4.31 1.42 ± 1.19 |
| Winter | 0.37–3.63 0.9 ± 0.81 | 0.31–3.9 1.53 ± 0.8 | 1.09–2.15 1.59 ± 0.33 | 0.00–0.24 0.09 ± 0.068 | 0.47–4.31 1.87 ± 1.08 |
| Summer | 0.49–2.24 0.94 ± 0.45 | 0.65–5.13 1.95 ± 1.01 | 0.94–2.88 1.69 ± 0.49 | 0.04–0.81 0.2 ± 0.17 | 0.68–3.75 2.76 ± 0.87 |
| Monsoon| 0.1–0.82 0.36 ±0.19 | 0.03–1.9 0.35 ± 0.49 | 0.47–2.22 0.88 ± 0.42 | 0.00–0.19 0.05 ± 0.056 | 0.01–1.25 0.45 ± 0.38 |
| Post-monsoon| 0.19–1.09 0.49 ±0.27 | 0.14–2.0 0.76 ± 0.57 | 0.44–1.56 0.94 ± 0.37 | 0.00–0.04 0.01 ± 0.015 | 0.09–1.58 0.85 ± 0.55 |
and seasons, it was concluded that the significant air pollutant affecting society’s health is fine dust particles, that is, PM$_{2.5}$. Under chemical characterization, the ion concentration of cations and anions shows higher values during the winter and summer seasons, whereas lower during monsoon and post-monsoon seasons. The metal concentration except Pb is found higher during the post-monsoon season, whereas Pb is found highest during the winter season. The variability of iron, zinc, sodium, copper, manganese and arsenic is found highest during the post-monsoon season; aluminum during monsoon season; and lead and magnesium during the summer season. The seasonal highest concentration range is found in sodium, that is, 7.5–10.1 ug/m$^3$. Non-sea salt concentration was found highest during the summer season, extending from March to June. Source contribution shows that contribution anthropogenic activities was very high during winter and summer season, whereas for monsoon and post monsoon, contribution from sea salt was high. It can be due to westerly winds from the Arabian sea, as it even reflects that wind direction is from during that period West to East or Southwest to the northeast. Overall, the pollution is higher during the winter and summer season, that is, December–May, and lowers during monsoon and post-monsoon season, that is, June–November.

**Authors’ contributions**

All persons who meet authorship criteria are listed as authors, and all authors certify that they have participated sufficiently in the work to take public responsibility for the content, including participation in the concept, design, analysis, writing or revision of the manuscript.

- **Abhishek Gupta**: Conceptualization, Methodology, Formal analysis, Writing - Original Draft, Visualization, Validation
- **Amit Dhir**: Supervision, Project administration, Writing-Reviewing and Editing

**Availability of Data and Material**

Data can be provided on special request as results and analysis part is from the study carried out at my lab for the completion of Doctorate of my student.

**Consent for publication**

Authors agreed for publication of this manuscript.
Disclosure statement

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Funding

This research did not receive any specific grant from any national or international funding agencies.

ORCID

Abhishek Gupta http://orcid.org/0000-0003-3301-3492
Amit Dhir http://orcid.org/0000-0002-6705-5888

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