

Source characterization of PM₁₀ using CMB receptor modeling for the western industrial area of India

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ABSTRACT

Introduction: Receptor models use the chemical characterisation of particulate matter to distinguish the source and analyse the source contributions. The main aim of this study is to carry out source apportionment of PM₁₀ for industrial locations of Vapi and Ankleshwar in Gujarat, using the Chemical Mass Balance (CMB) receptor model.

Materials and methods: At six distinct locations of Ankleshwar and Vapi, respirable dust samplers were used to collect particulate matter on quartz filter sheets for the current study. Filter papers containing PM₁₀ mass were subsequently examined for Water Soluble Ions (WSIs), major and trace elements, elemental and organic carbon followed by source apportionment study.

Results: Using CMB, the contributions obtained for Ankleshwar are 27.85% for crustal or soil dust, 26.31% for fossil fuel combustion, 21.06% for vehicle emissions, 14.20% for secondary aerosols, 9.30% for biomass, and 1.20% for industrial emissions. CMB for Vapi revealed the chief source signatures as fossil fuel combustion including industries contributing 35%, crustal or soil dust contributing 22.90%, biomass burning contributing 19.12%, vehicular emissions contributing 16.18%, and secondary aerosols contributing 6.79%.

Conclusion: By applying the CMB model, the primary source is found to be crustal or soil dust followed by burning fossil fuels, vehicular emissions, and secondary aerosols for Ankleshwar and Vapi, respectively. A quantitative assessment of source contributions to particulate matter is required to create emission control measures. The findings of this study will be beneficial for the environmental management of particle concentrations in the study region.

Introduction

Airborne particulate matter and other gaseous pollutants are becoming more prevalent,

especially in developing nations like India, as a result of rapid industrialisation, urbanisation, fossil fuel consumption, and economic expansion. According to research studies, increased morbidity and high particle concentration are strongly

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correlated. When inhaled, the respirable portion of particulate matter known as Particulate matter (PM₁₀ or PM_{2.5}) can cause several respiratory and heart health problems in people [1]. Numerous studies have demonstrated a correlation between particulate matter parameters, such as size, distribution, mass concentration, and the impacts on human health. Even better than any other indicator, this knowledge serves as a guide for predicting the effects of the particles on human health. [2, 3]. Due to its immediate as well as long-term detrimental impacts on health, chemical characterization of airborne particulate matter, particularly heavy metal tracer indicators, is of great interest. Along with having a negative impact on health, particulate matter also affects several atmospheric functions, such as solar radiation, visibility, precipitation, cloud formation, etc. Many stern measures have already been taken to reduce the threat of air pollution, but many big towns and cities are still dealing with this issue. The main anthropogenic sources of particulate matter include emissions from moving vehicles or traffic, industrial activity emissions, burning fossil fuels, burning biomass, construction and demolition activities, suspended or re-suspended road dust, and so on [4]. The concentration of particulate matter and its chemical characterization in ambient air can indicate characteristics of the activities involved in addition to providing details on human exposure to such heavy metal pollution [5]. Hence, thorough monitoring of ambient air quality is necessary to determine the current state of air quality in any given place.

Receptor models are often used to identify the sources of air pollution and assess the impact of each source on the receptor. Receptor models typically use the elemental features of particles identified from the source to recognize the presence of distinct sources and compute their contributions to the receptor. Different receptor models, including CMB, Principal Component

Analysis (PCA), PCA-MLR, UNMIX, Positive Matrix Factorisation (PMF), and others, have been used in research studies throughout the world to carry out source apportionment [6-8]. The CMB model, among these several receptor models, is quite reliable for source apportionment of both coarse and fine particulates. To analyze the contribution from various sources, the CMB model chooses the most optimal combination of the chemical composition of PM₁₀ and emission source characteristics [9]. Since Factor Analysis (FA) or PMF have been frequently employed, source apportionment studies with CMB in India are limited. It is crucial to understand the impact of each emission source separately to create efficient strategies for risk reduction and air pollution control. The CMB receptor model has been used in this work to evaluate the various sources of coarse particles in Ankleshwar and Vapi. For the industrial areas of Ankleshwar and Vapi in Gujarat, the current work presents the chemical characterization of atmospheric PM consisting of EC, OC, WSIs comprising cations and anions, major and trace elements in PM₁₀ mass. A source apportionment investigation using the CMB model, enrichment factor analysis, and mass closure is used to understand this. The findings of this study will help manage the environment of particle concentrations that exceed regulatory standards in the study area.

Materials and methods

Site description

The first study area, Ankleshwar, is the largest industrial complex in Asia and home to several chemical firms, is situated at 21.62° N and 73.01° E, about 10 km from Bharuch. Production of dyes, paints, insecticides, chemicals, and medicines are among the main industries of Ankleshwar. In Ankleshwar, the average air temperature ranges from 13.3 °C to 41.9 °C, while the average relative humidity

is between 12% and 99.4%. The average wind speed is observed to be between 3.1 m/s to 9 m/s, with prominent wind direction being south-west. Second study area, Vapi is located at 20°23'21.48" N and 72°54'38.16" E, with a mean sea height of approximately 30 m. The average annual temperature of Vapi is 27 °C, with 70% annual relative humidity and 2000 mm of average precipitation. The prevailing wind direction most of the year is West-South-West, with an average yearly wind speed of 3.6 m/s. The main contributors to atmospheric particulates in both the study areas include secondary aerosols, resuspended dust, fossil fuel burning, industrial pollutants, vehicle emissions and biomass burning. Fig. 1 displays the sampling locations for both Ankleshwar and Vapi. For both the sites, at each of the six sampling locations, respirable dust samplers were employed to measure the particle content. Filter papers were then further digested to measure the elements NO₃, SO₄, NH₃, K-S, Cl, Na, Ca, EC, OC, Al, Si, Br, Cr, Cu, Ni, Zn, Pb, Fe, K, Mn, S, Ti, and V.

Experimental techniques and methods

The PM₁₀ samples for Ankleshwar and Vapi were collected between December 2019 and February 2020 at the locations depicted in Fig. 1. Using a respirable volume sampler (RDS with Model 460 NL, make - Envirotech Pvt. Ltd) placed at a height of 1.5 m from the ground, PM₁₀ samples were collected for 24 hours on quartz filter sheets that are 20.3 cm long by 25.4 cm wide, with a flow rate of 1.13 m³/min. 120 samples were collected using filter sheets for both the study areas. The filter papers used in particulate matter monitoring were conditioned for two days in a desiccator at 25 °C temperature and 50% relative humidity, before and after sampling. A five-digit weighing balance was used to determine the gravimetric weight of fiber filters. The difference between the original and final weights of the filter was used to calculate the particulate concentration. The scientific techniques utilised in this study include gravimetric analysis for particulate matter concentration, ion chromatography for WSIC analysis, ICP-AES for heavy metal analysis, and EC-OC carbon analyzer for elemental and organic carbon analysis.

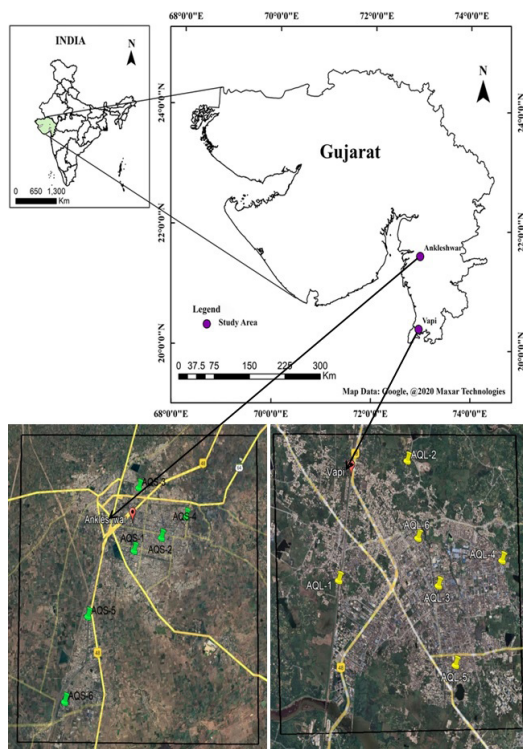


Fig. 1. Sampling locations in the study area

The filter sheets were subsequently separated into three portions for the examination of heavy metals, ions, and EC-OC after identifying the particulate matter concentration. Digestion and further heavy metal extraction from one part of the filter sheet was done on a hot plate. In a closed vessel, the filter papers were digested and dissolved in 15 mL HNO₃-HCl solution over the course of two hours at 150° C. Following digestion, the sample was filtered using Whatman filter paper, and it was then kept in a refrigerator until examination. The separated and chilled sample was utilised for the analysis of Al, Si, Br, Ca, Cl, Cr, Cu, Fe, K, Mn, Ti, Ni, Zn, Pb, S, and V using ICP-AES (Model ULTIMA 2000). According to the CPCB's standard process, the second portion of the filter paper was utilised for ion analysis, and it was extracted using ultra-pure or deionized water with a resistivity of 18 MU. A syringe filter was used to filter the extracted water sample, which was then saved for subsequent examination using an ion chromatograph (IC Basic 792: Metrohm). Four cations- ammonium (NH₃), potassium (K⁺), potassium (K-S) salt, and calcium (Ca²⁺) and two anions- nitrate (NO₃) and sulfate (SO₄) are included in the ion analysis. An EC-OC carbon analyzer (model DRI2001, Protocol Improve A) was used to analyse the third and final portion of the filter paper in accordance with U.S. Environmental Protection Agency (USEPA) protocol. The controlled oxidation of EC and OC, which liberates carbon compounds at various temperatures, is the basis for the operation of the EC-OC carbon analyzer.

Quality control and quality assurance

To keep the accuracy and precision throughout the investigation, a rigorous quality control program was put in place. The current sampling and analysis ensured the further quality control measures:

With clean forceps, filters were handled with caution.

It was made sure to collect representative samples with the appropriate labeling (such as sample type, location, time and date of collection, environmental factors, etc.).

The disposable materials, such as glassware, solvents, etc., were used appropriately.

Every precaution was taken to prevent contamination while sampling, sample handling, processing, and analysis.

Quality assurance was done during chemical reagent handling and field operations.

Collaborative sampling, flow audits, spot checks, and duplicate analysis to ensure data quality control.

Competency assessments were conducted for field operators and laboratory analysts.

Acceptance tests were performed on the tools and equipment being utilised.

Enrichment factor

The Enrichment Factor (EF) provides information about the element's fundamental characteristics, including whether it is of crustal origin or originates from human activity. The ratio of the two components is used to compute the enrichment factor. The numerator is obtained by dividing the element concentration by the reference element concentration in the sample whereas the denominator is derived by dividing the element concentration by a chosen reference element concentration in the earth's crust [10]. Fe, Al, and Si are the primary reference elements used to calculate EF, while Aluminum (Al), which has been widely used in numerous past research, has been chosen as the reference element for the current investigation [11].

EF is calculated through Eq. 1:

$$EF = (E_{\text{Sample}} / X_{\text{Sample}}) / (E_{\text{Crust}} / X_{\text{Crust}}) \quad (1)$$

Where E_{sample}=element concentration in the sample

X_{sample} =reference element concentration in the sample

E_{crust} =element concentration in the earth's crust.

X_{crust} =reference element concentration in the earth's crust.

Mass closure

To evaluate the relative contribution of measured elemental species and their correlation with an estimated mass of PM_{10} , the chemical species constituting PM_{10} mass are rebuilt (RCPM₁₀). The mass closure is accomplished using the IMPROVE equation, as illustrated in Eq. 2 below, and the reconstructed PM_{10} mass is referred to as RCPM₁₀ [12].

$$\text{RCPM}_{10} = [\text{AS}] + [\text{AN}] + [\text{POM}] + [\text{LAC}] + [\text{SS}] + [\text{SOIL}] \quad (2)$$

Where RCPM₁₀ is the reconstructed mass of PM_{10} , AS is ammonium sulfate, AN is ammonium nitrate, POM is particulate organic matter, LAC is light-absorbing carbon and SS is sea salt.

The product of each element's concentration and its conversion index is used to calculate the concentration of each factor specified in Eq. 2. By deducting the reconstructed mass RCPM₁₀ from the observed mass PM_{10} , the mass difference (MD) for PM_{10} is calculated (i.e., $MD = PM_{10} - RCPM_{10}$).

Chemical mass balance (CMB)

The fundamental idea underlying various receptor models is to utilise the classical theory of mass equilibrium to determine the likely sources of PM_{10} or $PM_{2.5}$ emissions while assuming that mass is conserved [13]. The concentration of chemical species bound to PM_{10} as well as specific source profiles constitutes the input dataset for the receptor model. By calculating the relative

source contributions of selected sources at the specific monitoring location, these input datasets are utilised to identify and carry out source apportionment of ambient particulates [14]. Due to the retroactive character of receptor models, it can only assess the effects of source profiles that have previously been examined. CMB is a novel receptor model that computes the source contributions by using the information on source profiles as well as the chemical composition of the elements in PM_{10} . To calculate the individual source contributions in comparison to similar emission sources, it is advised that the likely sources that are chemically different be employed [15]. The receptor element concentration is expressed as a direct aggregation of the sum of the products of the source contributions and source profiles in the CMB model's linear regression equation.

Thus, using multiple linear regression techniques, the CMB model uses source profiles and receptor concentrations with uncertainties as input to produce distinct source involvement [16]. However, it is advised to avoid linearity and the likelihood of identifying geographic locations in the source profile selection to maintain a high level of model relevance [17]. By combining a comparable set of sources, the linearity in source profiles can be decreased [18]. The application of the CMB model is appropriate when limited monitoring data is available. Utilizing in-depth information on source profiles may allow for a reduction in the number of samples or data that can be used as input, but a smaller dataset may raise the amount of uncertainty.

Watson provided the CMB model's fundamental equation (Eq. 3) in 1984 as a statement of mass conservation:

$$C_i = \sum_{j=1}^m F_{ij} S_j + E_i \quad (3)$$

Where i=number of species
j=number of sources

C_i =ambient concentration of species i

F_{ij} =fraction of species i in source j

S_j =source contribution of source j

E_i =residual error in species i

The fundamental premises on which the CMB model is applied are [2]:

- A linear independence between the source profiles
- The number of sources must be smaller than the number of species
- Source emission compositions remain stable during the monitoring period
- Chemical species do not interact with one another and accumulate linearly.
- Identification and characterization of receptor emissions from all likely sources that will affect the receptor
- The measured uncertainties are distributed normally, random, and not correlated.

For CMB model investigation, the following basic steps are applied:

- Measuring PM_{10} concentration and chemical species bound to PM_{10}
- Determining the details of selected source profiles used for the CMB analysis such as:
 - Vehicular source profiles
 - Refuse or biomass burning
 - Crustal or soil dust
 - Fossil fuel combustion
 - Industrial emissions
 - Secondary aerosols
- Using the CMB receptor model, the chemical mass balance equation is solved.
- Determining the contributing sources by averaging daily samples over the course of the monitoring period.

CMB model performance parameters

The CMB model must be used to assess contributions from chemically distinct sources since sources with identical physical or chemical features cannot be distinguished by them. The CMB model includes a variety of performance metrics for each model run, including the regression coefficient, degree of freedom, chi-square, and percent mass. For each of these diagnostic tests, the CMB guide from the USEPA lists a range of values. A Source Contribution Estimate (SCE) is the primary output provided by the CMB model. The overall mass concentration is often approximated by the sum of all source contribution estimations. When the SCE exceeds the standard error, it is taken into account for output; however, if the SCE is less than the standard error, the source contribution cannot be identified. The coefficient of determination (R^2), chi-square (χ^2), degree of freedom, and percent mass are typically the goodness of fit metrics used for computation using the least square approach [19].

- R^2 is derived using the linear regression of values obtained from the CMB model against observed concentrations. R^2 has values between 0 and 1. When R^2 is close to 1, the SCEs provide a better explanation for the observed concentrations, however, when R^2 is less than 0, the SCEs don't demarcate the source profiles.

- To calculate the weighted sum of squares, the difference between the estimated and measured concentrations for the fitted species is first determined and then divided by variance and degree of freedom. The chi-square value indicates the goodness of the data. Values of χ^2 smaller than one suggest a good fit data while values of χ^2 greater than 4 reveal that the linked species concentrations are not properly related to the SCEs.

- The percentage of mass is determined by dividing the total SCEs from the CMB model by the actual mass concentration. Percent mass

levels between 80% and 120% are regarded as sufficient.

- By deducting the number of fitting sources from species, the degree of freedom is calculated. According to the CMB handbook, a solution should be regarded as reasonable if its degree of freedom value is more than 5.

Results and discussion

Ambient air quality in the study area

For Ankleshwar, the mass concentration of PM_{10} varied between 100.98 to 225.47 $\mu\text{g}/\text{m}^3$, while for Vapi, it varied between 115.88 to 226.50 $\mu\text{g}/\text{m}^3$. Fig. 2 shows the levels of PM_{10} and $PM_{2.5}$ in the study area.

The average value of PM_{10} for six locations in Ankleshwar is 1.6 times higher than National Ambient Air Quality Standard (NAAQS, 2009) value of 100 $\mu\text{g}/\text{m}^3$, while for Vapi it is two times higher. Additionally, the average PM_{10} concentrations in Ankleshwar and Vapi are found to be almost 10 times higher than the PM_{10} air quality threshold set by the World Health Organization, which is 20 $\mu\text{g}/\text{m}^3$ (WHO, 2006). For Ankleshwar, the concentration of

$PM_{2.5}$ is found between 69.64 to 122.15 $\mu\text{g}/\text{m}^3$, while for Vapi, it is between 69.38 to 120.52 $\mu\text{g}/\text{m}^3$. Therefore, it can be seen that the ratio of $PM_{2.5}$ to PM_{10} in the study area ranges from 0.49 to 0.69, with an average value of 0.60, indicating the effect of combustion-related activities [19].

Chemical characterization of PM_{10}

Following the chemical characterization of PM_{10} , the elements are divided into four categories total carbon, WSIs, major and trace elements, as shown in Fig. 2. The carbon fraction has the largest concentration of the four identified components, followed by major elements, water-soluble ions, and trace elements. In Ankleshwar and Vapi, the mean concentration of water-soluble ions is found to be 26.90 and 25.87 $\mu\text{g}/\text{m}^3$, respectively whereas the mean concentration of total carbon is recorded as 49.72 and 51.18 $\mu\text{g}/\text{m}^3$, respectively. For Ankleshwar and Vapi, the mean concentration of the main elements is found to be 31.49 and 31.08 $\mu\text{g}/\text{m}^3$, respectively and the measured trace element concentrations are 1.60 and 1.58 $\mu\text{g}/\text{m}^3$, respectively

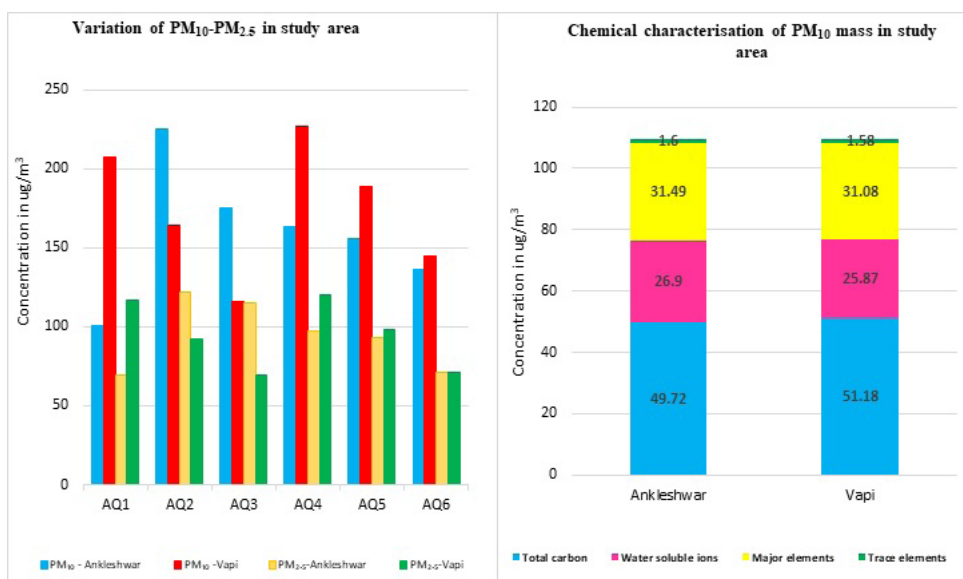


Fig. 2. Variation of PM_{10} - $PM_{2.5}$ and Chemical characterization of PM_{10} in the study area

As indicated in Fig. 3, the mean concentration of OC is recorded as 29.39 $\mu\text{g}/\text{m}^3$ for Ankleshwar and 29.40 $\mu\text{g}/\text{m}^3$ for Vapi, whereas the mean concentration of EC is obtained to be 20.33 $\mu\text{g}/\text{m}^3$ for Ankleshwar and 21.78 $\mu\text{g}/\text{m}^3$ for Vapi. The concentration of OC and EC is significantly influenced by vehicle emissions and the burning of agricultural waste [11]. The value of the OC/EC ratio between 0.3 and 1 denotes diesel vehicle emissions, whereas, the number between 1.4 and 4 denotes gasoline car emissions [11, 14]. According to the current study, the OC/EC ratio for Ankleshwar and Vapi is around 1.45 and 1.41 respectively, indicating emissions a mix of diesel as well as gasoline-powered automobiles. A similar trend is observed for OC and EC at both

the locations.

As shown in Fig. 3, the average concentrations of the water-soluble cations K, Ca, NH₃, and Na are 4.15, 3.32, 3.27, and 1.32 $\mu\text{g}/\text{m}^3$ for Ankleshwar and 3.99, 2.93, 2.79, and 1.32 $\mu\text{g}/\text{m}^3$ for Vapi, respectively. For Ankleshwar, the average concentration of water-soluble anions SO₄, NO₃, and Cl in PM₁₀ is 8.37, 3.66, and 2.81 $\mu\text{g}/\text{m}^3$, whereas, for Vapi, it is 8.04, 4.12, and 2.68 $\mu\text{g}/\text{m}^3$. The long-distance transmission of secondary aerosols, in addition to secondary emissions from nearby sources like factories and cars, can be blamed for the effect of water-soluble ions [14]. A similar trend is observed for WSIs that is cations as well as anions at both the locations.

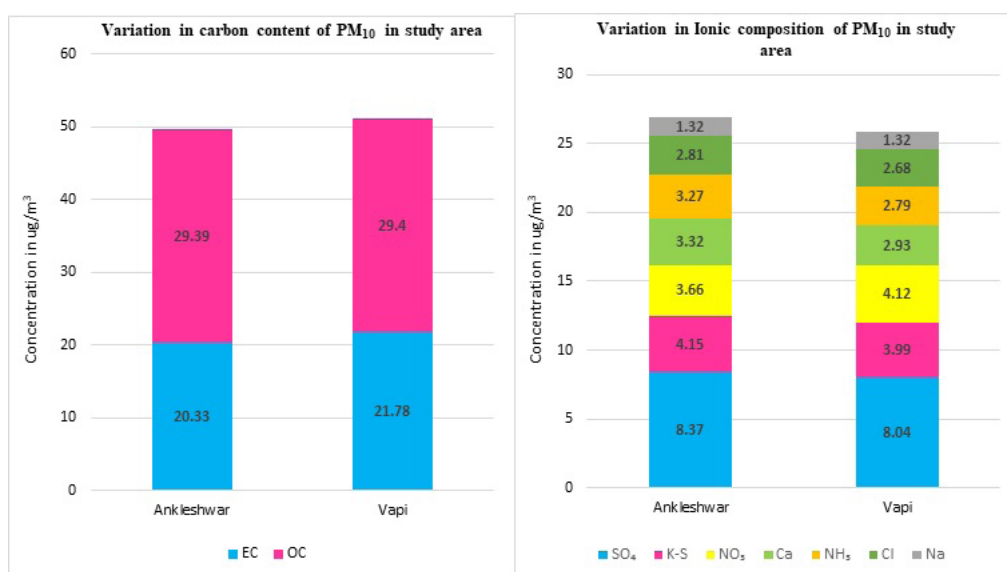


Fig. 3. Variation in Carbon content and Ionic composition of PM₁₀ in the study area

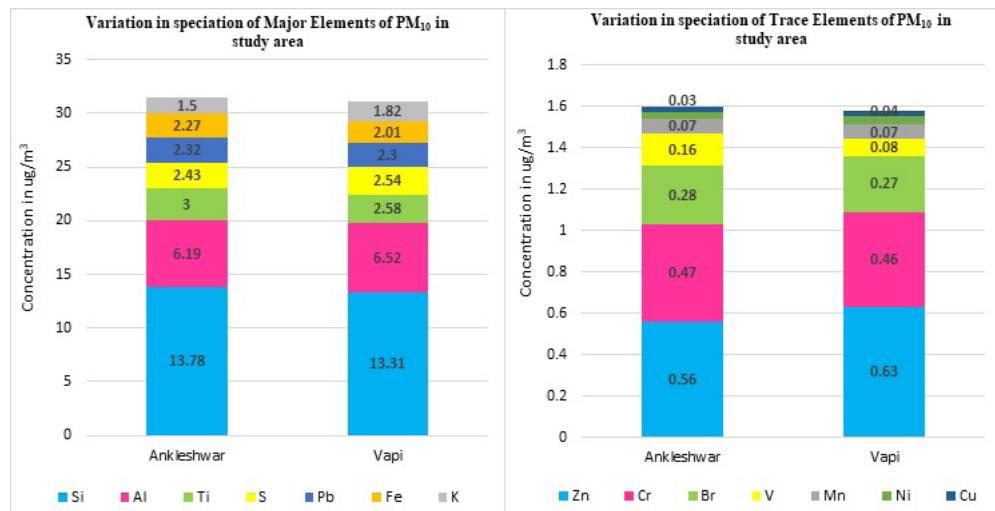


Fig. 4. Variation in speciation of major and trace elements of PM₁₀ in the study area

In this study, the elements are divided in two categories, major and trace elements. In general, the major elements are Si, Al, Ti, S, Pb, Fe, and K, with average concentrations of 13.78, 6.19, 3, 2.43, 2.32, 2.27, and 1.5 µg/m³ for Ankleshwar and 13.31, 6.52, 2.58, 2.54, 2.30, 2.01, and 1.82 µg/m³ for Vapi, as shown in figure 4.0. The trace elements include anthropogenic trace indicators such as Zn, Cr, Br, V, Mn, Ni, and Cu, with mean concentrations of 0.56, 0.47, 0.28, 0.16, 0.07, and 0.03 µg/m³ for Ankleshwar and 0.63, 0.46, 0.27, 0.08, 0.07, 0.04, and 0.03 µg/m³ for Vapi, respectively. Based on the location of the air mass and its path of travel, the main and trace elements can be identified as originating from either a natural or manmade source, which can be further substantiated using Enrichment Factor (EF) analysis [14]. The CPCB has established annual regulatory limits for several metals, including As, Pb, Cd, and Ni (MoEF, 2009). The mean Pb concentration is analysed as 2318 ng/m³ and 2305 ng/m³ for Ankleshwar and Vapi, respectively, comparing the CPCB limit of 500 ng/m³, while the concentration of Ni is found to be 34 ng/m³ and 37 ng/m³ for Ankleshwar and Vapi, respectively, exceeding the CPCB limit of 20 ng/m³.

Enrichment factor

Elements with EF values less than 10 are significantly associated with crustal sources and are marginally enriched. Elements with EF values between 10 and 100 indicate that the elements come from both crustal and anthropogenic sources, while elements with EF values greater than 100 imply that the majority of the elements come from anthropogenic sources [14]. For both Ankleshwar and Vapi, the order of the EF values for the elements taken into consideration in this study is Pb > Br > S > Zn > Cr > V > Ti > Cu > Ni > Al (Fig. 5). For the metals Fe, Mn, Si, and K, the values of EF are less than 10, indicating that the sources of these elements are crustal processes including natural rock weathering, forest fires, sea salt, and wind-blown soil components [20]. The measured EF values for Ni, Ti, Cr, Cu, and V range from 10 to 100, indicating moderate enrichment from both crustal and anthropogenic sources. Examples of anthropogenic sources include the burning of fossil fuels like coal, vehicle emissions, and industrial emissions. The elements Zn, S, Br, and Pb had EF values greater than 100, indicating that they probably originate from anthropogenic sources such as burning coke or biomass, traffic emissions, industrial emissions from the steel or foundry industries, and resuspended dust.

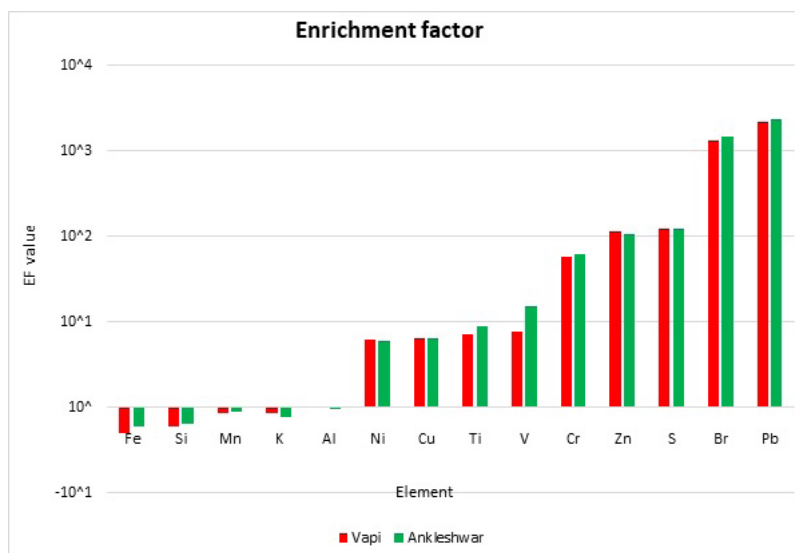


Fig. 5. Enrichment factors for elements in the study area

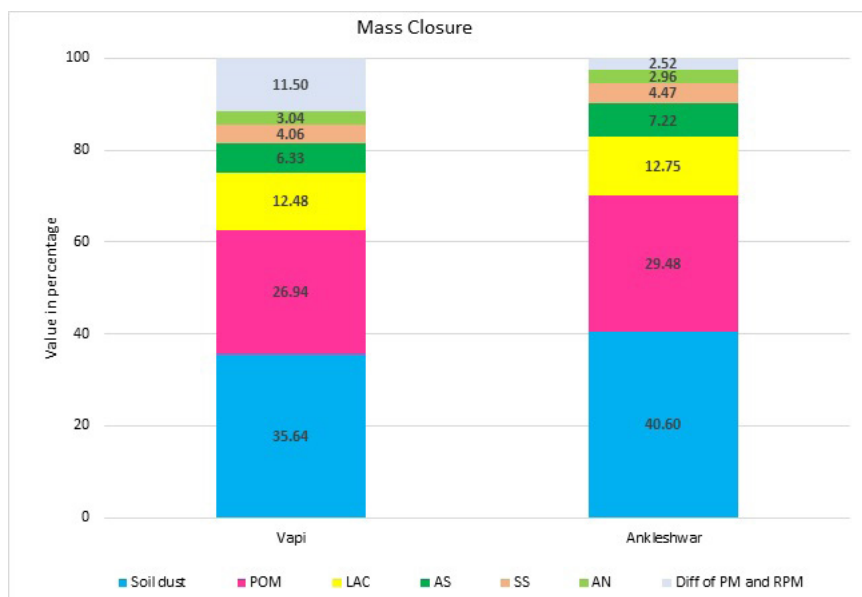


Fig. 6. Factors for Mass closure in the study area

Mass closure

Using IMPROVE equation, stated above, for Ankleshwar and Vapi, the MD for PM_{10} is determined as 2.52% and 11.5% of PM_{10} mass, respectively. The unidentified mass of PM_{10} is responsible for the mass difference. Using IMPROVE equation, the computed contribution of soil dust is obtained as 40.60% and 35.64% of the $RCPM_{10}$ mass, for Ankleshwar and Vapi respectively, which is greater than anticipated.

The effect of regional as well as transboundary migration of soil dust from neighbouring regions may be responsible for the high value of soil dust. For Ankleshwar and Vapi, the effect of POM is seen to be 29.48% and 26.94% of the $RCPM_{10}$ mass, respectively. The primary POM sources in the atmosphere include burning fossil fuels or burning biomass, whereas secondary sources are secondary aerosols released after the oxidation of gaseous precursors.

For Ankleshwar and Vapi, the estimated contribution of LAC to the RCPM_{10} mass is 12.75% and 12.47%, respectively. LAC typically consists of black, elemental, or graphite carbon that is released as a result of incomplete fossil fuel combustion or biomass burning. For Ankleshwar and Vapi, the contribution from AS is observed to be 7.22% and 6.33%, respectively. Typically, AS is created in the atmosphere as a result of several chemical reactions that occur with SO_2 , which is released through the combustion of fossil fuels. For Ankleshwar and Vapi, the effect of sea salt is determined to be 4.47% and 4.09% of PM_{10} mass respectively. The concentration of AN is 2.96% and 3.04% of RCPM_{10} mass for Ankleshwar and Vapi respectively. When NO_x from the burning of fossil fuels or vehicle emissions undergoes reversible interactions with the gaseous phases of NH_3 and HNO_3 , AN is created. According to Fig. 6, the percentage contribution of various factors

of RCPM_{10} mass is observed to be in the sequence of Soil>POM>LAC>AS>SS>AN.

Source apportionment-using CMB

For source apportionment investigation for the industrial districts of Ankleshwar and Vapi, the CMB receptor model is used. This scientific investigation is conducted to identify potential sources of PM_{10} emissions and to calculate the source contributions to PM_{10} mass. The estimations of the CMB model are not unique since they are based on least squares linear regression; as a result, it is difficult to demonstrate their correctness. For the current study, the CPCB-developed source profiles for the CMB model for several Indian metropolitan cities are used. The emission sources taken into account are biomass burning, vehicular emissions, crustal or soil dust, and fossil fuel combustion, including industrial sources.

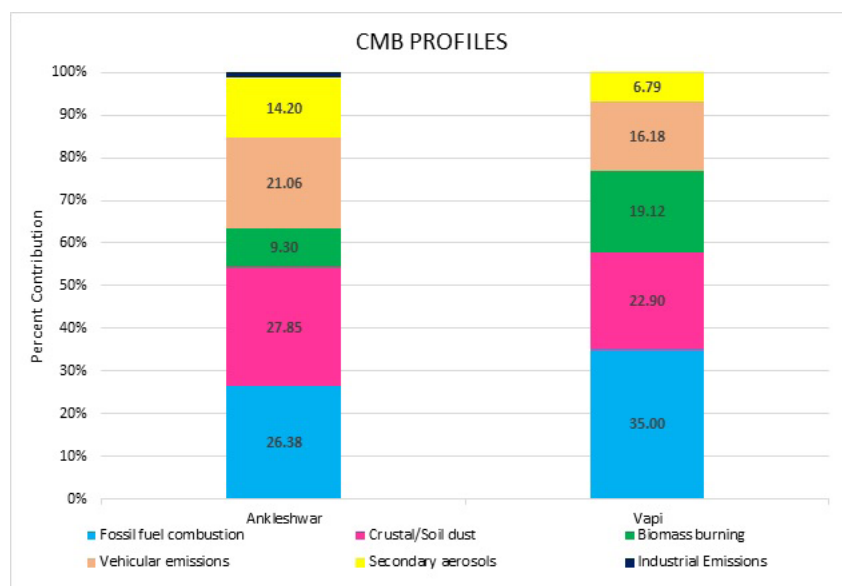


Fig. 7. PM_{10} Source contributions at Ankleshwar and Vapi using the CMB model

The factors for source apportionment using CMB are shown in Fig. 7, which reveals that the source contributions for Ankleshwar and Vapi are marginally different. With a percentage of 26.38% from Ankleshwar and 35% from Vapi, fossil fuel combustion is the leading source of emissions. The burning of any type of fossil fuel, such as coal, gasoline, diesel, natural gas, or oil, Light Diesel Oil (LDO), Heavy Diesel Oil (HDO) is a composite source of PM_{10} , and the several marker species linked to this source include Al, SO_4 , Cl, Fe, Cr, and Zn [21]. The second major source of emissions at both locations is crustal or soil dust, which Ankleshwar contributing 27.85% and Vapi contributing 22.90% of the mass of PM_{10} . Crustal or soil dust is a complex and heterogeneous mixture of dust that contains a high concentration of crustal elements like Si, Al, Ca, K, Na, and Mg. It can be produced by a variety of activities, including soil dust, resuspended dust, construction activities, fuel combustion, and vehicular emissions [22]. Vehicular emissions are the third-largest source of emissions, with EC, OC, Cu, Zn, Mn, Pb, and Ni serving as the primary marker species [23]. Vehicular emissions include combined emissions from several sources, such as gasoline and diesel cars, lubricants, beak liners, etc. Ankleshwar and Vapi as shown in Fig. 7, contribute 21.06% and 16.18%, respectively, to vehicular emissions. With an impact of 9.3% from Ankleshwar and 19.12% from Vapi, biomass burning is the fourth-largest component. Sources such as the burning of household fuelwood, agricultural waste, cow dung, solid waste, wildfires, and other biomass waste are included in biomass burning. The presence of element markers like SO_4 , NH_4 , or OC in combination with K^+ is often used to differentiate K^+ as a source of biomass-related burning [14].

Secondary aerosols, which comprise ammonium sulphate and ammonium nitrate, are identified as the fifth emission source. Secondary aerosols

of atmospheric particles that are created in the atmosphere can typically come from anthropogenic or natural sources and are mostly derived from their gaseous predecessors such as SO_2 , NO_x , and NH_3 [14]. Secondary aerosols are shown to contribute 14.20% for Ankleshwar and 6.79% for Vapi. For the current study, industrial emissions could not be distinguished as a separate source by the CMB model, however, for Ankleshwar, a very weak contribution of 1.2% is shown as the sixth emission source.

R^2 , chi-square (χ^2), degree of freedom, fit measure and percent mass are the several performance measurements and statistics used to assess the CMB model. The R^2 values are observed to be 0.77 and 0.86 for Ankleshwar and Vapi indicating that the SCEs provide a better explanation for the observed concentrations. The χ^2 is observed to be 3.56 and 5.80 for Ankleshwar and Vapi respectively depicting average linkage between SCEs and species concentration. The percentage of mass determined by the CMB model is 105.7% and 95.1% for Ankleshwar and Vapi, which can be termed as sufficient. The obtained solution by CMB can be regarded as reasonable with a degree of freedom values of 13 and 14 for Ankleshwar and Vapi respectively. The largest fit measures achieved for obtained solutions are 0.70 and 0.72 for Ankleshwar and Vapi, indicating a rational solution.

Table 1 provides an overview of the CMB source apportionment studies that are conducted in the Indian context.

Table 1. Summary of the percentage contribution of PM sources for CMB studies conducted in India

Sr. No.	Location	PM	Fossil fuel combustion	Crustal /Road dust	Vehicles	Industrial	Refuse/ Field burning	Secondary/ Marine aerosols	Other	Ref
1	Bangalore	PM ₁₀	4.2	50.6	19	4.5	---	8.7	13	[24]
2	Bangalore	PM _{2.5}	5.8	3.5	49.9	3.5	---	12.7	24.7	[24]
3	Delhi	PM ₁₀	---	64	29	3	---	---	4	[25]
4	Delhi	PM _{2.5}	---	35	62	2	---	---	1	[25]
5	Delhi	PM _{2.5}	---	35	20	20	16	---	9	[26]
6	Delhi	PM ₁₀	---	43	17	20	13	---	7	[26]
7	Hyderabad	PM ₁₀	12	40	22	9	7	---	10	[27]
8	Hyderabad	PM _{2.5}	9	26	31	7	6	---	21	[27]
9	Hyderabad	PM ₁₀	6.1	33.6	43.6	---	6.9	9.7	---	[28]
10	Hyderabad	PM _{2.5}	9.7	18.1	35.9	---	16.4	18.8	---	[28]
11	Kanpur	PM _{2.5}	13	6	37	---	23	15	---	[29]
12	Kolkata	PM ₁₀	42	21	---	---	7	---	29	[30]
13	Kozhikode	PM ₁₀	---	46	18	---	18	17	6	[31]
14	Mumbai	PM ₁₀	20.6	10	36.3	2.1	---	---	---	[32]
15	Nagpur	PM _{2.5}	---	6	57	---	15.1	16	6	[33]

Conclusion

The current research presents an exhaustive insight of PM₁₀ levels, elemental species bound to PM₁₀, and the emission sources contributing to PM₁₀ mass for Ankleshwar and Vapi industrial areas. The results showed that the PM₁₀ mass is higher than the NAAQS standard value of 100 µg/m³ and ranged between 100.98 and 225.47 µg/m³ for Ankleshwar and 115.88 to 226.5 µg/m³ for Vapi. According to the chemical examination,

the total mass of carbons ranged from 44 to 48 percent of PM₁₀ mass in Ankleshwar and from 45 to 48 percent in the industrial region of Vapi. For Ankleshwar and Vapi, water-soluble ions constitute 21 to 26% and 22 to 26% of the PM₁₀ mass, whereas significant elements ranged in proportion between 28 and 30% and 26 to 29% respectively. In all six locations for Ankleshwar and Vapi, the average lead and nickel concentrations are higher above the CPCB

limits of 500 ng/m³ and 20 ng/m³, respectively. The elements Ni, Cu, Ti, and V have a natural and anthropogenic source, while Fe, Si, Mn, and K are found to have crustal origins. The enrichment factors for the marker elements Cr, Zn, S, Br, and Pb showed that their source is anthropogenic. When assessing the sources that contribute to PM₁₀ mass, a well-known receptor model (CMB) is used and the best-fitting source profiles include fossil fuel combustion including industrial sources, crustal or soil dust, vehicle emissions, biomass burning, and secondary aerosols. According to the CMB model for Ankleshwar, source contributions are 27.85% from crustal or soil dust, 26.31% from burning fossil fuels, 21.06% from vehicle emissions, 14.20% from secondary aerosols, 9.30% from burning biomass, and 1.20% from industrial emissions. According to the CMB model findings for Vapi, the contribution from fossil fuel combustion, including industrial sources, is 35%, followed by contributions from crustal or soil dust (23%), biomass burning (19%), automobile emissions (16%), and secondary aerosols (7%). The current study is limited to the winter season because in the study area, winter is considered as worst climate scenario since dispersion of air pollutants is limited in winter season [34]. In developing countries, the generation of source profiles for specific areas takes long time. Hence, source apportionment study using the CMB model can give us a brief insight about source profiles present in the study area. The current research helps to estimate the pollutant load in the study region and creates a strategy for improving urban air quality. Further CMB, receptor model can be applied for PM_{2.5} in the future to study the health impact on the workers and people residing in nearby areas.

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Competing interests

The authors declare they have no conflicts of interest or competing interests.

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Ethical considerations

“Ethical issues (Including plagiarism, Informed Consent, misconduct, data fabrication and/or falsification, double publication and/or submission, redundancy, etc) have been completely observed by the authors.”

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