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Human health risk assessment of trace elements in PM_{10} for industrial areas in Gujarat

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ABSTRACT

Introduction: The present study examines human exposure to Particulate Matter (PM_{10}) and analyses potential health concerns in the industrial zones of Ankleshwar and Vapi in Gujarat.

Materials and methods: For Ankleshwar and Vapi, 120 samples were collected, and characterisation was carried out to determine the concentration of NO_3, SO_4, NH_3, K-S, Na, EC, OC, Al, Si, Fe, K, Ti, Ni, Br, Ca, Cl, Mn, Pb, Cr, Zn, S, V, and Cu in PM_{10} mass. The health risk from exposure to different trace elements, including both carcinogenic and non-carcinogenic, is evaluated for three distinct paths of ingestion, inhalation, and skin contact.

Results: The Excess Cancer Risk (ECR) values for Cr and Pb for the ingestion pathway and the carcinogenic risks for Cr, Ni, and Pb for the inhalation pathway are both found to be higher than the minimal permissible threshold (1×10^{-6}) for both children and adults for Ankleshwar and Vapi. However, for Ankleshwar and Vapi, the carcinogenic risks from dermal exposure to Cr and Pb are found to be lower than the permissible limit for both adults and children. It is observed that non-carcinogenic Hazard Index (HI) values for the skin contact and ingestion routes are less than 1 for both children and adults for Ankleshwar and Vapi. While the HI value for the inhalation pathway is found to be larger than the tolerable limit of 1 for both adults and children.

Conclusion: For the purpose of creating sustainable cities and improving the health of the urban population, this study will provide a fundamental basis and help the governing authorities design mandatory pollution prevention and control methods, restoration plans, and systematic monitoring programmes.

Introduction

Considering numerous environmental elements including air, soil, land, water, climate, etc., urbanisation and industrialisation have sparked significant environmental destruction [1]. Air pollution is mostly held responsible for environment-related problems in developing nations like Bangladesh, India, Nepal, and Sri Lanka. At the moment, air pollution is a major problem in India's cities, especially those that are developing quickly [2-3]. Industries and vehicular emissions, the two primary sources of

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air pollution, are both very significant. Particulate Matter (PM) continues to represent a sizable portion of air pollution that is closely linked to human diseases [4,5]. According to the World Health Organisation (WHO), particulate matter pollution is responsible for more than 8 million annual fatalities, ranking it as the thirteenth leading cause of death worldwide. The disorders of the heart, lungs, and brain are all directly associated with particulate pollution. However, studies have revealed that the relationship between particulate matter and fatalities is much more complicated [6].

Ambient particulate matter is a Group-1 carcinogen according to the International Agency for Research on Cancer (IARC) [7]. Additionally, it has been established that the particulate matter component of air pollution is closely related to the high prevalence of illnesses like lung cancer [8]. According to several studies, inhaling particulates is the primary cause of a number of health problems, including diminished lung function, aggravated asthma, increased respiratory problems like coughing, airway irritation, trouble breathing, irregular heartbeats, nonfatal heart attacks, and early death in people with comorbidities. [9, 10]. Based on the aerodynamic diameter, particulate matter is divided into two categories as PM_{10} and $PM_{2.5}$. According to this classification, coarse particulate matter has an aerodynamic diameter of 10 µm, while fine particulate matter has an aerodynamic diameter of 2.5 µm [11]. Pollen, forest fires, volcanoes, surface soils, marine aerosols, industrial activity, vehicle emissions, building and mining operations, various combustion processes, biomass burning, etc. are some of the natural and anthropogenic sources of particulate matter [12]. For the past 20 years, health concerns have been linked to the presence of atmospheric aerosols, which have resulted in declining air quality. Fine particulate matter that enters the lungs is closely associated with long-term health problems like respiratory or cardiovascular problems [13]. Recent research has connected traffic emissions to an increased risk of conditions like high blood pressure, systemic inflammation, and myocardial ischemia [14]. Arsenic (As), Nickel (Ni), and Cadmium (Cd) are classified by the IARC as being in class I, which is carcinogenic to humans. Lead (Pb) is classified as belonging to class 2A, which is known to be probably carcinogenic to humans, while Cobalt (Co) is classified as belonging to class 2B, which is known to be potentially carcinogenic to humans. There is not a single IARC carcinogenic classification group for elements like manganese (Mn), zinc (Zn), and Copper (Cu) [15].

According to a study, the specific physical and chemical PM characteristics can be employed as a crucial design element for epidemiological and toxicity research and assist in creating efficient control measures to enhance the air quality at these industrial clusters [16]. There is relatively limited literature on characterisation of particulates and risk assessment for Ankleshwar and Vapi. Thus, the current study is being carried out to characterise PM_{10} and analyse the associated risk for Gujarat's industrial areas of Ankleshwar and Vapi.

Materials and methods

Study area

Ankleshwar, a town in the Bharuch district of Gujarat, is situated at 21.62°N and 73.01°E, while Vapi, a town in the Valsad district, is situated at 20.38°N and 72.91°E. Ankleshwar is located in Gujarat's southern region, midway along the Ahmedabad to Mumbai industrial corridor, while Vapi is located in Gujarat's southernmost section, halfway between Surat and Mumbai. The Ankleshwar town has a plain environment with a mean elevation of around 15 m above mean sea level, which is lower than Vapi, which is situated 7 km from the Arabian Sea. The average annual rainfall in Ankleshwar is 860 mm, the average annual temperature is about 27°C, and the predominant wind direction is from the southwest or west. Vapi experiences 1403 mm of rain annually with an average yearly temperature of 26.5°C and a predominant west or southwest wind direction.

The industrial clusters of Ankleshwar and Vapi, which each house roughly 1700 and 1150 small or medium-sized enterprises, are dominated by the chemical and chemical products industries, pharmaceuticals, organic and inorganic chemicals, pigments, paints, dyes, and insecticides, etc. Different fuels used by these units include coke, lignite, firewood, furnace oil, light diesel oil, etc. The region uses extremely polluting fuels and chemical goods due to the nature of its manufacturing. Due to the increasing levels of air, water, and soil pollution, Ankleshwar and Vapi are thought to be Gujarat's most polluted industrial areas. The Comprehensive Environmental Pollution Index (CEPI) idea was created by the Central Pollution Control Board with the intention of analysing the environmental status of various industrial clusters throughout India. With an overall CEPI score of 89.09 for the 2019–2020 period, Vapi has been categorised as a very critically polluted cluster, and Ankleshwar follows closely behind with an overall CEPI score of 80.21. For the majority of the year in both Ankleshwar and Vapi over the past two years, the concentration of PM_{10} mass and $PM_{2.5}$ is higher than the permissible limit. This work aims to investigate the particulate matter concentration in the industrial estates of Ankleshwar and Vapi and evaluate the risk related to various elements in PM_{10}. The sampling locations were carefully selected in accordance with the site selection requirements of IS: 5182 Part XIV (BIS, 2000). Table 1 and Fig. 1 list the specifics of the monitoring locations.

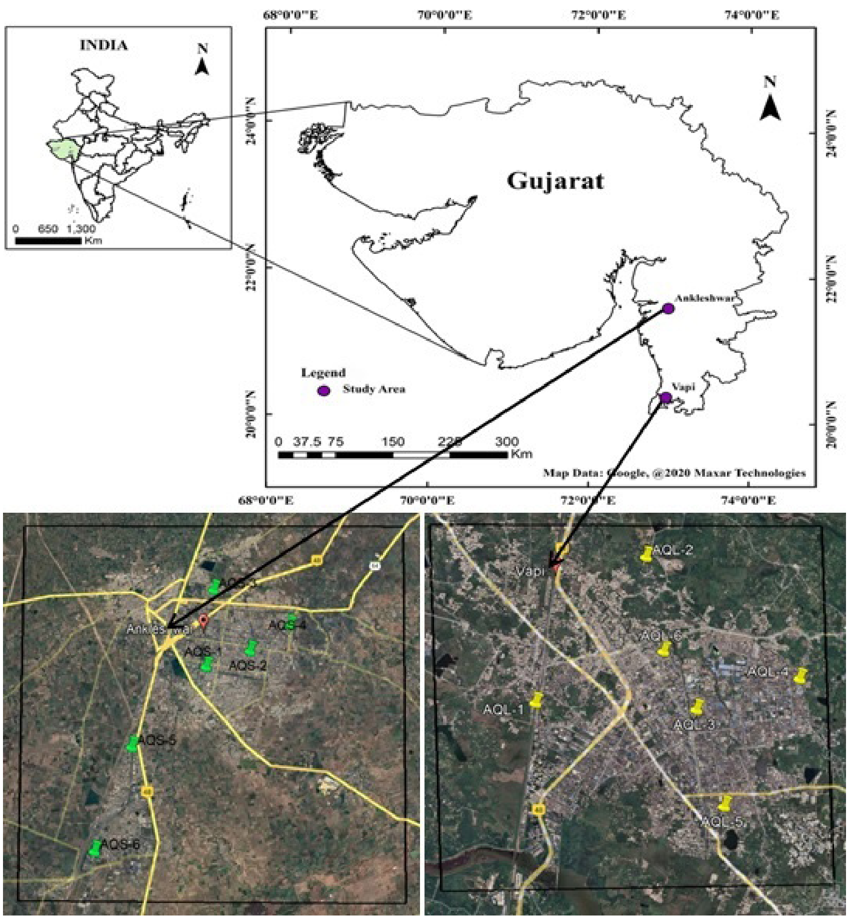

Fig. 1. Study area

Table 1. Sampling location details

Details	Ankleshwar			Vapi		
	Land use category	Latitude	Longitude	Land-use category	Latitude	Longitude
AQL-1	Residential	N 21° 36' 29.2"	E 73° 01' 2.2"	Commercial	N 20° 21' 54.3"	E 072° 54' 25.7"
AQL-2	Industrial	N 21° 36' 54.9"	E 73° 01' 59.9"	Green cover	N 20 °20' 46.8"	E 072° 55' 30.7"
AQL-3	Industrial	N 21° 38' 8.9"	E 73° 01' 1.2"	Industrial	N 20° 21' 50.5"	E 072° 56' 0.26"
AQL-4	Residential	N 21° 37' 32.8"	E 73° 02' 50.8"	Industrial	N 20°22' 08.6"	E 072° 57' 01.1"
AQL-5	Industrial	N 21° 34' 40.6"	E 72° 59' 34.74"	Industrial	N 20° 20' 54.6"	E 072° 56' 15.9"
AQL-6	Industrial	N 21° 32' 32.89"	E 72° 59' 3.34"	Industrial	N 20° 22' 24.8"	E 072° 55' 41.0"

Sample collection

As shown in Fig. 1, six locations in Ankleshwar and Vapi were sampled for PM_{10} from December 2019 to February 2020. PM_{10} samples were collected for 24 h on Quartz filter sheets with a size of 8 inches by 10 inches and a flow rate of 1132 lpm using a respirable volume sampler (RDS with Model 460NL, make - Envirotech Pvt. Ltd) positioned at a height of 1.5 m above the ground. Hence, a total of 120 samples were gathered for both research regions for all six locations. The filter sheets used in particulate matter monitoring were conditioned for two days in a desiccator at a temperature of around 25°C and relative humidity of 50%. The filter seets were then separated into three portions for further analysis of the particulate matter. The first component is used to analyse heavy metals, the second part is used to analyse ions, and the last part is used to analyse Elemental Carbon-Organic Carbon (EC-OC). Digestion and additional trace metal extraction from the filter sheets 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 material was filtered using Whatman filter paper and stored securely in the refrigerator for future analysis. Atomic Emission Spectrometer based on Inductively Coupled Plasma (ICP-AES, Model ULTIMA 2000) was used to analyse the extracted and chilled sample and determine the presence of the elements Al, Ca, Fe, Si, Cl, K, Br, Cr, Cu, S, Mn, Zn, Ti, Ni, Pb, and V. The CPCB-recommended standard approach was employed for ion analysis in the second section of the filter. In order to analyse the water-soluble ions under ideal circumstances, the filtered and extracted water samples were analysed using an ion chromatograph (IC Basic 792: Metrohm). The two anions, nitrate (NO_3), sulphate (SO_4), potassium salt (K-S) and the three cations, ammonium (NH_3), potassium (K^+), and calcium (Ca^{2+}), were examined. Using an EC-OC carbon analyser (model DRI2001, Procedure Improve A) and USEPA protocol, the third and final piece of the filter paper was examined. The EC-OC carbon analyzer's operation is based on the controlled oxidation of EC and OC, which releases carbon compounds at different temperatures.

Quality control and quality assurance

Throughout the research, a strict quality control procedure was implemented to maintain accuracy and precision. Further quality control procedures were made sure by the current sampling and analysis:

- During the handling of chemical reagents and fieldwork, quality assurance was performed.
- For lab analysts and field operators, competency evaluations were done.
- During sampling, sample handling, processing, and analysis, every safety measure was taken to avoid contamination.
- Appropriate labelling and representative samples were taken when gathering data (such as sample type, location, time and date of collection, environmental factors, etc).
- To assure data quality control, collaborative sampling, flow audits, spot checks, and duplicate analysis were done.
- The tools and equipment being used underwent acceptance tests.
- The disposable items, such as glassware, solvents, etc., were utilised appropriately.
- Filters were handled with clean forceps.

Risk assessment

The risk to human health associated with exposure to carcinogenic and other elements linked to atmospheric particulate matter is determined in the current analysis using the United States Environmental Protection Agency (USEPA) exposure model. Local residents in the research region may be exposed to airborne metals depending on their respiratory systems and other health-related factors. They can be further divided into adults and children. The following three pathways for exposure are taken into account when determining the exposure level for each element: 1. Particulate inhalation through the mouth and nose; 2. Particulate ingestion as a result of their deposition; and 3. Dermal absorption of particulate-bound trace elements when they adhere to exposed skin [17, 18]. Human health risks are further classified as carcinogenic and non-carcinogenic risks. Finding the exposure dose for each of the three exposure pathways, also known as the mean daily dose, is the first step in evaluating cancer risk and non-cancer risk. The non-carcinogenic risk is calculated as the hazard quotient for individual elements and the Hazard index for the combined effect of all elements using the mean daily dose. The Hazard Quotient (HQ), which is determined for all three routes and all trace elements taken into consideration in the study, is defined as the relationship between exposure dosage and specific Reference Dose (RfD). Every criterion used to calculate the average daily dose, Hazard quotients, and Hazard index is based on the USEPA reference. Pb, Ni, and Cr are three carcinogenic metals that are taken into account for this study's analysis of cancer risks. The exposure dose determined in the first stage is multiplied by the carcinogenic slope factor to determine the carcinogenic risk. Using USEPA-specified criteria, cancer risk is computed for each exposure pathway.

Exposure dose

Considering the exposure pathways for inhalation, ingestion, and skin contact, human health risk assessment is used extensively to distinguish toxic heavy metals. For calculating exposure dose and assessing the risk to human health, the USEPA criteria have been applied. The Average Daily Dosage (ADD) for each trace element taken into consideration in the study for all three exposure pathways is referred to as the exposure dose. The following equations are used to calculate exposure doses for inhalation, ingestion, and skin contact.

Exposure dose through inhalation pathway (ADD_{inh}, mg/kg/day)

$$ADD_{inh} = \frac{C * lnhR * EF * ED}{BW * AT * PEF} \quad (1)$$

Exposure dose through ingestion pathway (ADD_{ing}, mg/kg/day)

$$ADD_{ing} = \frac{C * lngR * EF * ED * CF}{BW * AT} \quad (2)$$

Exposure dose through dermal contact pathway (ADD_{derm}, mg/kg/day)

$$ADD_{derm} = \frac{C * SA * AF * EV * ABS * EF * ED * CF}{BW * AT} \quad (3)$$

Where, C is metal concentration in PM (mg / kg); InhR is the inhalation rate (20 m^3/day for children and 7.63 m^3/day for adults); IngR is ingestion rate (60 mg/day for children and 30 mg/day for adults); ED is exposure duration (6 years for children and 24 years for adults); EF is exposure frequency (180 days/year); BW is body weight (15 kg for children and 70 Kg for adults); SA is skin surface area parameter (2800 cm^2 for children and 5700 cm^2 for adults,); AF is adherence factor of soil to skin (0.2 mg/cm^2/event for children and 0.07 mg/cm^2/event for adults) ; EV is events frequency (1 event/day); ABS is dermal absorption fraction (0.001); PEF is particle emission factor (m^3/kg) (1.36 x 10^9 m^3/kg) ; AT is averaging time for non-carcinogens (ED * 365 days/year); CF is conversion factor (10^{-6} kg/mg). All the parameters used in the calculations in the current study are taken from US :EPA- 2007, US:EPA- 2009 [17, 18].

Non-carcinogenic health risk

The assessment of health risks for non-carcinogenic health consequences brought on by exposure to a trace element is often defined in terms of the hazard quotient for each element and each exposure pathway. The cumulative impact of all trace elements for a given pathway is then calculated for each pathway using the Hazard Index.

Hazard quotient (HQ)

The ratio of a trace element's likely exposure to the reference concentration that will not cause any harm is known as the hazard quotient. Thus, HQ is calculated by dividing the reference dose by the average daily dose (RfD).

$$HQ = \frac{ADD}{RfD} \quad (4)$$

Where ADD is the average daily dose and RfD is the reference dose (mg/kg/day).

The reference dosage is calculated using the average daily exposure dose and the highest tolerable risk for the total human population (including sensitive subgroups as well). If HQ<1, it suggests that the exposure must not have any negative impacts on health because the reference dose is more than the average daily dose. However, if HQ>1, it implies that the reference dose is lower than the estimated average daily dosage and that the exposure will have a negative impact on health [19]. In this investigation, reference dosage values from other research papers are used [20- 23].

Hazard index (HI)

Each exposure pathway's total non-carcinogenic risk is determined by performing an algebraic summation of all the calculated Hazard quotients for specific trace elements. According to this methodology for summarising, the health consequences of each trace element to which a receptor is exposed are cumulative for a certain exposure pathway. This cumulative non-carcinogenic health hazard for each exposure pathway is known as the Hazard index and is calculated using the equation shown below:

$$HI = \sum HQi \quad (5)$$

If HI is more than 1, it means that there are considerable non-carcinogenic risks, and the likelihood of these risks is inversely correlated with the value of HI. The likelihood of a noncarcinogenic risk increases with the HI score. Additionally, HI values below one suggest that there are no non-carcinogenic risks.

Excess cancer risk

The likelihood that a person will get cancer at any point in their lifetime as a result of exposure to carcinogens is known as carcinogenic risk [22]. Unless the exposure level is zero, an element is regarded to have no threshold if it is capable of producing harmful effects even at lower concentrations. The term "zero" refers to the safe exposure dose for carcinogens like chromium, cadmium, nickel, arsenic, mercury, etc. because they are classified as "no threshold" carcinogens, indicating that even minute amounts of exposure to them have the potential to cause any type of cancer. The probability of a person developing any type of cancer over the course of their entire lifespan as a result of cumulative exposure to possible carcinogens is expressed as excess cancer risk (ECR). The equation for calculating ECR is shown below:

$$ECR = \frac{C * ET * EF * IUR}{AT} \quad (6)$$

where, C is measured pollutant concentration (mg/m^3), EF is exposure frequency (180 days/year); ET is exposure time (8 h/day); AT is average exposure time for carcinogens (70 year x 365 days/year x 24 h/day); IUR is inhalation unit risk (mg/m^3). The tolerable limit of carcinogenic risk is between 1×10^{-6} to 1×10^{-4} for regulatory purposes and policy making. [19].

Results and discussion

Chemical characterisation of PM_{10}

Between December 2019 and February 2020, 120 quartz filter papers were used to gather PM_{10} mass, which is then subjected to additional chemical analysis. In Ankleshwar, the PM_{10} concentration ranged from 100.98 to 225.47 µg/m^3, with a mean value of 159.5 µg/m^3, while in Vapi, it varied from 115.88 to 226.50 µg/m^3, with an average value of 174.58 µg/m^3, as shown in Fig. 2. In comparison to the National Ambient Air Quality Standard (NAAQS, 2009) value of 100 µg/m^3, it has been observed that the average PM_{10} readings in Ankleshwar and Vapi were 1.6 and 2 times higher, respectively. Additionally, the average PM_{10} concentrations in Ankleshwar and Vapi were found to be almost 10 times higher than the ambient air quality threshold for PM_{10} set by the World Health Organization (WHO, 2006), which is 20 µg/m^3. In Table 2, the statistical distribution characteristics for PM_{10} and other elements such as EC, OC, NO_3, SO_4, NH_3, K-S, Na, Ca, Cl, Al, Si, Ti, Ni, S, K, Fe, Cr, Cu, Zn, Br, Pb, V, and Mn are provided for all the locations in Ankleshwar and Vapi.

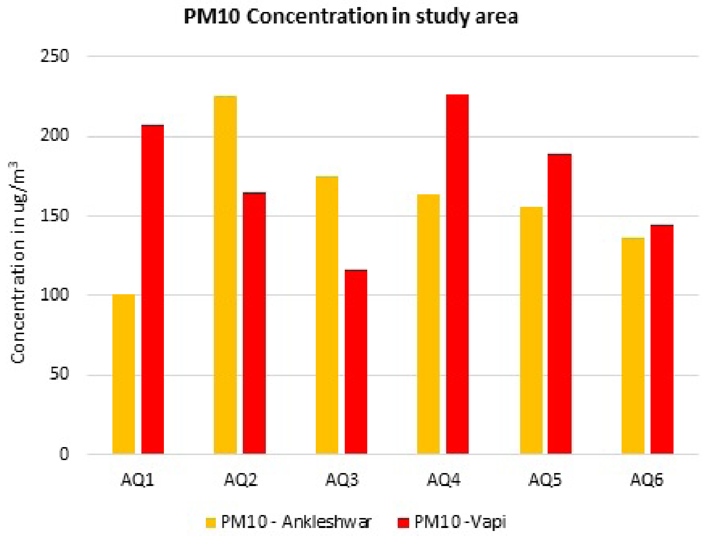

Fig. 2. Components of PM_{10} in Ankleshwar and Vapi

Table 2. Statistical distribution of PM_{10} and elemental concentration in the study area

Group	Ankleshwar					Vapi			
	Name of element	Mean value	Standard deviation	Minimum value	Maximum value	Mean value	Standard deviation	Maximum value	Minimum value
	PM	159.5	19.72	100.98	225.47	174.58	29.32	226.5	115.88
Carbon	EC	20.33	8.16	14.71	23.5	21.78	8.58	23.8	18.8
	OC	29.39	11.54	26.22	34.91	29.4	12.11	32.23	27.35
Water-soluble ions	SO_4	8.37	4.26	6.62	9.69	8.04	4.39	9.81	6.15
	K-S	4.15	1.56	3.62	4.62	3.99	1.77	4.43	3.72
	NO_3	3.66	1.91	2.48	4.35	4.12	2.12	4.6	3.5
	Ca	3.32	1.72	2.98	3.58	2.93	1.86	3.42	2.23
	NH_3	3.27	1.48	2.51	4.01	2.79	1.69	3.33	2.41
	K	1.5	1	1.29	1.7	1.82	1.03	2.07	1.51
Major elements	Si	13.78	7.02	11.91	16.08	13.31	7.23	14.39	12.65
	Al	6.19	3.23	5.41	7.17	6.52	3.54	6.87	6.09
	Ti	3	1.4	2.22	4.5	2.58	1.37	3.16	2.19
	Cl	2.81	1.54	2.37	3.09	2.68	1.25	2.94	2.25
	S	2.43	1.33	1.76	2.84	2.54	1.41	2.87	2.1
	Pb	2.32	1.31	1.95	2.69	2.3	1.3	2.66	2.09
	Fe	2.27	1.25	1.65	2.91	2.01	1.16	2.28	1.71
	Na	1.32	0.62	1.18	1.51	1.32	0.65	1.42	1.2
Trace elements	Zn	0.56	0.33	0.08	0.75	0.63	0.39	0.79	0.56
	Cr	0.47	0.26	0.36	0.57	0.46	0.27	0.57	0.37
	Br	0.28	0.09	0.26	0.32	0.27	0.09	0.3	0.23
	V	0.16	0.07	0.08	0.53	0.08	0.02	0.09	0.08
	Mn	0.07	0.03	0.05	0.08	0.07	0.03	0.08	0.05
	Ni	0.03	0.02	0.03	0.04	0.04	0.02	0.05	0.03
	Cu	0.03	0.01	0.02	0.03	0.03	0.01	0.03	0.03

- Values of all parameters are in $\mu g/m^3$

Following the chemical characterization of PM_{10}, the elements are divided into four categories, including total carbon, water-soluble ions, main elements, and trace elements, [24] as shown in Fig. 3. The largest concentration of the four detected components, is found in the carbon fraction, followed by elements and water-soluble ions. For Ankleshwar and Vapi, the mean concentration of total carbon is recorded as 49.72 µg/m^3 and 51.18 µg/m^3, which is 45% and 46% of the total PM_{10} mass. Ankleshwar and Vapi have mean OC concentrations of 29.39 and 29.40 µg/m^3, respectively, while Ankleshwar and Vapi have mean EC concentrations of 20.33 and 21.78 µg/m^3, respectively.

For Ankleshwar and Vapi, respectively, the mean concentration of water-soluble ions containing SO_4, NO_3, K-S, Ca, NH_3, and K is observed to be 26.90 and 25.87 µg/m^3, that is around 22% of the total PM_{10} mass. In Ankleshwar, the average concentration of the water-soluble cations Ca, NH_3, and K is 3.32, 3.27, and 1.5 µg/m^3, while in Vapi, it is 2.93, 2.79, and 1.82 µg/m^3. For Ankleshwar, the average concentration of water-soluble anions SO_4, K-S, and NO_3, is 8.37, 4.15 and 3.66 µg/m^3, but for Vapi, it is 8.04, 3.99, and 4.12 µg/m^3. For Ankleshwar and Vapi, the total mean concentration of major elements, including Si, Al, Ti, Cl, S, Pb Fe, and Na, is observed to be 31.49 and 31.08 µg/m^3, which is 30 to 31% of PM_{10} mass respectively. With average concentrations of 13.78, 6.19, 3, 2.81, 2.43, 2.32, 2.27, and 1.32 µg/m^3 for Ankleshwar and 13.31, 6.52, 2.58, 2.68, 2.54, 2.30, 2.01, and 1.32 µg/m^3 for Vapi, respectively, the major elements are often different earth crust elements like Si, Al, Ti, Cl, S, Pb Fe, and Na.

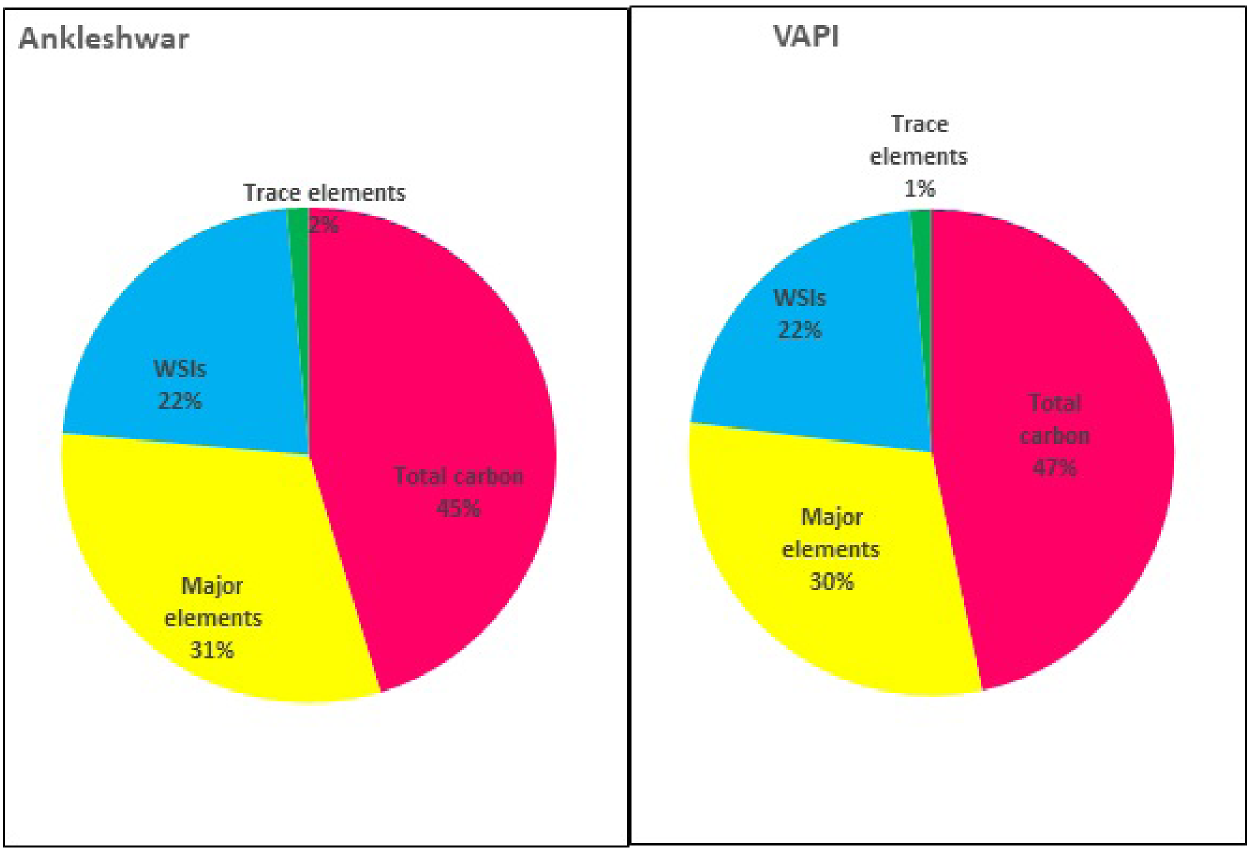

Fig. 3. Components of PM_{10} in Ankleshwar and Vapi

The total concentration of trace elements, such as Zn, Cr, Br, V, Mn, Ni, and Cu, is found to be 1.60 and 1.58 µg/m^3 which is around 1% of PM_{10} mass for Ankleshwar and Vapi, respectively. With mean concentrations of 0.56, 0.47, 0.28, 0.16, 0.07, 0.03, and 0.03 µg/m^3 for Ankleshwar and 0.63, 0.46, 0.27, 0.08, 0.07, 0.04, and 0.03 µg/m^3 for Vapi, respectively, the trace elements include anthropogenic trace indicators including Zn, Cr, Br, V, Mn, Ni, and Cu. The Central Pollution Control Board (CPCB) has set yearly regulation limits for a number of metals, including As, Pb, Cd, and Ni (Ministry of Environment and Forest -MoEF, 2009). The average lead concentration is found to be 2318 and 2305 ng/m^3 in Ankleshwar and Vapi, respectively, above the CPCB limit of 500 ng/m^3. Similarly, the average Ni concentration is found to be 34 and 37 ng/m^3 in Ankleshwar and Vapi, respectively, exceeding the CPCB limit of 20 ng/m^3. Table 3 compares the heavy metal concentrations discovered in the current study with past research conducted in a few other Indian towns.

Table 3. Comparison of Heavy metal concentration (ng/m^3) observed in the present study with other places in India

Place	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Pb	Cd	Reference
WHO	20	150	---	1	0.4	70	---	6	500	5	WHO-Limit [25]
Ankleshwar	470	70	2270	---	30	30	560	---	2320	---	Ankleshwar-present study
Vapi	460	70	2010	---	40	30	630	---	2300	---	Vapi-present study
Agra	238.57	206.57	2737.18	161.97	201.84	193.11	481.09	28.83	205.39	7.04	[26]
Agra	300	900	2900	---	200	100	500	---	1100	---	[27]
Lucknow	22.2	---	219.35	---	35.01	27.3	---	---	40.6	16.24	[2]
Delhi	230	250	11200	---	380	210	4100	---	460	19	[1]
Delhi	11-10268	163-10574	7119-349670	2.5-524	18-443	15-2224	67-12884	---	22-190	03.-11.7	[28]
Delhi	171	699	27047	23.3	37	169	264	---	129	---	[29]
Kolkatta	54	619	26700	16	42	44	159	23	1030	3.12	[30]
Kolkatta	101	249	11242	4.1	48	107	761	---	394	8.6	[3]
Chennai	64	15	1275	90	76	190	11700	1	96	BDL	[31]
Coimbatore	14.2	---	---	---	31.37	388.6	519.9	---	143.5	2.8	[32]
Dhanbad	22	164	4164	6	29	319	4754	9	89	7	[33]
Mining area-Odisha	5	0.8	70	2	3	50	0.2	---	40	0.7	[34]
Non-mining area-Odisha	4	2	210	3	2	90	0.4	---	60	0.8	[34]
Pune	241	395	5103	222	124	206	325	---	147	88	[35]
Mumbai	460	890	3340	---	720	820	7350	---	1600	---	[36]
Kharagpur	200.454	---	---	22.422	55.966	---	219.968	---	194.876	---	[37]
Dhanbad	290	1035	2970	36	33	915	560	22	210	30	[38]
Jharia Coalfield	120-330	170-2870	2880-8350		20-40	880-5200	220-1090		40-340	20-70	[39]
Dhanbad	34	65	1953	49	54	25	655	21	337	13	[40]
Dhanbad	110-420	140-1900	1430-28480	---	2-20	60-6320	160-2550	---	240-320	30-70	[41]

Non-carcinogenic risk assessment

HQ and HI values are calculated for adults and children for the three exposure pathways of ingestion, inhalation, and dermal contact, as indicated in Tables 4 and 5. The considerable discrepancy between the observed HQ/HI values for children and adults can be attributed to the distinct behavioural and physiological activities of each group [42]. Inhalation exposure is consistently observed to be the main route of direct exposure for particulate-linked trace elements in both adults and children. Since the threshold values for elements like Ca, Na, Fe, and Zn have not been defined or reported in other research papers, the HQ/HI values for these elements are not determined for this study. The absence of threshold values for these elements is due to the fact that Ca, Na, Fe, and Zn are thought to be necessary human constituents, and as a result, their observed concentrations may be lower than the reference doses [43]. For the Ankleshwar region, the inhalation pathway HQ value for adults for the elements Al, Cr, Mn, Ni, Ti, V, and Si is larger than the permissible value of 1, while the element Br is the only one whose value is below the allowed limit of 1. In contrast, the HQ value for the adult inhalation pathway in the Vapi study area is larger than 1 for the elements Al, Cr, Mn, Ni, Ti, and Si and less than 1 for the elements Br and V. Children's HQ values for the Ankleshwar and Vapi study areas are found to be larger than 1 for Cr, Ti, and Si, but less than 1 for Al, Br, Mn, Ni, and V. For Ankleshwar, the Hazard index HI, is observed to be 1.58 $x 10^2$ for adults and $5.51x10^1$ for children. HI due to inhalation exposure is seen to be 1.38 x 10^2 for adults and $5.51x10^1$ for children in the Vapi area, indicating a higher non-carcinogenic risk for all elements taken into account in the study. Furthermore, it can be deduced that the detrimental non-carcinogenic risk associated with inhalation is higher for adults than for children for both Ankleshwar and Vapi.

The exposure route for ingesting particulate-bound trace elements involves deposition on the surface of objects, food, beverages, etc., followed by transfer of the deposition of particles into the mouth [19]. For both Ankleshwar and Vapi, the HQ values for all the components taken into account in the study area for the ingestion pathway are lower than 1 for both adults and children. For Ankleshwar and Vapi, the observed HI values for adults are 4.85E-03 and 4.68E-03; for children, they are 4.53E-02 and 4.36E-02, respectively. This indicates that both the observed HI values for adults and children are below the permissible level of 1. This suggests that there is no non-carcinogenic risk from ingesting any of the elements, either alone or when combined. Additionally, it may be deduced that adults have a higher non-carcinogenic risk associated with the ingestion pathway for Ankleshwar and Vapi than children.

Tables 4 and 5 show the HQ and HI values for all components in the study area for the dermal contact pathway in both adults and children. The findings suggest that, when compared to the exposure pathways of inhalation and ingestion, all elements included in this investigation exhibit the lowest HQ values for dermal contact exposure. For both Ankleshwar and Vapi, the HQ values connected to dermal contact for both adults and kids have values lower than the permitted upper limit of 1. Furthermore, it is found that in Ankleshwar and Vapi, the integrated effect of all HQs expressed as HI had values of 5.56E-04 and 5.06E-04 for adults and 3.64E-04 and 3.49E-04 for children, respectively. Because of this, for both Ankleshwar and Vapi, all HI values for adults and kids are lower than the safe value of 1.

Table 4. HQ and HI for metals in PM_{10} via different exposure pathways–For adults

Element	HQingest		HQderm		HQinh	
	Ankleshwar	Vapi	Ankleshwar	Vapi	Ankleshwar	Vapi
Al	8.48E-06	8.93E-06	3.38E-07	3.56E-07	1.19E+00	1.25E+00
Br	5.48E-07	5.28E-07			6.71E-03	6.47E-03
Ca	1.74E-05	1.53E-05	6.93E-07	6.11E-07		
Cr	2.15E-04	2.10E-04	3.43E-04	3.35E-04	4.51E+00	4.41E+00
Cu	1.03E-06	1.03E-06	4.10E-08	4.10E-08		
Fe	4.44E-06	3.93E-06				
Mn	6.85E-07	6.85E-07	6.83E-07	6.83E-07	1.34E+00	1.34E+00
Ni	3.74E-06	4.98E-06	3.73E-06	4.97E-06	1.44E+00	1.92E+00
NO_3	3.13E-06	3.53E-06	1.25E-07	1.41E-07		
Pb	9.08E-04	9.00E-04	3.62E-05	3.59E-05		
Ti	5.01E-05	4.31E-05	5.00E-05	4.30E-05	1.44E+02	1.24E+02
V	4.38E-05	2.19E-05	6.73E-05	3.36E-05	1.53E+00	7.67E-01
Zn	2.56E-06	2.88E-06	1.02E-07	1.15E-07		
Cl	1.28E-03	1.22E-03	5.12E-05	4.88E-05		
Na	7.23E-05	7.23E-05	2.89E-06	2.89E-06		
Si	2.24E-03	2.16E-03			4.40E+00	4.25E+00
ΣHQ	4.85E-03	4.68E-03	5.56E-04	5.06E-04	1.58E+02	1.38E+02

Table 5. HQ and HI for metals in PM_{10} via different exposure pathways–For children

Element	HQingest		HQderm		HQinh	
	Ankleshwar	Vapi	Ankleshwar	Vapi	Ankleshwar	Vapi
Al	7.91E-05	8.34E-05	2.22E-07	2.12E-07	5.00E-01	5.00E-01
Br	5.11E-06	4.93E-06			2.59E-03	2.59E-03
Ca	1.62E-04	1.43E-04	4.54E-07	4.35E-07		
Cr	2.00E-03	1.96E-03	2.24E-04	2.15E-04	1.76E+00	1.76E+00
Cu	9.59E-06	9.59E-06	2.68E-08	2.57E-08		
Fe	4.15E-05	3.67E-05				
Mn	6.39E-06	6.39E-06	4.47E-07	4.29E-07	5.37E-01	5.37E-01
Ni	3.49E-05	4.65E-05	2.44E-06	2.34E-06	7.67E-01	7.67E-01
NO_3	2.92E-05	3.29E-05	8.19E-08	7.85E-08		
Pb	8.47E-03	8.40E-03	2.37E-05	2.28E-05		
Ti	4.68E-04	4.02E-04	3.27E-05	3.14E-05	4.95E+01	4.95E+01
V	4.09E-04	2.05E-04	4.41E-05	4.22E-05	3.07E-01	3.07E-01
Zn	2.39E-05	2.68E-05	6.68E-08	6.41E-08		
Cl	1.20E-02	1.14E-02	3.35E-05	3.22E-05		
Na	6.75E-04	6.75E-04	1.89E-06	1.81E-06		
Si	2.09E-02	2.02E-02			1.70E+00	1.70E+00
ΣHQ	4.53E-02	4.36E-02	3.64E-04	3.49E-04	5.51E+01	5.51E+01

The sequence of the HQ values for several heavy metals along the ingestion pathway in Ankleshwar and Vapi is Si>Cl>Pb>Cr>Na>Ti>V>Ca>Al>Fe>Ni>NO_3>Zn>Cu>Mn>Br for both children and adults. For the dermal contact pathway in Ankleshwar and Vapi, in both children and adults, the HQ values of several heavy metals appeared in the following order: Cr>V>Cl>Ti>Pb>Ni>Na>Ca>Mn>Al>NO_3>Zn>Cu. The HQ values of various heavy metals present in Ankleshwar and Vapi for both children and adults are in the following order: Ti>Cr> Si>V>Ni>Mn>Al> Br.

Carcinogenic risk assessment

Because the IARC has classified three trace elements, namely Cr, Ni, and Pb, as carcinogenic or certainly carcinogenic or possibly carcinogenic elements to humans, the carcinogenic risk is evaluated for these three elements in the current study. For exposure pathways connected to inhalation, ingestion, and skin contact, the carcinogenic risk is assessed. The individual cancer risks are calculated for each of the three routes for adults, kids, and elements Cr, Ni, and Pb separately, and the aggregate ECR for adults, kids, and each pathway for Ankleshwar and Vapi is then computed. The ECRs for various exposure pathways for Ankleshwar and Vapi are listed in Tables 6 and 7, respectively, for adults and kids.

Table 6. Cancer Risk for metals in PM_{10} via different exposure pathways–For adults

	Cringest		Cr derm		Cr inh	
Element	Ankleshwar	Vapi	Ankleshwar	Vapi	Ankleshwar	Vapi
Cr	1.29E-06	1.26E-06	5.14E-07	5.03E-07	3.79E-02	3.71E-02
Ni					7.48E-06	9.97E-06
Pb	1.14E-05	1.13E-05	3.55E-08	3.52E-08	1.78E-04	1.76E-04

Table 7. Cancer Risk for metals in PM_{10} via different exposure pathways–For children

Element	Cringest		Cr derm		Cr inh	
	Ankleshwar	Vapi	Ankleshwar	Vapi	Ankleshwar	Vapi
Cr	1.20E-05	1.18E-05	3.37E-07	3.23E-07	1.48E-02	1.48E-02
Ni					3.99E-06	3.99E-06
Pb	1.06E-04	1.05E-04	2.33E-08	2.23E-08	7.06E-05	7.06E-05

For inhalation exposure, the ECRs for Pb and Cr for adults are both higher than the maximum tolerated threshold (1×10^{-4}) for Ankleshwar and Vapi. The carcinogenic risk via the inhalation pathway for Ni (for adults and children) and Pb (for children) is also found to be higher than the tolerable minimum level ($1x10^{-6}$) for both Ankleshwar and Vapi. For both Ankleshwar and Vapi, the ECRs for Cr for both adults and children, as well as the ECRs for Pb in the case of children, are higher than the minimal tolerated limit ($1x10^{-6}$) for the ingestion pathway. In contrast, Ankleshwar and Vapi have ECRs for Pb that is higher above the upper acceptable limit (1×10^{-4}) for adults. For both adults and children in Ankleshwar and Vapi, the observed ECR values for Cr and Pb for the dermal contact pathway are observed to be lower than the permissible limit ($1x10^{-6}$ to 1×10^{-4}).

Conclusion

The goal of the current study is to evaluate the complete characterization of PM_{10}, including EC, OC, WSIs, and elements, followed by a risk evaluation of the elements for the Gujarat industrial locations of Ankleshwar and Vapi. In the Ankleshwar area, the mean PM_{10} mass concentration ranged from 100.98 to 225.47 μg/m^3, and in the Vapi area, it ranged from 115.88 to 226.5 μg/m^3, both of which are higher than the NAAQS standard value of 100 μg/m^3.. For both children and adults, the non-carcinogenic risk for the inhalation pathway had HQ and HI values of more than 1, indicating a negative effect on the inhalation pathway for Ankleshwar and Vapi. The HQ and HI values for the ingestion pathway and skin contact for both children and adults are less than 1, indicating that neither Ankleshwar nor Vapi will suffer any negative effects. In the research areas of Ankleshwar and Vapi, the potential carcinogenic risk for the inhalation route is higher than the tolerable limit ($1x10^{-6}$ to $1x10^{-4}$) for Cr, Ni, and Pb, for both adults and children. In addition, the ECR values for Cr and Pb for the ingestion pathway for Ankleshwar and Vapi are higher than the permissible limit ($1x10^{-6}$ to $1x10^{-4}$) for both adults and children. The ECR values thus imply a significant cancer risk for the population living in the research region for both ingestion and inhalation routes. The ECR values for Cr and Pb are below the acceptable limit only for dermal contact, suggesting no carcinogenic risk. The carcinogenic health consequences associated with the ingestion and inhalation exposure pathways are of concern for the current investigation. Policymakers will benefit from the present health risk assessment of carcinogenic and non-carcinogenic hazards in making decisions about air pollution management methods. The current study is only focused on the winter months because winter is considered as worst climate scenario since dispersion of air pollutants is limited and it further results in adverse effects on human health. Looking to dire health consequences of exposure to $PM_{2.5}$, a health risk assessment for $PM_{2.5}$ can be done 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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