Heavy Metal Assessment in Urban Particulate Matter in Industrial Areas of Vadodara City

S. A. Nihalani, A. K. Khambete, and N. D. Jariwala

Abstract Air pollution related to particulate matter is becoming a crisis of chief concern these days in urban areas. The concentration of ambient particulates is recently grabbing attention all over the world, owing to its harmful effects on people. The prime health risks linked with particulate pollution are breathing problems like asthma and long-term effects leading to premature death in the case of people with respiratory problems. This can essentially be attributed to mounting exposure to urban fine particulates termed as PM2.5. In the past several decades, exhaustive monitoring for ambient heavy metals focussing on long-term temporal trends and chemical characterisation has been done all over the world. The significant aspect of air pollution control depends on recognising the accurate sources of the pollutant. Sampling and monitoring for three sites at PCC industrial area in Vadodara for PM100, PM10, and PM2.5 including heavy metals have been carried out. PM100 concentrations were observed to be between 214 and 398 $\mu g/m^3$, PM10 was found to be between 70 and 93 $\mu g/m^3$, and PM2.5 concentration was in the range 10–35 $\mu g/m^3$. Highest concentrations of Fe, Zn, Cu, Ni, Pb, Cd, Hg, and Cr were found to be 10.86, 6.78, 0.995, 0.151, 0.077, 0.057, 0.025, and 0.014 $\mu g/m^3$, respectively. The chief sources of particulates and heavy metals at the site were emissions from industrial processes, traffic emissions, and re-suspension dust. It can be inferred that it is necessary to perform a detailed and exhaustive assessment of air pollutants and heavy metals in the study area.

Keywords Urban particulates · Heavy metal assessment · Suspended particulate matter

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1 Introduction

In developing countries like India, rapid industrialisation, urbanisation, and population explosion have led to an increase in fossil fuel combustion leading to a greater concentration of particulate matter and gaseous air pollutants [1]. The common air pollutants generally include total suspended particulate matter, respirable suspended particulates, carbon monoxide, sulphur dioxide, and nitrogen dioxide [2]. From the different air pollutants, urban particulates are considered to be of major concern due to its critical impact on air quality in an urban area and as well as a rural area [3]. Particulate matter is termed as a complex fusion of liquid or solid particulates that may vary in size. Airborne particulates are classified into coarse, fine, and ultrafine particles based on their aerodynamic diameters [4]. The natural sources of particulates may be dust, soil, or other crustal elements from, roads, mines, or volcanoes. The major anthropogenic sources of particulate matter may be industrial processes, fossil fuel burning, agricultural residue, or municipal solid waste incineration, construction activities, and emissions from paved and unpaved roads [5].

2 Sources and Effects of Heavy Metals Linked with Particulate Matter

Heavy metals are regarded as one of the most precarious groups of anthropogenic pollutants in the environment. This shall be attributed to their toxicity and persistent nature in the environment. Various studies have shown considerable links between health effects and different constituents of particulates like aluminium, arsenic, bromine, carbon, elemental carbon, chromium, copper, organic selenium, iron, lead, sulphate, mercury, nickel, nitrate, potassium, sodium, titanium, vanadium, and zinc, etc. Metals specifically cadmium, copper, and lead are capable of accumulating in the human body for a comparatively longer time period. The presence of heavy metals in urban particulates in significant concentration can lead to adverse health effects in human beings [6]. High levels of airborne heavy metals like lead, cadmium, and few organic pollutants may lead to neurological and behavioural problems in children. Lead is termed to be a community air pollutant. It is associated with increased blood lead in adults. Long-term exposure to Pb can lead to health problems such as tooth decay, anaemia, indigestion, and bone marrow alterations.

3 Study Area

Vadodara city is located in the central-eastern mainland region of Gujarat. Vadodara lies roughly between 22° 17′ North latitude and 73° 15′ East longitudes. The district covers an area of 7794 km^2 and accounts for 3.79% of the total geographical area of the state. Vadodara is considered a cosmopolitan city located on the banks of river Vishwamitri and to the South East of the city Ahmedabad [7]. Since all the major roads and railway lines connecting Delhi, Mumbai, and Ahmedabad pass through Vadodara, it is also known as the “Gateway to the Golden Corridor”. Due to urbanisation, various residential areas earlier have not been converted to the commercial areas, industrial areas, leading to severe air pollution. Since the late sixties and early seventies, the city has seen a spurt of industrial growth with the large refinery, petrochemicals, and fertilisers units being developed along with other downstream chemical units, and several ancillary units have been set up through the city in several industrial estates, which dot the city landscape. The major industries in the city include chemicals, petrochemicals, pharmaceuticals, and biotechnology. The monitoring locations were designed keeping the topography of the study area, wind speed as well as wind direction in mind [8].

From the several industrial areas, it was preferred to select the IOCL industrial area for study purposes since it houses various chemicals and pharmaceuticals. Three sampling locations were selected. One sampling station was selected on the upstream side of the industrial area, which is Koyali village, and two sampling stations were selected on the downstream of the industrial area that is Karachia and Ranoli villages. The annual wind rose diagram is shown in Fig. 1, and the sampling locations are shown in Fig. 2 and tabulated in Table 1.

4 Methodology

4.1 Sampling and Concentration of Particulate Matter

- Sampling was done at the stations for monitoring PM100, PM10, and PM2.5 using HVS, respirable dust sampler, and PM2.5 samplers.
- All three samplers were run simultaneously for 24 h in the open air, and flow rate was recorded [9].
- After the required time of sampling, the filter papers were taken out and stored carefully in envelopes within the desiccator.
- The filter papers were conditioned at 20–30 °C temperature and relative humidity between 40 and 50% [10].
- For all the three samplers, the initial weight (Wi) was taken for the filter papers.
- After sampling, the filter papers were again conditioned at 20–30 °C temperature and relative humidity between 40 and 50%.
- For all the three samplers, the final weight (Wf) was taken for the filter papers.

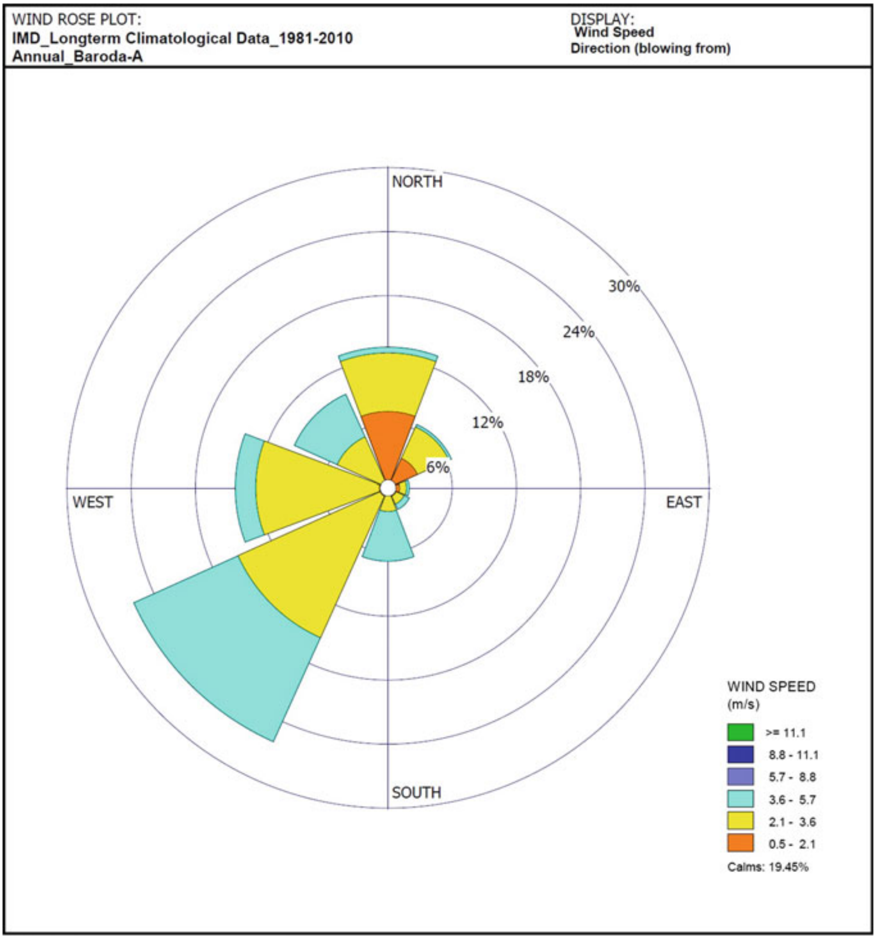

Fig. 1 Annual wind rose diagram

Calculations of the Mass of Particulate Matter

$$\text{RSPM}(\mu\text{g/m}^3) = (\text{W}_f - W_i) \times 10^6 / V$$

where

V air volume sampled in m^3.
W_f final filter weight in g.
W_i initial filter weight in g.

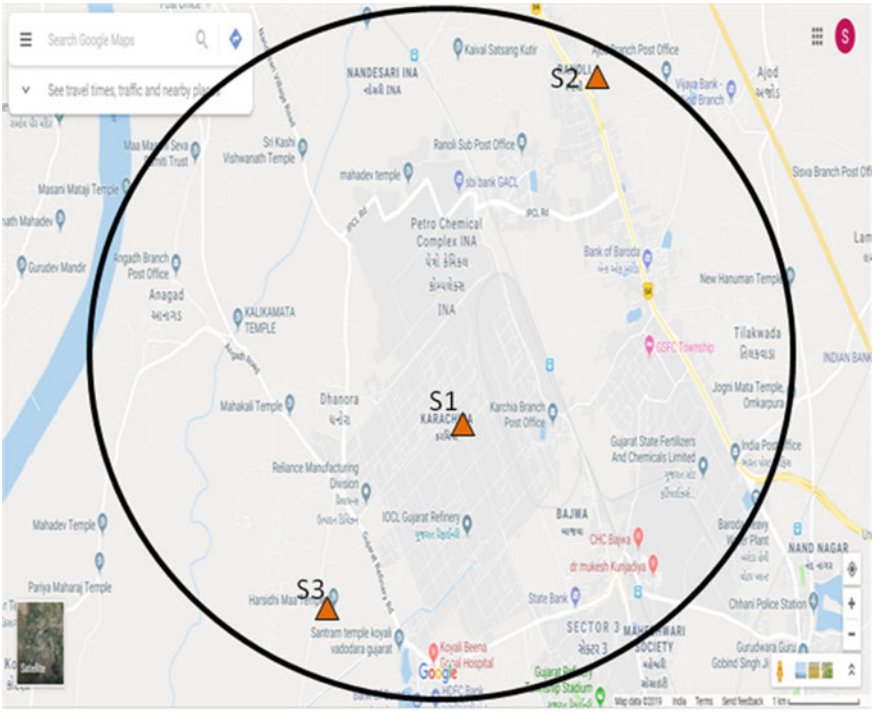

Fig. 2 Sampling locations in study area

Table 1 Details of sampling locations

Sr. No.	Station No.	Location	Rationale	Area category
1	AQ01	Karachia	d/w	Industrial
2	AQ02	Ranoli	d/w	Industrial
3	AQ03	Koyali	u/w	Industrial

4.2 Heavy Metal Analysis

- The size of the filter paper used for measurement of PM100/PM10 was adequate for further analysis for trace elements. Hence, toxic heavy metals, namely As, Cu, Cd, Cr, Hg, Fe, Mn, Ni, Pb, and Zn were analysed [11]. This method includes acid digestion of filter paper followed by chemical analysis using atomic absorption spectrometry.
- The exposed part of the filter was cut into three equal pieces. Once a piece of this filter paper was cut into small pieces and dip in a beaker having 100 ml acid (3% HNO_3 & 8% HCl) solution and beaker heated on the heating mantle for 10–15 min, till the volume reduces to 20 or 30 ml. Acid digestion was needed for

the metal estimation by AAS [12]. The contents of the beaker are cooled using filter paper, and the final volume made 100 ml be distilled water for estimation of heavy metal.

- Standard metal solutions were prepared in the optimum concentration range present by appropriate dilution of the CRM (certified reference metal) of As, Cu, Cd, Cr, Hg, Fe, Mn, Ni, Pb, and Zn solutions of 1000 ppm.
- The heavy metal determination was carried out using a Varian Spectra AA-220, atomic absorption spectrophotometer in the air–acetylene flame mode with background correction and hollow cathode lamps.

Calculations of Heavy Metals

The mass concentration of lead is expressed in micrograms per cubic metre in the air sample to the nearest 0.1 $\mu g/m^3$ using equation

$$\mathrm{Pb(conc)} = [\mathrm{Pb\,(sm)} - \mathrm{Pb(B1)}] \times \mathrm{V1/V}$$

where

Pb (conc)	mass concentration of particulate lead in $\mu g/ml$.
Pb (Sm)	concentration of particulate lead, in $\mu g/ml$ in the sample solution.
Pb (Bl)	concentration of particulate lead, in $\mu g/ml$ in blank solution.
V1	total volume of digested sample in ml, and.
V	volume of sampled air in m^3.

5 Regulatory standards

The National Ambient Air Quality Standards are ambient air quality standards put in place by the Ministry of Environment and Forests and applicable nationwide [13]. These standards specify major pollutants along with their concentrations, averaging time and assessment procedures, etc. [14] National ambient air quality standard (NAAQS) for particulates and heavy metals is represented in Table 2, and standard heavy metal concentrations are given in Table 3.

6 Results

Three locations, namely Karachia, Ranoli, and Koyali were selected based on the wind rose diagram for the summer season. Koyali is located upstream of PCC industrial area and Karachia and Ranoli on downstream. PM100, PM10, and PM2.5 were measured at the same time at each location during the first and second weeks of June 2019. Further, on the filter papers used for sampling of PM100 and PM10, heavy metals were analysed using standard procedure. The concentrations of PM100,

Table 2 National ambient air quality standards—New Delhi 18 November 2009

Pollutant	Time-weighted average	Ambient air concentration	
		Industrial, residential, rural, and other areas	Ecologically sensitive area
Particulate matter—PM_{10}, µg/m^3	Annual * 24 h **	60 100	60 100
Particulate matter—$PM_{2.5}$, µg/m^3	Annual * 24 h **	40 60	40 60
Lead (Pb), µg/m^3	Annual * 24 h **	0.50 1.0	0.50 1.0
Arsenic (As), ng/m^3	Annual *	06	06
Nickel (Ni), ng/m^3	Annual *	20	20

Table 3 Standard heavy metals concentrations in ambient air

Sr. No.	Heavy metal	Standard concentration µg/m3	Reference
1.	Cd	0.005	WHO, AAQC
2.	Pb	0.500	NEPC, AAQC
3.	Cr	0.010	TCEQ
4.	Ni	0.0038	WHO
5.	Cu	1.000	TCEQ
6.	Zn	100	EQA
7.	Mn	0.15	WHO

AQC Ambient Air Quality Criteria Act 1994, *EQA* Environmental Quality Act 1974, *NEPC* National Environmental Protection Council, *WHO* World Organisation Health, *TCEQ* Texas Commission on Environmental Quality

PM10, and PM2.5 are shown in Fig. 3, and the heavy metal concentrations are shown in Table 4.

7 Discussion of Results

- The concentration of PM100 was found to be between 214 and 398 µg/m^3 greater than the NAAQS standard of 230 µg/m^3.
- PM10 concentrations were observed to be between 70 and 93 µg/m^3, less than the NAAQS standard of 100 µg/m^3.

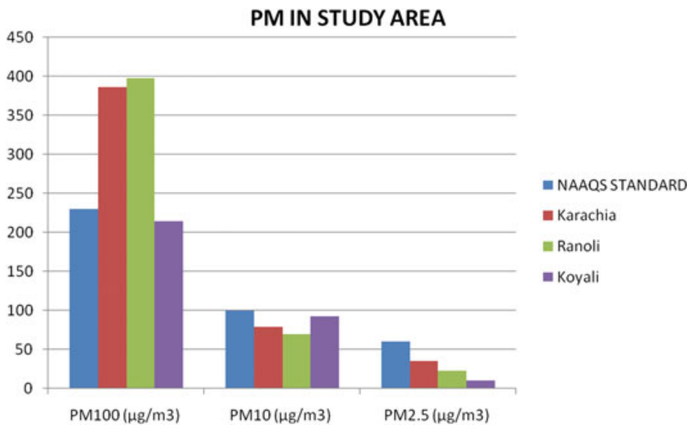

Fig. 3 Particulate matter status in the study area

Table 4 Heavy metal concentration in the study area

Sampling location			Karachia		Ranoli		Koyali	
Sr. No.	Heavy Metals	IS std	PM100	PM10	PM100	PM10	PM100	PM10
1	Arsenic (As)	**0.006**	ND*	ND*	ND*	ND*	ND*	ND*
2	Copper (Cu)	**1**	0.995	0.754	0.044	0.042	0.124	0.037
3	Cadmium (Cd)	**0.005**	ND*	ND*	ND*	ND*	0.057	ND*
4	Chromium (Cr)	**0.01**	0.014	0.01	0.008	0.006	0.011	0.009
5	Mercury (Hg)	**50**	0.025	0.017	0.003	0.003	0.004	0.001
6	Iron (Fe)	**10**	10.86	3.59	5.45	2.79	6.16	5.34
7	Manganese (Mn)	**0.15**	ND*	ND*	ND*	ND*	ND*	ND*
8	Nickel (Ni)	**0.02**	0.151	0.091	0.09	0.114	0.122	0.089
9	Lead (Pb)	**1**	ND*	ND*	ND*	ND*	0.077	0.03
10	Zinc (Zn)	**10**	2.19	4.1	6.78	3.5	5.19	4.39

- The average PM2.5 concentrations were found to be between 10 and 35 $\mu g/m^3$ less than the NAAQS standard of 60 $\mu g/m^3$.
- The highest concentrations for Cu, Cd, Cr, Hg, Ni, Pb, Fe, and Zn were found to be 0.995, 0.057, 0.014, 0.025, 0.151, 0.077, 10.86, and 6.78 $\mu g/m^3$, respectively, in PM100.
- The highest concentrations for heavy metals Cu, Cr, Hg, Ni, Pb, Fe, and Zn were found to be 0.754, 0.01, 0.017, 0.114, 0.03, 5.34, and 4.39 $\mu g/m^3$, respectively, in PM10.

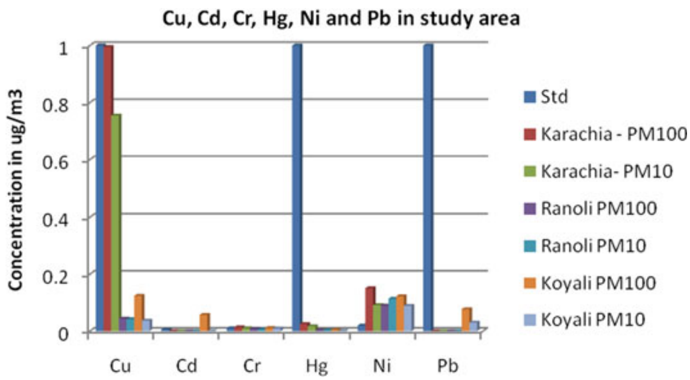

Fig. 4 Cu, Cd, Cr, Hg, Ni, and Pb in the study area

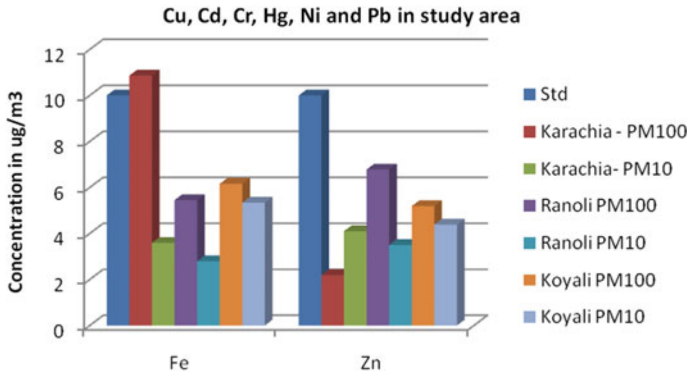

Fig. 5 Fe and Zn in the study area

- Figures 4 and 5 show the heavy metals concentrations in ambient particulates in the study area.
- The presence of copper indicates a probable source as vehicular emissions or coal combustion.
- The presence of chromium suggests emissions from coal and oil combustion.
- Presence of mercury points towards discharge from hydroelectric, mining, pulp, and paper industries.
- The presence of iron indicates emissions from soil or crustal sources.
- Presence of nickel points towards emissions from petroleum and coal combustion.
- The presence of zinc suggests emissions from the combustion of coal or coal-fired boiler.
- The presence of lead only at Koyali indicates proximity to traffic junction in addition to an industrial source.
- The absence of arsenic and manganese at all sites points towards the absence of steel smelting industries or coal combustion in the study area.

- The absence of cadmium at all sites except Koyali suggests the absence of probable sources of cadmium, which are steel, plastic, and pigment production.

8 Conclusion

The current study determines heavy metal levels in ambient particulates in Vadodara industrial area. The average PM2.5 concentrations were found to be between 10 and 35 $\mu g/m^3$ less than the NAAQS standard of 60 $\mu g/m^3$. Against the NAAQS standard of 100 $\mu g/m^3$, PM10 concentrations were found to be between 70 and 93 $\mu g/m^3$. The concentration of PM100 was found to be between 214 and 398 $\mu g/m^3$. In addition, all the six samples contained one or more metals at a concentration higher than the limit or guideline set by either CPCB or WHO [15]. Several of the detected metals, particularly chromium and arsenic, are carcinogenic to humans [16]. The detected heavy metals also give some indications as to the sources of particulate pollution [17]. High levels of copper, cadmium, chromium, nickel, and lead in particulates can be linked to industrial emissions, while high levels of iron and zinc can be linked to coal burning and ferrous metal melting [18]. High chromium and nickel can also be linked to traffic emissions. The heavy metal concentrations were observed to be more in PM100 as compared to PM10. The highest concentrations were found to be 0.995, 0.057, 0.014, 0.025, 0.151, 0.077, 10.86, and 6.78 $\mu g/m^3$ for Cu, Cd, Cr, Hg, Ni, Pb, Fe, and Zn in PM100, respectively. The highest concentrations of heavy metals were found to be 0.754, 0.01, 0.017, 0.114, 0.03, 5.34, and 4.39 $\mu g/m^3$ for Cu, Cr, Hg, Ni, Pb, Fe, and Zn in PM10, respectively. It is also a strong justification for more comprehensive monitoring programs of air pollution levels in middle-level cities like Vadodara, as well as the need for a renewed focus on the identification and control of sources for the toxic heavy metals associated with urban particulates.

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