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Analysis and Quantification of Airborne Heavy Metals and RSPMs in Dehradun City

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ABSTRACT

Air pollution is becoming a major environmental and public health problem worldwide. Exposure to different air pollutant have several adverse effects on human health. In the present study, we attempt to determine the concentration of respirable suspended particulate matters (RSPMs) and levels of the heavy metals in ambient air of Dehradun city. The RSPM concentration of all the areas under study were well under the NAAQ standard limit. The Ghantaghar area reported the maximum RSPMs of 87.5507 µg.m-3. The samples collected from four different locations of Dehradun were primarily analysed for heavy metals like Pb, Fe, Cr and Cd using atomic absorption spectrophotometer. The measured concentrations were compared with the standard safe limits provided by United States Environmental Protection Agency (USEPA). It is seen that all the heavy metals as well as the RSPM are well under permissible safe limits set by USEPA, OSHA and CPCB. It can therefore be concluded that the ambient air quality of Dehradun, in terms of heavy metal emissions in air should be done regularly to maintain the ambient air of Dehradun area as healthy.

INTRODUCTION

The immense growth of the human population lead to extensive utilization of natural resources and the technological advances have significantly affected the atmospheric air. The contamination of air occurs from both natural sources as well as anthropogenic sources. Usually, any substance that gets introduced to the atmosphere due to the above activities can become the cause of air pollution and they may have a detrimental effect on human health. The air pollutant generally includes particulate matter (smoke, dust, fumes and aerosols), gases (sulphur dioxides, nitrogen dioxides, hydrocarbons, etc.), radioactive materials, hazardous air pollutants (HAPs), heavy metals and many others (Godish 2004, Rana 2006). The presence of heavy metals in the environmental air above safe limits as approved by international and national agencies like U.S. Environmental Protection Agency (USEPA), Occupational Safety and Health Administration (OSHA), and Central Pollution Control Board (CPCB) are of important concern as they cause many health problems when they get absorbed, ingested/inhaled inside the human body (Duruibe et al. 2007).

It has been found that the natural emission of heavy metal pollutants are minimal and their concentration in the air is rising due to anthropogenic activities such as mining and smelting operations, industrial production and use, and domestic and agricultural use of metals and metal-containing compounds (Goyer 2001, He et al. 2005, Herawati et al. 2000, Shallari et al. 1998). Some studies have reported that the anthropogenic activity generates about 2000 tons of lead and 6000 tons of cadmium which contributed the most i.e. 333 times more than natural (lead) activities in the environment (Nriagu & Pacyna 1988, Chen & Graedel 2012).

Heavy metals are the metallic elements that have a relatively high density compared to water. With the assumption that heaviness and toxicity are inter-related, heavy metals also include metalloids, such as arsenic, that are able to induce toxicity at a low level of exposure. It has been described that metals such as cobalt (Co), copper (Cu), chromium (Cr), iron (Fe), magnesium (Mg), manganese (Mn), molybdenum (Mo), nickel (Ni), selenium (Se) and zinc (Zn) are essential nutrients that are required for various biochemical and physiological functions but these metals become toxic when present in larger quantities. Other heavy metals like Cr, Cd, Hg, Pb, etc. are extremely fatal for human health (Yu et al. 2011). Their presence is also associated with severe diseases in human bodies like metal plume fever, itai-itai (Tohyama et al. 1982), mina-mata, Hunter-Russel syndrome, etc. They promote insomnia, sleep disorder, blurred vision, speech and hearing impairment, etc. Due to the above concerns,

S. No.	Heavy Metal	Prescribed Conc. Limit ¹ Living Standards (in μ g.m ⁻³)	Max Permissible Limit ² Industrial Standards (in μ g.m ⁻³)
1	Lead (Pb)	0.5000 1	1.0000 ²
2	Iron (Fe)	5.0000 ⁻¹	10.000 ²
3	Chromium (Cr)	0.5000 1	1.0000 ²
4	Cadmium (Cd)	0.1000 1	0.5000 ²

Table 1: Maximum permissible limit for heavy metals as per USEPA¹ and OSHA²

Table 2. Maximum permissible limit for SPMs and RSPMs as per NAAQ standards.

S. No.	Туре	Prescribed Limit
1.	Suspended Particulate Matters (SPMs)	200 µg.m ⁻³
2.	Respirable Suspended Particulate Matters (RSPMs)	100 µg.m ⁻³

extensive study has been carried out to find out the heavy metal presence in water, air, and soil all around the world to inform the local and Government agencies for taking suitable measures for controlling toxic elements in the environment.

The prescribed concentration limits of the heavy metals set by the USPEA and OSHA are summarised in Table 1. Table 2 provides information about the permissible limit of respirable suspended particulate matter (RSPM) and suspended particulate matter (SPM) as per the National Ambient Air Quality Standards (NAAQ).

Different research work has been reported in various parts of India for determining the number of heavy metals in the air as well as their impacts on human beings (Kulshrestha et al. 2009, Mohanraj et al. 2004, Sharma et al. 2008, Sharma & Maloo 2005, Shridhar et al. 2010, Thakur et al. 2004). But till date, no such study has been performed to quantify the heavy metals particles in the ecologically sensitive region i.e. Dehradun city. The present study is extremely important as Dehradun is a valley and the dispersion of contaminated air entirely depends on the rain. Herein the present study, we have chosen four different locations of Dehradun city (Sahaspur, Ballupur, Dalanwala, and Ghantaghar) to determine the concentration of RSPM and levels of the heavy metals in the air of Dehradun. The RSPM levels were compared with the NAAQ standard limits. The samples collected from four different locations of Dehradun were further analysed for heavy metals like Pb, Fe, Cr and Cd using atomic absorption spectrophotometer (AAS). The measured concentrations were then compared with the standard safe limits provided by USEPA.

MATERIAL AND METHODS

Sites for sample collection: The air samples for the study were collected from four different localities of Dehradun city. The different locations were:

- Location I- Sahaspur: Sahaspur is an industrialised area with many manufacturing units of various MNCs and other small-scale industries.
- Location II- Ballupur: Ballupur is a residential cum market area with heavy population and witness a large no of vehicular movement throughout the day.
- Location III- Dalanwala: Dalanwala is an extensively populated area consisting of many slum areas and situated nearby the railway station.
- Location IV- Ghantaghar: Ghantaghar area is the prime location and main market place of Dehradun area, consisting of many residential complexes and shopping malls and other markets drawing huge population towards it. Different locations have been depicted in the Fig. 1.

Estimation of RSPM: The air samples were collected using Ecotech AAS127 Air Sampler for PM_{10} on a glass-fibre filter paper (GFF) cut-out of radius 2 cm. The initial weight of filter-paper cut-out were recorded after conditioning them in hot air oven at 105°C for 2 hrs and the kept in desiccator for 2 hrs. Each filter papers were weighed five times and the mean weight was recorded. The filter-papers were carried in a filter-paper holder to avoid any kind of contamination.

The instrument was operated for around 23 hrs approximately at a height of around 5 ft above the ground and the flow rates before and after each experiment run were recorded. After 24 hrs, the filter paper was removed from the instrument and was kept again in filter paper holder carefully to retain the actual deposition of particulate matters on filter paper. The filter papers were kept in desiccator for 2 hrs. Then the filter papers were first weighed and then digested to extract out the particulate matters.

Estimation of heavy metals: The extraction and analysis of heavy metals from the filter paper were conducted as per

USEPA method of hot-acid digestion (USEPA 1999). The filter papers were digested using 15 mL HCl and HNO₃ acid mixture (3:1). The concentration of the heavy metals was analysed using AAS (ThermoScientificiCE 3000 Series). For quality control, standard stock solutions were prepared for each metal. The standard Reference Materials (SRMS) were prepared using Certipur® standard solution (1000 ppm).

Detection range: The calibration plot method was used for the analysis. The air-acetylene gas was used for the analysis of Pb, Cd and Hg while nitrous-oxide gas along with air-acetylene gas was used for the analysis of Cr. The wavelengths for the determination of the elements were 217.0 nm, 228.8 nm, 248.3 nm and 357.9 nm for Pb, Cd, Fe and Cr respectively.

Quality control: For precision and accuracy, all the glassware's and filter assemblies were acid-washed and dried in hot-air oven. Only the calibrated glassware's were used. HPLC Grade de-ionised water was used for calibration of the device.

RESULTS AND DISCUSSION

Presence of respirable suspended particulate matters: The concentration of PM₁₀ in the air at different locations of Dehradun city were taken under study and the RSPMs data collected from the study locations is presented in Table 3. All the data at study stations are under $100 \,\mu g.m^{-3}$ that is under considered safe by NAAQ standards (for 24-hour duration; annual avg. of 60 µg.m⁻³) as shown in Fig. 2. The results show that high content and concentration of RSPMs are responsible for some difficulties for some age groups like toddlers and old-age groups, lung diseases causing difficulty in breathing and may trigger respiratory as well as cardiovascular diseases (Kim et al. 2015, Li et al. 2018). Hence, the results prove that the particulate matter present in the air can be very fatal and is severe for human health as they reach deep into the respiratory system. Particulate matter pollution in ambient air has been labelled as Group-1

Table 3: Respirable suspended particulate matters in air and their probable causes.

Sr. No.	Location Name	Initial Wt (Filter Paper)	Final Wt (Filter Paper)	Difference	Initial Flow Rate (L/min)	Final Flow Rate (L/min)	Avg. Flow Rate (L/min)	Total Sampling Time (min)	RSPM (µg.m ⁻³)	Activities around the sampling sites
1.	Sahaspur	1.14317	1.24695	0.10378	1.6	1.4	1.5	1380	50.2810	Industrial area
2.	Ballupur	1.25693	1.33635	0.07942	1.3	1.2	1.25	1380	46.0405	Vehicular emissions
3	Dalanwala	1.12291	1.22973	0.10682	1.2	1.1	1.15	1380	67.8006	Vehicular emission, construction sites, roadside piles of gar- bage
4	Ghantaghar	1.14133	1.32256	0.18123	1.6	1.4	1.5	1380	87.5507	Heavy pollution due to vehicles, generator, roadside dust piles, construction sites

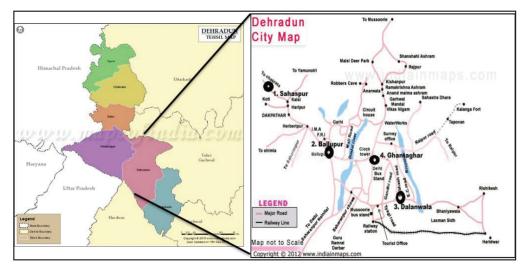


Fig.1 (a): Dehradun district map (b) Dehradun City map. (Image Courtesy: http://www.indiainmaps.com)

Carcinogen by the International Agency for Research on Cancer (IARC) (Loomis et al. 2013).

Presence of heavy metals in the air: The heavy metals concentration in the particulates were found by digesting the filter paper and analysing the presence of the metals in the sample using the atomic absorption spectrophotometer. Table 4 depicts the concentration of Pb, Cr, Cd, and Fe at different locations of Dehradun. From the acquired data it was found that Pb and Fe concentration is higher in Sahaspur and Ghantaghar area respectively, however the Cr and Cd concentrations found negligible in these areas. The concentrations of all the heavy metals taken into consideration are considered toxic if the concentrations in air are found beyond permissible safe limits.

The concentration of Pb in ambient air is demonstrated in the Fig. 3. The data confirmed that the concentration of Pb at different locations of study was slightly higher in the Sahaspur area $(0.1288 \ \mu g.m^{-3})$ but in other areas it is below the permissible safe limit set by USEPA.

The trend of Cr concentration in the environment can be seen steady and almost negligible as shown in Fig. 4. The concentration is way below than the standards set by USEPA for safe living. The Cd concentration was also studied at different areas of Dehradun (Fig. 5) which depicts that Cd is present at prescribed safe limits and are almost negligible as compared to other pollutants.

As shown in Fig. 6 the concentrations of Fe were found slightly higher in the Ghantaghar location (0.70068 μ g.m⁻³) and at Sahaspur area (0.56594 μ g.m⁻³). The level of Fe was not much higher in other two areas.

The data obtained for heavy metals from the four different locations was compared with the prescribed concentration limits set by USEPA considered safe for living for the inhabitants of the areas. The data predicts that the heavy metal presence is inconsequential as their concentrations in ambient air are negligible and are documented under the safe limits as shown in Table 5 which suggest that the peak concentration of Pb was recorded to be 74.24% less than the prescribed safe concentration by USEPA, which is the highest among the percentages of other heavy metals in air. On the other hand, the concentration of iron being maximum still is 99.86% less than that of the prescribed safe limits set by USEPA. It also confirms that the maximum concentrations of heavy metals taken for the under study were found in Ghantaghar area.

Fig. 7 depicts the bar graph showing the comparison of

S. No.	Location I.D.	Location Name	Pb (µg.m ⁻³)	Cr (µg.m ⁻³)	Cd (µg.m ⁻³)	Fe (µg.m ⁻³)
1.	Ι	Sahaspur	0.12882	0.01661	0.00664	0.56594
2.	Π	Ballupur	0.01434	0.01232	0.00115	0.14085
3.	III	Dalanwala	0.04607	0.01161	0.00280	0.22782
4.	IV	Ghantaghar	0.02185	0.02319	0.01220	0.70068

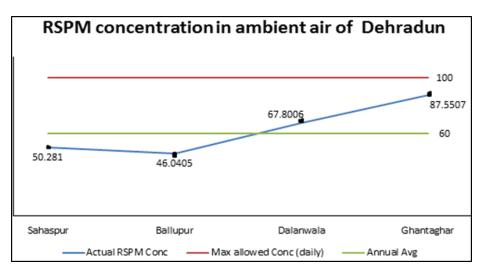


Fig. 2: Presence of RSPMs at different locations of the Dehradun city.

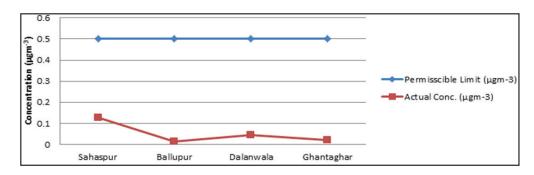


Fig. 3: Presence of lead at different locations of Dehradun.

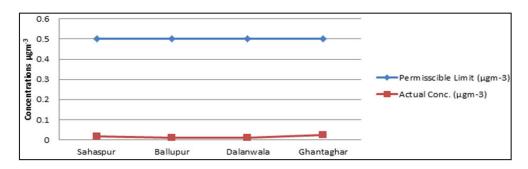


Fig. 4: The occurrence of chromium at different locations of Dehradun.

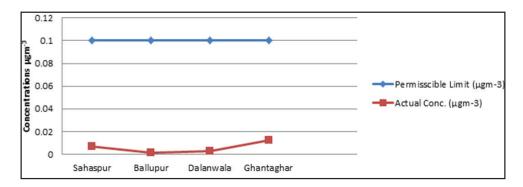


Fig. 5: The graph demonstrates the presence of cadmium as a pollutant in different locations of Dehradun.

the presence of different heavy metals (Pb, Cr, Cd, Fe) in the environment. The iron concentration has been found higher in almost all the study locations. Although its concentration is way more than the other heavy metals concentration, its impact on human health is negligible since it is about 99.86% less than the prescribed safe limits. The other significant heavy metal present in air is Pb whose concentration is maximum in Sahaspur area is comparatively higher with respect to the safe concentration limits. Other heavy metals are negligible and can be ignored safely.

Finally, we have compared our results with different study performed in various other locations as summarised

in the Table 6. Here, we have also taken up the study of the three other major cities (Delhi, Kanpur, Mumbai) of India into account. From all the comparative study we found the conclusion that the air quality of Dehradun is comparatively safe than other Indian cities.

CONCLUSION

The pollutants get added up in the environment through both the natural sources as well as anthropogenic sources. The air pollutant generally includes particulate matter, harmful gases, and heavy metals. In the study, we have obtained the data from different locations of Dehradun which firmly illustrates

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Table 5: Percentage of	peak concentration of heavy	y metals in air less than that of the	prescribed safe limits.

Peak Conc. of Heavy Metals (and their Study Area)	Peak Concentration Recorded	Safe limit set by USEPA	%age of Peak Conc. less than that of Prescribed Safe Limits
Lead (Sahaspur)	0.12882	0.50000	74.24%
Chromium (Ghantaghar)	0.02319	0.50000	99.95%
Cadmium (Ghantaghar)	0.01220	0.10000	99.88%
Iron (Ghantaghar)	0.70068	5.00000	99.86%

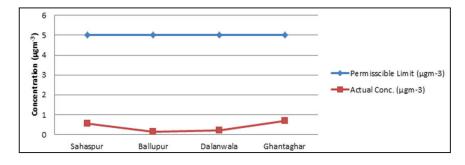


Fig. 6: The graph illustrates the occurrence of Iron in the environment at different locations of Dehradun.

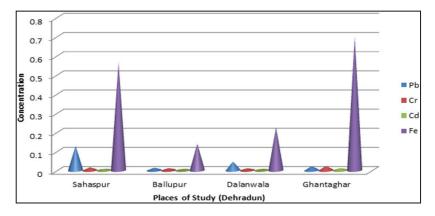


Fig. 7: Comparisons of the heavy metals in the air of different sites of study in Dehradun.

that all the parameters have not crossed the permissible safe limits set by the OSHA and USEPA which are considered safe for human inhabitation. While the respirable suspended particulate matters (RSPMs) are on rise at Ghantaghar and Dalanwala areas and nearing the prescribed limits of NAAQ standards set by CPCB. Ghantaghar area is the oldest inhabited market place of Dehradun and the centre point, making it the most crowded place in Dehradun which clarifies the significant RSPM concentration and slight increasing trend of the concentrations of heavy metals in the ambient air quality. Dalanwala and Ballupur are primarily residential areas where a sudden fall in concentration of heavy metals can be observed. Since Dalanwala is located near railway station of Dehradun and also a home of several slum areas, the RSPM concentration is little on the higher side. Almost all the major inhabited areas of Dehradun are located near the surroundings of these four locations. Hence, it can be concluded that the Dehradun city is free of any kind of heavy metals contamination in air but the RSPMs may pose threat to health conditions of certain special groups of the society like infants, children and aged people.

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Location	Pb	Cd	Cr	Fe	References
Spain	0.008 - 0.698	0.0001 - 0.004	0.0001 - 0.022	0.2 - 10.0	(Querol et. al. 2002)
Taiwan	0.133		0.656	6.99	(Fung & Wong 1995).
Norway	0.00036 -0.01036	0.00001 -0.00028	0.00021 - 0.00156		(NILU 2002b).
Delhi	0.6 - 1.9	0.020 - 0.150	0.3 - 0.7	5.0 - 20.0	(Balachandran et. al. 2000).
Mumbai	1.06		0.15		(Kumar et. al. 2001).
Kanpur	0.07 - 1.03	0.002 - 0.043	0.032 - 0.4	0.3 - 6.17	(Sharma & Maloo 2005).
Dehradun (Present Study)	0.0205	0.01178	0.0056975	0.4088	

Table 6: Comparison of concentration of heavy metals in air at different parts of the world.

tribution and its elemental composition in the ambient air of Delhi. Environ. Int., 26: 49-54.

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