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SOURCE IDENTIFICATION OF TRACE ELEMENTS IN PARTICULATE MATTER REFERENCE TO ENVIRONMENT OF QUETTA, PAKISTAN

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Abstract
The air quality in Balochistan's capital city of Quetta was the subject of a recent research. To do this, researchers analyzed trace element levels in PM_{10} and $PM_{2.5}$ particles collected daily from a significant urban region. With a value of 1,998.0 ng m^{-3}, $PM_{2.5}$ had the highest levels of Zn in the surrounding environment. To determine the relative contributions of different sources of specific metal components in airborne particles, multivariate receptor modeling techniques such as principal component analysis and cluster analysis were used. Based on the data, it seems that fossil fuel combustion in stationary sources and vehicle traffic are the main culprits responsible for the trace metals found in Quetta's urban aerosols as the air quality is much worse in underdeveloped countries. Low air quality, which is a result of both ignorance and bad social and economic conditions, claims the lives of millions of people every year. Air pollution monitoring in Pakistan has been the subject of several studies, despite a lack of comprehensive research in the field. It is well-established that both pollutants have negative impacts on human health when exposed to them for an extended period of time, and several studies have proven the different negative health outcomes that may occur as a result of this study too.

Keywords: Air pollution; Urban air Pollution; PM_{10} and $PM_{2.5}$; Fine particulate matter.

1. Introduction

Air is the essential ingredient of life which can provide us Oxygen to breath for the survivals of living things that is why air is to be considered the fundamental to our survivals. Because more pollution in the air means more pollution that people breathe in,so, air pollution is a major threat to people's health. Our indoor environment may not be as risk-free as it seems, but also there are many other sources of air pollution. To protect oneself from the elements and potentially harmful creatures, humans have been constructing buildings for a very long time. This means that many people spend the vast majority of their waking hours inside, either at work or at home (Hoppe and Martinac, 1998). Buildings can therefore be viewed as indoor ecosystem habitat is effected by factors including the people living there, the things they do, the building's architecture, the building's materials, and the surrounding environment which affects the airflow and ventilation. According to Goyal and Khare (2010), people's interactions with their internal environments are just as complex as their interactions with their outside environments. Even if it may not seem like it, there are still pollutants and other dangers in the air we breathe inside. It is possible that the indoor air quality is much worse than the outside air quality. Indoor air pollution accounts for 2.7% of the total worldwide sickness burden in 2002, according to the World Health Organisation (WHO).

Particulate matter is categorized according to particle size or diameter since this aspect affects several aspects of the particles, such as their airborne lifetime, potential settlement distance, and deposit location in the respiratory system. An important factor in understanding the degree of hazard is the efficiency with which certain particles settle into the respiratory system. Particulate matter (PM) fractions having an aerodynamic diameter of 10 µm (PM_{10}) or less are the ones that are often studied. Air quality laws and regulations pertaining to particle emissions place a heavy emphasis on PM_{10} and $PM_{2.5}$ because of their high inhalation potential and the influence they have on human health (Wiseman and Zereini, 2010).

According to Pope and Dockery (2006), of the six main air pollutants, particulate matter (PM) is the most harmful. A wide variety of sources, both natural and man-made, release particles into the atmosphere. Either primary or secondary particles may be their starting point.

A wide variety of air contaminants, both physical and chemical in nature, are collectively known as particulate matter. These air pollutants may come from a variety of organic and inorganic sources, and they are often a mixture of solid and liquid particles (Tiwary and Colls, 2010; and WHO, 2011). Respirable particulate matter (RSPM) and suspended particulate matter (SPM) are the two main types of particulate matter.

Particles larger than a certain size are considered part of total scattered particulate matter; the size limit is determined by factors such as wind speed and the direction of the sampler. According to the US Environmental Protection Agency (EPA), particles that are respirable have an aerodynamic diameter of 10 µm or less. Nevertheless, respirable particulate matter (PM) is defined by the American Conference of Government Industrial Hygienists (ACGIH) as particles with an aerodynamic diameter of 2 µm or smaller. Research by Goyal and Khare (2010), Parsia et al. (2010), and Tiwary and Colls (2010) lend credence to this knowledge.

Fine particulate matter, or PM $_{2.5}$, is made up of airborne particles with a size of 2.5µm or less. Differences between $PM_{2.5}$ and PM_{10} in terms of origin and chemical makeup are substantial. Oil, coal, gasoline, diesel, and wood all contribute to fine particulate matter when burned because they transform gasses into particles. Their formation is accomplished by a series of procedures that include chemical reactions, condensation, nucleation, coagulation, and processing of clouds and fog. These substances are hygroscopic and include elements such as sulfur, nitrogen, ammonium, organic compounds, water, and metals such as lead, cadmium, vanadium, nickel, copper, zinc, manganese, and iron. Fine particles, being so small, may stay in the air for days or weeks and travel hundreds or even thousands of kilometers from where they originated (Fierro, 2000). The increased danger to human health may be due to the huge surface area and chemical-absorption capabilities of finely split particles (Bates, 1995). There are many potential origins of fine particulate matter, as mentioned above. Both the interior and outdoor environments may contribute to the generation of aerosols. The process of identifying these sources and assessing their influence on air quality is intricated.

The atmospheric release of trace elements is caused by both natural and human-caused emissions. Most of the beryllium, cadmium, mercury, nickel, selenium, sulfate, and vanadium that humans produce comes from burning fossil fuels. A lot of arsenate, cadmium, copper, nickel, and zinc are released during industrial metallurgical processes. Lead (Pb), copper (Cu), zinc (Zn), nickel (Ni), and cadmium (Cd) are all present in gasoline exhaust emissions, but in different levels (Pacyna et al., 2001; Samara et al., 2003). Metal ions may be found in almost every fraction of aerosol size. This component greatly affects metal toxicity because particle size determines the amount of respiratory penetration during inhalation (Dockery et al., 2006).

According to the International Agency for Research on Cancer (2013), one of the main causes of lung cancer is exposure to air pollution in the outdoors. Nearly 2 million people die too soon in impoverished countries every year due to indoor air pollution. Nearly half of all deaths in children less than five years old are caused by pneumonia. Among the most significant air pollutants, particulate matter is known to pose the greatest threat to human health. The World Health Organization also estimates that 2.4 million people die too soon each year due to $PM_{2.5}$ inhalation (Tiwari and Colls, 2010). nearly 7.7 percent of all fatalities in 2012 were attributed to household air pollution (HAP), which was estimated by the World Health Organization (WHO) to be responsible for nearly 4 million premature deaths (Bruce et al., 2015).

The air we breathe, the water we drink, the plants we eat, and even our own bodies contain microbes come under the jurisdiction of aerosols particulates matter pollution . This class includes things like pollen, mites, spores, fungi, and bacteria. Biological aerosols, often called bio-aerosols, are a kind of airborne microorganisms and the compounds they create, which may include their cellular components. These organisms, which might be alive or dead, are the root of a lot of health problems. Whether you're inside or out, you might encounter microbial particle matter. In different ecosystems, bio-aerosols end up where they started. According to Hospodsky et al. (2012), indoor carpets are great at capturing and retaining these microscopic particles, which makes them perfect for persistence and eventual release into the air. Additionally, the ideal circumstances for the growth and survival of fungus and bacteria are provided by water-damaged regions. While outside sources account for the most majority of airborne fungus, bacteria may be found both inside and outside.

Two main indoor micro-environments, the kitchen and the living room, were examined in the research. We tested their air quality and looked for signs of environmental stresses by asking them directly. Since bio-aerosols and fine particulate matter are the main pollutants of relevance, this study focuses on their levels in the indoor air of residential structures.

Examining the concentrations of trace metals in Quetta's urban air via PM_{10} and $PM_{2.5}$ was the primary objective of this study. In addition, by analyzing climatic conditions, principal component analysis (PCA), and cluster analysis (CA), the research sought to identify the main sources of these trace elements. The results may provide empirical evidence for the creation of a strategy to control air pollution and also provide the groundwork for future studies examining the risks to human health from breathing in suspended particles.

The significance of this study lies in the fact that no previous work has presented data on PM and bio aerosol levels measured simultaneously in the urban center of Balochistan. People have paid little attention to the problem of indoor air quality as there are no hard and fast regulations governing it. Further in-depth studies should be conducted to track indoor micro-environment air quality and provide guidelines for controlling indoor pollutant levels.

2. Materials and Method

2.1. Samples collection

Particulate matter samples were obtained from Quetta, Balochistan, between 2022 and 2023.

2.2. Particle digestion

Particulate matter (PM) of a diameter smaller than 10 µm (PM_{10}) and 2.5 µm ($PM_{2.5}$) was measured at two sites in a city between June 2022 and July 2023. To gather the suspended particles, two Mini Vol air samplers were used, each having a 5 liter per minute flow rate with PM_{10} and $PM_{2.5}$ cutoff inlets. The filters used were Pure Teflon from Whatman and had a 47 mm diameter. There were 273 valid daily samples taken throughout the two-year period, with 209 PM_{10} samples and 64 $PM_{2.5}$ samples made up the total. Rajšić et al. (2004) provide a detailed description of the sampling sites and methodology. After the gravimetric analysis, graphite furnace atomic absorption spectrometry (GFAAS) was used to identify different trace elements in the particulate matter (PM) samples that had been treated with 0.1 mol dm^{-3} HNO_3 in an ultrasonic bath (Kyotani et al., 2002). Specifically, the Perkin Elmer AA 600 transversely-heated graphite atomizer was used for this task. For quality assurance purposes, NIST Standard Reference material 2783 was used.

2.3. Analysis

Temperature, turbidity, electrical conductivity (EC), and pH were among the factors routinely measured for particulate matter samples. The same methodology was used to analyze the bulk deposition (BD) samples. Each study needed a different set of data, so we took water samples from the tank and cut the BD samples into the appropriate portions. To ensure that all particles were evenly distributed, the sample was physically agitated before sub-sampling BD.

3. Results and Discussion

Particulate matter (PM) contributes significantly to environmental problems, global warming, and health hazards. It has been shown that small particles, namely $PM_{2.5}$ and PM_1 fractions with a diameter smaller than 2.5 µm and 1.0 µm, respectively, are associated with lung and heart

disorders, which may lead to sickness and mortality (Samet et al., 2000; Pope et al., 2002; WHO, 2003). Agricultural and natural environments might also be severely affected by these particles. They may potentially make it harder to see, which would be bad for both the vehicle's security and its appearance (Yuan et al., 2006). By both dispersing and absorbing solar and infrared radiation in the atmosphere, aerosol particles directly affect the Earth's energy balance, according to recent studies. Yu et al. (2002) and Cattani et al. (2006) found that they also change clouds' physical and radiative properties indirectly.

The daily mass (μg m^{-3}) and trace element (ng m^{-3}) concentrations in PM_{10} and $PM_{2.5}$ were analyzed using descriptive statistics, which showed that both the average and maximum values were highly raised (Table 1). The yearly limit of 40 μg m^{-3} proposed by the EU Directive 1999/30 EC was exceeded by the average mass concentration of PM_{10} (68.4 μg m^{-3}). Furthermore, the annual limit of 20 μg m^{-3} established by the EU Standard 14907 was exceeded thrice by the average $PM_{2.5}$ concentration (61.4 μg m^{-3}). The PM_{10} has the greatest concentration of iron (Fe) of any metal, measuring in at 1462.9 ng m^{-3}. There was an exceptionally high concentration of zinc (Zn) at 1389.2 ng m^{-3} and of aluminum (Al) at 873.8 ng m^{-3}. On average, zinc was the most abundant element in $PM_{2.5}$. Typical amounts of the very dangerous heavy metal copper (Cu) in PM10 were 71.3 ng m^{-3}, whereas in $PM_{52.5}$ they were 20.8 ng m^{-3}. According to Directive 2004/107/EC, the $PM_{.2.5}$ fraction had an average concentration of nickel (Ni) of 28.4 ng m^{-3} which is higher above the PM10 threshold limit of 20 ng m^{-3}.

Table 1. Presents the statistical characteristics for the daily mass (μg m^{-3}) and trace element (ng m^{-3}) concentrations in $PM_{2.5}$ in the Quetta urban area. The data covers the period from June 2022 to July 2023.

	$PM_{2.5}$	**Pb**	**Cu**	**Zn**	**Mn**	**Fe**	**Cd**	**Ni**	**V**	**Al**	**Cr**
N	64	64	64	64	64	64	64	64	64	64	64
Mean	61.4	21.0	20.8	1998.0	15.2	1081.2	0.9	28.4	59.8	1180.3	6.2
S.D.	52.5	27.0	19.2	1846.4	13.7	1360.3	1.2	43.1	56.3	1657.4	3.8
Max.	286.6	193.9	99.6	6642.4	50.7	5996.5	4.8	315.0	248.5	7875.0	26.0
Min.	8.8	0.5	0.2	115.2	2.1	49.7	0.0	0.4	5.2	159.1	1.6
Median	51.9	13.5	17.4	1153.3	10.1	488.4	0.4	17.3	50.2	500.7	5.9
98^{th} perc	237.3	66.8	80.6	6101.7	47.9	5380.6	4.1	107.9	208.7	7307.3	13.2

N- Number of samples; S.D. - Standard arithmetic deviation

PCA was used to determine where pollutants originated. By using a VARIMAX rotation, the factor loadings for PM were ascertained. The total variability for PM_{10} was found to be 73% explained by four components. The resuspension of road dust is responsible for factor 1, which accounts for 26% of the total. The presence of fuel oil markers V and Ni is closely related with Factor 2, which accounts for 17% of the total. Thirdly, there is the presence of Cu, Cd, and Pb in Factor 3, which is associated with transportation and local sources and makes up 17% of the total. Cr and Pb in vehicle exhausts account for 4% (13% of the total). Table 2 shows that out of the total variance in PM_{10} data, 88.5% can be explained by four different groups. The first component is the existence of airborne, stirred-up road dust. The second factor represents the lead and chromium emissions from oil refineries and vehicles. The third component is connected to the combustion of fossil fuels, and the fourth to the discharge of copper (Cu) and cadmium (Cd) from diesel-powered vehicles and nearby factories.

Table 2. PCA Factor loadings after Varimax rotation for the elements in $PM_{2.5}$

Element	Factor 1	Factor 2	Factor 3	Factor 4
Pb	0.27	**0.85**	-0.05	0.06
Cu	-0.1	0.14	0.46	**0.78**
Zn	**0.85**	0.17	0.25	-0.24
Mn	**0.8**	0.22	0.27	0.03
Fe	**0.78**	0.16	-0.09	0.16
Cd	0.1	-0.25	-0.36	**0.79**
Ni	0.06	0.1	**0.88**	0.08
V	0.3	-0.15	0.71	-0.11
Al	0.84	0.09	0.08	-0.01
Cr	0.16	0.91	0.05	-0.15
Var.(%)	29	17.8	17.7	13.5

Dendrograms showing four main clusters were the results of cluster analysis for the PM_{10} trace element data. There are two separate clusters for PM_{10} on the dendrogram. The first set is associated with pollutants from vehicles and includes the elements lead and copper in addition to cadmium. In the second category, you'll find Zn and Fe, which are mostly caused by the mechanical parts of road vehicles wearing down over time. Oil combustion is associated with the third cluster, which includes Ni and V. The fourth set is composed of soil-derived Mn, Al, and Cr. Bold marks indicate PCA loadings larger than 0.5.

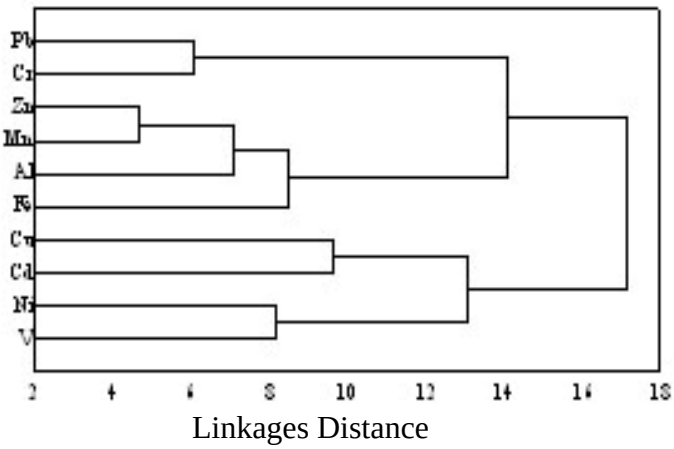

Figure 3.1. Hierarchical clustering diagram illustrating the relationships between trace components in PM 2.5.

According to Figure 3.1, which shows the dendrogram of trace elements in $PM_{2.5}$ there are several clusters. The first category consists only of lead and chromium, which are emitted into the air by vehicles using leaded gasoline and, perhaps, by oil refineries. Indicative of road dust is the second group, which includes Zn and Mn, which are closely linked to Al and Fe. There is a higher-level relationship between the third group (Cu and Cd) and the fourth group (V and Ni), suggesting that both groups originated from the same place.

In the end, we may divide the source profiles into two groups. Elements linked to industrial processes, such nickel (Ni), chromium (Cr), and copper (Cu), are visible in the first profile, together with elements typically present in soil dust and crustal debris, like iron (Fe) and manganese (Mn). Anthropogenic sources may be best described by the second profile, which includes lead, zinc, and cadmium. Emissions from road vehicles fueled by gasoline and diesel fuel mostly fall under this category. Our analysis shows that there is a clear pattern of traffic emissions related to $PM_{2.5}$.

Previous research on TSP and PM_{10} in the same area, however, relied on an iterative multivariate method that excluded concentration peaks (Ragosta et al., 2002; Ragosta et al., 2006) and only discovered this source profile.

More and more research have focused on particulate matter 2.5 ($PM_{2.5}$) due to its rising profile in recent years. (Braga et al., 2005; Fang et al., 2005; Giugliano et al., 2005; Hueglin et al., 2005; Lonati et al., 2005; Viana et al., 2005; Sudesh and Rajamani, 2006; Viana et al., 2006; Wu et al., 2006; Yatkin and Bayram, 2007) These studies not only measure the concentration of PM2.5 but also analyze its chemical composition. Understanding the origin of particles—whether they are naturally occurring or produced by humans—and the atmospheric processes in which they are involved are both greatly aided by their chemical makeup (Braziewicz et al., 2004; Karar and Gupta, 2007). The mechanisms that generate and release particulate matter (PM) into the atmosphere, as well as its toxicological and environmental impacts, may be better understood with its help (Astolfi et al., 2006). Heavy metals are very harmful to humans and other animals, hence a lot of work has gone into cataloguing them as chemical components.

We used the World Health Organization's criteria for $P_{2.5}$ and compared the microbiological levels to those given by other nations since the Pakistan Environmental Protection Agency has not set any standards for the acceptable levels of microorganisms and $PM_{2.5}$ in indoor environments. The World Health Organization has established air quality guidelines (AQG) that state the maximum permissible levels of particulate matter 2.5 ($PM_{2.5}$) should not exceed 25µg/m³ in a 24-hour period, with an average annual level of 10 µg/m³ (WHO, 2006). The average $PM_{2.5}$ levels found in the selected rooms were thirteen times higher than the World Health Organization's air quality guideline limits in the kitchen and living room. The annual average value for $PM_{2.5}$, which is 35 µg/m³, was exceeded by the results reported in this study. There has to be regulation since people's health might be negatively affected by prolonged exposure to high levels of fine particulate matter.

Because there is such a diverse array of microbes, each with its own set of health impacts, it is difficult to set a standard for airborne microbiological pollution. The current indoor air quality (IAQ) in the chosen residences was better understood by comparing the bio aerosol levels obtained in this study. Indoor bacterial and fungal contamination levels cannot exceed 500 cfu/m^3 and 300 cfu/m^3, respectively, according to standards in Singapore and Sweden. In the United States, air is deemed contaminated when the microbial load reaches 1000 cfu/m^3, according to the Occupational Safety and Health Administration (OSHA). However, according to the American Industrial Hygiene Association (AIHA) (2001), a concentration of 500 cfu/m^3 or less of fungal spores should not be present in inhabited buildings. The microorganism levels found in this analysis were clearly over the permitted limits, according to these standard values. Even though we asked the inhabitants about their respiratory health and didn't hear anything terrible, it's still important to keep an eye on the air quality inside to make sure nobody's becoming sick.

Conclusion

The study determined the methodology for identifying the origins of ambient trace metals in particulate matter (PM) by the use of multivariate receptor modelling. The elevated levels of trace elements were linked to calm weather conditions, indicating a significant impact from nearby sources. The principal component analysis (PCA) and correspondence analysis (CA) revealed that the primary origins of trace metals in particulate matter (PM) are combustion activities, such as emissions from both mobile and stationary units. The most significant contribution comes from traffic-related sources and road dust. The findings may serve as the foundational data for analyzing the health hazards associated with inhaling suspended particles. Additionally, they can give scientific evidence to support the development of an air pollution management plan. Ultimately, while examining the characterization of metal source profiles, the use of multivariate approaches enables us to identify two distinct profiles. The first profile is distinguished by the presence of Ni, Cr, and Cu, which are metals often found in industrial processes, as well as Fe and Mn, which are components typically found in soil dust and crustal debris. Additionally, it is seen that this profile contains significant amounts of Cr and Ni, indicating the likely existence of a distinct source of industrial emissions. The second profile is distinguished by the presence of lead (Pb), zinc (Zn),

and cadmium (Cd), and is mostly associated with emissions from transportation. Overall, it is emphasised that the analysed region exhibits elevated levels of some harmful elements, such as chromium and lead, despite the $PM_{2.5}$ concentrations being within the limit specified by the European Community. This implies that future initiatives for local air quality management must include both the amounts of atmospheric particles and their chemical makeup.

Recommendations

● It is necessary to conduct thorough and frequent measurements to assess the background levels and air quality of both rural and urban settings. Given the absence of established criteria for acceptable levels of several indoor contaminants, it is imperative to address this component as well. It is essential to establish specific criteria for PM2.5 and bio-aerosols. The background levels observed in this research exceed the WHO guideline of 25 $\mu g/m^3$. Hence, it is crucial to establish and enforce certain acceptable criteria to guarantee a sustainable ecosystem.

● It is very compulsory to identify the origin and intensity of particle emissions in different indoor micro-environments in order to develop an appropriate intervention strategy.

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