MONITORING AND ANALYSIS OF THE COMPOSITION OF PM2.5 IN LAHORE, PAKISTAN

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ABSTRACT: Lahore is grappling with severe air pollution, exacerbated by its rapid urban and industrial expansion. Regulatory oversight on vehicular and industrial emissions remains weak. Meteorological conditions, especially during winter with its low temperatures (around 20-30°C), stagnant winds, and lack of rain, trap pollutants, creating a smoggy environment. November sees the peak in PM2.5 concentration at 222 µg/m3. Conversely, summer brings relief due to higher temperatures, rainfall, and winds, reducing PM2.5 levels to as low as 31 µg/m3 in August. Around 26% of PM2.5 is made up of sulfate and nitrate. The latter's concentration is higher due to prevalent sources like vehicles and industrial outputs. This dominance of nitrate indicates that transportation and households are primary contributors to the city's air pollution, even more so than industries. Drains in Lahore, filled with untreated wastewater, are a significant source of the 16% ammonium found in PM2.5. Natural dust is evident from the substantial presence of Si (12.6%), Ca, and Fe in PM2.5. Emissions from vehicle exhausts and fossil fuel burning, both in industries and households, contribute to the combined 42% of Organic Carbon (OC) and Elemental Carbon (EC) in PM2.5. While sulfate, nitrate, ammonium, Si, OC, and EC show strong ties with PM2.5 levels, Pb, despite its minor presence, also correlates significantly with PM2.5. However, elements like Na, K, Fe, Ca, and Al don't show this strong correlation. The widespread presence of sulfate and nitrate stems from diesel and gasoline combustion, releasing SO2 and NO2 gases, which then convert into sulfates and nitrates.

Key words:

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INTRODUCTION

Lahore experiences severe levels of particulate matter pollution, especially during certain times of the year. The high concentrations of both PM2.5 (fine particles with a diameter of 2.5 micrometers or less) and PM10 (particles with a diameter of 10 micrometers or less) have caused significant health concerns and visibility issues in the city (Colbeck *et al*., 2010).

The major sources of particulate matter pollution in Lahore include Vehicle Emissions Industrial Activities, industrial processes, Biomass Burning, The burning of crop residues, Construction Activities, Waste Burning, Natural Sources. Lahore has witnessed rapid motorization in recent decades. The large number of vehicles, many of which are older and poorly maintained, contribute significantly to PM emissions (Ali *et al*., 2017). Various in and around Lahore, including factories, power plants, and brick kilns, emit substantial amounts of particulate matter. Many of these industries still employ outdated and inefficient technologies (Bashir *et al*., 2019). particularly in the neighboring agricultural regions, introduces substantial amounts of PM2.5 into the atmosphere, which then affects Lahore due to wind patterns and atmospheric conditions (Ghosh *et al*., 2020). Construction dust from various infrastructure development activities in the city adds to the particulate pollution. In the absence of comprehensive waste management systems, open burning of waste becomes a significant source of particulate pollution. Windblown dust from semi-arid regions nearby also contributes to the particulate levels in the city.

Health Implications: Prolonged exposure to high concentrations of particulate matter has been associated with a range of adverse health effects. Lahore's residents are at an increased risk of respiratory and cardiovascular diseases, and there is a heightened risk for vulnerable populations like children, the elderly, and those with pre-existing health conditions (Guttikunda & Calori, 2013).

The composition of PM2.5 in Lahore can vary based on factors such as season, local pollution sources, meteorological conditions, and more. Typical components of PM2.5 in Lahore include Black Carbon (BC), which primarily comes from incomplete combustion processes, such as vehicle exhaust, industrial emissions, and biomass burning (Chowdhury *et al*., 2007). Organic Compounds from a range of sources, such as vehicle exhaust, industrial processes, residential cooking and heating, and even vegetation (Zhang *et al*., 2007). Sulfates (SO_4^{2-}), which form in the atmosphere from sulfur dioxide (SO_2) emissions, predominantly from power plants and industries burning fossil fuels (Burr *et al*., 2011). Nitrates (NO_3^-), which come from nitrogen oxides (NOx) emissions mainly from vehicles, power plants, and certain industrial processes (Ansari & Pandis, 1998). Ammonium (NH_4^+), often connected to agricultural activities and the use of ammonia-based fertilizers (Seinfeld & Pandis, 2016). Mineral Dust from sources like soil and sand, which can be accentuated by human activities such as construction, agriculture, and road traffic (Hussein *et al*., 2008). Metallic Particles from industrial processes, vehicular emissions (especially brake and tire wear), and resuspension of road dust (von Schneidemesser *et al*., 2010). Secondary Organic Aerosols (SOA) that form from volatile organic compounds (VOCs) under the influence of sunlight and atmospheric processes (Jimenez *et al*., 2009). The specific challenges of Lahore, such as its proximity to agricultural zones, mean that during post-harvest seasons, the burning of crop residues can significantly contribute to PM2.5 levels and its composition (Stone *et al*., 2010).

PM2.5, or particulate matter with a diameter of 2.5 micrometers or less, is a significant air pollutant. The composition of PM2.5 is complex, and it can contain a variety of substances, both organic and inorganic. Organic Matter (OM) predominantly makes up a considerable fraction of PM2.5, originating from sources like vehicle exhaust, industrial processes, and biomass burning. This category encompasses hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), and volatile organic compounds (VOCs) (Zhang *et al*., 2007). Inorganic Ions are also prominent in PM2.5. These ions, including sulfate (SO_4^{2-}), nitrate (NO_3^-), ammonium (NH_4^+), and chloride (Cl^-), usually arise from the atmospheric chemical reactions of precursor gases such as sulfur dioxide (SO_2), nitrogen oxides (NOx), and ammonia (NH_3) (Seinfeld & Pandis, 2016). Metals such as lead (Pb), cadmium (Cd), copper (Cu), and zinc (Zn) can be found in PM2.5. Metallic Particles typically emanate from industrial processes, vehicle emissions (specifically from brake and tire wear), and the resuspension of road dust (Hinds, 1999). A product of the incomplete combustion of fossil fuels and biomass, Black Carbon (BC), constitutes a significant portion of PM2.5. BC is basically elemental carbon present as fine particles (Seinfeld & Pandis, 2016). Secondary Organic Aerosols (SOA) are formed in the atmosphere when VOCs undergo oxidation. These oxidized compounds can then react further and condense to form particulate matter (Zhang *et al*., 2007). Mineral Dust contributes to PM2.5, particularly in arid regions or in places with substantial construction or land disturbance. These dust particles consist of silicates and other minerals (Hinds, 1999). Biological components, such as pollen, spores, and certain microorganisms, are present in outdoor environments and add to the Biological Matter in PM2.5. Lastly, PM2.5 particles can absorb water molecules, leading to Water-Adsorbed Particles. These hygroscopic particles' chemical and physical properties can differ due to the presence of water (Seinfeld & Pandis, 2016). The composition of PM2.5 can undergo changes due to various factors such as emissions, chemical reactions, and meteorological conditions. Knowing this composition is essential for assessing the health impacts of PM2.5, identifying its sources, and establishing effective air quality control measures.

Experimental: Sampling was conducted at the rooftop of Pak Green Enviro-Engineering Laboratory situated at Gulberg III Lahore. The site is around 08 m above the ground and approximately 50 m from major roads. Sampling was started on 10 jan 2022 and ended on 15 Dec 2022.

Sampling and analysis: PM2.5 sampling was performed with medium-flow rate samplers. First sample was taken using a 47-mm, Gelman PTFE Teflon-membrane filter with a 2-mm pore size for PM2.5 mass concentrations and for elemental analysis. The second inlet uses a Teflon membrane filter and a nylon filter (Gelman 47-mm diameter, 1-mm pore size). These filters were used for the determination of ionic species (sulphate, nitrate and ammonium). The third inlet was followed by quartz filters (47-mm diameter Gelman quartz-fiber filters) that were used for determining organic and elemental carbon. Integrated weekly samples of PM2.5 were collected at a flow rate of 16 l/min through each sampling inlet. The front quartz filter was analyzed for organic and elemental carbon (OC and EC) by the thermal/optical reflectance (TOR) method. Nitrate, sulphate and ammonium were analyzed by titration method. Metal analysis was performed by Atomic Absorption Spectrophotometer. Blank filters were also used for quality control.

RESULTS AND DISCUSSION

Table 1 provides seasonal/monthly levels of PM2.5 and its constituents. Highest concentaration has been observed during winter season. Especially during month of November and December. This is due to stagnant metrological conditions i.e. low wind speed, low precipitation, low temperature and inversion phenomenon. PM2.5 levels remained at its highest level during November. The Monthly average was 222.02 µg/m3, but the PM2.5 levels may cross dangerous line of

500 µg/m3 during evening due to contribution from various sources like stubble burning, vehicles, household etc and stagnant conditions.

PM2.5 levels remained at its lowest level during summer/rainy season. This huge shift was due to a major shift in metreological conditions. High wind speed, high temperature and precipitation disperse out and cleans the pollution resulting in low levels of PM2.5. Table 1 points out very low level of PM2.5 i.e. 31.22 µg/m3 during August, 2022.

Table 2 provides percentage of PM2.5 constituents throughout the calendar year. Sulfate and nitrate are around 26% of PM2.5. Level of Nitrate is higher than the sulphate due to more sources of Nitrate in the form of vehicles and industrial engines. Diesel, furnace oil and coal are main sources of sulfur. Due to more gasoline vehicles in the city, vehicles do not contribute much to sulphate levels. But use of coal and furnace oil by power plants around the city may contribute to elevate the levels of sulphate. High level of nitrate also shows vehicles and households as a combine major contributor to air pollution as compared to industrial units. Ammonium level is around 16%. There are number of drains in Lahore containing untreated industrial and domestic water, which are main source of ammonium.

High level of Si (12.6%), Ca and Fe indicate high level of natural dust in PM2.5. OC and EC constitute around 42% of the PM2.5 indicating high contribution from the vehicular exhaust and use of fossil fuels in industry and household.

Table 3 shows correlation of different constituents.The precursors for nitrate and sulfate particles in the atmosphere primarily include nitrogen oxides (NOx) from combustion sources (e.g., vehicles, power plants) and sulfur dioxide (SO_2) from industrial processes and combustion of sulfur-containing fuels, respectively. Ammonia (NH_3), primarily emitted from agricultural sources and livestock, reacts with these acidic components to form ammonium salts (Pinder *et al*., 2007).

In the atmosphere, SO_2 can oxidize to form sulfate (SO_4^{2-}), and NOx can oxidize to form nitrate (NO_3^-). These anions can then combine with ammonia (NH_3) to form particulate salts like ammonium sulfate [$(NH_4)_2SO_4$] and ammonium nitrate (NH_4NO_3). Both of these salts can contribute significantly to the mass of PM2.5 in many regions (Seinfeld & Pandis, 2016).

The formation of ammonium nitrate is highly sensitive to temperature and humidity. In colder conditions, the gas-to-particle conversion of the precursors to form ammonium nitrate is favored, leading to increased PM2.5 concentrations. Conversely, ammonium sulfate remains particulate across a wider range of conditions (Zhang *et al*., 2012).

Both ammonium nitrate and ammonium sulfate in the PM2.5 fraction can have adverse health effects when inhaled, as the fine particles can penetrate deep into the lungs, potentially leading to respiratory diseases, cardiovascular problems, and other health issues (Seinfeld & Pandis, 2016).

Table 3 shows that major constituents of PM2.5 like sulfate, nitrate, ammonium, Si, OC and EC has high correlation with PM2.5. Although contribution of Pb is very low still it showed high correlation with PM2.5. Sulphate and nitrate are founnd everywhere in the cities due to presence of diesel and gasoline sources to produce SO2 and No2 gases, which ultimately converts to sulphates and nitrates. Other constituents like Na, K, Fe, Ca, and Al did not show high correlation with PM2.5.

Figure 1 shows linear regression of PM2.5 with its major constituents. Particulate matter of 2.5 micrometers or less in diameter (PM2.5) comprises various components, including elemental constituents like sodium (Na), potassium (K), iron (Fe), lead (Pb), and zinc (Zn). These elements, typically present in PM2.5 as particulate salts or metal oxides, can originate from various natural and anthropogenic sources. Their presence in PM2.5 and their correlations can be indicative of specific sources or atmospheric processes.

Table 1: Level of PM2.5 and its constituents throughout the calendar year (µg/m3).

	JAN	FEB	MAR	APR	MAY	JUNE	JULY	AUG	SEP	OCT	NOV	DEC
PM2.5	177.89	111.58	108.29	105.27	74.33	74.80	45.05	31.22	82.00	106.51	222.02	186.16
Sulfate	16.31	15.93	15.34	10.37	8.80	9.20	4.75	4.41	11.07	14.85	20.87	15.00
Nitrate	17.28	16.98	19.05	13.13	8.16	7.94	7.47	7.99	10.91	18.36	29.35	18.40
Ammonium	15.40	16.40	14.20	13.60	12.50	12.20	10.80	11.20	14.80	16.40	18.20	17.60
Si	12.70	13.40	11.20	10.40	10.20	9.20	8.40	8.20	9.80	13.40	17.20	16.10
OC	37.44	27.36	26.40	27.84	24.96	23.04	19.28	12.32	15.28	31.20	65.28	58.56
EC	17.28	13.44	12.24	9.84	10.56	9.12	10.56	8.08	11.52	12.24	19.68	15.36
Na	2.40	1.31	1.42	1.72	1.62	2.03	2.87	1.46	0.41	2.06	3.08	2.80
K	1.46	1.32	0.98	1.24	1.12	1.52	2.52	1.28	0.52	1.72	2.74	2.34
Fe	3.29	3.00	2.71	2.14	2.57	3.57	4.00	4.14	3.86	4.43	5.14	4.57
Ca	4.16	1.90	1.78	1.47	1.87	2.26	1.82	1.99	2.00	2.01	2.29	2.06
Al	0.95	1.11	1.51	0.88	0.67	0.97	0.95	1.01	0.54	0.55	1.01	0.87
Pb	0.93	0.71	0.50	0.68	0.70	0.57	0.44	0.48	1.02	1.20	1.58	1.44

Table 2: Percentage of constituents of PM2.5 during different months of the calendar year.

	JAN	FEB	MAR	APR	MAY	JUNE	JULY	AUG	SEP	OCT	NOV	DEC	Avergae
Sulfate	9.17%	14.28%	14.16%	9.85%	11.84%	12.30%	10.55%	14.12%	13.50%	13.94%	9.40%	8.06%	11.76%
Nitrate	9.71%	15.22%	17.59%	12.48%	10.98%	10.61%	16.59%	25.60%	13.30%	17.24%	13.22%	9.88%	14.37%
Ammonium	8.66%	14.70%	13.11%	12.92%	16.82%	16.31%	23.97%	35.88%	18.05%	15.40%	8.20%	9.45%	16.12%
Si	7.14%	12.01%	10.34%	9.88%	13.72%	12.30%	18.64%	26.27%	11.95%	12.58%	7.75%	8.65%	12.60%
OC	21.05%	24.52%	24.38%	26.45%	33.58%	30.80%	42.79%	39.47%	18.63%	29.29%	29.40%	31.46%	29.32%
EC	9.71%	12.04%	11.30%	9.35%	14.21%	12.19%	23.44%	25.88%	14.05%	11.49%	8.86%	8.25%	13.40%
Na	1.35%	1.18%	1.31%	1.64%	2.17%	2.72%	6.37%	4.68%	0.50%	1.93%	1.39%	1.50%	2.23%
K	0.82%	1.18%	0.90%	1.18%	1.51%	2.03%	5.59%	4.10%	0.63%	1.61%	1.23%	1.26%	1.84%
Fe	1.85%	2.69%	2.51%	2.04%	3.46%	4.77%	8.88%	13.27%	4.70%	4.16%	2.32%	2.46%	4.42%
Ca	2.34%	1.70%	1.64%	1.39%	2.52%	3.02%	4.04%	6.37%	2.44%	1.89%	1.03%	1.11%	2.46%
Al	0.53%	1.00%	1.39%	0.83%	0.90%	1.30%	2.11%	3.22%	0.66%	0.52%	0.45%	0.47%	1.11%
Pb	0.52%	0.64%	0.47%	0.65%	0.95%	0.76%	0.98%	1.54%	1.24%	1.13%	0.71%	0.78%	0.86%

Table 3: Correlation of different constituents with PM2.5

	PM2.5	*Sulfate*	*Nitrate*	*Ammonium*	*Si*	*OC*	*EC*	*Na*	*K*	*Fe*	*Ca*	*Al*	*Pb*
PM2.5	1.00												
Sulfate	0.89	1.00											
Nitrate	0.88	0.93	1.00										
Ammonium	0.87	0.92	0.88	1.00									
Si	0.92	0.89	0.90	0.95	1.00								
OC	0.93	0.77	0.83	0.80	0.93	1.00							
EC	0.94	0.87	0.87	0.83	0.88	0.86	1.00						
Na	0.52	0.24	0.39	0.23	0.48	0.69	0.52	1.00					
K	0.46	0.22	0.42	0.28	0.52	0.68	0.49	0.94	1.00				
Fe	0.33	0.22	0.38	0.39	0.45	0.48	0.42	0.49	0.65	1.00			
Ca	0.45	0.34	0.21	0.22	0.23	0.25	0.54	0.28	0.08	0.13	1.00		
Al	0.10	0.18	0.25	-0.06	0.04	0.07	0.11	0.11	0.07	-0.23	0.00	1.00	
Pb	0.81	0.72	0.74	0.87	0.87	0.84	0.77	0.39	0.46	0.64	0.22	-0.37	1.00

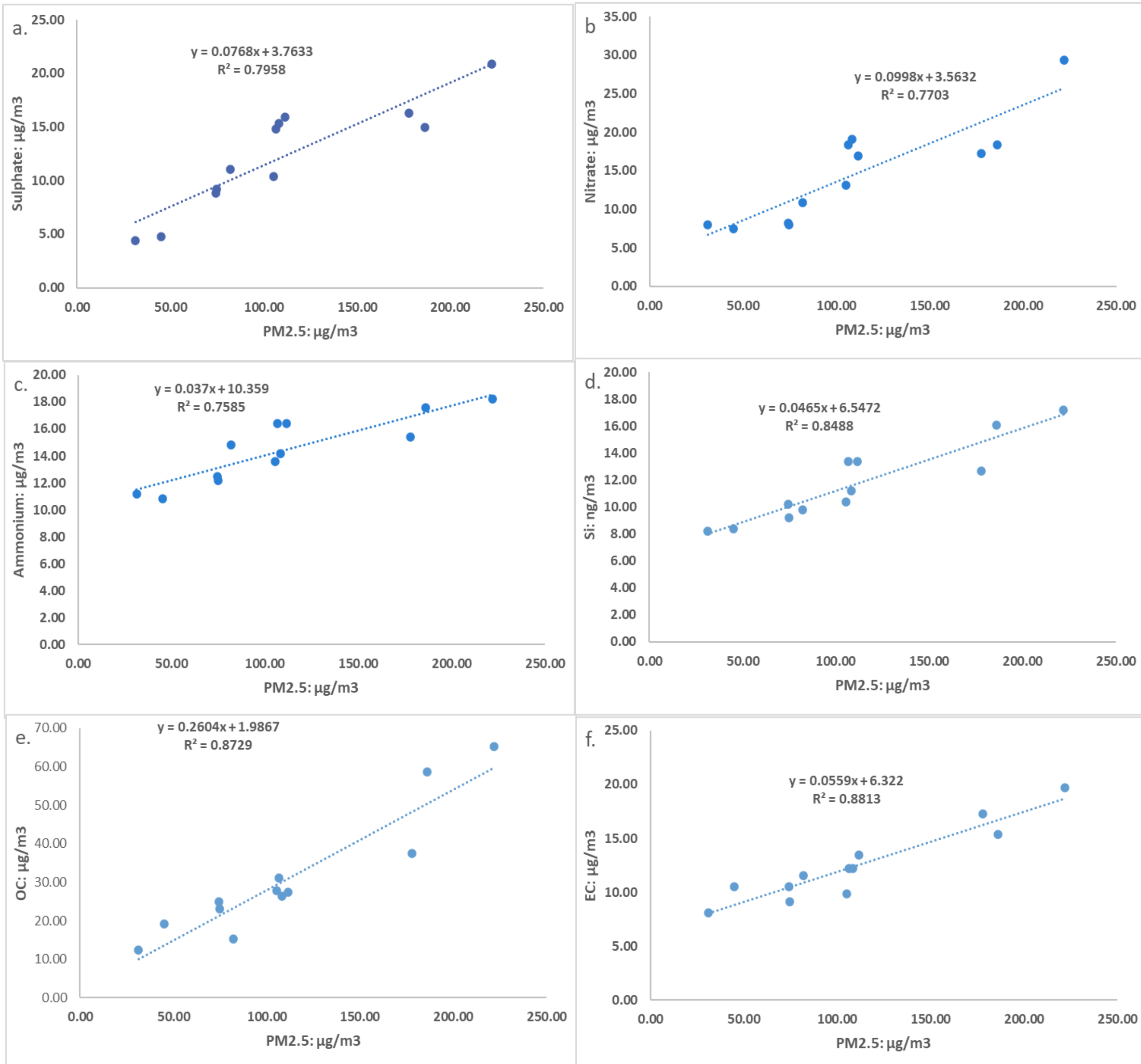

Figure 1: Relation of PM2.5 with its major constituents

Sodium and potassium are often associated with sea salt particles and biomass burning. For coastal regions, a strong correlation of Na in PM2.5 can indicate sea spray contributions (Lelieveld *et al*., 2015). On the other hand, elevated potassium levels often signify the influence of biomass burning, as K is a major component of plant material (Andreae & Merlet, 2001).

Iron in PM2.5 can originate from soil dust and industrial emissions. In urban areas with substantial industrial activities, elevated Fe levels in PM2.5 can signify industrial contributions (Han *et al*., 2016). Additionally, long-range transport of desert dust can also lead to significant Fe concentrations in PM2.5.

Historically, elevated Pb levels in PM2.5 were associated with leaded gasoline emissions. However, with the phasing out of leaded gasoline in many countries, current Pb levels in PM2.5 are more indicative of industrial processes, waste incineration, and the re-suspension of historically deposited lead (Mielke *et al*., 2011).

Calcium is predominantly associated with crustal or soil-derived dust. Elevated concentrations of Ca in PM2.5 typically indicate the influence of resuspended soil or road dust. In urban settings, construction activities, unpaved roads, or other soil-disturbing activities can lead to increased calcium levels in the ambient air. Additionally, in some regions, calcium can also derive from industrial sources or the burning of certain types of coal (Chow *et al*., 2015).

Similar to calcium, aluminum is a common crustal element, and its presence in PM2.5 is usually indicative of soil or mineral dust influence. Elevated levels of Al can be observed during events of long-range transport of desert dust, especially in areas downwind from deserts. Aluminum, as a component of aluminosilicate minerals, is abundant in the Earth's crust and is a useful tracer for mineral dust contributions to PM2.5 (Hussein *et al*., 2008).

Understanding the correlation of PM2.5 with calcium and aluminum is particularly useful in source apportionment studies. When observed alongside other elements and compounds, the contributions from soil or mineral dust, versus anthropogenic sources, can be better discerned.

The correlations between these elements and PM2.5 can provide insights into source contributions, especially when combined with other analytical methods like positive matrix factorization (PMF) or chemical mass balance (CMB).

Figure 2 shows low correlation of micro particles like Na, K, Ca, Al, Fe with the PM2.5. But amount of Ca and Al is high in the dust showing high contribution from the natural dust. But Pb shows high correlation with the Pm2.5 due to presence of lead in the dust from anthropogenic sources like gasoline and other industrial sources.

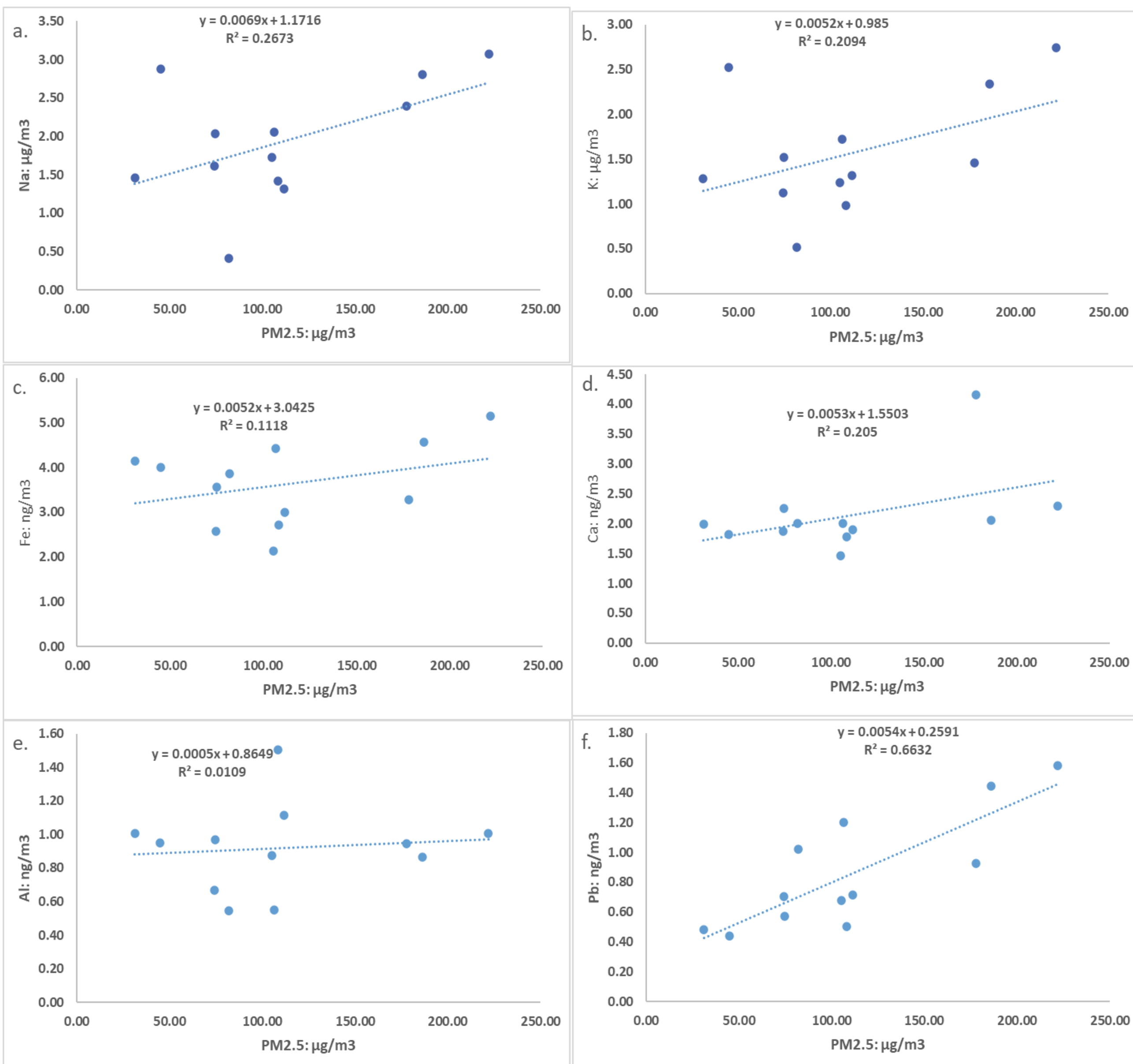

Figure 2: Relation of PM2.5 with minor constituents

Conclusion: Lahore city has been experiencing high level of air pollution of all times. The city has gone through a wide range of volumetric as well as numerical expansion. As a developing country the control on vehicular and industrial emissions is questionable. A more strange factor to enhance air pollution is the metreological factors. During winter season, due to low temperature (around 20 to 30 C^0), low wind speed and almost absence of rain, traps the air pollution in the city resulting in a hazy and smogy atmosphere. The highest average monthly PM2.5 concentration remained during November 222 µg/m3. While during the summer season due to high temperature, high precipitation and relatively high wind speed, air pollution either washes out or dispersed in the atmosphere resulting in better air quality. Minimum PM2.5 level observed during August i.e. 31 µg/m3.

Approximately 26% of PM2.5 consists of sulfate and nitrate. Nitrate concentrations surpass those of sulfate, largely attributed to its numerous sources such as vehicles and industrial machinery. The prominent presence of nitrate suggests that vehicles and residential sectors together are major culprits of air pollution, overshadowing the contributions from industrial entities. Ammonium constitutes close to 16% of PM2.5. In Lahore, numerous drains carry untreated wastewater from both residential and industrial sources, primarily accounting for the ammonium content.

The notable concentrations of Si (12.6%), Ca, and Fe in PM2.5 point towards a significant presence of natural dust. Organic Carbon (OC) and Elemental Carbon (EC) together make up roughly 42% of PM2.5, highlighting the substantial emissions from vehicle exhausts and the combustion of fossil fuels in both industrial and domestic settings.

Key components of PM2.5, including sulfate, nitrate, ammonium, Si, OC, and EC, exhibit a strong correlation with PM2.5 levels. Despite its minimal contribution, Pb also demonstrated a notable correlation with PM2.5. Sulfate and nitrate are omnipresent in urban areas, stemming from the combustion of diesel and gasoline that release SO2 and NO2 gases, respectively. These gases subsequently transform into sulfates and nitrates. However, other elements like Na, K, Fe, Ca, and Al did not manifest a significant correlation with PM2.5.

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