Research article

Geo-environmental approach to assess heavy metals around auto-body refinishing shops using bio-monitors

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HIGHLIGHTS

- Auto-body refinishing shops are one of the local businesses, which is the major issue of occupational and environmental health.
- Pigments used in color paints are metal-based.
- Use of bio-monitors are a very active way to assess health and environmental conditions.

ARTICLE INFO

ABSTRACT

The vehicular industry is looking for continuous challenges to develop the sustainability of its manufacturing, maintenance processes, and vehicle emissions due to marketability, environmental, economic, and policy concerns. The present study focuses on the impact of these processes on the environment. In Pakistan, most of the auto-body refinishing processes are carried out in an open atmosphere. The shades of Azadirachta indica (Neem Tree) are generally used for the outdoor practice of scrapping, grinding, and painting in auto-body refinishing shops of Pakistan. Azadirachta indica leaves were selected as bio-indicator. For the present work, 26 affected sites and 10 control sites were selected from Karachi city, which is the financial hub and biggest city of Pakistan. Concentrations of different metals (Fe, Co, Cd, Cr, Cu, Mn, Mo, Ni, Pb, and Zn) were determined by atomic absorption spectrophotometer. A geographic information system (GIS) is used to present the variation in concentrations within Karachi city. The only positive correlation was observed in Pb and Mn (0.750). Principal component analysis (PCA) is applied to identify the anthropogenic effect between auto-body refinishing areas and control areas. Almost all analyzed metals show higher concentration at affected sites but Pb (87.14 mg/kg), Mn (46.47 mg/kg) and Fe (146.95 mg/kg) were leading the values, as compared to their concentration at control sites, Pb (48.83 mg/kg), Mn (15.23 mg/kg) and Fe (43.07 mg/kg). All analyzed metals are frequently present in different color pigments, whereas Pb, Mn, and Fe may also come from other sources, like the anti-knocking agent, vehicular exhaust, and scraping of car surface.

1. Introduction

Several occupations are involved in metal pollution in the atmosphere within our society. Along with major natural and anthropogenic factors, minor occupations are also responsible for metal flow in the atmosphere and are always neglected by the governments and other private health care agencies. The auto-body refinishing is one of these minor occupations. Evaluation of paints, organic solvents, scrapping dust particles, and noise directly affects the close atmosphere around auto body refinishing shops (Tahir et al., 2010).

At present, elevated levels of chemical pollutants in the environment are observed as a result of rapid industrialization, agriculture, and urbanization. Inorganic and organic pollutants are observed in many environmental matrices such as soil, air, and water (Serbula et al., 2013). Excess metal concentration is toxic and has several side effects on public health, animals, and plants. The uplifted presence of heavy metals in food products is due to metallic pollution from various sources. Heavy metals are categorized as major inorganic pollutants because of their toxicity and physiological functions (Matin et al., 2016).

Heavy metals have a natural abundance in the environment, however, anthropogenic sources are also playing their role to contaminate the environment. Industries like textiles, processing, mining or refining ores, paints, alloys, sludge disposal, metal plating, batteries, production of electrical equipment, pesticides, etc., discharge their wastes in large quantity into the environment (Rezić, 2013). Human-created pollution changed the levels of heavy metal concentration in the atmosphere. The number of researches proved that heavy metals are broadly separated in the atmosphere, showing the capability to react with the natural environment and generate threats for the environment and human health (Park and Dam, 2010) (Aničić et al., 2011) (Pavlík et al., 2012) (Fumiyuki Nakajima, 2018) (Azzazy, 2020).

Airborne metallic pollution monitoring is still a challenge in developing countries due to the high cost of instruments and monitoring stations. Another difficulty associated with atmosphere research is widespread sampling in space and time. The effect of atmospheric pollutants on living organisms cannot be studied by commonly used monitoring stations. These cost issue and impact of pollutant issues of atmospheric studies naturally drags the scientist's interest towards the use of biomonitoring (Aničić et al., 2011). Due to the well-known advantages of a metal accumulation from the environment, low cost, and easy sampling, biomonitors/environmental monitors are used widely for environmental quality (Oliva and Valdés, 2004) (Fernández Espinosa and Oliva, 2006).

Plants are considered as natural qualitative and quantitative atmospheric pollution samplers. Plants are also very active in reducing atmospheric pollutants of all sizes, including respirable particulates (K. Paul Beckett, Peter Freer-Smith, 2000).

A sampling of bio-monitors is easy, cheap, and has high concentrations of heavy metals than rainwater and air. Different kinds of biomonitors are being used like grass, woody plants, and vascular plants (Ejidike and Onianwa, 2015). Isidora Deljanin et al., (2016) used biomonitors (Acer platanoides, Tilia spp., Aesculus hippocastanum, and Betula pendula) to find the distribution and correlation of trace elements in leaves from the atmosphere. Tilia spp. and A. hippocastanum were found most effective and least effective in the metal accumulation with 70% and 54% accumulation, respectively. It is already established that the selection of plant species and statistical techniques are very important in biomonitoring studies (Deljanin et al., 2016). Pedro Henrique (2015) used S. flexicaulis called "erva de passarinho" (bird grass) for the bio-monitoring study. The study suggested that leaves are the best part of the plant for biomonitoring. Herbs like S. flexicaulis have other advantages too, such as being abundant, low cost, and easy to sample (de Paula et al., 2015). Rossini Oliva and Mingorance (2007) conducted a study of heavy metals monitoring in soil, atmosphere, and plant leaves. He suggested that N. Oleander leaves are useful biomonitors for metals, especially for Cu analysis (Oliva and Espinosa, 2007). Despite plants, mosses

and testate amoebae can also be used as biomonitors for metal pollution (Asada and Warner, 2009). Numerous plant species were studied in order to investigate the tendency towards metal biomonitoring. Every plant has a tendency of heavy metal accumulation, but the level of accumulation is different (Weiss et al., 2003). Biomonitoring is not a new method of atmospheric monitoring. Many pieces of research conducted to prove the usefulness of different parts of plants as biomonitors, especially leaves and tree back (Ibrahim Hassan, 2013) (Guéguen et al., 2012) (Guéguen et al., 2011) (Norouzi et al., 2015) (Rodríguez-Germade et al., 2014) (SA et al., 2018) (Yasser A. El-Amier, 2018).

Table 1. GPS Locations of affected Leave sample from Karachi city.

S. No	Code	Location	GPS Location		Temperature (°C)
1	KL-1	Marton quarters	24° 53′ 16.84″ N	67° 2′ 37.19″ E	40–45
2	KL-2	Kashmir Road	24° 52′ 19.92″ N	67° 2′ 52.46″ E	40–45
3	KL-3	PECHS community hall	24° 52′ 6.28″ N	67° 3′ 6.32″ E	40–45
4	KL-4	PECHS (Block # 6)	24° 51′ 15.31″ N	67° 3′ 51.69″ E	40–45
5	KL-5	Ghosia Colony	24° 53′ 19.37″ N	67° 3′ 2.49″ E	40–45
6	KL-6	Teen Hatti	24° 53′ 29.31″ N	67° 2′ 42.20″ E	40–45
7	KL-7	Pehalwan Goth	24° 54′ 52.57″ N	67° 8′ 31.33″ E	35–40
8	KL-8	Lakhani Pride	24° 54′ 27.33″ N	67° 8′ 7.59″ E	35–40
9	KL-9	Rado Centre	24° 55′ 0.11″ N	67° 7′ 39.71″ E	35–40
10	KL-10	Karachi Centre	24° 53′ 25.73″ N	67° 3′ 29.42″ E	35–40
11	KL-11	Old Vegetable Market	24° 53′ 52.30″ N	67° 3′ 41.58″ E	35–40
12	KL-12	PIA planetarium	24° 54′ 25.97″ N	67° 4′ 46.23″ E	35–40
13	KL-13	Federal Urdu College	24° 54′ 45.46″ N	67° 5′ 16.38″ E	35–40
14	KL-14	PIB police station	24° 53′ 26.70″ N	67° 3′ 2.53″ E	35–40
15	KL-15	Orangi Police station	24° 56′ 19.96″ N	67° 0′ 13.36″ E	30–35
16	KL-16	Banaras Chowk	24° 55′ 53.03″ N	67° 0′ 55.85″ E	30–35
17	KL-17	Railway Colony	24° 50′ 38.56″ N	67° 3′ 2.26″ E	30–35
18	KL-18	Akbar Market	24° 51′ 40.98″ N	67° 1′ 0.45″ E	30–35
19	KL-19	Gulberg Square flats	24° 56′ 26.92″ N	67° 4′ 56.72″ E	30–35
20	KL-20	KMDC	24° 56′ 37.87″ N	67° 3′ 47.26″ E	30–35
21	KL-21	7-C last stop	24° 57′ 27.26″ N	67° 4′ 1.15″ E	30–35
22	KL-22	Saifi Poly Technique	24° 55′ 46.65″ N	67° 3′ 0.26″ E	30–35
23	KL-23	Habib Medical Centre	24° 55′ 9.89″ N	67° 3′ 10.13″ E	30–35
24	KL-24	Garibabad	24° 54′ 34.58″ N	67° 3′ 24.62″ E	30–35
25	KL-25	Karachi Zoo	24° 52′ 28.49″ N	67° 1′ 17.87″ E	30–35
26	KL-26	Talimi Bagh	24° 55′ 46.96″ N	67° 4′ 9.82″ E	30–35

Table 2. GPS Locations of control Leave sample from Karachi city.

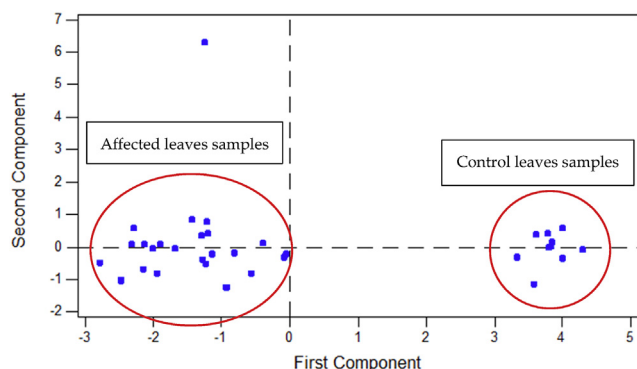| S. No	Code	Location	GPS Location		Temperature (°C)
1	CKL-1	Orangi Town (sector # 5)	24° 56′ 53.24″ N	66° 59′ 6.00″ E	28–38
2	CKL-2	Banarus Chowrangi	24° 56′ 6.93″ N	67° 0′ 39.46″ E	28–38
3	CKL-3	Zainab Market	24° 51′ 14.47″ N	67° 1′ 42.97″ E	28–38
4	CKL-4	Akbar Market	24° 51′ 38.88″ N	67° 1′ 6.02″ E	28–38
5	CKL-5	Jamshaid Road	24° 52′ 57.35″ N	67° 2′ 42.82″ E	28–38
6	CKL-6	Jahangir Road	24° 53′ 23.29″ N	67° 2′ 33.98″ E	28–38
7	CKL-7	Krimabad	24° 55′ 0.65″ N	67° 3′ 17.44″ E	28–38
8	CKL-8	Aysha Manzil	24° 55′ 23.60″ N	67° 4′ 4.54″ E	28–38
9	CKL-9	Gulshan Chowrangi	24° 55′ 29.75″ N	67° 5′ 30.13″ E	28–38
10	CKL-10	Rado Centre	24° 54′ 45.40″ N	67° 7′ 31.84″ E	28–38

Figure 1. Principal component analysis (score plot) of affected leaves and control samples collected from Karachi.

Leaves are considered as good biomonitors for targeted research (Samecka-Cymerman et al., 2009). Tree leaves are also used for studying atmospheric dust. In urban areas, atmospheric pollution monitoring is commonly carried out by roadside plants. In atmospheric research, an extensive area of plants is useful for sampling design (Lu et al., 2008). Azadirachta indica, (neem tree) is an evergreen rapid growing tree and is widely spread in Asian countries. Usually, the neem tree has a life span of 200 years. The average height is 7–15 m. Its branches are moderately thick and wide spreader by dense leaves (B. Abdullateef, B. G. Kolo, I. Waziri, 2014). The neem tree is a very famous plant among environmentalists and in 1992, the US National Academy of Science published an article "Neem: A tree for solving global problems". United Nations declared it as the "Tree of the 21st century" (Kumar and Navaratnam, 2013). Neem tree leaves have a good tendency to accumulate atmospheric dust due to the significant leaf area (Qadir et al., 2016) (B. Abdullateef, B. G. Kolo, I. Waziri, 2014) (A et al., 2016).

Auto-body refinishing shops are one of the main contributors to organic compounds and metal pollution in the atmosphere. The auto-body refinishing process is mainly based on scrapping, bonding work, and spray paints.

Around 5–20% of involved persons are affected by asthma in paint related occupations (Tahir et al., 2010) (Gyan Michael, 2016). The actual composition of paints or materials used in auto body refinishing is often unknown because these formulations are patented. Spray paints have generally complex formulations. Other than coloring pigment, solvents, and a binding medium, normally these modern paints contain biocides, stabilizers, fillers, plasticizers, emulsifiers, and antioxidants (Germinario et al., 2016).

Principal component analysis (PCA) was used to concise the details of a big data set. The use of PCA in environmental research is very common, for both monitoring and assessment of metals. In case of graphical limitations, PCA is a powerful tool to analyze data (Mishra et al., 2015).

The present study aimed to assess the concentrations of heavy metals (Cr, Co, Cu, Cd, Pb, Mn, Mo, Ni, Zn, and Fe) in Neem tree leaves. The Neem tree selection is because of its huge presence in local auto-body refinishing areas in Karachi, Pakistan. In most of the shops, the Neem tree is used as a shelter from sunlight during different stages of auto-body refinishing.

2. Material and method

2.1. Chemical and instruments

All analytical grades chemicals were used. HNO_3 (65% v/v), H_2O_2 (50% v/v), and other chemicals of MERCK and BDH company were used. Washing of glassware and dilution of the solution was done by distilled water. Grinder (DCFH 48-type) and hot plate (Stuart) were used for sample preparation. Atomic Absorption Spectrophotometer (Perkin

Table 3. Statistical parameters of heavy metals in affected and control leaves samples.

S. No.	Metal	Affected Sample			Control Sample			t-value	p-value	Remarks
		Range (mg/Kg)	$\overline{X}$	±SD	Range (mg/Kg)	$\overline{X}$	±SD			
1	Cd	1.300–13.70	4.558	2.466	0.200–1.400	0.620	0.394	7.880	0.000	Significant
2	Co	1.900–6.800	3.852	1.490	0.300–1.100	0.660	0.255	10.53	0.000	Significant
3	Cr	3.001–12.30	6.738	2.213	2.100–11.70	5.230	2.786	1.540	0.074	Insignificant
4	Cu	3.540–35.70	13.17	7.940	0.800–5.100	1.970	1.416	6.910	0.000	Significant
5	Fe	93.40–194.3	146.94	25.18	10.90–67.10	43.07	18.08	13.75	0.000	Significant
6	Mn	14.80–181.6	62.10	46.47	0.180–44.89	15.23	13.65	4.650	0.000	Significant
7	Mo	1.900–9.300	5.029	2.476	0.680–1.500	1.129	0.318	7.870	0.000	Significant
8	Ni	1.320–8.000	4.218	1.881	0.200–0.500	0.370	0.116	10.38	0.000	Significant
9	Pb	56.20–177.4	87.14	23.42	19.20–87.40	48.83	22.03	4.590	0.000	Significant
10	Zn	11.76–58.82	36.20	14.37	1.780–9.300	7.458	2.706	9.760	0.000	Significant
11	Na	198.1–591.5	365.0	97.30	62.50–96.70	83.59	10.75	14.52	0.000	Significant
12	K	889.4–1823	1283	264.4	341.9–856.4	676.1	166.1	8.220	0.000	Significant

Table 4. Correlations statistics between heavy metals in affected leaves samples.

Metal	Pb	Mn	Mo	Zn	Cu	Ni	Co	Cd	Cr	Fe	Na	K
Pb	1											
Mn	0.750	1										
Mo	-0.074	-0.228	1									
Zn	0.014	-0.264	0.277	1								
Cu	-0.179	-0.165	-0.005	0.069	1							
Ni	-0.021	-0.250	0.248	0.009	0.259	1						
Co	-0.070	-0.207	-0.002	-0.452	0.193	0.142	1					
Cd	0.212	0.218	0.237	0.010	-0.073	0.069	-0.219	1				
Cr	-0.210	-0.294	-0.450	0.111	-0.285	0.190	-0.011	-0.348	1			
Fe	0.046	-0.148	-0.162	-0.077	-0.187	0.033	-0.024	0.019	0.110	1		
Na	0.099	0.117	0.202	0.194	0.240	-0.193	-0.161	-0.137	-0.042	-0.246	1	
K	0.091	0.045	-0.263	0.208	0.024	-0.821	0.101	-0.107	-0.092	-0.010	0.161	1
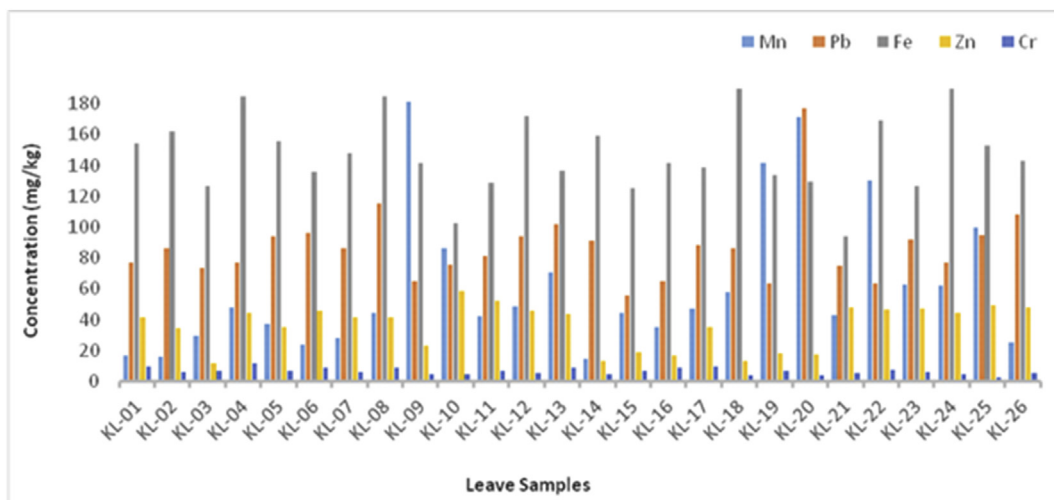
Figure 2. Concentration of heavy metals (mg/kg) in affected leaves samples.
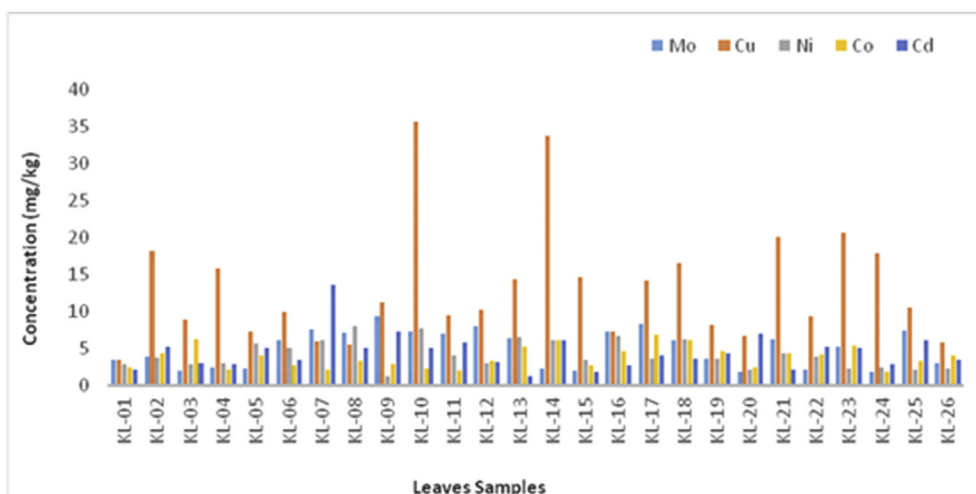
Figure 3. Concentration of heavy metals (mg/kg) in affected leaves samples.
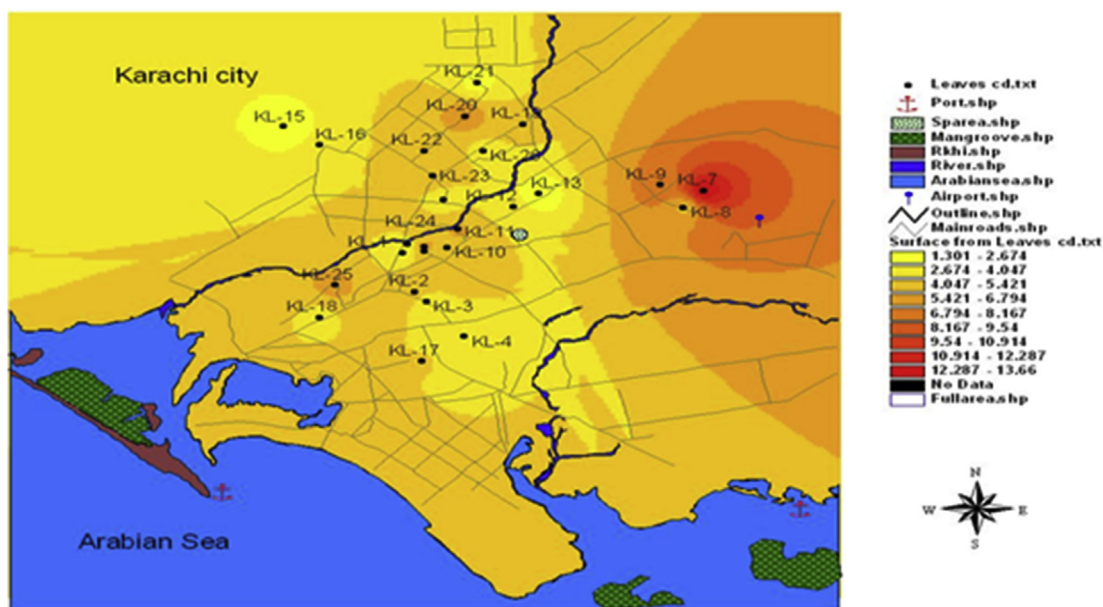
Figure 4. GIS Map showing concentration variation of Cd metals in leaves samples collected from Karachi city.
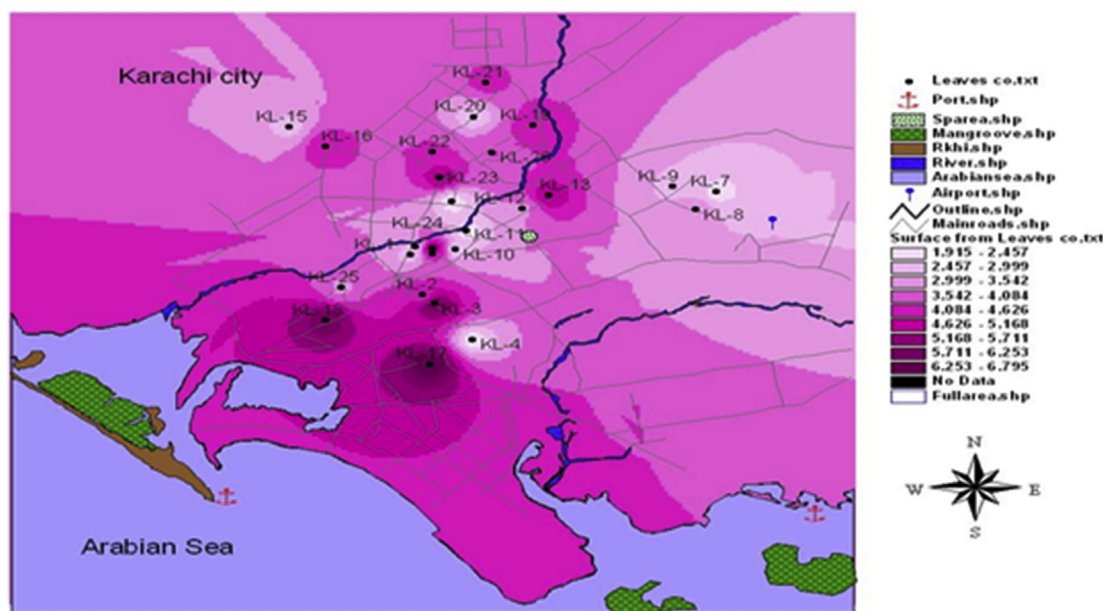

Figure 5. GIS Map showing concentration variation of Co metals in leaves samples collected from Karachi city.

Elmer, A Analyst- 700) and Flame photometer (410 Classic, Corning) were used for metal analysis.

2.2. Sampling

In Pakistan, painting and scraping processes of the auto-body refinishing shops are preceded in the open environment, under the shed of trees. The shade of the Neem tree is commonly used because of its dense shade.

Twenty-six effected and 10 control samples were collected from Karachi city. Three replicates of each sample were collected from each location and mixed to form composite samples. GPS (Global positioning system) locations and the ambient temperature of control and sampling sites, along with their codes are represented in Tables 1 and 2. GPS locations of all sampling sites were assessed and confirmed by using

"Garmin eTrex Vista" by Garmin. Metal concentration along with latitude and longitude coordinates were plotted in GIS (Geographic Information System) maps, Figures 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, and 15, by using ArcGIS 10.1 (software by Esri).

Leave samples were taken from singular plant species, Neem tree, botanically known as "Azadirachta Indica". Samples from two different types of locations of Neem trees were collected, one used by auto-body refinishing workers and other trees that were not used by auto-body refinishing activity, as controls. Affected leaves samples were collected which were used as a shadow during car painting and scraping processes, in Pakistan, it is common practice to repair or refinish the cars under the tree shades because shops are only used to secure the tools and equipment. Leaves samples were taken from the auto-body refinishing market, each sample was taken from 1.5 to 2 m height of the tree (from ground level) and inside the radius of 5 m from the scraping and painting process
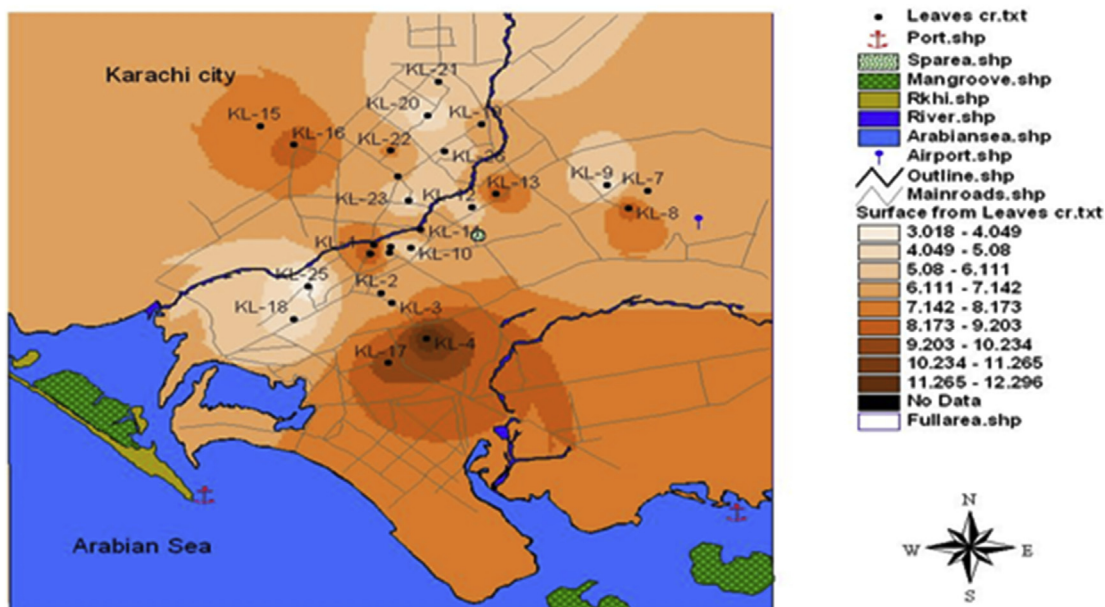
Figure 6. GIS Map showing concentration variation of Cr metals in leaves samples collected from Karachi city.
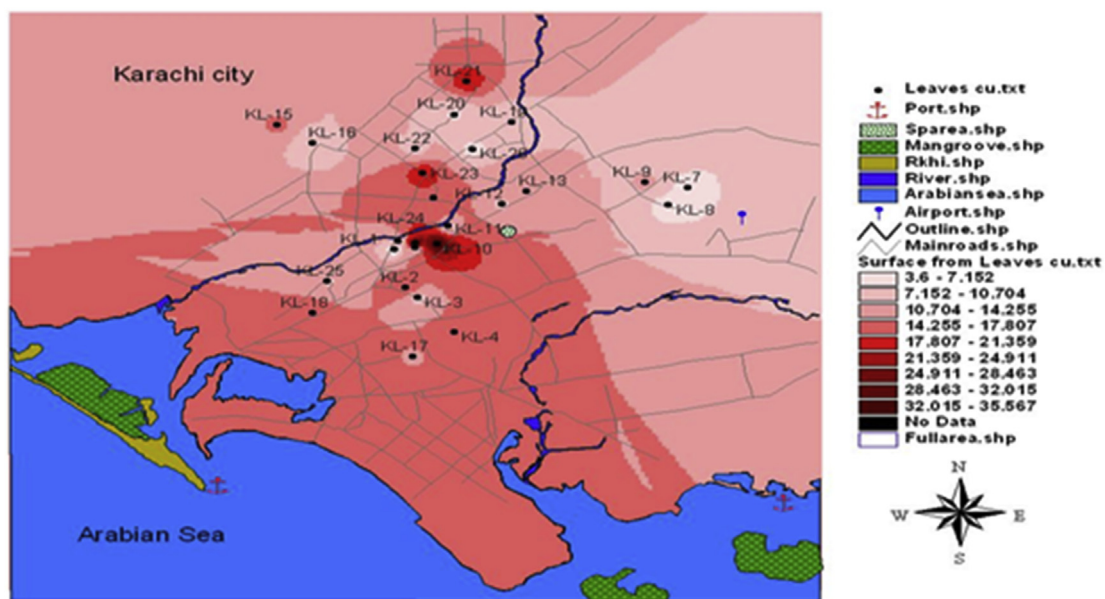

Figure 7. GIS Map showing concentration variation of Cu metals in leaves samples collected from Karachi city.

had done. The control leave samples were collected from selected locations where no auto-body refinishing shops or any other type of occupational activity were noticed within the diameter of 3 km. The sample collection conditions were kept the same, both for control and affected samples (Tahir et al., 2010) (Yasser A. El-Amier, 2018).

Leave samples were taken from only the Neem tree by using clean Teflon scissors while wearing polyethene gloves to avoid any contamination from bare hands. Polyethene bags were used to transport the samples. Under specifically guided conditions for the analysis of the concentration of trace metals (Markert et al., 1996) (Markert, 1996) (Z. Vukmirovic, S. Rajsic, D. Markovic, 1997) (Tomašević et al., 2005). Each sample bag was labelled so that its contents could be unequivocally identified.

2.3. Experimental

In the laboratory, the affected and control leaves samples were washed with deionized distilled water and dried for 24 h in an electric oven (Toyo Fs-type) at $70 \pm 2\,°C$ until constant weights were obtained. The dried leaves samples were ground to a fine powder with a grinder (DCFH 48-type), to homogenize, every sample was sieved using a 2 mm mesh and then stored in airtight desiccators (Eludoyin and Ogbe, 2017) (Iftikhar Imam Naqvi, Mohammad Ahmed Farrukh, 2005).

One gram (g) of effected and control leave samples were digested with a mixture of concentrated HNO_3/H_2O_2 (3:1. v/v) at 70–90 °C on a hot plate till the nitrous fumes had over and the solution became clear. After cooling, the digested samples were filtered (Whatman 540) and
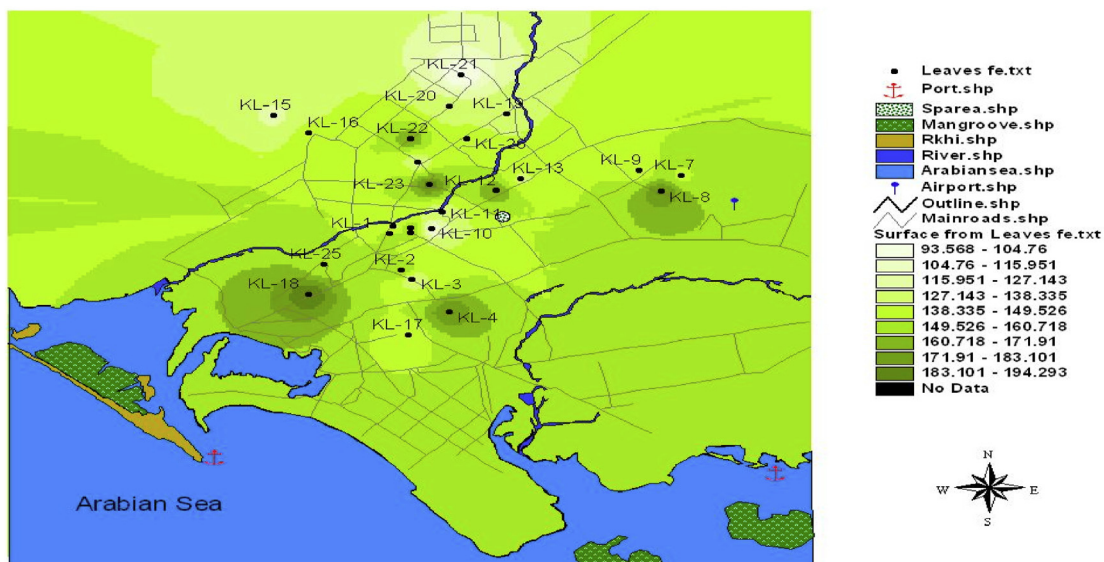
Figure 8. GIS Map showing concentration variation of Fe metals in leaves samples collected from Karachi city.
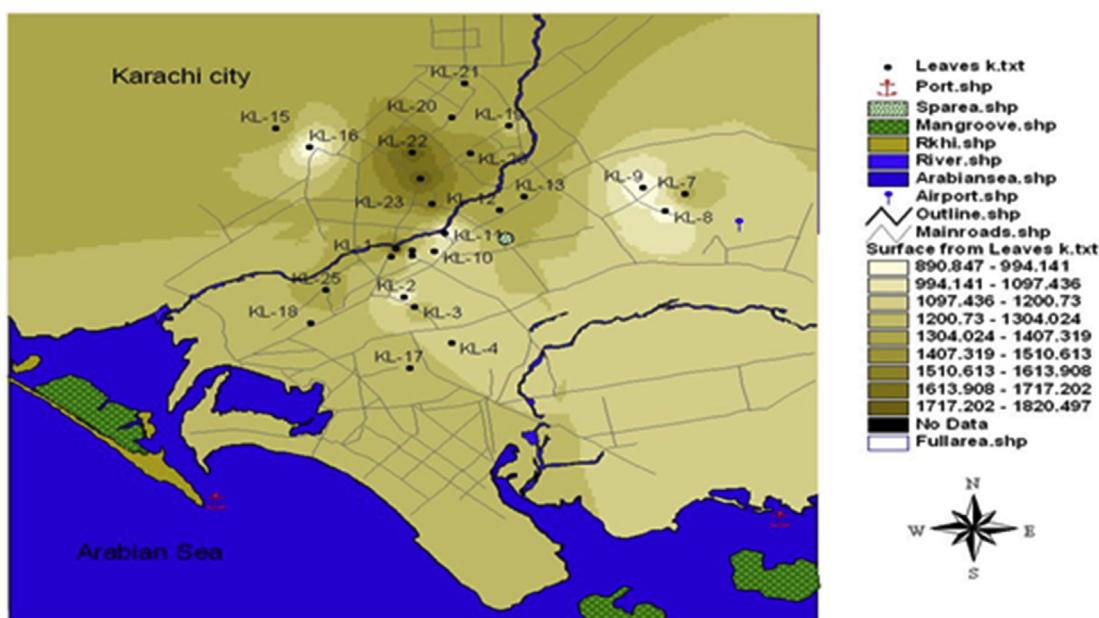

Figure 9. GIS Map showing concentration variation of K metals in leaves samples collected from Karachi city.

transferred into a 100 mL volumetric flask and marked up with deionized water (Yasser A. El-Amier, 2018) (Rossini Oliva and Mingorance, 2006). A combination of nitric acid and perchloric acid was not used, to avoid interference between K and perchlorate ion because potassium perchlorate has low solubility and volatilization (Zarcinas et al., 1987). 1000 ppm standard solution from Merck company were used for each metal analysis. Calibration standards were made as per concentration to signal data, provided with the AAS. Digested leave samples were analyzed for the concentrations of Cr, Co, Cu, Cd, Pb, Mn, Mo, Ni, Zn, and Fe by Flame technique using Atomic Absorption Spectrophotometer (Perkin Elmer, A Analyst- 700) under the optimized operating conditions (Allen et al., 1974). Whereas Na and K were analyzed by Flame Photometer (410 Classic, Corning). Every sample for each element was analysed 3 times and mean values were reported, it was a built-in option in the software of the instruments, in order to increase the accuracy.

2.4. Statistical analysis

Descriptive analysis and PCA was performed by using two software, Microsoft Excel and Minitab (a statistical software, developed by Pennsylvania State University). Raw data were used for statistical analysis, to calculate the concentrations of heavy metals with the affected and control samples, along with the correlation between metals and expected difference of concentration between affected and control samples. Score plot was created by using Minitab software.

3. Results

Table 1 and 2 show the GPS locations for the affected and control leave samples. Table 3 and 4 show the statistical results, and correlation analysis, of the analyzed metals in affected and control samples,
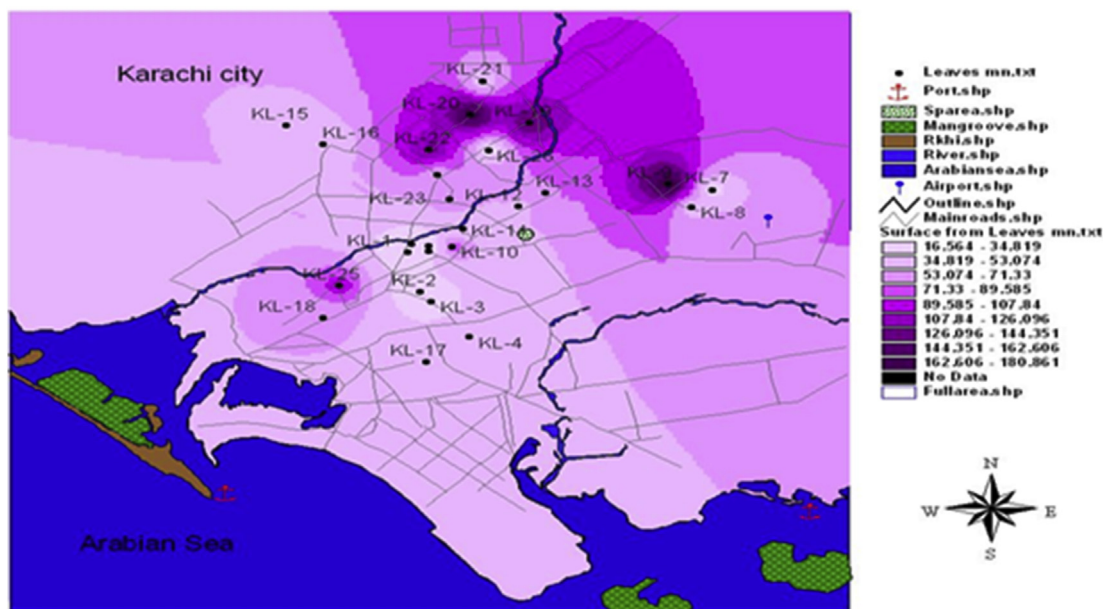
Figure 10. GIS Map showing concentration variation of Mn metals in leaves samples collected from Karachi city.
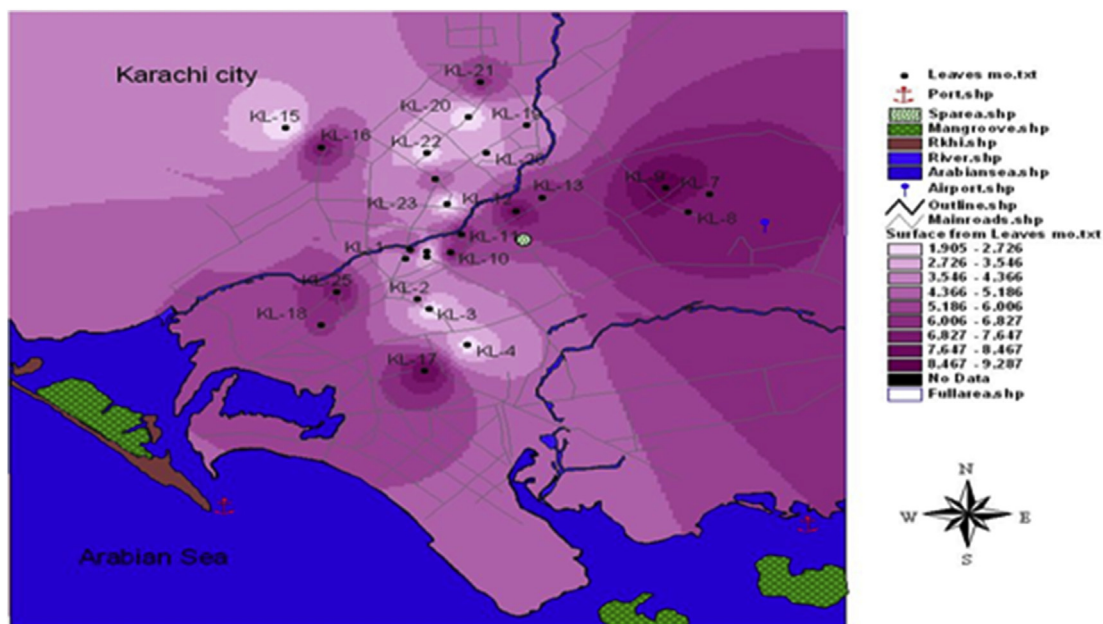

Figure 11. GIS Map showing concentration variation of Mo metals in leaves samples collected from Karachi city.

respectively. Figure 1 shows the score plot of affected and control samples. Figure 2 and 3 show the concentration of analyzed metals. Figures 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14 and 15 shows GIS maps of concentration variations of metals at sampling sites.

4. Discussion

Karachi is a metropolitan megacity among the top 20 megacities in the world. According to a study, conducted in 1991, Karachi had more than 650,000 registered vehicles and was calculated to emit almost 28.447 kg of lead per year, into the environment (Yousufzai., 1991). According to the provisional government's statistics, the total number of vehicles in 2004 was 1.5 million, and 3.32 million were estimated in 2011 (Arif Hasan, 2015).

The "Auto-body refinishing" is a sort of occupation that is continuously spreading metals into the environment, but still unnoticed. Most of the auto-body refinishing sites are located in residential areas and all processes are done with no protection measures. Heavy metals emitted during different processes of auto-body refinishing directly affects the workers, plants, and soil around the working area.

The data shows (Table 1) that the concentrations of heavy metals in affected samples are significantly higher than in the control samples, except Cr. In affected leaves samples, Pb, Mn, and Fe show the maximum average concentrations, 87.14, 62.10, and 146.94 mg/kg, respectively. Whereas, in control samples, Pb, Mn, and Fe show average concentrations, 48.83, 15.23, and 43.07 mg/kg, respectively. Principal component analysis (PCA) for the metal load of affected and control samples is shown in Figure 1, where it is distinctly observed that the groups of
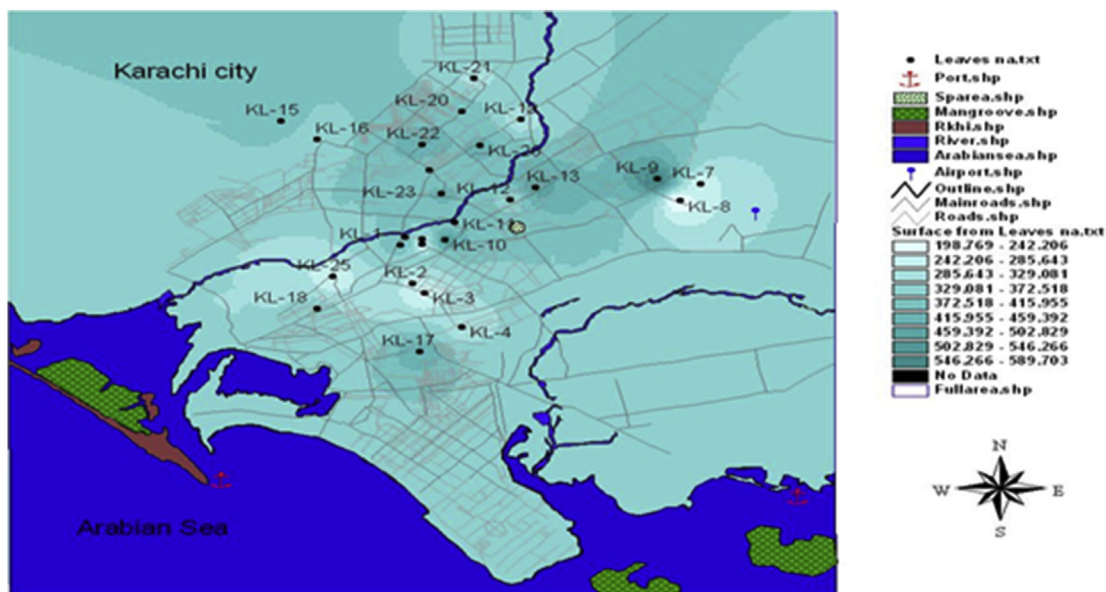
Figure 12. GIS Map showing concentration variation of Na metals in leaves samples collected from Karachi city.
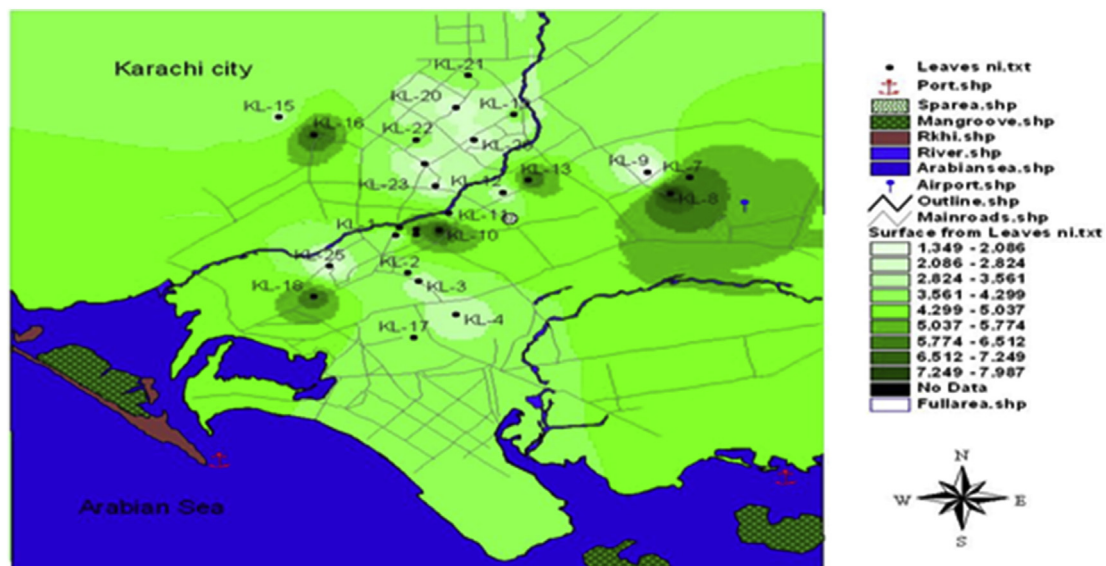

Figure 13. GIS Map showing concentration variation of Ni metals in leaves samples collected from Karachi city.

affected and control samples were separated clearly. It is evidence of the prominent difference in the pollution possibilities generated by the auto-body refinishing shops. One was of affected sample sites (KL-01 to KL-26) and the other is of controls samples sites (CKL-1 and CKL-10). Samples within the clusters were close with each other but the clusters of affected and control sites are far apart from each other, showing a significant difference between concentrations of affected and control sampling sites (Tahir et al., 2010). The auto-body refinishing process mainly involves the scraping of old paint, the hammering of the surface, and new paint. Many chemicals are used in refinishing process, especially organic solvents, and metal pigments. These metal pigments from old or new paints are additional sources, along with vehicle exhaust (Vitayavirasuk et al., 2005).

Ambient temperature and GPS locations are given in Tables 1 and 2, respectively, while, Table 3 summarizes relevant statistical parameters for various metals in affected and control leaves samples, in terms of average concentration ($\overline{X}$), range, standard deviation ($\pm$SD), t-test

analysis for the comparison of average concentrations and standard deviations. P-values were calculated for the significance of the results.

Statistical differences between mean results of control and samples were calculated and showed the P-values for control and affected samples were significantly different. They were significant for Cd, Co, Cu, Fe, Mn, Mo, Ni, Pb, Zn, Na, and K metals whereas for Cr (0.074) it is insignificant. Na and K show higher concentrations in both affected and control samples because of their natural abundance in Karachi (Arif Zubair, 2002). The correlation of paired variables of analyzed metals in affected samples is presented in Table 4. The only strong positive correlation was observed between Pb and Mn (0.750) which might be due to the traffic activity (Marković et al., 2013), whereas the only strong negative correlation was observed between Ni and K (0.821).

Figures 2 and 3 show the concentration of heavy metals (Fe, Mn, Pb, Zn, and Cr Mo, Cu, Ni, Co, and Cd) in affected leaves samples. In Figure 2, Pb, Mn, and Fe represent considerably higher concentrations in all samples, i.e., 177.4 mg/kg of Pb in sample KL-20, 171.6 mg/kg of Mn in
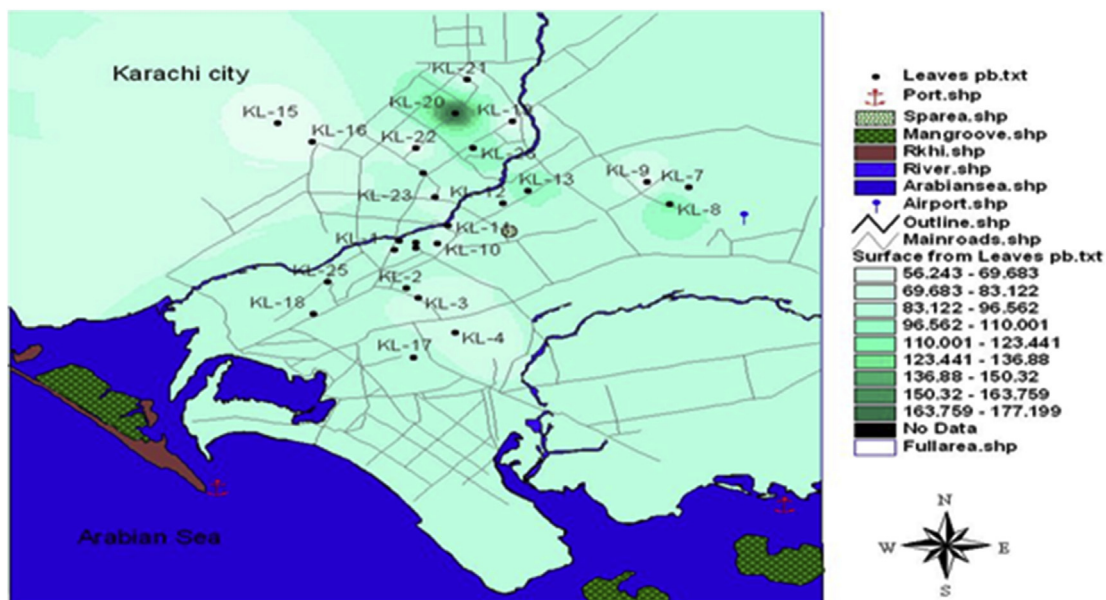
Figure 14. GIS Map showing concentration variation of Pb metals in leaves samples collected from Karachi city.
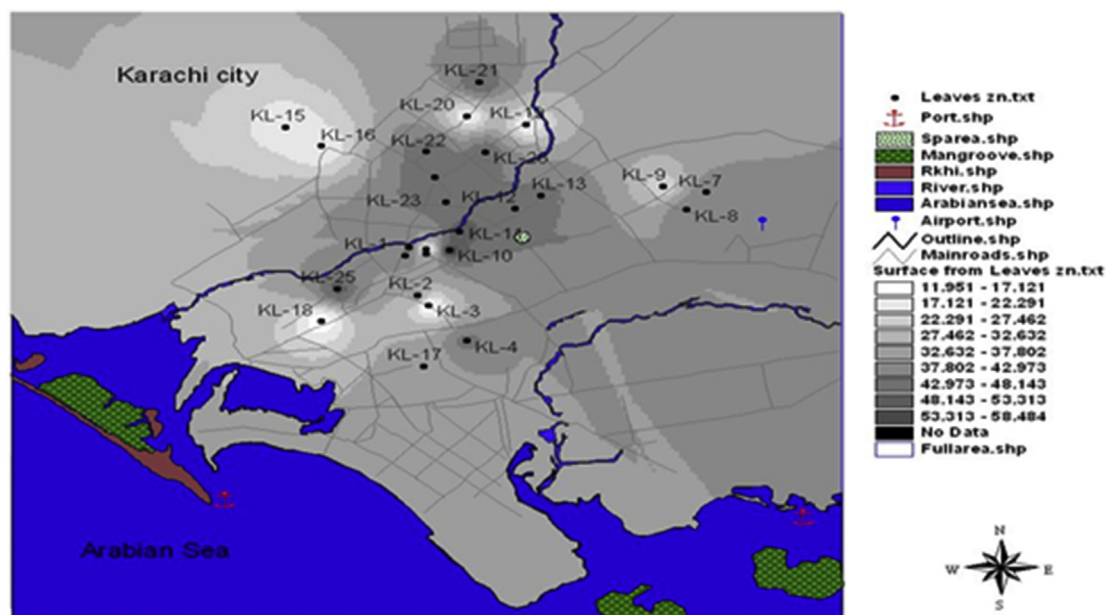

Figure 15. GIS Map showing concentration variation of Zn metals in leaves samples collected from Karachi city.

sample KL-09, and 194.3 mg/kg of Fe in KL-18. In Figure 3, Cu shows a higher concentration among other metals. 35.7 mg/kg of Cu in sample KL-10 was the highest concentration of Cu. Figures 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, and 15 show GIS maps for the concentration variation of metals in leaves samples collected from Karachi city. The concentration of the respective metal is mentioned at every single sampling site.

Affected and control sample locations are similar in all environmental and physical aspects, except these refinishing shops. These refinishing businesses are believed to be the key anthropogenic activity for these considerable differences. The concentrations of Pb, Cr, Co, Cd, Cu, Ni, Mn, Mo, and Zn in affected samples were significantly higher than in control samples. Color pigments with these metals were commonly used in car paint, i.e., used for refinishing vehicles. A higher concentration of Fe was sourced from color pigments and scrapping of the car's surface. Both, the surface of the car and the tools for scrapping are made up of Fe

and this frictional system allows Fe particles to enter the surrounding environment (Tahir et al., 2010). The main source of Pb in the environment is the automotive exhaust. The Pb metal is added to petrol to reduce the knocking and increase the performance of the engine. A major portion of Pb in the urban environment is in the form of aerosol and particulate matter (Iftikhar Imam Naqvi, Mohammad Ahmed Farrukh, 2005). Frequent movements of cars were observed near these shops for their refinishing. Generally, lead pigments are used as a primary coating on steel surfaces like auto-bodies. Metal pigments particularly lead, and zinc dust is good to use as coatings and protection from diffusion. The use of Pb pigments is destructive to the environment and worker's health (Werner Freitag, 2008). Metal bridges and all other metal structures are protected from moisture by coating with Pb pigments, particularly red lead. The Pb content is also used in different colors. Nearly 300 kg/year of lead-exposed or contaminated the environment only by the car

washing processes (Bergbäck et al., 2001). Karachi is a world-known seaport, industrial and metropolitan city with six major industrial areas (Bin Qasim, SITE, Malir Industrial Area, North Karachi Industrial Area, Hub Industrial Area, and Korangi Industrial Area). Karachi consumes tons of fuel (petrol, diesel, natural gas) because of huge numbers of vehicles (Yousufzai., 1991) (Arif Hasan, 2015). The increased level of Pb is due to vehicular volume, automobile exhaust, automobile paints, and restriction of Pb in the surroundings (Eludoyin and Ogbe, 2017) (Vitayavirasuk et al., 2005) (Tahir et al., 2010). The higher concentration of Mn in urban air will increase rapidly from the usage of Methyl-cyclopentadienyl Manganese Tricarbonyl (MMT), as an alternative anti-knocking agent for cars. Car batteries, steel parts, and alloy rims also contribute Mn near auto-body refinishing shops (Ter Haar et al., 1975). Cr is mostly utilized in auto paints pigments and Cr-plating. Cu is frequently consumed in auto-body refinishing workshops as auto paints (Eludoyin and Ogbe, 2017) (Tahir et al., 2010). Automobile radiators are the source of Fe and Cu concentrations when exposed directly to the atmosphere (Rabah, 2000). Fe and Cu particles from rusted parts of radiators or cars are directly entered into the atmosphere (Porter, 1985). Different metals come from different parts of automobiles like Zn comes from rubber tires; Cu comes from brake linings, Mn from moving metal parts, and gasoline products. Other auto-body refinishing activities like soldering, engine oils, brake fluids, metal corrosion, battery parts, and dumping of unsegregated waste are also contributors to heavy metals in the surrounding (Eludoyin and Ogbe, 2017) (Swaine, 2000).

5. Conclusions

The present study focused on heavy metal pollution in Karachi city, due to the auto-body refinishing procedures. Bio-adsorption of the analyzed metals by the leave tissues of the Neem tree (Azadirachta Indica) is evident around the auto-body refinishing shops and considerably higher than in leaves of control samples. The Neem tree also tends to absorb atmospheric heavy metals. The concentration of heavy metals in leave samples around auto-body refinishing shops followed up in the decreasing order of Fe > Pb > Mn > Zn > Cu > Cr > Mo > Cd > Ni > Co. The only positive correlation exists between Pb and Mn in sample tree leaves which represents the extraordinary traffic flow around sampling sites. All analyzed metals show higher concentrations at affected sites but Pb, Mn, and Fe were leading the values. GIS is used to present the variation in concentrations within Karachi city. PCA is applied to identify the difference of anthropogenic (auto-body refinishing shops) effect between sampling areas and control areas. Finally, it is recommended to take remedial actions, like shifting auto-body refinishing shops from residential areas to industrial areas or out of the city, installing commercially available exhaust solutions in the shops especially in the painting area, local government enforce to wear a gas mask and protective gears during the painting process, and floor must be covered with replaceable sand, pabals, or wood coating just to avoid leaching factors. . Furthermore, grow the surplus amount of Neem tree along with other trees, around auto-body refinishing shops and in industrial areas. Further studies are also recommended about the accumulation of heavy metals within auto-body refinishing workshops.

Declarations

Author contribution statement

Jahan Zeb: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Hajira Tahir: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data.

Abdullah Othman, Omar B. Ahmed & Shaikh Mohiuddin: Analyzed and interpreted the data; Wrote the paper.

Turki M. Habeebullah, Ali Sayqal & Hamza M. Assaggaf: Contributed reagents, materials, analysis tools or data; Wrote the paper.

Muhammad Sultan & Agha Zeeshan Mirza: Performed the experiments; Wrote the paper.

Saiyada Shadiah Masood: Performed the experiments; Analyzed and interpreted the data.

Bibi Hajira: Conceived and designed the experiments; Performed the experiments; Wrote the paper.

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