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Assessment of heavy metal exposure around auto body refinishing shops

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Significant number of occupations are present in our society which involves metal pollution. These small operational occupations which are always neglected by governments and other occupational health services are another major factor of metal flow in urban soil. The local auto body refinishing shops are one of these occupations. Workers, soil, plants, air and all environments around these shops are continually exposed by their organic solvents, dust, noise and metal pigments. In the present study, 36 top soil samples including controls were collected from 26 different auto body refinishing shops of the metropolitan city, Karachi. The soil samples were digested by EPA method 3050. The metal contents Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb and Zn were analyzed by Atomic Absorption Spectrometry (AAS). The results showed that metal contents in soil samples around auto body shops were mainly contaminated due to the exposure of metal pigments. The silent increase in metal concentration in soil samples may contribute to the accumulation of heavy metals in humans and livestock through soils and plants which will grow in these areas. The statistical methods of analysis were also applied to find out the t-values, p-values and correlation parameters. The Principal Component Analysis (PCA) was also applied to increase the significance of results.

Key words: Metal pollution, occupational health services, heavy metals, livestock.

INTRODUCTION

Heavy metals are toxic to all living organisms, if they exceed public health limits. They showed negative effects on microbial activities in soil and increases pollution (Duxbury, 1985; Baath, 1989). Many studies showed that dust and sediments are main transporters of heavy metals in the urban environment (Charlesworth and Lees, 1989; Zhou et al., 2007). Contaminated soil is a great threat for hyper accumulated plants, which can affect human health (Baker and Brooks, 1989; Knight et al., 1997). The soil of urban areas were mainly contaminated by the deposition of heavy metals which are emitted from industries, vehicles and burning of wastes. The natural variability in soil composition is very well indicated by the presence of trace elements (Jeffrey and Hudson, 2001;

Ozan, 2008). Soil contamination is also a well reported health risk issue (Farrell, 2002). Atomic Absorption Spectrometry (AAS) is the most valuable technique for the metal estimation in aqueous samples. Mineral constituents, organic matters, living organisms, air and water are the main composite parts of soil (ISO 11466k, 1995). Human activities like vehicular exhaust, lubricating oil residues, tyre wear particles, weathered street surface and paint components contaminate the soil (Rogge et al., 1993; Cocker et al., 2004). Urbanization and accelerated industrialization are the major factors which are disturbing the urban soil (Omar et al., 2007). Concentration of metals in soil is an indicator of environmental pollution (Manta et al., 2002). For example, traffic pollution can be estimated by measuring the levels of Pb, Cu and Zn in soil (Fergusson and Ryan, 1984). Soil pollution has been of great concern to scientists for many years (Guitao et al., 2008).

Along with other unnoticed occupations, the auto body refinishing is also a big contributor of heavy metals in whole environment and producing occupational hazards, especially in soil. The exposure of paints' affects human

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Abbreviations: AAS, Atomic Absorption Spectrometry; PCA, principal component analysis; VOC, volatile organic compounds; HAP, hazardous air pollutants; GPS, global positioning system; CNG, compressed natural gas.

health causing problems like asthma (Nielsen et al., 1985; Selden et al., 1989). About 5 to 20% exposed workers are facing asthma (Tornling et al., 1990). Auto body refinishing processes are under great pressure, in order to maintain the environmental regulations (Richards and Pearson, 1998). The auto body painting is the main process of auto body refinishing of shops and it directly affects the atmosphere (AAMA, 1997). In these shops over 80% of environmental pollution is due to paints (Lowell et al., 1993). It protects from corrosion, improve durability and color. These paints mainly consist of volatile organic compounds (VOC's) which are hazardous air pollutants (HAP's) (U.S. EPA, 1996). Auto body painting is the most costly process in the refinishing shops. Half of the cost of painting vehicles are expended for coating materials, especially paints (Nallicheri, 1993). According to EPA's Toxic Release Inventory, auto body sector has great concern with the reduction of pollutants in the environment (Praschan, 1994). These refinishing shops have serious concern relating to health issues such as cancer, asthma, kidney diseases and disordered central nervous system (Federal Register 61, 1996). VOC's from the exhausts of these locations reacts with atmospheric NO in the presence of sunlight and form ground level ozone layer, which is also a big threat to our environment (Richard et al., 1998).

A number of studies have been done on industrial waste, sediments and water (disaster of Tasman Sprit) (Tahir et al., 2000, 2004, Tahir, 2005; Tahir and Mushtaque, 2005). In this study, our objective is to calculate the concentration of selected metals that is, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb and Zn in soil around the auto body refinishing shops. According to our hypothesis, these soil samples are contaminated as compared to control soil samples.

Principal Component Analysis (PCA) is one form of multivariate data evaluation. It is a way of identifying pattern in data and expressing the data in such a way as to highlight their similarities and differences. Where the luxury of graphical representation is not available, PCA is a powerful tool for analyzing data. The other main advantage of PCA is that once we have found these patterns in the data and can compress the data, there could be the reduction of the number of dimensions, without much loss of information (Jolliffe, 2002).

MATERIALS AND METHODS

Sample collection

Generally in Pakistan, repairing cars are painted under the sheds of trees, on the soil and in open areas. 26 samples along with 10 controls were collected from Karachi city. The number of samples and controls are different in each town. They are based on the number of autobody refinishing shops in the towns. Soil samples were taken within the radius of 5 m from the car painting process. Three replicates were taken from each site, then the latter was mixed to get the composite sample. Each sample was taken to

represent the area of autobody refinishing shops. The locations were selected to present different areas of autobody refinishing shops in Karachi, Pakistan. Control soil samples were taken from these areas, which do not have autobody refinishing shops within the radius of 3 km. Similarly, three replicates of soil samples were taken from each site. Then, the latter was mixed to get the composite samples. The control locations were selected to present areas, without autobody refinishing shops but other conditions were almost the same. GPS locations and ambient temperature of sampling and control sites are given in Tables 1 and 2.

Method

The surface soil (about 0 - 3 cm in depth) samples from each site and control locations were collected by Teflon shallow scoop. The samples were stored in brown polyethylene bags, to avoid interaction of u.v radiations.

Sample preparation and analysis

Samples were oven dried at $60 \pm 2^\circ\text{C}$ until moisture contents were removed. 5.0 gm of soil samples (2 mm sieved) were weighted and digested by wet oxidation method, using HNO_3 (65%) at $60 \pm 2^\circ\text{C}$. After keeping at room temperature, the extract was filtered and the filtrate was collected in a volumetric flask and brought to volume by deionized distilled water. The concentrations of trace metals were estimated by Flame Atomic Absorption Spectrophotometer (A Analyst- 700, Perkin Elmer). Analytical grade reagents and standards were used for the analysis. Statistical analysis of data was also carried out by using Minitab soft ware.

RESULTS AND DISCUSSION

Tables 1 and 2 show the GPS locations and ambient temperature of sampling and control sites in Karachi city, respectively. Table 3 shows the evaluation of the statistical parameters like range, mean and standard deviation values of group data for the estimated metals of effected and controls samples.

Fe showed the maximum mean concentration value in all samples, among the other analyzed metals obtained during the scraping process of auto body's surfaces. In the scraping process, car's surface (mainly made up of Fe) was scrapped with the help of metal tools and this frictionating process allows Fe to drizzle directly on soil surface and later it mix in the soil. Prolong exposure of atomic Fe or Fe_2O_3 causes "siderosis" (Chronic inflammation of the lungs caused by excessive inhalation of dust containing iron salts or particles) (Toda et al., 2005).

Pb showed the higher mean concentration in the affected and control samples, among all analyzed metals. Karachi is the biggest metropolitan and industrial city of Pakistan, having four major industrial areas (SITE, KITE, HITE and Bin Qasim) and the largest number of petrol, diesel and compressed natural gas (CNG) vehicles are running. Due to vehicular and industrial emissions, the Pb content showed higher concentration in control samples as compared to other metals. The Pb exposure affects the membrane permeability of liver, kidney and brain cells

Table 1. GPS locations and ambient temperatures of sampling sites (Karachi).

S/N	Sample code	Location	GPS location		Temperature
1	KS-1	Marton quarters (Jahangir Road)	24° 53' 16.84" N	67° 2' 37.19" E	40 – 45 °C
2	KS-2	Kashmir Road	24° 52' 19.92" N	67° 2' 52.46" E	40 – 45 °C
3	KS-3	PECHS community hall (Shahra e Quaideen)	24° 52' 6.28" N	67° 3' 6.32" E	40 – 45 °C
4	KS-4	PECHS (Block # 6)	24° 51' 15.31" N	67° 3' 51.69" E	40 – 45 °C
5	KS-5	Ghosia Colony (Jamsheed Road)	24° 53' 19.37" N	67° 3' 2.49" E	40 – 45 °C
6	KS-6	Teen Hatti (Nishter Road)	24° 53' 29.31" N	67° 2' 42.20" E	40 – 45 °C
7	KS-7	Pehalwan Goth (Gulistan e Juhar)	24° 54' 52.57" N	67° 8' 31.33" E	35 – 40 °C
8	KS-8	Lakhani Pride (Gulistan e Juhar)	24° 54' 27.33" N	67° 8' 7.59" E	35 – 40 °C
9	KS-9	Rado Centre (Gulistan e Juhar)	24° 55' 0.11" N	67° 7' 39.71" E	35 – 40 °C
10	KS-10	Karachi Centre (Near Central Jail)	24° 53' 25.73" N	67° 3' 29.42" E	35 – 40 °C
11	KS-11	Old Vegetable Market (University Road)	24° 53' 52.30" N	67° 3' 41.58" E	35 – 40 °C
12	KS-12	PIA planetarium (University Road)	24° 54' 25.97" N	67° 4' 46.23" E	35 – 40 °C
13	KS-13	Federal Urdu College (University Road)	24° 54' 45.46" N	67° 5' 16.38" E	35 – 40 °C
14	KS-14	PIB police station (Martin Road)	24° 53' 26.70" N	67° 3' 2.53" E	35 – 40 °C
15	KS-15	Orangi Police station	24° 56' 19.96" N	67° 0' 13.36" E	30 – 35 °C
16	KS-16	Banaras Chowk (orangi town)	24° 55' 53.03" N	67° 0' 55.85" E	30 – 35 °C
17	KS-17	Railway Colony (Lily Bridge Road)	24° 50' 38.56" N	67° 3' 2.26" E	30 – 35 °C
18	KS-18	Akbar Market (M.A. Jinah Road)	24° 51' 40.98" N	67° 1' 0.45" E	30 – 35 °C
19	KS-19	Gulberg Square flats (Shahrah e Pakistan)	24° 56' 26.92" N	67° 4' 56.72" E	30 – 35 °C
20	KS-20	KMDC (Allama Rasheed Turabi Road)	24° 56' 37.87" N	67° 3' 47.26" E	30 – 35 °C
21	KS-21	7-C last stop (Shara e Shair Shah Suri Road)	24° 57' 27.26" N	67° 4' 1.15" E	30 – 35 °C
22	KS-22	Saifi Poly Technique (Allama Rasheed Turabi Road)	24° 55' 46.65" N	67° 3' 0.26" E	30 – 35 °C
23	KS-23	Habib Medical Centre (Shahra e Humayun)	24° 55' 9.89" N	67° 3' 10.13" E	30 – 35 °C
24	KS-24	Garibabad (Sir Shah Suleman Road)	24° 54' 34.58" N	67° 3' 24.62" E	30 – 35 °C
25	KS-25	Karchi Zoo (Garden Road)	24° 52' 28.49" N	67° 1' 17.87" E	30 – 35 °C
26	KS-26	Talimi Bagh (Shahrah e Pakistan)	24° 55' 46.96" N	67° 4' 9.82" E	30 – 35 °C

Table 2. GPS locations and ambient temperatures of control sites (Karachi).

S/N	Sample code	Location	GPS location		Temperature
1	CKS-1	Orangi Town (sector # 5)	24° 56' 53.24" N	66° 59' 6.00" E	28 – 38 °C
2	CKS-2	Banarus Chowrangi (Orangi town)	24° 56' 6.93" N	67° 0' 39.46" E	28 – 38 °C
3	CKS-3	Zainab Market (Abdualah Haroon Road)	24° 51' 14.47" N	67° 1' 42.97" E	28 – 38 °C
4	CKS-4	Akbar Market (M.A. Jinah Road)	24° 51' 38.88" N	67° 1' 6.02" E	28 – 38 °C
5	CKS-5	Jamshaid Road	24° 52' 57.35" N	67° 2' 42.82" E	28 – 38 °C
6	CKS-6	Jahangir Road	24° 53' 23.29" N	67° 2' 33.98" E	28 – 38 °C
7	CKS-7	Krimabad (Shahrah e Pakistan)	24° 55' 0.65" N	67° 3' 17.44" E	28 – 38 °C
8	CKS-8	Aysha Manzil (Shahrah e Pakistan)	24° 55' 23.60" N	67° 4' 4.54" E	28 – 38 °C
9	CKS-9	Gulshan Chowrangi (Rashid Minhas Road)	24° 55' 29.75" N	67° 5' 30.13" E	28 – 38 °C
10	CKS-10	Rado Centre (Johar More Road)	24° 54' 45.40" N	67° 7' 31.84" E	28 – 38 °C

(Stone and Droppo, 1996).

By applying the t and p-test, statistical differences between mean values of samples and controls were calculated, p-values for all analyzed metals showed that affected samples and control were significantly different. Since all physical and environmental conditions for both

sample and control locations were same except auto body refinishing shops. The auto body refinishing shops are the major source of these significant differences. The Pb, Cr, Co, Cd, Cu, Ni, Mn, Mo and Zn concentrations were also considerably higher as compared to control concentration. These metals were actively used in paints

Table 3. Range, mean, standard deviation, t and p-values of analyzed metals collected from Karachi city.

S/N	Metal	Sample			Control			t-value	p-value	Remarks
		Range (mg/Kg)	$\bar{X}$	$\pm$ SD	Range (mg/Kg)	$\bar{X}$	$\pm$ SD			
1	Cd	2.300 — 9.700	5.390	1.861	1.340 — 2.100	1.618	0.226	10.14	0.000	Significant
2	Co	1.300 — 13.10	6.100	3.578	0.820 — 1.800	1.224	0.452	6.810	0.000	Significant
3	Cr	43.20 — 100.3	72.42	17.51	3.560 — 36.72	23.70	13.18	9.020	0.000	Significant
4	Cu	14.00 — 267.3	47.40	52.10	1.820 — 10.60	3.908	2.616	4.250	0.000	Significant
5	Fe	905.1 — 1813	1327	183.9	26.40 — 98.70	71.45	19.19	34.34	0.000	Significant
6	Mn	31.00 — 735.8	215.3	142.3	20.40 — 98.54	61.32	26.83	5.280	0.000	Significant
7	Mo	4.167 — 14.33	8.942	2.882	0.033 — 3.000	1.547	0.776	12.00	0.000	Significant
8	Ni	5.800 — 41.20	12.48	6.610	0.760 — 1.700	1.110	0.274	8.750	0.000	Significant
9	Pb	173.4 — 339.6	254.7	35.85	25.50 — 386.8	122.5	106.0	3.860	0.002	Significant
10	Zn	172.2 — 336.5	206.7	43.64	1.700 — 25.16	13.06	7.490	21.81	0.000	Significant

Table 4. Statistical correlations between metals in soil samples (mg/kg) from different locations of Karachi city.

Parameter	Pb	Mn	Mo	Zn	Cu	Ni	Co	Cd	Cr	Fe
Pb	1									
Mn	0.260	1								
Mo	0.094	0.279	1							
Zn	-0.004	0.019	0.073	1						
Cu	0.125	0.272	-0.187	0.384	1					
Ni	-0.065	0.465	-0.003	-0.225	-0.168	1				
Co	-0.019	-0.139	-0.134	-0.137	-0.036	-0.019	1			
Cd	-0.0989	0.105	0.244	-0.065	-0.216	0.026	0.450	1		
Cr	-0.106	0.234	-0.103	-0.074	0.285	0.100	-0.271	-0.243	1	
Fe	-0.087	0.071	0.072	-0.110	0.065	0.125	-0.052	-0.035	0.075	1

to produce different colors, which were used for refinishing of vehicles. Table 4 shows the correlation matrix for paired variables for the metals in soil samples in Karachi city. There was no significant correlation between the metal contents in Karachi city; only Co and Cd show a weak correlation of 0.450.

One of the valuable statistical applications of PCA was also applied. Figure 1 shows score plots as a result of PCA for metal load, it showed a good evidence for prominent difference in pollution profile, in the graph, the right hand sides of samples were taken as controls.

Figures 2 and 3 show the concentration of metals in soils samples. Figure 2 represents the concentrations of Fe, Mn, Pb, Zn and Cr metals. The Fe content showed exponentially higher concentration in all analyzed samples. The reason of this Fe content is the scraping process. Sample KS-04 and KS-14 showed higher concentration of Mn, most of the autobody shops were using Mn based color paints. Sample KS-19, KS-23, KS-25 and KS-26 showed higher concentration of Zn as compare to Mn, Pb and Cr metals. Most of the auto body refinishing shops deals in white colors which are Zn based paint. The Pb content is also used in many colors, so all samples have considerable concentration of Pb. Cr is

mainly used in green color paints and also in Cr plating. Cr is dangerous to human health, because it causes stomach acidity leading to ulcer and lung cancer (Kenaga, 1980). Figure 3 represents the concentration of Mo, Cu, Ni, Co and Cd. The Cu contents were higher in all samples as compare to others five metals. Cu is frequently used in blue color paints. Cu may cause nausea, diarrhoea, salivation and gastrointestinal haemorrhage (Huang and Shin, 1993). The Mo, Cu, Ni, Co and Cd metals shown in Figure 3 are less used in auto paints as compare to other combination of metals (Fe, Mn, Pb, Zn and Cr) as shown in Figure 2.

Conclusion

There are many occupations and professions which are running in industrial and residential areas. The “Auto body refinishing” is such kind of occupation which affects the environment, especially on the workers and exposed soil. Particularly, the painting and scraping process were done without any safety measures. Metal pigments in paints and scrap are continuously deposited with effects on the workers and on soil. The results of the present

Figure 1. PCA for samples and control samples of Karachi.

Figure 2. Levels of trace metals (mg/kg) in soil samples of karachi city (Fe, Mn, Pb, Zn, Cr).

Figure 3. Levels of trace metals (mg/kg) in soil samples of karachi city (Mo, Cu, Ni, Co, Cd).

study showed that the soil around these auto body refinishing areas were contaminated exponentially due to gradually increase in the auto body refinishing shops which is a great threat to the environment. The levels of Pb, Mn, Fe, Cr, Zn Cd, Co, Ni, Mo and Cu contents were higher than the control samples. It shows an alarming situation. The remedial measures will be adopted to reduce the level of metal contents.

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