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An investigation of environmental impact of aerial metal deposition around the petrol filling stations and applying remedial measures to reduce the elevated level of lead metal

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ABSTRACT
The wide use of petroleum products causes contamination of air, water, soil and plants. The present study was related to monitor the aerial deposition of metals on soil and ryegrass around the fuel stations along central road of Karachi city, Pakistan. Samples of soil and ryegrass were collected from the selected locations of central road. Concentrations of selected trace metals were estimated through atomic absorption spectrophotometer. Multivariate analysis is also applied to authenticate the concentration difference between affected and control samples. Statistical analyses of metals in soil and ryegrass samples were reported in terms of average concentration of trace metals, standard deviation, median and mean values. The correlation coefficient (r) was also calculated between metals in soil vs. soil and ryegrass vs. ryegrass samples. By applying adsorption technique the beds of adsorbents like activated charcoal, cement, silica gel and calcium carbonate were placed at the petrol filling stations for the period of one month and monitor the deposited metal content.

Keywords: Petrol filling stations, Aerial metals, Bed method, Ryegrass.

1. INTRODUCTION

Historical back ground shows the use of metals from early ages. The great increases in metal concentrations were observed from 20th century. A large number of environmental studies were carried out to highlight the individual source of metals [1]. Environmental measurements revealed the higher concentrations of metals near the petrol filling stations, and most of the signs could be attributed due to petrol fumes [2]. The use of organic lead compounds such as tetraethyl lead and tetra methyl lead as an additive in petrol are added to improve the performance of engine is continual concern to environmental scientists [3]. Dispersion of petrol fumes near the local petrol filling stations becomes a serious environmental threat [4]. It links to effects on the skin and penetrate in the body tissues also causes genetic modification and intelligence of young childrens [5-6].

Vehicular pollution accounts about 70% of air pollution in metropolitan cities. Airborne lead is typically present in vehicular exhaust emissions in the form of particles, which have diameter of less than 1 µm and therefore may be transported to large distance in the atmosphere between one and four weeks lifetime depending on climatic factors. The main source of lead pollution is the emissions from automobile exhausts. The current emission of lead from automobile exhausts is around 7000 tones annually[7]. 10% of this level was falls out as dust on road side and reminder in air borne until it washed out of the air by rain or it can be remove by contact with vegetation or soil. The amount of lead was arising in this way about 10% [7].

The World consumption of petrol is about 82.4 million barrels per day (in 2004). Only United States consumes 20.5 million barrels per day (25% of the world total), China consumes 6.6 million barrels per day. Whereas Pakistan is the 36th bigger consumer of petrol[8]. The Figure No 1 shows the gradual increase in the total world oil consumption[9].

The aim of the present studies is to monitor the presence of airborne heavy metals Cadmium (Cd), Copper (Cu), Cobalt (Co), Lead (Pb), Molybdenum (Mo), Nickel (Ni), Chromium (Cr) and Zinc (Zn) in the environment near the petrol filling stations.

Soil and ryegrass (Lolium) were used as biomonitors for the heavy metal contents. The ryegrass is a genus of nine species of tufted grasses, family Poaceae. These plants are native to Europe, Asia and Northern Africa. They were widely cultivated and naturalized elsewhere and found worldwide and are used in lawns as a forage crop [10].

It has a great tendency to uptake heavy metals [11]. The elevated levels of airborne heavy metals were deposited in rye grass and soil. By employing bed adsorption around the filling stations and monitor the metal contents to how much extent they are adsorbed before dispersing in the environment [12-18].

2. EXPERIMENTAL

2.1 *Sample Collection, Preservation and Storage*

The soil and ryegrass samples were collected around the petrol filling stations along the central Road of Karachi city. Figure **2** shows the satellite locations of both control and affected sample collection sites. For the collection of samples all standard procedures were applied to avoid any contamination. CS-1 and CL-1 to CS-3 and CL-3 represent the

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control samples of both ryegrass and soil while L-1 to L-7 represents the ryegrass samples and S-1 to S-7 represent the soil samples. The locations for the colleted of affected samples of soil and ryegrass were same; similarly control samples of both soil and ryegrasses were taken from same locations. Global Positioning System (GPS) and local locations of affected and control samples of soil and ryegrass were shown in Table 1, along with their samples codes. Each sample was labeled so that its contents could be unequivocally identified. Soil and ryegrass samples were dried at 60 °C ± 2 °C in electric oven for 24 hours in order to remove the water content from the samples without reducing its dry matter contents. The samples were ground in a grinder (DCFH 48-TYPE) to 100 μm particle size and then stored in airtight desiccators.

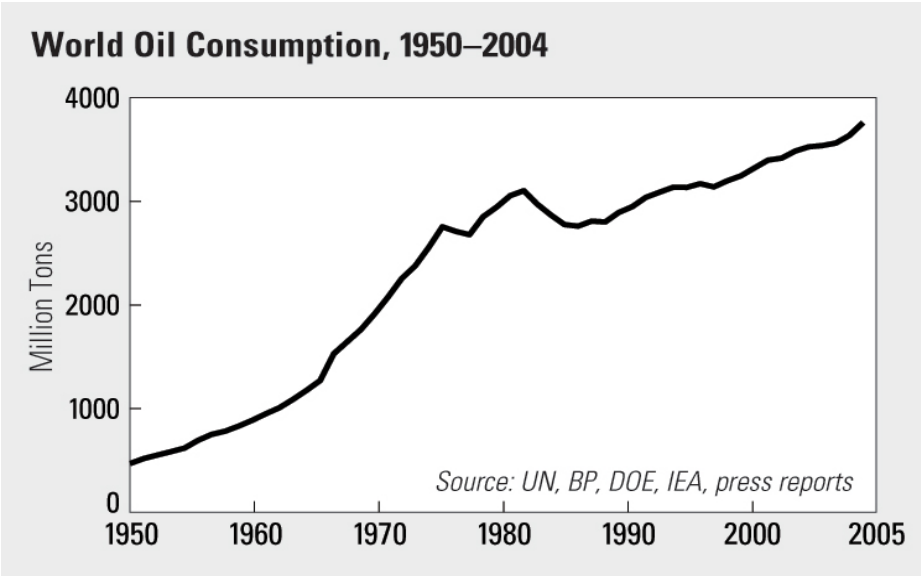

Fig-1: World Oil Consumption, (1950-2004)

Table-1: Sample code and their collection location

Sample Code	Local Location	G.P.S Location	
CS-1 & CL-1	Department of Chemistry, University of Karachi	24° 56' 30.72"N	67° 7' 9.86"E
CS-2 & CL-2	Safari Park, University Road	24° 55' 33.30"N	67° 6' 30.56"E
CS-3 & CL-3	PIA Planetarium, University Road	24° 54' 12.52"N	67° 4' 39.20"E
S-1 & L-1	PSO pump, University gate	24° 56' 2.83"N	67° 7' 43.70"E
S-2 & L-2	Shell pump, Opp to NED gate	24° 55' 46.81"N	67° 6' 58.78"E
S-3 & L-3	Shell pump, beside Usman Institute	24° 55' 37.80"N	67° 6' 34.70"E
S-4 & L-4	Caltex pump, beside IIEE	24° 55' 13.03"N	67° 5' 59.10"E
S-5 & L-5	Shell pump, beside Ashfaq hospital	24° 54' 30.45"N	67° 5' 0.66"E
S-6 & L-6	PSO pump, Gulshan e Iqbal	24° 54' 21.50"N	67° 4 51.56"E
S-7 & L-7	Caltex pump, near civic centre	24° 53' 55.13"N	67° 4' 13.55"E

2.2 *Digestion of Soil and Ryegrass Samples*

5.0 g of dried soil and ryegrass samples were digested with 25.0 ml of concentrated nitric acid (65% w/v). They were heated at 60 °C ± 2 °C on a hot plate (78 HW-1, Magnetic Pug Mill) till the volume was reduced to one third. The digested samples were filtered and the clear extract was transferred quantitatively into 100 ml volumetric flask and volume was made up to the mark with deionized water [19]. These samples were run through atomic absorption spectrophotometer (A Analsyt-700, Parken Elmner) to estimate the metal contents.

2.3 *Adsorption Studies*

For the adsorption of lead contents around petrol filling stations bed method was adopted. Beds of different synthetic adsorbents like activated charcoal, calcium carbonate, silica gel and cement were placed for the one month time period at the petrol filling stations. The lead content on these beds after adsorption were estimated by atomic absorption spectrophotometer.

3. RESULTS AND DISCUSSION

Figure 3 and 4 show the concentrations of selected metals in soil and ryegrass samples. Elevated level of zinc was found in soil samples compared to permissible limits. It may be due to the scratching of vehicles tyers on the roads. As the analysis show that level cadmium (17.9 mg/kg), copper (16.2 mg/kg) and zinc (12470 mg/kg) metals were appearing in significantly higher concentration showing that the smoke as combustion fuel, running vehicular

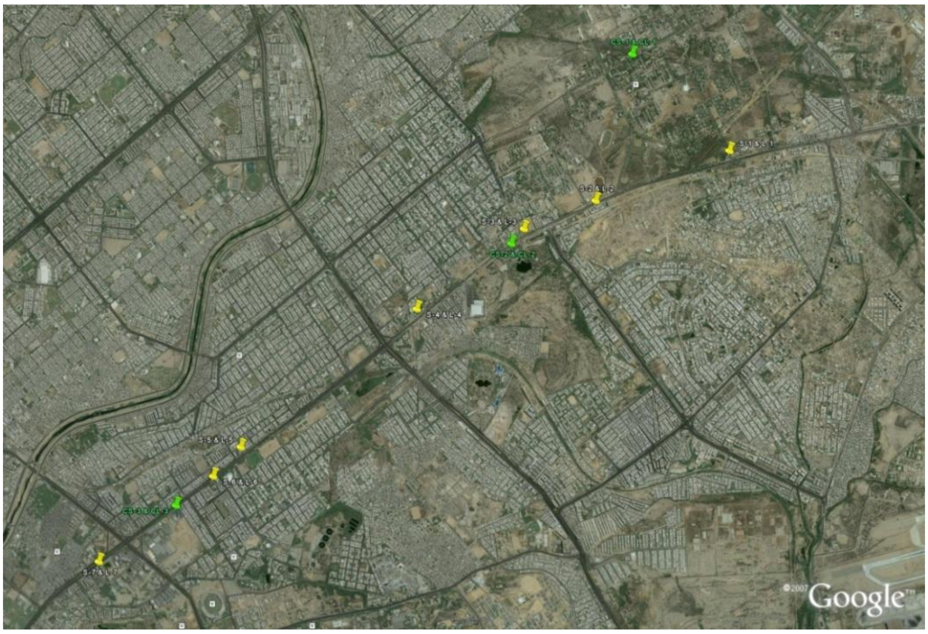

Fig-2: Location of Sampling Sites in Karachi city

friction of rubbing of tyers from road causes the higher level of metal [14]. Soil and ryegrass around fuel stations have higher concentration of lead. The level of lead in ryegrass samples were higher then control values. Where as the concentration of lead in soil is nearly equal in all samples which may be due to the use of leaded petrol and diesel. Both vehicular emissions and petrol fumes which are evaporating during filling are responsible for the higher concentration of lead [15]. Concentrations of nickel, chromium and cobalt were generally low, as compared to other metals. There is no other major source of these metals was located around the sampling locations.

Statistical analysis of metals in soil samples were reported in terms of average concentration of trace metals, standard deviation, median and mean values as shown in Table 2. The correlation coefficient (r) was also calculated between metals in soil vs. soil and ryegrass vs. ryegrass samples, as shown in Table 3 and 4. Soil system has strong positive co relation between Ni - Mo metals with corresponding (r) value 0.899. The ryegrass system shows strong positive co-relation between Pb-Co metals with corresponding (r) value 0.694. For soil samples score plot of multivariate analysis for the affected and control soil samples are shown in Figure 5. It shows a considerable difference between the two clusters of affected and control samples. In the affected soil samples MS-3 and MS-5 show outlier behavior, where as other five samples show closer values. Score plot of multivariate analysis for affected and control ryegrass samples are shown in Figure 6 shows a considerable difference between the two clusters of affected and control samples. In affected ryegrass sample only L-1 shows outlier behavior, where as other six samples shows closer values.

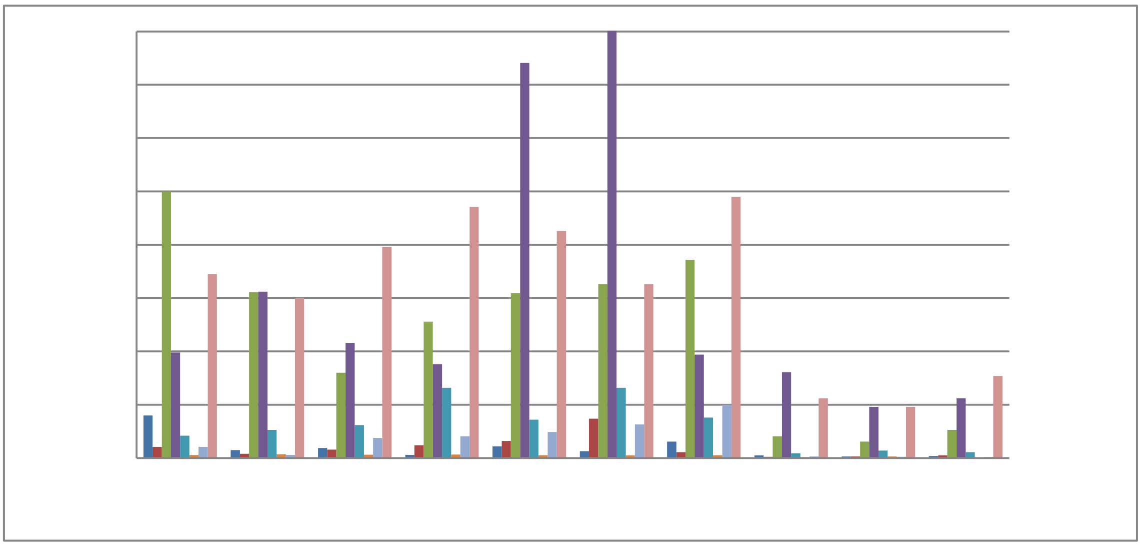

Fig-3: Concentrations of trace metals (mg/Kg) in soil samples near the petrol filling stations

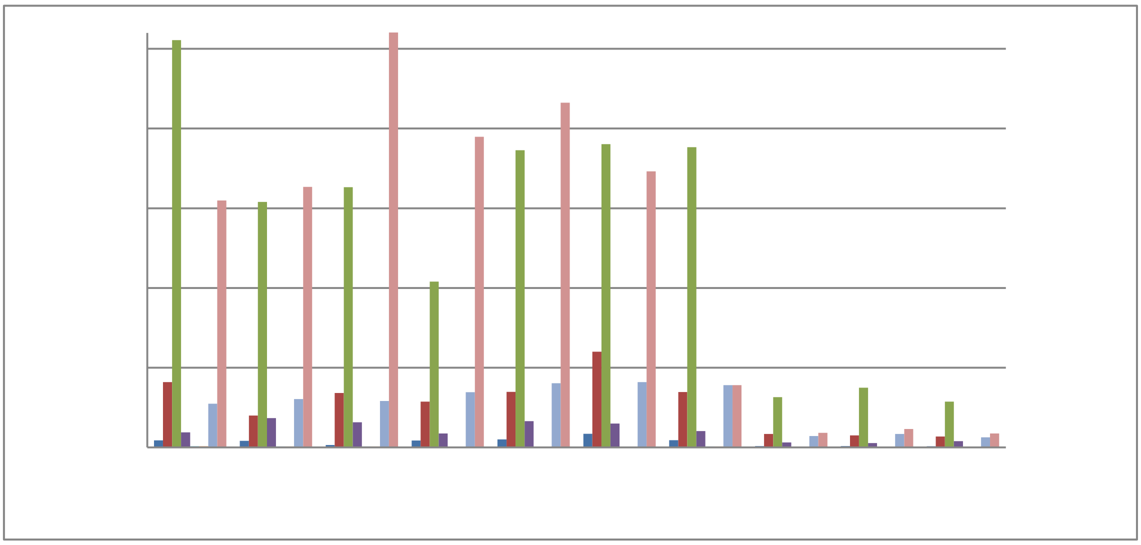

Fig-4: Concentration of trace metals (mg/Kg) in rye grass samples near the petrol filling stations

Table-2: Statistical Parameters of Selected Metals in Soil and Ryegrass Samples Collected From Various Petrol Filling Stations

S.No	METAL	RANGE		MEAN $\bar{X}$		MEDIAN		STANDARD DEVIATION (±SD)	
		Soil	Ryegrass	Soil	Ryegrass	Soil	Ryegrass	Soil	Ryegrass
3	**Ni**	6.000-80.00	14.70-84.70	29.71	46.44	10.00	37.50	34.59	24.95
4	**Mo**	8.000-74.00	BDL-BDL	26.57	BDL	22.5	BDL	22.42	BDL
5	**Cr**	160.0-500.0	200.0-600.0	331.4	367.9	360.0	300.0	117.1	147.7
6	**Pb**	176.0-1060	1040-2555	413.8	1735	264	1350	347.7	710.5
7	**Co**	42.00-132.0	87.00-184.0	85.43	130.6	92.00	1300	34.55	527.8
8	**Cd**	5.000-7.200	4.500-7.220	5.686	5.731	5.400	5.400	0.738	1.086
9	**Cu**	6.000-100.0	274.0-409.0	48.71	346.8	52.00	368.0	29.62	52.58
10	**Zn**	300.0-490.0	390.0-3800	393.4	1871	370.5	1800	73.07	1104

BDL= below detection limit

Table-3: Statistical Multiple Correlations in Soil Samples from Various Petrol Filling Stations

Metals	Cd	Cu	Co	Pb	Mo	Ni	Cr	Zn
Cd	1							
Cu	-0.198	1						
Co	-0.700	0.628	1					
Pb	-0.137	-0.432	-0.297	1				
Mo	0.088	-0.028	0.153	-0.671	1			
Ni	-0.171	0.107	0.304	-0.733	0.899	1		
Cr	-0.098	0.503	0.324	-0.680	0.763	0.786	1	
Zn	-0.639	0.148	0.472	-0.402	0.021	0.356	0.068	1

Table-4: Statistical Multiple Correlations in Ryegrass Samples from Various Petrol Filling Stations

Metals	Cd	Cu	Co	Pb	Ni	Cr	Zn
Cd	1						
Cu	0.483	1					
Co	0.662	0.289	1				
Pb	0.482	0.313	0.694	1			
Ni	-0.060	0.076	0.132	0.339	1		
Cr	0.018	-0.253	0.034	0.590	0.320	1	
Zn	-0.468	-0.355	0.288	0.298	0.190	0.333	1

The obvious source contributing these metals in ambient atmosphere is the aerial deposition of lead and other metals in soil and ryegrass samples near petrol filling stations due to higher density of vehicular exhaust and leakage of petrol fumes during filling of vehicles and scratching of vehicles tires on roads. Around the petrol filling stations, the lead content has a fairly direct and prompt effect on the urban air.

3.1 *Deposition of Lead by bed method*

Bed method was applied for the deposition of lead at different petrol filling stations of central road of Karachi. The beds of adsorbents like activated charcoal, calcium carbonate, silica gel and cement were placed at the filling stations for the period of one month. After that time period the amount of deposited lead ions were estimated by atomic absorption spectroscopy the results are shown in Table 5**.** It shows that activated charcoal shows better adsorption capacity compared to other adsorbents.

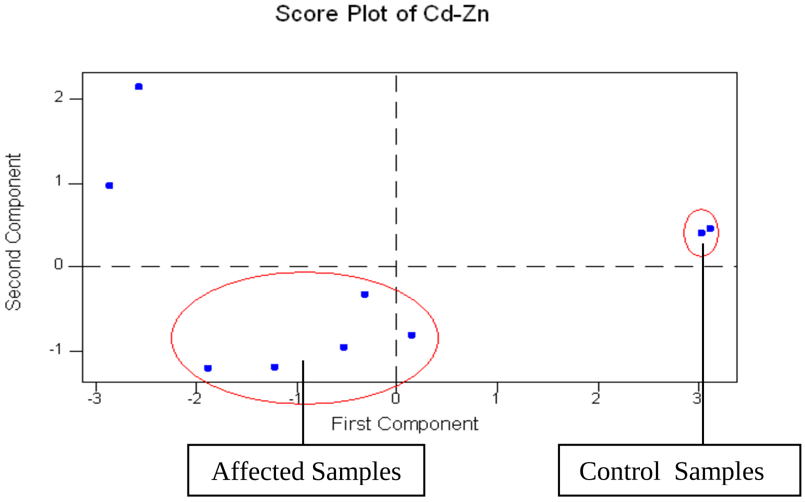

Fig-5: Score plot for the compression of soil samples

4. CONCLUSION

The present study shows that the environments around the petrol filling stations were polluted with metals. Most of the soil and ryegrass samples show higher level of lead and zinc metals compared to the permissible limits as mentioned by Environmental Protection Agency (EPA). Activated charcoal, silica gel, calcium carbonate and port land cement beds of adsorbent can be placed in petrol filling stations to monitor the dispersed metal content in the surrounding. Activated Charcoal was found to be a most active adsorbent among others. By applying the beds of activated charcoal around the petrol filling stations we can reduce the dispersion of toxic metals in the surrounding.

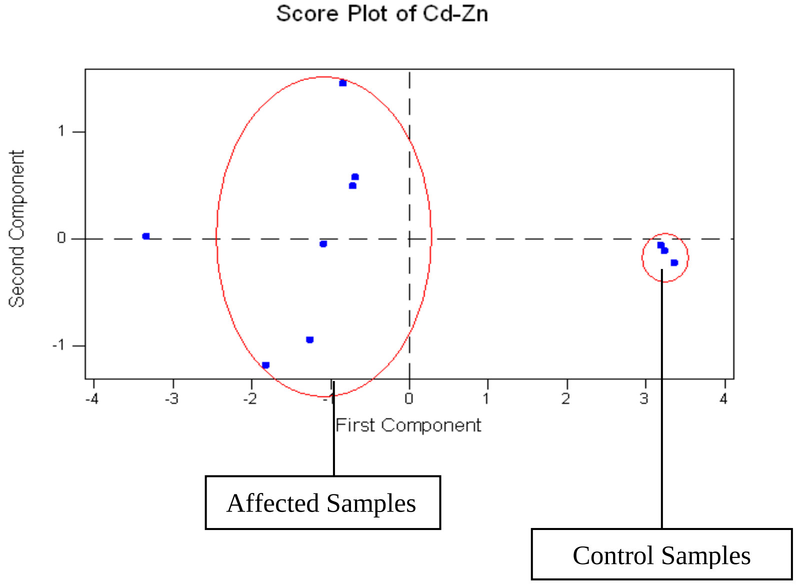

Fig-6: Score plot for the compression of Ryegrass samples

Table-5: Adsorption of Lead on different adsorbent beds

S.NO	ADSORBENTS	Concentration of Pb after adsorption (mg/kg)
1	Charcoal	12.18
2	Calcium Carbonate	11.06
3	Cement	10.70
4	Silica	2.48

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