IOSR Journal of Pharmacy and Biological Sciences (IOSR-JPBS)
e-ISSN: 2278-3008, p-ISSN:2319-7676. Volume 10, Issue 3 Ver. IV (May - Jun. 2015), PP 80-85
www.iosrjournals.org

Monitoring of Seasonal Variations in Heavy Metals Concentration in Roadside Soils of Agra, India – A Case Study

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Abstract: *Assessment of heavy metal contents in soil samples from seven roadside sites of Agra district was undertaken. The present study was conducted in pre and post monsoon seasons to find the variations in heavy metal contents in soil samples. Topsoil samples (0-15 cm) were taken at various sites, the metal analyzed were Cd , Cu , Pb , and Zn . Soil samples were taken at three different distances away from each roadside site. some physicochemical parameters of soils(pH, ECe ,OC ,* CO_3^{-2} *,* HCO_3^{-}*) in both seasons were also studied .The heavy metals concentrations in most of the soil samples were found to be significantly higher in pre monsoon season. The effect of season on heavy metals concentration was found significant at 5% levels in most of the soil samples which shows that the difference between the concentrations of metals in two seasons were significantly different. Levels of Pb, Cd, Cu and Zn in pre monsoon soils were ND- 7.8, ND- 14.7, 8.0- 41.4 and 17.7- 70.4 mg/kg respectively while in post monsoon soils, it were found to be ND-7.2, ND-13.9, 3.0-38.3 and 14.4- 68.6 mg/kg respectively.*

Keywords: *Heavy metal, seasonal variations, physicochemical parameters, pre monsoon soils, post monsoon soils*

I. Introduction

Soil is considered contaminated when chemicals are present or other alteration have been made to its natural environment. This is often caused by accidental releases of chemicals or the improper disposal of hazardous waste. Increased input of metals and synthetic chemicals in the terrestrial environment due to rapid industrialization coupled with inadequate environmental management in the developing country like India, has led to large- scale pollution of the environment. These chemicals in the terrestrial environment clearly pose a significant risk to the quality of soils, plants, natural waters and human health **(Adriano et al, 2001; Hooda et al, 2004; USEPA,2003; WHO,2004).** Heavy metals content of soil is of major significance in relation to their fertility and nutrient status. Many metals such as Zn, Cu, and Se are essential elements for growth of plants and living organism. However, high concentration of these metals become toxic. Others metals, which are not included in the group of essential elements, such as Pb or Cr, may be tolerated by ecosystem in low concentration, but become harmful in higher concentrations **(Alloway et al, 1997, Nriagu et al, 1988).**

Among anthropogenic sources, automobile exhaust and industrial emission contribute to a larger extent in this respect **(Vousta et al., 2002 & Nriagu et al., 2000).** The natural input of several heavy metals to soils due to pedogenic processes has been exceeded in some local areas by human input, even on a regional scale. In particular, agricultural soils can be long- term sink for heavy metals. These soils have also been influenced by other pollutant activities such as the use of manures, sewage sludge disposal or aerial fallout from industrial activities **(Van Camp et al., 2004)**. As a consequences, potentially toxic elements have accumulated in the soil profile. This can result in a loss of soil functions concerning environmental quality protection, maintenance of human health and productivity, which are relevant aspects of soil quality **(Doran and Parkin, 1994)**. Pollution activities can have implication for the quality of agricultural soils, including phytotoxicity at high concentration and the transfer of heavy metals to the human diet from crop uptake or soil ingestion by grazing livestock **(Nicholson et al., 2003).** Analysis of heavy metals concentration in soil is, therefore, critical for policy making oriented at reducing heavy metal input to soil and guaranteeing the maintenance or even improvement of soil function.

Recent years have seen as upsurge of interest on monitoring trace metal pollution in soil caused by traffic road dust, agricultural soil near motorways and sources identification **(Soyak et al 2000, Narain et al 1997, Ghaedi et al 2008, Ghaedi et al 2007)**. Along with industrial activities, automobiles are one of the major pollutant of soil, their consumption of gas, various oils and ware and tare; all contribute to soil contamination. Traffic – related elements such as Platinum group elements (PGEs), Zn and Cu have shown sharp decrease in concentration with increasing distance from the traffic lane **(Morcelli et al 2005).**

Emission reductions are substantial and importantly apply to all the vehicular fuels. In India, steps have been taken to ban leaded petrol. In the second phase, the Ministry of petroleum and natural gas (Govt. of India) introduced unleaded petrol (less than 0.013 g/l) in 1995 in four metro cities for 4- wheeler petrol vehicles fitted with catalytic converters. From 1998, unleaded petrol was introduced for all vehicles in Delhi. This was extended to the entire country from 1 April 2000.

The main objectives of the present study was to asses seasonal variations in heavy metal concentrations in surface soil samples collected from different sites of Agra District (INDIA).

II. Methods & Materials

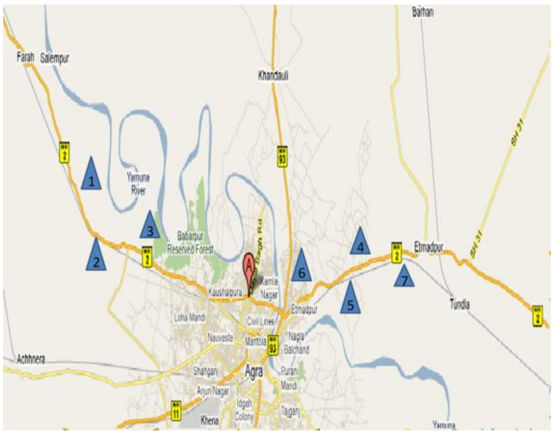
2.1 Study Area

Agra (27^o10'N, 78^0 05'E) is located in the north central part of India about 204 km south of the Delhi. It is the home to the world famous heritage monument Taj Mahal. It is bounded by the Thar Desert of Rajasthan on its South East, West and North peripheries and is therefore, a semi arid area Meteorologically the year is divisible into three distinct seasons; summer (March- June), monsoon (July- October) and winter (November-February) [14,15]. Summer season is associated with strong hot dry westerly winds and high temperature ranges between 30 and 46^0C. Relative humidity in the summer ranges between 18 and 48%. The monsoon season is hot and humid, temperature ranges from 24- 36^0C and the relative humidity ranges from 70- 90%. The pre-monsoon and monsoon season are dominated by strong northeast and southeast winds and in the winter season, the temperature ranges from 10 to 25^0C during day time and drops below 5^0C at night **(IMD, 1989)**.

Agra is fourth most populated city in Uttar Pradesh, India having three major National Highways (NH-2, NH-3 and NH-11) crossing the city. It has a population of about 2 million, which can generate about 700 tons of solid waste everyday that can be seen in the form of piles along roadside and streets due to poor municipality services. The major industrial activities are ferrous and non- ferrous metal casting, rubber processing, chrome and nickel plating units, copper wire and diesel engine, tanneries, lime oxidation, pulverization, engineering works and chemicals. Apart from local sources, Mathura refinery, Firozabad glass industries and brick kiln factories are situated within 40 km from Agra **(Kumar et al., 2007)**.

2.2 Samples Collection and Analysis

For this study, a total of 21 soil samples were carefully collected from the surface of 7 roadside sampling sites (in triplicate). Soil samples were dried at 110^0C for 2 hours, ground through a 200 mesh sieve and homogenized for analysis. An accurate mass (1 – 1.5 g) of the samples was digested with conc. HNO_3, H_2O_2 and $HClO_4$, filtered through a Whatman 42 filter paper, transferred to the volumetric flask (50ml). The solution was completed to the mark with deionised water and metal ions were determined with absorption spectrophotometer (Perkin Elmer, ANALYST 100).



City Map of Agra District, India

III. Results & Discussion

Table 1. Physico Chemical Parameters of soil samples in pre monsoon season (Jan- Jun)

S.No.	Site	S.P.%	pH(1:2.5)	EC(ds/m)	OC(%)	$CO3^{-2}$ (meq/L)	$HCO3^-$ (meq/L)
1	Keetham	29.16	7.6	0.53	0.58	0.35	2.65
2	Runakta	32.12	8.3	0.74	0.52	0.20	1.50
3	Sikandra	28.26	8.4	0.63	0.38	0.20	1.00
4	Panwari	36.18	7.5	0.34	0.40	0.35	1.65
5	Gobar Chauki	38.69	7.6	0.59	0.41	ND	2.00
6	Chhalesar	25.81	7.7	0.34	0.39	0.25	1.75
7	Nagla Paramsukh	31.98	7.9	0.41	0.47	0.25	1.75

Table 2. Physico Chemical Parameters of soil samples in post monsoon season (July- Dec)

S.No.	Site	S.P.%	pH(1:2.5)	EC(ds/m)	OC(%)	CO_3^{-2} (meq/L)	HCO_3^- (meq/L)
1	Keetham	26.17	7.7	0.20	0.47	0.50	1.50
2	Runakta	26.17	7.7	0.20	0.47	0.50	1.50
3	Sikandra	26.79	8.1	0.56	0.29	ND	0.68
4	Panwari	32.98	7.8	0.22	0.58	0.18	1.24
5	Gobar Chauki	33.34	7.8	0.54	0.33	ND	2.15
6	Chhalesar	23.84	8.1	0.17	0.39	0.19	1.65
7	NaglaParamsukh	30.31	8.1	0.35	0.30	0.15	1.13

Table 3. Heavy Metals in different Roadside Agricultural Soil Samples of Pre Monsoon (Jan- Jun)

	Pb			**Cd**			**Cu**			**Zn**		
S.NO	0-5m	5-10m	10-15m	0-5m	5-10m	10-15m	0-5m	5-10m	10-15m	0-5m	5-10m	10-15m
1	7.2+0.8	5.9+0.6	5.7+0.4	5.6+0.4	1.0+0.1	0.8+0.2	16.8+2.1	16.0+1.2	11.1+0.2	25.8+2.9	20.0+2.9	36.7+2.2
2	4.6+0.2	4.0+0.2	2.9+0.3	17.2+1.6	15.6+1.5	12.4+1.8	21.1+1.3	12.7+0.6	8.0+2.2	38.2+3.1	40.5+2.4	25.9+3.1
3	15.1+1.5	12.4+1.5	2.8+0.4	5.6+0.2	1.1+0.3	ND	27.1+1.7	9.2+1.5	13.0+1.2	28.9+2.0	26.8+3.7	23.2+3.3
4	0.8+0.0	0.6+0.1	ND	1.8+0.1	0.4+0.1	ND	17.3+1.9	18.0+0.7	11.1+1.8	24.9+2.6	18.7+2.6	33.9+0.7
5	4.1+0.4	3.7+0.3	2.4+0.4	5.0+0.3	2.6+0.1	ND	54.7+4.2	56.7+4.7	43.1+6.9	39.2+4.9	65.1+2.8	29.4+5.9
6	1.3+0.4	6.2+0.4	ND	14.8+0.7	13.8+0.9	2.5+0.4	12.7+1.2	19.3+1.7	4.4+0.5	33.2+3.8	45.5+2.2	17.7+0.9
7	3.5+0.2	1.9+0.1	0.8+0.2	1.8+0.1	0.5+0.1	ND	35.7+4.4	30.0+2.5	34.4+3.0	31.1+4.2	21.9+3.4	30.0+1.5

ND = Not detected

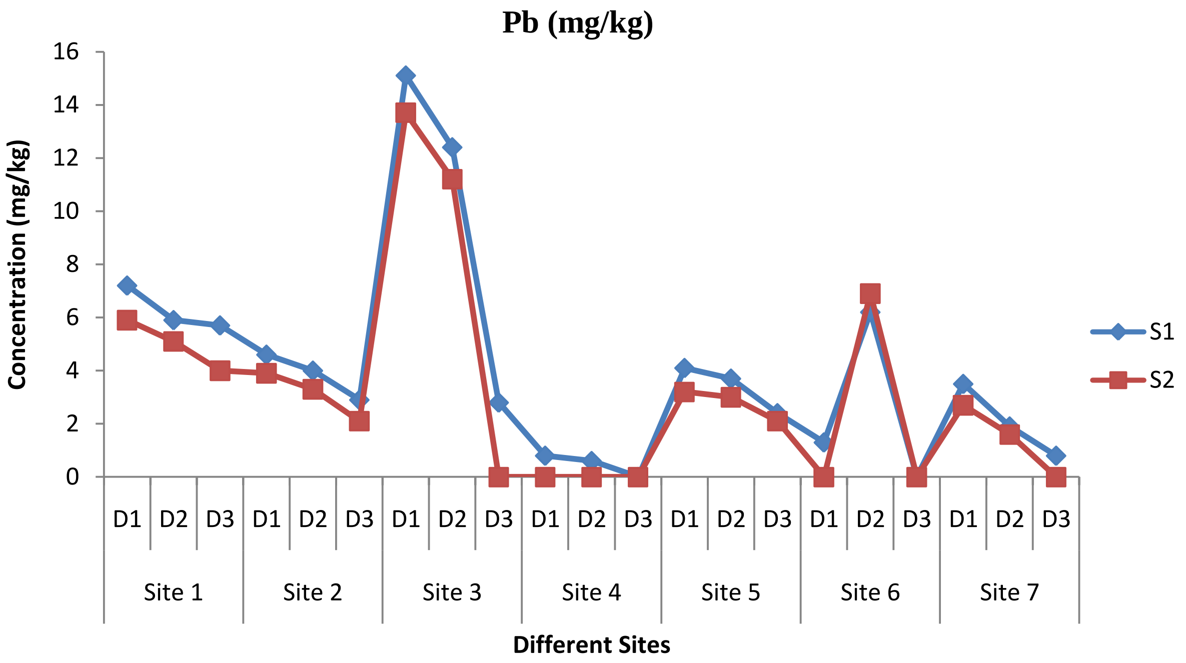
Table 4. Heavy metals in different roadside agricultural soil samples of post monsoon season (July- Dec)
ND = Not detected

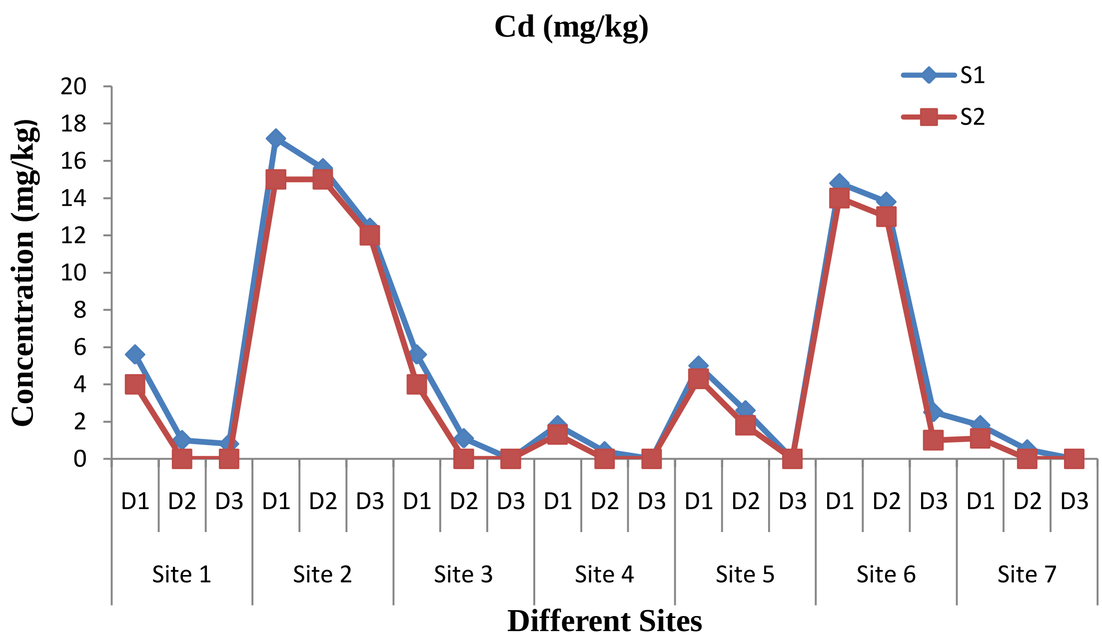
	Pb			**Cd**			**Cu**			**Zn**		
S.NO.	0-5m	5-10m	10-15m	0-5m	5-10m	10-15m	0-5m	5-10m	10-15m	0-5m	5-10m	10-15m
1	5.9+0.5	5.1+0.4	3.0+0.5	4.0+0.3	ND	ND	15.2+0.6	15.5+0.5	9.0+1.3	22.0+1.3	18.3+2.7	33.3+2.8
2	3.9+0.4	3.3+0.5	2.1+0.3	15.0+1.1	15.0+1.3	12.0+2.1	23.0+1.9	10.0+2.1	7.0+0.2	35.0+3.1	36.9+3.5	24.6+3.2
3	13.7+0.8	11.2+0.7	ND	4.0+0.2	ND	ND	22.0+1.1	7.0+1.6	12.3+1.7	27.6+2.9	24.6+3.8	20.0+1.5
4	Nd	Nd	ND	1.3+0.1	ND	ND	13.4+1.8	16.7+1.2	8.6+0.4	23.7+3.5	16.5+3.2	32.0+4.2
5	3.2+0.1	3.0+0.4	2.1+0.2	4.3+0.2	1.8+0.4	ND	50.3+6.4	53.9+5.5	39.8+4.7	37.6+4.6	61.5+5.7	26.2+4.5
6	ND	6.9+0.3	ND	14.0+0.9	13.0+1.3	1.0+0.5	11.0+0.3	15.0+0.8	3.0+0.8	29.7+0.9	36.2+5.4	44.4+3.8
7	2.7+0.4	1.6+0.1	ND	1.1+0.0	ND	ND	33.1+0.5	23.4+1.1	31.0+3.0	28.4+1.7	17.7+2.8	29.2+1.6

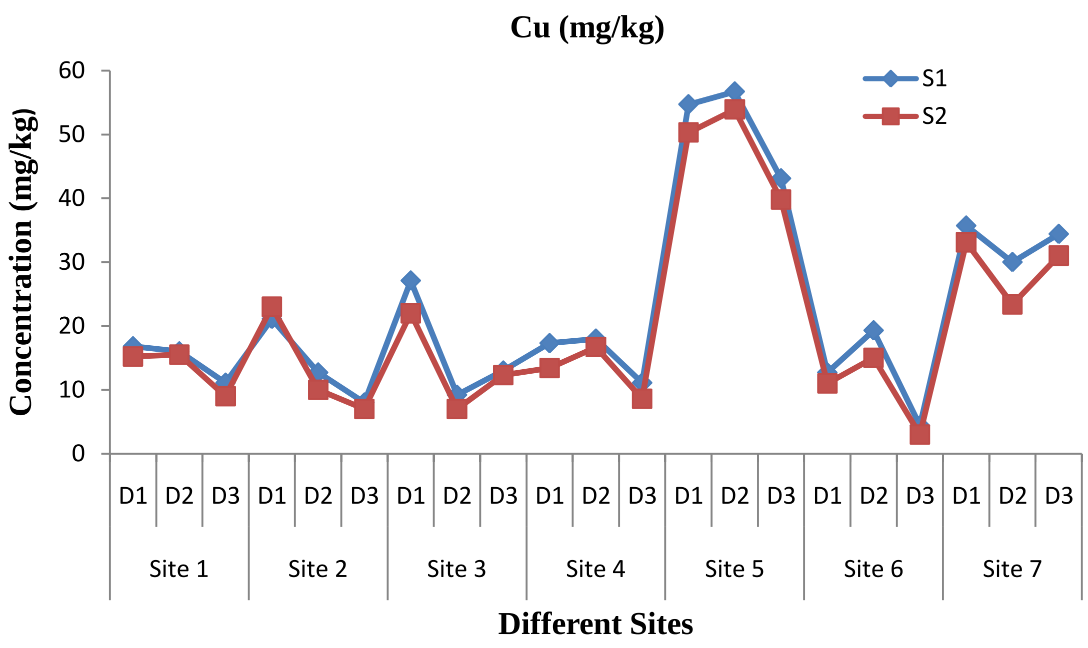
Table 5. Seasonal variation in heavy metals concentration in soil of pre and post monsoon seasons (P-values, Two way ANOVA)

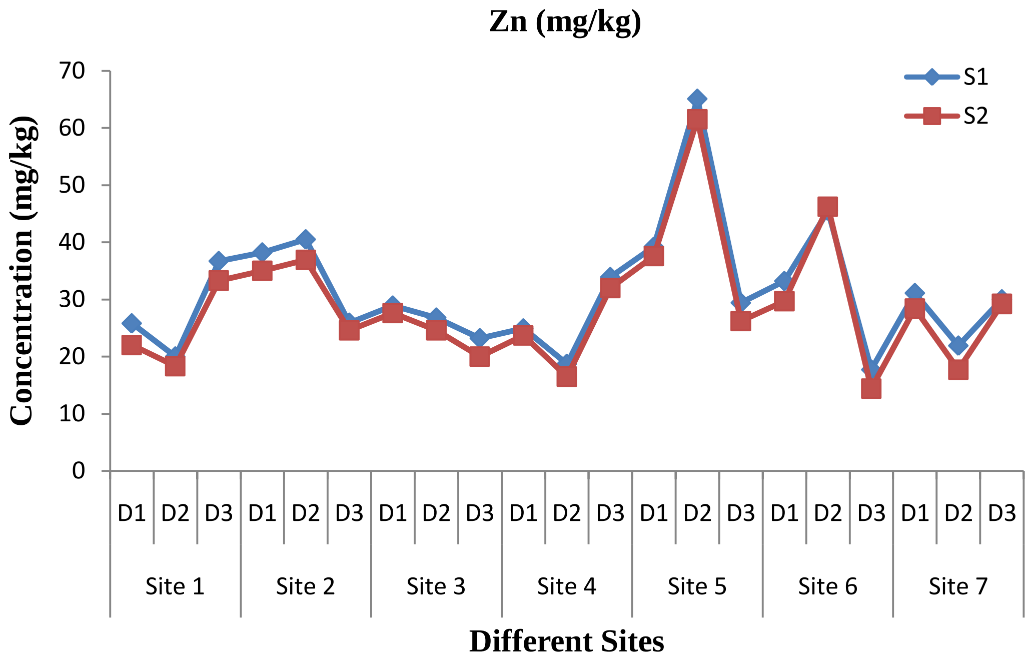
	Pb			**Cd**			**Cu**			**Zn**		
S.No.	S	D	S x D	S	D	S x D	S	D	S x D	S	D	S x D
1	#	#	#	#	#	#	#	#	NS	#	#	NS
2	#	#	NS	NS	#	NS	NS	#	NS	NS	#	NS
3	#	#	NS	#	#	#	#	#	NS	NS	#	NS
4	#	#	#	#	#	#	#	#	NS	NS	#	NS
5	#	#	NS	#	#	#	NS	#	NS	NS	#	NS
6	NS	#	#	#	#	NS	#	#	NS	NS	#	NS
7	#	#	NS	#	#	#	#	#	NS	NS	#	NS

S= Seasonal Variation
D= Distance wise variation
S×D = Combined effect of season and distance both
# = Significant variation
NS = Not significant









The physico-chemical properties of soil are tabulated in Table1. Soil pH varied from 7.5- 8.4 in pre monsoon while 7.7- 8.1 in post monsoon season soils, indicative of an alkaline environment. Electrical Conductivity values ranged from 0.34 – 0.74 in pre monsoon while 0.17- 0.56 in post monsoon soils. The pH can affect the availability of nutrients in the soil because at low pH, metals are more soluble in the soil solution and become more bioavalable to plants. Hence, toxicity problems are more severe in acidic soils in alkaline soils. The electrical conductivity in pre monsoon season soils were found to be higher than that of post monsoon season. The high value of EC may be due to the presence of organic and inorganic ions in the soil solution. Soils vary in the amount of soil organic carbon they contain, ranging from less than 1 % in many sandy soils to greater than 20% in soil found in wetlands. In the present study, all the samples show OC content below 1% in both the season.

In pre monsoon season , carbonate content was ranged from ND-0.35 meq/L while in post monsoon soils it was ND 0.50 meq/L. Bicarbonate values varied from 1.00- 0.65meq/L and 0.68-2.15 meq/L in both pre and post monsoon season respectively.

Due to low solubility and relative freedom from microbial degradation, Pb tends to accumulate in soils and remain bioavailable. The maximum allowable limit (MAL) in soil suggested by Kabata- Pendias and Pendias (1992) are 5mg/kg for Cd, 100mg for Cu and Pb and 300mg/kg for Zn. The concentration of Cu, Zn and Pb in the soil of Agra District were below the MAL and can be classified as uncontaminated whereas in case of Cd, sites S2 and S6 indicate highly contamination. This suggest the possibility for Cd and Zn, that in some cases, many sources are responsible, such as weae out of tyres, leakage of oils and corrosion of batteries and metallic parts such as radiators.

For the investigation of the seasonal variation, the year was divided into two seasons: pre monsoon (Jan- June), post monsoon (July- Dec).

Table 3, 4 & 5 states that Pb, Cd and Cu concentration in almost all soil samples were significantly higher than that in post monsoon season soils while the differences in Zn concentration in both season were not significant except that of site S1. This might be due to the runoff effect that is capable of removing heavy metals from the farmland and effect of rainfall which may facilitate the leaching of the soil and contribute to the dilution of the soil solution during post monsoon season. Concentration of all metals were found to be decreased significantly ($P<0.05$) in both season as the distance from the highway increased. This decline relationship between metal concentration in soil and distances from the road is in agreement with other studies [17,18]. The interaction or combined effect of season and distance factor (effect of S x D) on concentration of Pb and Cd was significant at 5% level which indicates that the combined effect of S x D together on the concentration of lead and cadmium was significantly different at 5% levels in these samples whereas combined effect of season and distance together on the concentration of Zn and Cu were not found significant at 5% levels. It states that the Zn and Cu content were significantly varied with corresponding changes in the season and distances simultaneously.

Acknowledgement

Authors are thankful to Dr. Ashok Kumar, Head, Department of Chemistry, St. John's College, Agra, for providing us the necessary facilities and Dr. A.K. Jain, for providing statistical assistance.

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