

# Fractionation of Heavy Metals in Soil of Industrial Area of Mysore City, India

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**Abstract**--The Metals are considered as most important toxic pollutants in the ecosystem. Metals are continuously released into the biosphere by natural processes like volcanoes, weathering of rocks and also by various anthropogenic activities, such as mining, combustion of fuels, industrial and urban sewage and agricultural practices. On a global scale there is evident that, through the anthropogenic activities surrounding environment has polluted heavy metals. Once metals were entered into the environment it goes on accumulation with the natural process. However, in general aspects it is very difficult to eliminate the metals from the environment. Traditional treatments for metal contamination in soils are expensive and cost prohibitive when large areas of soil are contaminated. In this present study the heavy metal pollution in industrial area of Mysore city has been taken and also heavy metal speciation, as well as abiotic and biotic factors affecting their bioavailability of heavy metal pollution was studied. The geochemical behavior of heavy metals was analyzed through speciation studies. The studies show that the heavy metals mobility is less in the Exchangeable metal fraction and Carbonate bound metal fractions. But in the Fe– Mn oxide metal fraction and Organic and sulfide metal fractions mobility of the metals is comparatively little higher than the other fraction. The final residual metal fraction has the non-mobile phase of the heavy metals. In this study period, the industrial surrounding area soil has become polluted and lost their natural fertility with the addition of some heavy metals by several processes taken up by the industries.

## I. INTRODUCTION:

Heavy Metals are considered very important and highly toxic pollutants in the various environmental aspects. Inputs of metals to the environment as a result of anthropogenic activities is difficult to measure due to the very large natural inputs from the erosion or rocks, wind-blowing dusts, volcanic activity and forest fires. Some metals that have received more attention are Hg, Cd, and Pb, because of their highly toxic properties and their effects on the environment and the living organisms. The inputs of metals to the environment from anthropogenic activities is complicated to distinguish as there are very large natural inputs from the erosion, wind-blown dust, volcanic activity and forest fires. Atmospheric and river inputs, dredging spoil, direct discharges, industrial dumping and sewage sludge are some of the important contributors to metal pollution, which lead to the release of metals to the marine environment. Some metals are deposited by gas exchange at the sea surface, by fallout of particles (dry deposition) or are scavenged from the air column by precipitation (rain) which is called wet deposition. Rivers make a major contribution of metals in the marine environment. The nature of metals depends on

ore-bearing deposits in the catchment area and the discharge of human waste and discharges when the river passes through urban areas. Dredging of shipping channels produces large quantities of metal pollution. Much smaller quantities of metals are being entered to the sea by direct discharges of industrial and other waste and the dumping of sewage sludge (Depledge MH *et al.*, 1998; Phillips DJH, 1995).

The extent of bioaccumulation of metals is depending on the total amount of the metal, the bioavailability of each metal in the environmental medium and the route of uptake, storage and excretion mechanisms. The requirements of different organisms for essential metals vary substantially but optimal concentration ranges are narrow and frequently under careful homeostatic control. Excess metal concentration in an organism must be actively excreted, compartmentalized in cells or tissues, or metabolically immobilized. Essential metals at high concentrations can have sub-lethal toxicity effects to some organisms or lethal consequences to others. Also, metals at deficient concentrations can have again adverse health effects. Thus essential metals can have a double “toxic” threshold (Rainbow PS, 2007). Living organisms exposed environmentally to high metal concentrations follow various mechanisms to counter potential toxicity.

## II. Speciation of Heavy Metals in Soil sample:

Speciation analysis is the analytical activity of identifying and/or measuring the quantities of one or more individual chemical species in a sample. The chemical species are specific forms of an element defined as to isotopic composition, electronic or oxidation state, and/or complex or molecular structure. The speciation of an element is the distribution of an element amongst defined chemical species in a system. Speciation analysis provides the necessary information to describe the effects of active species which is not available from the results of total trace element determinations. It is therefore predictable, that the concepts based on total trace element determination, such as

- Trace element determination
- Toxicity of elements
- Essentiality of elements
- Metals as environmental pollutants and workplace hazards
- Trace metals in human health and nutrition will be replaced gradually by the more meaningful concepts using the information of speciation, that mean
- Trace element speciation
- Toxicity of element species
- Essentiality of element species
- Element species as environmental pollutants and workplace hazards
- Trace element species in human health and nutrition

The additional information is very useful to direct actions enhancing the quality of products, improving production processes, reducing health risks associated with toxic species, leading to improved understanding of life and better control for the environment.

The chemical composition of soil influences to a great extent the speciation of heavy metals. In river water large proportion of metals is bound to organic and inorganic particulate matter. Other factors which influence speciation are: pH, hardness, and organic matter (Elbay-Poulichet F et al.,1987 ; Salomons W, et al.,1984) Large amounts of dissolved organic complexes and particulate matter with heavy metals are transported great distances to end up in the sediments of the estuaries. Some metals, such as Cd, can be released from their organic complexes by increasing Cl (chlorine) concentrations, which form chloride complexes (Zamuda CD, et al.,1982) Some metals are available for uptake into organisms from solution only as free ions, whereas others are transported over biological membranes as inorganic complexes. In experiments with Cu and Cd their toxicity and their bioavailability is correlated with the concentration of free metal concentration (Sunda WG,et al.,1978; Bienvenue E.1984). Inorganic Hg in the other hand is transported over lipid membranes principally as uncharged chloride complexes (Luoma SM, 1989). Sediments are more complex chemical environment than water and there are not reliable methods for assessing bioavailability of metals in such media (Alloway BJ.1990) It has been shown that heavy metal in soils are associated with several distinct geochemical phases, such as clay minerals, organic matter, carbonates and sulphates.<sup>48</sup> The types of reactions that are likely to control the partitioning of metals in soils are: adsorption and desorption, precipitation and solubilisation, surface complex formation, ion exchange and biological mobilization or immobilization (Chao TT,1984)

### III. MATERIALS AND METHODS

#### A. Study Area:

The study area Mysore is having more than 10 lakh populations and was capital of former state and  $11^{\circ}6'$  latitude and  $77^{\circ}7'$  longitude and general elevation is little more than 1800 feet above sea level. The climate of the city is moderated throughout the year with temperature during summer ranging from  $30^{\circ}\text{C}$  to  $34^{\circ}\text{C}$ . The rainy season is from June to October. The winter season starts from November to February. The source of water for domestic purpose is mainly from the Cauvery River and ground water.

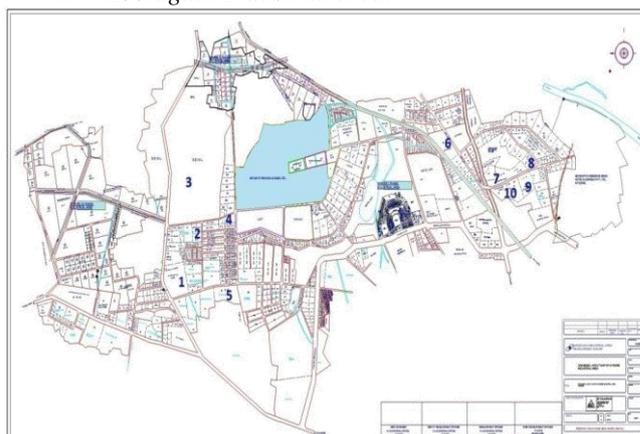
Mysore is one of the growing cities of Karnataka and it is largely due to presence of industrial resources and a well-developed communication network. Mysore has a rich and vibrant history and heritage and hence attracts a huge number of tourists. Also Mysore is now active centre for production and industrialization. The city has been growing as a country parallel to Bangalore, with a large presume of software companies and the population is growing at a faster rate due to the influx of many industrial and commercial activities.

In recent year's industrialization has become main cause of city's growth. There is diversity in industrial landscape of Mysore with haphazard distribution. The

industrial areas are distributed all over the city and its surroundings with lack of order and regulation in industrial location. A large number of small and medium scale industries exist in and around the Mysore city. Most of all medium scale industries like engineering, chemical, pharmaceutical, food, brewery, textile, steel and metal smelting etc.

Mysore city industrial area has been majorly divided in to three regions. Namely,

1. *Metagalli industrial area.*
2. *Hebbal Industrial area.*
3. *Hootagalli Industrial area.*



Source: KIADB

Fig. 1: Sampling location of study area

Metagalli Industrial area consisting of industries like tyre manufacturing, Aluminium industries, electric appliances manufacturing industry and metal industry. This industrial area is having medium and large scale industries.

In Hebbal industrial area, small scale industries and medium scale industries are more in number compared to large scale industries like electric appliances manufacturing industries, textile industry, metal product industries etc.

Hootagalli industrial area is smaller in its radius as compared to Metagalli and Hebbal industrial areas. Here the industries like textile, heavy earth movers manufacturing industry, chemical manufacturing industries and very few small scale industries are situated.

#### B. Sampling and pre-treatment of the sample

In the present study, sampling locations are included in all the 3 major industrial areas of Mysore city. The soil samples were collected at different points of the industrial zone of Mysore city, India. The samples were collected in polythene covers and immediately brought to the laboratory for analysis. Soil samples were dried with the help of oven in the laboratory and then ground in an agate mortar and pestle to pass through a 0.5mm stainless steel sieve. Then they were stored in polythene covers at room temperature. The soil samples were analyzed for basic physico-chemical properties using standard analytical methods and finally we digested the soil sample to quantify the total metal concentration by using di-acid mixture. The digested soil sample was analyzed for determination of total heavy metals concentration by using AAS.

Sr. No	Station code	Location	Industrial Area
1	P1	Automotive excel	Hootagahalli
2	P2	Chamundi Textiles	Hootagahalli
3	P3	BEML	Hootagahalli
4	P4	Wipro lightings	Hebbalu
5	P5	Rane madras	Hebbalu
6	P6	VikranthTyres	Metagalli
7	P7	Falcon Tyres	Metagalli
8	P8	Bhoruka Aluminium	Metagalli
9	P9	Triveni Gears.	Metagalli
10	P10	Shimoga steels	Hebbalu

Table. 1: List of sampling locations

#### IV. EXPERIMENTAL WORK

##### A. Determination of pH and Electrical conductivity:

Place two teaspoon of soil in a beaker. Add the same amount of distilled water, stir with glass rod and leave to stand for 10 minutes. Stir again and immerse the pH meter into the water/soil suspension.

##### B. Determination of Lime content:

1g soil was taken and its dried to remove the moisture content on hot plate. Add 25ml of 0.1N HCl. Keep aside for 30min. Then titrate the content against NaOH in the burette.

##### C. Determination of Organic carbon and Organic matter:

1g of soil taken in to conical flask which contains 0.1N  $K_2Cr_2O_7$ . Keep aside for 30min to get oxidation. Add 10ml of  $con.H_2SO_4$ . Titrate this solution against 0.5N FAS.

##### D. Determination of Sodium and Potassium:

Take 5g soil sample in a conical flask. To extract the calcium and magnesium add 100ml of 1N ammonium acetate and agitate the solution frequently at regular intervals for 1hr. Filter the solution and inject for flame photometer.

##### E. Determination of Calcium and Magnesium:

Take 5g soil sample in a conical flask. To extract the calcium and magnesium add 100ml of 1N ammonium acetate and agitate the solution frequently at regular intervals for 1hr. Filter the solution and titrate against

##### F. Determination of Total Heavy Metals:

1g of soil sample was taken in to the test tube and mixed well with the concentrated  $H_2SO_4$ , Perchloric acid and Nitric acid. Heat the test tube content till the solution become whitish color. If white color appears it indicates that the soil sample is digested completely. Cool the solution to room temperature and filter using whatman filter paper. Make up the filtered solution to 100ml using distil water and take the readings after injecting the solution to AAS.

##### G. Multi-step sequential extraction

The sequential extraction procedure used in this study is Tessier *et al.* 1979 method. According to Tessier *et al.* heavy metals are associated with the fractions as described as follows:

1) *The exchangeable fraction*, which is likely to be affected by changes in water ionic composition as well as sorption-desorption processes;

(2) *The carbonate fraction*, that is susceptible to changes in pH;

(3) *The reducible fraction*, that consists of iron and manganese oxides which are unstable under anoxic conditions;

(4) *The organic fraction*, that can be degraded leading to a release of soluble metals under oxidizing conditions and

(5) *The residual fraction* that contains mainly primary and secondary minerals, which may hold metals within their structure. These metals are not expected to be released in solution over a reasonable time span under the conditions normally encountered in nature. The extraction was carried out progressively on an initial mass of 1.00 g of sample of soil samples. The samples for sequential extraction were dried in an oven at 60°C for 24 h in order to avoid, as far as possible, the transformation of some chemical forms (exchangeable and carbonate). This fraction was calculated as the difference between the total metals and the sum of extracted metals. The selective extractions were conducted in 50 ml capacity centrifuge tubes. After each extraction step, the sample was subjected to 30 min of centrifugation at 4,000 rpm, the supernatant was separated from the residue with a pipette and transferred into a 25-ml calibrated flask. The residue was centrifugation and later washed thoroughly, the obtained second supernatant was added to the flask, which was diluted to the desired volume. The extracts obtained were acidified using aquaregia and stored in stopper polyethylene vessels until their analysis by using inductively coupled plasma atomic emission spectroscopy techniques (ICP-AES). The total content of metals was determined after digesting 1 g of sample with aquaregia. The concentration of particular heavy metals was expressed per 1 kg of air dry sample. The content of heavy metals in the obtained solution was determined by using ICP-AES.

##### H. Results and Discussion

The physico-chemical properties have been determined by standard methods to understand the quality of the industrial area soil. From the physico-chemical characteristics clearly indicated that the soil organic carbon and organic matter is very low with the range of 0.12% to 0.41%. In the present study the speciation of heavy metals was carried out according to Tessier method as described earlier. Table 4 shows the results of different fractions of the heavy metals in soil of the industrial area of Mysore city. The exchangeable fraction (F1) contains metal elements in the ionic form, which have a high mobility and can be drained by water. The fraction related to the carbonates (F2) is extractable and can be accumulated in the plants. The fraction related to the oxides of iron and manganese (F3) and that related to organic matter (F4) contain metals enclosed in the matrix. The fraction (F5) contains the inert metals.

Station code	pH	EC (µs/cm)	Lime content (mg/kg)	OC (%)	OM (%)	Na (ppm)	K (ppm)	Ca (mg/kg)	Mg (mg/kg)
P1	6.78	82.6	2.16	0.402	0.6930	4.0	6.8	148.2	56
P2	7.3	84.1	1.12	0.12	0.206	4.3	9.3	120.4	46
P3	7.1	80.6	1.98	0.16	0.2758	4.4	7.5	148.2	68
P4	7.4	83.9	7.24	0.5	0.862	3.7	5.7	112.0	56
P5	7.1	81.6	5.94	0.16	0.2758	3.8	13.2	142.3	72
P6	7.5	78.6	3.02	0.32	0.5516	4.9	10.3	176.7	112
P7	7.1	85.9	3.14	0.296	0.5103	4.5	10.9	136.1	86
P8	7.2	84.3	5.88	0.316	0.5447	5.2	12.7	132.4	72
P9	7.3	81.7	5.18	0.298	0.5137	6.0	12.2	322.7	236
P10	7.2	82.5	4.24	0.416	0.7171	4.7	10.6	166.6	122

Table. 2: Physico-chemical properties of Industrial area soil of Mysore city during Post Monsoon-2012

Station code	Fe	Cu	Cr	Zn	Ni
P1	3926.9	19.0	17.5	118.9	16.1
P2	4062.4	13.6	8.9	86.1	22.0
P3	6350.4	15.1	13.8	68.6	12.9
P4	5902.2	14.8	12.6	89.8	15.2
P5	6405.7	18.8	17.7	96.0	15.1
P6	4447.5	15.8	14.6	110.8	13.6
P7	4311.8	17.5	10.8	84.1	13.4
P8	2862.6	15.7	19.2	94.6	10.3
P9	3650.2	16.5	14.0	126.8	10.7
P10	3812.2	16.5	18.7	110.9	16.5

Table. 3: Heavy metal concentration in Industrial area soil of Mysore city during Post Monsoon-2012 (mg/kg)

	Fractions I	Fractions II	Fractions III	Fractions IV	Fractions V
<b>P1</b>					
Fe	2.9	23	467	817	2617
Cu	ND	ND	ND	4.8	14.2
Cr	ND	ND	2.9	5.2	9.4
Zn	ND	4.7	78	18.6	17.6
Ni	ND	ND	3.6	5.6	6.9
<b>P2</b>					
Fe	3.4	19	491	789	2760
Cu	ND	ND	ND	3.7	9.9
Cr	ND	ND	2	3.4	3.5
Zn	ND	3.9	48	27	7.2
Ni	ND	ND	3	2.9	16.1
<b>P3</b>					
Fe	7.1	16.3	791	1918	3618
Cu	ND	ND	ND	2.1	13
Cr	ND	ND	2	4.6	7.2
Zn	3.1	6.7	26	16.9	15.9
Ni	ND	ND	3	4.8	5.1
<b>P4</b>					
Fe	3.2	18	681	1410	3790
Cu	ND	ND	ND	3.6	11.2
Cr	ND	ND	ND	4.5	8.1
Zn	3.2	5.6	39	35	7
Ni	ND	ND	4.7	3.4	7.1
<b>P5</b>					
Fe	48	15.9	670	2515	3200
Cu	ND	ND	1.8	2.9	14.1
Cr	ND	ND	2.8	6.7	8.2
Zn	4.1	6.9	61	10.2	13.8
Ni	ND	ND	3.4	5.6	6.1

P6					
Fe	3.4	14.1	437	1177	2816
Cu	ND	ND	1.9	2.8	11.1
Cr	ND	ND	ND	3.8	10.8
Zn	3.6	7.2	51	27	22
Ni	ND	ND	2.8	3.6	7.2
P7					
Fe	3.8	20	376	1812	2100
Cu	ND	ND	ND	3.8	13.7
Cr	ND	ND	2.7	4.2	3.9
Zn	3.1	5.6	48	22.2	5.2
Ni	ND	ND	2.2	5.8	5.4
P8					
Fe	5.6	31	487	789	1550
Cu	ND	ND	ND	5.2	10.5
Cr	ND	ND	3.1	5.9	10.2
Zn	2.9	3.8	28	56.1	3.8
Ni	ND	ND	2	3.6	4.7
P9					
Fe	4.2	30	710	815	2091
Cu	ND	ND	ND	2.9	13.6
Cr	ND	ND	ND	6.8	7.2
Zn	2.8	36.6	48.2	35.2	4
Ni	ND	ND	4.3	3.6	2.8
P10					
Fe	4.2	41	383	417	2967
Cu	ND	ND	2.8	6.1	7.6
Cr	ND	ND	2.6	7.2	8.9
Zn	3.1	6.7	39	48	14.1
Ni	ND	ND	3.2	4.7	8.6

Table. 4: Speciation of Heavy metals in Industrial area soil of Mysore city during Post Monsoon-2012 (mg/kg)

	pH	EC	L.C	O.C	O.M	Na	K	Ca	Mg
pH	1								
EC	-0.24254	1							
L.C	0.290489	0.136031	1						
O.C	0.06055	0.143958	0.460441	1					
O.M	0.060271	0.143614	0.460782	0.999999	1				
Na	0.306186	-0.16862	0.039197	-0.02991	-0.0298	1			
K	0.122615	-0.01109	0.257142	-0.36989	-0.36961	0.54071	1		
Ca	0.167285	-0.37008	0.105757	0.013353	0.0136	0.792584	0.372069	1	
Mg	0.286856	-0.29771	0.213373	0.110997	0.111252	0.823741	0.449958	0.966178	1

Table. 5: Correlation matrix of physico-chemical properties

	Fe	Cu	Cr	Zn	Ni
Fe	1				
Cu	0.0279	1			
Cr	-0.1790	0.5277	1		
Zn	-0.5237	0.4273	0.4203	1	
Ni	0.1061	-0.2378	-0.3964	-0.1524	1

Table. 6: Correlation matrix of total heavy metals

In the result, the iron occurred mainly in residual fraction and which is varied from 48.7% and 67.94% at sampling station no.7 and 1 respectively and also 19.42% to 42.02% of iron is bound to organic matter. It is bound in much smaller amounts in the form of oxides, which is ranged from 8.72%–19.45% in different samples. Only minor amounts of iron were detected in the carbonate and bound to exchangeable fractions and they were in the range of 0.25% to 1.08%. and 0.07% to 0.19% respectively. The amount of zinc found in the residual fractions was varies

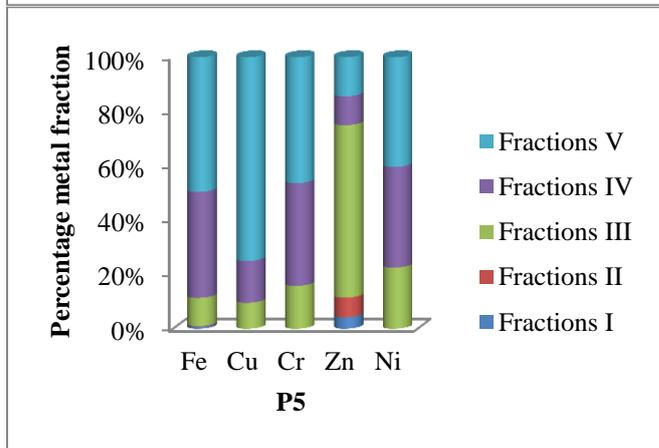
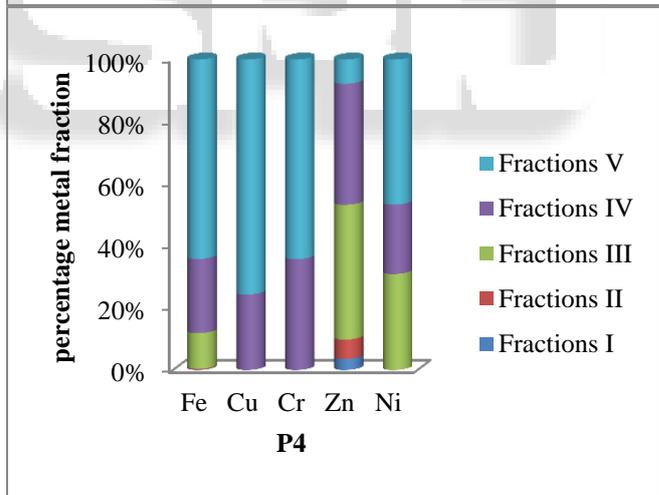
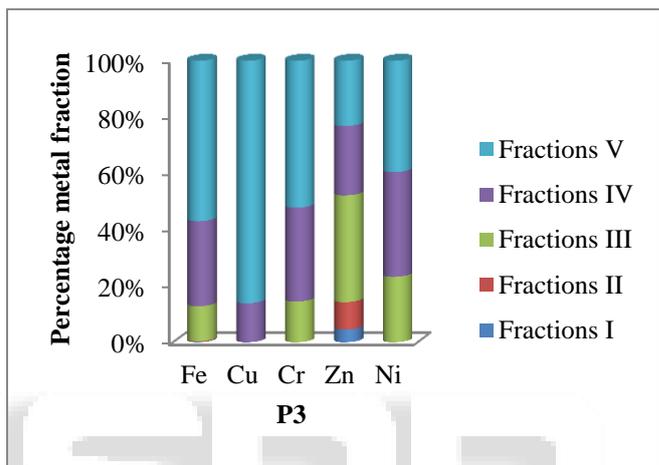
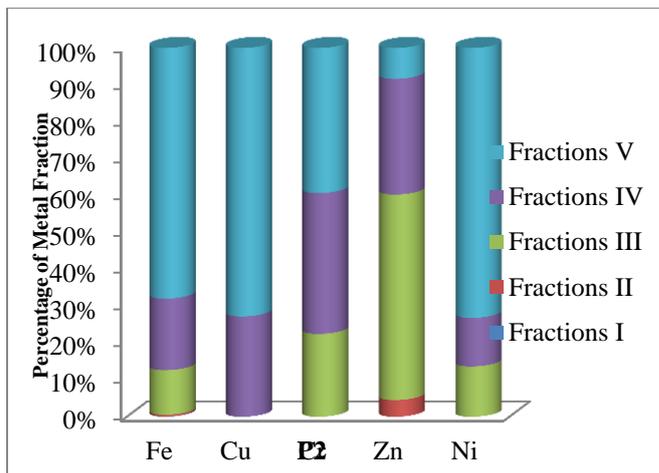
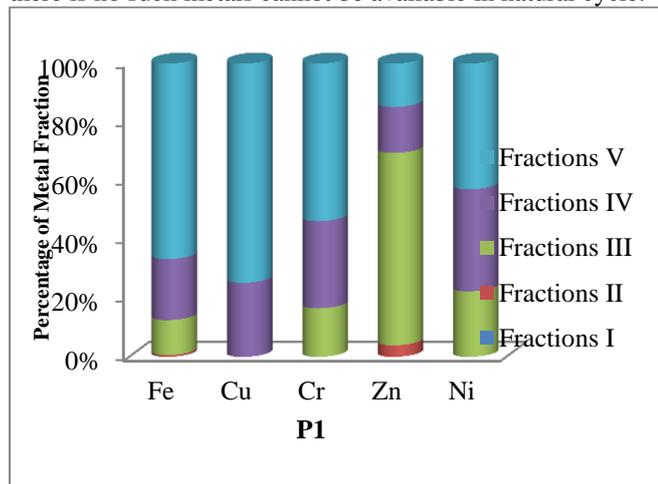
from 3.15%– 23.17%. The analysis shows that zinc has been bound to hydrated oxides of iron and manganese fraction in the range of 42.2– 68.9% and also was bound to organic matter fraction in range of 10.6%–59.3%. In exchangeable fraction the metal concentration was below the detection limit. The carbonate fraction was found that 3.95% to 28.86%.

In the present study, nickel concentration was found in the fraction bound to organic that is varies from 13.18% to 43.28%, whereas 26.16%–73.18% in residual fraction. It was bounded to oxide metal fraction for nickel is 13.63% to 40.18% and in carbonate bound fraction it is lower than the detection limit.. The concentration of nickel found in exchangeable metal fraction is once again lower than the detection limit. Toxicity of nickel is not important because of its low concentration in the mobile and bio-available fractions.

Copper concentration in the soil samples have been found in organic matter fraction ranged from 13.9%-33.12% and varied in the range of 66.87%-86.09% in residual form. In the exchangeable, carbonate fraction it was lower than the detection limit. The fractions bound to hydrated oxides of iron and manganese was estimated that 9.57% to 12.02%. Copper is bound in residual fraction than Ni and is much less likely to be displaced by the hydroxylamine hydrochloride reagent.

The analysis of fractionation of heavy metal shows in smaller amounts of chromium bound to hydrated iron and manganese oxides fractions ranges from 14.49% - 22.47%. The chromium in the soil sample is mainly found in the residual fraction in the range of 36.11%–73.97% and lesser in the range of 26.02%–48.57% bound to the organic matter.

In exchangeable fraction, except iron and zinc, the concentration of all metals in this fraction is lower than the detection limit. The amounts of metals released in the carbonate fraction represent a low proportion of the total metal concentration. Copper, chromium and zinc are below the detection range and iron has low concentrations in this fraction due to this fraction is susceptible to acid rain. In the fractions bound to hydrated iron and manganese oxides, the amounts of nickel, iron and zinc associated are relatively high. These amounts of metals would be released under reducing conditions. The metal levels in fraction associated with organic matter are relatively high and they represent a large fraction of the total metal concentrations. These amounts of metals are released in soil under strong oxidizing conditions and consequently this fraction constitutes an important source of potentially available trace metals. It can be observed that the greatest part of the metals studies, especially iron was associated with the residual fraction. This fraction, named as 'inert phase', corresponds to the part of the metals which cannot be mobilised. When the metal concentration is more in the residual fraction, the mobility is very less and even it cannot move. From this concentration there is no such metals cannot be available in natural cycle.



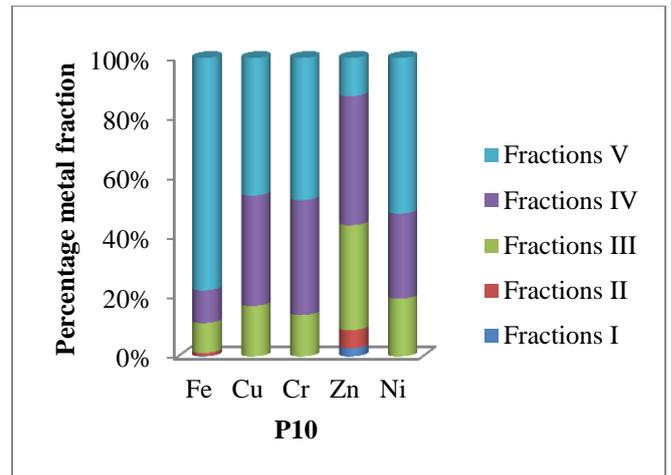
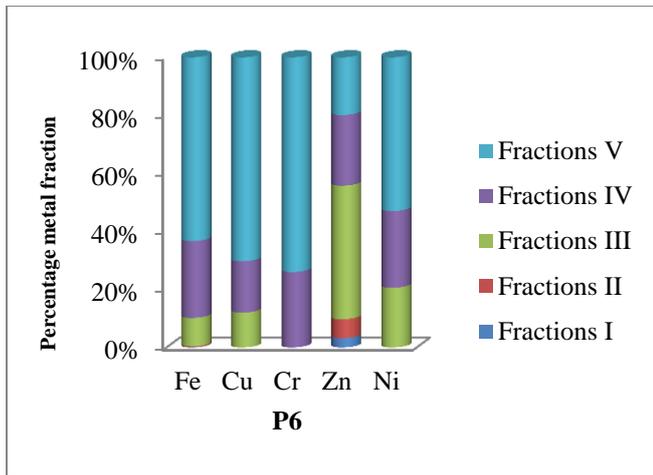
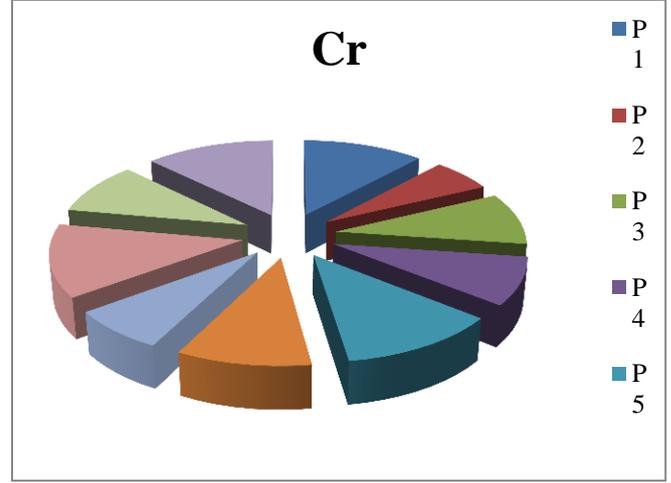
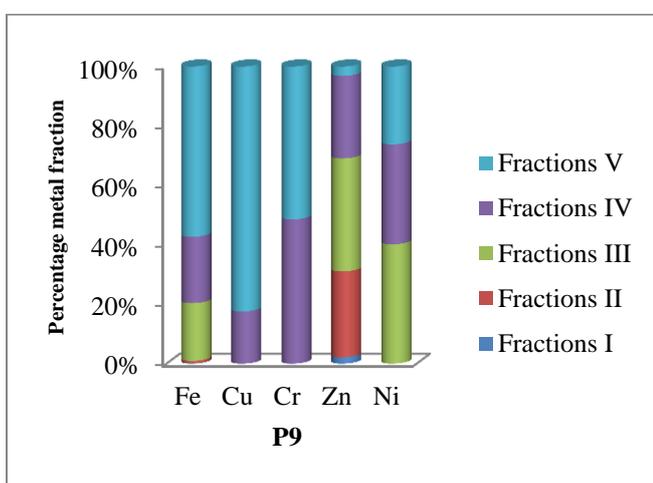
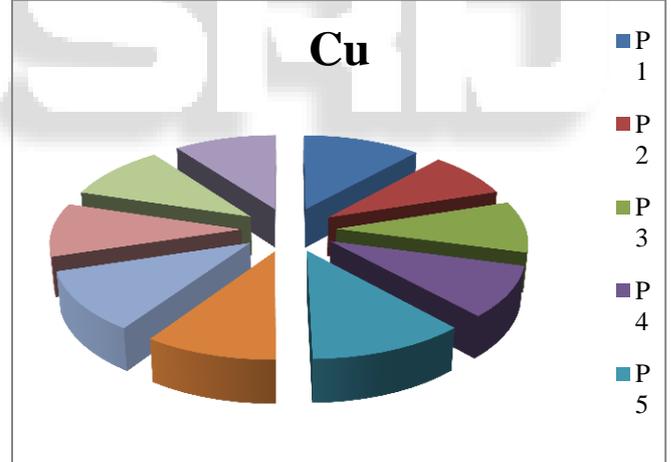
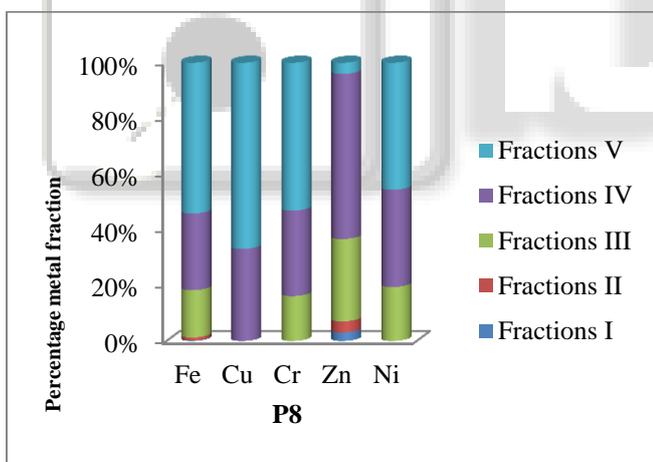
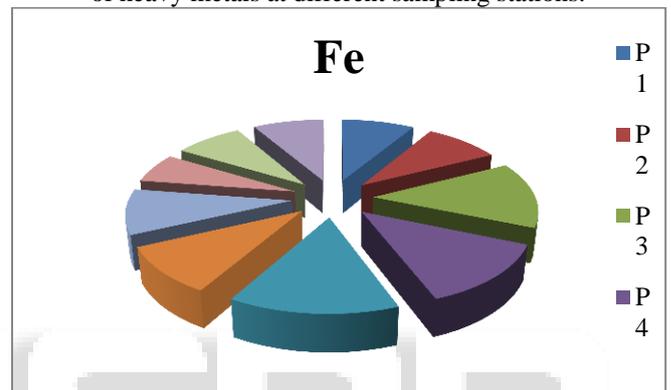
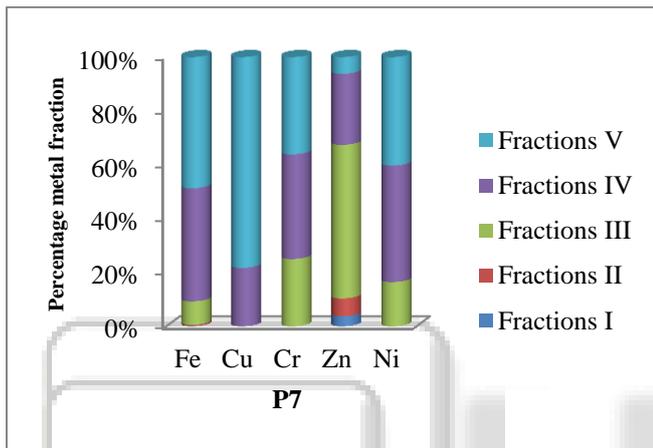


Fig. 2: Graphical representation of speciation of heavy metals at different sampling stations.



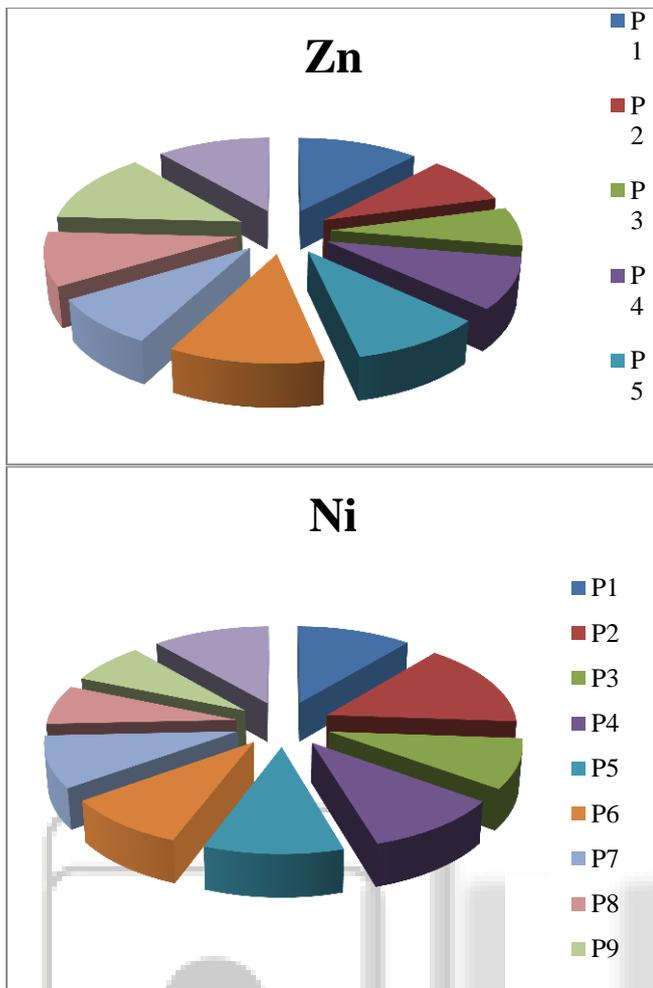


Fig. 3: Graphical representation of total heavy metal distribution at different sampling location

#### V. CONCLUSION

Pollution will occur from different sources in many ways either from natural or human made. When the pollution was caused by the nature, the effect of pollution is very low and pollution does not persist for a longer duration. When the pollution caused by the human beings the persistence capacity is more and it would cause very dangerous effects on the environment for the further more years. The present study of physico-chemical analysis of soil samples of Mysore city industrial area has shown optimum pH in all the soil samples. The organic matter and organic carbon (%) recorded showed minimum quantities during the study period. Increasing soil carbon can reduce the 25% of greenhouse gases created by agriculture and assist in ameliorating climate change. Increasing soil carbon will ensure good production outcomes and farm profitability. Soil carbon, particularly the stable forms such as humus increases farm profitability by increasing yields, soil fertility, soil moisture retention, aeration, nitrogen fixation, mineral availability, disease suppression, soil health and general structure. In this research work, results reveal that the soil has very low concentration of organic carbon and organic matter content. From the geochemical behavioral study the metals mobility is little low in the Exchangeable metal fraction and Carbonate bound metal fractions. But in the Fe- Mn oxide metal fraction and Organic and sulfide metal fractions mobility of the metals is comparatively little

higher than the other fraction. If the mobility of the metals is higher in initial two stages of speciation, the toxicity will be more in nature and it can be bio available. In addition to that the heavy metals are at risky levels in the study area. After reaching the maximum level of contamination, it would percolate in to ground water and it result in bioaccumulation in the natural cycle. From the different processes going in industries releases toxic chemicals, discharging of untreated waste water, dumping of untreated solid waste to the surrounding environment leads to release of heavy metals, acids etc. When pollutants get contaminate with soil, it will lose their fertility by the loss of its microbes present in the soil. Here, the organic carbon (%) showed a value of 0.12 % to maximum of 0.41%, which clearly indicates that, soil fertility has reduced. All these above said pollution problems are arises from the increased industrial process. For the future years the proper environmental management aspect should be taken care in the industrial areas by industries itself by making proper treatment and disposal of waste materials to the environment.

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