

**Full Length Research Paper****Evaluation of Heavy Metal Accumulation in Soil around Bhadravathi Taluk Shimoga District Karnataka****Neethu Patil, Ananth Nag.B* and E.T. Puttaiah*****Department of Civil Engineering, SJBIT, Kengeri, Bangalore-560060***Department of Environmental Science, Gulbarga-585106****Vice-Chancellor, Gulbarga University, Gulbarga- 585106****Corresponding Author: Ms. Neethu Patil*****Abstract**

Today, many developing countries are experiencing an Industrial Revolution of their own, capturing an ever-increasing share of industrial growth. The investigation deals with the characterization of Physico-Chemical properties of soil at Five different stations around Bhadravathi taluk. The emphasis was given to the heavy metal deposition / accumulation in the study area. The results of the study revealed heavy load of pollutants including Ni, Cu, Pb, and Cd metal ions from Irrigated areas of Bhadravathi taluk. The samples were collected from five Different stations. All the soil quality parameters were analyzed and heavy metals determined on Atomic Absorption Spectrophotometer (AAS). The result showed that the industrial area reported highly polluted and under the influence of anthropogenic activities, the high values were recorded during Pre-Monsoon season and comparatively less recorded during Monsoon and Post monsoon.

Key Words: - Atomic absorption spectroscopy (AAS), Heavy metals, Pollution, Soil contamination**Introduction**

Plants cannot usually access the total pool of a metal present in the growth substrate. Instead, that fraction of the metal which plants can absorb is known as the available or bioavailable fraction. Metals present in a soil can be divided into a number of fractions including; the soluble metal in the soil solution, metal-precipitates, metal sorbed to clays, hydrous oxides and organic matter, and metals within the matrix of soil minerals. These different fractions are all in dynamic equilibrium with each other (Norvell, 1991). However, while the soluble metal in the soil solution is directly available for plant uptake other soil metal pools are less available (Davis and Leckie, 1978; del Castillo *et al.*, 1993). For example, change in the concentration of metal in the matrix of soil minerals is slow relative to exchange and desorption reactions between clays, hydrous oxides, organic matter and the soil solution (Shuman, 1991; Whitehead, 2000).

Metals within the soil solution are the only soil fraction directly available for plant uptake (Fageria *et al.*, 1991; Marschner, 1995; Whitehead, 2000). Hence, factors which affect the concentration and speciation of metals in the soil solution will affect the bioavailability of metals to plants. Soil factors which have an affect on metal bioavailability include the total metal present in the soil, pH, clay and hydrous oxide content, organic matter and redox conditions.

Study area

Bhadravathi is a taluk head quarters located on the Banks of Bhadra River in Shimoga district of Karnataka state. It is located at 13052' North latitude and 75o40' East longitudes. The town is located at a distance of 270 km from Bengaluru and 20 km from Shimoga. The altitude of Bhadravathi is 548.70 m above MSL. It is the second largest city in Shimoga district with two major industrial units, viz. Vishweshwaraya Iron and Steel Ltd., (VISL) and Mysore paper mills. The population of the town as per 2001 is 1,60,392 and population in 2006 was 1,64,804, intermediate population in 2021 is 1,88,058 and the prospective population in 2036 is estimated to be 2,12,078. The area of Bhadravathi CMC is 67.08 sq. km.

Sampling Stations in and around Bhadravathi

Station Numbers	Sampling Sites
Station-1	Kadadakatte
Station-2	Seegebagi
Station-3	Holehonnur
Station-4	Kudli
Station-5	Agardhalli

Materials and Methods

Collection of Soil Samples

The soil samples from the agricultural fields wherein the UWW is used for irrigation is collected during the different seasons during 2009-2011. One time collection of various plant produces were collected in multiples from the UWW irrigated fields.

Analysis of Soil Samples

The samples were air dried and then ground in an agate mortar and pestle to pass through a 0.5mm stainless steel sieve. The powdered samples were stored in polythene covers at room temperature for further analysis of agronomical characteristics of soil samples and total metal concentration. The soil samples were analyzed for physico-chemical properties using standard analytical methods (APHA, 1998).

Organic matter

A known volume of soil sample is treated with an excess volume of standard potassium dichromate solution in the presence of concentrated H_2SO_4 . The soil sample is digested by the heat of dilution of sulphuric acid and organic carbon in the soil is thus oxidizing to carbon dioxide. The excess of potassium dichromate, unused in oxidation is titrated against standard solution of ferrous ammonium sulphate in the presence of fluoride or phosphoric acid and diphenylamine solution indicator. The organic carbon content of soil is calculated using the relationship of 1ml of 1N $K_2Cr_2O_7 = 0.003g$ of organic carbon. The % organic carbon is expressed in % organic matter by multiplying with the factor of organic matter percentage of carbon.

Collection of Plant Sample

Plant samples were collected, washed with distilled water and oven dried at the samples were powered by using Willey grinding mill and preserved further for analysis. Plant pre-treatment and chemical plant analyses Root tissues were washed with tap water and subsequently rinsed with de-ionized water. Large root and plant (stem, leave) tissue samples were shortened using a ceramic knife. Root, stem, leaves, husk and unpolished rice samples were dried at $70^\circ C$ for about 96 hr and ground to powder using a titanium-coated blade mill. Dried plant (except rice) material was digested with an acid mixture containing concentrated HNO_3 and $HClO_4$ mixed at a ratio of 5:1 (v:v) at $140^\circ C$ for 2 hr followed by a second step at $170^\circ C$ for 1 hr. After filtration (Whatman No. 42),

Analysis of Plant Samples

Micronutrients are estimated in plant digest obtained from dry ashing or from wet digestion by HNO_3 and $HClO_4$.

Principle - Atoms of metallic elements absorb energy when subjected to radiations of specific wavelength. The absorption of radiation is proportional to the concentration of atoms of that element. The AAS is a distinct advantage over flame emission spectroscopy because of wavelength of radiations and temperature of atoms. Chemical analysis of rice grains was done on unpolished or brown rice grain samples. Dried rice grain material was digested using concentrated HNO_3 at room temperature overnight. Subsequently, H_2O_2 was added followed by a second digestion in a microwave oven at $180^\circ C$ for 20 min.

Atomic Absorption Spectroscopy (AAS)

Heavy metals analyses were performed on an Atomic Absorption Spectrophotometer using acetylene gas as fuel (at 8 psi) and air as an oxidizer. Operational conditions were adjusted to yield optimal determination. The calibration curves were prepared separately for all the metals by running suitable concentrations of the standard solutions. Digested samples were aspirated into the fuel rich air-acetylene flame and the concentrations of the metals were determined from the calibration curves. Average values of three replicates were taken for each determination. Suitable blanks were also prepared and analysed in the same manner. The detection limits for iron (Fe), zinc (Zn), copper (Cu), nickel (Ni), chromium (Cr), lead (Pb) and cadmium (Cd) were 0.05, 0.008, 0.025, 0.04, 0.05, 0.06 and 0.009 ppm respectively.

Determination of Metals

Most metals are of geological origin, but contamination with them may be due to industrial, mining, agricultural, waste handling or other activity. Often a mixture of such metals occurs. The most common contaminants are cadmium, chromium, copper, lead, nickel, and zinc. In contrast to organic contaminants, metals cannot be degraded by microbes or plants. Thus the bioremediation strategy is based on the movement of metals, e.g., from soil to plants as in photo remediation, or on bioleaching. Some metals can undergo microbial oxidation-reduction or become methylated.

Soil characteristics

Brown clay loamy soil, Red soil, Sandy soil, Red sandy soil, Yellowish loamy soil, Lateritic soil, Mixed soils & black cotton soils are predominant in the region, which favours growth of cotton, paddy & oil seeds. Major crop grown in the town is sugarcane. The pH of soils is normal in Bhadravathi taluka. Soluble salt content is normal. Nitrogen and available P_2O_5 content is in medium range. The available K_2O content is high.

Geology

The predominant geological formations of Bhadravathi which is a part of Shimoga district are Quaternary (Alluvium), Dharwar super group (Ultra mafic complex, Grewake, Argoillite, Quartz Chlorite schist with orthoquartzite, Basal polymictconglomerate). Lower Precambrian (Metabasalt with thin Ironstone). Archaean formation (Granite Migmatites and Granodioritic to Tonolitic gneisses, Amphibolites and Pelitischists). Bhadravathi taluk falls under agriculture zone 7. Annual normal rainfall of the

district is 1805.5mm. South west monsoon starts normally from 2nd week of June and peak precipitation will occur during July and Augusts months.

Results and Discussion

The total metal concentration of a soil includes all fractions of a metal, from the readily available to the highly unavailable. Other soil factors, such as pH, organic matter, clay and redox conditions, determine the proportion of total metal which is in the soil solution. Hence, while total metal provides the maximum pool of metal in the soil, other factors have a greater importance in determining how much of this soil pool will be available to plants (Wolt, 1994). In addition, researchers have found that while total metal correlates with bioavailable soil pools of metal it is inadequate by itself to reflect bioavailability (Lexmond, 1980; Sauve *et al.*, 1996; McBride *et al.*, 1997; Sauve *et al.*, 1997; Peijnenburg *et al.*, 2000)

The inorganic and organic fertilizers (Fertilizer is a substance added to soil to improve plants growth and yield are the most important sources of heavy metals to agricultural soil include liming, sewage sludge, irrigation waters and pesticides, sources of heavy metals in the agricultural soils. Others, particularly fungicides, inorganic fertilizers and phosphate fertilizers have variable levels of Cd, Ni, Pb and Cu depending on their sources. Cadmium is of particular concern in plants since it accumulates in leaves at very high levels, which may be consumed by animals or human being. Cadmium enrichment also occurs due to the application of sewage sludge, manure and limes (Nriagu 1988 ; Yanqun *et al.* 2005). Although the levels of heavy metals in agricultural soil are very small, but repeated use of phosphate fertilizer and the long persistence, time for metals, there may be dangerously high accumulation of some metals.

Table 1: Heavy metal composition of typical uncontaminated soils and agricultural crops (Modified from Allaway 1968)

Heavy metals	Range in Soil (ppm d.wt)	Range in Agricultural crops (ppm d.wt)
Cd	0.01–0.7	0.2–0.8
Cu	2–100	4–15
Ni	10–00	1.0
Pb	2–200	0.1–10

Cadmium

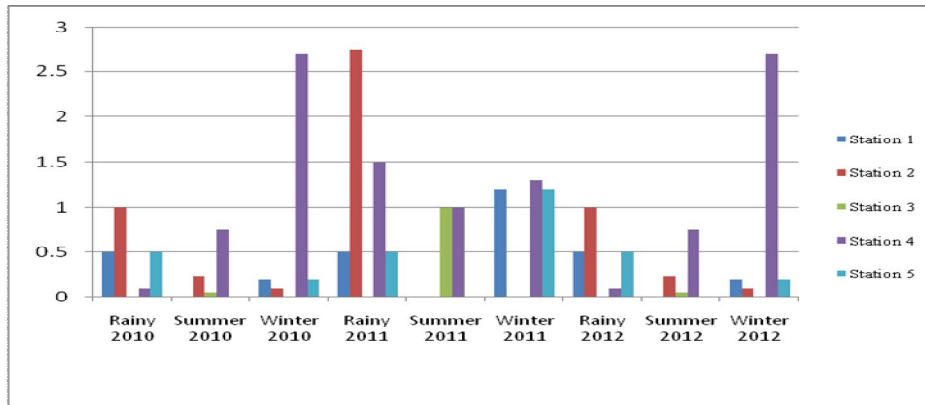
Cadmium is predominantly found in rechargeable batteries for domestic use (Ni-Cd batteries), in paints and photography. The main sources in urban wastewater are from diffuse sources such as food products, detergents and body care products, storm water [Ulmgren, 2000a and Ulmgren, 2000b]. Commercially Cadmium could originate from laundrettes, small electroplating and coating shops, plastic manufacture, and also used in alloys, solders, pigments, enamels, paints, photography, batteries, glazes, artisanal shops, engraving, and car repair shops. Data from ADEME [1995], estimated that worldwide, 16000 tonnes of cadmium were consumed each year; 50 - 60% of this in the manufacture of batteries and 20-25% in the production of coloured pigments. Among heavy metals, cadmium (Cd) is a non-essential and toxic metal, rapidly taken up by roots and accumulated in various plant tissues which hamper the crop growth and productivity worldwide. Plants employ various strategies to counteract the inhibitory effect of Cd, among which nutrient management is one of a possible way to overcome Cd toxicity. The heavy metal, Cd is commonly released into the arable soil from industrial processes and farming practices (Wagner 1993) and has been ranked No. 7 among the top 20 toxins (Yang *et al.* 2004).

The mean Cd concentration in seeds, shoots and roots was 0.034, 0.123 and 0.208 mg kg⁻¹ at the effluent irrigated locations, while the corresponding values were 0.013, 0.019 and 0.026 mg kg⁻¹ at canal irrigated sites and 0.010, 0.015 and 0.025 mg kg⁻¹ in tube well irrigated areas, respectively. Cadmium ranged from traces to 0.047 mg kg⁻¹ in seeds, 0.078 to 0.165 mg kg⁻¹ in shoots and 0.171 to 0.269 mg kg⁻¹ in roots receiving effluent for irrigation. Maximum concentration of Cd in seeds (0.047 mg kg⁻¹) and roots (0.296 mg kg⁻¹) was recorded at Uchkera and 0.165 mg kg⁻¹ in shoots at MW sampling site.

In view of its biological importance, soil samples are analyzed for the presence of cadmium at various sampling stations and results are given in Table 2. Cadmium is present in soil samples in negligible concentrations and in some stations, presence of cadmium is not recorded at all. Cadmium is found vary to from an low of 0.1mg/kg to 2.75 mg. Across the seasons, summer samples showed higher levels of cadmium.

Table 2: Cadmium in Soil (mg/kg)

	Rainy 2010	Summer 2010	Winter 2010	Rainy 2011	Summer 2011	Winter 2011	Rainy 2012	Summer 2012	Winter 2012
Station 1	0.5	Bdl	0.2	0.5	Bdl	1.2	0.5	Bdl	0.2
Station 2	1	0.23	0.1	2.75	Bdl	Bdl	1	0.23	0.1
Station 3	Bdl	0.05	Bdl	Bdl	1	Bdl	Bdl	0.05	Bdl
Station 4	0.1	0.75	2.7	1.5	1	1.3	0.1	0.75	2.7
Station 5	0.5	Bdl	0.2	0.5	Bdl	1.2	0.5	Bdl	0.2



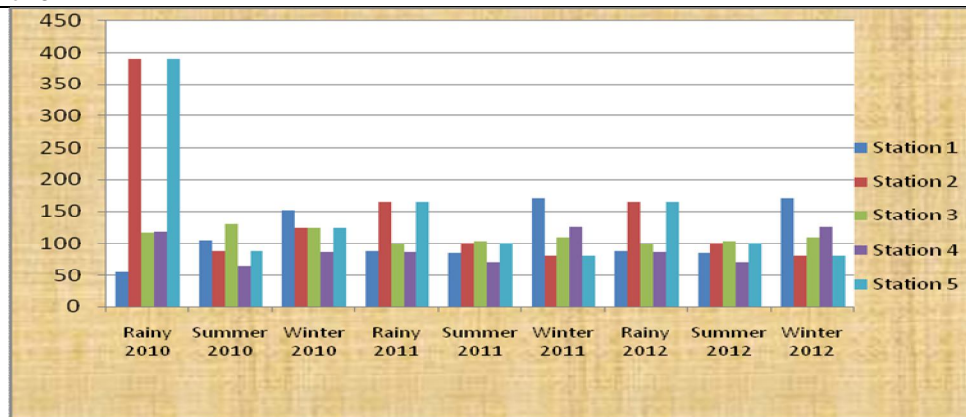
Copper

Copper comes mainly from corrosion and leaching of plumbing, fungicides (cuprous chloride), pigments, wood preservatives, larvicides (copper acetoarsenite) and antifouling paints. Commercially, Copper is used in electronics, plating, paper, textile, rubber, fungicides, printing, plastic, and brass and other alloy industries and it can also be emitted from various small commercial activities and warehouses, as well as buildings with commercial heating systems.

Copper concentration in samples of soil from various sampling stations is analyzed and results are given in Table 2. As can be seen from the table 3, the concentration of copper varied from 71mg to 391mg during the study period spanning over three years. The concentration in rainy season is found to be higher than the other two season. Summer season recorded lower values of copper. The highest concentration is recorded from Station 2 in rainy season and lowest concentration of copper is recorded from Station 4 during the summer season. Similar concentration levels are reported by Ramakrishnaiah and Somashekar (2002), Chopra and Pathak (2012).

Table 3: Copper in Soil (mg/kg)

	Rainy 2010	Summer 2010	Winter 2010	Rainy 2011	Summer 2011	Winter 2011	Rainy 2012	Summer 2012	Winter 2012
Station 1	55	106	151	88	85	170	88	85	170
Station 2	391	88	124	164	101	81	164	101	81
Station 3	117	130	124	100	104	110	100	104	110
Station 4	118	65	86	87	71	125	87	71	125
Station 5	391	88	124	164	101	81	164	101	81



Nickel

Nickel can be found in alloys used in food processing and sanitary installations; in rechargeable batteries (Ni-Cd), and protective coatings. Nickel is used in the production of alloys, electroplating, catalysts and nickel-cadmium batteries. The main emission of nickels are from corrosion of equipment from launderettes, small electroplating shops and jewellery shops, from old pigments and paints. It also occurs in used waters from hydrogenation of vegetable oils (catalysts).

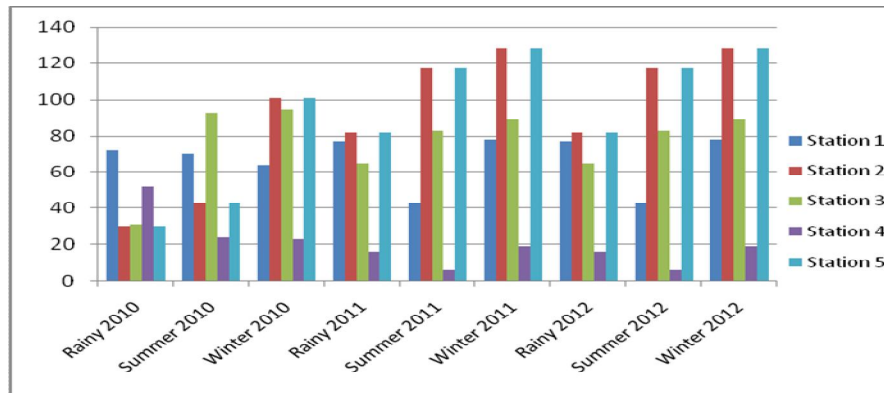
Nickel is considered to be a normal constituent of the diet and its compounds are generally recognized as safe when used as a direct ingredient in human food. little is known about the actual chemical forms of nickel in various foods or whether dietary nickel has distinct “organic” forms with enhanced bioavailability analogous to those of iron and chromium. Nickel levels in

foodstuffs generally range from less than 0.1 mg/kg to 0.5 mg/kg. A few foods may have obtained nickel during the manufacturing process but in most it apparently occurred naturally.

Soil samples are analyzed for the concentration of Nickel and results are given in Table 4. As can be seen from the table, the concentration of nickel in soil samples varied from 6mg to 128mg during the study period. Winter period samples are found to contain higher levels of nickel and rainy season samples recorded lower concentration of nickel. Across the sampling stations, station 2 is found to register higher values of nickel (in winter season). These observations are similar with the findings of R S Lokhande and N Kelkar (1999), Lokeshwari and Chandrappa (2006), Singh *et al* (2004).

Table 4: Nickel (mg/kg)

	Rainy 2010	Summer 2010	Winter 2010	Rainy 2011	Summer 2011	Winter 2011	Rainy 2012	Summer 2012	Winter 2012
Station 1	72	70	64	77	43	78	77	43	78
Station 2	30	43	101	82	117	128	82	117	128
Station 3	31	93	95	65	83	89	65	83	89
Station 4	52	24	23	16	6	19	16	6	19
Station 5	30	43	101	82	117	128	82	117	128



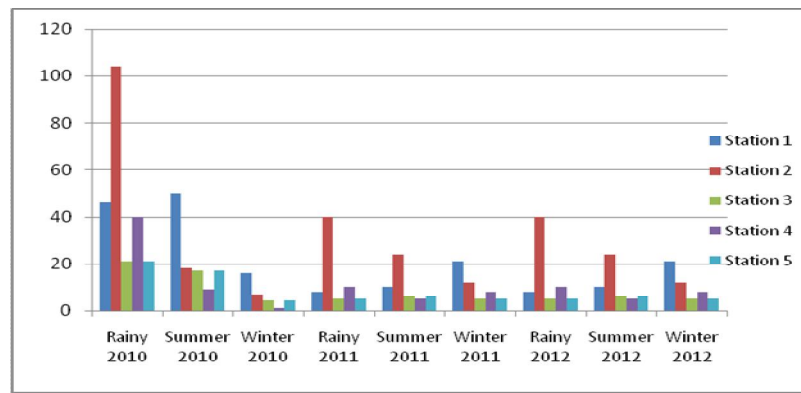
Lead

The main source of lead is from old lead piping in the water distribution system. It can be found in old paint pigments (as oxides, carbonates), solder, pool cue chalk (as carbonate), in certain cosmetics, glazes on ceramic dishes and porcelain (it is banned now for uses in glazes), also in "crystal glass". Lead has also been found in wines, possibly from the lead-tin capsules used on bottles and from old wine processing installations. Industrial Lead, as well as being used as a fuel additive (now greatly reduced or banned in the EU) it is also used in batteries, pigments, solder, roofing, cable covering, lead jointed waste pipes and PVC pipes (as an impurity), ammunition, chimney cases, fishing weights (in some countries), yacht keels and other sources.

Analytical results of soil for the heavy metal Lead are given in Table 5. The highest concentration recorded is 104mg in station 2 during the rainy season of 2010. However, all other samples recorded lower concentrations of lead during the study period. Therefore, this significantly higher concentration could be a random error. Otherwise the lead concentration varied from 1mg in winter season sample of 2010 to high level of 46mg in rainy season sample of year 2010. Across the seasons, the rainy season recorded higher values followed by summer season and then winter season. Chopra and Pathak (2012), Ramakrishnaiah and Somashekar (2002) reported similar variations in sewage irrigated soils.

Table 5: Concentration of Lead across Seasons (mg/kg)

	Rainy 2010	Summer 2010	Winter 2010	Rainy 2011	Summer 2011	Winter 2011	Rainy 2012	Summer 2012	Winter 2012
Station 1	46	50	16	8	10	21	8	10	21
Station 2	104	18	7	40	24	12	40	24	12
Station 3	21	17	4.5	5	6	5	5	6	5
Station 4	40	9	1	10	5	8	10	5	8
Station 5	21	17	4.5	5	6	5	5	6	5



Conclusion

Heavy metals accumulated in the surface soil layer may migrate into the deeper layers, and consequently pose a threat of groundwater contamination. The highest risk is related to the soil located under the constant pollution emitters such as sewage tanks. The speed and other parameters of pollutants transportation depend on the type of soil and its properties.

Heavy metals tend to accumulate in different organs and tissues depending on the type of element. This concerns plant tissues as well. Moreover, plants also make good bioindicators. This property may be used in the phytoremediation processes. Heavy metals also accumulate in soil, in the industrial areas.

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