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Metals in Environmental segments at Hirakud of Odisha, India

Mishra P.C.*, Dash A.K.[1] and Pradhan Khageswar[2]
*P.G.Department of Environmental Sciences, Sambalpur University, Jyoti Vihar, Orissa, INDIA
[1]Environmental Engineering, Department of Civil Engineering, ITER ,SOA University ,Bhubaneswar, INDIA
[2]NTPC ,Kaniha ,Angul ,Odisha, INDIA

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Abstract

Environmental segments in an industrial town in western Odisha were assessed in respect to seven metals including five heavy metals. The study includes horizontal distribution of the metals up to a distance of 2000 m from the source in four directions, east, west, north and south. Although the metal content was relatively negligible in aquatic environment, the soil and vegetable samples showed higher accumulation. The metals content in soil were 0.24 for Cd, 41.59 for Cr, 16253 for Fe, 22.08 for Pb, 47.06 for Zn, and 3.74 for As with 24.19, 4159.2, 34802.99, 1840.03, 3619.62 and 113.24 times magnification respectively over the respective value in water. The metal content in vegetation were 1.01 for Cd, 5.76 for Cr, 1096.80 for Fe, 4.01 for Pb, 104.88 for Zn and 4.2 for As with a magnification of 101.3, 575.9, 2348.61, 334.50, 8067.69, 127.30 respectively over the respective values in water. Flesh and Bone samples of amphibians also showed bioaccumulation in various range, in some cases more than the vegetation. The data reveals that although most of these pollutants are present in negligible quantity in water sources, the extent of biomagnification in quite visible particularly in respect to soil, vegetation, flesh and bone. All such contaminations may be due to the ongoing industrial activities because of continuous coal combustion in the thermal power plants and aluminium smelter operation as well as industries which were operating earlier but have been closed.

Key words: Smelter, power plant, Hirakud, metals, bioaccumulation.

Introduction

Aluminium Smelter and Thermal Power Plant of Hindalco Industries Limited are operating at Hirakud town of western Orissa. Hirakud smelter operating since 1958 is producing primary aluminium by Horizontal stud Soderberg Technology. Starting with a capacity of 10,000 T of aluminium per annum in 1959 it has increased its capacity to 30,000 T in 1996-97, 65,000 T in 2003 and 1,00,000 T in 2007. Hirakud Power Plant started with a capacity of 1 x 67.5 MW to run their smelter complex has now expanded to 200 MW. The coal consumption rate is 83.76 tons/hr. Coal requirement has been calculated by considering GCV of 3610 kcal/kg, sulphur content of 0.45 % and ash content of 40 %. Many small scale industries including rerolling mills were also operating in the town previously. Thus Hirakud Environment is expected to receive air pollutants in the form of emissions as well as from disposal of fly ash. Among environmental pollutants, metals are of particular concern, due to their potential toxic effects and ability to bioaccumulate in ecosystem[1,2]. Earlier studies have established metal contamination of crop field soil in near by zinc and lead smelter in Northen France[3,4]. The contamination up to a level of 1,132 mg kg^{-1} of Pb, 21 mg kg^{-1} of Cd and 2,167 mg kg^{-1} of Zn has been reported by these authors. Douay et al. have reported high (mg kg^{-1} soil) As (19-25.8) Cd (18.8-15.38), Cr (58.5-60.5), Cu (11.6-71.7), Pb (623-1118, Zn (3676.8-1340.6) in urban soil in an area of Northen France polluted by dust emission of two smelters[5]. Very few soils types of urban cities have been studied to assess contamination[6-10].

Material and Methods

Sixteen sampling sites were selected around the smelter and power plants i.e. four at each direction (East, West, North ant South) at a radius of 500m, 1000m, 1500m and 2000m (Figure1). Water (ground and surface water), soil and vegetation samples were collected in three seasons in a year from each sampling site. Amphibian and fish tissues were analyzed in one season only. A control site at an air distance of 5 Km was selected for sampling. Sodium and potassium (ppm) were estimated by flame photometer (Model- Systronics Flame Photometer-128). Heavy metals in water were analyzed using ion analyzer as per the methods prescribed by APHA[11]. For vegetation, animal and bone samples, analyses were performed after appropriate digestion. Statistical test was performed as per Snedecor and Cochran[12].

Results and Discussion

Metals in surface and ground water: Sodium: The salts of sodium are highly soluble in water and impact softness to water. The levels may vary from less than 1mg/L to more than 500mg/L. Domestic sewage is the important source of sodium to the freshwater. High concentration of sodium in the water affects the physical conditions of the soil[13]. Seasonal variations in sodium (ppm) in pond, well and stagnant water are presented in table.1.

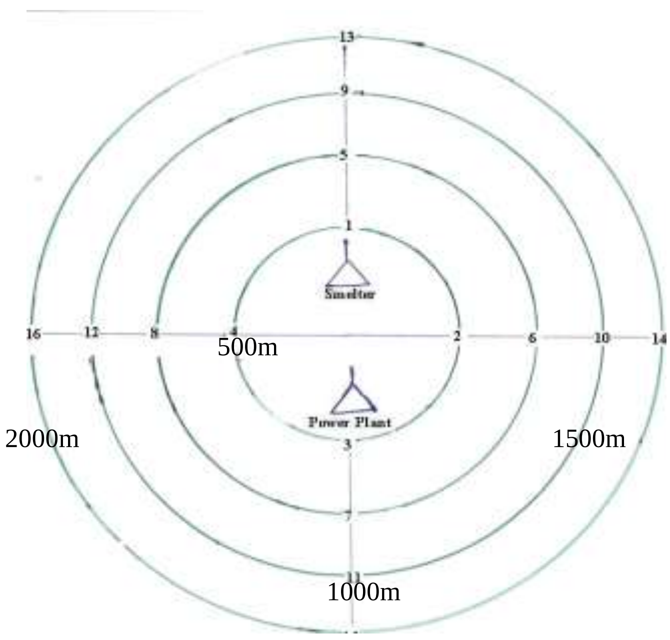

Figure -1
Sample collection sites around the smelter and power plant at Hirakud

The sodium content of pond water at control site of Burla was high (28.37) during summer and low (22.33) in rainy. On an average sodium content of pond was maximum during summer (31.96) followed by winter (28.76) and rainy (26.72). When the distance from the source of pollution is taken into consideration the maximum sodium content was observed in pond water at a distance of 0-500m in all the seasons. The test of analysis of variance indicated no significant difference in sodium content between the seasons but between the distances the difference is significant (F_2=9.0921, $p<0.05$).

The average sodium content of well water samples collected from different sampling points were 43.59, 29.54 and 27.27 in summer, winter and rainy respectively. Both control and experimental samples showed more sodium content in well water than pond water samples in respective seasons. In the well water samples the maximum values of sodium were observed at the distance 1500-2000m i.e. 47.47 in winter, 56.07 in summer and 43.68 in rainy season. In the control site, the sodium was high (41.30) during summer and low (32.83) in rainy. However the analysis of variance indicated significant difference of sodium in well water both between the seasons (F_1=46.768, $p<0.05$) and between the distances (F_2=37.002, $p<0.05$).

The stagnant water sample collected from crop fields varied from a minimum of 22.73 (rainy) to maximum of 77.63 (summer). Within 500m from the pollution source the maximum values of sodium were observed i.e. 36.84 (winter), 77.63 and 33.94 in winter, summer and rainy season respectively. On average sodium content of stagnant water was maximum during summer (45.49) and minimum in rainy (26.13).

The sodium of stagnant water in control site varied from 13.93 (rainy) to 15.35 (winter). The difference in sodium was only significant between the seasons (F_1=4.459, $p<0.05$).

Domestic sewage is the important sources of sodium to the fresh water. Sodium ions make the way in the water through weathering of rocks. Sodium is said to be utilized by blue green algae in high concentrations[14,15]. A thresh hold level of 4 mg/l is required for near optimal growth of several species[16]. High concentration of sodium in the water affects the physical conditions of the soil[13]. The threshold level of 400mg/L is required for near optimal growth of several species[16]. Seasonal lower values at all water sources during rainy due to the effect of dilution. The peak in winter may be due to microbial growth[17] mineralizing the decomposed organic matter and releasing the nutrients to the sediment, increasing sodium in to the nutrient pool there by making more sodium to solubilise.

Potassium: Potassium content in most drinking waters seldom reaches 20ppm. The concentration of potassium remains quite lower than the sodium, calcium and magnesium in an aquatic ecosystem. Although it is found in small amounts, it plays a vital role in the metabolism of fresh water environment. The seasonal variation of potassium (ppm) of pond, well and stagnant water samples are presented in table 2.

The average of potassium of pond water at Hirakud was high (5.37) during summer and low (4.06) in winter. The high values were observed in pond water at a distance 0-500m in winter (6.65) and rainy (5.49) where as in summer the highest value was 7.08 at 1500-2000m. In the control site, the potassium content of pond water was 7.50, 6.63 and 5.37 in summer, winter and rainy respectively. The analysis of variance indicated no significant difference in potassium content between the distances as well as between the seasons.

The potassium content of well water at control site of Burla was high (3.26) during rainy and low (2.14) in winter. On an average potassium content of well was maximum during winter (6.10) followed by summer (5.96) and rainy (5.59). The maximum values were found at a distance of 1500-2000m from the pollution source in all the seasons i.e. 8.20 (winter), 9.58 (summer) and 7.54 (rainy). The average potassium content of well water samples was more than pond water in respective seasons at Hirakud where as reverse was found at the control site. The analysis of variance showed no significant difference in potassium content of well water between the seasons, but the difference was significant between the distances (F_2=15.735, $p<0.05$). The potassium content of stagnant water samples were maximum at distance 0-500m in all seasons i.e. (5.71), summer (5.12) and rainy (5.41). The average potassium content was high

(4.51) during winter and low (3.90) in summer. The potassium of stagnant water samples at control site varied from 3.55 (rainy) to 7.37 (summer). The analysis of variance revealed no significant difference in potassium content between the seasons as well as between the distances.

Potassium is an essential nutritional element, but in excessive amounts it acts as a cathartic. Though potassium ranks seventh among the elements in the order of abundance, its concentration in most drinking water is trivial. Potassium in natural water is derived form weathering of rocks. The concentrations of potassium remain quite lower than the sodium, calcium and magnesium in aquatic ecosystems[18]. Although it is found in less quantity, it is also important in the ecology of blue-green algae[19,20]. Potassium has got a more or less similar chemistry like sodium and remains mostly in solution without undergoing any precipitation[18]. The low potassium content in rainy may be due to the effect of dilution. However high content in summer might be due to the fact that high evaporation tends to concentration.

Cadmium: Cadmium is insoluble in water but soluble in acids. It is an extremely toxic, non-essential metal, having no biochemical or nutritional function. The variations in cadmium content in water collected from both control and experimental sites are presented in table-3. Both in control and experimental site, the cadmium content is very low i.e. <0.01.

Cadmium salts are usually found in wastes from electroplating industries, textile printing, pigment works, lead mines and chemical industries. Cadmium is used as fungicides, insecticides, nematicides, polymerisation catalysts, pigments etc. and also as a contaminant of super phosphate fertilizers[21]. Cadmium has high toxic potential and minute quantities of cadmium are responsible for adverse renal arterial changes in human kidneys. Cadmium tends to concentrate in liver, kidneys, pancreas and thyroid of humans and animals. Once it enters the body it is likely to remain for long time[22,23,24,25]. Cadmium toxicity (50 mg/l) causes vomiting diarrohoea, abdominal pain, loss of bone, deformation, impaired kidneys functioning, impaired reproductive function, hypertension, tumor formation and teratogenic effects[26]. The WHO European Standard for cadmium in drinking water is 0.05mg/l.

Chromium: Chromium may exist in many different forms, though only trivalent (III) and hexavalent (VI) forms are considered to be biological importance. In aquatic environments, chromium (VI) is predominantly in soluble forms that may be stable enough to under go intra-media transport. Table-4 reveal the variation in chromium content in control as well as experimental sites. In both the sites the chromium content is very low i.e. <0.01.

Chromium salts impart colour to water. The salts of trivalent chromium are physiologically not harmful. It is reported that, the large doses of hexavalent chromium salts lead to corrosive effects in the intestinal tract and to nephritis[27]. It is one of the highly toxic metals responsible for various health hazards[23,25,24]. Chromium is hazardous and creates complication in the utilization of other nutrients by plants[28]. Chromium compounds are used extensively in industrial processes such as metal pickling, electroplating, aluminium anodizing, and leather tanning and in the manufacture of paints, dyes, paper, explosives and ceramics. In addition chromates are frequently added to cooling water for corrosion control. The chromium content in natural waters is usually very small. Elevated concentrations can result from mining and industrial processes[29]. The harmful effects of water borne chromium are digestive track cancer and sometimes lung cancer[26]. Chromium also discharged from electroplating units[30] galvanizing and tanning industries in river Rhine[31]. According to WHO International Standards for drinking water, the mandatory limit for hexavalent chromium is 0.05 mg/l.

Iron: Iron exists in the soluble ferrous state under reducing conditions. The oxides and hydroxides of iron and manganese constitute significant sinks of heavy metals into aquatic system. Table 5 reveals the variation in iron content in control as well as experimental sites.

The iron content in control sites at Burla varied from a minimum of 0.02 to a maximum of 0.05 mg/l. At Hirakud sites, the average iron content ranged from a minimum of 0.40 (pond) to 0.58 (well). In generals, the water samples collected from both the sites showed less than 1mg/l. The test of analysis of variance revealed no significant difference in iron content between the water types (pond, well and stagnant) where as the differences in distance from the source of pollution did contribute to difference in iron content.

Iron usually exists in natural water both in ferric and ferrous forms. Usually the ferric form is predominant in most of the natural water. On exposure to air or on addition of oxidants soluble ferrous iron is oxidized to insoluble hydrated ferric oxides rapidly by dissolved oxygen at neutral pH[11]. Under alkaline pH conditions of water, iron gets hydrolyzed[32] and forms insoluble hydroxide[33]. Ferric iron is only significantly soluble at pH less than 3.5. Iron was found harmful to the fishes even in low concentrations as ferric hydroxide, clogs up gills. At pH 6.5 to 7.5, 0.9 mg of iron per litre of water causes the death of fishes. The 1958 WHO international standards for drinking water specify a permissible limit of 0.3mg/l and an excessive limit of 1.0 mg/l iron. In the present study, iron was the most dominant metal throughout the study period. Highest mean concentration of iron and manganese was due to the iron-based industries. Similar sources of iron and manganese were reported by Prater[34].

Lead: When lead is released into the environment it has a long residence time compared to other and thus a potential threat to the environment. Table 6 presents the seasonal variation in lead content in water samples collected from both control and experimental sites. The average values in all sites are very negligible i.e. 0.01. The difference in lead content was not significant between the types of water, as well as distance.

Lead is not found in natural water supply. It may be due to the corrosion reactions and wastes contamination. Pollution due to lead is mainly attributed to the industrial effluents, coal combustion products and petroleum washes from various mechanical workshops garages, because lead is used as anti knocking compounds in petroleum[35] and also from domestic sewage discharge in the city[36,37]. Automobile exhaust also adds considerable amount of lead particulates to the river water[38] so also the traffic of diesel and petrol vehicles[39] and lead dust fall out. In aquatic ecosystems, the sediment is in a complex milieu with the overlying water. They affect water chemistry and are being affected by it[40]. Physico-chemical properties of a soil subsystem such as temperature, moisture content, pH, organic matter status and metal contents have direct or indirect impact on chemical, microbial and bio-chemical processes of sediment. Thus, a study on the physico-chemical properties of sediment gives an overview the functional dynamics of soil subsystem[41]. The organic pollutants, mineral particles and the metal oxides or hydroxide help in removing the dissolved contaminants from water but their concentration gradually build-up in the bottom sediment [42]. This could be visualized as sediment-water exchange between water and suspended particles in the water column and transfer of particles between sediment and water column[43]. Thus sediment is important indicators of anthropogenic activity and has a very important role to play the interaction between the pollutants and water. Water chemistry only assesses the impact of effluents at the time of sampling while the stream sediment geochemistry gives a cumulative assessment of the pollution in an aquatic ecosystem[42].

Zinc: Zinc occurs in the environment primarily in inorganic forms, with dissolved or as insoluble complexes and compounds. In the aquatic environment it will predominantly bind suspended material before finally accumulating in the sediment. Table 7 presents in variation in zinc content in soil in both control and experimental sites. In control site the zinc content is negligible (0.01). In experimental sites on an average it ranged from a minimum of 0.01 to a maximum of 0.02 (well). The analysis of variance reveals no significant difference in zinc content both between the water types and distances.

Zinc has no known adverse physiological effects upon human beings. In fact it is an essential and beneficial element in human nutrition. From aesthetic considerations however, high concentrations (above 5 mg/l) of zinc of domestic water are undesirable. A bitter astringent taste is produced by zinc. Concentration of zinc above 30 mg/l gives water milky appearance and causes a greasy film on boiling. It is now reported that even 5 mg/l can cause a greasy film on boiling. Zinc is commonly found in small quantities on domestic water supplies and industrial waters due to corrosion of galvanized iron and brass in condensing, cooling and distributing systems. Zinc may also enter into a water supply through the discharge of industrial effluent such as galvanizing water, zinc plating wastes, viscose rayon wastes and rubber factory waste[27]. A relatively higher concentration of zinc may be toxic to aquatic life[44]. The concentration of heavy metal is inversely proportional to pH and highest solubility occurs at pH 7.0[45]. At alkaline pH, Zn is precipitated from the water to the sediment[46].

Arsenic: Arsenic as a metalloid element can exist in several different valence states and as many different inorganic and organic compounds. In the aquatic environment, the transport and partitioning of arsenic is dependent on the forms of arsenic present.

Table - 1
Seasonal variation in sodium (ppm) in control and experimental site

Sampling Points	Pond			Well			Stagnant Water		
	Winter	Summer	Rainy	Winter	Summer	Rainy	Winter	Summer	Rainy
0-500m	43.45	52.79	32.72	24.31	41.69	23.31	36.84	77.63	33.94
500-1000m	27.42	21.78	25.23	23.29	38.32	21.82	23.65	42.39	22.73
1000-1500m	24.93	35.03	29.57	23.08	38.27	20.26	27.50	29.94	24.84
1500-2000m	19.26	18.25	19.37	47.47	56.07	43.68	24.26	32.00	22.99
G.Average	28.76	31.96	26.72	29.54	43.59	27.27	28.06	45.49	26.13
Control	25.78	28.37	22.33	34.55	41.30	32.83	15.35	14.52	13.93

Table - 2
Seasonal variation in potassium (ppm) in control and experimental site

Sampling Points	Pond			Well			Stagnant Water		
	Winter	Summer	Rainy	Winter	Summer	Rainy	Winter	Summer	Rainy
0-500m	6.65	5.67	5.49	4.92	3.63	5.11	5.71	5.12	5.41
500-1000m	4.22	2.90	4.98	5.43	3.63	4.42	5.24	3.75	5.00
1000-1500m	2.63	5.84	4.30	5.85	7.00	5.27	4.41	2.78	4.11
1500-2000m	2.74	7.08	3.99	8.20	9.58	7.54	2.70	3.93	2.84
G.Average	4.06	5.37	4.69	6.10	5.96	5.59	4.51	3.90	4.34
Control	6.63	7.50	5.37	2.14	2.25	3.26	4.94	7.37	3.55

Table - 3

Seasonal variation in cadmium (mg/l) in control and experimental site

Sampling Points	**Pond**	**Well**	**Stagnant Water**
0-500m	0.01	0.01	0.01
500-1000m	0.01	0.01	0.01
1000-1500m	0.01	0.01	0.01
1500-2000m	0.01	0.01	0.01
G.Average	0.01	0.01	0.01
Control	0.01	0.01	0.01

Table - 4

Seasonal variation in chromium (mg/l) in control and experimental site

Sampling Points	**Pond**	**Well**	**Stagnant Water**
0-500m	0.01	0.01	0.01
500-1000m	0.01	0.01	0.01
1000-1500m	0.01	0.01	0.01
1500-2000m	0.01	0.01	0.01
G.Average	0.01	0.01	0.01
Control	0.01	0.01	0.01

Table - 5

Seasonal variation in iron (mg/l) in control and experimental site

Sampling Points	**Pond**	**Well**	**Stagnant Water**
0-500m	0.50	0.80	0.70
500-1000m	0.60	0.80	0.20
1000-1500m	0.20	0.20	0.30
1500-2000m	0.30	0.50	0.50
G.Average	0.40	0.58	0.43
Control	0.05	0.02	0.04

Table - 6

Seasonal variation in lead (mg/l) in control and experimental site

Sampling Points	**Pond**	**Well**	**Stagnant Water**
0-500m	0.01	0.01	0.01
500-1000m	0.01	0.01	0.01
1000-1500m	0.01	0.02	0.02
1500-2000m	0.01	0.01	0.01
G.Average	0.01	0.01	0.01
Control	0.01	0.01	0.01

Table - 7

Seasonal variation in zinc (mg/l) in control and experimental site

Sampling Points	Pond	Well	Stagnant Water
0-500m	0.01	0.02	0.01
500-1000m	0.02	0.01	0.01
1000-1500m	0.01	0.02	0.01
1500-2000m	0.01	0.01	0.01
G.Average	0.01	0.02	0.01
Control	0.01	0.01	0.01

Table 8

Seasonal variation in arsenic (mg/l) in control and experimental site

Sampling Points	Pond	Well	Stagnant Water
0-500m	0.01	0.06	0.03
500-1000m	0.04	0.05	0.01
1000-1500m	0.03	0.03	0.09
1500-2000m	0.01	0.02	0.02
G.Average	0.02	0.04	0.04
Control	0.01	0.01	0.01

Table - 9
A comparative picture in physicochemical characteristics of water between control and experimental sites

Parameter	Type	Control	Experimental	t value
Sodium (mg/l)	Pond	25.49±0.55	28.50±23.20	NS
	Well	36.23±0.11	33.28±16.43	NS
	Stagnant	14.60±0.07	31.40±7.49	6.67
	Average	25.44±10.8	31.06±2.41	NS
Potassium (mg/l)	Pond	6.50±0.09	4.76±2.16	2.21
	Well	2.55±0.10	6.10±3.70	2.84
	Stagnant	5.29±0.07	4.41±1.38	NS
	Average	4.78±2.02	5.09±0.89	NS
Cadmium (mg/l)	Experimental	0.01	0.01	0.01
	Control	0.01	0.01	0.01
Chromium (mg/l)	Experimental	0.01	0.01	0.01
	Control	0.01	0.01	0.01
Iron (mg/l)	Experimental	0.40	0.58	0.43
	Control	0.05	0.02	0.04
Lead (mg/l)	Experimental	0.01	0.01	0.01
	Control	0.01	0.01	0.01
Zinc (mg/l)	Experimental	0.01	0.02	0.01
	Control	0.01	0.01	0.01
Arsenic (mg/l)	Experimental	0.02	0.04	0.04
	Control	0.01	0.01	0.01

NS-Not significant

Table 8 presents the variations in water arsenic content in control and experimental sites. In control site it was same i.e. 0.01 mg/l in all the type of water samples. In experimental sites, it varied from a minimum of 0.02 in pond water to a maximum of 0.04 in well and stagnant water samples. Test of analysis of variance reveals no significant difference in water arsenic content both between the different types of water samples as well as the distances.

However, most arsenic compounds can readily dissolve in water, and soluble forms may be leached by rainwater or snowmelt into surface waters or groundwater[47]. In the aquatic environment, the transport and partitioning of arsenic is dependent on the forms of arsenic present. It may be adsorbed from water on to sediments or soils, especially onto clays or compounds of iron, aluminum, manganese and calcium. Soluble forms may be carried long distances through rivers[48,49,47]. Arsenic is toxic to many plants, animals and humans, though lethal doses in animals are somewhat higher than the estimated lethal dose in humans[50,47]. In addition, bioconcentration of arsenic can occur in aquatic organisms, primarily in algae and lower invertebrates[51]. Most cases of human toxicity from arsenic have been associated with exposure to inorganic arsenic. Long-term low-level human exposures may lead to damage to the vascular system and can cause injury to the nervous system[47]. Of greater concern is the increased risk of carcinogenicity through prolonged ingestion of inorganic arsenic. As a result of its carcinogenicity, in 2002 the USEPA set a limit of 10 µg/l (0.01 mg/l) for arsenic in drinking water[52].

Table 9 presents a comparative view in the metal content of water between control and experimental sites. Student ‘t’ tests revealed no significance difference in average water quality relating to any of the water quality parameters mentioned above, although with regard to type of water (pond, well and stagnant) there may be some differences. With regard to heavy metals in water source, the experimental site showed negligible higher value (mg/l) in Iron (+ 0.433), Zinc (+0.003) and As (+0.023). The data indicate that the water quality at Hirakud almost remains uncontaminated and fit for use following prescribed guidelines for various usages.

Metals in Soil: Sodium: Sodium, a major macronutrient in soils, is encountered in its exchange state and as salts of $NaCO_3$, $NaHCO_3$, Na_2SO_4, NaCl and $NaNO_3$. Being highly soluble and mobile, it is removed from moist soils more readily. Table 10 presents in variations in soil sodium content in control and experimental sites. In control site it varied from a minimum of 263.0 in crop fields to a maximum of 1433.0 mg/kg in fallow land. In experimental sites, the variation was limited to a range of 603.9 (fallow)- 764.53 (grassland). Test of analysis of variance reveals a significant difference in soil sodium content between the distances only.

Sodium is easily accumulated in the zone of capillary moisture evaporation. Electronegative colloidal particles soils, when represented by humus substances and clay are capable or retaining cations of H, Al, Ca, Mg, K and Na hydrated ion (Na) when absorbed into colloidal particles are absorbed most intensively (Mn, Cu, Zn), they are not replaced by other ions and are resistant to washing[53]. In the present study high sodium content found in the Fallow land soil may be the available of unutilized sodium due to low microbial activity.

Potassium: Although weathering of rocks is a natural source of potassium to soil, the disposal of wastewater to terrestrial habitat significantly contribute K to soil. Seasonal variations in potassium content in soil collected from both control and experimental sites are presented in table 11. The soil potassium content in control site ranged from a minimum of 115.17 in grassland to a maximum of 360.0 mg/kg in cropfield soil. In experimental soil fallow land soil showed a higher range of potassium ranging from 438.93 to 564.21 with minimum in crop fields in the range of 214.12 to 360.23. The difference in K content in soil was not significant between seasons. In respect to distance, the difference was significant in grassland as well as fallow land.

Potassium is a naturally occurring element the major source of which is weathering of rocks. However the quantity increases with disposal of wastewater[40]. It is one of the macro-nutrients for living organisms and is readily retained by soil constituents[54]. Potassium is an important element in plant nutrition[53]. The micro-flora does have an influence on the level of available potassium. The quantity of potassium in soil fluctuates with the physical and chemical environment. In crop field soil, maximum potassium is due to the application of fertilizer. But in the experimental site high potassium content in fallow land soil may be the available of unutilized potassium.

Cadmium: Cadmium occurs in nature in association with zinc minerals. Growing plants acquire Zn and they also take up and concentrate Cd with the same biochemical set up. At the high levels, Cd causes kidney problems, anemia and bone marrow disorders. Table 12 reveals the variation in cadmium content (mg/kg) in soil of control as well as experimental sites. The cadmium content in control sites at Burla varied from a minimum of 0.11 (grassland) to a maximum of 0.24 (cropfield). At Hirakud sites, the cadmium content ranged from a minimum of 0.17 in fallow land to a maximum of 0.29 in grassland. The test of analysis of variance revealed no significant difference in cadmium content in soil both between the type of soil samples as well as the difference in distance from the source of pollution.

Cadmium is insoluble in water but soluble in acids. It is highly corrosion resistant and is used as a protective coating for iron steel and copper. It is generally applied in electroplating. It is used as fungicides, insecticides, nematicides, polymerization catalysts, pigments etc, and also as a contaminant of super phosphate fertilizers[21]. Cadmium is a well known carcinogen in human system[22] and is a highly toxic metal considered responsible for health hazards[23,25,24]. Cadmium has been implicated in human prostate carcinomo[55,24]. Cadmium toxicity (50mg) causes vomiting, diarrhea, abdominal pain, bone deformation, impaired kidney functioning, impaired reproductive function, hypertension, tumor formation and teratogenic effects[26]. Cadmium is not essential for plant growth but under certain conditions can accumulate in some plants to certain level that are hazardous.

Chromium: In soils, chromium (III) is relatively immobile due to its strong adsorption capacity on to soils. In contrast, chromium (VI) is highly unstable and mobile, since it is poorly adsorbed on to soils under natural conditions. The variations in chromium content (mg/kg) in soil of the controlled as well as the experimental sites are presented in table 13. In control sites the chromium content varied from a minimum of 24.60 in cropfield to a maximum of 29.75 mg/kg in grassland. In experimental sites the average chromium content varied from a minimum of 51.67 mg/kg in fallow land to a maximum of 50.64 in crop fields. The analysis of variance revealed no significant difference in chromium both between the type of soil samples and the different distances.

Chromium is one of the highly toxic metals responsible for various health hazards[23,25,24]. It is hazardous and creates complicating in the utilization of other nutrients by plants[28]. The chromium content in natural waters are usually very small. Elevated concentrations can result from mining and industrial processes[29]. It is absorbed through both gastrointestinal and respiratory tracts and necessary for glucose lipid metabolism and for utilization of amino acids in several systems. The harmful effects of water borne chromium are digestive tract cancer and sometimes lung cancer[26]. Chromium trioxide (CrO_3) is used in chrome plating, copper stripping, aluminium anodizing as a catalyst, refractory, inorganic synthesis and photography[21].

Iron: Iron is abundantly present in the rocks and soils in ferrous and ferric states. It is received by both plants and animals and has special role in the oxidation under anaerobic conditions. The variations in iron content (mg/kg) in soil collected from both control and experimental sites are presented in table 14. In control site, iron content ranged from a minimum of 12489 mg/kg in cropfield to a maximum of 16076 mg/kg in fallow land. In experimental sites on an average it ranged from a minimum of 14335 mg/kg in grassland to a maximum of 19831 mg/kg in cropfield. The analysis of variance reveals no significant difference in iron content both between the type of soils and the different distances.

Iron is abundantly present in the rocks and soils in ferrous and ferric states. It occurs in respiratory pigments required for elctron transfer processes in both plants and animals and has special role in the oxidation process as external electron accpetors under anaerobic condition[56]. Iron is allloyed with carbon to produce steel. The addition of their elements e.g. manganese, silicon, chromium, vanadium, tungsten, molybdenum, titanium, phosphorous, zirconium, aluminium, copper, cobalt and nickel impart special characteristics to the steel[21]. Iron might have entered the aqueous system from various metal industries. It is insoluble in ewater, iron oxide is soluble in hydrochloric acid. Iron is not toxic, yet its presence in excess interferes with certain chemical estimations[57]. It occurs in respiratory pigments, required for electron transfer processes in both plants and animals and has special role in the oxidation process as external electron acceptors under anaerobic condition[56].

Lead: Lead tends to accumulate in soils and sediments, due to low solubility; it can remain accessible to the food chain and to human metabolism far into the future. Lead has no known nutritional biochemical or physiological function. The variations in lead content (mg/kg) in soil in control and experimental sites are presented in table 15.

The lead content in soils of control site was maximum in crop field (12.65) and minimum in fallow land (12.30). In experimental sites it ranged from 15.48 in Crop field to 29.59 in fallow land. The difference in lead content in both between the type of soil and the different distances are not significant. Pollution due to lead is mainly attributed to the industrial effluents, coal combustion products and petroleum washed from various mechanical workshops garages, because lead is used as anti-knocking compounds in petroleum[35] and also from domestic sewage discharge in the city[36,37]. Automobile exhaust also add considerable amount of lead particulate to the river water[38] so also the traffic of diesel and petrol vehicles[58] and lead dust fall out. Lead is a minor element in the earth crust but is widely distributed in low concentrations in uncontaminated sedimentary rocks and soil. Significant contributions of lead come from the atmosphere. Lead in high doses has been recognized as cumulative general metabolic poison[55]. Lead is classified as highly toxic element in nature[23,25,24].

Zinc: In soils it often remains strongly absorbed and in aquatic environment it will predominantly bind to suspended material before finally accumulating in the sediment. Variations in zinc content (mg/kg) in the control and experimental sites are presented in table 16. The zinc content in soil varied from 25.95 in cropfield to 47.10 in fallow land in control sites. In experimental site the range was from 41.98 in cropfield to 52.86 in fallow land. The difference in zinc content was not significant in both type of soil and the distances.

Zinc is an abundant element in rocks and ores but it is present in natural water only as a minor constituent because of lack of solubility of the free metal and its oxides[59]. Zinc is essential in human metabolism. A deficiency of zinc in the diet of children lead to growth retardation. It is necessary for functioning of various enzyme systems including alkaline phosphatase, carbonic-anhydrase and alcohol dehydrogenase[26]. Zinc is an industrial pollutant of considerable magnitude. Domestic sewage also contains higher zinc contents[60]. Zinc has important role in plant nutrition, essential and stimulatory to the growth of a number of fungi and bacteria[54]. It is a very essential micronutrient. Zinc may be present in high concentration in the soil, due to disposal of the wastes form pharmaceuticals, galvanizing, paint, pigments, several insecticides and cosmetics etc[40].

Arsenic: When arsenic released to land, it is relatively immobile through binding to soil particles. It may adsorb from water on to sediments of soils, especially onto clays or compounds of iron, aluminium, manganese and calcium. Table 17 presents the variation in arsenic content (mg/kg) in soils of control and experimental sites. In control site, arsenic content ranged from a minimum of 1.80 in grassland to a maximum of 7.90 in cropfield. In experimental sites, it ranged from a minimum of 3.46 in fallow land to 4.09 in cropfield. Test of analysis of variance revealed no significance difference in between both the type of soil as well as the different distances.

Contamination of the environment with arsenic from both anthropogenic and natural sources has occurred in many parts of the world and is a global problem. The most important anthropogenic emission sources to the environment for metalloids are the non-ferrous mining and smelting industries and the burning of coal and petroleum. Gross contamination of surface soils and plants by dust and smelter fumes from copper and lead smelters have been reported; the nearest samples to mine industries present the highest concentrations but the levels decrease with increasing distance[61,62]. Slight contamination by these metalloids may also arise from the application of sewage sludge and fertilizer to soil. While a worldwide community of researchers work on arsenic speciation, transformation, transport, seasonal cycling, accumulation, geochemistry and toxicology, scarce information is available about the mobilization and transformation of antimony in the different compartments of the environment. Many arsenic compounds are toxic and potentially carcinogenic, which raises much concern from the environmental, occupational and nutritional points of view according to ATSDR (Agency for Toxic Substances and Disease Registry)[63]. In agricultural soils, toxic elements have received a great deal of attention because of their long term effects on crop yields, soil quality, accumulation in crop tissue and potential source of risk to animals, farmer and consumer. But the mobility of trace elements, their bioavailability and related eco-toxicity to plants depend strongly on their specific chemical forms or types of binding rather than the total element contents. The physico-chemical characteristics of soils result in important control of the adsorptive capacities and therefore will affect the availability of elements to plants[64]. But these interactions vary with the element, soil type and the form in which the metal or metalloid itself is present or enters the soil[65,66].

Table - 10

Seasonal variation in sodium (mg/kg) of soil in control and experimental site

Sampling Points	Crop field			Grass land			Fallow land		
	Winter	Summer	Rainy	Winter	Summer	Rainy	Winter	Summer	Rainy
0-500m	966.83	736.00	958.43	643.68	651.75	603.49	349.86	364.41	324.22
500-1000m	758.66	641.03	659.12	708.18	594.54	594.90	799.10	392.88	538.18
1000-1500m	705.31	759.99	659.21	761.58	867.54	749.70	685.10	763.17	609.05
1500-2000m	584.19	526.02	372.08	843.74	944.29	767.78	1140.33	983.75	944.16
G.Average	753.75	665.76	662.21	739.29	764.53	678.97	743.60	626.05	603.90
Control	342.53	263.00	284.40	355.70	253.33	320.93	1060.55	1433.00	945.37

Table - 11

Seasonal variation in potassium (mg/kg) of soil in control and experimental site

Sampling Points	Crop field			Grass land			Fallow land		
	Winter	Summer	Rainy	Winter	Summer	Rainy	Winter	Summer	Rainy
0-500m	689.50	294.43	279.48	298.18	797.29	430.46	275.53	286.82	261.88
500-1000m	224.94	196.51	239.20	523.15	498.41	353.85	347.33	398.44	370.12
1000-1500m	270.15	158.23	242.35	210.40	261.73	210.26	256.66	368.14	335.32
1500-2000m	256.32	207.32	150.59	272.03	309.91	260.19	876.18	1203.44	1032.58
G.Average	360.23	214.12	227.91	325.94	466.83	313.69	438.93	564.21	499.97
Control	360.00	243.37	281.70	273.77	238.34	115.17	342.13	203.63	297.43

Table - 12

Seasonal variation in Cadmium (mg/kg) of soil in control and experimental site

Sampling Points	Crop field	Grassland	Fallow land
0-500m	0.21	0.13	0.15
500-1000m	0.30	0.28	0.18
1000-1500m	0.17	0.26	0.19
1500-2000m	0.07	0.31	0.16
G.Average	0.27	0.29	0.17
Control	0.24	0.11	0.21

Table - 13

Seasonal variation in Chromium (mg/kg) of soil in control and experimental site

Sampling Points	Crop field	Grassland	Fallow land
0-500m	28.40	38.80	23.05
500-1000m	47.67	38.68	32.99
1000-1500m	67.90	30.60	31.65
1500-2000m	40.10	39.10	41.50
G.Average	50.64	42.47	31.67
Control	24.60	29.75	29.20

Table - 14

Seasonal variation in iron (mg/kg) of soil in control and experimental site

Sampling Points	Crop field	Grassland	Fallow land
0-500m	13484	14801	12063
500-1000m	19573	13253	15915
1000-1500m	19359	12149	11140
1500-2000m	19208	16418	12701
G.Average	19831	14335	14594
Control	12489	15187	16076

Table - 15

Seasonal variation in lead (mg/kg) of soil in control and experimental site

Sampling Points	Crop field	Grassland	Fallow land
0-500m	10.55	49.25	40.70
500-1000m	15.59	13.88	12.90
1000-1500m	23.25	20.25	53.45
1500-2000m	25.40	17.90	81.90
G.Average	15.48	21.19	29.59
Control	12.65	12.55	12.30

Table - 16

Seasonal variation in zinc (mg/kg) of soil in control and experimental site

Sampling Points	Crop field	Grassland	Fallow land
0-500m	21.90	73.65	59.75
500-1000m	56.83	42.43	52.58
1000-1500m	33.47	28.60	64.70
1500-2000m	68.10	31.60	98.50
G.Average	41.98	46.32	52.86
Control	25.95	42.60	47.10

Table - 17

Seasonal variation in arsenic (mg/kg) of soil in control and experimental site

Sampling Points	Crop field	Grassland	Fallow land
0-500m	2.60	5.25	4.25
500-1000m	4.01	1.81	3.52
1000-1500m	8.70	5.65	6.05
1500-2000m	5.20	4.70	4.40
G.Average	4.09	3.66	3.46
Control	7.90	1.80	2.80

Table – 18a

A comparative picture in physicochemical characteristics of soil between control and experimental sites

Parameter	Type	Control	Experimental	't' value
Sodium (mg/kg)	Crop field	296.64±1.47	704.50±476.62	2.54
	Grassland	309.99±2.99	727.62±501.06	2.58
	Fallow land	1146.31±5.77	657.85±449.44	3.04
	Average	584.31±486.74	696.65±35.53	NS
Potassium (mg/kg)	Crop field	295.02±0.61	266.73±177.84	NS
	Grassland	209.09±0.57	368.82±334.09	1.85
	Fallow land	281.06±1.99	501.04±418.04	NS
	Average	261.73±46.12	378.86±117.48	3.80

Table 18.b

Parameter	Type	Crop field	Grass land	Fallow Land	Average	Standard Deviation
Cadmium (mg/kg)	Experimental	0.27	0.28	0.17	0.24	0.06
	Control	0.24	0.11	0.21	0.19	0.07
Chromium (mg/kg)	Experimental	50.64	42.47	31.67	41.59	9.52
	Control	24.60	29.75	29.20	27.85	2.83
Iron (mg/kg)	Experimental	19831	14335	14594	16253.33	3101.06
	Control	12489	15187	16076	14584.00	1867.98
Lead (mg/kg)	Experimental	15.48	21.18	29.59	22.08	7.09
	Control	12.65	12.55	12.30	12.50	0.18
Zinc (mg/kg)	Experimental	41.98	46.32	52.86	47.06	5.48
	Control	25.95	42.60	47.10	38.55	11.14
Arsenic (mg/kg)	Experimental	4.09	3.66	3.46	3.74	0.32
	Control	7.90	1.80	2.80	4.17	3.27

Table 18a and b presents a comparative view in the quality of soil between control and experimental sites. Students't' tests reveal significant difference in potassium only. With regard to type of soil (cropfield, grassland and fallow land) there may be some differences. With regard to heavy metals in soil, the experimental site showed much higher value (mg/kg) in cadmium (+0.06), chromium (+13.74), iron (+1669.33), lead (+9.58) and zinc (+8.51).

Metals in vegetation: Cadmium: By different means the cadmium gets incorporated into the soil, since some of them are washed in with the rain. They also get incorporated into the food chain and create serious problems for the biological systems. Table 19 shows the variation in cadmium content (mg/kg) in vegetation of control and experimental sites. The cadmium content varied from a minimum of 0.07 mg/kg in grasses to a maximum of 0.30 in plant leaf in control sites. In experimental sites, the cadmium content varied from a minimum 0.33 in grasses to a maximum of 2.04 in crop leaf. However, the difference in cadmium content was not significant between different type of vegetation as well as the different distances from the source of pollution.

Cadmium is a rare metal, found naturally as very low concentrations. However, as anthropogenic emissions far exceed those from natural sources, elevations above these natural, background levels, are often found. In soils, the agricultural use of phosphate fertilizers or cadmium-containing sewage sludge can dramatically increase cadmium concentrations.

Furthermore, cadmium is readily available for uptake in grain, rice and vegetables, and there is a clear association between the cadmium concentration in soil and the plants grown on that soil[67,68,69]. When present in a bioavailable form, both aquatic and terrestrial organisms are known to bioaccumulate cadmium. Studies have shown accumulation in aquatic animals at concentrations hundreds to thousands of times higher than in the water[70]. With reported bioconcentration factors ranging from 113 to 18,000 for invertebrates and from 3 to 2,213 for fish. Cadmium accumulation has also been reported in grasses and food crops, and in earthworms, poultry, cattle, horses, and wildlife[70,69]. Evidence for biomagnification is inconclusive. However, uptake of cadmium from soil by feed crops may result in high levels of cadmium in beef and poultry (especially in the liver and kidneys). And this accumulation of cadmium in the food chain has important implications for human exposure, whether or not significant biomagnification occurs[70]. Cadmium has no biochemical or nutritional function, and it is highly toxic to both plants and animals[70,69,49].

Chromium: The greatest chromium toxicity risk to plants is in acidic, sandy soils with low organic content. In plants chromium interferes with uptake, translocation and accumulation by plants of calcium, potassium, magnesium, phosphorous, boron, copper and aggravates iron deficiency chlorosis by interfering with iron metabolism. Table 20 reveals the variation in chromium content (mg/kg) in control as well as experimental sites.

The chromium content in control sites at Burla varied from a minimum of 1.45 mg/kg in plant leaf to a maximum of 21.25 in crop vegetation. At Hirakud sites, the chromium content ranged from a minimum of 0.12 in plant leaf to a maximum of 8.82 in crop vegetation. In both the control and experimental sites, the crop vegetations contain much higher than the grasses and plant leafs. The analysis of variance revealed a significant difference in chromium content both between the different types of vegetation and between the different distances from the source of pollution.

Chromium can exist in many different forms, though only the trivalent (III) and hexavalent (VI) forms are of biological importance. In general, chromium (VI) is the predominantly soluble form in aquatic environments[47]. Both chromium (III) and chromium (VI) can accumulate in many aquatic species[71]. Whilst chromium (III) is an essential trace element in animals, chromium (VI) is non-essential and toxic at low concentrations[47,72]. Chromium (VI) compounds are corrosive, and allergic skin reactions readily occur following exposure. Damage to the kidney and liver has also been reported[47]. Hexavalent chromium (VI) has been classified by The International Agency for Research on Cancer as a known carcinogen[73]. Also, the US Department of Health and Human Services in its 9th Report on Carcinogens, lists classifies chromium (VI) compounds as “known to be human carcinogens”[74].

Iron: It is non-toxic, yet its presence in excess interferes with certain chemical estimations. It occurs in respiratory pigments required for electron transfer process in both plants and animals and has special role in the oxidation process as external acceptor under anaerobic conditions. The variations in iron content (mg/kg) in vegetation in the control as well as the experimental sites are presented in table 21.

In control site, the iron content varied from a minimum of 241.0 mg/kg in plant leaf to a maximum of 2065.0 mg/kg in grasses. The same trend was found in the experimental samples i.e. the minimum of 413.0 in plant leaf and maximum of 1487.0 in grasses. In different type of vegetations the difference in iron content was significant.

Lead: Many plants and animals can accumulate lead from water, soil and sediments, with organic forms being more easily absorbed than inorganic. It can remain accessible to the food chain and to human metabolism. The variations in lead content (mg/kg) in soil collected from both control and experimental sites are presented in table 22. In control site, lead content ranged from a minimum of 0.70 mg/kg in grass to a maximum of 5.450 in plant leaf. In experimental sites on an average it raged from a minimum of 2.40 in crop vegetation to a maximum of 5.067 in grasses. The analysis of variance reveals no significant difference in lead content between the different types of vegetation as well as the different distances.

Lead is present in uncontaminated aquatic and terrestrial ecosystems at relatively low levels. However, as anthropogenic emissions far exceed those from natural sources, elevations above these natural, background concentrations are often found. When lead is released into the environment it has a long residence time compared with most pollutants. As a result, it tends to accumulate in soils and sediments. Where, due to low solubility, it can remain accessible to the food chain and to human metabolism far into the future[75,70,49]. However, as with all metals, speciation is critical when assessing bioavailability and the potential threat to the environment. Two oxidation states of lead, +2 and +4, are stable, but the environmental chemistry is dominated by the Pb+2 ion, its compounds and complexes. In general the free +2 ion is more toxic than inorganic complexes, and therefore any factor, which increases complexation and decreases the concentration of the free ion is bound to affect lead toxicity adversely. Toxic organic forms of lead are also present in the environment. From direct inputs (manufacture, transport and storage of leaded petrol and consequent car exhaust emissions) and the possible chemical / biological methylation of inorganic lead in anaerobic sediments[76,77]. Plants and animals can accumulate lead from water, soil and sediment, with organic forms being more easily absorbed than inorganic. In general, the highest lead concentrations are found in aquatic and terrestrial organisms that live near to lead mining, smelting, and refining facilities; storage battery recycling plants; areas affected by high automobile and truck traffic; sewage sludge and spoil disposal areas; sites where dredging has occurred; areas of heavy hunting (spent lead shot); and in urban and industrialized areas[70].

Zinc: Zinc is an essential element, present in the tissue of animals and plants even at normal, ambient concentrations. However, if plants and animals are exposed to high concentrations of bioavailable zinc, significant bioaccumulation can results, with possible toxic effects. Table 23 presents the variations in zinc content (mg/kg) of vegetation samples collected from both the control and experimental sites.

Both in control and experimental sites, the zinc content is low in crop vegetation i.e. 25.45 in control and 55.24 mg/kg in experimental. In plant leaf its concentration is much higher 85.00 in control and 150.55 in experimental. Test of analysis of variance reveals no significant difference in vegetation zinc content in between the type of vegetation as well as the different distances.

Zinc is an essential element, present in the tissues of animals and plants even at normal, ambient concentrations. However, if plants and animals are exposed to high concentrations of bioavailable zinc, significant bioaccumulation can results with possible toxic effects[47]. Plants studies have shown that although an essential element for higher plants, in elevated concentrations zinc is considered phytotoxic, directly affecting crop yield and soil fertility. Soil concentrations ranging from 70-400 mg/kg are classified as critical, above which toxicity is considered likely[49].

intake of inorganic forms of arsenic. The variation in arsenic content in vegetation in control and experimental sites are presented in table 24.

The arsenic content in control site was minimum in crop vegetation (2.45 mg/kg) and maximum in plant leafs (4.40 mg/kg). In experimental site, the reverse was found i.e. minimum (2.47) in plant leaf and maximum (5.38) in crop vegetation. Test of analysis of variance did not revealed any significant difference in arsenic content in both between the different type of vegetations and the different distances from the source of pollution.

Arsenic is toxic to many plants, animals and humans, though lethal doses in animals are somewhat higher than the estimated lethal dose in humans[50,47]. In addition, bioconcentration of arsenic can occur in aquatic organisms, primarily in algae and lower invertebrates[51]. Most cases of human toxicity from arsenic have been associated with exposure to inorganic arsenic. Long-term low-level human exposures may lead to damage to the vascular system and can cause injury to the nervous system[47]. Of greater concern is the increased risk of carcinogenicity through prolonged ingestion of inorganic arsenic. Arsenic and certain arsenic compounds are known to be carcinogenic to humans by both the oral and inhalation routes. Arsenic is toxic to many plants, animals and humans. Most cases of human toxicity have been associated with the intake of inorganic forms of arsenic[78,47]. The lethal dose for humans has been estimated to be 70-180 mg, or 1-3 mg per kg body weight[47]. Lethal doses in animals are somewhat higher than the estimated lethal dose in humans[50].

Table 25 presents a comparative view on accumulation of heavy metal content between control and experimental site. The experimental site showed relatively higher value (mg/kg) cadmium (+0.85), iron (+205.33), lead (+1.37), zinc (+58.62) and arsenic (+0.68) over the control site.

Table 26 shows the bioaccumulation and the extent of biomagnification of heavy metals in relation to their availability in water source.

Table - 19

Variation in cadmium (mg/kg) content in crop, grass and leaf in control and experimental site

Sampling Points	Crop	Grass	Leaf
0-500m	0.20	0.14	0.20
500-1000m	2.09	0.32	0.77
1000-1500m	0.10	0.50	0.13
1500-2000m	0.12	0.08	1.10
G.Average	2.04	0.33	0.68
Control	0.13	0.07	0.30

Table - 20

Variation in chromium (mg/kg) content in crop, grass and leaf in control and experimental site

Sampling Points	Crop	Grass	Leaf
0-500m	8.10	9.15	2.50
500-1000m	10.18	8.21	2.95
1000-1500m	7.55	6.00	1.35
1500-2000m	0.90	2.40	0.60
G.Average	8.82	8.33	0.12
Control	21.25	18.50	1.45

Table - 21

Variation in iron (mg/kg) content in crop, grass and leaf in control and experimental site

Sampling Points	Crop	Grass	Leaf
0-500m	1216	1117	481
500-1000m	1797	1737	603
1000-1500m	494	377	162
1500-2000m	397	1074	308
G.Average	1391	1487	413
Control	369	2065	241

Table -22

Variation in lead (mg/kg) content in crop, grass and leaf in control and experimental site

Sampling Points	Crop	Grass	Leaf
0-500m	4.60	4.70	3.25
500-1000m	1.28	6.45	4.73
1000-1500m	2.80	4.00	4.30
1500-2000m	4.50	2.40	15.60
G.Average	2.40	5.07	4.58
Control	1.80	0.70	5.45

Table - 23

Variation in Zinc (mg/kg) content in crop, grass and leaf in control and experimental site

Sampling Points	Crop	Grass	Leaf
0-500m	17.50	295.30	74.10
500-1000m	54.35	69.43	146.73
1000-1500m	17.40	27.95	190.30
1500-2000m	30.80	94.40	447.00
G.Average	55.21	108.88	150.55
Control	25.45	28.35	85.00

Table - 24

Variation in arsenic (mg/kg) content in crop, grass and leaf in control and experimental site

Sampling Points	Crop	Grass	Leaf
0-500m	4.38	0.80	2.60
500-1000m	4.80	5.40	2.35
1000-1500m	6.10	9.70	2.70
1500-2000m	7.40	3.10	3.70
G.Average	5.38	4.75	2.48
Control	2.45	3.70	4.40

Table - 25
Heavy metal content in vegetation between control and experimental sites

Parameter	Type	Crop	Grass	Leaf	Average	Standard Deviation
Cadmium (mg/kg)	Experimental	2.04	0.33	0.677	1.01	0.90
	Control	0.13	0.07	0.3	0.17	0.12
Chromium (mg/kg)	Experimental	8.82	8.33	0.12	5.76	4.89
	Control	21.25	18.50	1.45	13.73	10.73
Iron (mg/kg)	Experimental	1391	1487	413	1097.0	594.30
	Control	369	2065	241	891.67	1018.15
Lead (mg/kg)	Experimental	2.40	5.067	4.575	4.01	1.419
	Control	1.80	0.7	5.45	2.65	2.48
Zinc (mg/kg)	Experimental	55.21	108.88	150.55	104.88	47.80
	Control	25.45	28.35	85.00	46.27	33.58
Arsenic (mg/kg)	Experimental	5.38	4.75	2.48	4.20	1.53
	Control	2.45	3.70	4.40	3.52	0.99

Table 26
Bioaccumulation and Biomagnification of metals in vegetation, animal flesh and bone

Parameter	Water	Soil	Vegetation	Flesh	Bone
Cadmium (mg/kg)	0.01	0.24 (24.19)	1.01 (101.3)	0.01 (1.0)	0.4 (40.0)
Chromium (mg/kg)	0.01	41.59 (4159.2)	5.76 (575.9)	0.01 (1.0)	2.40 (240.0)
Iron (mg/kg)	0.467	16253 (34802.99)	1096.80 (2348.61)	111.60 (238.97)	1078 (2308.35)
Lead (mg/kg)	0.012	22.08 (1840.33)	4.01 (334.50)	2.55 (212.50)	16.50 (1375.0)
Zinc (mg/kg)	0.013	47.06 (3619.62)	104.88 (8067.69)	68.7 (5284.62)	704 (54153.85)
Arsenic (mg/kg)	0.033	3.74 (113.24)	4.20 (127.30)	3.40 (103.03)	12.24 (370.90)

(Numbers within parentheses are the unit of magnification)

The data reveals that although most of these pollutants are present in negligible quantity in water sources, the extent of biomagnification in quite visible particularly in respect to soil, vegetation, flesh and bone. Analysis of trace elements in soil, tomato leaves and fruit samples collected from the vicinity of a paint industry in Nigeria[79] has also indicated the mobility of lead, copper, nickel, zinc, manganese and iron from soil to plants. Reports on the bioaccumulation of Mn, Pb, Cd, Cr, Ni and Cu in gills, muscle and tails of three fish species collected from river Nigeria are also available[80].

Conclusion

The presented data reveals no visible accumulation of metals in the water sources and the values are within the permissible limit. The experimental sites showed higher level of all metals compared to control sites possible due to a long exposure period to industrial emissions. Arsenic, the metalloid was an exception showing lower values in experimental site than control. Analysis of metal content in vegetation (crop, grass and tree leaf and their biomagnifications level shows biomagnifications in vegetation over the metal content in water extending up to 2349 times for iron and d minimum of 101 times for cadmium. Even analysis of flesh and bones of dead animals reveals biomagnifications indicating the metals as a potential threat in the future unless proper strategies are undertaken to mitigate the mobility of metals to the environment.

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References

1. Censi P., Spoto S.E., Saiano F.,Sprovieri M., Mazzola S. and Nardone G., Heavy metals in coastal water system: A case study from the northenwestern Golf of Thailand, *Chemosphere*, **64**, 1167-1176 **(2006)**

2. Fernandes C., Fontainhas-Fernandes A., Carbral D. and Salgado M.A., Heavy metals in water , sediments and tissues of *Liza saliens* from Esmoriz –Paramos lagoon, Portugal, *Environ. Moint, Assess*, **136,** 267-275 **(2008)**

3. Frangi J.P. and Richard D., Heavy metals soil pollution cartography in northen France, *Scince of the Total Environment*, **205**, 71-79 **(1997)**

4. Godin P., Feinberg M. and Dueauze C., Modelling of soil contamination by air-borne lead and cadmium around several emission sources, *Environmental Pollution*, **10(B)**, 97-114 **(1985)**

5. Douay F., Pruvot C., Roussel H., Ciesielski H., Fourrier H., Proix N. and Wateriot C., Contamination of urban Soils in an area of Northen France Polluted by dust emissions of two smelters, *Water Air Soil Pollu.*, **188**, 247-260 **(2008)**

6. Chen T.B., Wong J.W.C., Zhou H.Y. and Wong M.H., Assessment of trace metal distribution and contamination in surface soils of HongKong Environmental pollution, **96**, 61-68 **(1997)**

7. Brike M., and Rauch U., Urban Geochemistry: Investigations in the Berlin Metropolitan Area, *Environmental Geochemistry and Health*, **22**, 233-248 **(2000)**

8. Linde M., Bengtsson H. and Oborn I., Contamination of Pools of heavy metals in urban soils in Stockholm, Sweden. *Water, Air and Soils pollution :Foucs*, **1**, 83-101 **(2001)**

9. Manta D.S., Angelone M., Bellance A., Neri R. and Sprovieri M., Heavy metals in urban soils, A case study from the city of Palermo (Sicily), Italy, *Science of the Total Environment*, **300**,229-243 **(2002)**

10. Imperato M., Adamo P., Naimo D., Arienzo M., Stanzione D. and Violente P., Spatial distribution of heavy metals in urban soil of Neples city(Italy), *Environmental Pollution*, **124**, 247-256 **(2003)**

11. APHA, Standards methods for the examination of water and wastewater, 18th ED., APHA- AWWA-WPCP, American Publish Health Association, Washington, D.C., (**1991)**

12. Snedecor G.W and Cochran W.G., Statistical Methods, Oxford and IBH, Calcutta **(1967)**

13. Rawal N.C., Quality of river water of India, Proceedings of 47th Research Session of CSIB, Hubli, Dharwad, Karnataka, **2,** 139-160 **(1978)**

14. Gerloff G.C., Fitzgerald G.P. and Smog F., The mineral nutrition of microcystis aeruginosa, *Amer. J. Bot*. **39,** 26-33 **(1952)**

15. Provasoli L., Algal nutrition and eutrophication, In Eutrophication: Causes, Consequences, Correctives, Natural Academy of sciences, Washington D.C, **574-593**, *Pure and Appl. Limnology* (Ed. A.D. Adoni), *Bull. Bot. Soc*., Sagar **(1969)**

16. Kulshrestha S.K., George M.P., Saxena R., Johri M. and Srivastava M., Seasonal variations in the limnochemical characteristics of Mansarovar reservoir of Bhopal, In Mishra, S.R. and Saksena, D.N. (Eds), *Aquatic Ecology*, Ashish Publishing House, New Delhi, India. 275-292 **(1992)**

17. Pradhan S. and Mohanty R.K., Occurrence of microbes in steel plant effluents, *IJEP*, **11**, 201-205 **(1991)**

18. Trivedy R.K., Goel P.K. and Trisal C.L., Practical methods in Ecology and Environmental Science, Environmental Publications, Karad (India) **(1987)**

19. Provasoli L., Nutrition and ecology of protozoa and algae, *Annual Rev. Microbial*, **12,** 279-308 **(1958)**

20. Wetzel R.G., Variation in productivity goose and hypertrophic Sylvan Lakes, Indiana, Invest. *Indian lakes stream*, **7,** 147-184 **(1966)**

21. Sittig M., Hazardous and toxic effects of industrial chemicals, Noyes Data Corporation, Park Ridge, New Jersey, U.S.A. **(1979)**

22. Nayak M. S. and Sawant A.D., Seasonal variation in heavy metal concentration in water of lakes supplying water to Bombay City, *Journal of Indian Water Works Assoc*., **24**, 241-243 **(1994)**

23. Forstner U., Metal concentrations in metal pollution in fresh water sediments natural background and cultural effects: Interactions between sediments and freshwater, Goltorman, H. L. (Ed.) Washington / The Hague, Pudoc/Junk, B. V. Pub., 94-103 **(1977)**

24. Kudesia V. P., Physico-chemical properties of Ganga river at Farrukhabad, *Indian J. Environ. Agric.*, **3,** 81-82 **(1989)**

25. Forstner U. and Wittman G.T.W., Metal pollution in the aquatic environment, Springer- Verlag, Berlin **(1981)**

26. Chatterjee C.C., Human physiology, Medical Allied Agency, Calcutta **(1984)**

27. Manivaskam N., Physico-chemical examination of water, sewage and industrial effluents, Pragati Prakashan, Post Box. No. 62, Begum Bridge, Meerut 250001, 380, **(1989)**

28. Khan S. and Khan N. N., Influence of lead and cadmium on the growth and nutrient concentration of tomato (*Lycopersicum esculentum*) and egg-plant (*Solanum melongena*), *Plant and Soil*, **74**, 387-394 **(1983)**

29. Datar M. D. and Vashishtha R. P., Investigation of heavy metals in water and silt sediments of Betwa river, *IJEP*, **10**, 666-672 **(1990)**

30. Mathur A., Sharma Y. C., Rupainwar D. C., Murthi R. C. and Chandra S., A study of river Ganga at Varanasi with special emphasis on heavy metal pollution, *Poll.Res*., **6,** 37-44 **(1987)**

31. Weijden V.C.H. and Middelburg J.J., Hydro-chemistry of the river Rhine: long term and seasonal variability, elemental budgets, base levels and pollution, *Water Res*., **23,** 1247-1266 **(1989)**

32. Stumm W. and Lee G.F., The Chemistry of aqueous iron, Schweiz. *Z. Hydrol.*, **21**, 295-319 **(1960)**

33. Stumm W. and Morgan J.J., Aquatic Chemistry (2nd ed.), Wiley interscience, New York **(1981)**

34. Prater B.E., The metal content and dispersion characteristics of steel work effluents discharging to the Tees Estuary,*Wat.Pollut.Control*,**74,** 63-78 **(1975)**

35. Katariya H.C., An evaluation of water quality of Kaliasot river, *IJEP*, **14**, 690-694 **(1994)**

36. Hydn H.S., Distribution of uranium and other metals in crude oils, U.S., *Goel. Surv. Bull*, **1100(3)**, 72-89 **(1961)**

37. Harrison R.M. and Laxen D.P.H., Lead in atmosphere, in Lead Pollution - Causes and Control, Chapman and Hall Ltd., London, 10 **(1984)**

38. Pophali S., Siddiqui S. and Khan L.H., Sources and distribution of heavy metals in the abiotic components of a polluted urban stream in Bhopal, *IJEP*,**10**, 600-603 **(1990)**

39. Agarwal M. and Singh J., Impact of coal power plant emission on the foliar elemental concentration in plants in a low rainfall tropical region. Environment Monitoring and Assessment, 60(3), 261-282 (**2002**)

40. Trivedy R.K. and Goel P.K., Practical methods in Ecology and Environmental Science, Environmental Publications, Korad, (India) **(1984)**

41. Mishra S., Quantification of heavy metals in Brahmani river ecosystem at Rourkela and its modeling, A Ph. D. thesis submitted to Sambalpur University (Orissa) **(1999)**

42. Chattopadhyay R.M. and Roy N.N., Sediment chemistry parameters in rivers around Jamsedpur, *IJEP*, **10,** 683-689 **(1990)**

43. Ramaswamy S., Muralidharan K. V. and Ramesh L., Pollutants in sediment samples of Madras city, Tamilnadu, *Poll Res*, **14**, 487-495 **(1995)**

44. Kothandaraman H. and Viswannathan S., Cooum, a perspective study, In river Cooum; Let it be a Resource. Univ. of Madras, 4.1-4.10 **(1986)**

45. Metzner A.V., Removing soluble metals from wastewater, *Water and Sewage Works*, **124,** 98-101 **(1997)**

46. Jain S. and Salmon S., Heavy metal concentration in a highly eutrophic lake sediments and overlying water, *Poll Res*., **14,** 471-476 **(1995)**

47. USPHS, Toxicological profile on CD-ROM, Agency for Toxic Substances and Disease Registry, **(2000)**

48. Welch A.H., Lico M.S. and Hughes J.L., Arsenic in ground water of the western United States, *Ground water*, **26,** 333-347 **(1988)**

49. Alloway B.J., Heavy metals in soils, John Wiley and Sons, Inc. New York, (**1990**)

50. Kaise T., Watanabe S. and Itoh K., The acute toxicity of arsenobetaine, *Chemosphere*, **14,** 1327-1332 **(1985)**

51. USEPA, Review of the environmental effects of pollutants, IX. Fluoride, Cincinnati, Ohio, (EPA-600/1-78-050) **(1980)**

52. USEPA, http://www.epa.gov/safewater/arsenic.html, **(2002)**

53. Zonn S.U., Tropical and subtropical soil science, Mir Publishers, Moscow **(1986)**

54. Alexander M., Introduction to soil microbiology, Wiley Eastern Ltd, New Delhi (India) (**1983**)

55. Suess M.J., Examination of water for pollution control, 1st edition, Vol.II, Pergamon Press, Oxford **(1982)**

56. Munch J.C., Hillerbrand T.H. and Ottow J.C.W., Transformations in the Feo/Fed ratio of pedogenic iron oxides affected by iron reducing bacteria, *Can.J.soil,Sci*, **58,** 475-485 **(1978)**

57. Michael P., Ecological methods for field and laboratory investigations, Tata MaGraw Hill Publishing Co. Ltd., New Delhi (India) **(1984)**

58. Agrawal M., Singh B., Rajput m., Marshall F. and Bell J.N.B., Effect of air pollution on peri-urban agriculture; a case study, *Environ poll*, **126(3)**, 323-329 **(2003)**

59. David E.G., Irvin and Knights B., Pollution and the use chemical in agriculture, Butterworths, London **(1970)**

60. Jalan G. and Pande G. S., Composition of domestic sewage sludge, *IJEP*, **8,** 593-594 **(1988)**

61. Lepp N.W., Effect of heavy metals pollutions on plants, *Applied Science Publishers,* London, UK, 299–325 **(1981)**

62. Alloway B.J., Heavy metals in soils, Blackie Academic and Professional, Glasgow, UK, (**1995**)

63. ATSDR (Agency for Toxic Substance and Disease Registry), Toxicological profile of arsenic, US Public Health Service, (**1993)**

64. Peterson P.J., Benson L.M. and Zieve R., Metalloids, in pollution monitoring series, Effect of heavy metals on plants, Volume 1- Effect of Trace Metals on Plant Function, ed. N. W. Lepp, Applied Science Publisher, London **(1981)**

65. Bower C.A. and Hatcher J.T., Adsorption of fluoride by soils and minerals, *Soil Sci*, **103,** 151–154 **(1967)**

66. Boone R.J. and Manthey M., The anatomical distribution of fluoride within various body segments and organs of Antarctic krill (*Euphausia superba* Dana), *Arch Fischereiwiss*, **34(1)**, 81–85 **(1983)**

67. Elinder C.G. and Jarup L., Cadmium exposure and health risks: recent findings. *Ambio.*, **25(5)**, 370-373 **(1996)**

68. Cabrera C., Ortega E., Gallego C., Lopez M.C., Lorenzo M.L. and Asensio C., Cadmium concentration in farmlands in southern Spain: possible sources of contamination, *The Science of the Total Environment*, **153,** 261-265 **(1994)**

69. WHO, Cadmium, Environmental Health Criteria **(1992)**

70. USPHS, Toxicological profile for lead on CD-ROM, Agency for Toxic Substances and Disease Registry, U.S. Public Health Service **(1997)**

71. Goyer R.A., Toxic effects of metals. In Casarett and Doull’s Toxicology, The Basic Science of Poisons, Fifth Edition, Klaassen, C.D. [Ed], McGraw-Hill Health Professions Division, **(1996)**

72. Kimbrough D.E., Cohen Y., Winer A.M., Creelman L. and Mabuni C., A critical assessment of Chromium in the environment:Critical Reviews in Env.Sc. and Technology, **2991**, 121-125 **(1999)**

73. IARC, Chromium and certain chromium compounds. In: IARC monographs on the evaluation of the carcinogenic risk of chemicals to humans. Chemicals, industrial processes and industries associated with cancer in humans. *IARC monographs*, **Vol. 1 to 29**, **(1998)**

74. USPHS, 9th Report on Carcinogens, U.S. Department of Health and Human Services **(2001)**

75. Sauve S., McBride M.B. and Hendershot W.H., Speciation of lead in contaminated soils, *Environmental Pollution,* **98 (2)**, 149-155 **(1997)**

76. Sadiq M., Toxic metal chemistry in marine environments, Marcel Dekker Inc., New York, Basel, Hong Kong **(1992)**

77. Forsyth D.S., Dabeka R.W. and Cleroux C., Organic and total lead in selected fresh and canned seafood products, *Food Additives and Contaminants,* **8(4)**, 477-484 **(1991)**

78. Levin-Scherz J.K., Patrick J.D., Weber F.H. and Garabedian C., Acute arsenic ingestion, *Annals of Emergency Medicine*, **16(6),** 702-704 **(1987)**

79. Nwajei G.E., Okwagi P., Nwajei R.I. and Obi-Iyeke G.E., Analytical Assessment of Trace Elemets in soils, tomato leaves and fruits in the vicinity of paint industry, Nigeria, *Research Journal of Recent Sciences,* **1(4)**, 22-26 **(2012)**

80. Nwajei G.E., Obi-Iyeke G.E. and Okwagi P., Distribution of selected trace metals in Fish parts from the river Nigeria, *Research Journal of Recent Sciences,* **1(1)**, 81-84 **(2012)**