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ANALYSIS OF HEAVY METALS CONTAMINATION ON GROUNDWATER RESOURCES AND SURFACE SOILS IN THE VICINITY OF BUDDHA NULLAH STREAM IN LUDHIANA, PUNJAB

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Abstract:

Industries produce tons of pollutants and effluent every year. The disposal of untreated municipal, industrial and agricultural wastewaters into water resources have degraded the standard of surface waters in different parts of the planet. Theses Industrial pollutants include different kinds of Heavy metals. These metals in soils are of great environmental concern, the aim of this study is to determine heavy metal content in the surface soil from the vicinity of Buddha Nullah stream and Sutlej River's from village Walipur and Ladhowal of Punjab and also in groundwater samples via hand pumps/Tube wells at villages near Buddha Nullah in Ludhiana district namely Walipur and Ladhowal, and evaluate the contamination levels of nearly 20 soil samples and 20 underground water samples which were collected and analyzed for Cu, Zn, Cd, Pb, Fe and Ni contents using atomic absorption spectroscopy. Soil texture, physical phenomenon, pH, total organic content, and ion exchange capability were collectively measured additionally with this Metal pollution load index (MPLI) of Cr, Mn, Cu, Zn, As, Sb, Cd, Hg, and U were analyzed at both the selected sites of Ludhiana city. In the investigated soils, the mean recorded concentrations of the heavy metals were 10.41 mg/kg f ff or Cu, 0.083 mg/kg for Ni, 0.107 mg/ kg for Cd, 68.72 mg/kg for Fe, 8.59 mg/kg for Zn and 37.11 mg/kg for Pb. The reported results indicate that the enrichment factors of the measured heavy metals were 3.05, >0.1, 0.41, and 3.47 for copper, nickel, zinc, and lead respectively. Many of the essential elements were also either found to be in higher concentrations or deficient than permissible limits. Hand pump water has not been found a secure supply of water because its faucets into shallow aquifers having several significant metals in terribly higher concentrations. I-geo (accumulation index) values of the metals within the soils below the study indicate that they're uncontaminated to slightly contaminate with nickel and iron however extremely contaminated with copper and lead. The Buddha Nullah pollutes the Sutlej watercourse as numerous reports showcased that several factories rather than treating the effluents, inject these into the earth through deep-bore wells.

Keywords: Soil Contamination, Heavy Metals, Geoaccumulation Index, Industrial, and urban effluents

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Introduction:

There is increasing awareness that heavy metals present in soil may have negative consequences on human health and the environment (Abrahams, 2002; Schroeder et al., 2003; 2004; Mielke et al., 2005; Selinus et al., 2005). From the environmental point of view, all heavy metals are important because they cannot be biodegraded and are largely immobile in the soil system, so they tend to accumulate and persist in urban soils for a long time. This results in levels that are harmful to humans upon both acute and chronic exposure (Sheppard, 1998). Groundwater quality depends upon both geogenic factors and anthropogenic factors. There are naturally occurring minerals in aquitards in different regions of Punjab which control the concentration of geogenic pollutants, such as selenium (Se), fluoride (F), boron (B), and arsenic (As) in alluvial aquifers. Agricultural activities that influence water quality include the application of fertilizers and chemicals. Although the concentration of heavy metals in sewage effluents is low, long-term use of these wastewaters on agricultural lands often results in the build-up of the elevated levels of these metals in soils (Rattan et al. 2002). The most frequently reported heavy metals with regards to potential hazards and the occurrence in contaminated soils are Cd, Cr, Pb, Zn, Fe, and Cu (Alloway, 1995). The concentration of these toxic elements in soils may be derived from various sources, including anthropogenic pollution, weathering of natural high background rocks, and metal deposits (Senesi et al., 1999). although heavy metals distribution in soils is well documented for many cities of developed countries, comparatively little is studied in less developed countries (Thuy et al., 2000). However, in recent years, a few of these countries have achieved significant strides in their quest for rapid economic growth through industrialization. Thus, several factories, usually sited haphazardly, have developed. Population explosion and the increased use of automobiles have become very common in urban areas. The impact of pollution in the vicinity of overcrowded cities and from industrial effluents and automobile exhausts has reached a disturbing magnitude and is arousing public awareness. At present, relatively little data are available on the extent of environmental pollution because there are few agencies with inadequate capacity charged with the routine monitoring and protection of the environment (Olade, 1987).

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The study area covers high levels of contaminants, such as heavy metals, might have been released into the soil. Most of the land in this area is intensively used for different purposes including residence and agriculture. Thus, it is necessary to carry out an investigation of heavy metals in the soils of this urban area. This study of heavy metal content in urban soils provides baseline information on the anthropogenic impact of environmental pollution in the Sutlej Rivers. A recent study conducted by Dheri et al. (2005) showed that the concentration of heavy metals like Pb, Cr, Cd, and Ni was not only significantly higher in water samples of Buddha Nullah drain but also in those collected from shallow hand pumps located within the vicinity of 200 meters as compared to the deep tube well water. These caused contaminants in the surface and groundwater by leachates of nutrients, metals, organic contaminants in the surface and groundwater. This study is important because it can be used as the basis for planning management strategy to achieve better environmental quality and substantial development of this area.

Heavy Metals Pollution:

Heavy metals are dangerous because they tend to accumulate. Compounds accumulate as living things any time they are taken up and stored faster than they are broken down or extracted (metabolized). These metals can enter the water supply by industrial or consumer waste or even from acidic rain breaking down soils and releasing heavy metals into streams, lakes, rivers, and ground waters. Lenntech (2005a). This exit over than 18 different heavy metals toxins that have impacts on human health and each toxin will produce different behavioral physiological and cognitive changes in exposed individuals. The toxicity of heavy metals can be listed in order of decreasing toxicity as Hg>Cd>Cu>Zn>Ni>Pb>Cr> Al>Co, also this is only approximate as the vulnerability of species to individual metals varies. Toxicity also varies according to the environmental conditions that control the chemical speciation of metals

Hossain (2006) observed that the 'As' concentrations of drinking water from deep wells in 64 districts in Bangladesh and found that 59 had concentrations >10 μ g L–1 and 43 had concentrations >50 μ g L–1. Contaminated groundwater is also used for irrigation of paddy





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rice, which is the main staple food for the population. This practice enhances the level of 'As' in the soils rendering them unsuitable for agriculture. A few recent studies have reported that 85–95% of total 'As' in rice and a vegetable was inorganic. Arsenic concentration is higher in Bangladeshi soils, groundwater, and plants (data based on 4% area of the country) than the permissible limits or normal range reported.

Nangare et al. (2008) studied the impact of the textile industry on groundwater quality of the industrial estate area of Ichalkaranji. The results showed that the pH value ranged from 6.5 to 9.0, but within the permissible limit and only two samples showed the pH 9.0. The value of turbidity was also within the range of permissible limits for all samples except only one sample which showed more turbidity because this sample consisted of effluents or wastewater coming from the industries, and collected from sewer outlets

Materials & Methods:

Study Area

The present study was conducted at two places near each other. The first area was chosen for the study was the Ludhiana district. Ludhiana city was founded on a ridge of Buddha Nullah a tributary of River Sutlej and the untreated sewage of the city is discharged into Buddha Nullah. Buddha Nullah runs parallel to Sutlej, on its south for a fairly large section of its course in the district. The water of the stream becomes polluted after it enters Ludhiana City. With the industrialization/ urbanization of the area, Buddha Nullah has become the sullage/ sewage as well as an industrial effluent carrier for the Ludhiana city leading to River Sutlej. The primary data collected from a village name Walipur Kalan, situated in Tehsil Jagraon and block Sidwan Bet, under district Ludhiana at a distance of 1-1.5 km from Buddha Nullah, and the other site was Ladhowal, 18 Kms from Walipur. The underground water samples were collected from various tube wells in January 2021. During this month the irrigation is at its peak level. The water samples were analyzed for pH, EC, Ca2+, Mg2+, CO32–, HCO3–, Cl– and SO42– quantitatively. To provide a satisfactory geographical representation of the sites, the vicinity was divided into two zones; zone S1 was to the north-east, S2 south-west of

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the selected site point. Sampling sites were distributed among these zones to ensure that each zone had an equal number of sites. A bulk sample was prepared by collecting about 1 kg of surface soil (0–20 cm) by hand digging at 5 sampling sites within a maximum area of 20 m2. Ten composite samples were collected from each zone. Samples were collected with a stainless-steel spatula and kept in labelled plastic bags for laboratory analysis. After air drying, samples were passed through a 2 mm sieve and stored in plastic bags until they were analyzed. The texture was investigated by using the pipette method (ISO, 2001a). A weighted sample was oven-dried at 105 °C for twelve hours and cooled in desiccators. The weight loss was used for calculating the soil water content. Organic matter contents were determined by soil ignition at a temperature of 450 degree C (Allen et al., 1974). Electrical conductivity (EC) and pH were measured in a soil deionized water suspension (soil: water, 1:2.5 by volume) by a calibrated pH meter and conductivity meter respectively (ISO, 2002a). Soil samples were analyzed for CEC, using the ammonium acetate method at pH 7 (Chapman, 1965). The samples were digested using aqua regia (ISO, 2002b). The solutions of the digested samples were analyzed using air/acetylene atomic absorption spectroscopy with the use of prepared standards for Fe, Cu, Ni, Cd, Zn, and Pb. Analytical grade of nitrate salt of lead, analytical granules of copper and zinc and iron, and general-purpose reagent cadmium nitrate of maximum purity of 99% were used in the preparation of standard solutions. Calibration curves were used to calculate the concentration of the metals. A reagent blank was used to zero the instrument. This was followed by aspiration of standard solution and finally, the soil sample extract was aspirated.

Twenty samples of Hand pump/Tube well water from the households were collected during the period (Jan to April). Groundwater samples are presumably away from other potential sources of contamination (fertilizers, animals, human sewage. Before sample collection, the hand tube wells were pumped out at least for 3 minutes. The pre-cleaned and dried polyethylene bottles (100 ml) rinsed with sample water were used for sample collection and preservation. All the water samples tested were used for drinking by farmers and families and farm workers. The concentration of essential elements (Zn, Cu, Fe, K, Mn, Mg, P, Se) and heavy metals (Cd, Cr, Ni, Pb, Ti, Sr, Co, Bi, Hg, U, As, Sn), were determined by using

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atomic absorption spectroscopy in groundwater. The degree of water pollution for each metal was measured using the Metal pollution load index (MPLI) depending on soil metal concentrations compared with internationally accepted standards. The following modified equation was used to assess the (MPLI) level in water. MPLI = Mean value of the samples / Mean value of the permissible limits.

Results & Discussion:

The results of the physicochemical analysis of the study area are given in Table 1. The relative percentage of clay, silt, and sand in the soils were in the range (5.89-8.17 %) for clay, (11-19 %) for silt, and (71.56-76.58 %) for sand. The soils were classified as loamy sand. The values of pH ranged in a narrow interval from 6.58 to 7.89 which suggests slightly acidic to neutral conditions for all the topsoils in the entire study area. The cation exchange capacity (CEC) of the soil samples ranged between 16.85 and 27.58 meg/100g with a mean value of 26.115 and 19.20 meq/100g. As shown in Table 1 the soil samples collected from the north displayed the highest mean CEC value, those from the east had the least value. The total organic matter content (TOM) in the samples ranges between 20.44% and 11.89%, with an average of 15.67 and 18.165 % (Table 1). There was a significant difference in the TOM distribution in the entire study area. The relatively high content of TOM in samples due to the high organic content of used lubricants that were discharged at the site. Furthermore, loamy textured soils generally have higher organic matter due to their ability to support vegetation compared to light textured soils (Brady and Weil, 1999). Soil organic matter is important because it improves both the physical and chemical properties of soil. It decreases soil erosion by stabilizing soil particles. It also enhances aeration, increases water holding capacity, and restores and supplies nutrients for the growth of plants and soil microorganisms. Concentrations of Pb, Zn, Cu, Cd, Ni, and Fe in the soil samples from the vicinity of the railway servicing workshop in Kumasi are listed in (Table 2) together with mean values, standard deviations, and variance. Iron had the highest mean value (48.38 & 47.145 mg/kg), followed by Pb (24.56 & 29.72 mg/kg). Compared to average concentrations in urban soils in the world, the mean values of the Pb in the analyzed soils are much lower than

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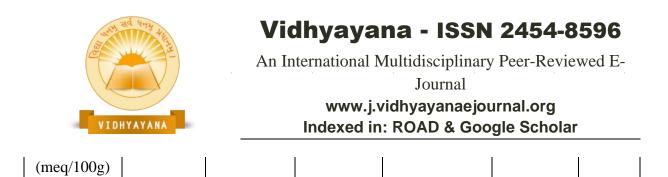
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those reported from samples from large and industrialized cities such as Palermo (Sisily) 202 mg/kg (Manta et al., 2002), Central London 647 mg/kg (Rundle and Duggan, 1980), and Rome 330.8 mg/kg (Angelone et al. (1995). Cadmium and Ni concentrations were generally low, close to those reported for the unpolluted soils. Moreover, these metals display quite homogeneous distributions across the sampling area and therefore had lower standard deviations, thus suggesting a major natural (i.e., indigenous lithologic) source. However, there were significant differences in the distribution of Pb and Cu. In this study, Cu had the maximum mean concentration value of 9.2 mg/kg in the samples from the Walipur area and a minimum value of 7.05 mg/kg in the Ladhowal Area. Zinc plays an important role as an essential element in all living systems, in this work the concentration of Zn was found ranging from an average of 6.382 mg/kg to 8.01 mg/kg in Walipur and Ladhowal Area respectively near to Buddha Nullah.

	S1 Walipur	S2 Walipur	Mean	S3 Ladhowal	S4 Ladhowal	Mean
Texture class	Loamy sand	Loamy sand		Loamy sand	Loamy sand	
Sand %	75.51	76.58	76.045	71.56	73.56	72.56
Clay %	6.23	5.56	5.89	6.78	9.56	8.17
Silt %	19	15	17	15	11	13
рН	7.89	7.25	7.57	7.01	6.58	6.79
Moisture content %	3.5	1.56	2.53	2.11	7.5	4.805
Organic content %	15.89	20.44	18.165	11.89	19.45	15.67
Conductivity (mS)	0.2	0.11	0.155	0.14	0.25	0.195
CEC	27.58	24.65	26.115	16.85	21.56	19.205

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Element	S1 Walipur	S2 Walipur	Mean	S3 Ladhowal	S4 Ladhowal	Mean
Cu (mg/kg)	9.2	7.45	8.32	7.72	7.05	7.38
Fe (mg/kg)	45.65	48.64	47.145	47.55	49.22	48.38
Pb (mg/kg)	33.56	15.56	24.56	19.89	39.56	29.725
Cd (mg/kg)	0.03	0.05	0.04	0.06	0.1	0.035
Zn (mg/kg)	8.01	6.42	7.21	6.38	7.71	7.045
Ni (mg/kg)	0.02	0.03	0.025	0.03	0.04	0.035

 Table 2: Parameters of Extracted Heavy Metals at different zones of selected areas

On the basis of the study, an enrichment factor was used to assess the level of contamination and the possible anthropogenic impact in soils from the vicinity on a ridge of Buddha Nullah a tributary of River Sutlej. To identify anomalous metal concentration, geochemical normalization of the heavy metals data to a conservative element, such as Al, Fe, and Si were employed. Several authors have successfully used iron to normalize heavy metals contaminants (Baptista Neto et al., 2000; Mucha et al., 2003). In this study, iron was also used as a conservative tracer to differentiate natural from anthropogenic components. According to Ergin et al., (1991) and Rubio et al., (2000), the metal enrichment factor (EF) is defined as follows:

EF= M/Fe (sample) / M/Fe (Backgroud)

Where EF is the enrichment factor, (M/Fe) sample is the ratio of metal and Fe concentration of the sample, and (M/Fe) background is the ratio of metals and Fe concentration of a background. The background concentrations of metals were taken from soils from an undisturbed area from both the areas of study. Table 3 shows EF values and Igeo of Cd, Zn,



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Fe, Ni, Pd, and Cu in soils along with the background concentrations of these metals. According to Zhang and Liu (2002), EF values between 0.5 and 1.5 indicate the metal is entirely from crust materials or natural processes, whereas EF values greater than 1.5 suggest that the sources are more likely to be anthropogenic. The results of the present study show that Pb and Cu were significantly enriched in the soils from the vicinity of the workshop since EF values of these two metals are greater than 1.5 (Table 3). The highest average EF is seen for Pb with a value of 3.21. Copper has the second-highest EF with an average value of 2.51. This suggests that Pb and Cu are anthropogenic and the soils have been contaminated by these two metals in recent years. The difference in EF values may be due to the difference in the magnitude of input for each metal in the sediment and/or the difference in the removal rate of each metal from the soil. The EFs of Zn, Cd, and Ni were less than 0.5 which suggests a natural source of these metals in the study area. The geoaccumulation index (Igeo) introduced by Muller (1969) was also used to assess metal pollution in soils. It is express as:

Cn

2 1.5*Bn*

Where Cn is the measured concentration of the examined metal in the soil and Bn is the geochemical background concentration of the same metal. Factor 1.5 is the background matrix correction factor due to the lithogenic effect. The index of geoaccumulation includes seven grades (0-6) ranging from unpolluted to very highly polluted. The pollution levels of these metals in the environment expressed in terms of geoaccumulation indices indicate that the environment is high to very highly pollute with Pb and Cu. The level of pollution with Zn was moderate. The results reveal that the samples are uncontaminated to slightly contaminate concerning Ni and Fe.

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Table 3: Geo-accumulation index, Enrichment Factor and background concentration ofheavy metals in the soils of the vicinity of the railway workshop

Element	Enrichment Factor (EF) accumulation	Geo-Index (Igeo)	Background conc. (mg/kg)	
Cu	2.51	7.1	0.25	
Fe	N. D	0.95	4.5	
Pb	3.21	4.65	0.98	
Cd	< 0	< 0	N.D*	
Zn	0.368	1.8	1.58	
Ni	> 0.1	0.19	0.31	

*N. D = not detectable

The results of analytical analysis of water samples are presented in Table 1. The Table clearly revealed the contents of the heavy metals: cadmium, chromium, antimony, lead, uranium and higher than the desirable standards advocated by different mercury were international/national bodies engaged in environmental pollution control. There are certain other heavy metals like selenium, molybdenum and nickel are present within the permissible limits. Analysis revealed that metal pollution load index (MPLI) of nine metals: Cr, Mn, Cu, Zn, As, Sb, Cd, Hg, U was higher in both of the selected sites. These results reveal that ground water system in the vicinity of the Buddha Nullah seemed to be much polluted due to higher concentration of heavy metals. Copper (Cu) is an essential element in human metabolism and was considered to be non-toxic up to 1.5 mg/L concentration in drinking water (ISI 1991; WHO 1993). The concentrations of Cu were found in present study ranged from 0 to 47.6 mg/L with mean value 25.07mg/L at Ludhiana and ranged from 4.76 to 23.4 mg/L with mean value 15.18 mg/L at Patiala and thus majority of samples had values higher than maximum permissible limit of 0.5 mg/L. Some essential elements Co, Ag, Sn, Sr and Bi are found in higher concentration at Ladhowal than at Walipur. These metals may leach into water naturally are through anthropogenic factors. Bismuth occurs naturally as the metal

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itself and is found as crystals in the sulphide's ores of nickel, cobalt, silver and tin. Strontium (Sr) minerals are widely distributed throughout the earth and are released to the groundwater by the natural re-crystallization of rocks and weathering of rocks and soils (Greve et al. 2007). Many of the essential elements were also found to be in higher concentrations than permissible limits. For example, like Ca and Ti were found in higher concentration at Walipur than in Ladhowal village. Ca in groundwater are known to originate mainly by the dissolution of carbonate minerals, but a fair amount of Ca can also contribute by silicate weathering (Subramani et al. 2010), so its higher concentration at any place may be partly due to natural processes alone. Zinc (Zn) is another essential trace element found in virtually all kind of food and potable water in the form of either salt or organic complexes. Zinc concentration was found in present study in range of 13.4 to 66.6 mg/L with mean value 18.7mg/L at Walipur, while it ranged from 1.95 to 4.25 mg/L with mean value 3.035 mg/L at Ladhowal. So observed Zn concentration value was much higher than the permissible limit of 5-15 mg/L at Walipur, but was within the normal range at Ladhowal. The ground water in the present study was deficient of certain essential element. For example, Iron (Fe) is an essential element for the humans. In this study, the Fe concentration was found between 0.0 mg/L in all the samples at both the places. Hence the ground water was deficient for Fe. Corrosion of hand pumps is known to lead to the presence of Fe in some studies (Langaneger 1987). Similarly another essential element Se was not found in the ground water in the present study. Concentration of many toxic elements like Pb, As, Bi, Sb in ground and surface waters increases mainly through anthropogenic activities. For example, the possible sources of lead in groundwater can be diesel fuel consumed extensively in farm lands, discarded batteries, paint and leaded gasoline. Lead is also used in some pesticides such as lead arsenate. Arsenic (As) is however introduced into ground water from industrial effluents, atmospheric deposition and also from pesticides & insecticides.

Conclusion:

This survey has allowed us to determine total metal levels (Cu, Fe, Ni, Pb, Cd, and Zn) in surface soils from selected sites. Soil pollution in the present study was assessed using

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enrichment factor and geoaccumulation index values. The calculation of the enrichment values showed that Pb and Cu are enriched with 3.21 and 2.51 respectively. The results of geoaccumulation index based on Muller's classification allows us to conclude that, for analyzed metals, the concentrations of Cd and Ni can be generally considered as background levels moderately polluted with Zn and highly to very highly polluted with Pb and Cu. Some of the elevated concentrations of Pb, Cu, and Zn are due to anthropogenic sources. The soils from the vicinity can be described as moderately to very highly polluted since all the samples collected showed moderately high levels of contamination in at least one metal. Regarding the Groundwater results, it shows that pump water isn't a secure supply of potable. It faucets into shallow aquifers and is serious chemically. The untreated industrial effluents together with dyes from tanning, nickel, and chrome plating unit's area unit discharged into Buddha Nullah. The Buddha Nullah pollutes the Sutlej stream. The area units report that a lot of factories rather than treating the effluents inject them into the world through deep-bore wells. The high concentration of trace components and heavy metals, as revealed in the present study, maybe causing a detrimental effect on the inhabitants of the locality. The health status of the individuals in these areas is being investigated. Many heavy metals like lead, cobalt, chromium, zinc, and copper are known to cause damage to the intestinal tract.

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