

EXTENT OF HEAVY/TRACE METALS/ELEMENTS CONTAMINATION OF GROUNDWATER RESOURCES IN LUDHIANA AND PATIALA, PUNJAB

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Background: Water is an important constituent of the ecosystem on the earth and essential component of life. The discharged effluents into water resources are a risk to human health. Industries produce a lot of pollutants and effluent. The disposal of untreated municipal, industrial and agricultural waste waters into water resources has degraded the quality of surface waters in different parts of the world. Extensive irrigation of agricultural lands as well as the drinking water supplies is mainly based on canal water / surface water. **Aims and Objectives:** To explore the amount of micro/trace elements and /or heavy metals in ground water samples from hand pumps at villages near two water channels; one at Arnetu under Patiala district of Punjab along Ghaggar River and another at three villages near *Buddha Nullah* in Ludhiana district. **Research Methodology:** The primary data collected from three villages of the Ludhiana District, namely, Bhamian Kalan, Khasi Kalan and Wallipur. The water samples were analyzed using the energy dispersive x-ray fluorescence (EDXRF). These samples were analyzed without any chemical pretreatment. **Results and Conclusions:** The results reveal that groundwater system in the vicinity of the *Buddha Nullah* seems to be polluted than in Patiala district. Metal pollution load index (MPLI) of Cr, Mn, Cu, Zn, As, Sb, Cd, Hg, and U was higher at Wallipur and other villages situated near *Buddha Nullah* in Ludhiana than that at Arnetu village near Ghaggar River in Patiala district; while MPLI of Nickel and lead was higher at Arnetu than at Ludhiana. 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 safe source of drinking water as it taps into shallow aquifers having many heavy metals in very higher concentrations. The untreated industrial effluents including dyes from tanning, nickel and chrome plating units are discharged into *Buddha Nullah*. The *Buddha Nullah* pollutes the Sutlej River. There are reports that many factories instead of treating the effluents, inject these into the earth through deep-bore wells. The increased influx of heavy metals into water resources may result in their transportation and accumulation in dangerous quantities in different plant parts would result in a serious health hazard to animals and ultimately humans.

Keywords: Groundwater, Industrial and urban effluents, Heavy metals, Water pollution and Punjab

Introduction

Water is an important constituent of the ecosystem on the earth and essential component of life. Planning and management of water resources and its optimal use are a matter of urgency for most countries of the world, and even more so for India with a huge population. India supports more than 16% of the world's population with only 4% of the world's fresh water resources (Singh 2003). Ground water is used domestically for drinking, cleaning and bathing purposes and also

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for irrigation purposes. Heavy metals and trace elements are present in the ecosystem and humans and other organisms are exposed to them through various pathways. Presence of these elements in sub surface water comes from both natural and anthropogenic sources. The weathering of minerals is one of the major natural sources. Anthropogenic sources of soil contamination include waste water irrigation, solid waste disposal, sludge applications, vehicular exhaust, industrial effluents, fertilizers and insecticides. All these factors are related with urbanization and industrialization. The urbanization in any area is characterized by high density of residential and commercial buildings, extensive areas of impervious surfaces and extensive construction of subsurface drainage systems such as flushing water pipes, sewers and storm water drains.

The major source of surface and ground water pollution in industrial and urban areas is injudicious discharge of untreated effluents directly into the surface water bodies resulting in serious surface and ground water pollution. The quality of water resources is deteriorating due to the continuous pollution with undesirable discharge of these pollutants and effluents into the water resources.

The initial effect of water pollution is to degrade the physical quality of the water. Later biological degradation becomes evident in terms of number, variety and organization of the living organisms in the water (Gray 1989). Often the water bodies readily assimilate waste materials they receive without significant deterioration of some quality criteria; the extent of this is referred to as its assimilative capacity (Fair *et al.* 1971). The input of waste into water bodies therefore does not always impact negatively on aquatic environment because of the self-purification property of the water bodies. But there is always some limit to which water bodies can sustain pollutants. A high level of discharged effluents into water resources are a risk to human health. Industries produce a lot of pollutants and effluent. The disposal of untreated municipal, industrial and agricultural waste waters into water resources has degraded the quality of surface waters in different parts of the world. Extensive irrigation of agricultural lands as well as the drinking water supplies is mainly based on canal water / surface water.

Extensive irrigation of agricultural lands and drinking water supplies are mainly based on canal water. Irrigation water percolating through soil and dissolves carbon dioxide gas produced at high pressures from the plant root respiration and microbial oxidation of the agricultural matter.

Although the concentration of heavy metals in sewage effluents are low, long-term use of these waste waters on agricultural lands often results in the build-up of the elevated levels of these metals in soils (Rattan *et al.* 2002). Agricultural sources of contamination include runoffs, agrochemicals such as pesticides and nitrates used on farm lands.

Chemical pollution of surface water can create health risks, because such waterways (flowing water) are often used directly as drinking water sources or

connected with shallow wells used for drinking water. The waste water contains substantial amounts of beneficial nutrients and toxic heavy metals, which are creating both opportunities and problems for agricultural production (Chen *et al.* 2005). Heavy metals are basically present in groundwater and play an important role in determining the quality of water for drinking purposes (Siddiqi and Hassan 2006). Essential metals for humans are Iron (Fe), Copper (Cu), Cobalt (Co), Manganese (Mn), Zinc (Zn), Chromium (Cr) and their deficiency would result in many clinical abnormalities (Caussy *et al.* 2003), but high doses of these essential elements can also cause toxic effects. Other metals such as Hg, Pb, Cd, and As are not known to be essential for any animals (Académie des Sciences 1998). The damage that they cause on the cellular level can result into cancer and many other diseases. Heavy metal toxicity can also result in damaged or reduced mental and central nervous function, lower energy levels, and damage to blood composition, lungs, kidneys, liver, and other vital organs. The heavy metals like lead, cobalt, chromium, zinc and copper cause damage to the intestinal tract. Repeated long-term contact with some metals or their compounds may even cause cancer (International Occupational Safety and Health Information Centre 1999).

Symptoms indicative of acute metal toxicity is not difficult to recognize because the symptoms are usually severe, rapid in onset, and associated with a known exposure or ingestion: cramping, nausea, and vomiting; pain; sweating; headaches; difficulty in breathing; impaired cognitive, motor, and language skills; mania; and convulsions (Ferner 2001). Heavy metals like cadmium, cadmium and lead are carcinogenic (Trichopoulos 1997, Turkdogan *et al.* 2002).

Studies on Extent of Water Pollution by Heavy Metals

Tripathi *et al.* (1997) assessed the dietary intake of heavy metals in Bombay city. Results indicated that the total intakes of Zn, Cu, Pb and Cd through air, water and food were 10500µg/day, 1500µg/day, 30µg/day and 4.3µg/day respectively. Hanaa *et al.* (2000) found strong relationship between contaminated drinking water with heavy metals from some of the Great Cairo Cities, Egypt and chronic diseases such as renal failure, liver cirrhosis, hair loss, and chronic anaemia has been identified in the present study. These diseases are apparently related to contaminant drinking water with heavy metals such as Pb, Cd, Cu, Mo, Ni, and Cr. Renal failure in the study is related to contaminated drinking water with lead and cadmium, liver cirrhosis to copper and molybdenum, hair loss to nickel and chromium, and chronic anemia to copper and cadmium. Fytianos *et al.* (2001) conducted the study to determine the distribution of heavy metals in contaminated agricultural soil in Northern Greece. Samples of vegetables showed highest lead concentrations for spinach and low values for leek and carrot respectively. The lead contents in vegetables from industrial areas were higher than in rural areas. Spinach and lettuce grown in the industrial soil were enriched

in Cd whereas the Zinc content in vegetables was in normal range. Copper is an essential nutrients for plants. Copper concentration in vegetables in both the areas is in normal range. The iron concentrations were higher in some species of vegetables in rural areas and for some other species it was higher in industrial areas.

Sharma *et al.* (2007) did an assessment of the impact of wastewater irrigation on heavy metal contamination of *Beta vulgaris* (*palak*) which is highly nutritious leafy vegetable that is widely cultivated and consumed in urban India. The field study was conducted at three major sites that were irrigated by either treated or untreated wastewater in the suburban areas of Varanasi, India according to normal practice. Samples of irrigation water, soil, and the edible portion of the palak were collected monthly during the summer and winter seasons and were analyzed for Cd, Cu, Zn, Pb, Cr, Mn, and Ni. Heavy metals in irrigation water were below the internationally recommended (WHO) maximum permissible limits set for agricultural use for all heavy metals except Cd at all the sites. Similarly, the mean heavy metal concentrations in soil were below the Indian standards for all heavy metals, but the maximum value of Cd recorded during January was higher than the standard. Also in the edible portion of *B. vulgaris*, the Cd concentration was higher than the permissible limits of the Indian standard during summer, whereas Pb and Ni concentrations were higher in both summer and winter seasons. The study concluded that the use of treated and untreated wastewater for irrigation had increased the contamination of Cd, Pb, and Ni in edible portion of vegetables causing potential health risk in the long term.

Hossain (2006) observed that the 'As' concentrations of drinking water from deep wells in 64 districts in Bangladesh and found that 59 had concentrations $>10 \mu\text{g L}^{-1}$ and 43 had concentrations $>50 \mu\text{g L}^{-1}$. Contaminated groundwater is also used for irrigation of paddy 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 textile industry on ground water 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 range of permissible limits for all samples except only one sample which showed the more turbidity because of this sample totally consisted of effluents or waste water coming from the industries, and collected from sewer *nallahs*.

Siddiqui and Sharma (2009) carried their work in the Okhla industrial area phase-II, New Delhi, India in the year 2007. The result showed that discharge of

untreated effluents by the industries was leading to contamination of groundwater of the surrounding areas. Lead, mercury, fluoride, TDS, sulphate was above the desirable limit in effluent water (ISI standard for effluent water discharge). Subsequent analysis of groundwater of nearby areas was rated as unacceptable for drinking because of presence of fluoride in all the samples above the desirable limit. Lead, mercury, cadmium, chloride was also detected in many samples.

Aims and Objectives of the Study

This study explores heavy metal and trace element distributions in groundwater samples collected from villages situated along some water channels in Punjab. The results would help us to understand the potential threat to our ground water resources due to dumping of industrial waste into surface water channels/ rivers.

Materials and Methods

Study Area

The present study was conducted at two places. First area chosen for the study was 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*. *Budha Nullah* runs parallel to Sutlej, on its south for fairly large section of its course in the district and ultimately joins Sutlej at Gorsian Kadar Baksh in the north western corner of 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 industrial effluent carrier for the Ludhiana city leading to River Sutlej. The study areas of Bhamian Kalan, Khasi Kalan and Wallipur Kalan are situated in Tehsil Jagraon and block Sidwan Bet, under district Ludhiana at a distance of 1-1.5 km from *Buddha Nullah*. Walipur Kalan is surrounded by Tehsil towards South, Shahkot Tehsil towards North, Nurmahal Tehsil towards North, Nakodar Tehsil towards North.

The second area chosen for the study was a village Arnetu in Patiala district. Patiala district is situated at south-eastern part of the state; it lies between 29°49' and 30°47' north latitude, 75°58' and 76°54' east longitude. Ghaggar River originates from Siwalik Hills and runs along its foothills through Haryana and Punjab to Rajasthan and then disappear itself in the sands of the Thar Desert. The Ghaggar River was selected to evaluate the heavy metal characteristics of its surface water in upper reaches. There are 5 tehsils, 8 blocks, 1084 villages in the district. Rural population of Patiala generally uses tube well water for drinking and irrigation. People of rural area of Patiala district generally use tube well as the sources of water for drinking and irrigation purposes. The study area, village Arnetu, is situated

in Patran tehsil. There are 68 villages in Patran Block. This village is situated near the Ghaggar River at distance of half a kilometer. A number of industries and towns discharge their effluents and chemical waste in various tributaries of Ghaggar River. The study areas and sample collection sites are shown in Figure 1.

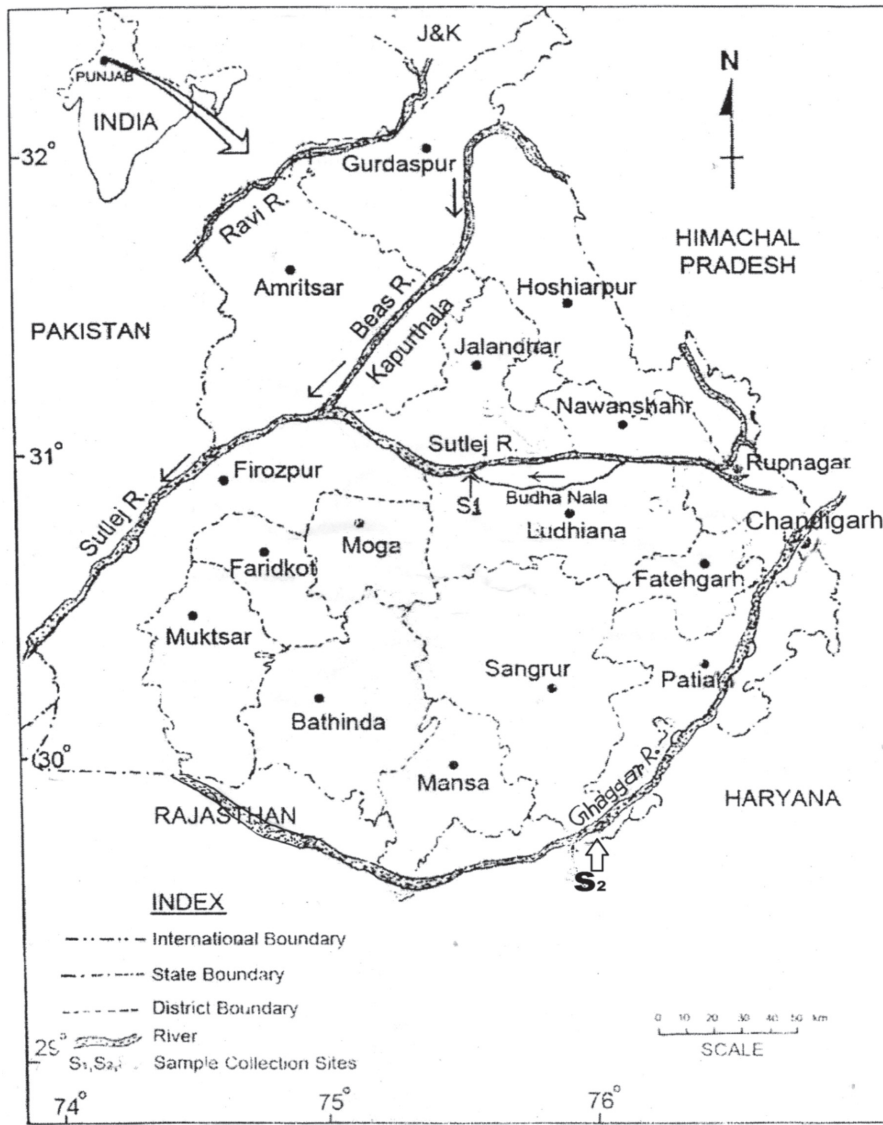


Fig 1: Location Map of the Area

Figure 1

Hydrogeology

Ludhiana District: The Ludhiana district is drained by Satluj and Buddha Nullha and is occupied by Indo-Gangetic alluvium deposits of the Quaternary age. The subsurface geological formations of the area comprise of sand, clay and *kankar* in various proportions. In general ground water of the district is fresh except in and around Ludhiana city where the ground water is polluted due to industrial effluents. The lithological data from drillings in the area by Central Ground Water Board (2007) revealed the presence of many sand beds forming the principal aquifers separated by clay beds at various depths. Five prominent sand horizons have been found up to 400 meters depth. The first aquifer is between 10-30m in Ludhiana district.

Patiala District: Just like Ludhiana, this district is a part of Indo-gangetic plain and composed of alluvial deposits of the Quaternary age. These deposits consist of sandy clay, sand, clay, gravel, pebble and *kankar* deposited by Ghaggar River. The alluvial deposits have rich ground water potential, having shallow unconfined aquifers. Hand pumps and shallow tube wells tap shallow aquifers for domestic purpose. Patiala district is mineral poor, except nitrates of Na, K and Ca. Soils are deficient in nitrogen, phosphorus and potassium. In Patran and Samana blocks, soils are arid brown soils occur. Nitrate values ranges between 0.40 to 200 mg/l and fluoride concentration ranges from 0.20 to 2.8 mg/l, but at few places high fluoride and nitrate have been observed (Central Ground Water Board 2007). According to the board, the ground water in these places is harmful for human consumption.

Groundwater Sampling and Analysis

Hand pump water samples from the households were collected during the post monsoon period (October to May). Ground water 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), total elements were 22 in number, were determined by Energy Dispersive X-Ray Fluorescence (EDXRF) Spectrometry in ground water. The components of an energy-dispersive X-ray spectrometer consisted of a primary X-ray source, sample holder, an X-ray detector, a multi-channel analyzer (MCA) and associated NIM electronics for data acquisition and processing. A microcomputer was dedicated to this system for XRF data analysis. The source of primary X-rays for the excitation of characteristic X-rays was a high intensity Cd¹⁰⁹ annular sealed X-ray source. The sample holder was

simply a receptacle to hold the sample. The sample was directly irradiated from the source. All the samples were tested four times and the mean of the three most consistent values were taken.

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. $MPLI = \text{Mean value of the samples} / \text{Mean value of the permissible limits}$.

Results and Discussion

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 mercury were higher than the desirable standards advocated by different international/national bodies engaged in environmental pollution control. The Table also shows that certain other heavy metals like selenium, molybdenum and nickel are present within the permissible limits. Table 1 also shows that metal pollution load index (MPLI) of nine metals: Cr, Mn, Cu, Zn, As, Sb, Cd, Hg, U was higher in Ludhiana than that at Arnetu village of Patiala; while MPLI of Nickel and lead was higher at Ametu than at Ludhiana. These results reveal that ground water system in the vicinity of the Buddha Nullah seemed to be more polluted due to higher concentration of heavy metals than that at Patiala district. The pollution status of drinking water systems in the study area is of great environmental and health concerns. Punjab Pollution Board has identified number of sources of pollution of Ghaggar where industrial units are discharging their toxic waste water into water streams. These units are situated in Banur, Dera Bassi, and Bahadurgarh. Besides industrial units, waste water from domestic sources at Zirakpur, Dera Bassi, Mohali, Bassi Pathana and Sirhind is discharged into Ghaggar River.

Some essential elements like Ca and Ti were found in higher concentration at Walipur than Arnetu 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. Co, Ag, Sn, Sr and Bi are found in higher concentration at Arnetu than at Walipur. These results were slightly intriguing. These metals may leach into water naturally are through anthropogenic factors. Bismuth occurs naturally as the metal itself and is found as crystals in the sulphides 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). Since Patiala district is not known to be rich in metals, so higher amount of these in shallow water aquifers may be attributed to extraneous factors rather than natural processes.

TABLE 1: ELEMENTAL ANALYSIS: MEAN, STANDARD DEVIATION, RANGE AND MPLI OF THE HOUSEHOLD WATER SAMPLES

Element	Wallipur (Ludhiana) N=10				Arnetu (Patiala) N=23				
	Mean (ppm)	S.D	Range	MPLI	Mean(ppm)	S.D	Range	MPLI	Permissible limits (mg/l)
Ca	9.71	4.596	0 to 53.9	-	0.23	0.319	0.03 to 1.66	-	No value proposed
Cr	27.99	4.454	14.6 to 42.9	559.8	2.80	0.452	3.76 to 2.06	56	0.05 (IS:1991)
Mn	88.83	3.464	41.7 to 167.2	888.3	0.97	0.460	0.53 to 1.26	9.7	0.1 (IS:1991)
Fe	0	0	0 to 0	0	0	0	0 to 0	0	0.3 (IS:1991)
Co	1.34	0.565	0.3 to 2.8	-	4.05	1.081	6.26 to 2.3	-	-
Ni	0	0	0 to 39.2	0	0.53	0.920	0 to 3.25	26.5	0.02 (WHO:1993)
Cu	25.07	0.494	0 to 47.6	16.713	15.18	4.912	23.4 to 4.76	10.12	0.05-0.5 (IS:1991, WHO 1993)
Zn	18.7	7.495	13.4 to 66.6	1.24	3.035	0.777	4.25 to 1.95	0.202	5-15 (IS:1991, WHO 1993)
As	0.07	0.141	0 to 0.3	1.4	0	0	0 to 0	0	0.05 (IS:1991)
Sb	42	12.727	0 to 306	8400	37.36	63.096	233 to 0	7472	0.005 WHO:1993)
Ag	1.51	2.474	0 to 4.3	-	13.24	10.803	0 to 39.8	-	-
Sn	2.65	0.070	1.7 to 6.1	-	3.71	0.601	4.66 to 3.06	-	-
Mo	0	0	0 to 0	0	0	0	0 to 0	0	0.07 ((WHO:1993)
Bi	0.06	0.212	0 to 0.3	-	0.48	0.726	0 to 2.46	-	-
Pb	2.69	0.0707	1.6 to 3.3	269	7.039	0.514	7.96 to 6.3	703.9	0.01 (WHO:1993)
Sr	1.06	0	0 to 5.9	-	1.202	1.435	0 to 6.56	-	-
Cd	3.63	5.091	0 to 11.4	1210	0.34	0.374	0 to 1.53	113.3	0.003 (WHO:1993)
U	1.06	0.565	0 to 3.3	35.33	0.42	0.428	0 to 1.4	14	0.03 US EPA
Hg	0.04	0	0 to 0.4	40	0	0	0 to 0	0	0.001 (WHO:1993)
Se	0	0	0 to 0	0	0	0	0 to 0	0	0.05 US EPA
Ti	1.63	2.969	0 to 4.7	-	0.83	0.898	0 to 2.85	-	-
I	0	0	0 to 0	-	0	0	0 to 0	-	-

Many of the essential elements were also found to be in higher concentrations than permissible limits. For example, 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 was 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. 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 Ludhiana, while it ranged from 1.95 to 4.25 mg/L with mean value 3.035 mg/L at Patiala. So observed Zn concentration value was much higher than the permissible limit of 5-15 mg/L at Ludhiana, but was within the normal range at Patiala. The ground water samples therefore were not Cu- and Zn- deficient.

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. These results are contrary to many other studies who found high level of Fe concentrations in some parts of western Uttar Pradesh (Kalicharan 2007). 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. Lead is known to be toxic to the central and peripheral nervous systems, including subencephalopathic neurological and behavioral effects and its consumption in higher quantity may cause hearing loss, blood disorders, and hypertension (ISI 1991, WHO 1993). Antimony is used in making certain types of semiconductor devices, such as diodes and infrared detectors. Antimony is alloyed with lead to increase lead's durability. Antimony alloys are also used in batteries, low friction metals, type metal and cable sheathing, among other products. Antimony compounds are used to make flame-proofing materials, paints, ceramic enamels, glass and pottery. Bismuth is a by-product from lead and copper smelting. Arsenic (As) is introduced into ground water from industrial effluents, atmospheric deposition and also from pesticides, insecticides and herbicides.

The study clearly shows that hand pump water is not a safe source of drinking water. It taps into shallow aquifers and is heavy with chemicals. The untreated industrial effluents including dyes from tanning, nickel and chrome plating units

are discharged into *Buddha Nullah*. The *Buddha Nullah* pollutes the Sutlej River. There are reports that many factories instead of treating the effluents, inject it into the earth through deep-bore wells. The high concentration of trace elements and heavy metals, as revealed in the present study, may be causing the detrimental effect on the inhabitants of the area. The health status of the people in these areas is being investigated. The prevalence of Hepatitis C and gastrointestinal problems was much high in Walipur area near *Buddha Nullah*. Many heavy metals like lead, cobalt, chromium, zinc and copper are known to cause damage to the intestinal tract. Prevalence of congenital bony problems was higher at Arnetu village.

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