(WHO, 2011):

"Not all of the chemicals with guideline values will be present in all water supplies or, indeed, all countries. If they do exist, they may not be found at levels of concern. Conversely, some chemicals without guideline values or not addressed in the Guidelines may nevertheless be of legitimate local concern under special circumstances."

4.1 General

Apart from being a potential source of radiation exposure through ingestion of radionuclides like uranium and radon, drinking-water has important chemical aspects of health concern. The health concerns associated with chemical constituents via drinking water is often a subject of prolonged periods of exposure, unless there is not massive contamination of drinking-water. Guideline values have been established for every possible chemical entity that may constitute drinking water naturally or may be added in it via external pathways (WHO, 2011). Guideline values for heavy metals in particular, have been described in Table 1.4.

Water quality targets are the most common form of health-based target applied to chemicals that may be found in drinking-water (WHO, 2011). Metals are a ubiquitous class of inorganic chemical both in the natural environment and in the workplace. The common occurrence of numerous natural and artificial forms of metals in the human environment is dictated by their wide natural distribution and by their intensive use in an ever-growing number of industrial processes (Friberg *et al.*, 1986). Human exposure to metals and metal compounds therefore is clearly inevitable. Metallic agents, once concentrated in the biosphere, generally persist and are not broken down by natural forces, at least not beyond the elemental form. Environmental persistence in combination with intensive use by modern society has, over the years, concentrated metals within the human environment and this trend continues generally unabated and provides ample opportunity for human exposure to metals.

In recent times, attention is also being paid to the natural background concentrations of metals in ground water in order to study the anthropogenic and geogenic sources affecting groundwater quality, since the background levels of major ions, minor and trace elements are related to the rock type through which water flows. In this context hydro geochemical study of a localized area, in the absence of major polluting sources, helps us to understand the baseline concentrations of that area.

As discussed in the chapter 1, the term heavy metal is used inconsistently as a group name for metals and semimetals (metalloids) that have been associated with contamination and potential toxicity or ecotoxicity. This practice has led to a tendency to assume that all so-called heavy metals have highly toxic or ecotoxic properties. The prefix ‘heavy’ in conventional usage implies high density. But unfortunately scientific community has differed rather failed, to set a reference density value, above which a metal is said to be heavy metal (Grant and Grant, 1987; Parker, 1989; Lozet and Mathieu, 1991). Atomic number was proposed as another basis of defining heavy metal; where metals with atomic numbers above 23 (of sodium) (Bennet, 1986) or metals of atomic weights greater than 40, thus starting with scandium (Rand *et al.*, 1995) were defined as heavy metals. But the problem with citing metals of atomic number greater than sodium as being “heavy” is that it contradicts the historic definition based on density, as it includes elements of density lower and includes essential metals such as magnesium and potassium. To add to the confusions in the use of term heavy metal, the term ‘trace element’ is sometimes used for toxic elements in soils, foods and water or for elements of low nutritional importance. To overcome these inconsistencies and confusions, adopting “understanding bioavailability as the key to assess the potential toxicity of metallic elements and their compounds” has been recommended (Duffus, 2002).

A heavy metal as per above discussion, thus is a member of a loosely defined subset of elements that exhibit metallic properties and includes transition metals, some metalloids, lanthanides, and actinides that concern us because of occupational or residential exposure. Water is important source of injecting trace elements in human body. A water sample can comprise possibly all of the elements appearing in the periodic table. The elemental analysis of water for health risk assessment thus, is inexactly referred to as heavy metal analysis. Semimetals, arsenic, boron and tellurium and the nonmetal selenium are often included in such analysis to take into account their toxic exposures. Antimony, bismuth, barium, cadmium, cerium, chromium, cobalt, copper, gallium, gold, iron, lead, manganese, mercury, nickel, platinum, silver, tellurium, thallium, tin, uranium, vanadium, and zinc are other heavy metals in this sense.

Arsenic is an important element of health concern among acute elemental poisoning in adults (ATSDR, 2007). Exposure to elevated levels of arsenic, a class I human carcinogen (IARC, 2004), is now a global concern most significant environmental causes of cancer in the world. World Health Organization recommends a guideline value of 10 μg^{-1} in drinking water. The origin and mobility of arsenic in the groundwater environment has received significant attention in recent years. In drinking water, arsenic is considered as one of the most significant environmental causes of cancer in the world (Smith *et al.*, 1992; Mukherjee *et al.*, 2006). There are however, several non-cancer effects of arsenic ingestion including cardiovascular disease, diabetes, and anemia, as well as reproductive and developmental, immunological, and neurological disorders. It is this severity of arsenic toxicity, that forced WHO and USEPA to decrease health limit for As in groundwater from 50 μgl^{-1} to10 μgl^{-1}, to take care of risks of long-term exposure from low As concentrations in drinking water causing skin, bladder, lung, and prostate cancer (Jiménez-Valverde, 1999; Prasad, 2008). WHO in fact, states that the health-based drinking water guideline for arsenic should be 0.17 μg^{-1}. The existing detection limit 10 μgl^{-1} has been adopted; to accommodate the fact that detection limit for most laboratories is 10 μgl^{-1}.

Barium in water comes primarily from natural sources. Whereas acetate, nitrate and halides of barium are soluble in water, carbonate, chromate, fluoride, oxalate, phosphate and sulfate are quite insoluble. Although barium compounds have variety of industrial applications, barium in water comes primarily from natural sources and whereas food is the primary source of intake for the non-occupationally exposed population, drinking-water may contribute significantly to total intake, where present in high levels in water. The solubility of barium compounds is a function of pH in the terms that highest levels to be found in drinking-water are likely to be associated with groundwater of low pH from granite-like igneous rocks, alkaline igneous and volcanic rocks and manganese-rich sedimentary rocks (USEPA, 1985a). Generally found concentrations of barium in drinking-water are less than 100 μgl^{-1} (WHO, 2011).

Guideline value of barium concentration in drinking water by WHO is 700 μgl^{-1}. Guideline value for barium in drinking-water is derived using the TDI (total daily intake) approach, as there is no evidence that barium is carcinogenic (Schroeder and Mitchener, 1975a). By definition (WHO, 2011), TDI is an estimate of the amount of a substance in food and drinking-water, expressed on a body weight basis (milligram or microgram per kilogram of body weight), that can be ingested over a lifetime without appreciable health risk, and with a margin of safety. Hence, TDI is kind of quantity like that of reference average daily dose (R_fD) to estimate chemical, non-carcinogenic harms incurred due to the exposures calculated for uranium in chapter 3. Various other terms are in use to measure and monitor uptake of trace elements, both essential and toxic, through water and foods. These may be- Life time Average Daily dose (LADD), Maximum Contaminant Level (MCL), Tolerable Daily Intake (TDI), Minimum Desirable Concentration (MDC), No-observed adverse-effect-level (NOAEL), Lowest-observed adverse-effect-level (LOAEL) and Benchmark dose (BMD).

Guideline values in drinking water are established for these chemical elements on the basis of international risk assessments of the health effects associated with exposure through water. Arsenic, Barium, Boron, Chromium and Selenium are listed as "naturally occurring chemicals that are of health significance in drinking-water" (Table 8.8, WHO, 2011), whereas cadmium and mercury are "chemicals from industrial sources and human dwellings that are of health significance in drinking-water" (Table 8.10, WHO, 2011).

Water also ingests in our body essential elements with physiological relevance like iron, magnesium, manganese, molybdenum, potassium, selenium, sodium, zinc; which of course, can become toxic at high concentrations and elements that are altogether toxic like antimony, arsenic, barium, beryllium, cadmium, lead, mercury. Among these, cadmium and mercury are not expected to be found in detectable amounts in routine drinking water samples, as they don't have natural origin. Highest risk of exposure to cadmium for example may be due to processes involving heating cadmium-containing materials such as smelting and electroplating. Major route of cadmium exposure is through inhalation of dust and fumes or incidental ingestion from contaminated hands, food (ATSDR, 2008). A possible classification can be carried out to take account of health concerns associated with a particular element (Prasad, 2008):

- Elements essential in nutrition: calcium, cobalt, chromium (III), copper, fluorine, iodine, iron, magnesium, manganese, molybdenum, potassium, selenium, sodium, zinc.
- Elements with possible beneficial effects: boron, nickel, silicon, vanadium.
- Toxic or (without any beneficial effects) elements: aluminium, antimony, arsenic, barium, beryllium, cadmium, lead, mercury, silver, strontium, thallium, tin. This list encompasses elements that can be found in the environment and for which human exposure should be limited.

Physico-chemical parameters (Conductivity, pH, salinity, total dissolved solids (TDS) and temperature etc.) of water are important in the sense that these parameters can provide important first hand in-situ information about the suitability of water for drinking purposes apart from being helpful in studying and modeling of speciation of radionuclides and anthropogenic elements in aquatic environment (Kumar *et al.*, 2011). Total dissolved solids (TDS) comprise inorganic salts (principally calcium, magnesium, potassium, sodium, bicarbonates, chlorides and sulphates) and small amounts of organic matter that are dissolved in water. The source of these solids in drinking-water may be a natural one or a sewage, urban runoff and industrial wastewater. Concentrations of TDS in water vary considerably in different geological regions owing to differences in the solubility of minerals.

Like any other solution, pH scale runs from 0 to 14 in natural waters, i.e. a pH value of 7 is neutral; a pH less than 7 is acidic and greater than 7 represents base saturation or alkalinity. The pH is monitoring parameter to assess aquatic ecosystem health, irrigation sources and discharges, live stock, drinking water sources, industrial discharges and intakes. In unpolluted or pure waters, pH is governed by the exchange of carbon dioxide with the atmosphere. Carbon dioxide is soluble in water and the dissolution of CO_2 in the water is a function of temperature and the concentration of CO_2 in the air. As the gaseous CO_2 becomes aqueous, the CO_2 will be converted into H_2CO_3 which will acidify the water to a pH of about 6. If any alkaline earth metals such as sodium are present, the carbonates and bicarbonate formed from the solublization of CO_2 will interact with sodium increasing the alkalinity shifting the pH up over 7. In addition to organic acids and the carbonate chemistry, the acidity of natural waters could also be controlled by mineral acids produced by the hydrolysis of salts of metals such as aluminum and iron. The solubility of most metals increases in water as the pH decreases. The excesses of dissolved metals in water in turn, will negatively affect the health of the aquatic organisms.

ORP (Redox Potential) is a measurement of water's ability to oxidize contaminants. Higher ORP simply indicates the greater number of oxidizing agents. In generalized terms for human health, a lower ORP is preferred for consumption due to the high anti-oxidant value. There are numerous applications for ORP, each with its own specific optimum value. For example, the minimum ORP for pool and spa disinfection (set by the World Health Organization) is 650 mV. Though the WHO has not set a standard for ORP in drinking water, anything below -550 mV is considered too strong and not recommended for drinking.

The present study was taken up to determine the levels of trace elements in drinking water samples to estimate exposure to the heavy metals through drinking water to the residents of study region and to assess the water quality/suitability for drinking purposes. For this, 36 water samples out of 90 water samples analysed for uranium discussed in chapter 3 have been analysed for elemental analysis. Other water quality chemical parameters viz. pH, conductivity, TDS and salinity have also been monitored. Obtained values of metal concentrations and other parameters are compared with the guideline values issued by health agencies like world health organization.

4.2 Experimental Techniques

4.2.1 Heavy Metal Analysis

Inductively Coupled Plasma Mass Spectrometer (ICP-MS) at National Geophysical Research Institute (NGRI), Hyderabad, India has been used for elemental analysis in water samples. In these water samples eighteen metals/metalloids Be, Al, V, Cr, Mn, Fe, Ni, Co, Cu, Zn, As, Se, Mo, Ag, Cd Sb, Ba and Pb have been analysed. The present study however, is aimed mainly at knowing individual concentrations of As, Ba, Cd, Cr, Pb, Se and Zn in drinking water samples from these areas from health hazard point of view. Other heavy metals are also analyzed because of the calibration of the instrument with the default ICP-MS standard. The details of instrument used and principle of inductively coupled plasma mass spectrometry (ICP-MS) have already been discussed in chapter 2.

Water samples were filtered through 0.45 μm membrane filters and then samples were acidified by conc. HNO_3. Filtered samples were directly introduced into ICP-MS instrument by conventional pneumatic nebulization, using a peristaltic pump with a solution uptake rate of about 1 ml min^{-1}. The nebulizer gas flow, sample uptake rate, detector voltages and lens voltage were optimized for a sensitivity of about 50,000 counts s^{-1} for 1 ng ml^{-1} solution of In. The instrumental and data acquisition parameters are published elsewhere (Balaram *et al.,* 2003). Calibration was performed using the certified reference material NIST 1640 (National Institute of Standards and Technology, USA), to minimize matrix and other associated interference effects. Certified reference material for trace elements in river water SLRS-4 (National Research Council, Canada) was analyzed as an unknown to check the precision and accuracy of the analysis. Blanks were analyzed along with the samples and corrections were carried out accordingly. The RSD was found to be better than 6% in majority of the cases, which indicates that the precision of the analysis is reasonably good.

4.2.2 Water Quality Analysis

The Physico-chemical parameters measured for these water samples were measured during sample collection using water quality kit due to Naina solaris Ltd, New Delhi. Technical specifications of the microcontroller solution analyser lit have already been discussed in section 2.5.

4.3 Results and Discussion

Heavy Metal Analysis

Table 4.1 details the results of ICP-MS analysis of 36 water samples from Faridkot, Ferozepur and Muktsar districts of Punjab. Ranges and averages of respective elements are given in Table 4.2. Table 4.3 is for Lifetime Average Daily Dose (LADD) and hence Hazard Quotients (HQ) due to obtained concentrations in these water samples for some important heavy metals.

Arsenic, Barium, Chromium, Lead and Selenium comprise first group of elements for discussion here. Arsenic, Barium, Chromium and Selenium are of *natural origin* and have potential toxic effects when present in drinking water above permissible limits. Lead also occurs naturally in the environment. However, most of the high levels of lead found throughout the environment come from human activities. More than 99% of all publicly supplied drinking water contains less than 5 parts of lead per billion parts of water (ATSDR, 2007). Arsenic, Barium, Chromium, lead and Selenium ranged between (in μgl^{-1} units) 0.46- 13.82, 0.24-148.68, 1.09- 67.12, 0.48- 182 and 0.43-24.56 respectively, with respective mean values 4.34, 20.68, 22.27, 25.10 and 7.49 μgl^{-1}. Average daily doses (LADDs) given in the table 4.5, for these elements are calculated for water ingestion rate of 4.05 $l$day^{-1}, exposure frequency of 350 days, life expectancy for both males and females of 63.7 years and average body weight equal to 51.5 kg.

Table 4.1 Concentration (average) of heavy metals (μgl^{-1}) in drinking water samples collected from Faridkot, Ferozepur and Muktsar districts of Punjab using ICP-MS

Sample Locations→ Metals (Mass Number)↓	**1. Faridkot city**	**2. Kotkapura**	**3. Ramana**	**4. Jaito**	**5. Bhagtuana**	**6. Karirwali**	**7. Machaki**	**8. Sadik**	**9. Mallan**
Be (9)	0.008	0.002	0.540	0.040	0.004	0.002	0.005	0.164	0.004
Al (27)	29.09	9.34	27.20	111.50	30.80	22.86	25.18	25.22	41.63
V (51)	2.22	3.91	2.29	7.02	3.37	4.42	7.17	3.43	5.70
Cr (52)	7.02	41.13	5.24	1.09	6.10	13.75	47.75	6.94	17.12
Mn (55)	22.29	31.66	84.76	14.76	21.44	20.21	17.71	33.37	20.40
Fe (57)	48.15	18.75	7.67	12.58	31.31	11.68	28.82	12.3	45.86
Ni (58)	14.55	10.29	7.02	13.37	4.42	10.71	6.94	3.43	1.35
Co (59)	0.075	0.070	0.086	0.110	0.041	0.110	0.360	0.087	0.098
Cu (63)	3.79	4.47	70.40	62.02	33.14	8.09	20.88	45.15	5.04
Zn (64)	24.44	7.03	7.67	12.58	11.31	46.68	13.02	11.31	47.66
As (75)	1.35	1.47	1.44	2.8	5.24	1.70	12.38	3.90	3.003
Se (82)	1.44	2.81	5.24	1.09	6.10	13.21	24.56	10.14	5.24
Mo (98)	2.18	4.76	2.37	3.11	13.80	3.43	4.79	8.00	56.54
Ag (107)	0.48	0.06	0.08	0.07	0.24	0.24	0.54	0.50	0.56
Cd (114)	0.12	0.06	0.24	0.40	0.21	0.12	0.19	0.22	0.28
Sb (121)	0.21	0.50	0.46	0.63	0.55	0.45	0.85	0.50	0.47
Ba (138)	46.08	3.60	6.50	140.68	20.02	6.07	36.36	30.07	6.50
Pb (208)	62.02	0.64	182.00	66.75	1.59	22.05	0.48	157.05	1.60

Cont..

Sample Locations→ Elements (Mass Number)↓	10. Kauni	11. Mukatsar city	12. Marh Mallu	13. Rupana	14. Aulakh	15. Pind Malout	16. Malout City	17. Badal	18. Kabbarwal
Be (9)	0.004	0.006	0.016	0.062	0.115	0.004	0.007	0.002	0.044
Al (27)	15.62	15.43	11.25	45.50	50.80	12.52	37.24	17.23	10.34
V (51)	2.10	3.95	3.57	6.82	1.14	2.54	4.54	4.54	1.75
Cr (52)	67.12	15.37	39.89	52.67	22.58	35.86	27.46	50.41	3.00
Mn (55)	31.68	21.69	15.14	16.35	12.47	12.61	22.55	20.01	10.32
Fe (57)	51.45	22.82	17.36	7.67	12.58	31.24	102.34	34.73	31.31
Ni (58)	9.01	12.25	3.12	7.02	2.37	4.22	11.18	7.47	22.55
Co (59)	0.080	0.090	0.050	0.077	0.054	0.129	0.260	0.096	0.082
Cu (63)	2.98	6.14	6.15	21.52	18.40	3.73	15.00	11.47	18.10
Zn (64)	12.58	11.30	50.65	11.32	7.67	14.34	18.40	132.98	11.31
As (75)	5.82	3.39	3.11	6.41	6.1	1.32	3.12	3.54	3.90
Se (82)	1.09	6.12	12.65	5.20	12.64	3.90	20.82	4.96	12.65
Mo (98)	4.37	3.10	13.80	8.15	6.50	4.75	7.64	13.96	2.37
Ag (107)	0.31	0.16	0.08	0.03	0.16	0.97	0.38	0.25	0.30
Cd (114)	0.07	0.07	0.05	0.06	0.22	0.08	0.02	0.12	0.071
Sb (121)	0.93	0.55	0.36	0.50	3.74	0.28	0.58	3.74	0.47
Ba (138)	148.68	5.02	5.36	6.02	15.35	7.72	16.40	5.60	6.02
Pb (208)	0.81	1.05	0.72	13.05	11.50	31.05	10.03	14.50	24.33

Cont..

Sample Locations→ Elements (Mass Number)↓	19. Balluana	20. Abohar	21. Nihal Khera	22. Fazilka	23. Behakbobla	24. Bambha Battu	25. Bagge Ke	26. Jalalabad	27. Jiwan Arain
Be (9)	0.056	0.025	0.020	0.002	0.064	0.038	0.090	0.030	0.006
Al (27)	30.12	18.34	20.45	40.63	45.87	51.45	22.82	17.36	23.57
V (51)	1.35	2.01	3.25	3.12	3.98	3.37	5.42	7.47	3.43
Cr (52)	25.82	3.39	1.09	14.82	3.30	50.82	23.10	45.11	11.78
Mn (55)	13.12	23.54	20.70	13.09	11.35	12.01	14.25	25.12	52.25
Fe (57)	10.68	8.82	12.37	51.35	31.34	11.68	181.82	12.3	21.84
Ni (58)	1.29	4.02	26.93	4.42	15.25	20.12	3.02	3.37	14.98
Co (59)	0.058	0.068	0.129	0.180	0.096	0.066	0.098	0.073	0.073
Cu (63)	60.18	30.52	19.76	13.36	88.03	11.30	64.14	56.10	8.70
Zn (64)	45.68	11.31	25.67	21.76	11.68	20.31	30.67	21.76	12.55
As (75)	13.82	5.97	8.97	7.09	4.55	1.29	4.02	3.37	1.57
Se (82)	4.24	12.60	1.02	6.42	12.66	6.12	10.68	3.90	6.19
Mo (98)	3.11	13.80	8.15	19.15	5.50	4.75	20.64	15.96	13.72
Ag (107)	0.16	0.09	0.38	0.64	030	0.16	0.10	0.38	0.21
Cd (114)	0.02	0.24	0.07	0.48	0.07	0.02	0.24	0.07	0.17
Sb (121)	0.60	0.15	0.45	1.58	0.36	0.52	0.29	1.15	0.10
Ba (138)	5.36	7.72	25.40	5.74	4.02	8.35	7.72	16.40	3.52
Pb (208)	26.00	11.50	15.80	2.82	51.05	45.08	22.82	29.88	2.15

Cont..

Sample Locations→ Elements (Mass Number)↓	**28. Pindi**	**29. Lakho Ke Behram**	**30. Khai Kheme Ki**	**31. Ferozepur city**	**32. Khosa Dal Singh**	**33. Zira**	**34. Khui Khera**	**35. Bhadana**	**36. Makhu**
Be (9)	0.060	0.400	0.080	0.050	0.030	0.004	0.030	0.060	0.020
Al (27)	22.40	14.40	17.12	6.84	15.37	20.51	40.63	45.86	8.73
V (51)	5.70	3.21	1.47	2.01	3.95	3.57	3.72	3.25	3.12
Cr (52)	3.30	48.19	5.24	1.09	26.10	26.10	7.04	5.86	57.46
Mn (55)	23.20	12.57	23.47	21.41	12.55	12.42	21.25	24.12	26.68
Fe (57)	10.68	23.25	10.68	8.82	12.3	51.45	22.82	17.36	22.04
Ni (58)	3.37	6.93	9.25	16.12	3.02	7.93	4.55	4.00	2.72
Co (59)	0.097	0.052	0.053	0.084	0.081	0.090	0.356	0.179	0.040
Cu (63)	70.50	4.28	22.00	48.43	104.35	6.94	50.01	96.80	3.19
Zn (64)	23.76	17.85	30.55	29.76	22.85	38.25	18.55	24.76	27.85
As (75)	4.028	6.93	3.25	3.12	0.95	7.93	4.55	0.45	4.35
Se (82)	3.90	0.74	5.96	12.65	6.10	8.40	5.97	12.65	0.43
Mo (98)	7.64	9.33	8.64	14.96	13.73	3.55	5.50	4.75	0.96
Ag (107)	0.30	0.43	0.08	0.62	0.24	0.24	0.16	0.09	0.07
Cd (114)	0.19	0.11	0.07	0.17	0.12	0.20	0.27	0.17	0.03
Sb (121)	0.47	0.45	2.50	0.36	1.18	0.35	1.74	0.4	0.67
Ba (138)	16.60	31.37	16.40	3.52	22.40	1.55	31.37	28.4	0.24
Pb (208)	21.04	0.68	0.91	2.38	1.06	14.14	10.76	30.30	14.55

Table 4.2 Results in brief corresponding to the data in Table 4.2

Element →	Be (9)	Al (27)	V (51)	Cr (52)	Mn (55)	Fe (57)	Ni (60)	Co (59)	Cu (63)
Mean	0.058	27.81	3.63	22.27	22.03	29.17	8.42	0.106	30.97
Range	0.002-0.540	6.84-111.50	1.14-7.47	1.09-67.12	10.32-84.76	7.67-181.82	1.29-26.93	0.040-0.360	4.98-104.35
Element →	**Zn (66)**	**As (75)**	**Se (82)**	**Mo (98)**	**Ag (107)**	**Cd (114)**	**Sb (121)**	**Ba (138)**	**Pb (208)**
Mean	24.70	4.34	7.49	9.38	0.26	0.15	0.55	20.68	25.10
Range	5.68-132.90	0.46-13.82	0.43-24.56	0.97-56.53	0.06-0.64	0.02-0-0.48	0.10-1.18	0.24-148.68	0.48-182

Table 4.3 Table for chemical doses (LADD) and Hazard Quotients calculated for some important heavy metals (As, Cd, Cr, Pb, Se and Zn) in water samples

Elements (alphabetically)	Guideline value in water ($\mu g l^{-1}$)	Mean and range Concentration ($\mu g l^{-1}$)	Calculated LADD ($\mu g kg^{-1} day^{-1}$)	R_fD ($\mu g kg^{-1} day^{-1}$)	HQ ($\frac{ADD}{RfD}$)
As	10	4.34 (0.46-13.82)	0.15 (0.02 .49)	0.36	0.43 (0.05-1.38)
Ba	700	20.68 (0.24- 148.68)	0.73 (0.01-5.28)	24.86	0.03 (0-0.21)
Cd	3	0.15 (0.02- 0.48)	0.01 (0 .00-0.02)	0.11	0.05 (0.01- 0.16)
Cr	50	22.27 (1.09-67.12)	0.79 (0.04-2.38)	1.78	0.45 (0.02-1.34)
Pb	10	25.10 (0.48- 182)	0.89 (0.02- 6.46)	0.36	2.51 (0.05-18.20)
Se	40	7.49 (0.43- 24.56)	0.27 (0.02 .87)	1.42	0.19 (0.01- 0.61)
Zn	10	24.70 (5.68-132.90)	0.88 (0.20-4.72)	0.36	2.47 (0.57-13.29)

In the present analysis, the mean of the arsenic concentration in the water samples is found to be 4.34 μgl^{-1} and contents ranged as 0.46-13.82 μgl^{-1}. Out of 36 samples, arsenic concentration exceeded the safe limit 10 μgl^{-1} for 6 samples. (Average) concentration of the arsenic is thus below the recommended safe limit. In their study in some adjoining areas of Punjab, Jain and Kumar (Jain and Kumar, 2007) however, have reported the concentration of arsenic in ground water as high as 688 μgl^{-1} (3.5-688μgl^{-1}) and recognized 46 percent ground water sites containing high arsenic concentration. The range of arsenic obtained in the present work however, agreed with the findings of Blaurock-Busch *et al.* in 2010, who reported an Arsenic range of 1.0-8.0 μgl^{-1} in some water samples from the present study region (Blaurock-Busch *et al.,* 2010). Arsenic is an extremely toxic element for humans, not only in high concentrations, but also the exposition during a long period to low concentrations (Tripathi *et al.*, 1997). The arsenic contaminated groundwater in Bangladesh and in West Bengal (India) is the region with largest case of poisoning of a population (Chatterjee *et al.*, 1995; Bhattacharya *et al.*, 1997; Dhar *et al.*, 1997; WHO, 2003). Kavcar *et al*. (2009) have reported non-carcinogenic risk due to arsenic concentration exceeding safe limit 10μgl^{-1} in 20% of the drinking water in their recent study for exposure to trace metals via drinking water ingestion for Province of Izmir, Turkey.

Level of barium varied as 0.24-148.68 μgl^{-1} and average for the 36 samples came out to be 20.68 μg^{-1}. Guideline value of barium concentration in drinking water recommended by WHO is 700 μgl^{-1}. Therefore, concentration of the barium in all the water samples is below the recommended safe limit. This also corroborates findings of above referred work by Blaurock-Busch *et al.* (2010), who also reported barium concentration in the safe limit, with a range of 9.0- 436 μgl^{-1}.

For the present water samples, whereas cadmium ranged as 0.02- 0.48 μgl^{-1} with mean value 0.15 μgl^{-1}, mercury was found to be below detection limits for all the samples. Whereas WHO has put a guideline value of 3 μgl^{-1} for cadmium in drinking water, EPA has mandated the water suppliers to be controlled for cadmium concentrations in drinking water to less than 5 μgl^{-1}. Moreover, water is not considered to be major sources of cadmium ingestion. Therefore, it can be concluded that exposure to cadmium and mercury through public drinking water sources is not a concern for the study region.

Table 4.4 Table briefing health effects associated with some important heavy elements and their sources of contamination in water

Element (atomic mass)	Potential Health Effects from Long-Term Exposure Above MCL[1]	Sources of Contamination in Drinking Water
Arsenic (75)	Skin damage or problems with circulatory systems, and may have increased risk of getting cancer	Erosion of natural deposits; runoff from orchards, runoff from glass & electronics production wastes
Cadmium (114)	may promote several disorders in the metabolism of Ca and vitamin D, leading to bone degeneration and kidney damage	Corrosion of galvanized pipes; erosion of natural deposits; discharge from metal refineries; runoff from waste batteries and paints
Chromium (52)	Allergic dermatitis	Discharge from steel and pulp mills; erosion of natural deposits
Lead (208)	Infants and children: Delays in physical or mental development; children could show slight deficits in attention span and learning abilities. Adults: Kidney problems; high blood pressure	Corrosion of household plumbing systems; erosion of natural deposits
Mercury (202)	hemorrhagic gastritis and colitis; the ultimate damage is to the kidney	Natural weathering of mercury-bearing minerals in igneous rocks
Selenium (82)	Symptoms in people with high urinary selenium levels included gastrointestinal disturbances, discoloration of the skin, decayed teeth, hair or nail loss, nail abnormalities and changes in peripheral nerves.	Selenium is present in Earth's crust, often in association with sulfur-containing minerals.

[1] Maximum Contaminant Level (MCL) - The highest level of a contaminant that is allowed in drinking water.

Cd in the range 0.08-39.62 μgl^{-1} has been reported in drinking water samples from adjacent Bathinda district in a recent study (Kumar *et al.*, 2006). Elevated cadmium levels in water sources reported by them might be due to local industrial emission e.g. presence of in the vicinity of cadmium-emitting industries. As said above, Cd comes into human environment as a result of industrial emission and doesn't have a natural origin.

The concentration of aluminum, iron, manganese, molybdenum, nickel, silver and zinc in μgl^{-1} units ranged as 1.14-7.47, 1.29-26-93, 10.32-84.76, 0.97-56.53, 1.29-26.93, 0.26-0.64 and 5.68-132.90 respectively with average values 3.63, 8.42, 22.03, 9.38, 8.42, 0.26 and 24.70 μgl^{-1}.

As per above classification of elements, whereas aluminum is categorized as element 'without any beneficial effect' and toxic only at abnormally high values; iron, manganese, molybdenum and zinc are among essential trace elements. Nickel was categorized under category 'elements with possible beneficial effects'. World Health Organization in fact, has not established guidelines for some of elements/chemicals (of natural origin in particular), on the grounds that their occurrence is only at concentrations well below those that would be of concern for health. Apart from Aluminum, iron, manganese, molybdenum, potassium, sodium, silver; physico-chemical parameters pH and total dissolved solids (TDS) come under this category (WHO, 2003; WHO, 2011).

Nickel ranged 1.29-26.93 μgl^{-1} and averaged at 8.42 μgl^{-1}, well below the guideline value of 70 μgl^{-1} (WHO, 2005). Nickel in fact, is normally not found in concentrations above 20 μgl^{-1} (WHO, 2005), except in special cases including nickel emission from natural or industrial nickel deposits in the ground. Higher Ni contents in water are found reported however. One example of higher contents (31.37- 388.4, average 31.37 μgl^{-1}) is that reported by Kavcar *et al.* (2009) in Izmir province, Turkey.

Zinc with average value of 24.70 μgl^{-1} in the present analysis has been found well above the permissible limit 10 μgl^{-1} by WHO. Zn has also been reported above permissible limit (in the range 3-1044 μgl^{-1}) in a previous study by Kumar *et al.* (2006) in drinking water samples from adjacent Bathinda district. Cobalt and copper ranged as 0.040- 0.360 μgl^{-1} and 4.98-104.35 μgl^{-1} with average values 0.106 and 30.97 μgl^{-1}.

Hazard Quotient

Hazard Quotient (HQ) has been calculated for the obtained average value of some heavy metals in the Table 4.3 on the lines of that calculated for uranium in chapter 3. For each metal reference dose (R_fD) was calculated corresponding to WHO guideline value in drinking water. For example, for barium, with 700 μg^{-1} as reference value, reference average daily dose or LADD comes out to be 24.86 $\mu gkg^{-1}day^{-1}$ for water ingestion rate of 4.05 $l day^{-1}$, exposure frequency of 350 days, life expectancy for both males and females of 63.7 years and average body weight equal to 51.5 kg are taken for an adult Indian reference man (see chapter 3). For barium mean concentration of 20.68 μgl^{-1} for the 36 water samples here, HQ is much lesser than 1 corresponding to average daily chemical exposure 0.74 $\mu gKg^{-1}day^{-1}$.

Hazard Quotients for Arsenic, Cadmium, chromium and selenium remained less than 1, for average water contents 4.34 μgl^{-1}, 0.15 μgl^{-1}, 22.27 μgl^{-1} and 1.35 μgl^{-1} respectively. Hazard Quotient for lead however, has been found to be considerably greater than 1, with value 2.51 corresponding to mean value 25.10 μgl^{-1} and range 0.05-18.20 μgl^{-1}. Reference average daily dose (R_fD) value 0.36 corresponding to guideline value of 10 μgl^{-1} in water has been used to calculate these values for R_fD. Hence lead is above the permissible value in ground water samples. Lead has also been reported exceeding safe limit in the water samples by Kumar *et al.* (2006) in the adjoining Bathinda district, ranging between 6.7-460.0 μgl^{-1}.

Similarly, as seen in Table 4.4, at an average concentration 24.70 μgl^{-1}, zinc in the ground water of study region, imparts an average daily dose of 0.88 $\mu gkg^{-1}day^{-1}$ to the residents against permissible (R_fD) dose 0.36 $\mu gkg^{-1}day^{-1}$, leading to a hazard quotient value of 2.47.

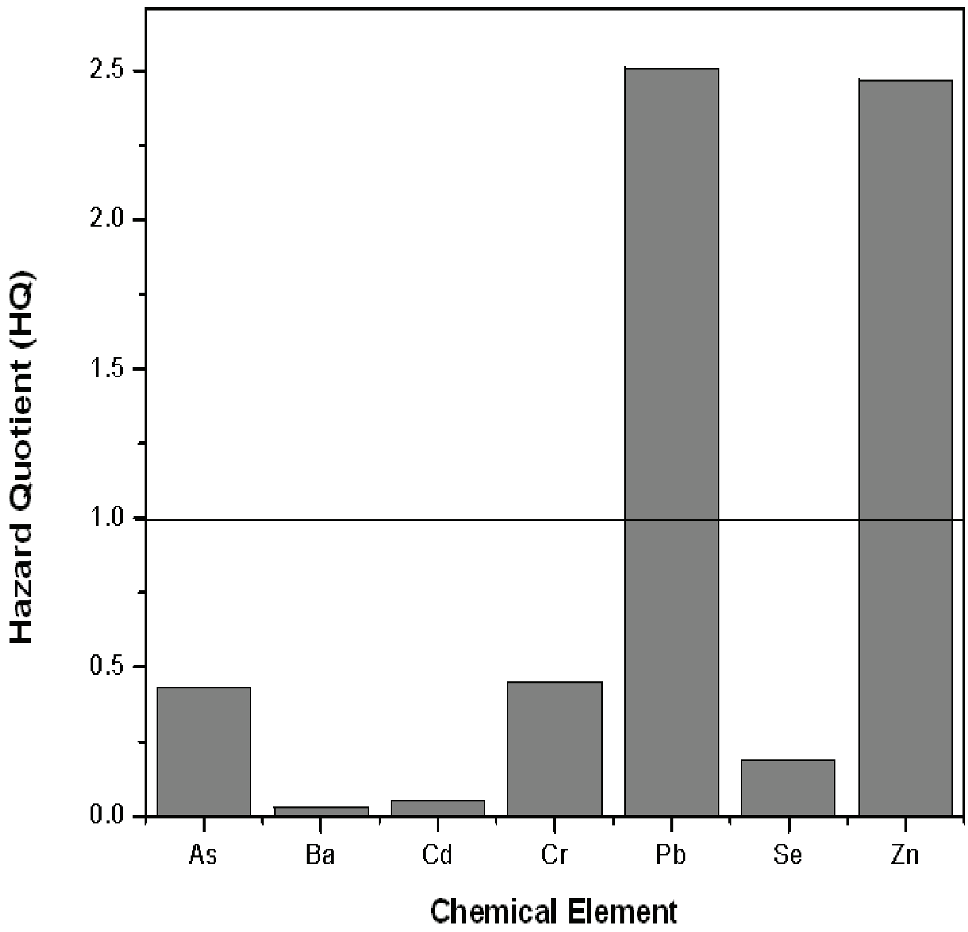

Figure 4.1 Hazard Quotients for some important heavy metals in water samples

Physico-chemical Parameters

Table 4.5 summarizes average and ranges of physical parameters for these water samples. TDS concentrations of the water samples for the present study, varied from a minimum of 60.0 mgl^{-1} to maximum 2020.0 mgl^{-1}. For total dissolved solids (TDS), values less than 600 mgl^{-1} are generally considered to be desirable in drinking water (WHO, 2011). Average of the TDS for the 36 samples 550.6 mgl^{-1} is thus just below the desirable value of 600 mgl^{-1}.

The pH of the samples ranged in 6.55-8.31 with average 7.45. The recommended values of pH for drinking water by Bureau of Indian Standards is 6.5-8.5, while no health-based guideline value is proposed by World Health Organisation for pH (WHO, 2011). Hence pH for these water samples is in safe range. The ranges of other water qualities i.e. ORP, conductivity and salinity for these water sample have been obtained as -716-(-9) mV, 0.12-3.98 $mScm^{-1}$ and 0.01-2.80 ppt respectively.

Physico-chemical parameters in the ground waters for the respective areas have been reported by different working around India. Few among the most recent studies are those in Karnataka (Nirmala *et al.,* 2012), Madhaya Pradesh (Parihar *et al*., 2012), and Rajsthan (Jain and Aggarwal, 2012). In these studies, TDS values as high as 2600 mgl^{-1} and 3780 mgl^{-1} are found reported.

Water quality/physico-chemical parameters TDS, ORP, pH, conductivity and salinity in fact, have no direct and immediate health implications unless found in very abnormal range. Measurement of these parameters in groundwater is finding more important applications now days. For example, monitoring anomalies of TDS and conductivity in ground water has been correlated with seismic event by some workers in seismically active NW Indian Himalayas (Kumar *et al*., 2010).

Table 4.5 Table for water quality parameters of drinking water samples from Faridkot, Ferozepur and Muktsar districts

Location	pH	ORP (-mV)	Conductivity (mS cm^{-1})	TDS (mgl^{-1})	Salinity (ppt)
Faridkot city	7.76	98	1.40	798.5	1.0
Kotkapura	7.61	102	0.99	496.0	0.3
Ramana	7.52	110	1.57	785.2	0.2
Jaito	7.46	62	0.35	175.7	0.2
Bhagtuana	7.16	77	0.12	60.6	0.2
Karirwali	7.54	222	0.21	104.4	0.6
Machaki	7.46	90	0.31	153.9	0.3
Sadik	7.48	54	0.15	87.7	0.1
Mallan	7.66	74	3.98	2020.0	0.1
Kauni	6.55	09	1.4	701.1	0.8
Mukatsar city	6.88	76	0.89	448.5	0.2
Marh Mallu	7.39	716	0.51	257.4	1.0
Rupana	7.24	45	2.00	1001.0	0.4
Aulakh	7.53	239	0.28	139.6	0.3
Pind Malout	7.70	38	1.18	591.5	0.3
Malout City	7.22	86	1.19	594.5	0.2
Badal	7.21	86	1.34	798.4	0.3
Kabbarwal	7.18	94	2.38	1188.2	0.2
Balluana	8.06	99	1.77	885.3	2.3
Abohar	8.12	101	0.12	60.6	1.2
Nihal Khera	7.16	45	0.46	228.2	0.6
Fazilka	7.85	107	1.78	889.4	1.2
Behakbobla	8.03	97	0.17	98.1	0.2
Bambha Battu	8.08	100	1.78	932.0	1.3
Bagge Ke	8.31	193	1.31	742.7	0.3
Jalalabad	8.09	100	2.85	142.3	0.1
Jiwan Arain	7.46	63	1.70	933.8	0.2
Pindi	7.96	92	1.20	648.8	0.2
Lakho ke	7.15	43	1.54	768.0	0.2
Khai Kheme Ki	7.49	64	1.19	596.4	1.1
Ferozepur city	7.66	74	0.97	485.2	0.3
Khosa Dal Singh	7.41	64	0.12	60.0	0.3
Zira	7.83	77	0.66	328.4	0.6
Khui Khera	6.85	21	1.38	689.5	0.2
Bhadana	7.86	86	0.16	98.1	1.5
Makhu	7.69	66	1.66	832.0	1.2
Average	7.45	-105	1.14	550.6	0.67
Range	6.55- 8.31	-716-(-9)	0.12- 3.98	60.0- 2020.0	0.01-2.80

4.4 Conclusions

Chemical doses to masses due to ingestion of elemental composition of drinking water have been estimated on the basis of individual concentrations of these elements using ICP-MS. A particular reference dose was set for each of these corresponding to WHO guideline value to obtain Hazard Quotient.

1. Hazard Quotient for metal of health significance like As, Ba, Cd, Cr, and Se, on the average remained less than 1 and rarely exceeded 1.
2. For Zn and Pb however, HQ averaged has been calculated at a level of 2.47 and 2.51.
3. Among water quality parameters, TDS of the samples averaged at 550.6 mgl^{-1}, which is below the recommended limit of 600 mgl^{-1}, but ranged up to as high as 2020 mgl^{-1}. The pH of the waters samples however, varied in the safe zone as 6.55-8.31.