

### Uranium Analysis in Soil and Water Samples

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#### 3.1 General

Uranium is one of the most important natural radionuclides of primary origin in the Earth's crust. It was identified as an element by the German chemist Martin Klaproth, who isolated it from samples of pitchblende in 1789 and later in 1841 was isolated in metallic form by the French chemist Eugene-Melchior Peligot. Acid igneous rocks contain concentrations of the order of  $3 \text{ mgkg}^{-1}$ , about 100 times greater than that in the ultra-basic igneous rocks. The phosphate rocks of Florida and southeastern Idaho and neighboring areas contain as much as  $120 \text{ mgkg}^{-1}$  and have been used as a commercial source of uranium (Clegg and Foley, 1958). The high uranium content of phosphate rocks can be observed as correspondingly high uranium concentrations in commercial phosphate fertilizers. The overall effect of soil development results in the average soil concentration of uranium being less than the average rock concentration. Most natural waters at the same time also contain detectable amounts of uranium. The uranium concentration of ground and surface waters varies greatly, from a low of less than  $0.1 \text{ ngl}^{-1}$  to several  $\text{mg l}^{-1}$ . The average concentration in the ocean water is about  $3 \text{ } \mu\text{gl}^{-1}$  (Rona *et al.*, 1956). The concentration in ground waters associated with secondary uranium deposits such as the Shirley Basin uraniumiferous area in Wyoming sometimes exceeds several milligrams per liter (Harshmann, 1966).

Radionuclides are a special group of contaminants in terrestrial media and have high ecological significance because they accumulate in media and enter the food chain. Uranium is one such radionuclide of high significance in this respect. It enters into human tissues mainly through drinking water, food, air and the other occupational and accidental exposures. Since distribution and enrichment of radionuclides are generally influenced by soil texture, a routine monitoring of radionuclides in crust soil, can be of great help in detecting any such accumulation via natural or anthropogenic route. Estimation of uranium is also essential in a number of nuclear applications such as fuel

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*Some part of this chapter has been published in the journal 'Human and Ecological Risk Assessment (17: 2, 381- 93\2011)' as paper, entitled "Risk Assessment for Natural Uranium in Subsurface Water of Punjab State, India"*

preparation, reprocessing apart from environmental monitoring (Berthoud *et al.*, 1988; Mauchien *et al.*, 1989; Moulin *et al.*, 1990; Brina and Miller, 1992). Example are estimation of residual uranium (high active waste) in the aqueous phase, estimation of uranium in leached hull (un-dissolved solid waste obtained after dissolution of spent fuel) etc (Sood *et al.*, 1996). Uranium minerals display an extraordinary wide structural and chemical variability, resulting from the different chemical conditions under which U minerals are formed. Improved understanding of uranium mineralogy gives insight into the evolution of uranium deposits, possible mechanisms for uranium and radionuclide retardation following the weathering of nuclear waste materials, and the fate of other anthropogenic sources of uranium of environmental concern.

In the present work, Fission track technique has been used for uranium estimation in soil samples collected from three districts viz. Faridkot, Ferozepur and Muktsar of Punjab, India. For drinking water samples, Laser fluorimetry is used for uranium analysis. Corresponding radiological and chemical risks are calculated for the uranium concentrations in water samples. Few water samples were analyzed by Fission track method for comparison.

## 3.2 Experimental Techniques

### 3.2.1 Uranium Estimation in Water Samples using Fluorimetry

Laser fluorimeter manufactured by Quantalase Enterprises Pvt. Ltd., Indore, India was used for analyses of water samples for uranium concentrations in this work.

#### Analytic Procedure

Analytic procedure begins with taking 10 ml aliquot of filtered water sample in duplicate for wet digestion ( $\text{HClO}_4$  and  $\text{HNO}_3$ ) on hot plates to destroy organic material in the sample. The residue was then dissolved in Millipore elix-3 water followed by mixing with fluorescence reagent (5% sodium pyrophosphate) to make the total volume 25 ml and to adjust pH to 7.2 levels. The sample solution was then taken into a cuvette for the measurement of U concentration. The instrument was calibrated in the range of  $1\text{--}100\ \mu\text{g l}^{-1}$  using a stock solution of standard that was prepared by dissolving 1.78 g of uranyl acetate dihydrate ( $(\text{CH}_3\ \text{COO})_2\text{UO}_2\cdot 2\text{H}_2\text{O}$ ) in 1 l of Millipore elix-3 water

containing 1mL of HNO<sub>3</sub> (70% pure). 5 % phosphoric acid in ultra pure water was used as fluorescence reagent. To obtain blank counts, a blank sample containing same amount of fluorescing reagent was measured for U concentration. All the reagents used for experimental work were of ultrapure/analytical grade (Merck, Mumbai, India). Quality assurance was made by analysis of IAEA standard reference materials, spike recovery, replicate analysis, and cross method checking. The concentration of uranium in samples using Laser Fluorimeter can be calculated by

$$U(\mu\text{gl}^{-1}) = \frac{D_1}{(D_1 - D_2)} \times \frac{V_1}{V_2} C \quad (3.1)$$

where,

$D_1$  is fluorescence due to sample only,  $D_2$  is fluorescence due to sample and Uranium standard spiked,  $V_1$  is the volume of U standard added,  $V_2$  is the volume of sample taken and  $C$  is the a concentration of U standard solution. The relative standard deviation (RSD) of measurements was calculated to be approximately 10 %.

### Quenching Effects in Fluorimetric Methods

A real-life geological sample is not without complications in fluorimetric estimations, as the fluorescence may be quenched by a number of other species that may be present in the analyte solution. The presence of organic matter and other metal ions can cause the quenching effect. In the presence of quenching, the decay of fluorescence intensity becomes more complex than a single exponential decay, due to transient effects which occur immediately following excitation of the fluorophore. Effects of some quenchers on the slope of the plots of  $\text{UO}_2^{2+}$  fluorescence against uranium concentration is explained elsewhere (Maji *et al.*, 2001). Quenching results in reduced fluorescence intensity which if not corrected, may lead to an apparently lower concentration of the analyte. It is here to be pointed out that problem of quenching is not unique to uranium but applies to almost all fluorophores (Lakowicz, 1991). The quenching can proceed through dynamic and/or static quenching mechanisms (Lakowicz, 1991). Time resolved fluorimetry, which utilizes the reduction in the lifetimes of the fluorophore in the presence of quenchers is a measure to correct quenching, at least in those cases where dynamic quenching is dominating (Hieftje and

Haugen, 1981). A number of reports exist in the literature addressing the problem of quenching in fluorimetric estimations of uranium (Yokoyama *et al.*, 1976; Moriyasu *et al.*, 1977; Whitkop, 1982). The quenching effect due to presence of high acidic concentration can be removed by proper pH adjustment. Another method is to chemically separate the quenchers from the analyte, and then conduct the estimation in quencher-free environment. However such a method would be time-consuming and is not feasible every time and everywhere.

Quenching of fluorescence by various elements occurs in any type of flux, although it seems to be most pronounced in high carbonate fluxes. Moriyasu *et al.*, (1977) list Cr, Mn, Co, Ni, Ag, La, Pt, Au, Pb, Ce, Pr, and Nd as strong quenchers (1-10 µg quench uranium fluorescence by 10 percent or more) and Fe, Cu, Zn, Sn, and Th as moderately strong quenchers (Moriyasu *et al.*, 1977). In general, separation of uranium from quenching elements by solvent extraction or ion exchange is preferable to making a large dilution. Both techniques may be avoided, however, if the quenching does not reduce the fluorescence by more than about 30 percent. Most non-saline natural waters can be analyzed for uranium by this procedure without preliminary treatment (Barker *et al.*, 1965). Standard addition method used in this work, for the uranium analyses by Laser fluorimeter is quiet effective in minimizing the matrix effect (Skoog *et al.*, 1998; Sahoo *et al.*, 2009).

### 3.2.2 Uranium in Water using Fission Track Method

Lexan, another detector material from Solid State Nuclear Track Detectors category, has been used for uranium estimation in water samples under Fission Track Registration technique (Fleischer and Lovett, 1968). Basic principal of the technique has already been explained in section 2.3.2. Sample and standard disks covered with track detectors were stacked in an irradiation capsule and irradiated with a neutron dose of  $2 \times 10^{15}$  nvt at BARC, Mumbai. Commercial aluminum foil is a convenient secondary standard for this purpose; disks of it, covered with Lexan, may be placed throughout the capsule (Aumento, 1971). After irradiation, the track detectors were removed and etched. The background of tracks due to uranium in the track detector material can be

determined by irradiating and etching the blank samples. Lexan was etched in 6M aqueous NaOH for about 24 hours. Uranium concentration followed the expression:

$$C(\mu\text{g l}^{-1}) = \frac{TM}{VG\sigma N\phi E} \quad (3.2)$$

where,

N is the Avogadro number ( $6.023 \times 10^{23}$ ), T is the total number of tracks, V, the volume of drop (ml); M, the atomic weight of uranium isotope  $^{238}\text{U}$ ; G, the geometry factor (assumed unity);  $\phi$ , the total thermal neutron dose;  $\sigma$ , the fission cross section and E is the etching efficiency factor for lexan, taken unity.

### 3.2.3 Uranium Estimation in Soil

Uranium concentration in the soil samples was also measured by using fission track registration technique (Fleischer *et al.*, 1975). Samples were dried in an oven at  $70^\circ\text{C}$  for few hours, were powdered and sieved through a  $100\ \mu\text{m}$  mesh sieve. 50 mg of sample powder was mixed with 100 mg of methyl cellulose powder used as a binding material. This mixture was pressed into a thin and flat pellet of 1.3 cm in diameter using a hydraulic pellet making machine. Each of the pellets was sandwiched between a pair of lexan discs. Induced fission tracks were recorded in these sets after irradiating the pellet with a thermal neutron dose of  $2 \times 10^{15}$  nvt at BARC, Mumbai. After irradiation the detector discs were etched in 6.25N NaOH solutions at  $70^\circ\text{C}$  for 25 min to reveal the fission tracks. The developed fission tracks were scanned using an optical microscope at a magnification of 400 x. The uranium concentration was calculated using the equation:

$$U_x = U_s \left\{ \frac{T_x}{T_s} \right\} \left\{ \frac{I_s}{I_x} \right\} \left\{ \frac{R_s}{R_x} \right\} \quad (3.3)$$

where,

Subscripts x and s represents the samples and standard respectively. U, the uranium content; T, the fission tracks density and I, the isotopic abundance ratio of  $^{235}\text{U}$  and  $^{238}\text{U}$  and R the range of fission fragments in  $\text{mg cm}^{-2}$ . The factor  $R_s/R_x$  is taken to be unity.  $I_s/I_x$  has been taken as unity assuming that the isotopic abundance ratio is the same for the samples and standard.

### 3.3 Health Risk Assessment

As explained in chapter 1, health effects of uranium due to ingestion via drinking water can be divided into two types: carcinogenic (radiological risk) and non-carcinogenic (chemical risk) (Health Canada 1999a; WHO 1998). Below is described methodology adopted to estimate radiological and chemical toxicity due to calculated uranium concentrations in the water samples of the study region.

#### 3.3.1 Radiological Risk Assessment

The radiological risk (excess cancer risk) due to ingestion of natural U in drinking water has been evaluated based on the general USEPA standard method (USEPA, 2000a).

$$\text{Excess Cancer Risk} = \text{Activity Concentration of Uranium (Bq l}^{-1}\text{)} \times \text{Risk Factor (per Bq l}^{-1}\text{)} \quad (3.4)$$

The risk factor (per Bq l<sup>-1</sup>) R, is associated with intake of Uranium nuclide can be estimated by product of the risk coefficient (r) of Uranium (1.19×10<sup>-9</sup>) for mortality and per capita activity intake I as

$$R = r \times I \quad (3.5)$$

Per capita activity intake I of Uranium again can be calculated using 63.7 years i.e. 23250 days as life expectancy and daily consumption of water as 4.05 l day<sup>-1</sup>.

$$I = 4.05 \text{ l day}^{-1} \times 23250 \text{ days} \quad (3.6)$$

#### 3.3.2 Chemical Toxicity Risk

Uranium heavy metal, associates with it, chemical risk in addition to that of radiological (Orloff *et al.*, 2004). Nephrotoxicity is most likely due to chronic exposure to uranium. Kidney injuries are reported in several studies as being directly associated with a continuous intake of U contaminated water, even if at low concentrations (Weir, 2004). The chemical toxicity risk for a given element is defined in terms of Average Daily Dose (ADD) of the element through drinking water intake. For an observed Exposure Point Concentration (EPC), in µg l<sup>-1</sup> units, of a given contaminant, average

daily dose is the quantity of chemical substance ingested per kilogram of body weight per day is given by (Lee *et al.*, 2005)

$$ADD = \frac{C \times IR \times ED \times EF}{BW \times AT \times 365} \quad (3.7)$$

C is the concentration of the contaminant in the environmental media ( $\text{mgkg}^{-1}$  or  $\text{mg l}^{-1}$ ), IR is the ingestion rate per unit time ( $\text{mgday}^{-1}$  or  $\text{l day}^{-1}$ ), ED is the exposure duration (y), EF is the exposure frequency ( $\text{days y}^{-1}$ ), BW is the body weight of the receptor (kg), and AT is the Averaging time (years), equal to the life expectancy, and 365 is the conversion factor from year to days. Toxic risks refer to the non-carcinogenic harms incurred due to the exposures. The extent of the harm is indicated in terms of a hazard quotient (HQ):

$$HQ = \frac{ADD}{R_fD} \quad (3.8)$$

where,

$R_fD$  is the reference dose.

The reference dose is the daily dosage that enables the exposed individual to sustain this level of exposure over a prolonged time period without experiencing any harmful effect. Reference doses for heavy metal have been calculated using permissible limits in drinking water given by World Health Organization (WHO, 2011).

### 3.4 Results and Discussion

Results of uranium concentration in 90 water samples from districts Faridkot, Ferozepur and Muktsar analyzed using laser fluorimetric technique are given in Table 3.1. Table 3.2 is a district wise summary corresponding to Table 3.1, while Table 3.3 summarizes over all data of the study region for 90 water samples for uranium concentration, corresponding radiological (excess cancer risk) and chemical risk (HQ). Results of uranium concentrations in 36 soil samples from the study region using fission track technique are given in Table 3.6.

### Uranium in Water

Starting discussion with uranium concentration in the water samples of three districts individually, Table 3.2 shows that 30 water samples of water collected from Faridkot district averaged at  $68.6 \mu\text{g l}^{-1}$  with range 16.5- 473.5  $\mu\text{g l}^{-1}$ , 45 samples of Ferozpur averaged at  $62.1 \mu\text{g l}^{-1}$  with range 2.8- 184.4  $\mu\text{g l}^{-1}$  and 15 samples of Muktsar stood at an average of  $53.3 \mu\text{g l}^{-1}$  and range 13.2-157.0  $\mu\text{g l}^{-1}$ . Hence, uranium concentration averages for Faridkot and Ferozpur districts are above permissible limits of all world agencies including that of  $60 \mu\text{g l}^{-1}$  by AERB. For Muktsar average of samples  $53.28 \mu\text{g l}^{-1}$  is again above recommended limit of  $30 \mu\text{g l}^{-1}$  by WHO and US Environmental Protection Agency and not far below of  $60 \mu\text{g l}^{-1}$  by AERB. Median values for the three respective districts are 38.35, 54.8 and 49.7 in  $\mu\text{g l}^{-1}$  units. 5<sup>th</sup>, 25<sup>th</sup>, 75<sup>th</sup> and 95<sup>th</sup> percentile values for the uranium values of three districts are also calculated. By definition, a percentile is the value of a variable below which a certain percent of observations fall. For example, table shows that for Faridkot district, 5% of the 30 observations lie below  $3.3 \mu\text{g l}^{-1}$  and 95% of the samples are below value  $242.9 \mu\text{g l}^{-1}$ .

To take a collective look of study region for water uranium contents, a bar graph is drawn for uranium values in the 90 water samples (Figure 3.1). Overall, uranium ranged between 2.8- 473.5  $\mu\text{g l}^{-1}$  with an average of  $61.3 \mu\text{g l}^{-1}$ . To compare the data with permissible values of  $30 \mu\text{g l}^{-1}$  by World Health Organization and  $60 \mu\text{g l}^{-1}$  by AERB, pie chart of over all 90 samples is shown in Figure 3.2. In total, 58 (65%) of the 90 water samples were found to exceed permissible limit of  $30 \mu\text{g l}^{-1}$  by World Health Organization and 32 (36%) of the 90 samples exceed the limit  $60 \mu\text{g l}^{-1}$  by AERB.

**Table 3.1** Uranium concentrations in 90 water samples from Faridkot (30 samples, Fkt codes), Ferozepur (45 samples, Fzr codes) and Muktsar (15 samples, Mkt codes) districts using Laser fluorimetry

Sample code	GPS location	Uranium value ( $\mu\text{g l}^{-1}$ )	Sample code	GPS location	Uranium value ( $\mu\text{g l}^{-1}$ )
Fkt1	N30°42.287' E74°35.189'	31.8±2.8	Fzr1	N30°55.532' E74°36.577'	34.0± 3.1
2	N30°41.439' E74°38.208'	25.8± 2.3	2	N30°55.532' E74°36.577'	37.0± 3.4
3	N30°41.204' E74°39.497'	77.1± 8.2	3	N30°52.494' E74°29.588'	8.9± 0.1
4	N30°40.531' E74°44.567'	21.0± 1.8	4	N30°49.030' E74°27.030'	20.1± 2.0
5	N30°40.511' E74°44.567'	16.5± 1.2	5	N30°49.030' E74°27.030'	44.6± 4.2
6	N30°40.530' E74°44.547'	2.8± 0.1	6	N30°44.400' E74°22.122'	55.1± 4.9
7	N30°39.292' E74°46.119'	16.4± 1.1	7	N30°41.337' E74°19.255'	46.7± 4.7
8	N30°41.351' E74°47.492'	4.2± 0.1	8	N30°41.337' E74°19.255'	59.8± 6.0
9	N30°42.476' E74°49.534'	245.0± 19.4	9	N30°38.210' E74°16.012'	50.9± 4.1
10	N30°47.267' E74°41.548'	46.0± 4.3	10	N30°38.210' E74°16.012'	33.4± 2.7
11	N30°43.516' E74°43.459'	54.0± 4.9	11	N30°36.222' E74°14.510'	102.0± 9.1
12	N30°37.255' E74°47.249'	8.9± 1.0	12	N30°35.510' E74°11.414'	98.1± 9.3
13	N30°35.396' E74°48.439'	82.0± 7.5	13	N30°32.193' E74°07.205'	60.4± 4.3
14	N30°35.396' E74°48.439'	17.0± 1.3	14	N30°27.185' E74°04.423'	56.2± 3.8
15	N30°35.396' E74°48.439'	34.3± 2.9	15	N30°18.018' E74°05.458'	15.2± 1.5
16	N30°34.194' E74°51.465'	123.0± 10.2	16	N30°14.038' E74°08.194'	9.0± 0.1
17	N30°34.194' E74°51.465'	98.0± 9.7	17	N30°09.164' E74°12.274'	157.6± 15.0
18	N30°36.183' E74°54.024'	51.1± 4.3	18	N30°09.164' E74°12.274'	5.2± 0.1
19	N30°33.115' E74°53.162'	138.2± 13.7	19	N30°16.233' E74°06.478'	118.4± 11.1
20	N30°33.115' E74°53.162'	4.5± 0.1	20	N30°23.549' E74°01.555'	127.0± 12.2
21	N30°31.272' E74°56.480'	26.0± 1.9	21	N30°52.284' E74°36.472'	129.0± 11.6
22	N30°31.272' E74°56.480'	473.5± 35.2	22	N30°46.240' E74°36.378'	135.1± 12.8

conti..

Sample code	GPS location	Uranium value ( $\mu\text{g l}^{-1}$ )	Sample code	GPS location	Uranium value ( $\mu\text{g l}^{-1}$ )
Fkt 23	N30°27.331' E74°58.561'	16.5± 1.4	23	N30°46.286' E74°10.570'	81.2± 6.9
24	N30°26.490' E74°54.222'	130.0± 11.6	24	N30°51.168' E74°55.364'	100.1± 9.5
25	N30°26.485' E74°50.158'	58.0± 4.4	25	N30°50.079' E74°55.347'	3.4± 0.1
26	N30°26.485' E74°50.158'	18.9± 1.6	26	N30°57.349' E74°58.517'	41.0± 3.6
27	N30°29.442' E74°51.461'	75.0± 6.6	27	N30°58.240' E74°55.249'	42.1± 3.3
28	N30°32.272' E74°50.278'	75.6± 7.4	28	N30°58.221' E74°50.541'	27.2± 2.4
29	N30°32.272' E74°50.278'	88.1± 7.8	29	N30°57.114' E74°46.104'	50.4± 4.9
30	N30°34.238' E74°43.735'	24.7± 2.0	30	N30°53.335' E74°38.400'	184.6± 18.5
Mkt1	N30°24.190' E74°44.330	88.2± 6.4	31	N30°53.335' E74°38.400'	54.6± 4.6
2	N30°19.666' E74°39.597'	32.4± 1.1	32	N30°51.444' E74°39.437'	100.5± 12.8
3	N30°28.419' E74°31.917'	33.0± 2.2	33	N30°51.444' E74°39.437'	85.3± 8.6
4	N30°33.878' E74°32.792'	157.0± 4.7	34	N30°50.144' E74°40.276'	21.2± 1.5
5	N30°23.971' E74°39.571'	18.6± 1.5	35	N30°51.141' E74°51.559'	87.1± 7.3
6	N30°17.061' E74°31.772'	83.8± 7.9	36	N30°52.490' E74°43.203'	37.1± 3.4
7	N30°12.844' E74°29.099'	35.9± 3.2	37	N30°55.526' E74°36.584'	78.2± 7.4
8	N30°11.782' E74°29.943'	27.2± 3.0	38	N30°59.522' E74°32.475'	2.7± 0.1
9	N30°03.745' E74°31.107'	49.7± 4.6	39	N30°57.579' E74°34.471'	28.1± 2.6
10	N30°11.485' E74°24.689'	13.2± 1.0	40	N30°57.400' E74°36.175'	57.6± 5.0
11	N30°28.410' E74°31.867'	58.0± 4.9	41	N30°00.185' E74°40.341'	26.7± 2.6
12	N30°03.236' E74°31.102'	18.9± 1.6	42	N31°02.171' E74°44.336'	16.2± 1.5
13	N30°11.733' E74°29.140'	75.0± 7.4	43	N31°03.332' E74°49.172'	58.3± 5.7
14	N30°57.114' E74°46.104'	50.4± 4.2	44	N31°06.309' E74°57.168'	15.5± 1.3
15	N29°50.593' E75°44.647'	58.0± 5.7	45	N31°06.213' E74°58.376'	44.1± 4.0

**Table 3.2** Summary of uranium concentrations of subsurface water in Farikot, Muktsar and Ferozepur districts of Punjab state in India (all data in  $\mu\text{g l}^{-1}$ )

Districts (number of samples)	Mean	Median (50 <sup>th</sup> percentile)	P <sub>5</sub> (5th percentile)	P <sub>95</sub> (95th percentile)	P <sub>25</sub> (25th percentile)	P <sub>75</sub> (75 <sup>th</sup> percentile)	Min	Max
Farikot (30)	68.6±8.3	38.4	3.3	242.9	16.5	81.7	16.5	473.5
Ferozpur (45)	62.1±7.3	54.8	3.4	142.5	27.4	95.7	2.8	184.4
Muktsar (15)	53.3±6.2	49.7	16.9	108.8	29.8	66.5	13.2	157.0

**Table 3.3** Over all summary for the study region summarizing uranium concentration, corresponding radiological (excess cancer risk) and chemical risk (HQ) for 90 drinking water samples

Parameter	Uranium Concentration ( $\mu\text{g l}^{-1}$ )	Excess Cancer Risk	LADD ( $\mu\text{g kg}^{-1} \text{ day}^{-1}$ )	HQ
Mean	61.3	$1.63 \times 10^{-4}$	4.62	1.02
Range	2.8± 0.2- 473.5±3.8	$7.45 \times 10^{-6}$ - $1.26 \times 10^{-3}$	0.21-35.71	0.04-7.97

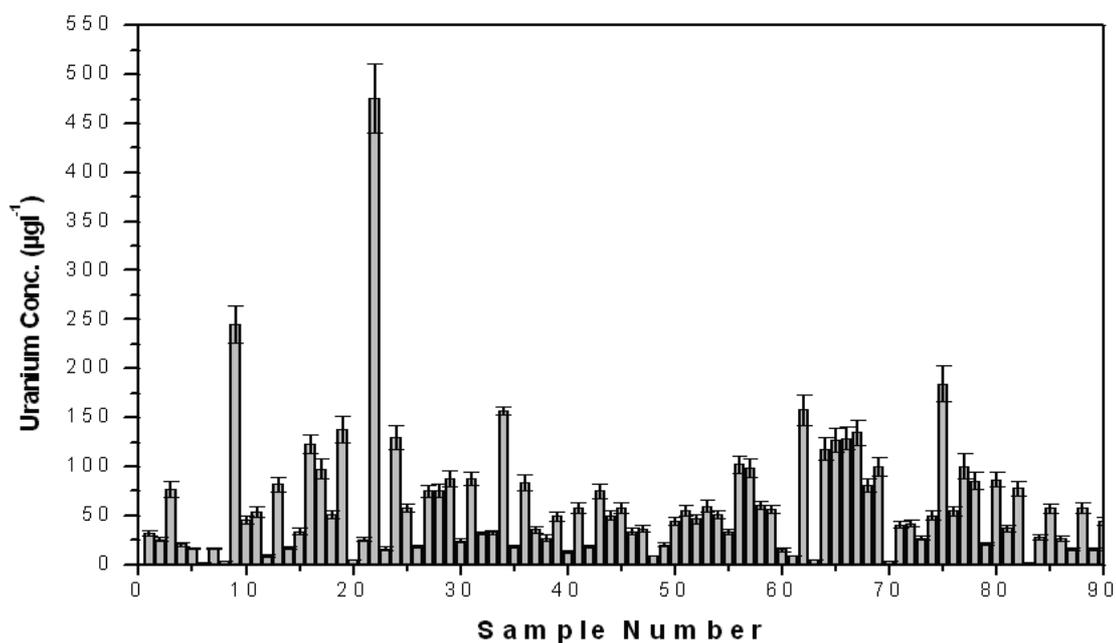


Figure 3.1 Bar graph corresponding to uranium values in 90 water samples from the study region analysed using Laser Fluorimetry

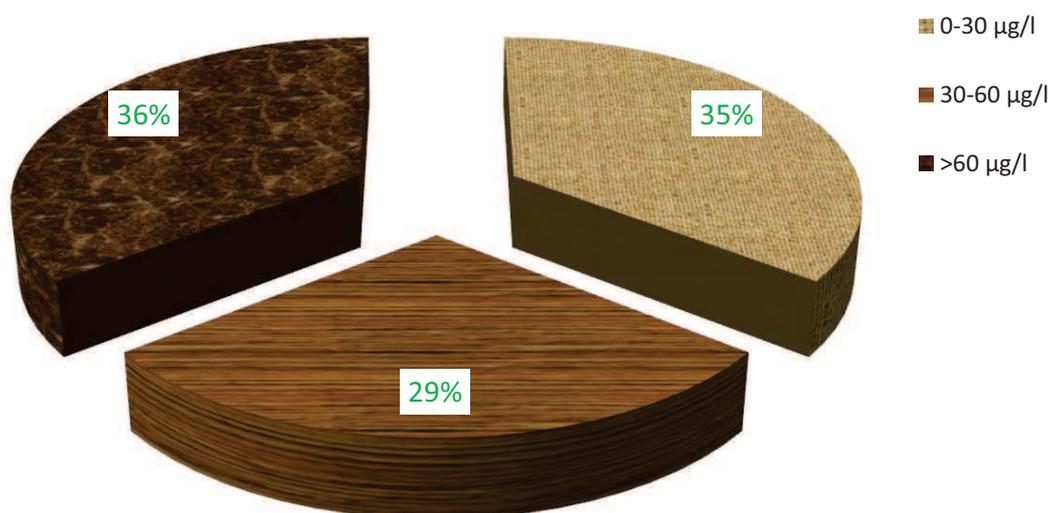


Figure 3.2 Pie chart showing range intervals of uranium contents in 90 water samples from three districts

Uranium concentration in water samples has been being reported at times, by various workers worldwide with sources varying from groundwater of Punjab, India (Singh *et al.*, 1995; Kumar *et al.*, 2006), springs of Himalaya (Virk, 1997), Bottled river water from Argentina (Bomben *et al.*, 1996) to mineral waters from high background region in Brazil (deCamargo and Mazzilli, 1996) and sea waters (Rona *et al.*, 1956). Table 3.4 compares the results obtained in the present investigation with the uranium concentrations in various water samples reported by some other workers from India and worldwide.

As is evident from Table 3.4, uranium in water can vary from few microgram per litres to up to several hundreds microgram per litres. For example, uranium has been reported to vary in Jordan drinking supply waters with large range of 0.01- 1186  $\mu\text{g l}^{-1}$  (Gedeon *et al.*, 1995). Uranium concentrations in US, as reported by Cothorn *et al.* (1983) are 0.01-652 $\mu\text{g l}^{-1}$ . Kumru (1995) meanwhile reported comparatively lower values of uranium concentration in waters of Turkey in range of 0.24-17.65  $\mu\text{g l}^{-1}$ .

The uranium concentrations reported by Bansal *et al.* (1985, 1988) in ground waters from Aligarh region in India ranged as 0.67-471  $\mu\text{g l}^{-1}$ , very similar range to one obtained in the present study. In a study comprising uranium analysis in water samples from wider parts of India, Singh *et al.* (2010) found uranium contents ranging from 0.09 to 35.4  $\mu\text{g l}^{-1}$ . The uranium concentrations found for the present study region are significantly high and witnessed a sharp contrast with the North-western regions of Punjab, where uranium in water samples was reported to vary from 3.19 to 45.59  $\mu\text{g l}^{-1}$  (Singh *et al.*, 2003). In a recent study for uranium concentration in drinking water samples from some areas of Punjab and Himachal Pradesh, Rani and Singh (2006) measured concentration varying from 1.39 to 98.25  $\mu\text{g l}^{-1}$  with a mean value of 19.84  $\mu\text{g l}^{-1}$  using laser induced fluorimetry technique and reported most of the drinking water samples from Punjab exceed the safe limit recommended by the World Health Organization.

Coefficients of radiological and chemical toxicity due to oral ingestion are calculated for this data of uranium concentrations and are given in Table 3.3. The Radiological risk (excess cancer risk) due to ingestion of natural uranium in drinking water at an average  $4.05 \text{ lday}^{-1}$  over the average all India lifetime expectancy of 63.7 years for both males and females was found to be in the range of  $7.45 \times 10^{-6}$ - $1.26 \times 10^{-3}$  with a mean value of  $1.72 \times 10^{-4}$ , narrowly higher than the maximum acceptable level ( $1.67 \times 10^{-4}$ ) as per guide lines of AERB, India. This infers that over a lifetime consumption of groundwater at an average  $4.05 \text{ lday}^{-1}$  with the present uranium level, the mean of excess cancer risk in all districts appeared to be about less than 2 per 10 thousand people.

The mean chemical toxicity risk defined as life time daily dose (LADD) came out to be  $4.62 \mu\text{gkg}^{-1}\text{day}^{-1}$  with a range of  $0.21$ - $35.71 \mu\text{gkg}^{-1}\text{day}^{-1}$ , considering the body weight as  $51.5 \pm 8.5 \text{ kg}$  of an adult Indian reference man. The mean of hazard quotient (LADD/ $R_fD$ ) was also found to be greater than 1. For uranium, reference dose ( $R_fD$ ) has been taken  $4.53 \mu\text{gkg}^{-1}\text{day}^{-1}$ , corresponding to  $60 \mu\text{gl}^{-1}$  as maximum acceptable level in drinking water as per guidelines of India's Atomic Energy Regulatory Board (AERB, 2004). Water ingestion rate of  $4.05 \text{ lday}^{-1}$ , 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 (HDR, 2009).

**Table 3.4** Ranges of uranium in water samples from various parts of world

S. No.	Country	Range of uranium Conc. ( $\mu\text{g l}^{-1}$ )	Reference
1	Argentina	0.04- 11.0	Bomben <i>et al.</i> , 1996.
2	Brazil	0.08- 2.0	deCamargo and Mazzilli, 1996
3	Canada	0.05- 4.21	OMEE, 1996
4	Cyprus	0.005- 38.0	Smith <i>et al.</i> , 2000
5	France	0.18-37.2	UNSCEAR 2000
6	India	0.09- 35.4	Singh <i>et al.</i> , 2010
		0.1- 19.6	Sahoo <i>et al.</i> , 2009
		1.39- 98.25	Rani and Singh, 2006
		3.19- 45.59	Singh <i>et al.</i> , 2003
		11.71-113.70	Singh <i>et al.</i> , 1995
		38.37- 471.27	Bansal <i>et al.</i> , 1985
7	Jordan	0.01- 1186	Gedeon <i>et al.</i> , 1995
8	Kuwait	0.02- 2.48	Bou-Rabee, 1995
9	Norway	0.02- 170	Banks <i>et al.</i> , 1995
10	Pakistan	0.05- 5	WHO, 2001
11	South Greenland	0.5-1.0	Brown <i>et al.</i> , 1983
12	Syria	14 (highest observed value)	Othman and Yassine, 1996
13	Turkey	0.24-17.65	Kumru, 1995
14	Uganda	<0.05-17	Smith <i>et al.</i> , 1996, 1998
15	United Kingdom	0.1-10	Edmunds <i>et al.</i> , 1989
16	United States	0.01- 3.08	UNSCEAR, 2000
		0.03- 0.08	Fisenne and Welford, 1986
		0.01-652	Cothorn and Lappenbusch, 1983
	<b>South-Western Punjab, India</b>	<b>2.8-473.5</b>	<b>Present Study</b>

### Comparison of Techniques

A comparison of the Laser Fluorimetry and Fission Track techniques was attempted. For this, 15 water samples in random from the total samples analysed using fluorimeter method were taken. Ratios of the concentrations obtained using two techniques are given the Table 3.5. A very satisfying range 0.85-1.11 for this ratio was obtained.

Such comparative study of these two techniques viz. laser induced fluorimetry and fission track registration is found in the literature attempted by some workers (Shi-Lun Guo *et al.* 1986; Rani and Singh, 2006). It has been observed here that value of uranium measurements by one of these methods may be larger or smaller than other.

A possible reason as reported by Rani and Singh (2006) for the ratio (laser fluorimetry to fission track)  $>1$ , may be suspended uranium particulates matter recorded by the laser fluorimeter in the larger volume of sample used for analysis than in the fission track technique. They attributed ratio  $<1$  to the incomplete dissolution of the particulates left attached to the walls of the container used during digestion of the sample. Shi-Lun Guo *et al.* (1986) concluded on fairly good reproducibility of fission track method for environmental studies, uranium exploration and other purposes and favored fission track method for better sensitivity in comparison to laser-fluorometry and fluorocolorimetry to be used for determination of uranium concentration in natural water.

### Uranium in Soil

Uranium concentration in 36 soil samples from three districts of Punjab using fission track registration technique is given in Table 3.6. Sampling locations are shown in Figure 3.3.

Uranium in the soil samples averaged at  $2.27 \text{ mgkg}^{-1}$  with range 1.14-3.82  $\text{mgkg}^{-1}$ . Figure 3.4 is a graphical representation. One of the obvious inferences out of normal uranium contents calculated in the soil samples is that region is not significant

for uranium prospection. Uranium mineralization for example, has been observed in some areas of Himachal Pradesh (India) particularly in Siwalik formations; where uranium contents up to 20 mgkg<sup>-1</sup> (1.62-19.82 mgkg<sup>-1</sup>) in soil and up to 25 mgkg<sup>-1</sup> (1.65-24.72 mgkg<sup>-1</sup>) have been reported by some workers (Singh *et al.*, 2001).

Uranium in the soil samples averaging at 2.27 mgkg<sup>-1</sup> for the present region is comparable to world average of 2.1 mgkg<sup>-1</sup> (Kaul *et al.*, 1993). In a recent study, Geraldo *et al.* (2010) used similar (fission track registration technique) for uranium content and corresponding dose assessment in SP, Brazil to report values 3.12-18.3 mgkg<sup>-1</sup> in sediments and relatively higher values 3.21-11.5 mgkg<sup>-1</sup> for soils. Uranium content in soil samples in the present analysis agreed with that reported by Singh *et al.*, (2005) in these areas of Punjab, who reported values ranging from 1.14 to 2.44 mgkg<sup>-1</sup>. Values observed in the present study are also comparable to those determined in the soils of Una district (Himachal Pradesh, India), where reported ranges of uranium have been 1.07-2.47 mgkg<sup>-1</sup> (Singh *et al.*, 2002), while concentration of uranium in the soil of Palmpur area has been reported bit higher ranging from 1.18 to 5.12 mgkg<sup>-1</sup> with mean value of 2.13 mgkg<sup>-1</sup> (Singh *et al.*, 2005). Uranium has also been found to be reported in Jammu and Kashmir part of India by Kumar *et al.* (2009), varying in the rather normal range of 2.53-3.65 mgkg<sup>-1</sup>.

In terms of activity concentrations, average and range turned out to be 57.88 Bqkg<sup>-1</sup> and 29.07- 97.41 Bqkg<sup>-1</sup> respectively, which are obtained by using conversion factor 1 mgkg<sup>-1</sup> of natural uranium= 25.5 Bqkg<sup>-1</sup> (or 1 µg U<sub>total</sub>/g<sub>soil</sub> = 0.690pCi U<sub>total</sub>/g<sub>soil</sub>) (Davidson, 1988). Further to estimate enrichment of uranium by external factors, such as anthropogenic sources, the percentage enrichment factor (EF %) is defined as (Zonta *et al.*, 1994):

$$EF\% = \frac{C_{ave} - C_{min}}{C_{max} - C_{min}} \times 100 \quad (3.9)$$

where,

**Table 3.5** Comparison of Uranium concentration in a few drinking water samples using two techniques viz. Laser Induced Fluorimetry and Fission track technique ( $\mu\text{g l}^{-1}$  units)

Sample Code	Uranium concentration (Fluorimeter method)	Uranium concentration (Fission track method)	Ratio (Fluorimetry to fission track technique)
Fkt 2	25.8	23.3± 0.1	1.11
5	16.5	20.7± 0.1	0.80
14	17.0	15.6± 0.1	1.09
26	18.9	19.2±0.1	0.98
Mkt 2	32.4	34.0± 0.2	0.95
3	32.9	29.2± 0.2	1.13
8	27.2	25.2± 0.2	1.08
9	49.7	55.8± 0.2	0.89
Frz 3	8.9	14.5± 0.1	0.61
7	46.7	42.3± 0.2	1.10
9	37.3	39.0± 0.2	0.96
15	15.2	16.5± 0.1	0.93
36	37.1	40.5±0.2	0.92
25	3.4	7.4± 0.1	0.46
41	26.2	30.8± 0.2	0.85
Min			0.85
Max			1.11

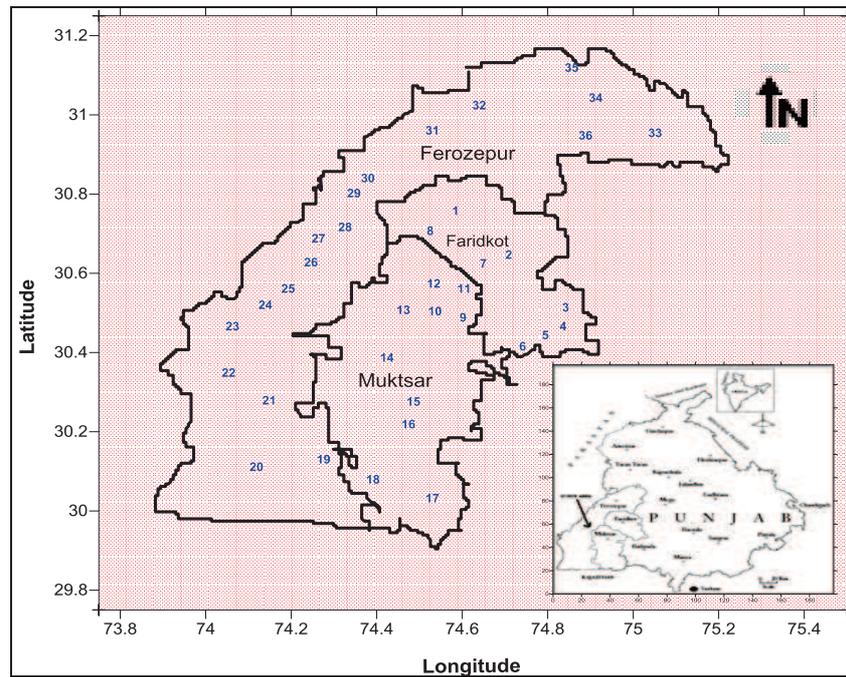
\*Statistical counting error

$1\sigma = (1/\sqrt{N}) \times \text{Uranium concentration}$ , N is the number of tracks

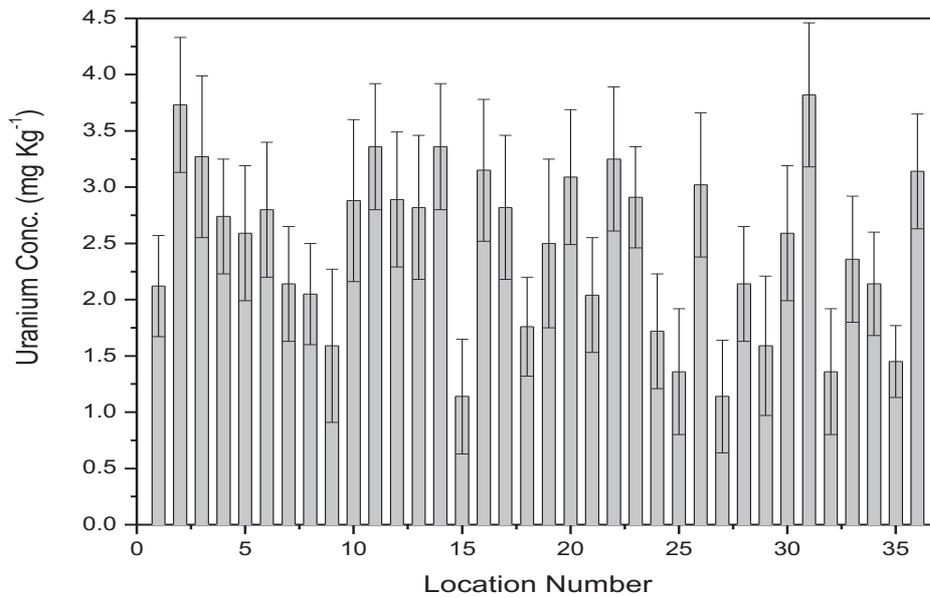
**Table 3.6** Uranium concentrations in 36 soil samples from different locations in Farikot, Muktsar and Ferozepur districts of Punjab, India using fission track registration technique

S. No	Location	GPS Coordinates	Uranium concentration (mgkg <sup>-1</sup> )	S. No	Location	GPS Coordinates	Uranium concentration (mgkg <sup>-1</sup> )
<b>Faridkot District</b>				<b>Ferozepur District</b>			
1	Faridkot city	N30°40.531' E74°44.567'	2.12±0.45	19	Balluana	N31°19.322' E74°51.867'	2.5±0.75
2	Kotkapura	N30°35.396' E74°48.439'	3.73±0.60	20	Abohar	N30°09.164' E74°12.274'	3.09±0.60
3	Ramana	N30°30.634' E74°51.430'	3.27±0.72	21	Nihal Khera	N30°14.038' E74°08.194'	2.04±0.51
4	Jaito	N30°26.485' E74°50.158'	2.74±0.51	22	Fazilka	N30°23.549' E74°01.555'	3.25±0.64
5	Bhagtuana	N30°24.612' E74°56.623'	2.59±0.60	23	Behakbobla	N30.28.200' E74.05.486'	2.91±0.45
6	Karirwali	N30°24.423' E74°37.243'	2.80±0.60	24	Bambha Battu	N30°32.193' E74°07.205'	1.72±0.51
7	Machaki	N30°41.204' E74°39.497'	2.14±0.51	25	Bagge Ke	N30°35.510' E74°11.414'	1.36±0.56
8	Sadik	N30°42.287' E74°35.189'	2.05±0.45	26	Jalalabad	N30°36.222' E74°14.510'	3.02±0.64
9	Mallan	N30°24.432' E74°44.456'	1.59±0.68	27	Jiwan Arain	N30°41.337' E74°19.255'	1.14±0.50
10	Kauni	N30°19.276' E74°48.654'	2.88±0.72	28	Pindi	N30°44.400' E74°22.122'	2.14±0.51
<b>Muktsar District</b>				29	Lakho ke	N30°49.030' E74°27.030'	1.59±0.62
11	Mukatsar city	N30°26.234' E74°48.612'	3.36±0.56	30	Khai Kheme Ki	N30°55.532' E74°36.577'	2.59±0.60
12	Marh Mallu	N30°33.675' E74°32.453'	2.89±0.60	31	Ferozepur city	N30°55.526' E74°36.584'	3.82±0.64
13	Rupana	N30°16.876' E74°30.654'	2.82±0.64	32	Khosa Dal Singh	N30°58.221' E74°50.541'	1.36±0.56
14	Aulakh	N30°24.634' E74°15.243'	3.36±0.56	33	Zira	N30°57.349' E74°58.517'	2.36±0.56
15	Pind Malout	N30°12.645' E74°28.876'	1.14±0.51	34	Khui Khera	N30°18.018' E74°05.458'	2.14±0.46
16	Malout City	N30°11.645' E74°29.466'	3.15±0.63	35	Bhadana	N30°18.853' E75°02.577'	1.45±0.32
17	Badal	N30°03.678' E74°30.623'	2.82±0.64	36	Makhu	N31°06.213' E74°58.376'	3.14±0.51
18	Kabbarwal	N30°11.432' E74°24.678'	1.76±0.44	<b>Range</b>			1.14±0.51- 3.82±0.64
<b>Average</b>							2.27±0.42

The errors shown in the results are the ( $1\sigma$ ) statistical uncertainties in track counting:  $1\sigma = 1/\sqrt{N}$  where N is the number of tracks.



**Figure 3.3** Map showing sampling sites of uranium analysis in soil samples using fission track technique across the study region corresponding to Table 3.6 (axis units in decimal degrees).



**Figure 3.4** Bar graph for uranium concentrations in soil samples corresponding to Table 3.5

$C_{\min}$  is minimum concentration of an element in soil of investigated region, assumed as the geochemical background value. With an average  $57.88 \text{ Bqkg}^{-1}$  and range  $29.07\text{-}97.41 \text{ Bqkg}^{-1}$  respectively, enrichment percentage comes out to be 42 %. This enrichment of uranium in agricultural soil may be a consequence of the variety of human activities like excess use of phosphate fertilizers and presence of chemical and cement factories in the investigated area. The relevance of enrichment of uranium in soil due to fertilizers particularly is of significance for this region, as entire of the study region is prime agricultural land. It is an established fact that agricultural use of fertilizers is the one of the major source of groundwater pollution, including natural radioactive elements. These *Technically-Enhanced, Naturally- Occurring Radioactive Materials* (TENORMs) contains levels of uranium series radionuclides about 50 times higher than typical soils, and can accumulate a large fraction of its radioactive content in the soil (Rutherford *et al.*, 1994).

Coming back to very high levels of uranium values found in ground waters of the region discussed above, excess use of fertilisers may also be held responsible because it is known that portion of the radionuclides contained in fertilizers leaches through the soil and can reach the groundwater table (El-Mrabet *et al.*, 2003; Guzman *et al.*, 2002). However, some of the experts see the leaching of uranium from adjoining granitic Tosham region of Bhiwani district in Haryana state, as possible region behind elevated uranium concentration in underground water. It becomes imperative here to mention that uranium contents as high as  $62 \text{ mgkg}^{-1}$  in the rock samples has been reported from Tosham region of neighbouring Bhiwani district in Haryana (Singh *et al.*, 2008). More precise identification of the mechanisms responsible for higher uranium concentrations in underground water and study of uranium speciation are thus needed to be carried out in future.

### 3.5 Conclusions

1. The analysis of 90 water samples of the study region showed an average uranium concentration of  $61.32 \mu\text{g l}^{-1}$ , which is much higher than  $30 \mu\text{g l}^{-1}$  permissible value, recommended by WHO and slightly higher than  $60 \mu\text{g l}^{-1}$  that recommended value by AERB.
2. A very large variation  $2.8- 473.5 \mu\text{g l}^{-1}$  in the uranium concentrations has been found. Major geological construction of the entire study region being very similar, this variation may be attributed to the vertical distribution of uranium content and different local soil texture and different levels of surface mineralization. Depth profile of uranium concentration is discussed in the publication “*Risk assessment for natural uranium in subsurface water of Punjab state in India*” (Kumar *et al.*, 2011), in addition to data presented in this chapter.
3. Average radiological risk (excess cancer risk) due to ingestion of natural uranium in drinking water at an at an average  $4.05 \text{ l day}^{-1}$  over the average all India lifetime expectancy of 63.7 years has been found to be  $1.72 \times 10^{-4}$ , marginally higher than the maximum acceptable level ( $1.67 \times 10^{-4}$ ) as per guide lines of AERB, India.
4. The mean chemical toxicity risk defined as life time daily dose (LADD) came out to be  $4.62 \mu\text{g kg}^{-1} \text{ day}^{-1}$ , considering the body weight as  $51.5 \pm 8.5 \text{ kg}$  of an adult Indian reference man. The mean of hazard quotient (LADD/R<sub>f</sub>D) was also found to be greater than 1.
5. Uranium concentration in soil came out to be in the normal range  $1.14 \pm 0.51- 3.82 \pm 0.64 \text{ mg kg}^{-1}$  and averaged at  $2.27 \pm 0.42 \text{ mg kg}^{-1}$ .