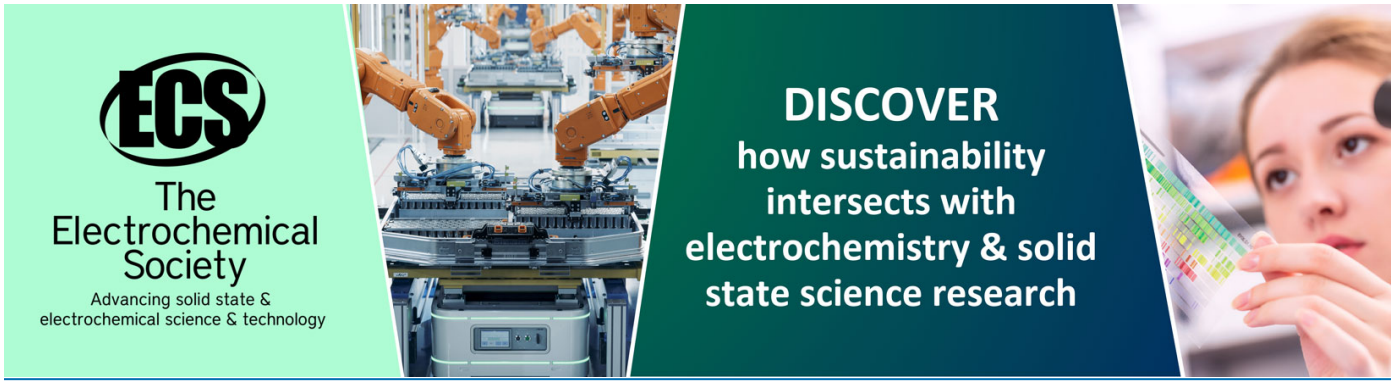
# Chemical Toxicity Risk Assessment of Uranium in the Fly Ash from Thermal Power Plant (GNDTPP) of Bathinda City, India





# Chemical Toxicity Risk Assessment of Uranium in the Fly Ash from Thermal Power Plant (GNDTPP) of Bathinda City, India

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**Abstract**
Uranium can be released into the environment from various activities such as the use of phosphate fertilizers, combustion of coal in thermal power plants, mining, and depleted uranium used in the wars. One of the talked about sources for such water contamination in Bathinda city is the fly ash from the coal-fired thermal power plants. To assess the role of fly ash and Chemical toxicity risk associated with uranium from the fly ash to the water, the coal, dry fly ash, ash slurry and water samples collected from the surrounding of Guru Nanak Dev Thermal Power Plant (GNDTPP) in the Bathinda city of Punjab state, India. The samples were analyzed using the X-ray fluorescence set up. In the present work, we found that uranium concentrations in the dry fly ash and coal samples were higher than permissible limit i.e. < 2 ppm but the concentrations in the ash slurry and water samples was below the safe limit of 30 μg $l^{-1}$ as recommended by World Health Organization (WHO, 2011) .The $_{38}$Sr concentrations are also found to be 0.103-1.210 ppm and with average value 0.576 ppm in the various types of water in surrounding of the thermal power plant. The concentrations of $_{42}$Mo are found to be 0.002-0.050 ppm and the average value 0.022 ppm below the safe limit of 0.07 mg/l as recommended by World Health Organization (WHO, 2011) and Bureau of Indian Standards (BIS, 2012). Chemical toxicity risk calculated in the form of lifetime average daily dose (LAAD) and hazard quotient. The lifetime average daily dose (LAAD) values of ash slurry and water samples were found to be lower than WHO (2011) recommended level of 1 μg $kg^{-1}$ $d^{-1}$, and the values of hazard quotient of the study samples were found to be lower than unity expect dry fly ash and coal samples were higher than permissible limit. The present study is concluded that uranium contamination in water of Bathinda city is not due to the Thermal Power Plant, and there is indicating no chemical toxicity risk due to uranium from the fly ash to the water.

**Keywords:** Uranium, Thermal power plant, fly ash, Chemical toxicity risk

## 1. INTRODUCTION:

Uranium is a naturally occurring element and is widespread in nature. It is found in low levels within all rock, soil, and water. This is the heaviest element to be found naturally in significant quantities on earth. A number of reports continue

appearing in the media that fly ash from the thermal power plants in Bathinda city is the cause of uranium contamination of water. It is estimated that more than 70 million tons of fly ash is produced annually in India from the combustion of coal in power plants [1]. Fly ash associated with various useful constituents such as $_{20}$Ca, $_{12}$Mg, $_{25}$Mn, $_{26}$Fe, $_{29}$Cu, $_{30}$Zn, $_{35}$Br, and $_{38}$Sr along with appreciable amounts of toxic elements such as $_{24}$Cr, $_{82}$Pb, $_{80}$Hg, $_{28}$Ni, $_{33}$As, $_{23}$V, and long-lived radioactive elements, $_{90}$Th and $_{92}$U and their decay products. Depending upon the source and makeup of the coal being burnt, the components of fly ash vary considerably, but all fly ash includes substantial amounts of silicon dioxide ($SiO_2$) (both amorphous and crystalline) and calcium oxide (CaO), both being endemic ingredients in many coal bearing rock strata. The quality of coal depends on the ash content, which is an important factor determining the caloric value of coal. Bhabha Atomic Research Centre (BARC) Mumbai is of the opinion that most of the Indian coals has very low levels of radioactivity which is well below the hazardous limit. Central Fuel Research Institute, Dhanbad observed that there is no significant uptake of radioactive elements by plants and also that there was negligible cumulative buildup of these contaminants in soil when fly ash applied for agriculture purposes [2]. There are two coal-fired power stations in Bathinda district. Guru Nanak Dev Thermal Power Plant (GNDTPP) near the Bathinda city and Guru Hargobind Thermal Power Plant (GHTPP) in nearby Lehra Mohabat town have been in operation since 1974 and 1998, respectively [3,4].

To assess the role of fly ash from thermal power plants (GNDTPP) for water contamination in the Bathinda city, the dry fly ash, coal, ash slurry and water samples collected from various locations have been analyzed using the Energy dispersive X-ray Fluorescence (EDXRF) technique. The EDXRF technique has the advantage due to its multielement analytical capability, lower detection limit, capability to analyze metals and non-metals alike and easy sample preparation can be utilized.

The purpose of this study is to investigate the chemical toxicity risks due to ingestion of the water, using international standards established by the WHO, adjusted with local parameters.

## 2. Materials and methods:

### *2.1. Sample collection and measurement*

The Fly ash samples were collected from the GNDTPP at Bathinda city of Punjab state, India Fig. 1. The samples were prepared to determine the various elements presented in fly ash. The prepared pellets were irradiated with the X-ray beam emitted from the $_{42}$Mo-anode based X-ray tube. The reflection mode experimental setup used in the present measurements is shown in Fig 2. It consists of water cooled single window $_{42}$Mo anode glass X-ray tube, (Be window of thickness 300 $\mu$m) along with the 4 kW X-ray generator, (PW3830) procured from PanAnalytic, Netherland. The tube emits $_{42}$Mo K X rays along with the continuous radiations (Bremsstrahlung) ranging upto the maximum applied tube operational voltage. The detection system consisted of a Si(Li) detector (28.27 mm$^2$ x 5.5 mm, 8-$\mu$m Be window, Canberra, US) in horizontal configuration and having an energy resolution of 180 eV for the Mn $K\alpha$ X rays. The detector was also shielded using $_{82}$Pb sheets in order to reduce the background. The tube was equipped with $_{50}$Sn collimator of diameter 3 mm to direct the incident flux on to the sample. The optimum operating conditions for the X-ray tube were found to be 38 kV and 10 mA. In order to improve the detection limit in the energy regions of interest, the $_{42}$Mo *K* X rays and the high energy Bremsstrahlung was absorbed with the help of selective absorbers of $_{39}$Y (53 mg/cm$^2$), $_{30}$Zn (10 mg/cm$^2$) and $_{38}SrCo_3$ ( 20 mg/cm$^2$). The X-ray spectra were collected using a PC-based multichannel analyser (Multiport II, Canberra, US). The $_{13}$Al chamber was evacuated ($10^{-2}$ torr) to avoid attenuation of low energy X rays in air and to eliminate the *K* X-ray ($E_{Kx}$ = 2.975 keV) peak due to $_{18}$Ar gas present in the air. The chamber is equipped with a 2 mm $_{50}$Sn collimator and a 2-$\mu$m Mylar window. The target was mounted at 45$^o$ with the detector and X-ray tube axis. The X-ray tube and detector were kept outside the chamber. The $_{13}$Al chamber containing the target was mounted on the detector head. The alignment of the X-ray tube collimator and chamber collimator was done using laser beam.


Fig. 1: Map of GNDTPP at Bathinda district of Punjab state in India.

### *2.2 Measurement of Uranium and other elements in fly ash Samples*

The concentration of various elements present in fly ash samples were determined using the procedure detailed elsewhere [5]. The standard targets procured from Micromatter, Deer Harbor, WA, US were used as reference and fundamental parameter approach was used to determine concentration various elements present in coal, fly ash, ash slurry and water residue.

The elemental composition for fly ash sample from the GNDTPP at Bathinda is given in Table 1. Sixteen elements, namely $_{22}$Ti, $_{23}$V, $_{24}$Cr, $_{25}$Mn, $_{26}$Fe, $_{29}$Cu, $_{31}$Ga, $_{32}$Ge, $_{37}$Rb, $_{38}$Sr, $_{39}$Y, $_{40}$Zr, $_{41}$Nb, $_{82}$Pb, $_{90}$Th, and $_{92}$U, were detected using the above-mentioned operating conditions of the EDXRF set-up. A typical spectra is shown in Fig. 3. and Fig 4.shows the variation of uranium concentration with different other samples.

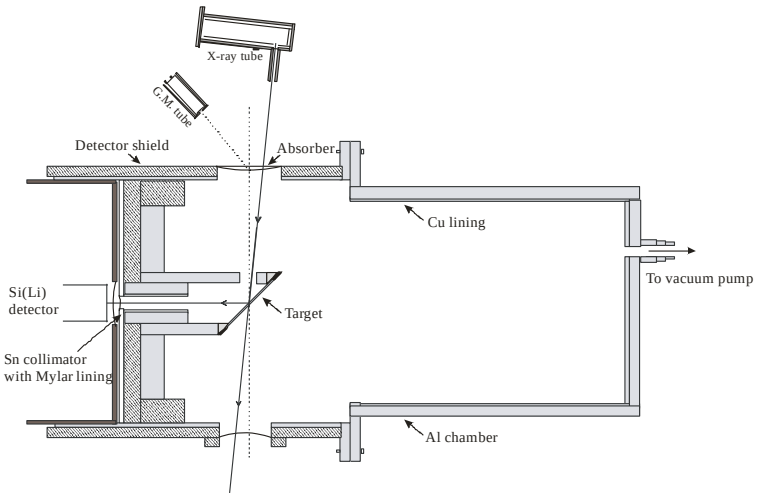


Fig 2. X-ray tube based geometry in the reflection mode.

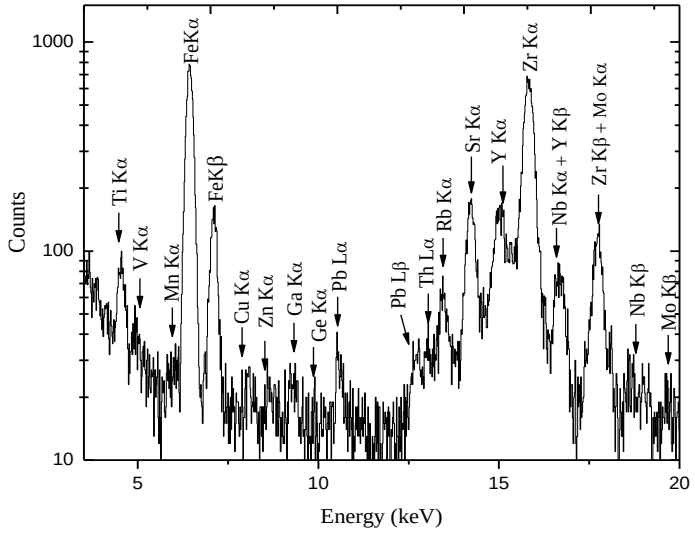


Fig 3. XRF spectrum of fly ash collected from Guru Nanak Dev thermal power plant.

Table 1: Concentration of uranium and elements (ppm) present in fly ash and other samples collected from ash dykes of GNDTP thermal power plant.

| **code** | **Sample name** | **$_{92}$U** | **$_{38}$Sr** | **$_{42}$Mo** | **$_{35}$Br** | **$_{26}$Fe** | **Other element** |
|---|---|---|---|---|---|---|---|
| *Fly ash, Coal and Ash slurry from thermal power plant plants (GNDTPP)* | | | | | | | |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **A1** | Ash slurry1 | < 0.003 | 0.266 | 0.028 | 0.006 | 1.427 | $_{20}$Ca, $_{37}$Rb |
| **A2** | Ash slurry2 | < 0.003 | 0.281 | 0.021 | 0.002 | 0.677 | $_{20}$Ca, $_{37}$Rb |
| **A3** | Dry fly ash | < 2 | 117 | < 10 | Below DL | 14000 | ($_{37}$Rb =24, $_{39}$Y=78, $_{40}$Zr=330 ) ($_{22}$Ti, $_{25}$Mn, $_{29}$Cu, $_{30}$Zn, $_{31}$Ga, $_{33}$As, $_{41}$Nb) < 50 ($_{82}$Pb =20, $_{90}$Th=7) |
| **A4** | Pulverized coal | < 1 | 38 | < 10 | Below DL | 28000 | ($_{37}$Rb =11, $_{39}$Y=30, $_{40}$Zr=175) ($_{82}$Pb ~7, $_{90}$Th =3) |
| *Water sample from surrounding of the thermal power plant plants (GNDTPP)* | | | | | | | |
| A5 | Canal | 0.002 | 0.103 | 0.002 | 0.003 | 0.537 | $_{20}$Ca, $_{33}$As (<0.010) |
| A6 | Tube well | 0.005 | 0.255 | 0.050 | 0.114 | 0.739 | Zn, Pb, |
| A7 | Hand pump | 0.018 | 1.210 | 0.005 | 0.016 | 0.691 | Zn, Pb |
| | Min value | 0.002 | 0.103 | 0.002 | 0.003 | 0.002 | |
| | Max value | 0.018 | 1.210 | 0.050 | 0.1 | 0.018 | |
| | Average | 0.009 | 0.576 | 0.022 | 0.050 | 0.009 | |
| | WHO | 0.03 | N.A | 0.07 | 0.5 | 0.3 | |

Below DL-below detection limit, N.A- not available

### *2.3 Risk measurement*

### *Chemical toxicity assessment*

The chemical toxicity risk in the fly ash and other samples from the Guru Nanak Dev thermal power plant due to the uranium concentration was estimated in terms of the lifetime average daily dose using equation given by USEPA [6]:

$$\mathrm{LADD} = \frac{\mathrm{C_U} \times \mathrm{IngR} \times \mathrm{EF} \times \mathrm{ED}}{\mathrm{AT} \times \mathrm{BW}} \times 10^{-6} \quad (1)$$

Where LADD = lifetime average daily dose (mg.kg$^{-1}$.day$^{-1}$), $C_U$ is the concentration of uranium element in the fly ash (mg/l) ("exposure point concentration"), IngR is the ingestion rate (l/day), EF is the exposure frequency (days/year), ED is the total exposure duration (years), AT is the average time (days) and BW is the body weight.

The ingestion rate = 4.05 l/day [7]. The exposure frequency = 350 days. The total exposure duration = 65 years [8]. The average time calculated (65 × 365 days) = 23, 270 days and the average body weight taken of an Indian man = 53 kg [9].

The Hazard quotient (HQ) is given by:

$$\mathrm{HQ} = \frac{\mathrm{LADD}}{\mathrm{RFD}} \qquad (2)$$

Here, RFD is the reference dose calculated on the basis of the AERB permissible limits (60 μg/l) and turned out to be 4.53 $\mu g.kg^{-1}.day^{-1}$ [10].

Table 2: Uranium concentration ($\mu g\ l^{-1}$), life time average daily dose and Hazard quotient dose of various samples from GNDTPP thermal plant in Bathinda distract.

| **Sample. Code** | **Sample. Name** | **Uranium Con. ($\mu g\ l^{-1}$)** | **LADD (μg/kgd)** | **Hazard Quotient** |
|---|---|---|---|---|
| *Fly ash, Coal and Ash slurry from thermal power plant plants (GNDTPP)* | | | | |
| **A1** | Ash slurry (ash dyke) | < 3 | 0.124 | 0.027 |
| **A2** | Ash slurry (pipe) | < 3 | 0.124 | 0.027 |
| **A3** | Dry fly ash | < 2 (mg $l^{-1}$) | 82.576 | 18.229 |
| **A4** | Pulverized coal | < 1 (mg $l^{-1}$) | 41.288 | 9.114 |
| *Water sample from surrounding of the thermal power plant plants (GNDTPP)* | | | | |
| **A5** | Canal | 2 | 0.083 | 0.018 |
| **A6** | Tube well | 5 | 0.206 | 0.046 |
| **A7** | Hand pump | 18 | 0.743 | 0.164 |
| **Min value** | | 2 | 0.083 | 0.018 |
| **Max value** | | 18 | 0.206 | 0.164 |
| **Average** | | 8.3 | 0.743 | 0.082 |
| **WHO** | | 30 | 1 | 1 |

## 4. Results and discussion:

### *4.1. Estimation of uranium concentration in water from fly ash*

In the present study, we analyzed the fly ash, coal, ash slurry samples from ash dyke, Ash slurry sample coming out from pipe , water samples from the canal running along fly ash

dykes of the Guru Nanak Dev thermal power plant, standing water on ash dyke from thermal power plant, Bathinda, Private Tube well 150 m away from ash dykes, Hand pump opposite GNDTPP .The concentration of uranium and other elements present in these fly ash, coal, ash slurry and water samples shown in (table 1). The uranium concentration in fly ash (< 2 ppm) from the thermal power plants is well below the range found in some granitic rocks, phosphate rocks, and shales (10-85 ppm) [11, 12] and even soil samples from Punjab (~ 3 ppm). The present analysis revealed the major element observed is Fe with concentration 1.4 % and 2.8 % in coal and flyash sample, respectively. Other elements like $_{22}$Ti (~50 ppm), $_{23}$V (~20 ppm), $_{25}$Mn (~50 ppm), $_{29}$Cu (~30 ppm), $_{30}$Zn (~30 ppm), $_{31}$Ga (~30 ppm), $_{33}$As (~30 ppm), $_{37}$Rb (~20 ppm), $_{38}$Sr (~100 ppm), $_{39}$Y (~ 80 ppm), $_{40}$Zr (~300 ppm), $_{41}$Nb (~20 ppm), $_{42}$Mo (~10 ppm), $_{82}$Pb (~20 ppm) and $_{90}$Th (~7 ppm), are also present in significantly high concentrations compared to uranium (< 2 ppm). The concentration of these elements in the coal sample was found to be 30-50 % diluted as compared to fly ash.

Uranium in the fly ash is generally in its oxide form which is not soluble in water. The apparent absence of abundant, surface bound, relatively available uranium suggests that the rate of release of uranium is dominantly controlled by the relatively slow dissolution of host ash particles. Further, pozzolanic properties of the produced fly ash [13] do not allow any seepage in to the ground water. For contribution of uranium to the water via fly ash, the other elements with much higher concentrations should have also been present. The average of uranium concentration in the ash slurry from the ash dyke and water samples from the canal, tube well and hand pump (< 0.003 ppm), (0.009 ppm) , respectively was below the safe limit of 30μg $l^{-1}$ as recommended by World Health Organization (WHO, 2011) table 1. These results indicate that fly ash from thermal power plants (GNDTPP) is not a possible source of uranium contamination in drinking water. Because none of various water samples from the surrounding of the Guru Nanak Dev thermal power plant shows unusual high concentration of uranium Fig 4.

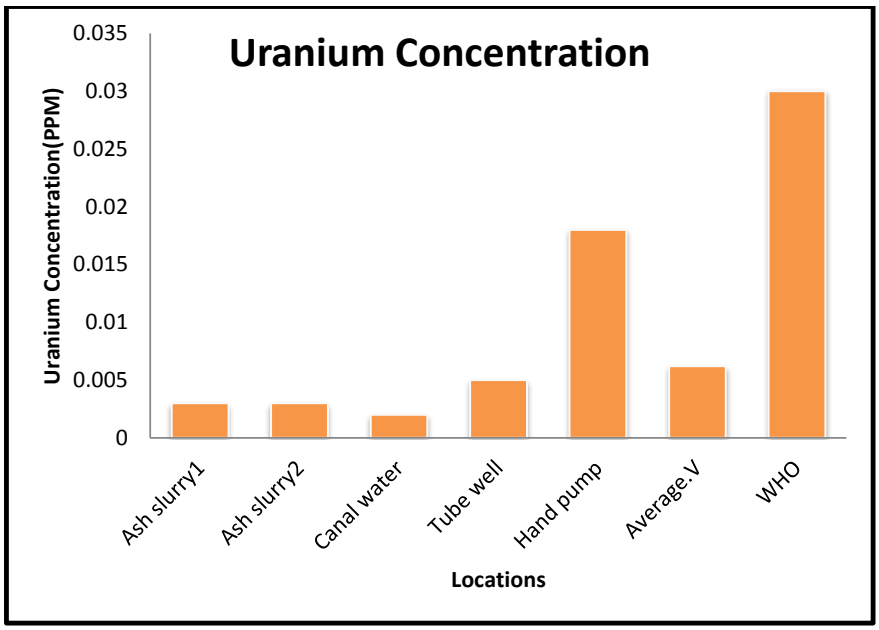


Fig 4. Ash slurry and water samples versus Uranium Concentration

The $_{38}$Sr concentrations were found to be 0.103-1.210 ppm and with average value 0.576 ppm in the various water samples from the surrounding of the thermal power plant, the $_{38}$Sr concentrations is not known to have harmful effects except that regular consumption of $_{38}$Sr affects the colour of teeth [14]. The concentrations of $_{42}$Mo were found to be 0.002-0.050 ppm and the average value (0.022 ppm) was below the safe limit of 0.07 mg/l as recommended by World Health Organization (WHO, 2011) and Bureau of Indian Standards (BIS, 2012) [15]. The concentration of $_{26}$Fe was observed in the various water samples with range 0.002- 0.018 ppm and with the mean value 0.009 ppm below the safe limit of 0.3 mg/l as recommended by World Health Organization (WHO, 2011) and Bureau of Indian Standards. The $_{35}$Br concentration was found to be 0.003-0.114 ppm and with mean value 0.050 ppm below the safe limit of 0.5 mg/l as recommended by World Health Organization (WHO, 2011) and Bureau of Indian Standards [16, 17].

In the samples of fly ash and coal $_{35}$Br is not observed, but it is present in the samples from the ash dykes and water in surrounding of the Guru Nanak Dev thermal power plant.

### *4.2. Chemical toxicity risk*

The lifetime average daily dose of uranium from the fly ash to the different type of water varied from 0.083 to 0.206 (µg $kg^{-1}day^{-1}$) with the mean value 0.743 (µg $kg^{-1}day^{-1}$). The mean value of LADD in ash slurry was 0.124 µg$kg^{-1}day^{-1}$ (Table 2). The ash slurry and water samples were found to have lifetime average daily dose value below the safe limit Fig. 5. The study showed that maximum value of the lifetime average daily dose was in the dry fly ash and coal samples and which exceeds the permissible limits. The permissible LADD recommended by World Health Organization is 1.0 mg/kg/d [18].

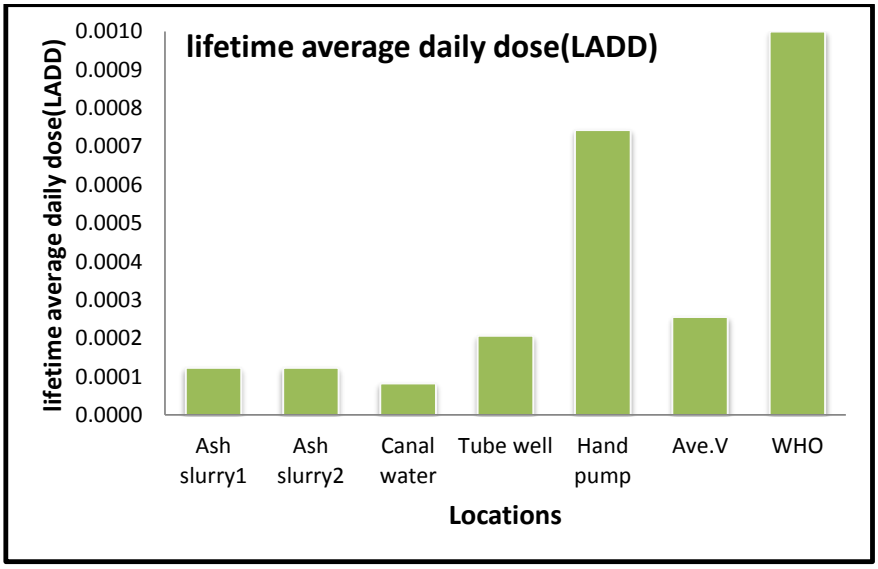


Fig. 5: Location versus lifetime average daily dose LADD).

The hazard quotient (HQ) was calculated using RfD recommended by World Health Organization and AERB, i.e., 4.53 mg $kg^{-1}day^{-1}$. The HQ varied from 0.018 to 0.164 with the mean value 0.082 in the various water samples. The mean value of hazard quotient was 0.027 in ash slurry samples (Table 2). The ash slurry and water samples were found to have hazard quotient value below the safe limit of 1.0 Fig. 6, indicating no chemical toxicity risk due to uranium from the fly ash to water. The HQ values were higher than 1.0 in the dry fly ash and Pulverized coal samples. The higher values of LADD and HQ in the dry ash and coal are due to higher contain of uranium in the soil of bathinda region ~3 ppm [19].

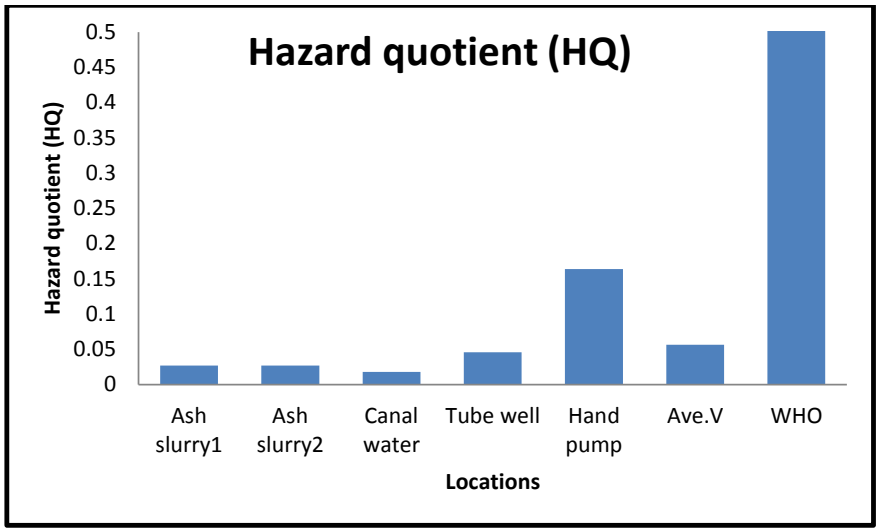


Fig. 6: Location versus Hazard Quotient (HQ).

## 5. CONCLUSIONS

The present studies show that the fly ash from thermal power plant plants (GNDTPP) is not source of uranium contamination in drinking water in the Bathinda city. Because none of various water samples from surrounding of the GNDTPP shows unusual high concentrations of uranium. The water samples were found to have hazard quotient value below the safe limit of 1.0, indicating no chemical toxicity risk due to uranium from the fly ash to the different type of water.

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