# Chromium toxicity in the Yamuna River ecosystem at Brij Region – Uttar Pradesh, India

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#### **abstract**

Chromium (Cr) is a dangerous industrial pollutant that harms surface water resources and is associated with serious adverse health effects that eventually lead to mortality. In present study Cr concentrations were detected spectrophotometrically by atomic absorption spectrophotometer from October 2018 to October 2020 (in the month of October, January, April, and July) in abiotic (water and sediment) and biotic [plant (*Eichhornia crassipes* (Mart.) Solms) and fish (*Labeo rohita*)] components of Yamuna River ecosystem. Samples were collected from Vihar Ghat (Vrindavan), Mathura – 27.58387, 77.69317 (i.e., M2 site), 100 m upstream (M1 site) and downstream (M3 site) and from Renuka Ghat, Agra – 27.25190, 77.87535, India (i.e., N2 site), 100 m upstream (N1 site) and downstream (N3 site). Root, stem and leave of studied plant while gill, muscle, liver, and kidney samples of fish were used for determination of Cr toxicity. Results revealed higher concentration of Cr in water throughout the study when compared with permissible limits by WHO and BIS (0.05 mg/L). While sediment sample had the highest metal content with a mean concentration of 51.3 ± 2.34 mg/L in summer 2019. The Heavy Metal Pollution Index for water, sediment, plant and fish samples at Mathura sampling site were shown to be extremely high, that is, 2,555; 31,254; 269 and 2,600 respectively, when compared to the samples from Agra sampling site. The bioconcentration factor in fish tissues was highest in gills (6.4167 in post-monsoon 2018 at Agra), and lowest in kidney (1.0417 in winters 2020 at Mathura). Such studies pave the path for future to establish the highest risk in term of time and components in the river ecosystem for their utility. Besides, such approaches and findings will help policy makers to ensure a safe and sustainable environment in terms of socioeconomics and human health aspects.

*Keywords:* Chromium (Cr); *Eichhornia crassipes* (Mart.) Solms; *Labeo rohita*; Heavy Metal Pollution Index; Bioconcentration factor (BCF)

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## **1. Introduction**

"The Yamuna," a holy river in India, originates from the glaciers of Yamunotri near Bandar punch in the Mussoorie range of the lower Himalayan region. It is the biggest tributary of the Ganga River [1]. A large Indian population uses water for drinking, irrigation, household, and industrial needs. From its origin, the quality of water is good, but when it flows from the Himalayas to Prayagraj (U.P.), where it merges with Ganga, most of the pollutants get dissolve in the Yamuna River and make it in the count of polluted rivers of the nation [2]. The Yamuna River is an important river in Uttar Pradesh and is being used for both abstractive and instream purposes. The catchment area of Yamuna River in U.P. (including Uttrakhand) is 74,208 km<sup>2</sup> which is about 21.5% of the total catchment area of the river. Environmental pollution due to human activities such as urbanization, unsafe agricultural practices, mechanical growth and rapid industrialization are still main contributors for deteriorating water quality [3]. Metal toxicants are transferring to river sediments from contaminated water via hydrolysis, adsorption, and precipitation, which later enter into the biotic components (flora and fauna) of ecosystem.

Depending on the concentration, these metals can be beneficial or harmful to plants, animals, and humans. Certain heavy metals have detrimental effects while some are biologically necessary for human health as well as for the plants and other biota present in ecosystem [4]. However beneficial heavy metals can be toxic to life when exposed in higher concentrations. When toxic metals are ingested, they may interact with biomolecules in the body, such as enzymes and proteins, to form stable bio-toxic compounds, mutating their structures and preventing them performing various biochemical reactions [5]. Cr exists in divalent Cr(II), trivalent Cr(III), and hexavalent Cr(VI) oxidation states in nature, with Cr(III) and Cr(VI) being the most stable of the heavy metal contaminants. Cr(VI) is a hazardous pollutants produced by anthropogenic activities that has been classified as a carcinogen with mutagenic, congenital, and physical abnormality-inducing properties [6].

Cr contamination is an issue in aquatic ecosystems that can be caused by natural, anthropogenic, or both sources. Some examples of anthropogenic causes are domestic wastewater, pesticides, inorganic fertilizers, leaching, seepage, paper manufacture, industrial wastes, and tanning companies [7].

It can deposit in marine biotic components (algae, plants, fish, etc.) via the food chain mechanism, and become harmful after permissible limits [8]. Water hyacinth plants developed apparent stress symptoms, chlorosis of the leaves, petiolar chlorosis, and necrosis, in response to the Cr(VI) supply and plant also show toxicity when exposed to Cr for a long duration [9]. Moreover, Cr can accumulate in tissues of aquatic animals especially liver, spleen, kidney, and bone marrow [10]. Cr may enter in fishes via gills, skin, and oral tracts after reaching the aquatic ecosystem, and eventually accumulate in lungs, muscles, and other tissues. According to several studies, chromium has been discovered to have severe hematological and biochemical effects on fish, resulting in a decrease in protein and glycogen levels [11].

Directly or indirectly when humans are exposed, Cr can cause serious health problems, due to its nondegradable, accumulation, and magnifying capabilities [12]. After absorption, oxidation states of Cr influence its fate. Chromium is detectable in both plasma and RBCs following absorption through the gastrointestinal tract [13]. Cr(VI) can enter through the membrane of a cell, whereas Cr(III) cannot. Cr(VI) is rapidly reduced to Cr(III) after passing through the cell membrane and it binds to macromolecules in the body finally causes neurological and cardiovascular manifestations and can even accelerate chronic situation leading to death [14]. Keeping in the view to the literature, present investigation aims with biannual monitoring (October 2018 to October 2020) of Cr concentrations in water, sediment, plant, and fish of Yamuna River ecosystem at Brij Region.

## **2. Materials and methods**

## *2.1. Study area*

The Yamuna River flows from upstream to downstream from Delhi NCR region to Mathura, followed by Agra. The main sampling locations for present study were Vihar Ghat (Vrindavan), Mathura (27.58387, 77.69317), and Renuka Ghat (Runkata), Agra (27.25190, 77.87535), India, as illustrated in Fig. 1. For the present study, water, sediment, plant, and fish



Fig. 1. Sampling sites (a) Vihar Ghat (Vrindavan), Mathura, India and (b) Renuka Ghat (Runkata), Agra, India.

samples were taken from Vihar Ghat, (i.e., M2 site), 100 m upstream (M1 site) and downstream (M3 site) and from Renuka Ghat, (i.e., N2 site), 100 m upstream (N1 site) and downstream (N3 site).

Because of their holy practises, these important ghats are visited by a great number of people. The polluted Delhi water (containing discharges from tanning businesses, welding, electroplating, and paint manufacturers) enters into Vihar Ghat at Vrindavan, Mathura. Renuka Ghat is located in Runkata, Agra, where water from the Yamuna River runs through an oil refinery (Mathura oil refinery). These places are linked to areas where human activity is higher and there is more human-animal interaction with the river environment.

## *2.2. Collection of samples*

From Yamuna River, water, sediment, plant, and fish samples were collected in four different seasons, that is, winter, summer, monsoon and post-monsoon for 2 y (2018 to 2020) as shown in Table 1. Surface water were collected in sterilized screw-capped polythene bottles at a depth of 10–15 cm from the midstream as per the Moyo and Rapatsa protocol [15]. River sediment was collected in sterile polythene bags from 5 to 10 cm depth from both of the sites [16]. Sterile plastic bags were used for plant sample collection. Plants were gently taken and washed with river water to remove particulate matter followed by rinsing with distilled water [17]. Fish samples were gathered with the assistance of a local fisherman by using clean fishing net and samples were transported to Styrofoam box preserved with ice packs. Collected sample were transported to the Department of Biotechnology, GLA University, Mathura (U.P.).

## *2.3. Physicochemical analysis – water and sediment*

Water quality parameters total dissolved solids (TDS), pH, dissolved oxygen (DO), biochemical oxygen demand (BOD) and chemical oxygen demand (COD) were carried out as per the 23rd edition of the Renowned Water Manual 'Standard Methods' APHA 2017 [18]. Temperature and pH were measured in situ with the help of portable thermometer (HM TM 1 Digital thermometer) and pH meters (Systronics digital pH meter 335) respectively.  $MnSO_{4}$ , alkali azide, and  $H_2SO_4$  were added to the collected water samples at sampling site for fixing DO concentration. While sediment analysis was carried out at Department of Soil Testing, Banasthali Vidyapith, Rajasthan. Determination of macro and micro-nutrients were performed as per the standard protocols described by Kayode and Agboola [19]. Electrical conductivity and pH of the sediment sample were performed by digital pH meter and electrical conductivity meter, respectively.

## *2.4. Sample digestion for AAS analysis*

#### *2.4.1. Water*

Between October 2018 and October 2020, 54 samples from both sampling sites were collected for present study as shown in Table 1. Three samples were taken from each site (Vihar Ghat and Renuka Ghat) during each season, and one litre of water was obtained from each sample collected for further processing. The samples were treated with  $3 \text{ mL of } 1 \text{ N HNO}_3$  before being thoroughly mixed and filtered using Whatman filter paper. A 15 mL diacid solution  $(HNO<sub>3</sub>/HCLO<sub>4</sub>, 9:4)$  was gently blended with 100 mL filtered water specimens. After the solution had entirely evaporated, the conical was allowed to cool to ambient temperature. Finally, before the AAS examination, each powdery deposit was mixed with 100 mL of triple distilled water [17].

## *2.4.2. Sediment*

For the current study, 54 samples were gathered over a 2-y period as shown in Table 1. From both sites, 1 g of ovendried soil was finely crushed and filtered individually with a 2 mm sieve to prepare sediment samples for AAS. The soil samples were treated with a  $(HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, HCLO<sub>4</sub>)$  triple acid combination in a 10:1:4 ratio. When the blend was totally evaporated at 80°C, it was allowed to cool to ambient temperature. Before the AAS investigation, triple distilled water (30 mL) was added to the residue and filtered, followed by makeup to 50 mL quantity [20].

## *2.4.3. Plant*

A total of 54 samples were obtained from both sites during the investigation period as shown in Table 1. Samples of plant (leaf, stem, and root) were prepared individually from both sites. All plant parts were oven dried at 60°C followed by powder preparation. 1 g of plant powder sample was mixed with 20 mL of concentrated  $HNO<sub>3</sub>$  and 5 mL of HCLO<sub>4</sub>. The mixture was heated for complete evaporation, and after cooling at room temperature, 30 mL of triple distilled water were added to the mixture followed by filtration, the volume was increased to 50 mL and assessed for AAS [17].

#### *2.4.4. Fish*

#### *2.4.4.1. Pre-treatment*

After reaching to the laboratory, fishes were again washed with distilled water before proceeding of dissection and excessive moisture on the surface of fishes were wiped using Whatman filter paper. The length and weight of collected fishes were measured by scale and weighting machine respectively.

#### *2.4.4.2. Treatment*

18 fishes were collected for the study, in which one fish was collected from each sampling site (between M1 and M3 stretch and N1 and N3 stretch of Mathura and Agra sampling site respectively) during every seasons as shown in Table 1. For sample preparation of fish, 10 mL of diacid mixture  $HNO<sub>3</sub>$  and  $H<sub>2</sub>SO<sub>4</sub>(1:1)$  was taken in vials and incubated for 10 min followed by addition of 1 mL  $H_2O_2$ . Fish was dissected, and the organs of fish such as liver, kidney, gills, and muscles were washed with 0.9% saline and liver, kidney, 5 g of oven dried muscles and kidney was added in





the prepared tubes separately and incubated for overnight at room temperature. After overnight incubation tubes were kept in the oven at 105°C for 2 h for further digestion [21]. After digestion, the samples were cooled and filtered by the help of Whatman filter paper (No. 42). The quantity was make up to 25 mL using deionized water or HNO<sub>3</sub> and stored at 4°C in a sterile container.

## *2.5. AAS analysis*

Determination of Cr concentration among digested samples were carried out by Z express 8000 AAS model at ICAR – Division of Soil Science and Agricultural Chemistry, Indian Agricultural Research Institute's (IARI).

## *2.6. Modeling and statistical analysis*

#### *2.6.1. Heavy Metal Pollution Index analysis*

To estimate the Heavy Metal Pollution Index (HPI), the quality of the river was assessed by taking the weighted average values of the concentrations of samples (water, sediment, plant and fish). The HPI rating of 100 is fundamental. It was determined by using Eq. (1) given by Mohan et al. [22].

$$
HPI = \frac{\sum_{i=1}^{n} W_i Q_i}{\sum_{i=1}^{n} W_i}
$$
 (1)

where  $W_i$  is the reciprocal value of  $S_i$ ,  $S_i$  denotes the standard values (WHO standard limits) of heavy metal for the sample taken, *Qi* denotes sub-indexing of the *i*th parameter as computed by Eq. (2), and *n* denotes a number of parameters.

$$
Q_i = \sum_{i=1}^{n} \frac{M_i}{S_i} \times 100
$$
 (2)

where *Mi* denotes the measured heavy metal value and *Si* denotes the standard parameter of *i*th in ppm (mg/L). The lowest quality of water, sediment, plant and fish is when the concentration of metal exceeds the allowed limit. A value of > 1 on the Metal Quality Index (MQI) is considered a warning threshold [23]. Eq. (3) is used to determine the MQI [24].

$$
MQI = \sum_{i=1}^{n} \frac{M_i}{S_i}
$$
 (3)

#### **3. Heavy metal evaluation index**

If the concentration value of a metal exceeds its acceptable limits, it indicates that the samples (water, sediment, plant and fish) are of poor quality. The threshold of warning is a MI value greater than one. The metal index [Eq. (4)] is determined using the formula [25]:

$$
HEI = \sum_{i=1}^{n} i = 1 - n \left( \frac{C_i}{MAC_i} \right)
$$
 (4)

where  $C<sub>i</sub>$  denotes the metal concentration detected and MAC denotes the maximum acceptable limit (permissible limit).

## **4. Bioconcentration factor**

The ratio of Cr in tissues of *Labeo rohita* and Cr concentration in water is defined as Bioconcentration factor (BCF). BCF is calculated as described by Eq. (5) [26]. The other terminology against the BCF is BAF (Bioaccumulation factor) [27,28].

$$
BCF = \frac{Cr\,\text{concentration in fish tissues}}{Cr\,\text{concentration in water}}\tag{5}
$$

## **5. Human health risk evaluation using quantitative methods**

#### *5.1. Estimated daily intake of Cr*

Human health risk is assessed using estimated daily intake (EDI) of Cr and target hazard quotients (THQ). Only the fish muscles were employed. The following on Eq. (6) can be used to calculate the anticipated daily consumption of Cr.

$$
EDI = \frac{C \times FIR}{BW}
$$
 (6)

where *C* is the mean concentration of Cr of dry weight basis in the fish muscle  $(\mu g/g)$ .

Conversion factor 4.8 is taken for conversion from dry weight to wet weight. FIR (food intake rate) is the daily intake of freshwater fish ( $g/d$  ( $g^{-1}$ )/cap. The average FIR was 1.53 g person<sup>-1</sup> d<sup>-1</sup> [India Nutrition Security Freshwater Fish Reference: FAO Data Evidence] [29]. BW is the mean body weight for adults, 70 kg [57].

#### *5.2. Target hazard quotient*

The non-carcinogenic level of risk assessed as a result of heavy metal exposure is known as the target hazard quotient (THQ). Eq. (7) below is used to compute it.

$$
THQ = \frac{Efq \times ED \times FIR \times C \times 10^{-3}}{RfD \times BW \times AT}
$$
 (7)

where Efq (exposure frequency) is 365 d/y, ED is the exposure duration, that is, 70 y (as set for this study), FIR and *C* are already defined earlier, RfD is the Dosage that evaluates the health risk of fish consumption (considered 0.003 µg/kg d by the United States Environmental Protection Agency), and AT is the time for noncarcinogenic average exposure (365 d  $\times$  No. of exposure years).

## *5.3. t-test analysis*

To scrutinize the trends in Cr levels among the various environmental compartments (i.e., water, sediment, fish and plant) the statistical comparison is performed using descriptive *t*-statistics. Eq. (8) is used for calculating the *t*-value for paired sample.

$$
t = \frac{\overline{X}_a - \overline{X}_b}{\sqrt{\frac{s_a^2}{n_a} - \frac{s_b^2}{n_b}}}
$$
(8)

where  $X_a \& X_b$  are the sample means,  $S_a \& S_b$  are the standard deviations and  $n_a \& n_b$  are the number of sample observation in 1st and 2nd group respectively. The null hypothesis  $(H_0)$  and alternate hypothesis  $(H_1)$  are defined as:

- *H*<sub>0</sub>: there was no significant difference in the Cr concentration between the water (mean =  $\mu$ <sub>1</sub>) and sediment (mean =  $\mu$ <sub>2</sub>) samples or fish (mean =  $\mu$ <sup>'</sup>) and plant (mean =  $\mu_2$ <sup>'</sup>) samples, that is,  $\mu_1 = \mu_2$  or  $\mu_1' = \mu_2'$ .
- *H*<sub>1</sub>: the Cr concentration in sediment sample is significantly higher than that for water sample, that is,  $\mu_1 < \mu_2$ or  $\mu_1' < \mu_2'.$

This is left-tailed *t*-test. Here, the null hypothesis  $(H_0)$ will be rejected if the calculated *t*-value is obtained more than the critical tabulated value at a pre-defined significant level ( $\alpha$  = 0.05). If the calculated value is less than the tabulated value then the null hypothesis will be accepted.

All statistical analysis has been carried out through *R* software.

#### *5.4. Statistical analysis*

The overall results from above equations were analyzed statistically by using *R* software package to determine the average, standard deviation, and Pearson's correlation coefficient with a level of significance  $p < 0.05$ . *t*-test was also performed to specify the significant difference between groups. The data were carried out in triplicate form, and its mean was taken as results.

#### **6. Results and discussion**

Water is a natural resource that is almost unavoidable, as well as a life-supporting system for life. Domestic, agricultural and industrial effluents account for the majority of the pollution load in the Yamuna River. Heavy metals, organic waste, untreated sewage, pesticides, dead body dumping, livestock washing, and other pollutants are the principal contaminants. Diverse parameters were investigated for the current study to evaluate the physicochemical state of river water and sediment from studied sites (Mathura – 27.58387, 77.69317 and Agra – 27.25190, 77.87535) from October 2018 to October 2020. Besides, Cr concentration was estimated in abiotic (water and sediment) and biotic (plant and fish) components of river ecosystem. Such information can be used to establish the maximum risk time of the year, the highest risk part of plants and fish for ingestion. The findings of this study will have a substantial impact on the improvement of river health and will help in the improvement of socioeconomics, public health, and environmental status.

Throughout the study for both sampling sites, water was alkaline with a temperature ranged from  $19^{\circ}$ C ±  $0.1^{\circ}$ C to  $35^{\circ}$ C ±  $0.15^{\circ}$ C and pH range of  $6.8 \pm 0.3$  to  $8.2 \pm 0.1$ . The alkaline river water is not only toxic for the river fauna but also lethal for humans and may be attributed to draining of sewage and industrial effluents from urban areas. The DO of the Yamuna River was deficient with a range of  $1.2 \pm 0.1$ to  $5.73 \pm 0.07$  with the mean BOD ranged from  $8.32 \pm 0.16$ to  $32.73 \pm 0.57$  mg/L which suggested an increased load of contamination from upstream to downstream as shown in Table 2. In winters the highest DO  $(5.73 \pm 0.07)$  observed in water samples (Mathura) which could be due to the great dissolution property of  $O_2$  in lower temperature while in summer (2019), maximum BOD value (32.73 ± 0.57 mg/L) was observed in water samples (Mathura). Similar patterns were found for physicochemical analysis in the study carried out by Hassan et al. for Yamuna River water [30]. Dissolved oxygen determines the purity of water, it depends upon the relative biological activity and is used for the quality check. The concentration of DO was low due to urban water waste addition in downstream rather than the presence of water hyacinth. As the river was not stagnant in its path and water was in a well flowing condition there were no signs of eutrophication. Due to decreased concentration of DO in water, organisms unable to decompose the organic components, so from upstream to downstream, there was an increase in a load of organic pollutants, and may be the reason for enhancing the temperature and BOD of river water. In addition, there was a significant reduction in BOD and COD values during impact assessment of COVID-19 pandemic confinement on physicochemical analysis of Yamuna water (Table 2). Similar results were reported in CPCB may be due to decreased effluent load and drain contaminants results in improvements of water quality [31–33].

Determination of sediment properties is a very valuable method for determining river quality. The electrical conductivity of the Yamuna sediment was found to be normal with moderate alkaline pH as shown in Table 3 [34]. Organic carbon, accessible nitrogen, phosphorus, potassium, and sulphur were found at average concentrations, whereas iron, zinc, manganese, and copper were found at sufficient concentrations [35]. The fish was identified as *Labeo rohita* by Fisheries Department, Mathura, Government of Uttar Pradesh, India. The average length and weight of fishes collected from Mathura site was 35.07 ± 2.05 and 659.67 ± 66.13 and from Agra site length and weight was  $36.08 \pm 2.11$  and 635.44 ± 58.71. The plant was identified by Patanjali Research Institute, Patanjali Yogpeeth, Haridwar, Uttrakhand.

#### *6.1. Chromium concentration in samples*

As per WHO [36] and FEPA [37], permissible limits of Cr in water, plant and fish samples are 0.05 mg/L, 1.30 mg/ kg and 0.15 µg/g respectively. Results of present study revealed higher concentration of Cr in all of the studied samples except for stem and kidney samples from plant and fish respectively as shown in Fig. 2. During biannual study, significant high Cr concentration was observed in summers for all of the samples while Mathura sampling site (27.58387, 77.69317) have higher contamination when compared with Agra site (27.25190, 77.87535). Besides, in summer 2019, sediment was found to be the most polluted component of Yamuna River ecosystem with highest Cr concentration, that





is,  $51.3 \pm 2.34$  mg/L and  $39.8 \pm 2.22$  mg/L at the Mathura and Agra site respectively. Similar results were reported by Kaur and Mehra in 2012 for study conducted on determination of various heavy metal load in Yamuna ecosystem at Delhi region [38]. May be due to the dropping of water level, concentration of metals rises over the summer, resulting in an increase in pollution deposition. However, due to a complete lockdown because of a covid outbreak in summer 2020, the values were low. Gupta et al. [39] observed that the value of heavy metals reduced during the Monsoon season as a result of higher water levels caused by heavy rains. The key component of the aquatic ecosystem is sediment, which is created by the deposition of eroded soil, crops, and livestock. This deposition is caused by vectors such as soil, ice, and water, which aid in the transport of these deposits into river streams and ultimately into the basin [40]. Because of the nutrients that sustain tremendous biodiversity, it has its own importance due to its fertility. Sediment is often regarded as the most polluting component of an aquatic ecosystem, as it contains a variety of contaminants released by natural and anthropogenic events.

In plants, highest Cr concentration was observed in roots followed by leaves and stem. *Eichhornia crassipes* (Mart.) Solms. is a very good phytoremediator and many experiments have been performed in which *Eichhornia* showed high absorption of heavy metals especially via roots from different industrial effluents [41–43]. The data confirm Cr accumulation in roots was from nearby water that is already contaminated with Cr because the roots were within the water, as well as a small uptake of Cr were also from sediment. Since the stem is the binding tissue that transports absorbing material (water and nutrients) from the roots to

the vascular tissues, such as the leaves, it may because of transportation, stem has the lowest Cr toxicity. Furthermore, leaves store nutrients and water, as well as being the site of photosynthesis and other key metabolic pathways. Cr transferred from polluted sediment in very small quantity, mainly from surrounded water Cr accumulates in roots followed by leaves, causing them to have higher Cr levels than the stem.

In "Rohu" the widely consumed fish in the area, the order of accumulation was discovered to be highest in the gills, liver, muscles, and least in the kidney [44]. *Labeo rohita* is an omnivorous fish, still there are no signs of trophic transfer from plant to fish so probably the source of Cr contamination in fish is the river water. Rohu prefers zooplankton in its early stages of life, comprised primarily of rotifers and cladocerans, with phytoplankton. At the fingerling stage, there is a strong positive selection for all zooplanktonic species as well as certain smaller phytoplankters such as desmids, phytoflagellates, and algal spores. Adults, on the other hand, demonstrate substantial positive selection for the majority of phytoplankton. Rohu is primarily an herbivorous column feeder in its juvenile and adult stages, favouring algae and submerged plants. Its restricted eating habits are indicated by the presence of degraded organic debris, sand, and mud in its stomach. The fish eat on soft aquatic vegetation that does not need seizure or crushing because to the nibbling mouth, smooth fringed lips, sharp cutting edges, and lack of teeth in the bucco-pharyngeal area. The modified thin, hair-like gill rakes of fish further indicate that they feed on minute plankton by sifting water. In ponds, fry and fingerlings engage in schooling activity primarily for the purpose of eating; however, adults do not





engage in this behaviour [45]. Cr enters in the body of fish through gills [46], where it accumulates in high concentration in comparison to other tissues and organs of fish and it is due to pH levels of surrounding water from which Cr diffuses passively and may be the reason for higher accumulation of Cr in gills than the liver [47–49]. Liver is one of the most metabolically active tissue responsible for storage and detoxification of body, is the next organ where metal accumulation takes place. In the liver, the metals accumulate due to its thin epithelium. The increased quantity in the liver is owing to the metallothionein protein's affinity or strong coordination with these metals [50].

Cr(VI), due to its higher solubility in water readily penetrates the gill membrane by the process of passive diffusion, and can be influenced by surrounding pH and temperature as it is responsible for higher metal concentration. The pattern of Cr distribution in fishes is as follows: Gills > Liver > Skin > Muscles. Cr associate with the hardness of water and then get accumulate in fish from that water through gills and then blood and reaches to different organs. Finally, eliminate out of the body in the form of faces through alimentary canal [51]. This might be the explanation for the fish species for poor Cr build up in their muscles when compared to other organs exposed directly to the water.

#### *6.2. Pollution risk analysis*

The HPI values in Table 4 were calculated using mean sample levels from both sites. The mean HPI for Yamuna water, sediment, plant, and fish samples were found to be

extremely high, that is, 2,555; 31,254; 269 and 2,600, revealing high chromium pollution in the Yamuna ecosystem for the Mathura region, when compared to Agra samples (2,093; 28,252; 243 and 2,376). For the measurement of total chromium contamination in the Yamuna ecosystem, the Metal Quality Index (MQI) was calculated in Table 4 with HPI value [52]. Both locations along the examined length were substantially contaminated with chromium  $(MQI > 1)$  [53]. MQI values for water, sediment, plant, and fish samples were 25.56, 312.54, 2.70, and 26.01 for Mathura region and 20.93, 282.52, 2.43, and 23.76 for Agra region, indicating a substantial difference.

Pearson's correlation matrix is used to demonstrate the relationship between the components in Table 5. Features in different samples have a statistically significant strong positive association. The high favorable relationship values between all the samples for the Mathura region  $(r = 1)$ 

#### Table 4

Heavy Metal Pollution Index (HPI) and Metal Quality Index (MQI) in an ecosystem

Sample		<b>HPI</b>	MOI		
	Mathura	Agra	Mathura	Agra	
Water	2,555.56	2,093.33	25.56	20.93	
Sediment	31.254.44	28,252.22	312.54	282.52	
Plant	269.52	243.33	2.70	2.43	
Fish	2,600.62	2,376.11	26.01	23.76	



Fig. 2. Showing Cr concentration in seasonally collected samples (water, sediment, plant and fish) in (a) Vihar Ghat (Vrindavan), Mathura and (b) Renuka Ghat (Runkata), Agra.

Table 5 Pearson's correlation analysis of Cr concentration in the samples

Sample		Mathura			Agra			
	Water	Sediment	Plant	Fish	Water	Sediment	Plant	Fish
Water		0.82	0.77	0.87		0.86	0.65	0.90
Sediment			0.91	0.93			0.75	0.93
Plant				0.95				0.84
Fish								

demonstrate a significant association, as do the high positive correlation values for the Agra region.

Cr in fish tissue as a percentage of total Cr to surrounding water is known as BCF. The BCF of Cr in species-specific metals in distinct fish tissues, such as gill, liver, muscles, and kidney, revealed that there was a significant likelihood of Cr metals bioaccumulation in the fish organs and tissues in the current study. During the examined season, the BCF in gills of fish was greater, whereas the BCF of liver, muscle, and kidney was lower for both sites. Similar results were reported by Maurya et al. (2019) in River Ganga in *Labeo rohita*, *Cirrhinus mrigala*, and *Cirrhinus reba* [54]. The BCF in this investigation revealed that the Cr concentration in the tissues was in the following order: gill > liver > muscle > kidney. A boxplot depicting the different comparisons between the BCF of both sites is shown in Fig. 3. The human population as a whole consumes fish muscles. As a consequence, as indicated in Table 6, the human health risk was calculated using target hazard quotients (THQ) values of Cr content in

fish muscles and an EDI of Cr. People who consume fish on a daily basis in the surrounding towns are concerned about the buildup in freshwater fish of certain heavy metals. The acceptable levels for EDI 0.003 g/kg d and THQ is 1, according to the USEPA (2011) [55]. The EDI was substantially lower than expected, and the THQ in all of the fish muscle samples was less than one. As a result, the fish is now safe to consume, but higher Cr levels in the future may constitute a



Heavy metal evaluation index for all samples





Fig. 3. Boxplot showing bioconcentration factor in (a) Vihar Ghat (Vrindavan), Mathura and (b) Renuka Ghat (Runkata), Agra.





Critical values: EDI: 0.003 µg/kg d; THQ > 1 (*Source*: USEPA, 2011).

Site	Mathura			Agra				
Sample	Sediment	Water	Fish	Plant	Sediment	Water	Fish	Plant
Mean	31.25	1.27	3.91	3.48	28.25	1.04	3.56	3.15
Variance	62.46	0.11	1.08	1.24	30.75	0.06	0.58	0.71
<b>Observations</b>	9	9	9	9	9	9	9	9
Hypothesized mean difference	$\Omega$		$\Omega$		0		$\overline{0}$	
df	8		16		8		16	
t-stat.	11.3675		1.8303		14.7014		1.8083	
$P(T \le t)$ one-tail	0.000000162		0.0292		0.00000052		0.0309	
t-Critical one-tail	1.8595		1.7458		1.8595		1.7458	

Table 8 *t*-statistics for Cr concentration in the studied sites

public health concern. Heavy metal evaluation index (HEI) of sediment samples from Vrindavan (Vihar Ghat) location was determined to be 312.54, whereas the HEI of sediment samples from Agra (Renuka Ghat) site was 282.52. Plant samples from both sites had the lowest levels of HEI (2.20 for Mathura and 2.43 from Agra). Low pollution is indicated by a score of less than 10, moderate pollution by a score of 10 to 20, and severe pollution by a score of more than 20 [56]. Table 7 shows that sediment, in contrast to water and fish, was heavily contaminated, although plant samples were unaffected. The results were over the threshold values in both sites, showing that all samples were contaminated. Vrindavan's (Vihar Ghat) water is more polluted than Agra's. In Table 8, *t* test results shows that, the null hypothesis is significantly rejected for both the studied sites for Cr concentration. The *t*-value between sediment and water samples is 11.3675, which is significantly higher than the critical *t*-value (1.8595), showing significantly greater Cr content in sediment than in water for the Mathura region (p-value  $= 0.05$ ) at the 5% level of significance. The Agra region appears to be following the similar pattern. While Cr concentration in fish was found to be slightly higher than in plant.

#### **7. Conclusion**

When Cr levels in all samples obtained from the Yamuna River were compared to the BIS and WHO standard limits, it was concluded that the river water was unfit for the use of living beings without treatment. There was a significant reduction for Cr contamination in all component of river ecosystem during lockdown 2020 resulting in improvement in quality. The majority of the water samples collected had higher Cr concentrations than allowed. In summer 2019, the highest concentration of Cr  $(51.3 \pm 2.34 \text{ mg/L})$ was found in sediment in the Mathura region, followed by  $(38.80 \pm 2.22 \text{ mg/L})$  in Agra region. As compared to Agra, the pollution load in Mathura was slightly higher. In all samples, the lowest Cr concentration was observed in October 2019. Both sites were seriously threatened by Cr contamination, according to the HPI and MQI studies. BAF for Cr in fish, demonstrate that it is readily consumed and accumulated. The gills were the most abundant, followed by the liver. All fish samples had a THQ of less than 1. The bioaccumulation of toxic metals in these edible fish poses a health risk to humans. In future such studies and their findings will help decision makers to ensure the outputs of running and completed policies and programs for welfare of river ecosystem.

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