International Journal of Zoological Investigations

Contents available at Journals Home Page: www.ijzi.net

ISSN: 2454-3055

Human Health Risk Associated with Multiple Pathway Exposure to Arsenic in Contaminated Wetlands Cultivating Invasive Fish

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Received: 2nd April, 2020

Accepted: 30th April, 2020

Published online: 7th May, 2020

<https://doi.org/10.33745/ijzi.2020.v06i01.012>

Abstract: The fish, water and sediment samples were examined for the presence of arsenic from six lakes in Ballia (Surha, Dah, Maniyar) and in Unnao (Nawabganj, Ajgaine and Asiwani) districts of Uttar Pradesh commonly producing water chestnut *Trapa bispinosa* locally known "singhara". Spraying of herbicides especially monosodium methanearsonate (MSMA) is very common in these water bodies. The estimated Arsenic (As) concentration in lake water ranged from $43.89 \pm 6.54 \mu\text{g/l}$ to $31.39 \pm 3.12 \mu\text{g/l}$ in Ballia and $22.21 \pm 4.4 \mu\text{g/l}$ to $10.78 \pm 2.32 \mu\text{g/l}$ in Unnao district at different sampling sites. The calculated total exposure of As level for adult was observed from $0.0042 \mu\text{g/kg}$ body weight per day, while in children the exposure level was $0.0092 \mu\text{g/kg}$ body weight/day. Muscular concentration of As in *Clarias gariepinus*, *Oreochromis niloticus* and *Cyprinus carpio* captured from district Ballia was found higher (0.017 ± 0.009 to $5.46 \pm 1.95 \mu\text{g/kg}$) than the concentration found in Unnao (0.002 ± 0.001 to $1.75 \pm 0.39 \mu\text{g/kg}$). The combined hazard index (HI) value for As was 3.6 for Ballia and 1.8 for Unnao through different exposure routes. Human health risk assessment for As contaminants from different routes was calculated as per the processes and the probability of occurrence and the probable magnitude of adverse health effects over a specified time period. Food safety issue concerning human health has been addressed in this paper keeping in view of As bioaccumulation in hardy invasive fish species available particularly in Arsenic prone areas.

Keywords: Fish, *Trapa bispinosa*, Methanearsonate, Arsenic, Hazard index, Risk assessment

Citation: Singh Atul K.* and Srivastava Sharad C.: Human health risk associated with multiple pathway exposure to arsenic in contaminated wetlands cultivating invasive fish. Intern. J. Zool. Invest. 6 (1): 148-161, 2020.

<https://doi.org/10.33745/ijzi.2020.v06i01.012>

Introduction

Over the past two decades, occurrence of high concentrations of arsenic in water has been recognized as a major public-health concern in several parts of the world (Liu, 2010).

There are few reviews published covering the arsenic-contamination scenario around the world (Smedley and Kinniburgh, 2002; Mandal and Suzuki, 2002). With the discovery

of newer sites in the recent past, the arsenic-contamination scenario especially in Asian countries has changed considerably. Before 2000, there were only few major incidents of arsenic contamination in aquatic bodies reported from Bangladesh, India and China. Arsenic contamination in groundwater from the Padma-Meghna plain in Bangladesh was first reported in 1995 (Dhar *et al.*, 1997). WHO reported that at least 140 million people of 50 countries are exposed to arsenic through arsenic-contaminated groundwater at levels above 10 µg/L and a majority of them live in India and Bangladesh (WHO, 2018). The areas and population of 50 arsenic-affected districts in Bangladesh was 118,849 km² and 105 million respectively compared to the total area and population of the country-148, 393 km² and 120 million respectively (Ahmad *et al.*, 2018).

In India, the first case of arsenicosis was identified in 16 patients from one village of a district in West Bengal in July 1983 (Chakraborti *et al.*, 2002). In arsenic-affected areas, a preliminary study showed the presence of elevated levels of inorganic arsenic in rice and vegetables (Chowdhury *et al.*, 2001; Hassan *et al.*, 2017). The source of arsenic is geogenic and is present in alluvial sediment of the Delta. The mechanism and cause of arsenic leaching from source has been suggested via theories of oxidation (Chowdhury *et al.*, 1999; Chakraborti *et al.*, 2001), reduction (Nickson *et al.*, 2000), carbon reduction (Harvey *et al.*, 2002), and microbial reduction (Islam *et al.*, 2004). During June 2002, arsenic in groundwater was first reported in Semria Ojha Patti village of Sahapur police station in Bhojpur district of Bihar state in India (Chakraborti *et al.*, 2003). In December 2003, arsenic contamination of

water was found in Sahibganj district, Jharkhand state, which is situated in the Middle Ganges Plain (Anon, 2005). In the northeastern region of India for the first time, arsenic contamination was detected in water of the Upper Brahmaputra plain (Chakraborti *et al.*, 2004). A preliminary study in 1976 on arsenic in dug-wells, hand-pumps, and spring-water was reported from Chandigarh and different villages of Punjab, Haryana, and Himachal Pradesh in northern India (Datta *et al.*, 1976). In Uttar Pradesh, arsenic contamination in many blocks and villages of Ballia, Ghazipur and Varanasi district has also been reported during 2004 and the issue is coming to the forefront.

The water chestnut herb is a host of traditional water crops besides fish, providing precious income for the community during the off-season. Fishermen use to raise different kinds of fish in local natural water bodies particularly lakes, which happens to be breeding sites of those fish as well. Some rice varieties such dooshavadlu, palagadda and kamalaksha are also among the other crops that are cultivated in the periphery of these lakes (Singh, 2011). *Clarias gariepinus*, *Oreochromis niloticus* and *Cyprinus carpio* are popular invasive exotic aquaculture species which are cultivated in several lakes and wetlands of Uttar Pradesh including the water bodies containing water chestnut as a crop (Singh, 2014). During the last few years, availability of tilapia, African catfish and common carp in commercial catches has increased (Singh and Lakra, 2011; Singh *et al.*, 2014). Year-round availability and lower price of these fishes are probably indicators of their increased consumption (Singh *et al.*, 2012, 2014). Fishes have been reported to have high tolerance and absorption of arsenic (Kar *et al.*,

2011). The amount of arsenic (As) found in fish is usually related to the concentration in the water and soil, especially the concentration of water soluble As, since water soluble As travels more easily from the aquatic environment (Sharma and Dwivedi, 2009). Since fishes are constantly exposed to pollutants in contaminated water, they could be used as excellent biological markers of arsenic (Canli and Atli, 2003).

Spraying of herbicides especially the monosodium methanearsonate (MSMA) is very common in paddy and water chestnut suffering from Straighthead disease including lakes particularly cultivating them (Gilmour and Wells, 1980). There are also reports revealing that straighthead is closely associated with the arsenic concentration in soil, and the severity of straighthead was found to increase significantly with the increase of arsenic concentration (Rahman *et al.*, 2008; Datta and Sarkar, 2004). Since water bodies receiving arsenate contents are supposed to be contaminated with arsenic for which we do not have any scientific report. Consumption of As contaminated paddy, waterchestnut or even fishes have been reported to have risk potential for human (USEPA, 2019; Michael *et al.*, 2011; Imar and Carlos, 2011; Ali *et al.*, 2019). This paper reports the bioaccumulation of Arsenic in some fish species available in different lakes of the Ballia and Unnao districts of Uttar Pradesh which have recently been identified as arsenic prone areas (MoSPI, 2007; Sankararamakrishnan *et al.* 2015). We have attempted to correlate the bioaccumulation with the mobile phase episodes of arsenic contamination in Uttar Pradesh, demonstrated a spatially explicit ecological risk assessment that closely conforms to the

general framework developed for the assessment of risks due to environmental toxicants (WHO, 2001; USEPA, 2016).

Materials and Methods

Study area:

The study area was natural lakes in the Nawabganj (S1) (26°37'3. 56 N, 80°39'13. 80E), Ajoin (S2) (26°36'59. 39 N, 80°37'32. 32 E) and Asiwan (S3) (26°37'40. 08 N, 80°38'1. 17E) of the Unnao district of Uttar Pradesh. The main source of water for these lakes is only rain water. It is a potential source for capture fisheries and forms the lifeline for rural economy and environment of the area. The study was also extended in famous SurhaTal (S4) (25°51'7.75 N, 84°10'28.92E), Dah Tal (S5) (25°51'01.22 N, 84°22'12.56 E) and Maniyar Tal (S6) (26°2'59.27 N, 84°3'10.45E) located in the district of Ballia. It is an open natural lake in the floodplain of river Ganga. It is an important natural resource of fisheries in the Ballia district and eastern Uttar Pradesh.

Sampling procedure and analysis:

The fish, water and sediment samples were taken from the lakes of Unnao and Ballia following the Standard method (APHA, 2012) and quality monitoring was done as per the procedure of Central Pollution Control Board (CPCB, 2008; Singh *et al.*, 2012). The invasive fish species used in this study were *Clarias gariepinus*, *Oreochromis niloticus* and *Cyprinus carpio* since they are hardy and tolerate harsh and pollution conditions. Each fish species was caught from the selected samplings lake sites using drag net, which were usually left over night in the Lake by local fishermen. Fishes (*Clarias gariepinus*, *Oreochromis niloticus* and *Cyprinus carpio*) were caught at

S1 to S6 locations in the Unnao and Ballia districts.

Muscle:

The netted fish were recovered each morning in a sample box with some quantity of lake water and brought to the laboratory. The scales were removed using plastic knife. Approximately 2.0 g muscle of sample was weighed and placed in glass tubes. One gram of dried tissue (in three replicates) was then digested with standard method (APHA, 2012; Singh *et al.*, 2014).

Surface sediment:

Surface sediment from each study sites was collected into pre-cleaned polythene bag using a stainless van-ven grab. Sediment samples were digested according Singh *et al.* (2014) and the volume was made 10 ml with deionized water for further analysis.

Water:

A water sample was collected using plastic containers. 5 ml of concentrated hydrochloric acid was added to 250 ml of water sample and evaporated to 25 ml. The concentrate was transferred to a 50 ml flask and diluted to mark with distilled water. Analyzing these variations and the collected data, we tried to find reliable relations between the variables and data, as well as helpful trends. Total As was detected in water samples, surface sediment sample and digested tissue samples by UNICAM-flame atomic absorption spectrophotometer (FAAS, Agilent) method through hydride generation technique (Jones and Laslett, 1994; APHA, 2012).

Quality Control:

Analysis of sample was done according to standard, reagent blank and sample replicate

which were randomly inserted in the analysis process to assess contamination and precision. A sample of double distilled water divided into two, where one part was kept in the laboratory and other part was transported to the sample sites. The error from contamination due to transportation was 0.1020 to 0.1098. Recovery studies of As metals determination were conducted to demonstrate the efficiency of the method. The recovery rates ranged from 83.3% to 92.2%.

Risk assessment:

The hazard identification was done by monitoring of arsenic in surface water as well as fish muscle as described above. Quantification of exposure in relation to consumption of As was done by a multiple pathway exposure model (SEDISOIL) (Harma *et al.*, 1999) using parameters in the exposure values (Table 1). The model was based on individual exposure routes: the surface water, sediment, and fish consumption. The following equations are incorporated into the model to calculate total exposure (Singh *et al.*, 2014):

$$\text{Ingestion of contaminated sediment (mg kg}^{-1}\text{day}^{-1}) = \frac{CS \times IRs \times EF \times AF}{BW} \quad (1)$$

where CS = concentration of the As in sediment (mg kg⁻¹dw), IRs = ingestion rate of sediment (kg/dw exposure day), AF = absorption factor (unitless), and BW = body weight (kg).

$$\text{Ingestion of surface water (mg/kg/day)} = \frac{CW \times IRw \times EF \times AF}{BW} \quad (2)$$

where CW= concentration of the As in surface water (mg l⁻¹) and IRw = ingestion rate of surface water (per liter exposure day).

$$\text{Ingestion of suspended material (mg/kg/day)} = \frac{CM \times CMW \times IRw \times EF \times AF}{BW} \quad (3)$$

where CM= concentration of AS contaminant in suspendedmatter (mg/kg/dw) and CMW= suspended matter content of surface water (kg/l).

$$\text{Dermal contact with contaminated sediment (mg/kg/day)} = \frac{CS \times SAs \times AD \times ASs \times Mf \times EDs \times EF \times AF}{BW} \quad (4)$$

where SAs = dermal surface area for sediment exposure (m²), AD = dermal adherence rate for sediment (mg⁻¹ cm²), ASs = dermal absorption rate for sediment (l/h), Mf= matrix factor (unitless), and EDs = exposure duration from dermal exposure to sediment (h/day).

$$\text{Dermal contact with contaminated surface water (mg/kg/day)} = \frac{CW \times SAw \times ASw \times EF \times EDw \times AF}{BW} \quad (5)$$

$$ASw = \frac{5000 \times (0.038 + 0.153 \times K_{ow}) \times \exp(-0.016 \times M)}{5000 + (0.038 + 0.153 \times K_{ow}) \times 1.5} \quad (6)$$

where SAw = dermal surface area for exposure in surface water (m²), ASw = dermal absorption rate for exposure in surface water [(mg/m²)/(mg/l)/h], EDw = exposure duration from dermal exposure to surface water (h/day), K_{ow} = octanol/water partition coefficient, and M = molecular weight (g mol⁻¹).

$$\text{Ingestion of fish (mg/kg/day)} = \frac{CF \times IRf \times FI \times AF}{BW} \quad (7)$$

where CF = concentration of the contaminant in fish [mg kg⁻¹ fresh weight (fw)], IRf= ingestion rate of fish (kg/fw/day), and FI = fraction contaminated (unitless)

Calculated As exposure levels were compared with the tolerable daily intake (TDI). The TDI refers to the reference dose of a substance that can be taken in daily without identifiable risk at lifetime exposure. Additionally, the hazard index was calculated, which refers to the ratio of the calculated lifetime daily exposure divided by the reference dose (TDI). Daily exposure (mg/kg/day) averaged over a lifetime (eg. 70 years) was calculated:

$$\frac{6 \times \text{daily exposure child}}{70} + \frac{64 \times \text{daily exposure adult}}{7}$$

Carcinogenic risk:

The following equation was used for each exposure route (USEPA, 1989; Yongli *et al.*, 2010):

$$\text{Carcinogenic risk} = \text{TDI} \times \text{slope factor} [(\text{mg/kg/day})^{-1}]$$

The reference dose (RfD) and carcinogenic potency slope factor (CPS) were used for health risks evaluation as provided by USEPA (USEPA, 2011). The cancer slope factors for ingested arsenic are 1.5. RfD is the reference

dose (As= 0.003, µg g⁻¹day⁻¹) (USEPA, 2011) that is likely to be without appreciable risk of deleterious effects during a lifetime (averaging time of 365 day⁻¹yr for 70 yr).

Acceptable Risk Distribution:

The lower end of the range of acceptable risk distribution was defined by a single constraint on the 95th percentile of risk distribution that was equal or lower than 10⁻⁶ for carcinogens and was up to 10⁻⁴ in some circumstance. The health protection standard of lifetime risk for HI was 1 (USEPA, 2011).

Statistical Analyses:

All values from chemical analyses were presented as mean ± SD. Data obtained from the experiment were subjected to one-way analysis of variance (ANOVA) test using the Statistical Package for the Social Sciences.

Results

Different levels of arsenic concentration have been observed in water, surface sediments and fish samples and the same are presented in Table 2. The results indicated that presence of As in fish tissues (muscle) was reasonably lower than it was present in surface sediments and water. Muscular concentration of As bioaccumulation in fishes in district Ballia was found higher (0.017±0.009 -- 5.46±1.95 µg/kg) than it was present in Unnao (0.002±0.001--1.75±0.39 µg/kg). The level of muscular As was high (4.33±1.21-- 5.46±1.95 µg/kg) in *Oreochromis niloticus* caught from lakes in Ballia. However, the As level in the same species was lower (1.428±0.32 --1.75±0.59 µg/ kg) in Unnao. The level of muscular As in *Clarias gariepinus* was much elevated and it was 2.04 ±1.16 to

Table 1: Parameters in used in the health risk estimations

Use of symbol	Description	Unit	Value	References
IRs	Ingestion rate of sediment	Kg dw exposure day ⁻¹ (dw=dry weight)	10 ⁻³ for child; 0.35×10 ⁻³ for adult	Harma <i>et al.</i> , 1999
IRf	Ingestion rate of fish	kgfw day ⁻¹ (fw= flesh weight)	0.015 for child; 0.055 for adult	Heijna and Hof, 1993
IRw	Ingestion rate of surface water	Liter exposure day ⁻¹	50 × 10 ⁻³ for child and adult	Van Wijnen, 1982
AF	Absorption factor	Unit less	1 for child and adult	Harma <i>et al.</i> , 1999
ASs	Dermal absorption rate	L hr ⁻¹	0.01 for child; 0.005 for adult	Hawley, 1985
SAs	Dermal surface area for sediment exposure	m ²	0.17 for child; 0.28 for adult	Hawley, 1985
SAw	Dermal surface area for exposure in surface water	m ²	0.95 for child 1.80 for adult	Veerkamp and Ten Berge , 1990
AD	Dermal adherence rate for sediment	mg ⁻¹ cm ²	0.51 for child 3.75 for adult	Veerkamp and Ten Berge , 1990
Mf	Matrix factor	Unit less	0.15 for child and adult	Hawley,1985
EF	Exposure frequency	Days ⁻¹ 365 days	30 for child and adult	Harma <i>et al.</i> , 1999
BW	Body weight	Kg	15 for child 70 for adult	Veerkamp and Ten Berge , 1990
CMW	Suspended matter content of surface water	kg l ⁻¹	30 × 10 ⁻⁶ for child and adult	Riza,1989
EDs	Exposure duration to sediment	hr day ⁻¹	8 for child and adult	Hawley, 1985
EDw	Exposure duration in surface water	hr day ⁻¹	2 for child 1 for adult	Harma <i>et al.</i> , 1999
Fl	Fraction contaminated	Unit less	0.5 for child and adult	Fiore <i>et al.</i> , 1989
Ow	Octanol/ water partition coefficient	L Kg ⁻¹	1 for child and adult	Allison, 2005
SF	Carcinogenic potency slop,	Mg ⁻¹ g ⁻¹ day	1.5 for child and adult	USEPA, 2011

Table 2: Arsenic levels in fish muscle, surface sediment and lake water of Ballia district

Locations	Species	Muscle ($\mu\text{g kg}^{-1}$)	Lake Surface Sediment ($\mu\text{g kg}^{-1}$)	Lake Water ($\mu\text{g l}^{-1}$)
Surha lake	<i>Clarias gariepinus</i>	2.26 $\pm$ 1.1	2579.48 $\pm$ 147.81	31.39 $\pm$ 3.12
	<i>Oreochromis niloticus</i>	5.46 $\pm$ 1.95		
	<i>Cyprinus carpio</i>	0.08 $\pm$ 0.024		
Dah lake	<i>Clarias gariepinus</i>	2.27 $\pm$ 1.13	1813.98 $\pm$ 306.54	43.89 $\pm$ 6.54
	<i>Oreochromis niloticus</i>	5.18 $\pm$ 1.33		
	<i>Cyprinus carpio</i>	0.08 $\pm$ 0.062		
Maniyar lake	<i>Clarias gariepinus</i>	2.04 $\pm$ 1.16	1030.87 $\pm$ 397.92	31.89 $\pm$ 8.58
	<i>Oreochromis niloticus</i>	4.3 $\pm$ 1.21		
	<i>Cyprinus carpio</i>	0.017 $\pm$ 0.009		
Nawabganj	<i>Clarias gariepinus</i>	0.322 $\pm$ 0.12	1026.04 $\pm$ 192.52	14.92 $\pm$ 2.67
	<i>Oreochromis niloticus</i>	1.750 $\pm$ 0.39		
	<i>Cyprinus carpio</i>	0.004 $\pm$ 0.001		
Ajgaine	<i>Clarias gariepinus</i>	0.394 $\pm$ 0.18	997.68 $\pm$ 101.21	22.21 $\pm$ 4.4
	<i>Oreochromis niloticus</i>	1.605 $\pm$ 0.42		
	<i>Cyprinus carpio</i>	0.003 $\pm$ 0.001		
Asiwan	<i>Clarias gariepinus</i>	0.385 $\pm$ 0.22	635.61 $\pm$ 302.54	10.78 $\pm$ 2.32
	<i>Oreochromis niloticus</i>	1.428 $\pm$ 0.32		
	<i>Cyprinus carpio</i>	0.002 $\pm$ 0.001		

2.27 $\pm$ 1.13 $\mu\text{g/kg}$ in Ballia district and 0.32 $\pm$ 0.12 to 0.394 $\pm$ 0.18 $\mu\text{g/kg}$ in Unnao as compared to its level in *Cyprinus carpio* (Table 2). The highest As concentration in sediment samples was found 2579.48 $\pm$ 147.81 $\mu\text{g/kg}$ in Suraha lake followed by, 1813.98 $\pm$ 306.54 $\mu\text{g/kg}$ in Dah lake and 1030.87 $\pm$ 397.92 $\mu\text{g/kg}$ in Maniyar lake in Ballia district. The highest value of arsenic (2579.48 $\pm$ 147.81 $\mu\text{g/kg}$) in surface sediments was present in Surha Lake

in Ballia as compared to other sampling sites. The As level in surface sediment at three sampling stations in Unnao district were 1026.04 $\pm$ 192.52 $\mu\text{g/kg}$ in Nawabganj, 997.68 $\pm$ 101.21 $\mu\text{g/kg}$ in Ajgain and 635.61 $\pm$ 302.54 $\mu\text{g kg}^{-1}$ in Asiwan, respectively (Table 2). The water quality constituents of surface water, reference freshwater values of the lake and other global published values have been considered. In water samples the

Table 3: Carcinogenic risk and average exposure levels ($\mu\text{g kg}^{-1}\text{day}^{-1}$) of Arsenic

Exposure routes	Ballia		Unnao	
	Adult	Child	Adult	Child
Ingestion of sediment	0.27×10^{-3}	3.61×10^{-3}	0.13×10^{-3}	1.77×10^{-3}
Ingestion of surface water	0.87×10^{-3}	4.07×10^{-3}	0.34×10^{-3}	1.59×10^{-3}
Ingestion of suspended matter	1.9×10^{-6}	4.3×10^{-6}	1.8×10^{-6}	3.8×10^{-6}
Dermal contact with sediment	1.6×10^{-4}	3.7×10^{-4}	0.7×10^{-4}	1.7×10^{-3}
Dermal contact with surface water	0.3×10^{-3}	1.2×10^{-3}	0.1×10^{-3}	0.2×10^{-3}
Ingestion of fish	0.7×10^{-6}	0.3×10^{-5}	0.9×10^{-6}	0.7×10^{-6}
Total	0.0016	0.0092	0.0006	0.005
Hazard indices (HI)	3.6		1.8	

concentration of the arsenic was 43.89 ± 6.54 $\mu\text{g/l}$ to 31.39 ± 3.12 $\mu\text{g/l}$ in Ballia and 22.21 ± 4.4 $\mu\text{g/l}$ to 10.78 ± 2.32 $\mu\text{g/l}$ in Unnao district. The concentrations of arsenic in samples from all sites were found above the detection limits (0.002 $\mu\text{g/l}$). The adsorption and accumulation of metals by suspended solids and the concentration of metals in surface sediments were found higher than in the water column below the surface sediments where it ranged from 635.61 ± 302.54 to 1026.04 ± 192.52 $\mu\text{g/kg}$ in Unnao and 1030.87 ± 397.92 to 2579.48 ± 147.81 $\mu\text{g/kg}$ in Ballia (Table 2).

The calculated total exposure level for As was observed from 0.0016 $\mu\text{g/kg}$ body weight /day for adult, 0.0092 $\mu\text{g/kg}$ body weight/day for children in Ballia while it was 0.0006 $\mu\text{g/kg}$ body weight/day for adult; 0.005 $\mu\text{g/kg}$ body weight /day for children in Unnao. The combined HI value for As was 3.6 and 1.8 in Ballia and Unnao, respectively. The HI value

for metal was more than 1 under exposure routes (Table 3) which indicated that there might be some concern for adverse health effects. According to Equation 1 to 7, the carcinogenic risks caused by several single factors and the total risks caused by multiple factors have been presented in Table 3. Total exposure through different routes was maximum in children in Ballia district. Total exposure route value also indicated that it was observed maximally in children in both the districts. Arsenic maximally exposed through dermal contact with surface water and it exposed to children at higher level than adults. Arsenic also exposed through the ingestion of fish but exposure level through this route was maximum in adults 0.7×10^{-6} in Ballia and 0.9×10^{-6} in Unnao rather than children in both districts (Table 3). The risk due to ingestion of fish was, 0.7×10^{-7} for children and 0.6×10^{-7} for adults for *Cyprinus carpio*, 0.1×10^{-4} for children and 0.1×10^{-4} for adults for *Oreochromis niloticus* in Unnao

district and 0.9×10^{-6} for children and 0.8×10^{-6} for adult for *Clarias gariepinus*. The calculated risk range through ingestion of fish was 0.2×10^{-8} for children and 0.2×10^{-8} for adults in case of *Cyprinus carpio*; 0.7×10^{-5} for children and 0.5×10^{-6} for adults, in case of *Oreochromis niloticus* and also for *Clarias gariepinus* in Ballia district. The calculated carcinogenic risk in Ballia was 6.24×10^{-3} and 1.39×10^{-3} in adults and children, respectively while it was 0.7×10^{-3} for adults and 0.1×10^{-3} for children in Unnao district. Comparing the carcinogenic values with guideline values of 10^{-6} – 10^{-4} given in USEPA (2011), it was found that the risk through fish consumption from lakes of Ballia as well as in Unnao were although not alarming at present, might pose carcinogenic risk of As exposure in future.

Discussion

Analyses of 54 samples collected from 6 locations in the state of Uttar Pradesh revealed that values of arsenic varied in different locations. This study revealed that the surface water of the Ballia district showed higher degree of As contamination which is in conformity with the earlier report (Sankararamakrishnan *et al.*, 2015). Analysis of arsenic in fish muscle showed species wise bio-concentration of the arsenic level. Sediment arsenic level was high particularly in Ballia district of Uttar Pradesh. Arsenic is toxic to both plant and animals and inorganic arsenicals are proven carcinogens in humans (Shrivastava *et al.*, 2015). A wide range of arsenic toxicity has been determined that depends on arsenic speciation (Sharma and Sohn 2009; Shrivastava *et al.*, 2015). Generally inorganic arsenic species are more toxic than organic forms to living organisms, including humans and other animals (Sharma and Sohn,

2009; Shrivastava *et al.*, 2015). Results of samples analyzed in different lake showed a mean level of surface sediment arsenic of 1808.44 $\mu\text{g/kg}$ in Ballia district and 886.44 $\mu\text{g/kg}$ in Unnao district, which could be due to use of arsenic herbicide. Maximum value of arsenic was found in *Oreochromis niloticus* which is currently understood as As hyper-accumulator species. An extensive survey of cooked Canadian foods elucidated an increase in total arsenic levels of cooked relative to uncooked food such as marine and freshwater fish. Similarly, total arsenic content of fresh sea bass fillets increased greatly upon microwave oven cooking of the fillets. The decrease in moisture content during cooking was suggested as the reason for increase in arsenic content (Sharma and Sohn, 2009; Kumarathilaka, 2019). There are very few reports on the wildlife poisoning by arsenic, however, Eisler (1988) reported it for the first time showing that catfish in the reservoir water contained 5 and 12 mg kg^{-1} of As which is relatively persistent in the aquatic environment (Bears *et al.*, 2006). Tanner and Clayton (1990) reported elevated concentrations of arsenic in macrophytes where it was 193–1200 mg kg^{-1} dry weight and surfacial sediments 540–780 mg/kg dry weight in Lake Rotoroa, New Zealand. 24 years after an application of sodium arsenite herbicide; arsenic levels in a nearby reference lake (lake Rotokauri) was found $<20 \text{ mg/kg}$ dry weight in macrophytes and 16.5–40 mg/kg dry weight in surface sediments. Variation of arsenic, under the influence of water sand and fishes in lakes has been found and it differed between the lakes of the two districts (Ballia and Unnao). Arsenic in Ballia was greater than that in Unnao which correlates between various arsenic forms,

supporting the possibility that arsenic partition in suspended particulates in lakes was driven mainly by biotic factor (Sankar *et al.*, 2014). Arsenic mobility is greatly influenced by the concentration and nature of adsorbent surfaces and the adsorption process itself which is affected by many factors including but not limited to pH. Under environmentally relevant conditions, dissolved organic matter tends to compete with dissolved arsenic species for active sites. As a result, the calculated risk that three persons per capita (1000 persons) would be in danger of skin diseases in the Ballia district and one person would be in skin diseases in the Unnao district has been reported (Tripathi, 2008).

Risk assessment for As contaminants was calculated as per the processes and the probability of occurrence of an event and the probable magnitude of adverse health effects over a specified time period (Kolluru *et al.*, 1996). Human health risk assessment was carried out in three stages: (1) hazard identification, (2) exposure assessment and (3) risk characterization (Yongli *et al.*, 2011). Risk-specific doses have been derived from the slope factor or unit risk to estimate the dose associated with a specific risk level (USEPA, 2005). Carcinogenic risks have been estimated as the incremental probability of an individual developing cancer over a lifetime as a result of exposure to a potential carcinogen (Kar *et al.*, 2011). If a site has multiple carcinogenic contaminants, cancer risks for each carcinogen and each exposure route are added (assuming additivity of effects) and compared with the accepted risk (Liu *et al.*, 2010). Risk assessment is the process of obtaining quantitative or qualitative measures

of risk levels (USEPA, 1998; Singh *et al.*, 2012). Risk assessments have traditionally focused on quantifying the probability of negative consequences from one or a number of identified or unknown sources. Sample variance and standard deviations were high, possibly due to wide variations in the levels of As in lake water. The surface water of the region showed elevated levels of arsenic, which could be influenced by the arsenic mix herbicides. Health risks from long-term ingestion of arsenic concentrations was found in the range of 10–100 $\mu\text{g l}^{-1}$, and this ecological study was the first step in suggesting that moderately elevated arsenic concentrations in fish muscles are associated with mortality from cerebrovascular diseases, diabetes mellitus and kidney diseases by consumption of the fish in As prone areas and the possibilities are supported by the earlier report of Jaymie *et al.* (2007) and Oguri *et al.* (2014). The potential health risks associated with consumption of arsenic-contaminated fish and also from other routes are reported for arsenicosis, skin cancer, and other arsenic-related diagnoses concentrations (WHO, 2004; Krishna *et al.*, 2009; Majumdar *et al.*, 2009; Roychowdhury *et al.*, 2003; Uchino *et al.*, 2006). Other researchers have performed risk assessments similar to that reported in Bangladesh and other countries, reporting elevated cancer risks (Chowdhury, 2010; Chen *et al.*, 2005).

The United States Environmental Protection Agency (USEPA), considering hyperpigmentation, keratosis and possible vascular complications (blackfoot disease) as the critical effects of As, accepted the value of 0.3 $\mu\text{g/kg/day}$ as the reference dose in the case of human chronic exposure (Lyon, 1987).

There is sufficient evidence that arsenic compounds are skin and lung carcinogens in humans. In our findings the calculated risk values through the ingestion of fish was maximum in Unnao i.e. it was 0.9×10^{-6} $\mu\text{g}/\text{kg}/\text{day}$ in adult and 0.7×10^{-6} $\mu\text{g}/\text{kg}/\text{day}$ in children and minimum in Ballia where it was 0.7×10^{-6} $\mu\text{g}/\text{kg}/\text{day}$ in adult and 0.3×10^{-5} $\mu\text{g}/\text{kg}/\text{day}$ in children but overall exposure through different routes was higher in Ballia. In both the districts (Ballia and Unnao) the calculated risk value was more than 0.3 $\mu\text{g}/\text{kg}/\text{day}$ as per reference dose reported by USEPA which can create carcinogenic risk in human beings.

Arsenic is released into the environment through natural processes such as weathering, and may circulate in natural ecosystems for long time. A well-recognized arsenic problem of water in Uttar Pradesh was first reported in the late 1980s. Comparatively higher concentration of arsenic accumulation was observed in *Oreochromis niloticus* in this study; however lower concentrations of As accumulation has been reported by other workers (Bhupander and Mukherjee, 2011). The observed concentration of arsenic in muscle tissue of fishes from Ballia was higher than fishes from Unnao. The arsenic forms are more hazardous to humans than the organic ones, which are generally of low toxicity. In fact, several days after its ingestion it gets excreted unchanged from the human body. Both organic and inorganic forms of arsenic occur in food. It has been established that fish can accumulate sizeable quantities of arsenic from their environment (Kar *et al.*, 2011). The daily intake of arsenic by humans reflects generally the quantities of Rfd in the diet. As a result, there is no safe level of arsenic intake from food and water. There is a linear dose-

response relationship between arsenic intake and health hazards down to very low levels of intake. Arsenic causes serious skin lesions and various forms of cancer and it can cause deaths from a wide range of other serious diseases (Meharg, 2005). Symptoms may not appear for 2 to 10 years from the start of chronic exposure and they may also appear long after exposure ceases (Jarup, 2003). Therefore, it is important to generate information on the arsenic and efforts need to be made to minimize arsenic intake from all sources as soon as possible. The results of this study revealed that consuming fish from lakes of Uttar Pradesh, where As is present in water and sediment may not be harmful to consumers because observed values of arsenic were below the permissible limits issued by FAO/WHO.

Conclusion

Assessing the bio-concentration as well as the bio-magnification potential of arsenic in fish is an important issue for the environmental and human health risk containment. Accumulation of As among the fish *Clarias gariepinus*, *Oreochromis niloticus* and *Cyprinus carpio* reflected differences in their bioaccumulation capabilities and further translocation to fish muscle. Hazard index of As suggested that contamination in most of the fish species had potential for human health risk due to consumption of edible part of the fish. Thus, regular monitoring of As contamination in the fish species especially cultivated in contaminated water is necessary and consumption of such contaminated fish should be avoided in order to reduce the health risk.

Acknowledgement

Authors are thankful to the Uttar Pradesh Pollution Control Board, India for their help in

the analysis of samples.

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