Agricultural Research & Technology
Open Access Journal
ISSN: 2471-6774

Research Article
Volume 10 Issue 3 - August 2017
DOI: 10.19080/ARTOAJ.2017.10.555788

Agri Res & Tech: Open Access J

Study of Chattri Dam for Selected Metal Concentrations in Water, Sediments and Fish Species

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Submission: February 02, 2017; **Published:** August 24, 2017

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Abstract

The research was conducted on Chattri dam in Haripur district. The study was aimed to find metal (Zn, Cu, Fe, Mn, Cd and Ni) concentrations in water, sediment and fish tissues (muscles, gills and liver) with an idea to know about the possible metal hazard and potential health risk assessment. 24 samples of water, 16 sediment samples and 3 samples of fish species were selected for analysis. Water samples were directly analyzed by atomic absorption spectrometer while sediment and fish samples were extracted and then aspirated to atomic absorption spectrometer (Model AAS 700 Acetylene Flame). Results showed the concentration of metals in water samples were within the permissible limit when compare with international guidelines in water (World Health Organization) [1].

Higher concentrations of metals in some samples were reported collected after rainy season. In sediments, average values of metals were investigated below the range in order of Fe>Zn>Mn>Ni>Cu>Cd and Fe>Zn>Mn>Ni>Cu>Cd at upstream and downstream respectively. Enrichment factor value of Cu (1.0) was found minor and linked with anthropogenic sources, Zinc (9.7) showed moderately severe contamination while Cd (0.24), Ni (0.80), Fe (0.07) were within limits but the concentration was toward increase. In Cirrhinus mrigala, Hypophthalmic hthysmolitrix and Cteno pharyngo donidella, concentration of metals were observed below the USEPA limit. It is indicated that there is no metal with THQ>1. But there is a possibility of harmful impacts of sediments on fish species in future, which will contaminate food chain. It is therefore, recommended to monitor the dam for pollution load, tune agriculture activities and initiate reforestation activities in surrounding.

Keywords: Chattri dam; Contamination; Enrichment factor; Health quotient and risk assessment

Abbreviations: NGOs: Non Government Organizations; THQ: Target Hazard Quotient; USEPA: United States Environmental Protection Agency; EF: Enrichment Factor

Introduction

Water scarcity becomes a worldwide problem. In Pakistan, water is scarce in arid and semiarid region. Small dams are constructed to store water for dry season to overcome water scarcity [2]. The concept of small dam construction increasing throughout the world, major purpose for construction of dam is irrigation. In rural areas of Pakistan (almost 64% of total population) where livelihood directly or indirectly depends upon the agricultural activities, available water is not sufficient (Agricultural Census [3], Pakistan Report). Some Non Government Organizations (NGOs) and government agencies constructed many dams as an artificial source of water to reduce water shortage problems [2].Dams receive suspended load and sediments from nearby mountain and agriculture fields due to erosion and weathering. Sometime sediment load contributes toward metals contamination in reservoirs [4]. More than 90% of heavy metal contamination has been associated with suspended solids and sediments. Sediments have a high nutrient content, accelerate various microbial activities and there is a possibility to release metals and its accumulation in food chain [5]. In China, Rauf [6] investigated metal contamination in sediments. Highest concentrations of Cu, Zn and Cr were recorded in Fo-Tan tributaries, while Al and Cd were found in the Shing Mun River. Metal pollution in sediment of reservoir has also been investigated in the Kurang Nallah, Feeding tributary of the Rawal Lake, Pakistan [5,6].

Presence of suspended solids is one of the threats to aquatic fauna worldwide in aquatic ecosystem, turbidity and sediments are common pollution indicators. Literature indicated the contamination of metals in muscle and liver tissues of fishes in Pakistan [7-10]. Accumulation of higher level of these metals in an environment is toxic to aquatic as well as terrestrial life [11]. For human, toxic effects include headache, hypertension, irritability, abdominal pain, nerve damages, liver and kidney problems, anemia, intellectual disabilities and carcinogenesis [12].

Various other sources of metal pollution have been identified due to rapid increase in population, unplanned human settlements, domestic and recreational activities in a catchment area of a reservoir [5]. Agriculture activities like application of various agro-chemicals within a catchment area of a dam contribute to higher metal concentration [13]. Geology of a catchment area of a reservoir has got role in quality and quantity of sediment load and metal contents. Rocks along the spring contribute metal contamination in dams. The literature revealed that excessive metals enter in water through spring would cause health risk for both human and aquatic life [11]. Health risk assessment commonly used for determination of potential health hazard related to human activities. For determination of potential health risk due to metals, two methods are commonly use that are carcinogenic and non-carcinogenic method [5]. Non-cancer risk assessment included Target Hazard Quotient (THQ) as adopted by United States Environmental Protection Agency (USEPA) [5,14].

Enrichment factor is being used to differentiate the source of pollution either by natural or manmade means. Enrichment factor is a method commonly used to compare the concentration of metal in sediments with pre-civilization background levels to present day metal concentration with their concentrations in standard earth materials such as average shale [15]. Risk related to human from metal contaminated foods, actual dietary intakes of metals should be estimated and compared with oral toxicity reference dose [14]. The estimation of actual intake of metals is essential to determine effect on humans by frequent ingestion of particular pollutants. The target hazard quotient (THQ) was developed by the United States Environmental Protection Agency (USEPA) for estimation of potential health risks associated with long-term exposure to chemical contaminants [16,17].

Chattri dam is located in Haripur district (Khyber Pakhtunkhwa) has a possibility for metal contamination. As besides irrigation, the dam is being used for fish farming and animal watering. Concentration of metals in water and sediments affect the fish species. Fish is a part of aquatic food chain so there is a risk potential of human. Therefore, this study was aimed to analyze sediment, water and fish for various metals and to assess the level of metal contamination by using enrichment factor (EF). Possible potential health risk assessment was made by using target health quotient (THQ).

Materials and Methods

Study area

The study was conducted on Chattri Dam (33.94414 N, 73.030634 E) located in district Haripur, Khyber Pakhtunkhwa (Pakistan). The Dam is located about 800m above the sea level and was constructed in 1967 by blocking natural spring coming from mountains. Dam is a source of water for irrigation, fish farming and provides opportunities for recreation [18]. The catchment area of Chattri Dam is 6.68km2. Maximum height of the dam is 85 feet, crest length 530 feet and throw back 560m. Fish species in the Dam are Tor *putitora* (Mahseer), *Cirrhinus mrigala* (Mori), *Catlacatla* (Thela fish), *Hypophthalmic hthysmolitrix* (silver carp), *Cteno pharyngo donidella* (Grass Carp), *Labeorohita* (Rohu), and *Puntiuschola* (Chiddu).

Methodology

For determination of water quality of Chattri Dam, 24 composite water samples were collected over a year (January to December 2012) twice a month. Water samples were analyzed in laboratory for concentrations of selected metals (Zn, Cu, Fe, Mn, Cd, and Ni) by using atomic absorption spectrometer Model AAS 700 (Acetylene Flame), Detection limits for Cd, Cu, Zn, Fe, Ni and Mn were 0.8, 1.5, 1.5, 5, 6 and 1.5 ppb respectively. Method adopted according to the standard methods for the examination of water and waste water analysis [19]. Total of 16 sediment samples were collected from upstream and downstream locations in dry season (May, June, December, and January in 2012). Sediments were then analyzed in laboratory for determination of metals (Zn, Cu, Fe, Mn, Cd, and Ni) by microwave aqua-regia digestion method [20]. In this method, 1 gram of each sample was digested with 15ml of aqua regia (HCl, HNO3 and HClO4 with ratio of 3:1:1) and flask were covered and allowed to sit overnight. Samples were placed inside digester at 120 °C until vapor and sample inside the flask turned clear. Samples were then cooled at room temperature, filtered, diluted with distilled water up to 50ml and were aspirated into atomic absorption for analysis. Model AAS 700 (Acetylene Flame), Detection limits for Cd, Cu, Zn, Fe, Ni and Mn were 0.8, 1.5, 1.5, 5, 6 and 1.5ppb respectively [20].

Three frequently consumed fish species; *Cirrhinus mrigala* (Mori), *Hypophthalmic hthysmolitrix* (Silver Carp) and *Cteno pharyngo donidella* (Grass Carp) were collected from dam for analysis. Fish species were sampled with help of fisherman by using fishing net. The organs (muscles, gills and liver) were digested with aqua-regia on digestion block. In brief, 1 gram of each organ was digested with 15ml of aqua-regia (HCl, HNO3 and HClO4 with ratio of 3:1:1) and flask were covered and allowed to sit overnight to dissolve tissue completely. Samples were placed in digester at 120 °C until vapor and sample inside the flask turned clear. Samples were cooled at room temperature, filtered and diluted to 50ml. Finally samples were subjected to

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atomic absorption spectrophotometer for analysis of Cd, Cu, Zn, Fe, Ni and Mn, Detection limits were 0.8, 1.5, 1.5, 5, 6 and 1.5ppb respectively [20].

Enrichment factor (EF)

Source and extent of metal contamination either by natural sources or anthropogenic sources in the Chattri Dam was determined by metal enrichment factor to compare metal concentrations in sediments with respect to reference value of elements. EF was calculated with the following Equation used by Zahra et al. [5].

$$EF = \frac{Cx / CMn \left(sample\right)}{CX / CMn \left(refrence\right)}$$ ....Equation (1)

Where, is the ratio of concentration of concern metal to that of in sediment sample (mg kg-1) while is the same ratio of unpolluted refrence sample. Manganese ( ) was used as a reference element to calculate anthropogenic metal enrichments. World's average concentrations of unpolluted metals (Zn, Cu, Fe, Mn, Cd, and Ni) were used as reference values [5]. Based on EF values, sediments were categorized into different classes. EF <1 natural, EF 1-3 minor, anthropogenic enrichment, EF 3-5 moderate, and EF value 5-10 moderately severe enrichment and EF 10-25 severe contamination, EF 25-50 very severe >50 extremely severe [21].

Health risk assessment (THQ)

For non-carcinogenic health effects, hazard quotient (THQ) was calculated as risk by the equation given by Iwegbue [17] & Akoto et al. [22].

$$THQ = \frac{C \times FI \times EF \times EP \times 10-3}{RFD \times BW \times AT}$$ ....Equation (2)

Where (Concentration of metals mg kg-1), (average food intake rate g/day), exposure frequency 365 d/year), (exposure period 70 years), (body weight 70 kg) and (average life span (365 days/year × number of exposure years) [17].

Table 1: Metals of Chattri Dam in Water (mg/l), Sediments (mg/kg) and Enrichment factor (mg/kg).

		Zn	Cu	Fe	Mn	Cd	Ni
Summer Dams water	Max	0.9	0.02	1.31	0.01	0.002	0.04
	Minimum	0.03	0.001	0.03	0.007	0.001	0.01
	Average	0.21	0.03	0.54	0.02	0.002	0.031
Winter Dams water	Max	1.2	0.05	1.9	0.06	0.003	0.034
	Minimum	0.09	0.01	0.9	0.001	0	0.01
	Average	0. 178	0.04	1	0.03	0.002	0.029
	WHO	3	2	ND	ND	0.003	0.07
Upstream sediments	Max	14.1	0.63	46.3	13.6	0.9	0.91
	Minimum	17.9	0.86	54	15.8	0.13	1
	Average	16.9	0.72	52.4	14.8	0.1	1.5
Downstream sediments	Max	11.1	0.3	40	9.8	0.2	0.6
	Minimum	17.9	0.7	56.3	15.8	1.3	1.8
	Average	15.1	0.54	48.4	11.2	0.43	1.3
	Pheiffer,2014	123	16	ND	460	0.57	18
EF values	Max	10.2	1.08	0.07	1.1	0.27	0.82
	Minimum	7.31	0.91	0.06	0.9	0.22	0. 79
	Average	9.7	1	0.07	1	0.24	0.8

Results and Discussion

The concentrations of Zinc (Zn), Copper (Cu), Iron (Fe), Manganese (Mn), Cadmium (Cd) and Nickel (Ni) in water samples were observed within normal range when compared with guidelines given by WHO (Table 1). The trend was recorded as Fe>Zn>Cu> Ni>Mn>Cd in summer season while in winter the order of metals was Fe>Zn>Cu>Mn>Ni>Cd. The results suggested that metals concentration in summer and winter season was almost same. Higher concentrations were observed in samples collected in the rainy period. This is in agreement with the study, Zahra, et al. [5] suggested that concentration of metals may be due to dilution during rainfall which mixes polluted and unpolluted water and decrease the heavy metal concentrations in post-rainy season.

Overall Fe showed higher concentrations over other metals. Perez et al. [23] reported higher concentrations of Fe in water and sediments of the Alzate Reservoir because Lerma River drains terrigenous sedimentary formation, rich in Fe-oxyhydroxides. Our findings go in favor of Perez et al. [23]. In our study the metals contamination is resulted from both natural and anthropogenic sources such as erosion and discharge of municipal waste. This is in support with the study of Perveen et al. [24] which reported that metals contamination in water caused by both natural and human activities. In future, continuous pollution of such water over longer period of time may cause accumulation of Cd up to toxic levels for living biota.

In sediments, concentrations of metals were found below the range when compared with International Sediment Quality

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guidelines (Table 1). The order of metals was Fe>Zn>Mn>Ni>Cu>Cd at upstream and Fe>Zn>Mn>Ni>Cu>Cd at downstream. Higher concentration of metals at upstream was recorded. However, anthropogenic activities like sewage discharge municipal waste and agricultural activities in the surrounding village were suggested to attribute higher concentration of metals at upstream. Other sites were less contaminated while decline was observed at downstream. This finding supports Iqbal et al. [25] study of Rawal lake, Pakistan. Sediments collected from upstream showed high concentration of all metals which are receptor sites for domestic waste, agricultural runoff and entrance of natural spring from mountains [25].

Fe was found high in sediments as compared with other elements. Relatively higher concentration of Fe was also recorded in the sediments of Rawal Lake, Pakistan [25]. However, presence of metals in sediments is associated with nature of source from where it enters into reservoirs and anthropogenic activities within surrounding areas i.e. runoff from cropland. For example, cadmium is found as impurities in phosphate fertilizer and is a possible source of the sediment coming from the surrounding agriculture field [13]. Similarly, as farmers are using natural fertilizer and is a big source of Ni and Cd as people disposed off re-chargeable batteries along with the solid waste used in compost preparation. The possible sources of Cu and Zn are sewage water used for irrigation in the surroundings coming from the compost [26].

In comparison, metal contamination in water and sediments clearly indicated that sediments were more contaminated as compared to water. Higher concentration of metals (Cu, Mn, Zn, Cr, Ni) in sediments, with comparison of water may be as a result of adsorption to sediment particles [6]. Concentration of selected metals in sediments increased many folds as compare to the Dam's water. Water quality in Dam was relatively better as compare to sediments.

EF values were compared with categories given by Pheiffer et al. [21]. Zinc, EF value 9.7 showed moderately severe enrichment, Copper, EF value 1, showed minor anthropogenic enrichment at downstream and other metals showed no enrichment (Table 1). Metals enrichment values showed that accumulation of metals such as Cd, Ni and Fe were due to the natural source (erosion) while Cu showed anthropogenic sources of contamination (municipal sewage discharge) according to categories [21].

In selected fish species, Concentration of selected metals was observed lower than the adverse level (Table 2). Metals concentration observed in the Cirrhinus mrigala in order of Fe>Ni>Zn>Cu>Cd>Mn, Hypophthalmic hthysmolitrix Fe>Ni>Cu>Cd>Mn>Zn and Cteno pharyngo donidella Fe>Ni>Cu>Zn>Mn>Cd. The level of metal accumulation varied among tissues. Among selected organs (muscles, gills and liver), liver is observed contaminated as compare to other organs. A higher concentration of metals in the liver is in the agreement with the finding of Khan, et al. [9] from Shah Alam River Pakistan. Khan reported that the muscles were not considered as an active tissue for accumulation of metals while higher concentration of metals in liver is attributed with storing ability [9]. Cirrhinus mrigala, Hypophthalmic hthysmolitrix and Cteno pharyngo donidella, average values of Fe and Cu were observed high as compare to other selected metals but considered as negligible with the comparison of USEPA [27]. Thus high concentration of Fe is considered as safe due to its beneficial effects for organism and plays a vital role in hemoglobin formation. Presences of metals are indicator of extent of pollution of the dam. Metals are not bio-degradable, stay in tissues of fishes for long time and enter into food chain by consumption [13].

Table 2: Metals in fishes tissues (mg kg^{-1}) of Chattri Dam.

		Zn	Cu	Fe	Mn	Cd	Ni
Cirrhinus Mrigala	Mussels	0.06	0.42	0.65	0.04	0.02	0.31
	Gills	0.09	0.11	0.91	0.06	0.09	0.12
	Liver	0.9	0.5	0.98	0.09	0.81	1.13
	Average	0.35	0.34	0.85	0.07	0.31	0.52
	THQ value	0.0006	0.004	0.005	0.002	0.15	0.012
Hypophthalmic Hthysmolitrix	Mussels	0.08	0.34	0.39	0.09	0.04	0.29
	Gills	0.02	0.02	0.87	0.12	0.03	0.07
	Liver	0.007	0.78	1.63	1.13	0.54	0.91
	Average	0.04	0.38	0.96	0.15	0.2	0.49
	THQ value	0.0005	0.004	0.005	0.005	0.09	0.012
Cteno pharyngo Donidella	Mussels	0.03	0.61	0.51	0.06	0.05	0.24
	Gills	0.04	0.07	0.85	0.07	0.1	0.09
	Liver	0.03	0.49	0.93	0.91	0.61	0.86
	Average	0.3	0.39	0.76	0.29	0.25	0.4
	THQ value	0.0007	0.004	0.004	0.01	0.29	0.009
Average	0.14	0.37	0.86	0.29	0.25	0.45	

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Daily Intake	0.005	0.012	0.06	0.09	0.0008	0.011	
TDI (USEPA, 2009)	0.3	0.04	0.08	0.14	0.001	0.02	

Results of health risk assessment considered in this study are presented in Table 2. Results indicated that there is no metal with all metals THQ>1. This level of exposure will not cause any harmful effect in humans [28]. So, no risk was associated by consumption of these fishes from the Chattri dam. Exposure of metals was within limits but Cd showed a potential risk for future.

From human health point of view Cu, Zn and Cd values were found safe and less than tolerable daily dietary intake limit of USEPA [27] given in Table 2. It is concluded that concentrations of metals in all parts of fish species were within acceptable levels. Aquatic environment accumulate metals nearly 100 times as compare to concentration of metals in water. Therefore metals are of high concern [29]. Although metals contamination in the Dam are not alarming but their accumulation can be dangerous in future.

Conclusion and Recommendation

Enrichment factor showed that value of Cu was found minor and linked with anthropogenic sources, Zinc showed moderately severe contamination while Cd, Ni, Fe and Mn were within limits but the concentration was toward increase. The dam under study can be considered safe in terms of Target Hazard Quotient (THQ) for all studied metals. To overcome on the increasing level of different metals, periodic monitoring is recommended [30-32]

Acknowledgement

The authors are grateful to the Department of Environmental Sciences, and centralized resource laboratory (CRL) University of Peshawar, Pakistan for analysis.

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DOI: 10.19080/ARTOAJ.2017.10.555788

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