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Advances in Applied Science Research, 2016, 7(5): 34-45

ISSN: 0976-8610
CODEN (USA): AASRFC

Assessment of seven heavy metals in water of the river Ghaghara, a major tributary of the Ganga in Northern India

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ABSTRACT

Water quality of the River Ghaghara has been examined in special reference to seven heavy metals namely cobalt (Co), copper (Cu), chromium (Cr), nickel (Ni), cadmium (Cd), zinc (Zn), lead (Pb), and on seasonal basis for two consecutive years 2013-14 and 2014-15. Samples were collected from five stations namely Katernia ghat, Colonelganj, Ayodhya, Dohrighat, and Chhapra. In the water of the river maximum value of Co, Cu,Cr, Ni, Cd, Zn, Pb and was recorded as 0.027, 0.032, 0.007, 0.018, 0.043, 0.031and 0.019 mg/l respectively whereas the minimum value was recorded 0.005, 0.016, 0.001,0.005, 0.003, 0.013, 0.005 mg/l respectively at different sites. Most of the above values were found either below or closed the permissible limit set by World Health Organization (WHO) except Cd. Cadmium concentration exceeded the WHO limit. Cd contamination in the river water of this area is a serious concern for human health. Correlation analysis among all considered heavy metals shows positive correlation with each other in both the years. The data generated may provide useful information to Governmental agencies to control the heavy metal pollution of the river at these urban centers which may even be worst in future scenario. The present experimental data indicates that the pollution level along the river Ghaghara is not very high but the increasing population load in the basin may cause irreparable ecological harm in the long-term well masked by short term economic prosperity

Keywords: Ghaghara River water. Environmental pollution. Heavy metals contamination. Correlation matrix.

INTRODUCTION

Rivers are the major geological agents in tropical and sub-tropical regions. Year by year, rivers transport about 37000 km^3 of water [1] and 13.5 x 109 tonnes of sediments [2] from terrestrial environments to the world oceans. During transportation, water and sediments undergo considerable changes in their physico-chemical properties depending on terrain characteristics and climate of the region through which the river flows [3]. It is now well understood that river transport of particulates, nutrients and minerals plays a major role in maintaining the productivity of the rivers. But, unfortunately, increased human interventions like domestic sewage, industrial effluent, runoff from chemical fertilizers and pesticides used in agriculture within the basin, and large quantities of solid waste, including thousands of animals' carcasses and hundreds of human corpses are dumped in the river every day in recent years have imposed tremendous pressure on the river systems. The scenario is being complicated further by the huge discharge of toxic contaminants from point and non-point sources. All these, in one way or the other, have negatively affected the natural productive capacity of these life support systems of tropics and sub-tropics.

In India, incidence of toxic heavy metal accumulation in fish, oysters, sediments and other components of aquatic ecosystems have been reported regularly [4, 5]. These toxic heavy metals entering in aquatic environment are adsorbed onto particulate matter, although they can form free metal ions and soluble complexes that are available for uptake by biological organisms [6]. Untreated or allegedly treated industrial effluents often contains variable amounts of heavy metals such as arsenic, lead, nickel, cadmium, copper, mercury, zinc and chromium which have the potential to contaminate crops growing under such irrigation [7]. These heavy metals have a marked effect on the aquatic flora and fauna which through bio-magnification enter the food chain and ultimately affect the human beings as well. Heavy metal pollution is an ever increasing problem of aquatic bodies. Weathering of minerals, industrial effluents, atmospheric precipitation and nonpoint discharges are important sources of high heavy metal concentrations in river systems.

To study the water quality of the river Ghaghara with special reference to seven heavy metals, namely Chromium (Cr), Cobalt (Co), Nickel (Ni), Copper (Cu), Zinc (Zn), Cadmium (Cd), and Lead (Pb) were investigated in the present study. The metals selected for investigation were assumed to be both from point and nonpoint sources has been identified in the river Ghaghra. Zn, Cu, Pb and Cd are the most frequently researched heavy metals in bioaccumulation studies [8]. Ni and Cr were considered because they have been found to be in high concentrations in urban runoff due to corrosion-induced release from metal alloys [9, 10].

The present study is an attempt to address certain aspects of the water systems of the rivers river Ghaghara flowing through different districts of Uttar Pradesh and Bihar. The study includes a systematic analysis of heavy metals distribution in water of the river system. The specific objectives of the study are firstly to investigate the current status of the heavy metals availability registered in the water of the river, secondly to assess the seasonal variations in the water quality of the river and to provide scientific basis to understating the environmental problem in the ecosystem context.

Study area

Ghaghara River is one of the most important left bank tributeries of the river Ganga. In the upper reaches, the river Ghaghara is known as the Manchu and Karnali in Nepal. It rises in the Himalayan glaciers near Lampia-pass at an elevation of 4800 meter at latitude 30° 38′N and longitude 80˚ 57′E about 60 km South-West of Mansarowar. After flowing for about 72 km in a south-easterly direction, the river enters Nepal. Ghaghra enters into India at Kotia Ghat near Royal Bardia National Park, Nepal Ganj, where it is known as the river Girwa for about 25 km. A barrage called Girijapuri Barrage has been constructed at the end of the Girwa. Below the barrage the river attains the name of the Ghaghra. The river receives the Mugu Karnali and the Tiha on its left bank. In the reach between Churiaghat and Dhundras, The River is joined by the Seti on its right bank. The river Bheri joins its left bank near Kueghat. After traversing for some length in the plains, the river branches off into several channels downstream of Chisapani. The Kauriala and the Girva are the important tributeries. The Kauriala, before leaving Nepal, receives the Mohan River on its right. The Kauriala and the Girva rejoin at Bharatpur in Bahraich district of Utter Pradesh. Near Gularia the river receives the Sarjuon on its right and furthers downstream the Baheri Sarjuon on its length. The Sarda, most important tributeries of the river Ghaghara joins the Kaurial River at Rampur. After the junction with the Sarda, the river is known as the Ghaghra. River Ghagra continues its journey through Ayodhya where it is known by the name Sarjuon. The River Ghaghra flows in many channels through the district of Gorakhpur, Deoria, Azamgarh, and Ballia. Near Dhuriapar, the Kuwana River joins the Ghaghra. The course of the Ghaghra is confined to a single channel at Dohrighat. The Rapti and the little Gandak join it from the left. After receiving the Jharahi and the Daha, two small streams on its left, the river finally joins the river Ganga few km. downstream of chhapra town in Bihar sub-basin of the River Ghaghara (excluding river Rapti).

The Ghaghara flows for a total length of about 1080 km, the upper half of which lies in Tibet and Nepal and the lower half in India. Out of the total catchment area of 1, 27,950 sq. km, the area in India is only 57,647 sq. km, which falls 45% of the total area. The critical locations along Ghaghra in India where major shifting has occurred are Tanda, Ayodhya, Golabazar, Barhaj and Bansdih. Heavy mining of sand from its course and variation in flow is the possible reasons for shifting in river Ghaghra. The sampling sites are shown in the Fig:1.

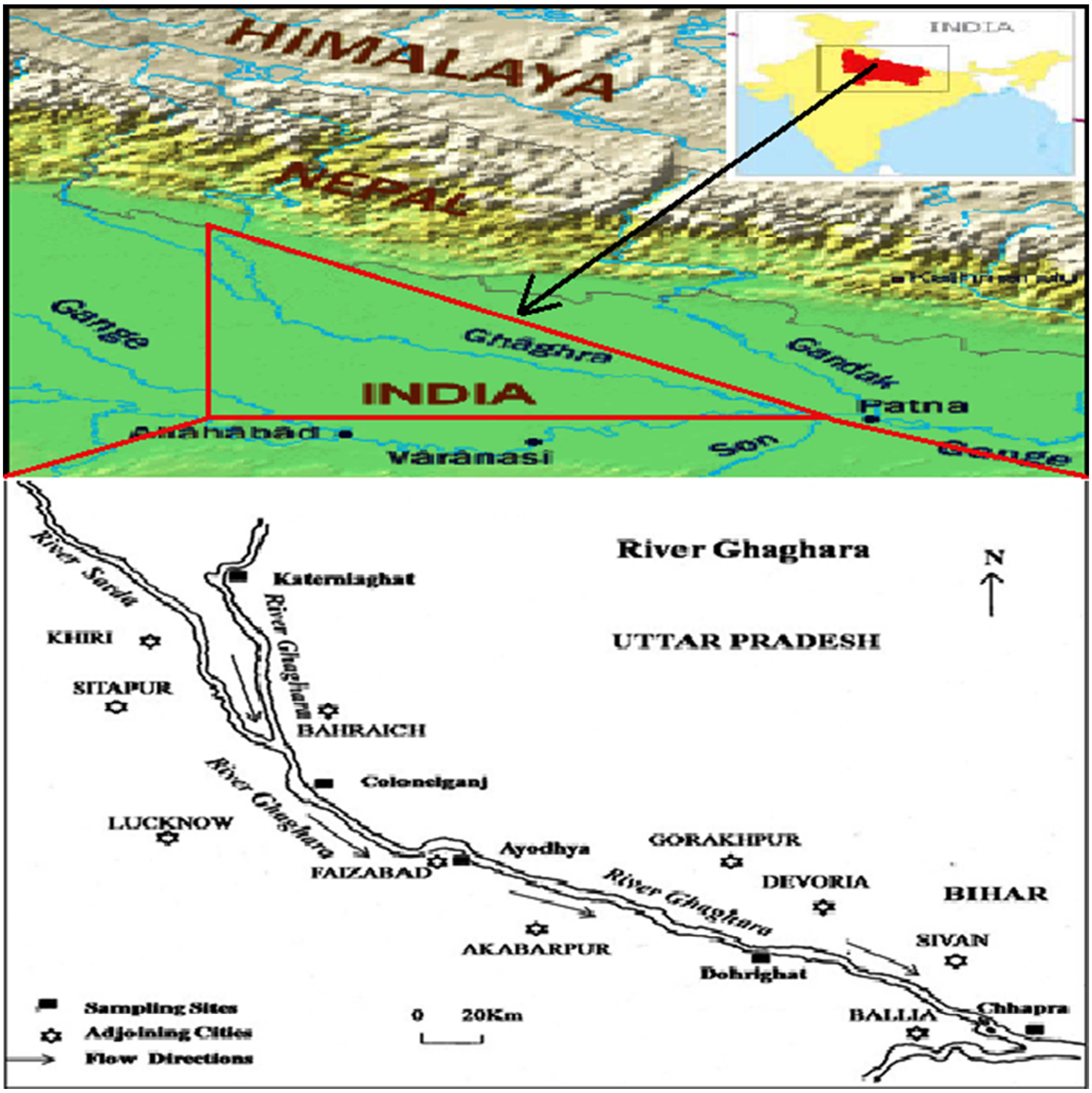

Fig: 1 Sampling stations of the River Ghaghara with the adjoining cities

Sampling stations of the River Ghaghra

There were five sampling stations were selected for the study purposes of the river Ghaghara in Indian Territory from Katerniaghat, Bahraich (UP) to confluence point of the River Ganga at Chhapra, Bihar. The geographical co-ordinates of sampling sites are given in the Table: 1

Table: 1 Sampling sites of the River Ghaghara with their geographical co-ordinates

Study sites	Latitude	Longitude	Elevation(ft)	District	State
Katernia ghat	$28^0$19′46′N	$81^0$07′44′N	462	Bahraich	UttarPradesh
Colonelganj	$27^0$08′10′N	$81^0$41′58′E	352	Gonda	UttarPradesh
Ayodhya	$26^0$47′49′N	$82^0$11′53′E	298	Faizabad	UttarPradesh
Dohrighat	$26^0$16′37′N	$83^0$30′33′E	213	MauNathBhanjan	UttarPradesh
Chhapra	$25^0$47′05′N	$84^0$43′37′E	196	Saran	Bihar

Katernia Ghat is located near the Indo-Nepal Border of India in the Bahraich district of Uttar Pardesh at is a fragile eco-system spread over an area of around 440 square kilometers with sal and teak forests , lush grasslands and wetlands along with the ever flowing. Girwa River and is a jungle known as the Katerniaghat Wildlife Sanctuary. The river is dominated by the Gharials and Muggar (Crocodile) which can be seen basking on the sand bars. The sanctuary is an important breeding area of the Ghariyal which builds its nests on these sand bars. Turtle of various kinds can also be seen basking in the sun and the sudden splash in the water alerts one of the presences of the

Gangetic Dolphin which playfully jump in the waters. There are many small scale industries like textile (coloring reagents), tanneries, automobile, laundries chemicals, agricultural manufacturing units and sugarcane industries have established in this region. As of India census-2011, Baharaich had a population of 3,478,275.

Colonelganj is a historic place in Gonda District of Uttar Pradesh. Gonda is around 40 km east of Colonelganj. Colonelganj is located at 27.07°N 81.402°E. As of 2001 India census, Colonelganj had a population of 24,163. This City is situated on the bank of Saryu River which is 2 Km away from Main city. In the range of Tahseel the area of sangam of two rivers as Ghaghara and Sarju are situated. Sarju is a small river which merges in the Ghaghara near Paska village. This river system is again called as Sarju when it reaches Ayodhya in Faizabad district. The untreated domestic and industrial wastes are released into the river by open drains.

Ayodhya is an ancient city of India adjacent to Faizabad city in Faizabad district of Uttar Pradesh. It is located at 26º 47′ 49″ N latitude and 82º 11′ 53″ E longitude. As a result of rapid settlement and development Ayodhya has been merged to Faizabad city. Ayodhya is located on the right bank of the river it Saryu (also called Ghaghara) Just 6 km from Faizabad,. Ayodhya has a warm humid subtropical climate, typical of the Indian heartland. Summers are long, dry and extremely hot, lasting from late March to mid-June, with average daily temperatures near 32 °C (90 °F). As per provisional reports of Census India, population of Faizabad in 2014 is 167,544. The untreated domestic and industrial wastes are released into the river by open drains.

Dohrighat is a small town of the district Mau Nath Banjan, Uttar Pradesh, spread in 5 km^2 area. It is located between 26º 16′ 37″ N latitude and 83º 30′ 33″ E. Mau (Mau Nath Bhanjan) is situated on the fertile plains of the Ganges–Ghaghara doab. According to sensus 2014 the total population of this district is 2,205,170. This district represents geographical characteristics of mid Gangetic plain. “Khachari” and “Khadar” are types of soil found in the areas of north of Azamgarh - Ballia. In some high places “Bangar” soil is also found. In the southern part of the district, river flow is absent, due to which that area has Bangar type of soil, which is not fertile. Industries like leather tanning, small textile units, laundry chemicals, paints and dyes, radiators, brake wires, tire wear, anticorrosive plating are main contributors of heavy metals contamination in the river.

Chhapra is a city and headquarters of Saran district in the state of Bihar, India. It is situated near the junction of the Ghaghara and the Ganges River. Chapra is located at 25º 47′ 05″N latitude and 84º 43′ 37″E longitudes. The district is shaped like a triangle with its apex at the confluence of boundary of Gopalganj district and the Gandak – Ganges River. There are three rivers, namely the Ganges, Ghaghra, Gandak, which encircle the district from South, North, East and Western side respectively. The district is entirely constituted of plains but there are quite a few depressions and marshes, which create three broad natural divisions. Industries such as multiproductive agro-manufacturing unit, alcohol manufacturing unit, polythene manufacturing units, leather tanning, small textile units, laundry chemicals, paints and dyes, radiators, brake wires, tire wear, anticorrosive plating are main contributors of Cd, Zn, Cr,Cu, and Ni contamination in the river.

MATERIALS AND METHODS

The experimental work has carried out in two phases firstly, the field study and secondly the laboratory work. To collect the water and sediment sample from the river Ghaghra five sites have selected Sampling sites were located by using Global Positioning System (GPS) Technology.

Water sampling procedures

The periodic samplings were carried out in monsoon, winter and summer seasons with three replicates in two consecutive years 2013-2014 and 2014-2015. The site of sampling is selected randomly by considering the population, location and source of pollutions. There were five sampling stations were selected for the study proposes. River water samples were collected at depths varying from 15 to 30 cm with the help of a water sampler which consisted of a glass bottle and a cord tied to a lid. The whole assembly was lowered into water to the desired depths and the cord of the lid was pulled and released only when displaced air bubble ceased to come to the surface. The whole assembly was withdrawn and the water was then transferred into pre-cleaned polypropylene bottles. All the containers which used in sampling purposes were thoroughly washed and rinsed with 10% HNO_3 following by double distilled water. The bottles were filled leaving no air space, and then the bottle was sealed to prevent any leakage. Each container was clearly marked with the name and address of the sampling station, sample description and date of sampling. All the procedures were adopted according to the standard methods recommended by APHA [11]

Preparation of water sample for the analysis of heavy metals

All chemicals used in the study were of analytical grade and obtained from E. Merck, Mumbai, India. Double distilled water was used throughout the study. All the glassware and other sample containers were thoroughly cleaned and finally rinsed with double distilled water prior to use. The trace metal concentration in the sediment sample was determined by using Perkin-Elmer Atomic Absorption Spectrophotometer model 800.

For determination of heavy metals in water, water samples (50 ml) were digested with 10 ml of conc. HNO_3 at 80^0C until the solution became transparent [12]. The solution was filtered through Whatman No. 42 filter paper and diluted to 50ml with double distilled water. These samples were used to determine heavy metal concentrations by Atomic Absorption Spectrophotometer (Perkin-Elmer model 800, USA).

Heavy metals were determined by atomic absorption spectrophotometer (AAS). Atomic Absorption spectroscopy is an absorption methods where radiation absorbed by metal ions, excited atoms in the vapors state. In atomic absorption spectroscopy, the sample is first converted at a selected wavelength, which is characteristic of each individual element. The same experimental condition was also applied for the determination of the reference samples of known composition.

Cobalt (Co^{++}) was directly aspirated in to an air C_2H_2 flame of an Atomic absorption spectrophotometer and the absorbance of the standard Cd samples were monitored at the wavelength of 242.5 nm.

Copper (Cu^{++}) was determine by directly aspirate in to an air -C_2H_2 flame of an atomic absorption spectrophotometer and absorbance was measured at wavelength of 325 nm.

Chromium (Cr^{+++}) was determinate by directly aspired into air C_2H_2 flame of an atomic absorption spectrophotometer and absorbance measured at wavelength of 283.3 nm.

Cadmium (Cd^{++}) was directly aspirated in to an air C_2H_2 flame of an Atomic absorption spectrophotometer and the absorbance of the standard Cd samples were monitored at the wavelength of 228.8 nm.

Nickel (Ni^{++}) was determinate by directly aspirated in to an air- C_2H_2 flame of and atomic absorption spectrophotometer was measured at wavelength of 232 nm.

Zinc (Zn^{++}) was determined by directly aspirated in to an air C_2H_2 flame of an atomic absorption spectrophotometer and absorbance measured at wavelength of 279.5 nm.

Lead (Pb^{++}) was directly aspirated in to an air C_2H_2 flame of an atomic absorption spectrophotometer and absorbance was measured at wavelength of 358 nm.

Statistical and computational analysis
Mean
For a data set, the mean is the sum of the observations divided by the number of observations. It identifies the central location of the data, sometimes referred to in English as the average. The mean is calculated by stat software

Statistica 8, using, and the following formula.
Σ(X) M = N
Where Σ = Sum of
X = Individual data points
N = Sample size (number of data points)

Standard Deviation (SD)
The standard deviation is the most common measure of variability, measuring the spread of the data set and the relationship of the mean to the rest of the data. If the data points are close to the mean, indicating that the responses are fairly uniform, then the standard deviation will be small. Conversely, if many data points are far from the mean, indicating that there is a wide variance in the responses, then the standard deviation will be large. If all the data values are equal, then the standard deviation will be zero. The standard deviation is calculated by stat software

Statistica 8, using the following formula.
Σ(X-M)2 S2 = n - 1

Where Σ = Sum of
X = Individual score
M = Mean of all scores
N = Sample size (number of scores)

Correlation study

The word correlation is made of Co-(meaning "together"), and Relation. When two sets of data are strongly linked together we say they have a high correlation. Correlation is Positive when the values increase together; and correlation is negative when one value decreases as the other increases

Correlation can have a value:

- 1 is a perfect positive correlation
- 0 is no correlation (the values don't seem linked at all)
- -1 is a perfect negative correlation

RESULTS AND DISCUSSION

Water and sediment quality of the River Ghaghara Ghaghara River passes through mainly villages, towns and small cities. However big city like Ayodhya is also located on right bank of the river in Faizabad district of Uttar Pradesh. Domestic effluents are added into river from the towns and cities. Untreated industrial effluents are also added from some small scale industries in to the river. The study area covers a stretch of the river Ghaghara in Indian Territory from Katerniaghat, Bahraich (U.P) to Chhapra (Bihar). The experimental findings of physico-chemical analysis and heavy metals content in water and sediment of river Ghaghara presented in Tables :2 to Table: 6

Table: 2 Water and sediment quality of the River Ghaghara at Katerniaghat, Bahraich (U.P.)

Heavy metals in river water								
araParameter	Year 2013-2014				Year 2014-2015			
	Monsoon	Winter	Summer	Mean ± SD	Monsoon	Winter	Summer	Mean ± SD
Co(mg/l)	0.005	0.008	0.022	0.011± 0.009	0.008	0.018	0.021	0.015± 0.006
Cu (mg/l)	0.021	0.028	0.031	0.026± 0.005	0.010	0.023	0.033	0.022± 0.011
Cr (mg/l)	ND	ND	ND	0± 0.00	ND	ND	ND	0± 0.00
Ni (mg/l)	0.007	0.013	0.0	0.013± 0.003	0.013	0.017	0.022	0.017± 0.004
Cd(mg/l)	0.001	0.002	0.005	0.003± 0.002	0.002	0.003	0.007	0.004± 0.002
Zn (mg/l)	0.002	0.017	0.021	0.013± 0.010	0.005	0.021	0.028	0.018± 0.011
Pb (mg/l)	0.001	0.007	0.021	0.009± 0.010	0.003	0.005	0.009	0.005± 0.003

Table: 3 Water and sediment quality of the River Ghaghara at Colonelganj, Gonda (U.P.)

Heavy metals in river water								
araParameter	Year 2013-2014				Year 2014-2015			
	Monsoon	Winter	Summer	Mean ± SD	Monsoon	Winter	Summer	Mean ± SD
Co(mg/l)	0.03	0.008	0.027	0.021± 0.011	0.005	0.025	0.030	0.02± 0.013
Cu (mg/l)	0.012	0.017	0.023	0.017± 0.005	0.013	0.025	0.031	0.023± 0.009
Cr (mg/l)	ND	ND	ND	0± 0.00	ND	ND	ND	0.00± 0.00
Ni (mg/l)	0.007	0.013	0.025	0.015± 0.012	0.003	0.008	0.025	0.012± 0.011
Cd(mg/l)	0.018	0.021	0.028	0.022± 0.15	0.011	0.025	0.027	0.021± 0.008
Zn (mg/l)	0.015	0.018	0.025	0.019± 0.005	0.013	0.021	0.030	0.021± 0.008
Pb (mg/l)	0.005	0.018	0.029	0.017± 0.012	0.008	0.016	0.022	0.015± 0.007

Table: 4 Water and sediment quality of the River Ghaghara at Ayodhya, Faizabad (U.P.)

Heavy metals in river water								
araParameter	Year 2013-2014				Year 2014-2015			
	Monsoon	Winter	Summer	Mean ± SD	Monsoon	Winter	Summer	Mean ± SD
Co(mg/l)	0.020	0.028	0.031	0.026± 0.005	0.018	0.027	0.038	0.027± 0.010
Cu (mg/l)	0.015	0.023	0.047	0.028± 0.016	0.012	0.034	0.047	0.031± 0.017
Cr (mg/l)	0.002	0.005	0.009	0.005± 0.003	0.004	0.009	0.010	0.007± 0.003
Ni (mg/l)	0.010	0.018	0.021	0.016± 0.005	0.009	0.015	0.032	0.018± 0.011
Cd(mg/l)	0.015	0.030	0.057	0.034± 0.021	0.017	0.033	0.043	0.031±0.013
Zn (mg/l)	0.021	0.030	0.042	0.031± 0.010	0.019	0.028	0.038	0.028± 0.009
Pb (mg/l)	0.008	0.005	0.016	0.010± 0.005	0.010	0.020	0.028	0.019± 0.009

Table: 5 Water and sediment quality of the River Ghaghara at Dohrighat, Maunath Bhanjan (U.P.)

Heavy metals in river water								
araParameter	Year 2013-2014				Year 2014-2015			
	Monsoon	Winter	Summer	Mean ± SD	Monsoon	Winter	Summer	Mean ± SD
Co(mg/l)	0.002	0.015	0.028	0.015± 0.013	0.004	0.017	0.028	0.016± 0.012
Cu (mg/l)	0.024	0.036	0.035	0.032± 0.006	0.021	0.032	0.039	0.030± 0.009
Cr (mg/l)	ND	ND	ND	0± 0.00	ND	ND	ND	0±0.00
Ni (mg/l)	0.002	0.004	0.009	0.005± 0.003	0.005	0.006	0.010	0.007± 0.002
Cd(mg/l)	0.024	0.038	0.042	0.035± 0.009	0.027	0.032	0.048	0.036± 0.001
Zn (mg/l)	0.014	0.018	0.021	0.017± 0.003	0.011	0.017	0.023	0.017± 0.006
Pb (mg/l)	0.002	0.004	0.008	0.005± 0.003	0.003	0.007	0.009	0.006± 0.003

Table: 6 Water and sediment quality of the River Ghaghara at Chhapra, Saran (Bihar)

Heavy metals in river water								
araParameter	Year 2013-2014				Year 2014-2015			
	Monsoon	Winter	Summer	Mean ± SD	Monsoon	Winter	Summer	Mean ± SD
Co(mg/l)	0.003	0.021	0.027	0.017± 0.01	0.004	0.024	0.028	0.019± 0.012
Cu (mg/l)	0.010	0.014	0.025	0.016± 0.007	0.018	0.028	0.044	0.019± 0.014
Cr (mg/l)	0.002	0.006	0.008	0.005± 0.003	0.001	0.004	0.007	0.005± 0.003
Ni (mg/l)	0.003	0.009	0.017	0.009± 0.007	0.010	0.014	0.019	0.014± 0.005
Cd(mg/l)	0.031	0.042	0.051	0.041± 0.010	0.037	0.049	0.043	0.043± 0.008
Zn (mg/l)	0.020	0.029	0.031	0.027± 0.005	0.018	0.023	0.019	0.020± 0.005
Pb (mg/l)	0.005	0.015	0.027	0.015± 0.011	0.006	0.017	0.025	0.016± 0.009

Table: 7 showing Minimum and maximum value of seven heavy metals compared with WHO standards

Parameters	Minimum value at different sites in different years			Maximum value at different sites in different years			Permissible limit (mg/l)	Standards
Co(Mg/l)	0.011	katerniaghat	2011-12	0.027	Ayodhya	2011-12		
Cu (Mg/l)	0.016	Colonelganj	2010-11	0.032	Dohrighat	2010-11	1.0	WHO
Cr (Mg/l)	0.005	Ayodhya	2010-11	0.007	Ayodhya	2011-12	0.05	WHO
Ni (Mg/l)	0.005	Dohrighat	2010-11	0.018	Ayodhya	2011-12	0.1	WHO
Cd(Mg/l)	0.003	Colonelganj	2010-11	0.043	chhapra	2011-12	0.005	WHO
Zn (Mg/l)	0.013	Katerniaghat	2010-11	0.031	Ayodhya	2010-11	5.00	WHO
Pb (Mg/l)	0.005	Katerniaghat	2011-12	0.019	Ayodhya	2011-12	0.05	WHO

Table: 8 Presenting the Correlations coefficient between seven parameters in the year 2013-14

	co	Cu	Cr	Ni	Cd	Zn	Pb
co	1						
Cu	.982	1					
Cr	.966	.900	1				
Ni	.899	.966	.756	1			
Cd	.977	1.000*	.888	.972	1		
Zn	.941	.988	.822	.994	.992	1	
Pb	.999*	.990	.952	.920	.986	.957	1
*. *Correlation is significant at the 0.05 level (2-tailed).*							

Table: 9 Presenting the Correlations coefficient between seven parameters in the year 2014-15

	co	Cu	Cr	Ni	Cd	Zn	Pb
co	1						
Cu	.982	1					
Cr	.966	.900	1				
Ni	.899	.966	.756	1			
Cd	.977	1.000*	.888	.972	1		
Zn	.941	.988	.822	.994	.992	1	
Pb	.999*	.990	.952	.920	.986	.957	1
*. *Correlation is significant at the 0.05 level (2-tailed).*							

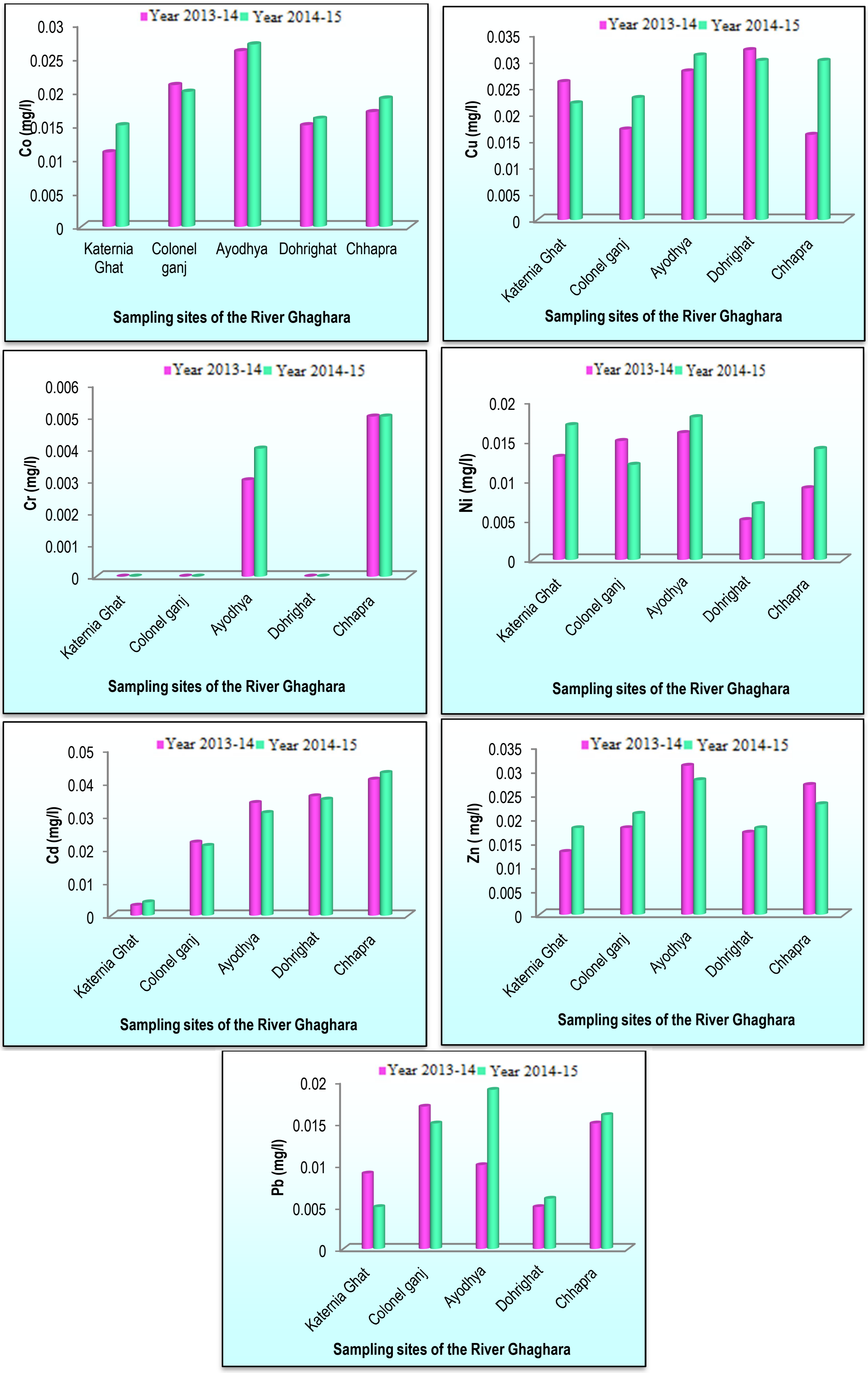

Fig: 2 Distribution of heavy metals at various sites of the river Ghaghara in the Year2013-14 and 2014-15

Cobalt (Co^{++})
Ghaghara River shows variability in cobalt concentration at different sites. At Katerniaghat the average value of Co^{++} in water was recorded as 0.011 ± 0.009 mg/l in the year 2013-14 and 0.015 ± 0.006 mg/l in 2014-15. The minimum value was observed in Monsoon season whereas the maximum value was recorded in the summer season. At Colonelganj the average value of Co was recorded 0.021 ± 0.011 mg/l in the year 2013-14 and 0.02 ± 0.013 mg/l in 2014-15. At Ayodhya the average concentration of Co was recorded 0.026 ± 0.005 mg/l in the year 2013-14 and 0.027 ± 0.010 mg/l in 2014-15. At Dohrighat the average value of Co was recorded 0.015 ± 0.13 mg/l in the year 2013-14 and 0.016 ± 0.012 mg/l in 2014-15. At Chhapra the average value of Co was recorded 0.017 ± 0.001 mg/l in the year 2013-14 and 0.019 ± 0.012 mg/l in 2014-15. The Co concentrations of water of the River Ghaghara at different sites are presented in the Table: 2 to Table: 6 In the river Ghaghara maximum concentration of Co was noted 0.021 mg/l at Ayodhya in the year 2013-14 whereas it was minimum 0.002 mg/l at Colonelganj in the year 2014-15.

Copper (Cu^{++}) Concentration of Copper in the River Ghaghara varies site to site. At Katernia the average value of Cu in the water of the River Ghaghra was recorded 0.026 ± 0.005 mg/l in the year 2013-14 and 0.022 ± 0.011 mg/l in 2014-15. At Colonelganj the average value of Cu was recorded 0.017 ± 0.005 mg/l in the year 2013-14 and 0.023 ± 0.009 mg/l in 2014-15. At Ayodhya the average value of Cu was recorded 0.028 ± 0.016 mg/l in the year 2013-14 and 0.031 ± 0.017 mg/l in 2014-15. At Dohrighat the average value of Cu was recorded 0.032 ± 0.006 mg/l in the year 2013-14 and 0.030 ± 0.009 mg/l in 2014-15. Chhapra the average value of Cu was recorded 0.016 ± 0.007 mg/l in the year 2013-14 and 0.019 ± 0.014 mg/l in 2014-15. The Cu concentrations of water of the River Ghaghara at different sites are presented in the table: 2 to table: 6. In the river Ghaghara maximum concentration of Cu was noted 0.032 mg/l at Dohrighat in the year 2014-15whereas it was minimum 0.002 mg/l at Colonelganj in the year 2013-14. In present investigation it was noted that the observed values were below the permissible limit of 0.05mg/L set by WHO [13] (Table 7). It is important here to note that Cu is highly toxic to most fishes, invertebrates and aquatic plants than any other heavy metal except mercury. It reduces growth and rate of reproduction in plants and animals. The chronic level of Cu is 0.02–0.2mg/L [14]. Aquatic plants absorb three times more Cu than plants on dry lands [15]. Excessive Cu content can cause damage to roots, by attacking the cell membrane and destroying the normal membrane structure; inhibited root growth and formation of numerous short, brownish secondary roots. Cu becomes toxic for organisms when the rate of absorption is greater than the rate of excretion, and as Cu is readily accumulated by plants and animals, it is very important to minimize its level in the waterway.

Chromium (Cr^{++}) concentration varies from site to site and season to season for the River Ghaghara. Chromium was not detected in water of the river Ghaghra at Katerniaghat, Colonelganj and Dohrighat but it was detected at Ayodya and Chhapra. At Ayodhya the average value of Cr was recorded 0.005 ± 0.003 mg/l in the year 2013-14 and 0.007 ± 0.003 mg/l in 2014-15. At Chhapra the average value of Cr was recorded 0.005 ± 0.003 mg/l in the year 2013-15 and similar value was also recorded in 2014-15. The Cr concentrations of water of the River Ghaghara at different sites are presented in the table: 2 to table: 6. In the river Ghaghara maximum concentration of Cr was noted 0.007 mg/l at Chhapra in the year 2014-15 whereas it was minimum as 0.002 mg/l at Ayodhya in the year 2013-14. Cr was not detected from other sites of the river Ghaghara In the present investigation the average Cr content in water samples was found below the permissible limit of 0.05mg/L set by WHO [13]. [16] observed that chromium is a transition metal that is discharged into the environment through the disposal of wastes from industries like leather tanning and metallurgical, leading to contamination of river water and sediment both. Chromium is the main tanning agent and most hazardous chemical used in chrome tanning process. The excessive use of this chemical leads to higher concentration in the effluent [17]. Chromium levels in the target area were found in very low amount in the undertaken rivers. It is the major chemical present in the effluent, which, when released into water percolates the layers of sediments. Cr compounds are used as pigments, mordents and dyes in the textiles and as the tanning agent in the leather. The sources of emission of Cr in the surface waters are from municipal wastes, laundry chemicals, paints, leather, road run off due to tire wear, corrosion of bushings, brake wires and radiators, etc. The high level of Cr in waste water effluent indicates excessive pollution from textile industries and tanneries [18]. Acute toxicity of Cr to invertebrates is highly variable, depending upon species [19]. For invertebrates and fishes, its toxicity is not much acute.

Nickel (Ni^{++}) Nickel concentrations were varies from one sampling station to the other. At Katernia the average value of Ni in the water of the River Ghaghra was recorded 0.013 ± 0.003 mg/l in the year 2013-14and 0.017 ± 0.004 mg/l in 2014-15. At Colonelganj the average value of Ni was recorded 0.015 ± 0.012 mg/l in the year 2013-14 and 0.012 ± 0.011 mg/l in 2014-15. At Ayodhya the average value of Ni was recorded 0.016 ± 0.005 mg/l in the year 2013-14 and 0.018± 0.011 mg/l in 2014-15. At Dohrighat the average value of Ni was recorded 0.005 ± 0.003 mg/l in the year 2013-14 and 0.007 ± 0.002 mg/l in 2014-15. At Chhapra the average value of Ni was recorded 0.009 ± 0.007 mg/l in the year 2014-15 and 0.014 ± 0.005 mg/l in 2014-15. The Ni concentrations of water of the River Ghaghara at different sites are presented in the table Table: 2 to Table: 6. In the river Ghaghara maximum concentration of Ni was noted 0.018 mg/l at Ayodhya in the year 2013-14 whereas it was minimum 0.005 mg/l at Dohrighat in the year 2013-14 The average Ni content in the water samples of the river Ghaghara were found between 0.003 mg/l to 0.030 mg/l which was below the maximum limit of 0.1mg/L set by WHO (Table 7.5). Short-term exposure to Ni on human being is not known to cause any health problems, but long-term exposure can cause decreased body weight, heart, liver damage and skin irritation Tiwana *et al* (2005). The carcinogenic action of nickel carbonyl on rat was reported earlier by [20]. Ni can accumulate in aquatic life, but its magnification along in food chain is not confirmed.

Cadmium (Cd^{++}) Ghaghara River shows different level of concentrations from site to site. At Katerniaghat the average value of Cd in the water of the River Ghaghra was recorded 0.003 ± 0.002 mg/l in the year 2013-14 and 0.004 ± 0.002 mg/l in 2014-15. At Colonelganj the average value of Cd was recorded 0.022 ± 0.015 mg/l in the year 2013-14 and 0.021 ± 0.008 mg/l in 2014-15. At Ayodhya the average value of Cd was recorded 0.034 ± 0.021 mg/l in the year 2013-14 and 0.031 ± 0.013 mg/l in 2014-15. At Dohrighat the average value of Cd was recorded 0.035 ± 0.009 mg/l in the year 2013-14 and 0.036 ± 0.001 mg/l in 2014-15. At Chhapra the average value of Cd was recorded 0.041 ± 0.010 mg/l in the year 2013-14 and 0.043 ± 0.008 mg/l in 2014-15. Cd concentrations of water of the River Ghaghara at different sites are presented in the Table: 2 to Table: 6. In the river Ghaghara maximum concentration of Cd was noted 0.036 mg/l at Dohrighat in the year 2014-15 whereas it was minimum 0.002 mg/l at Katerniaghatin the year 2013-14. The values of Cd obtained for the river Ghaghara Dohrighat was found to be higher than the permissible limit of 0.01mg/L set by WHO (Table 7). Cd is contributed to the surface waters through paints, pigments, glass enamel, deterioration of the galvanized pipes etc. The wear of studded tires has been identified as a source of Cd deposited on road surfaces. The average Cd content in water samples was found to vary from river to river and place to place. Higher values of Cd in waste water effluent samples suggest the high level of pollution due to dyes paints and pigments manufacturing industries around. There are a few recorded instances of Cd poisoning in human beings following consumption of contaminated fishes. It is less toxic to plants than Cu, similar in toxicity to Pb and Cr. It is equally toxic to invertebrates and fishes [19].

Zinc (Zn^{++}) In the River Ghaghara the concentration of Zinc varies between one site to the other. At Katerniaghat the average value of Zn was recorded 0.013 ± 0.010 mg/l in the year 2013-14 and 0.018 ± 0.011 mg/l in 2014-15. At Colonelganj the average value of Zn was recorded 0.019 ± 0.005 mg/l in the year 2013-14 and 0.021 ± 0.008 mg/l in 2014-15. At Ayodhya the average value of Zn was recorded 0.031 ± 0.010 mg/l in the year 2013-14 and 0.028 ± 0.009 mg/l in 2014-15. At Dohrighat the average value of Zn was recorded 0.017 ± 0.003 mg/l in the year 2013-14 and 0.017 ± 0.006 mg/l in 2014-15. At Chhapra the average value of Zn was recorded 0.027 ± 0.005 mg/l in the year 2013-14 and 0.020 ± 0.005 mg/l in 2014-15. The Zn concentrations of water of the River Ghaghara at different sites are presented in the Table: 2 to Table: 6. In the river Ghaghara maximum concentration of Zn was noted 0.031 mg/l at Ayodhya in the year 2014-15 whereas it was minimum 0.013 mg/l at Katerniaghat in the year 2014-15. Level of Zn was also found below the permissible limit of 5.5mg/L as per United State Public Health Services (USPHS,1997) standard. Excessive concentration of Zn may result in necrosis, chlorosis and inhibited growth of plants**.** The overall concentration of Zinc as obtained from the analysis of water samples collected from different undertaken rivers varied from 0.004 mg/l to 0.096 mg/l. Since the desired level of Zinc is 5.0 mg/l, none of the samples has exceeded the limiting value. However result indicates leaching of Zinc from the waste dumping site confirming the presence of Zinc in the waste dumped.

Lead (Pb^{++}) concentration at Katerniaghat was recorded 0.009 ± 0.010 mg/l in the year 2013-14 and 0.005 ± 0.003 mg/l in 2014-15. At Colonelganj the average value of Pb was recorded 0.017 ± 0.012 mg/l in the year 2013-14 and 0.015 ± 0.007 mg/l in 2014-15. At Ayodhya the average value of Pb was recorded 0.010 ± 0.005 mg/l in the year 2013-14 and 0.019 ± 0.009 mg/l in 2014-15. At Dohrighat the average value of Pb was recorded 0.005 ± 0.003 mg/l in the year 2013-14 and 0.006 ± 0.003 mg/l in 2014-15. At Chhapra the average value of Pb was recorded 0.015 ± 0.011 mg/l in the year 2013-14 and 0.016 ± 0.009 mg/l in 2014-15. The Pb concentrations of water of the River Ghaghara at different sites are presented in the Table: 2 to Table: 6. In the river Ghaghara maximum concentration of Pb was noted 0.019 mg/l at Ayodhya in the year 2014-15, whereas it was minimum 0.005 mg/l at Katerniaghat in the year 2014-15. It is one of the oldest metals known to man and is discharged in the surface water through paints, solders, pipes, building material, gasoline etc. Lead is a well known metal toxicant and it is gradually being phased out of the materials that human beings regularly use. Combustion of oil and gasoline account for >50% of all anthropogenic emissions, and thus form a major component of the global cycle of lead. Atmospheric fallout is usually the most important source of lead in the fresh waters [19]. The average concentration of Pb in water samples collected from the river Ganga and it's tributaries was found below the permissible limit for lead in drinking water is <0.05mg/L according to the USPHS drinking water standards. Acute toxicity generally appears in aquatic plants at concentration of 0.1–5.0mg/L. In plants, it initially results in enhanced growth, but from a concentration of 5 ppm onwards, this is counteracted by severe growth retardation, discoloration and morphological abnormalities. There is an adverse influence on photosynthesis, respiration and other metabolic processes. Acute toxicity of Pb in invertebrates is reported at concentration of 0.1–10mg/l, [19]. Higher levels pose eventual threat to fisheries resources.

Correlation Coefficients matrix is a associations between variables that can show the overall coherence of the data set and indicate the participation of the individual chemical parameters in several influence factors. The correlation coefficient between every parameter pairs was computed by taking the average values of each season (mansoon, winter and summer) for the five sites of the River Ghaghra for the year 2013-14 and 2014-15. Correlation analysis among all considered heavy metals shows positive correlation with each other in the year 2013-14 (Table 8). Approximately similar pattern of correlation was also found in the year 2014-15 (Table 9).

CONCLUSION

On the basis of experimental findings it was found that the river water in summer, monsoon and winter seasons show different level of fluctuations in heavy metals from place to place. The seasonal changes in the water quality of the rivers were imparted mainly due to catchment characteristics and seasonal effects. These variations were noted due to the change in the volume of industrial and sewage waste being added to river at different stations of the stretch. Concentrations of trace metals like Co, Cu, Ni, Zn and Pb in water of the river were recorded below the permissible limit at most of the selected sites, whereas the level of Cd in water exceeded the permissible limit. The present experimental data indicates that the pollution level along the river Ghaghara is not very high but the increasing population load in the basin may cause irreparable ecological harm in the long-term well masked by short term economic prosperity. The experimental data suggests a need to implement common objectives, compatible policies and programmes for improvement in the industrial waste water treatment methods. It also suggests a need of consistent, internationally recognized data driven strategy to assess the quality of waste water effluent and generation of international standards for evaluation of contamination levels. The existing situation if mishandled.

Acknowledgments
The authors wish to thank University Grant Commission (UGC), New Delhi for financial assistance, Prof. M. C. Chattopadhyay, Department of Chemistry, University of Allahabad for help in heavy metal analysis and Prof. G.K. Srivastava, Department of Botany, University of Allahabad for technical guidance in manuscript writing.

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