Pollution Status in river Yamuna with reference to Trace and Toxic metals

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ABSTRACT

Deteriorating water quality has become a serious problem in developing countries. Almost 70% of Indian's surface water resources have become contaminated due to the discharge of untreated sewage and industrial effluents. The water quality of the Yamuna river has been studied with reference to toxic metals during November, 2011; February, 2012 and June 2012 at 12 water quality monitoring stations. The results reveals that water samples collected from 8 water quality stations (viz. Poanta, Kalanour, Mawi, Palla, Auraiya, Etawah, Hamirpur and Pratappur) are found to be within the permissible limit for all purposes. While at 4 stations (viz. Delhi R Bridge, Mohana, Mathura and Agra) water quality was unsuitable due to presence of cadmium, lead and iron toxic metals. Cadmium and lead metal show higher concentrations in the month of June. The main sources of metal pollution in the Yamuna River include municipal and industrial effluents. The river water is not safe due to the toxic metals. The water supply for domestic purposes from the Yamuna River at Delhi, Mohana, Mathura and Agra should be treated for toxic metal ions, and immediate action should be taken to control the quality of the river water.

1. INTRODUCTION

Fresh water is of vital importance for human existence. Man uses water for domestic, industrial and agricultural purposes. The past decade has seen remarkable impact of man on the environment due to unprecedented increase in population and rapid rate of urbanization as well as the intensification of the use of fragile and marginal ecosystems. This has led to progressive and continual resources degradation especially surface water. Polluted water is an important vehicle for the spread of diseases. In developing countries about 1.8 million people, mostly children, die every year as a result of water related diseases (WHO, 2006). In most urban-rural communities in the developing countries surface waters (rivers, streams, and lakes among others) have been the most available sources of water used for domestic purposes. The water from these sources are contaminated with domestic, agricultural, and industrial wastes and likely to cause water related diseases.

Every human use of water, whether for drinking, irrigation and industrial processes or for recreation has some quality requirements in order to make it acceptable. This quality criterion can be described in terms of physical, chemical and biological properties of such water (Gore, 1985). According to the World Commission on water for the 21st century, more than half of the world's major rivers are so depleted and polluted that they endanger human health and poison surrounding ecosystems (Inter-press, 1999). The infiltration of rainfall into landfill, together with the biochemical; and chemical breakdown of the waste, produces leachate, high in suspended solids and of varying organic and inorganic content. If the leachate enters surface or ground water before sufficient dilution has occurred, serious pollution incidents can occur. In surface water leachate high in organic material and reduced metals will cause severe oxygen depletion and result in death of fish. Leachate high in non-biodegradable synthetic organic compounds is a particular threat, through bioaccumulation. Concentration of these substances may increase to toxic levels and thus endanger animal and human life. Trace metals are those having density greater than 5 gcm^{-3}. Most often this term denotes metals that are toxic. These include Al, As, Cd, Cr, Co, Pb, Hg, Ni, Se, and Zn (Rodier, 1975). These metals or their compounds may be discharged from industries, farmlands, municipal urban water runoffs, and agricultural activities into surface water and can cause pollution. They vary in type and include large quantities of raw materials, by-products, co-products and final products of human activities. Many of these wastes are toxic and they find their ways into land water/sediments and air.

In view of the hazardous nature of metal ions, an attempt has been made to study the pollution potential of toxic metals in the Yamuna River at Delhi (India). It warrants immediate attention for the enhancement of the water quality of the river.

2. STUDY AREA

The Yamuna River originates from the Yamunotris glacier, 6387 meter above mean sea level (msl), at the Banderpoonch peak in the Uttarkashi district of Utter Pradesh. The river flows 1,367 km from here to its confluence with the Ganga at Allahabad. The annual flow of the river is about 10,000 cumecs. The annual usage is 4,400 cumecs, irrigation accounting for 96% of this (Ministry of Environmental Forest, 1994).

On the basis of different geological and ecological characteristics, the Yamuna River has been divided into five segments- Himalayan, Upper, Delhi, Eutrophicated and Diluted-of which Delhi is the most polluted stretch of the river. The 172 km long stretch of the river through the Haryana from the source to the Tajewala barrage is called the Himalayan segment. The stretch from the Tajewala barrage to the Wazirabad barrage, when the river flows 224 km through Haryana, is the upper segment. The delhi segment comprises the 22 km that the river traverses in Delhi from the Wazirabad barrage to the Okhla barrage. From here to its confluence with the Chambal, 490 km downstream is the eutrophicated segment. Beyond this point is the Diluted segment.

At estimated 57 million people are dependent on the waters of the Yamuna River. It is the main source of drinking water for the most of the town along its course. The water quality of the river Yamuna deteriorates almost the moment it reaches the plains. The agricultural belt of Haryana, and the industrial town all along the river, discharge significant amounts of wastes into the river. However, throughout its course through Haryana and Delhi, the Yamuna becomes a drain, receiving agricultural runoff containing pesticides and fertilizer as well as industrial and domestic effluents. With several towns and cities discharging their untreated or partially treated wastes into the river, the water quality deteriorates constantly.

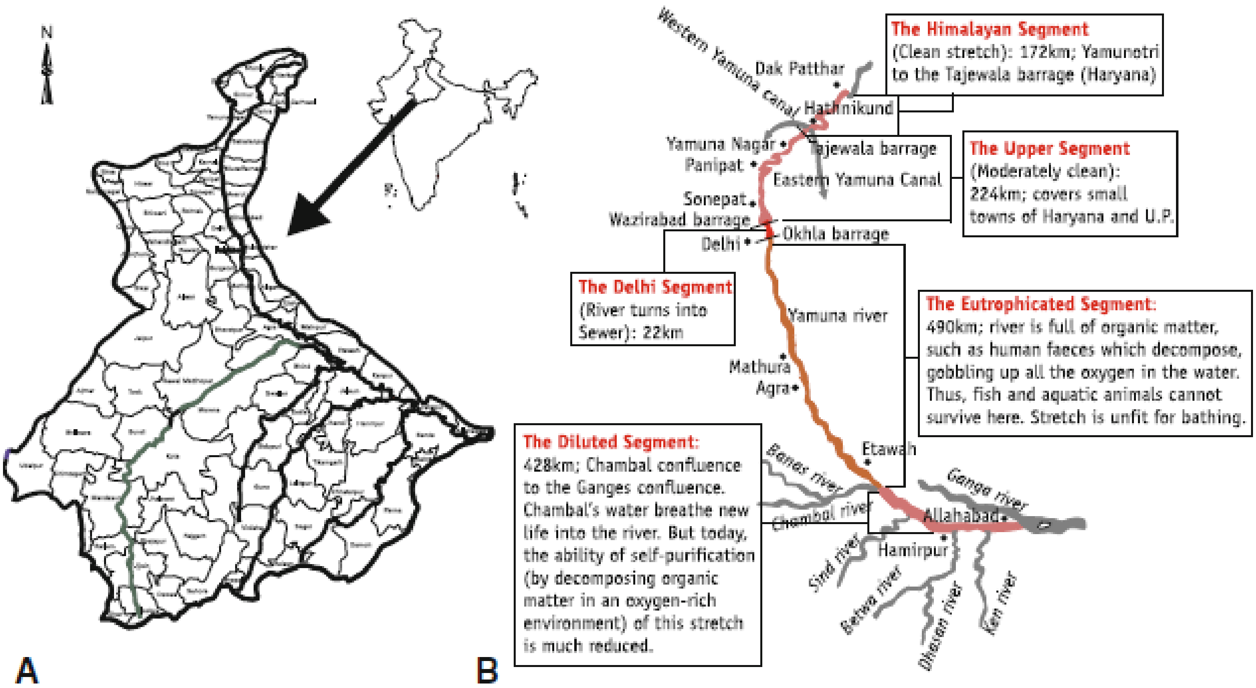

Fig. 1 Description of the study area. A. Basin map of River Yamuna.
B. River classification according to pollution.

3. EXPERIMENTAL METHODOLOGY

Grab samples were collected from midstream of the Yamuna river at a depth of about 0.3 meters from all the sampling locations. The sample bottles were soaked in 10 percent HNO_3 for 24h and rinsed several times with double distilled water prior to use. 500ml of water samples were collected and immediately acidified with 2ml ultra pure nitric acid (1:1 or 50ml Con HNO_3 + 50 ml DW) and 2ml HCL for arsenic to bring down the pH to <2.0. The samples thus preserved were stored at 4^0C in sampling kits and brought to the laboratory for metal analysis. In the laboratory water samples were filtered through 0.45 µm membrane filter. Samples were collected in the months of November, 2011; February, 2012 and June 2012.

All the chemicals and reagents used were of analytical grade and were procured from Merck, India. The standard solutions of metals were obtained from Merck, Germany. Deionized water was used throughout the study. All glass wares and other containers were thoroughly cleaned and finally rinsed with deionized water several times prior to use. Trace metal analysis was carried out using Agilent 240 FS Atomic Absorption Spectrometer (AAS) following the standard methods given in APHA, 2012.

4. QUALITY CRITERIA

As it is a well-known fact that the sources of usable water on the earth are limited, any kind of pollution in them will further reduce its availability. Polluted water cannot be utilized for drinking because of its inherent health risk. Water with high salt contents is not suitable for agriculture and most industries. The quality of water also interferes with the aesthetic and economic pursuits of water bodies by affecting marine and fresh water life. However, the water, which is not suitable for irrigation, may be quite suitable for industrial cooling. Every use of water requires a certain minimum quality standards with regards to the presence of dissolved and suspended materials of both chemical and biological nature. The desirable quality of water ensures no harm to the user.

To maintain the minimum quality standard for diverse user has led to the formulation of water quality criteria, and water quality standards. Water quality criteria can be considered as specific requirements on which a decision or judgment to support a particular use will be based. The criteria for the various uses are developed based on the experimental data, and our current knowledge of the health, ecology and other issues and assessing its overall economical effect these are not a set of fixed values, but subject to modification as the scientific data get updated and more and more knowledge is gathered. The term standard applies to any definite principle or measure established by an authority by limiting concentration of different constituents in water to ensure the safe use of water and safeguard the environment.

Drinking Water Standards

In view of the direct consumption of water by human beings, the domestic water supply is considered to be most important use of water and drinking use has been given first priority on utilization of water resource in the National Water Policy. In India, agencies like the Bureau of Indian Standards (BIS) and Indian Council of Medical Research (ICMR) have formulated drinking water standards. The World Health Organization (WHO) has also laid down drinking water standards, which are considered international standards. Values of the trace and toxic metals covered in this research paper and given in table 1 are according to BIS 10500, 2012 as given below.

Table 1: Drinking Water Standards for Trace & Toxic metals (BIS:10500;2012)

S. No	Toxic metal	Unit	Requirement (Acceptable Limit)	Permissible Limit in the Absence of Alternative Source
1	**Total arsenic as As**	mg/l	0.01	No relaxation
2	**Cadmium as Cd**		0.003	No relaxation
3	**Total Chromium as Cr**		0.05	No relaxation
4	**Copper as Cu**		0.05	1.5
5	**Iron as Fe**		0.3	No relaxation
6	**Lead as Pb**		0.01	No relaxation
7	**Mercury as Hg**		0.001	No relaxation
8	**Nickel as Ni**		0.02	No relaxation
9	**Zinc as Zn**		5	15

5. RESULT AND DISCUSSION

Heavy metals or trace elements is the term referred to those elements that occur at very low levels of few parts per million in a given system. They are among the most harmful of the elemental pollutants. Some of them like Pb, Sn, Hg, Zn and Cu can be very toxic to the system (Bhatia, 2006). Trace metals include essential elements like Iron as well as toxic metals like Cd and Hg. Most of them have strong affinity for Sulphur and disrupt enzyme function by forming bonds with sulphur groups in enzyme. Heavy metals are highly persistent and can easily enter a food chain and accumulate until they reach toxic levels. These may eventually kill fish, birds and mammals (USEPA, 1999). Many countries in the world have experienced menace of metal pollution in water and large number of people has been affected. Causes of this pollution have been well documented. However, the main sources of metal toxicity in surface water have been thought to be natural occurrence and subsequent degradation of the environment.

Arsenic

Arsenic is a natural element that is widely distributed throughout the Earth's crust. Arsenic is classified as a human carcinogen. The maximum acceptable concentration for arsenic in drinking water was established based on the incidence of internal (lung, bladder, and liver) cancers in humans, through the calculation of a lifetime unit risk. This guideline for arsenic has been set at a level that is higher than the level that would be considered to be associated with an "essentially negligible" risk, based on limitations of available treatment technology. Bureau of Indian Standard (10500, 2012) have recommended acceptable limit of arsenic is 0.01 mg/l or 10μg/l in drinking water. 36 samples from 12 water quality stations were analyzed for a period of November, 2011; February, 2012 and June 2012. Arsenic concentration has been observed ranged 1.38 – 8.47 μg/L. All the samples having arsenic concentration in Yamuna river with in the acceptable limit prescribed by Bureau of Indian Standard IS:10500, 2012. Etawah water quality station on river Yamuna reported to have the highest arsenic values 8.47 μg/L during June, 2012.

Copper

Copper is an essential element in human metabolism, and it is well-known that deficiency results in a variety of clinical disorders, including nutritional anaemia in infants. BIS, 10500, 2012 has recommended a acceptable limit of 0.05 mg/l (50μg/l) of copper in drinking water; this concentration limit can be extended to 1.5 mg/l (1500 μg/l) of copper in case no alternative source of water with desirable concentration is available. The intake of large doses of copper has resulted in adverse health effects. Copper and its compounds are widely distributed in nature, and copper is found frequently in surface water and in some groundwater. 30 samples from 12 water quality stations were analyzed for a period of November, 2011; February, 2012 and June 2012. Copper concentration of the Yamuna river was found between 0.01- 8.81 μg/L. The maximum concentration (8.81 μg/L) was found in Agra (PG) and minimum (0.01 μg/L) at Kalanour water quality station. In the study area all the river water quality stations having copper concentration is well within the acceptable limits of Bureau of Indian Standard (BIS) and there is no toxicity of Cu in the river water.

Cadmium

Cadmium is a relatively rare element. It is uniformly distributed in the Earth's crust, where it is generally estimated to be present at an average concentration of between 0.15 and 0.2 mg/kg. A maximum acceptable concentration for cadmium in drinking water has been established on the basis of health considerations. BIS proposed the maximum desirable limit of cadmium is 0.003 mg/l or 3μg/l and no relaxation maximum permissible limit in absence of another source. The concentration of cadmium in unpolluted fresh waters is generally less than 0.001 mg/L. Surface waters containing in excess of a few micrograms of cadmium per litre have probably been contaminated by industrial wastes from metallurgical plants, plating works, plants manufacturing cadmium pigments, textile operations, cadmium-stabilized plastics, or nickel–cadmium batteries, or by effluents from sewage treatment plants. 27 samples from 12 water quality stations were analyzed. Cadmium concentration in the river Yamuna varies from 0.02-12.10 μg/L. In the study area the concentration of cadmium of Delhi Rly Bridge, Mohana, Mathura, Agra (P.G.) at Yamuna River exceed acceptable limit. Yamuna River have maximum 12.10 μg/L cadmium concentration is observed at Mohana during June, 2012.

Table 3 shows the name of the water quality stations, river affected by high cadmium water (>3μg/L) and these WQ stations are hot spots from point of view of cadmium.

Chromium

Chromium can exist in di to hexa valent forms but is present in the environment mainly in the trivalent or hexavalent state. Trivalent chromium (Cr^{+3}) is the most common naturally occurring state; hexavalent chromium (Cr^{+6}) present in the environment are generally the result of industrial and domestic emissions. A maximum acceptable concentration of 0.05 mg/L (50μg/L) for chromium in drinking water has been established on the basis of health considerations. Trivalent chromium, the most common naturally occurring state of chromium, is not considered to be toxic. Toxic effects of chromium in man are attributed primarily to this hexavalent form. BIS (Bureau of Indian Standard), 10500; 2012 have recommended acceptable limit of 0.05 mg /l or 50 μg/l of chromium in drinking water. 36 samples from 12 water quality stations were analyzed. Data reveal that all water quality stations having the chromium concentration below 0.05 mg/L (50μg/L) in river Yamuna.

Iron

Iron is the fourth most abundant element in the earth's crust and the most abundant heavy metal; it is present in the environment mainly as Fe^{+2} or Fe^{+3}. Iron an essential element in human nutrition, is an integral component of cytochromes, porphyrins and metalloenzymes. The ingestion of large quantities of iron results in haemochromatosis. It is a condition in which normal regulatory mechanisms do not operate effectively which leads to tissue damage as a result of the accumulation of iron. Tissue damage has occurred, however, in association with excessive intake of iron from alcoholic beverages in some cases of alcoholism. Iron is generally present in surface waters as salts containing Fe (III) when the pH is above 7.

According to BIS the acceptable limit of Iron is 0.3 mg/L. The occurrences of iron in river water above maximum acceptable limit (>0.3mg/L) have been shown on the table 2. Thirty six water quality samples from 12 water quality stations were analyzed. High concentration of iron > 0.3 mg/l at 9 river water samples during Nov, 2011; Feb, 2012 and June, 2012 was observed. The highest concentration 2.29 mg/l is observed at Agra (P.G.) on river Yamuna. Table 3 shows the name of the water quality stations, river affected by high iron water (>0.3mg/l) and these WQ stations are hot spots from point of view of Iron.

Lead

Lead is the one of the most common of the heavy elements. It has therefore been used extensively since Roman times and, as a result, has become widely distributed throughout the environment. The acceptable limit (AL) for lead in drinking water is 0.010 mg/L (10μg/L). Above the acceptable limit lead is a cumulative general poison, with foetuses, infants, children up to six years of age and pregnant women (because of their foetuses) being most susceptible to adverse health effects. Lead can severely affect the central nervous system. Overt signs of acute intoxication include dullness, restlessness, irritability, poor attention span, headaches, muscle tremor, hallucinations and loss of memory. Signs of chronic lead toxicity, including tiredness, sleeplessness, irritability, headaches, joint pain and gastrointestinal symptoms, may appear in adults. After one or two years of exposure, muscle weakness, gastrointestinal symptoms, lower scores on psychometric tests, disturbances in mood and symptoms of peripheral neuropathy were observed in occupationally exposed populations.
Bureau of Indian Standard (10500, 2012) have recommended a acceptable limit of lead is 0.01 mg/l or 10μg/l in drinking water. In India some rivers have lead concentration above the acceptable limit prescribed by Bureau of Indian Standards, 10500; 2012. Twenty eight samples from 12 water quality stations were analyzed. Agra (P.G.) water quality station was reported to have the highest lead concentration 34.17 μg/L during June, 2012. Six samples have lead greater than maximum desirable limit (10μg/L). Table 3 below shows the name of the water quality stations, river affected by high lead water (>10μg/L) and these water quality stations are hot spots from point of view of lead.

Nickel

The average abundance of nickel in the earth's crust is 1.2 mg/L; in soils it is 2.5 mg/L; in streams it is 1 μg/L, and in groundwater it is <0.1 mg/L. Nickel is obtained chiefly from pyrrhotite and garnierite. It is suspected to be an essential trace element for some plants and animals. The standards of BIS, 10500;2012 for drinking water is 20 µg/L. Mohana water quality station was reported to have the highest nickel concentration 15.53 µg/L during June, 2012. Toxic behavior of river water with respect to nickel was not observed at all water quality stations of Yamuna river. 36 samples from 12 water quality sites have nickel concentration within the acceptable limit (0.02 mg/l or 20 µg/L).

Zinc

Zinc is an essential element for all living things, including man. Zinc-containing proteins and enzymes are involved in every aspect of metabolism, including the replication and translation of genetic material. BIS has recommended 5mg/l acceptable concentration of zinc in drinking water, which can be extended to 15 mg/l in case no alternative source of water is available. If water have zinc concentration of more than 5 mg/l are not suitable for drinking purposes. 36 samples from 12 water quality stations were analyzed for a period of November, 2011; February, 2012 and June 2012. The Zinc concentration varies from 0.01- 55.40 µg/L. High zinc level is found at Mohana water quality site during November, 2011. In the study area all the water quality stations having zinc concentration is well within the acceptable and permissible limits of Bureau of Indian Standard (BIS) and there is no toxicity of Zn in the river water. Zinc is an essential element for human nutrition. The daily requirement is between 4 and 10 mg depending on age and sex, but pregnant women and new mothers may require up to 16 mg/day. Food constitutes the most important source of zinc.

6. CONCLUSION

Metals occur naturally and become integrated into aquatic organisms through food and water. Trace metals such as iron, copper selenium, and zinc are essential metabolic components in low concentrations. However metals tend to bio-accumulate in tissues and prolonged exposure or exposure at higher concentrations can lead to illness. Elevated concentrations of trace metals can have negative consequences for both wildlife and humans. Human activities such as mining and heavy industry can result in higher concentrations than those that would be found naturally.
Comprehensive study of the results reveals that out of 12 water quality stations monitored, water samples collected at 8 water quality stations (Poanta, Kalanour, Mawi, Palla, Auraiya, Etawah, Hamirpur and Pratappur) are found to be within the permissible limit for all purposes. While Delhi R Bridge, Mohana, Mathura and Agra stations were beyond the permissible limit due to presence of cadmium, lead and iron toxic metals.

The contents of metal ions were higher during June month. This may be due to flushing out of the effluent discharge from various industrial units through surface runoff. The concentration of metal ions in Yamuna river water was found much higher than the permissible limits except for cadmium, lead and iron. Delhi is the largest contributor of pollution to the Yamuna River, which receives almost 80 percent of its pollution load through various drains. The untreated sewage with a significant quantity of partially treated sewage, is discharged into the Yamuna River every day. The river receives sewage and industrial wastes through nineteen drains, which join the Yamuna River between Wazirabad and Okhla. It is clear from the results that the Yamuna River is polluted due to some toxic metals. The quality of the Yamuna River water is not safe for domestic use. In order to preserve the quality of river water, effluent discharge from various industries should be treated to an adequate extent.

Table: 2. Trace and toxic metal concentration in Water Quality Sites of river Yamuna

S. No.	Water Quality Sites	Month of Sampling	As	Cd	Cr	Cu	Ni	Pb	Zn	Fe
			µg/L							mg/l
1	**Paonta**	Nov, 2011	2.04	-	4.58	-	3.80	0.09	28.60	0.04
		Feb, 2012	2.73	-	0.95	0.28	1.43	-	23.30	0.04
		June, 2012	1.60	1.00	0.05	4.63	4.63	0.59	0.01	0.02
2	**Kalanaur**	Nov, 2011	2.36	-	3.81	-	6.90	0.07	19.80	0.01
		Feb, 2012	3.38	-	24.75	0.01	1.23	-	33.50	0.18
		June, 2012	1.70	1.02	0.02	1.28	4.83	0.76	0.01	0.03
3	**Mawi**	Nov, 2011	1.71	-	1.26	-	2.23	1.09	29.80	0.01

S. No.	Water Quality Sites	Month of Sampling	As	Cd	Cr	Cu	Ni	Pb	Zn	Fe
			µg/L							mg/l
		Feb, 2012	3.05	-	4.83	1.41	0.78	-	26.10	0.06
		June, 2012	1.38	0.15	0.02	0.39	4.41	3.21	0.02	0.01
4	**Palla**	Nov, 2011	2.38	-	1.79	-	3.08	1.68	30.90	0.08
		Feb, 2012	3.27	-	1.94	2.74	6.44	1.76	31.40	0.17
		June, 2012	1.84	1.02	0.00	1.41	4.47	4.13	0.01	0.02
5	**Delhi Rly Bridge**	Nov, 2011	2.39	-	3.44	2.87	8.69	13.35	44.00	1.20
		Feb, 2012	1.96	0.09	7.24	2.63	8.68	18.31	40.90	1.30
		June, 2012	2.16	7.00	0.10	1.97	12.40	27.45	0.01	1.10
6	**Mohana**	Nov, 2011	4.19	0.03	3.13	-	7.91	3.11	55.40	1.20
		Feb, 2012	6.51	0.03	5.81	5.19	10.85	8.65	39.50	0.95
		June, 2012	4.19	12.10	0.01	2.25	15.53	24.11	0.09	0.80
7	**Mathura**	Nov, 2011	7.81	0.07	2.13	-	1.45	4.95	14.00	0.08
		Feb, 2012	7.55	0.16	4.39	1.38	9.37	5.10	7.50	0.21
		June, 2012	4.26	4.00	0.03	1.52	13.40	34.17	0.03	0.31
8	**Agra (P.G.)**	Nov, 2011	2.51	0.04	46.46	8.81	0.30	-	1.65	2.29
		Feb, 2012	2.60	0.09	3.79	2.88	5.27	3.78	6.70	0.02
		June, 2012	5.68	7.00	0.13	7.09	7.12	24.58	0.09	0.03
9	**Auraiya**	Nov, 2011	2.62	0.07	22.12	6.95	0.28	-	0.14	0.25
		Feb, 2012	2.15	0.33	1.48	2.64	5.60	2.02	32.90	0.06
		June, 2012	3.64	1.00	0.10	2.65	5.24	7.01	0.11	0.01
10	**Etawah**	Nov, 2011	2.40	0.06	34.48	8.38	0.27	-	0.57	0.25
		Feb, 2012	2.18	0.24	2.25	2.94	8.03	4.04	23.80	0.02
		June, 2012	8.47	1.20	0.15	6.06	9.50	8.55	0.10	0.04
11	**Hamirpur**	Nov, 2011	2.63	0.06	31.98	6.95	0.32	-	0.29	0.18
		Feb, 2012	3.02	0.16	1.39	2.85	5.88	1.48	16.40	0.05
		June, 2012	3.66	0.23	0.11	1.30	5.10	6.03	0.09	0.02
12	**Pratappur**	Nov, 2011	2.30	0.05	47.28	8.43	0.42	-	1.08	0.22
		Feb, 2012	2.10	0.02	2.07	2.35	3.89	2.09	33.80	0.04
		June, 2012	2.34	2.99	0.12	2.34	4.14	4.69	0.08	0.01

Table 3 : Water Quality Hot Spot in River Yamuna

S. No.	Name of the Water Quality Sites	Month of Sampling	Cd	Pb	Fe
			µg/L		mg/l
1	**Delhi Rly Bridge**	Nov, 2011	-	13.35	1.20
		Feb, 2012	-	18.31	1.30
		June, 2012	7.00	27.45	1.10
2	**Mohana**	Nov, 2011	-	-	1.20
		Feb, 2012	-	-	0.95
		June, 2012	12.10	24.11	0.80
3	**Mathura**	June, 2012	4.00	34.17	0.31
4	**Agra (P.G.)**	Nov, 2011	-	-	2.29
		June, 2012	7.00	24.58	-

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