Assessment of Heavy Metals in Summer & Winter Seasons in River Yamuna Segment Flowing through Delhi, India

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Abstract

In the present investigations, monitoring of seasonal variations in the concentrations of heavy metals (Pb, Fe, Zn, Mn, Cd, Co, Cu, Cr and Ni) in the Yamuna river water flowing through Delhi have been carried out during the year 2011. Yamuna River, Delhi segment has been chosen for this study as Delhi is a major industrial centre in the country, leading to addition of loads of contaminants into the river Yamuna.   For this purpose, sampling was done from ten selected study sites (most likely to be affected by industrial & anthropogenic activities) during two seasons i.e. summer (May) and winter (January). The technique of Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS) was used to determine the concentration of heavy metals in the water samples in both the seasons. Results have shown wide variations in the heavy metal levels varying from high concentration during summer and low concentrations during winter season. The concentrations of Pb, Cd, Cr, Cu, Zn and Co were found to be under the permissible limits of ICMR, CPCB, WHO and EPA. Elevated concentrations of Fe, Ni & Mn were found at Boat club, Yamuna Bazar, Nigambodh Ghat, Delhi old Bridge, ITO, Nizamuddin Bridge & Mayur Vihar. Also, Pb, Cd, Cu and Co have shown significant variation ($p<0.05$) in their concentration between summer and winter

seasons, with less accumulation during winter and high during summers. High heavy metal concentration during summer may be attributed to increased water temperature during summer that may result in increased metal toxicity. The high levels of heavy metal at these sites can be related to the untreated industrial discharge, lead battery-based industrial units, vehicular pollution & surface run-off from contaminated areas.

Keywords: Heavy metals, Yamuna River pollution, Seasonal variations, River water analysis, industrial pollution, Metal toxicity, Bio-accumulation

1. Introduction

In the recent years, heavy metal toxicity has grown up as a serious concern all over the world, as these heavy metals pose adverse effects on all forms of living organisms in the biosphere. These heavy metals are not readily degradable in the environment and accumulate in the animal and human bodies to a very high toxic levels leading to undesirable effects. The increased population and the progress in agriculture and industry, in the recent years, have further complicated this situation (Giguere *et al*., 2004). The discharge of untreated or partially treated industrial waste waters containing heavy metals into the water bodies, especially rivers, prevail in aquatic bodies and get bioaccumulated along the food chain. Biomagnification of these heavy metals along the food chains occurs leading to various health hazards to both humans and other living organisms. Heavy metals affect the structural, biological functioning of biomolecules (McCormick *et al*., 2005). They are also known to interfere with synthesis & metabolism of the hormones (Manjappa and Puttaioh, 2005; Riddell *et al*., 2005; Gupta *et al*., 2009). The River Yamuna also considered as prominent and sacred as the great 'River Ganga' itself, is the leading branch of River Ganga. The key tributary of river originates from the Yamunotri glacier (Saptrishi Kund) near Bander punch peaks 380 59' N 78027'E) in the Mussoorie range of the lower Himalayas in Uttarkashi district of Uttaranchal and also commended as a 'sacred river'. Various religious centers of Yamunotri (Uttaranchal), Paonta Sahib (Himachal Pradesh), Mathura, Vrindavan, Bateshwar and Allahabad (all in Uttar Pradesh), are situated at the banks of Yamuna River. Large urban centers, including, Yamuna Nagar, Sonepat, Delhi, Gautam Budh Nagar, Faridabad, Mathura, Agra and Etawah are also established on its banks. Industrialization has occupied most part of the Yamuna bank. Also, due to its soil fertility, Yamuna River basin is most widely used for agriculture production. Yamuna water after proper treatment is supplied for domestic activities and untreated water is used for various agricultural activities. Population density, Industrialization, Urbanization & agricultural activities in & around the Delhi region, have deteriorated the quality of Yamuna River to maximum extent that affects the aquatic biodiversity & impact on the public health also. Therefore, the present investigations have been carried out to assess the heavy metals concentration of Pb, Fe, Zn, Mn, Cd, Co, Cu, Cr and Ni in the Yamuna river water flowing through the city of Delhi during two seasons viz. summer (May) and winter (January). Similar kind of studies have already carried out by several workers all over the world (Sehgal *et al*., 2012; Chakrabarty and Sarma, 2011; Puthiyasekar *et al*., 2010; Dan'azumi and Bichi, 2010; Ahmed *et al*., 2010; Pandey *et al*., 2010; Borah *et al*., 2009; Kaushik *et al*., 2009; Huang *et al.,* 2008; Gaur *et al*., 2005; Neal *et al*., 2000; Zereen *et al*., 1999; etc.).

2. Material and Methods

2.1 Sampling Area

These investigations were performed in summer season & winter season in 2011 for the ten selected sites of river Yamuna flowing through Delhi: Loni Border; Wazirabad Pump House, Sonia Vihar; Sur Yamuna Ghat, Wazirabad; Boat club, Yamuna Bazar 3; Nigam Bodh Ghat;

Delhi Old Bridge; Income Tax office (ITO); Nizammudin Bridge; Mayur Vihar and Okhla Barrage. The location map of the ten selected sites is presented in the Figure 1.
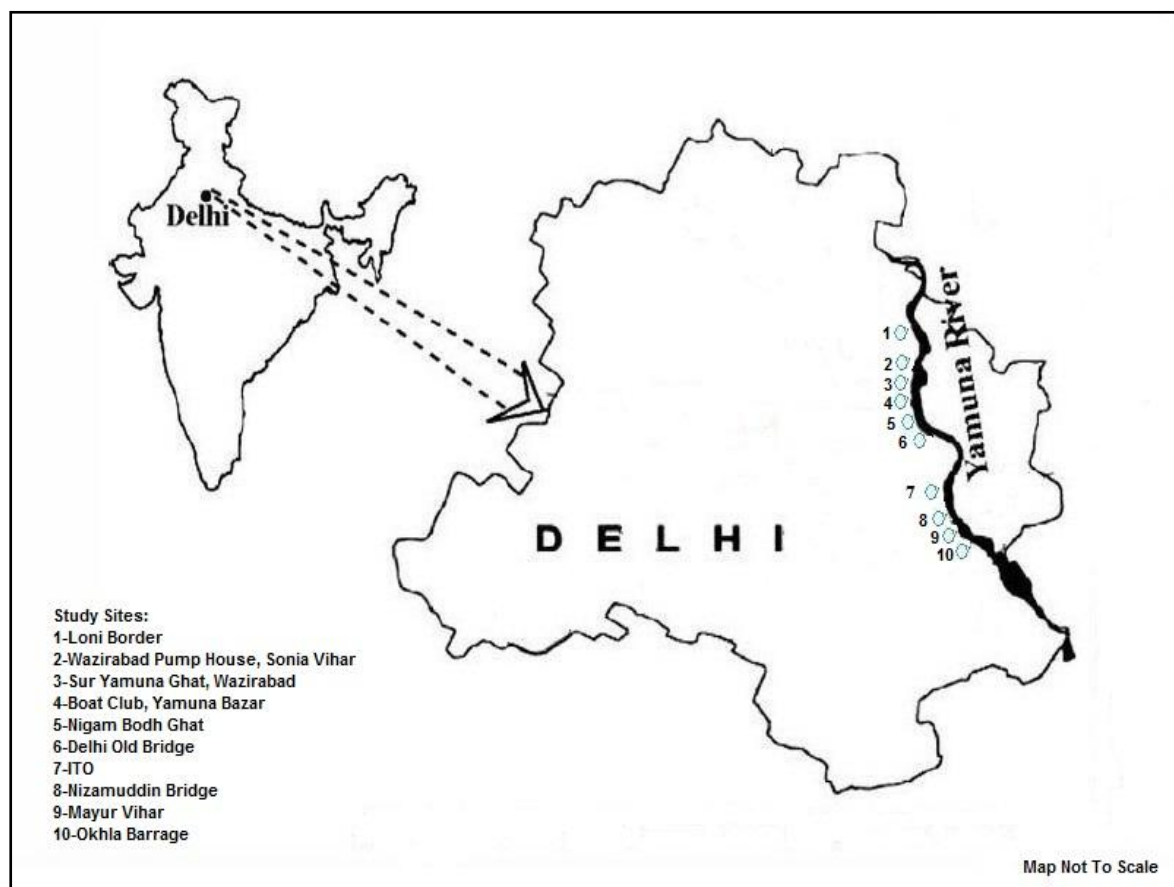
Figure 1. Map showing the location of the ten selected sampling spots

2.2 Sample Collection

Water samples were collected in triplicates from the ten sampling stations during the year 2011 for two seasons i.e. summer (May) and winter (January). The water sampling was done in high grade plastic bottles. The bottles were dipped into the river water and after being filled, they were capped tightly, inside the river water, itself.

The following sampling spots were selected for present investigations:

1=Loni Border; 2=Wazirabad Pump House, Sonia Vihar;   3=Sur Yamuna Ghat, Wazirabad; 4=Boat Club, Yamuna Bazar;   5=Nigam Bodh Ghat; 6=Delhi Old Bridge; 7=ITO; 8=Nizamuddin Bridge; 9=Mayur Vihar; 10=Okhla Barrage.

2.3 Sample Precautions

All the glassware was carefully rinsed before use to avoid contamination of the samples. Sampling cans and bottles should be rinsed with de-ionized water and soaked in 3% HNO_3 for 24 hours. After the acid bath the bottles for storing of precipitation samples should be rinsed thrice and then filled with 1% HNO_3 and stopped. Also, the sampling bottles were

rinsed thrice with de-ionized water, dried, stopped and packed in two clean plastic bags with zip-locks. The rings and filter supports from the filter packs were soaked in 1% HNO_3 for 12 hours, rinsed properly with de-ionized water. Autosampler tubes and cups were also rinsed with de-ionized water, soaked in 1% HNO_3 for minimum 12 hours and rinsed thrice with de-ionized water before use.

2.4 Heavy Metal Analysis

Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS) method was used for the assessment of heavy metal concentrations at all the ten selected spots. During these investigations, total of nine elements viz. Pb, Fe, Zn, Mn, Cd, Co, Cu, Cr, Ni were determined for each water sample (i.e. ten study spots X two seasons i.e. summer and winter).

2.5 Principle

ICP-MS is a technique where ions produced in inductively coupled plasma, are separated in a mass analyser and detected. The sample solution is fed into a nebulizer by a peristaltic pump. The nebulizer converts the liquid sample into a fine aerosol that is transported into the plasma by an Air gas flow, most often called carrier gas or nebulizer gas. With an ordinary pneumatic nebulizer, only 1-2% of the sample reaches the plasma. In the plasma the sample is evaporated, dissociated, atomised and ionised to varying extent. The produced positive ions and molecular ions are extracted into the mass analyser. A simple quadruple gives a resolution of 1 amu or more at a peak width of 10% of the peak height. The ions are separated by mass to charge ratio (m/z) and measured by a channel electron multiplier. Methodology followed for ICP-MS technique was same as described by Montaser, 1998.

2.6 Statistical analysis

Data obtained were statistically analyzed at 5% level of significance by using one-way ANOVA.

Estimation

3. Result and Discussion

Pb, Cu, Co & Cd have shown significant variation ($p<0.05$) in their concentration in summer and winter seasons, with less accumulation during winter and high during summers. No significant variation in the concentrations of Cr, Fe, Ni, Mn, Zn were observed during summer and winters, but the seasonal pattern for all the heavy metals was same i.e. high values during summer and low values during winter season [Figures 2-10].

Also, Pb, Cd, Cr, Cu, Zn and Co concentrations were within the permissible limits of ICMR, CPCB, WHO and EPA when compared with table1.

Table 1. Prescribed limits for heavy metals concentration in water

Standards	Pb	Fe	Zn	Mn	Cd	Co	Cu	Cr	Ni
ICMR(mg/L)	0.1	0.3	5	0.1	0.01	NA	0.05	0.05	0.02
CPCB(mg/L)	0.1	3	5	2	2	NA	3	2	3
WHO(µg/L)	15	300	3000	100	3	40	2000	50	20
EPA(µg/L)	15	300	5000	50	3	---	1300	100	---

Lead (Pb): Pb poisoning causes gastrointestinal, neuromuscular (known as lead lapsy) and central nervous system disorders. It can also cause liver and kidney damage, reduced haemoglobin formation and infertility and birth defects.
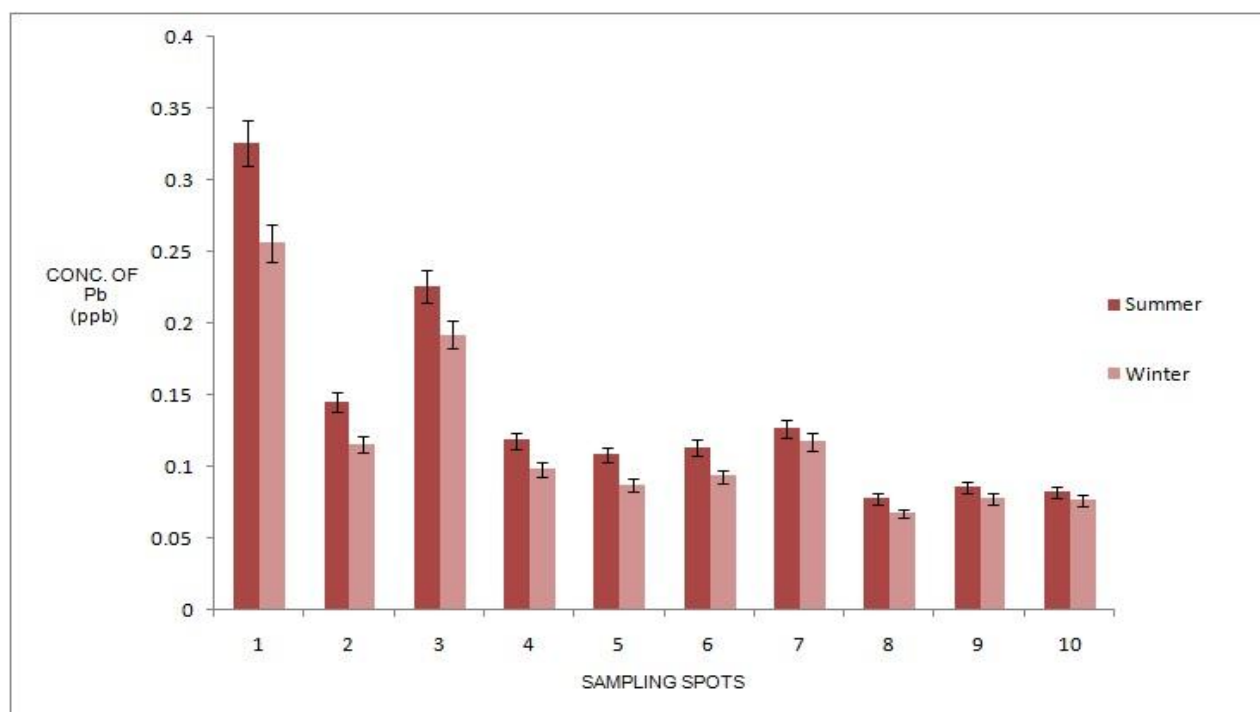
Figure 2. Concentration of Pb at ten selected sampling spots of Yamuna River, Delhi, in summer & winter season

The Pb concentration varied from 0.077-0.326 ppb, with a mean of 0.141 ppb during summer and from 0.067-0.256 ppb, with a mean of 0.118 ppb during winter season (Figure.2). The high concentration of Pb in the river water can be related to the lead-based battery making industrial units across the Delhi's industrial areas & also through vehicular emissions. In some cases, Pb is used to stabilize the land pipes/plastic pipes that results in Pb contamination of the drinking water (Pillai, 1983).

Iron (Fe): High level of Fe results in nausea, vomiting, brain haemorrhage, anxiety, tension, cardiac arrest, metabolic disorder.
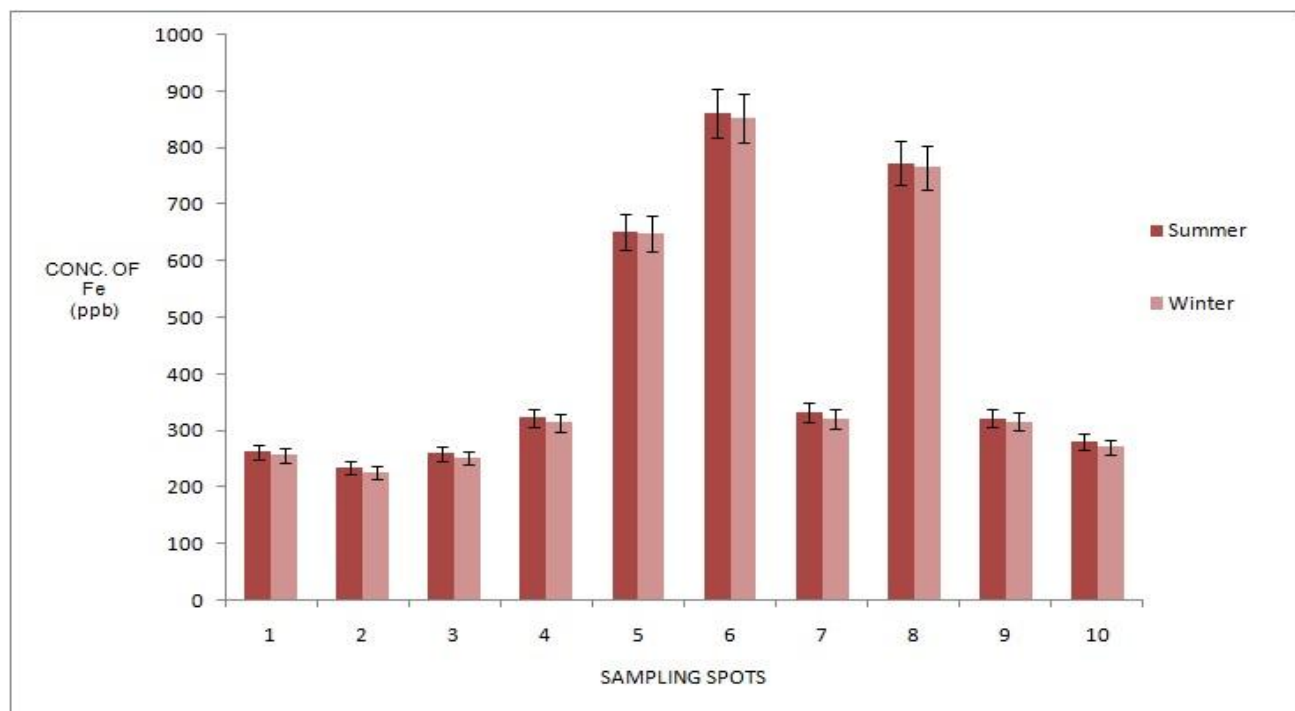
Figure 3. Concentration of Fe at ten selected sampling spots of Yamuna River, Delhi, in summer & winter season

Fe concentrations were found to be extremely high in the river water during seasons, ranging from 233.235-861.266 ppb, mean of 429.581 ppb during summer season and ranging from 224.589-852.074 ppb, mean of 421.908 ppb during winter season. Boat Club, Nigam Bodh Ghat, Delhi Old Bridge, ITO, Nizamuddin Bridge and Mayur Vihar showed the presence of elevated concentrations of Fe (Figure.3). Higher levels of iron at these sites could be due to the fact seeped through soil and entered the river along with the rainwater run-off.

Zinc (Zn): Zn is involved in various physiological and metabolic activities of many organisms. But increased level of Zn can cause many health disorders (Pillai, 1983). The sources of Zn into the water bodies could be effluents of electroplating industries, sewage effluents (Boxall *et al*., 2000; Dean *et al*., 1972). Reddy *et al*., 2012, while assessing the water quality of Hussainsagar Lake, have mentioned that the Zn concentration probably increased in the Lake body due to the immersed idols painted with multicolor.
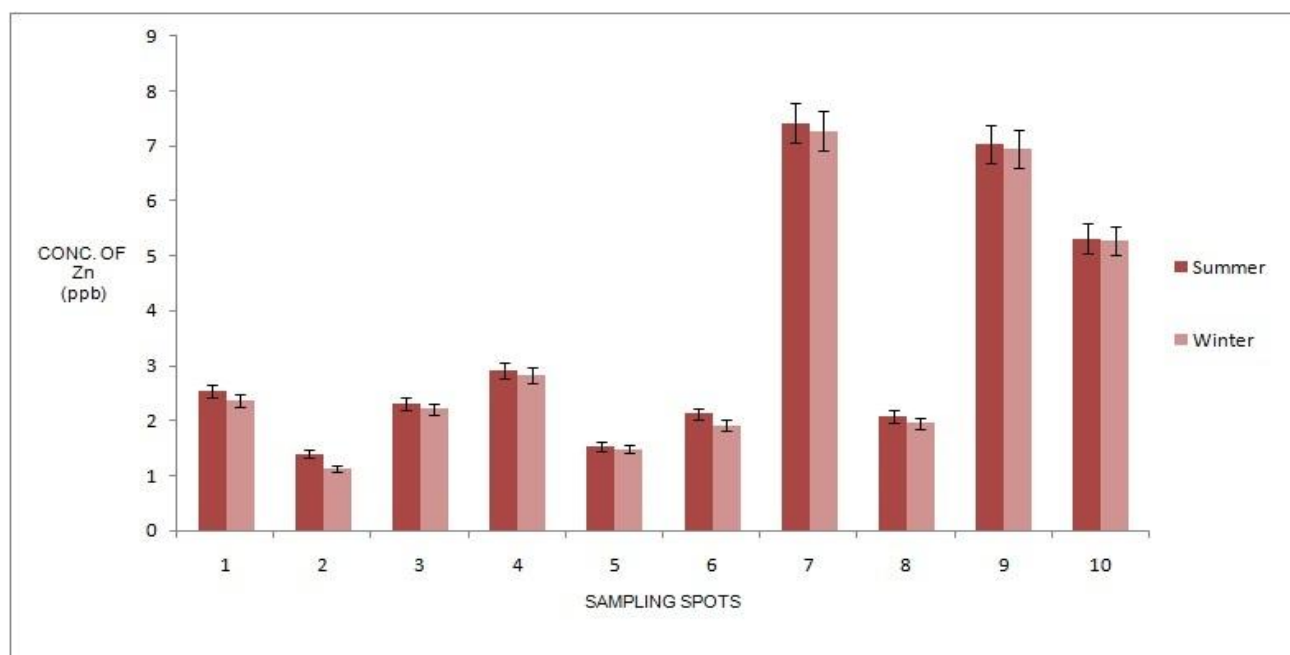
Figure 4. Concentration of Zn at ten selected sampling spots of Yamuna River, Delhi, in summer & winter season

Zn was found in the range of 1.393-7.426 ppb and the mean was found to be 3.467 ppb during summer season and in the winter season, the range was 1.139-7.27 ppb and the mean was 3.338 ppb (Figure.4).

Manganese (Mn): High concentration of Mn results in kidney failure, lever & pancreas malfunctioning but its optimum concentration is very much essential for respiratory enzymes connective tissues developement (Underwood, 1977).
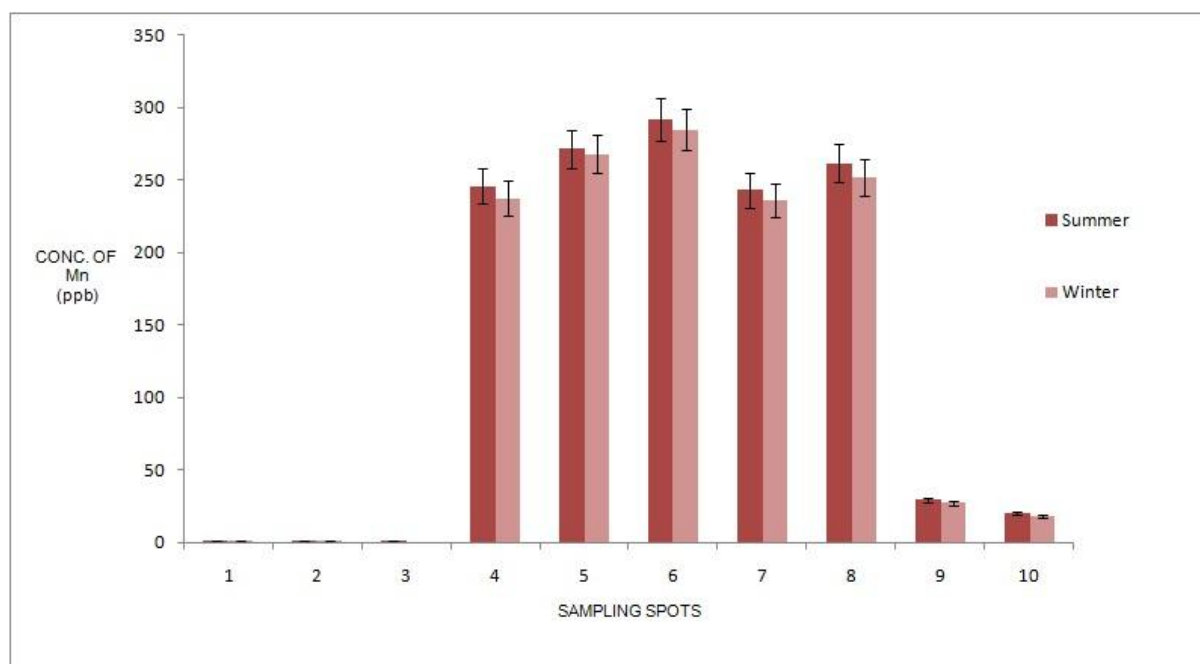
Figure 5. Concentration of Mn at ten selected sampling spots of Yamuna River, Delhi, in summer & winter season

Mn was in the range of 0.992-291.78 ppb (mean=136.671 ppb) during summer season and 0.0851-285.15 ppb (mean = 132.624 ppb) during winter season The sites of Boat Club, Nigam Bodh Ghat, Delhi Old Bridge, ITO, Nizamuddin Bridge also showed the elevated Mn concentration (Figure.5). Mn levels were found above the IS-105000 levels and were highest at Wazirabad Barrage and Okhla Barrage. This observation may be linked to the industrial units situated at Wazirpur, Badli and Jhilmil vicinity, where, steel processing industries are common & these industries discharge their treated and untreated waste water into the various drains which further meet the river Yamuna at Wazirabad Barrage. Mn is frequently found in iron-bearing waters and is present most frequently as a manganous ion. Mn can also enter the river through industrial effluents from steel industries (Sehgal *et al*., 2012).

Cadmium (Cd): Cd is a poisonous metal and can cause serious health problems even if ingested in small concentration. It has the tendency to get accumulated in the body tissues that results in lung problems and kidney damage (Fleischer *et al*., 1974; Friberg *et al*.,1974). Effluents from industries like battery making, dye making, pigment making, alloy making are the major sources of Cd into the water bodies (Rao and Yoshida, 2004). Cd concentration varied from 0.024-0.044 ppb, mean of 0.031 ppb during summer and 0.018-0.035 ppb, mean of 0.024 ppb during winter (Figure.6).
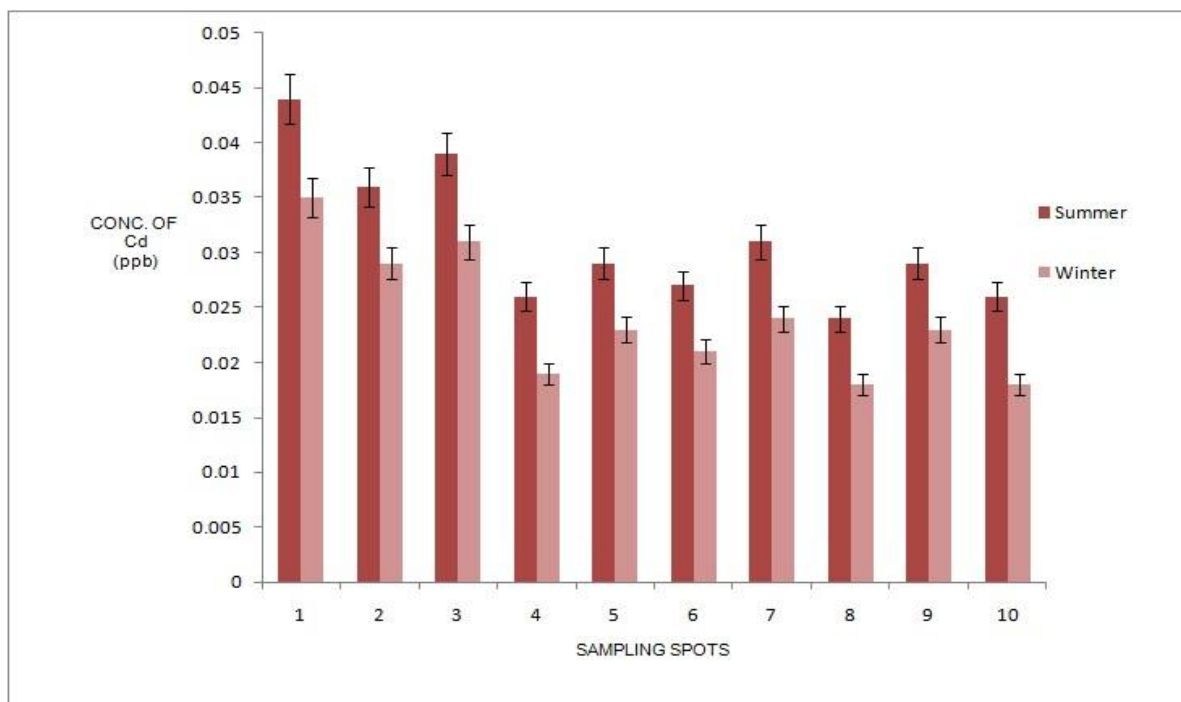
Figure 6. Concentration of Cd at ten selected sampling spots of Yamuna River, Delhi, in summer & winter season

Cobalt (Co): Earlier research findings confirm that Co is carcinogenic in nature. In low concentration, it causes vomiting, weakness, giddiness, lack of concentration, hearing impairment, thyroid problems, memory loss & cardiovascular disease. Co enters the water bodies from the effluents coming from industries dealing with corrosion and wear-resistant alloys. The other sources of Co contamination are colors and pigments used to color glass and ceramic objects, lithium-cobalt batteries and permanent magnets. Petroleum based industries are also the cause of Co contamination into the environment.
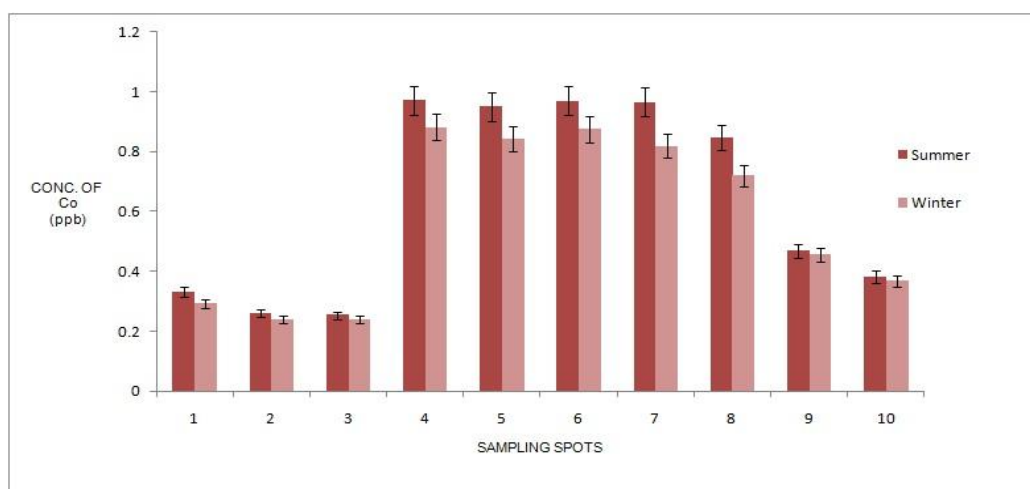
Figure 7. Concentration of Co at ten selected sampling spots of Yamuna River, Delhi, in summer & winter season

The range for Co was 0.254-0.972 ppb and 0.24-0.881 ppb during summer and winter respectively and the mean was found to be 0.640 ppb and 0.574 ppb during summer and winter season, respectively (Figure.7). Decreased water level during summer seasons may be responsible for increased Co level. This can also be related with the increased water temperature during summers that depletes the dissolved oxygen & amplify the toxicity.

Similar type of study have already conducted by Sehgal *et al*., 2012 to estimate the concentrations of heavy metals in the Yamuna River in the Delhi segment, starting from Wazirabad Barrage till the Okhla Barrage by selecting different spots. Sen *et al.,* 2011 found high concentrations of heavy metals (Ca, K, Mg, Na and P) in fish of Yamuna River indicating that the Yamuna River is highly contaminated with heavy metals. It was found out that the probable sources of heavy metals in the river may be caused by various industry outlets which come to the river.

Copper (Cu): Cu is an essential nutrient. At lower concentrations, Cu ions cause headache, nausea, vomiting and diarrhea and at high concentrations, it causes anemia, gastrointestinal disorder & also leads to liver and kidney malfunctioning in extreme cases. (USEPA, 1999).
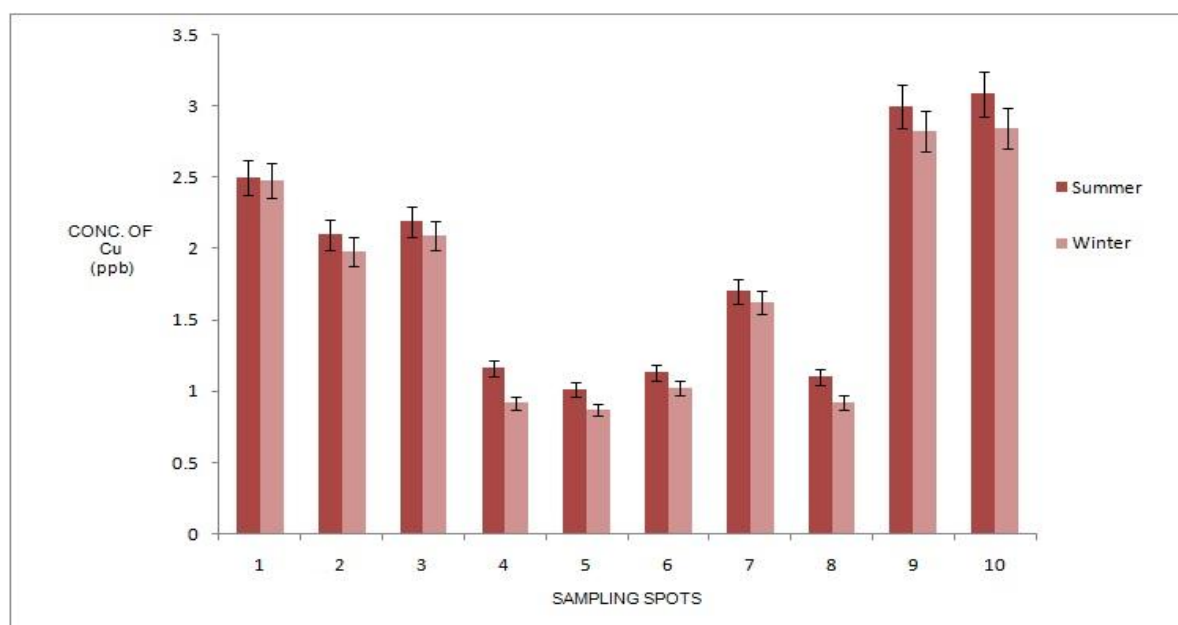
Figure 8. Concentration of Cu at ten selected sampling spots of Yamuna River, Delhi, in summer & winter season

The concentrations for Cu ranged from 1.011-3.087 ppb and 0.871 to 2.85 ppb during summer and winter season, respectively, and the mean values were 1.898 ppb and 1.759 ppb for summers and winters respectively (Figure.8).

Chromium (Cr): Research says that Cr (+6) gets adsorbed through intestinal tract at a higher rate than than Cr (+3). Therefore, Cr (+3) is found to be less toxic than Cr (+6). Also, Cr (+6) gets converted in to Cr (+3) under natural environment, thereby reducing the toxic impact of Cr discharges. Epidemiological studies have shown that some Cr components have carcinogenic effects (Moore and Ramamoorthy, 1984).

Cr is used by stainless, tool and alloy steel, heat and corrosion resistant materials, alloy cast iron, pigments, metal plating, leather tanning industries.
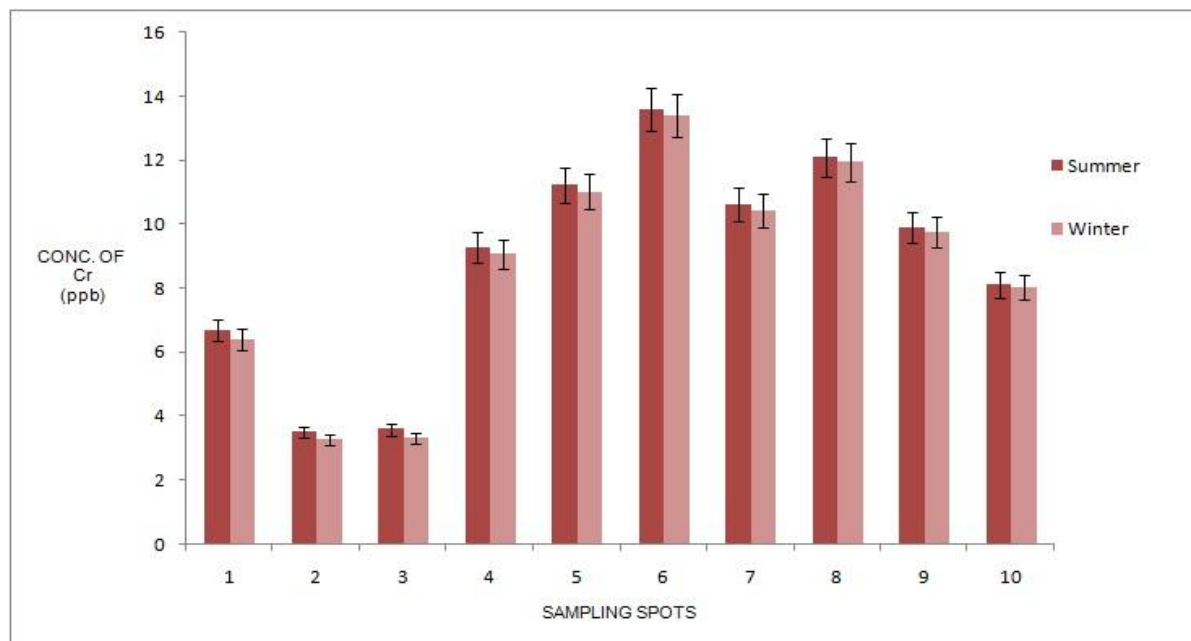
Figure 9. Concentration of Cr at ten selected sampling spots of Yamuna River, Delhi, in summer & winter season

The maximum and minimum Cr concentration values for summer were 13.58 to 3.5 ppb, with a mean of 8.856 ppb, and that of winter were 3.245 to 13.424 ppb, with a mean of 8.661 ppb (Figure.9). The presence of Cr in the Yamuna River is attributed to electroplating industries situated in Wazirabad, Badli and Mangolpuri areas. High level of Cr in the industrial effluents has already been reported by Rawat *et al.* (2003).

Nickel (Ni): Symptoms of nickel toxicity include skin rash (called nickel dermatitis), giddiness, diarrhea & other health problems like contact with nickel vapor can lead to swelling of the brain and liver; degeneration of the liver; irritation to the eyes, throat and nose; and various types of cancer. Nickel toxicity sources are cocoa plant foods (nuts) and hydrogenated oils. Stainless steel manufacturing, electroplating, coal and oil combustion also release Ni as their effluents. Industries dealing with electrical equipment and household appliances, catalysts, pigments, batteries (NiCad) are also sources of Ni contamination in the water bodies.
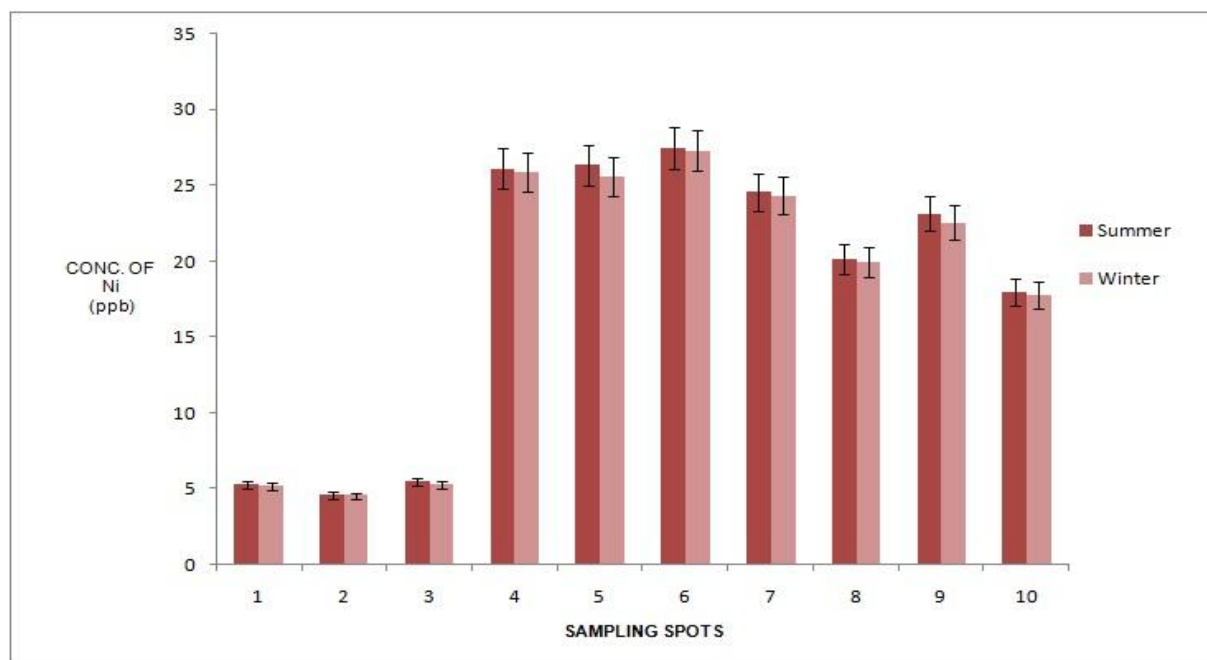
Figure 10. Concentration of Ni at ten selected sampling spots of Yamuna River, Delhi, in summer & winter season

Ni lied between 4.559-27.487 ppb, with an average of 18.092 ppb, during summer and 4.515-27.296 ppb, with an average of 17.821 ppb, during winter season (Figure.10). The elevated levels of Ni were found at the sites of Boat Club, Nigam Bodh Ghat, Delhi Old Bridge, ITO, Nizamuddin Bridge and Mayur Vihar. Ni must have entered these sites through various industrial processes & other domestic activities. Dumping of municipal sewage into the river Yamuna can also lead to elevated Ni in the river. Higher concentrations of Ni at the site of Boat Club, Yamuna bazaar, was present as this site is used for idol immersion of God and Goddesses during the festival of Vinayaka Chathurthi, Durga Puja and Saraswati Puja. These idols contain multicolored paints, which contain Ni.

4. Conclusion

Fe, Ni, Mn have shown elevated levels of heavy metals at Boat Club, Nigam Bodh Ghat, Delhi Old Bridge, ITO, Nizamuddin Bridge and Mayur Vihar. A possible reason for this could be the industrial effluents, as the industrial areas of Delhi contain various metal and ferro alloy industries. The increased levels of heavy metals in the water lead to accumulation of heavy metals in the agricultural soils and plants grown on these contaminated soils, leading to great harm to humans and animals. Hence, it is obligatory to rectify the various heavy metals resources which lead to addition of these metals into the river bodies. In addition, water should be tested regularly to keep an eye on the heavy metal pollutant into the water and purify the water, if necessary.

5. Further Investigations

As the heavy metals enter the food chain and get accumulated at each level from producers to consumers. As the water of Yamuna River is widely used for agricultural activities at the sites of ITO, Mayur Vihar and Nizammudin Bridge, therefore, further, investigations are in progress to test the heavy metal concentration in soil and in various crops being grown in these areas. Further, we would like to determine some interventions that could reduce heavy metal contamination in the food crops. This work will increase awareness among producers, consumers and policy makers (as currently there is no regulatory system to test heavy metals in food crops).

Acknowledgements

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