Monitoring of Seasonal Variations in Heavy Metals Concentration in Sirhind Canal, Moga, Punjab, India

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ABSTRACT---- ***During these investigations, water samples were collected from ten different sites of Sirhind Canal along its course in Moga Region, Punjab, India in summer & winter season. The purpose to select this Canal for present research is as very little work has done on water quality analysis of this. Increasing population, Urbanization & Industrialization along its course has been deteriorating the water quality of the Canal. Eight heavy metals (As, Cr, Cu, Fe, Mn, Ni, Pb & Zn) analyzed have shown significant variations in their concentration between summer & winter seasons at ten different study sites. Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) was used to estimate 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 all the heavy metals were found to be under the permissible limits of ICMR, CPCB & WHO except Cr that has elevated levels at some study sites. Increased concentrations of Fe, Cr, Cu & Mn at some sampling spots make the situation troublesome. Also, Fe, Cu & Cr have shown significant variation ($p<0.05$) in their concentration between summer and winter season. In contrast, As, Pb & Zn have shown less variations in both the seasons.***

Keywords---- Heavy metal pollution, Water analysis, Water pollution, Sirhind Canal.

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1. INTRODUCTION

Natural as well as anthropogenic activities both are responsible for heavy metal occurrence in environment. Heavy metals chemistry differs significantly from the organic pollutants. All heavy metals, including those that are essential micronutrients (e.g. copper, zinc etc.) are toxic at high concentrations. Some heavy metals can be harmful to human health even in very low concentrations. Some heavy metals get accumulated in the food chain and continue its cycle by passing from one organism to another through the food chain, the process known as biomagnification. Biomagnification of heavy metals along the food chain occurs leading to various health hazards to both humans and other living organisms & affect the structural, biological functioning of biomolecules [1]. Since metals act as endocrine disruptors, they can interfere with metabolism, synthesis, and transport of hormones or receptors [2-4]. During these investigations, eight heavy metals *(*As, Cr, Cu, Fe, Mn, Ni, Pb & Zn) were studied in Sirhind Canal along its course in Moga, Punjab, in summer and winter season. The concentrations of all the heavy metals were found to be under the permissible limits of ICMR, CPCB & WHO except Cr that has elevated levels at some study sites. Similar kind of studies on heavy metal estimation have conducted by various workers [5-10] on different water bodies that have shown the adverse effects of increased heavy metal concentration on the environment.

2. MATERIALS & METHODS

2.1 Sampling Area

2.1.1 Geographical Location

Sirhind canal in Punjab, India, opened in 1882. It consists of an extensive canal system that irrigates more than 2,000 square miles (5,200 square km) of farmland. The system's headworks, where it draws its water, are on the Sutlej River at

Ropar, near the border of Himachal Pradesh state. From there the canal runs west-southwest to Doraha, where it splits into three branches. One flows west and then northwest to rejoin the Sutlej near the Pakistan border; one runs southwest past Bhatinda to the border of Rajasthan state; and the third flows southeast to Patiala. There are many distributaries, in addition to the three principal branches. The Sirhind Canal was completed by 1887. It irrigated 728,424 hectares in the districts of Firozepur, Ludhiana and parts of the princely states of Patiala, Nabha, Faridkot, Jind, Malerkotla and Kalsia. During this study, samples were collected in summer season & winter season in 2012 for the ten selected sites of Sirhind River flowing through Moga, Punjab: Raunta, Mardi Mustafa, Bhaga Purana, Sivian, Daatewala, Langian, Bhalour, Phulewalan, Ranian & Daudhar.

2.2 Sampling

Water samples were collected in triplicates from the ten sampling stations during the year 2012 for two seasons i.e. summer (April) and winter (November). Polyethylene bottles were used to collect the water samples. The bottles were tightly closed after being filled & stored at room temperature. 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.

2.3 Methodology

Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) method was used for the assessment of heavy metal concentrations at all the ten selected spots. During these investigations, total of eight elements *viz.* As, Cr, Cu, Fe, Mn, Ni, Pb & Zn were determined for each water sample in both seasons.

2.3.1 Principle

The sample is exposed to the extremely high temperature of argon plasma (up to 10,000 K) that breaks the sample into atoms, ionizes these atoms, and electronically excites the resulting ions. When the excited electrons in these ions fall back to lower energy levels, they emit light. The wavelengths of light emitted by a particular element serve as a "fingerprint" for that element. Therefore, by measuring the wavelengths of light emitted by the sample, elements in the sample can be identified; and by measuring the amount of light emitted by a particular element in the sample, the concentration of that element can be identified.

2.3.2 Method

The sample solution is pumped by a peristaltic pump into the nebulizer where it is broken into an aerosol of fine droplets by a fast stream of argon gas. From the nebulizer it passes through the spray chamber (which eliminates the larger droplets) and on to the quartz plasma torch. The plasma ionizes and excites the atoms of the sample. Emitted light from the ions in the plasma then passes through the entrance window to the monochromator where it is separated into its various wavelengths. The monochromator is a high-resolution "Echelle" design that makes use of both a diffraction grating and a prism to generate a two-dimensional pattern of individual wavelengths of light. This light hits the charge-coupled device (CCD) detector where thousands of individual picture elements capture the light and turn it into a digital signal that can be measured. Data obtained were statistically analyzed at 5% level of significance by using one-way ANOVA.

3. RESULTS & DISCUSSION

These scientific findings on seasonal variations (summer & winter seasons) in Sirhind Canal, Moga (Punjab) have shown significant variations in heavy metal concentration indicating the severity of pollution load in this River. Heavy metal analysis of As, Cr, Cu, Fe, Mn, Ni, Pb & Zn was done to analyze the pollution impact.

3.1 Results

Arsenic (As): Arsenic compounds are released during mining, weathering of rocks, soils and spread throughout the environment. Arsenic concentrations in groundwater are particularly high in areas with geothermal activity. In aquatic ecosystems inorganic arsenic derived from rocks such as arsenic trioxide, orpiment, arsenopyrite, most prevalent. Arsenic is very important compound as it plays a role in protein synthesis. The total amount of arsenic in a human body is about 0.5-15 mg. Many arsenic compounds are easily excreted and humans can develop resistance to certain arsenic compounds. Drinking limit for arsenic is 10µg/L. Excessive intake of arsenic results in to organ damage, hair fall, skin pigmentation, nausea, vomiting, diarrhoea, cyanosis, cardiac arrhythmia, hallucinations, depression, numbness & sleeping disorders& in some cases skin cancer also.

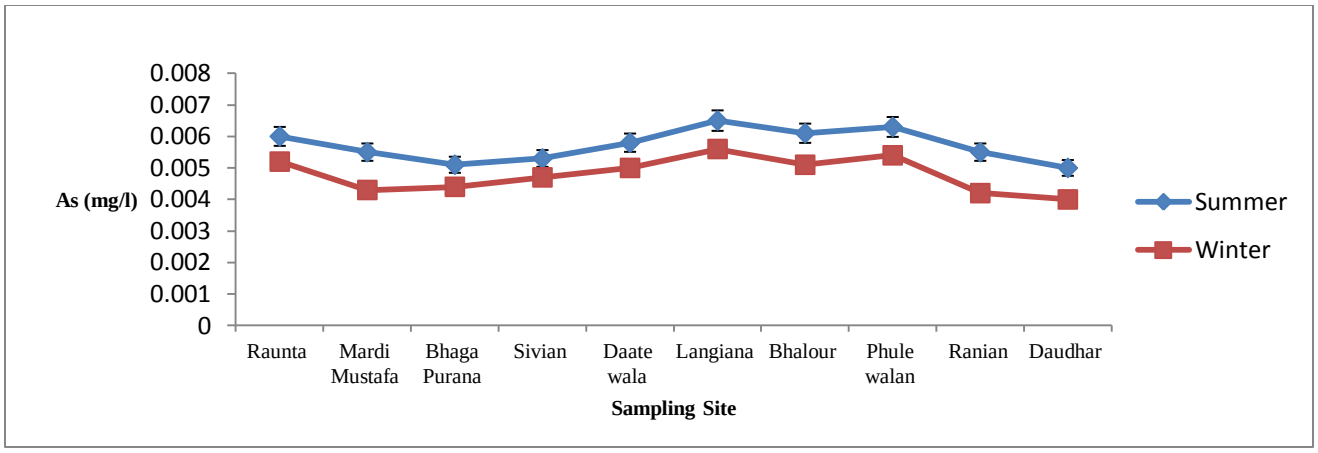

Figure 1: Seasonal Variations in As concentration in ten selected sites of Sirhind Canal, Moga, Punjab, India

In this study, Arsenic has shown highest concentration at Langian followed by Phulewal, Bhalour & Raunta and minimum concentration at Daudhar both in summer as well as in winter season.

Chromium (Cr): Chromium compounds can be found in waters only in trace amount. Most commonly chromium mineral is chromite. The element and its compounds can be discharged in surface water through various industries as it is applied for example for metal surface refinery and in alloys. In dissolved form chromium is present as either anionic trivalent $Cr(OH)_3$ or as hexavalent CrO_4^{2-}. Trivalent chromium is a dietary requirement for a number of organisms. It removes glucose from blood in conjugation with insulin. Chromium deficits may enhance diabetes symptom s. Hexavalent chromium is found to be very much toxic to flora and fauna. It causes cancer, diarrhoea, stomach and intestinal bleedings, cramps, liver, kidney& respiratory tract damage.

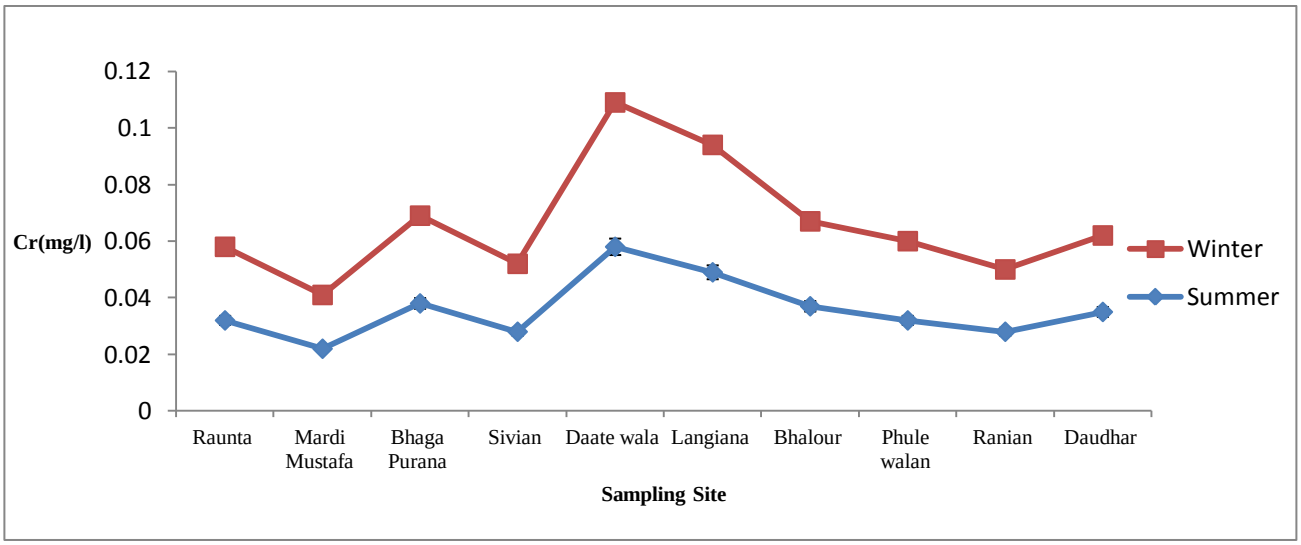

Figure 2: Seasonal Variations in Cr concentration in ten selected sites of Sirhind Canal, Moga, Punjab, India

In this study, Cr has shown maximum concentration at Daatewal followed by Langian, Bhaga Purana and minimum concentration at Mardi Mustafa in both summer as well as in winter.

Lead(Pb): Under normal conditions (at 20°C), elementary lead does not dissolve in water. It may however occur dissolved in water as $PbCO_3$ or $Pb(CO_3)_2^{2-}$. Lead frequently binds to sulphur in sulphide form (S^{2-}), or to phosphor in phosphate form (PO_4^{3-}). In these forms lead is extremely insoluble, and is present as immobile compounds in the environment. Lead

compounds are generally soluble in soft, slightly acidic water. Both organic as well as inorganic lead is toxic in nature. Lead poisoning includes colics, skin pigmentation and paralysis. Organic lead causes necrosis of neurons. Inorganic lead causes axonal degeneration and demyelination. Lead enters in to the food chain & causes biomagnification. According to WHO, permissible limit of Pb in drinking water is 10 ppb.

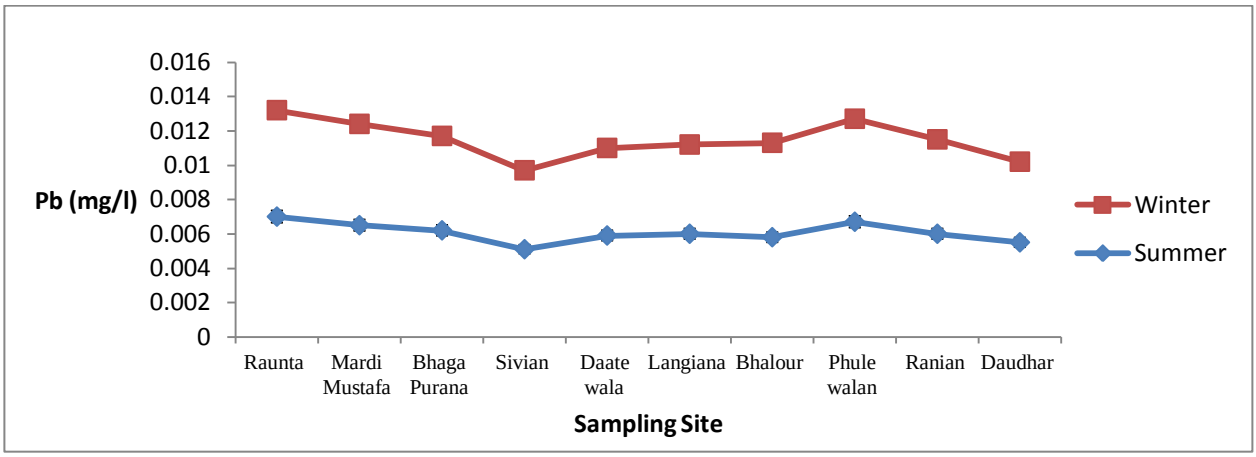

Figure-3: Seasonal Variations in Pb concentration in ten selected sites of Sirhind Canal, Moga, Punjab, India

In this study, Pb has shown highest concentration at Raunta followed by Phulewal, Murdi Mustafa, Bhaga Purana and minimum at Sivian in both the seasons.

Iron (Fe): Under normal conditions, elementary iron dissolves in water under normal conditions. Naturally occurring iron oxide, iron hydroxide, iron carbide and iron penta carbonyl are water insoluble. The water solubility of some iron compounds increases at lower pH values. Iron is a dietary requirement for most organisms, and plays an important role in natural processes in binary and tertiary form. Fe carries fresh oxygen from lungs to other parts of body and takes back Co_2 to lungs where it can be breathed out. Iron deficiency leads to anaemia, tiredness, headache, loss of concentration, weak immune system. In young children its deficiency affects mental development and causes concentration disorder.

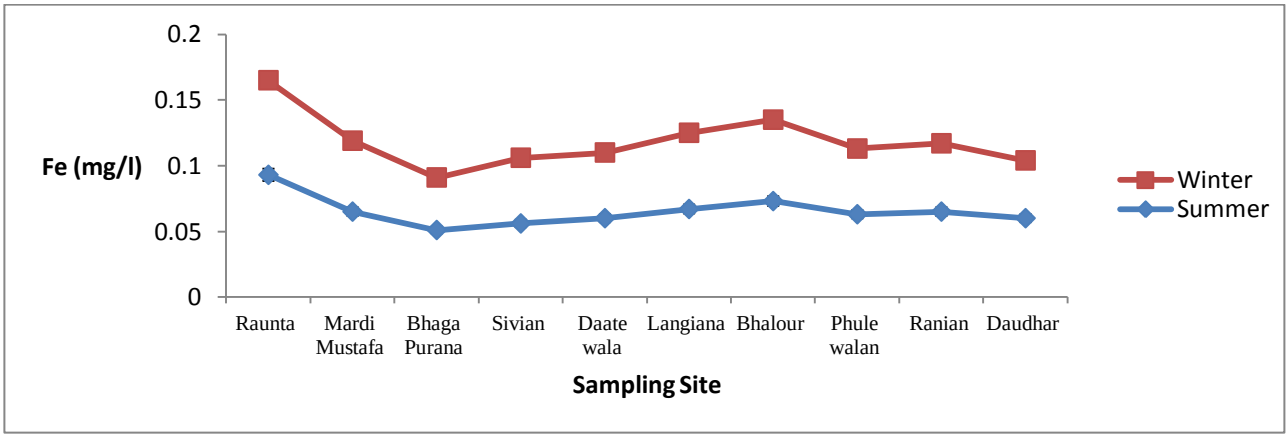

Figure 4: Seasonal Variations in Fe concentration in ten selected sites of Sirhind Canal, Moga, Punjab, India

In this study, it has inferred that Fe has shown maximum value at Raunta followed by Bhalour, Langian, Murdi Mustafa and minimum at Bhaga Purana in both summer as well as in winter.

Zinc (Zn): Elementary zinc is insoluble in water at neutral pH. Zinc dissolves in water as $ZnOH^+$ (aq) or Zn^{2+} (aq). Zinc as zinc hydroxide ($Zn(OH)_2$ forms a protective, water insoluble layer& causes a milky turbidity in water in higher concentrations. Sometimes, Zn may add an unwanted flavor to water. Zinc is a dietary mineral for humans and animals & is responsible for mainly enzymatic processes and DNA replication. Daily intake of 2-3g is recommended. Zn deficits cause tastelessness and loss of appetite. Overdoses (4-8g) may negatively influence human and animal health. Excessive intake of

Zn results in to nausea, vomiting, dizziness, colics, fevers and diarrhea.

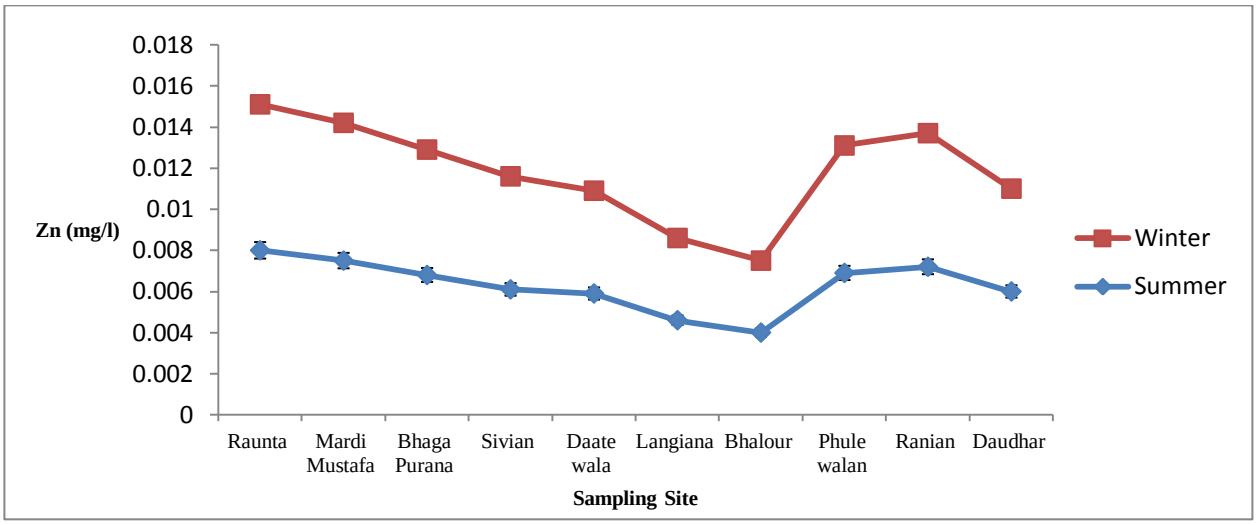

Figure 5: Seasonal Variations in Zn concentration in ten selected sites of Sirhind Canal, Moga, Punjab, India

In this study, Raunta has shown highest concentration of Zn followed by Mardi Mustafa, Ranian, Phulewal and low concentration at Bhalour in both the seasons.

Copper (Cu): The presence of copper in water is complex and influenced by pH, dissolved oxygen and the presence of oxidizing agents and chelating compounds or ions. In pure water, the copper (II) ion is the more common oxidation state. Copper is an essential nutrient. At high doses it has been shown to cause stomach and intestinal distress, liver and kidney damage and anemia [11]. Acute Cu toxicity causes headache, nausea vomiting, gastrointestinal irritation, haemorrhage, haemolysis, multiorgan dysfunction syndrome. Cu could increase in the water bodies due to the inflow of sewage and intense ecotourism boating activity [12].

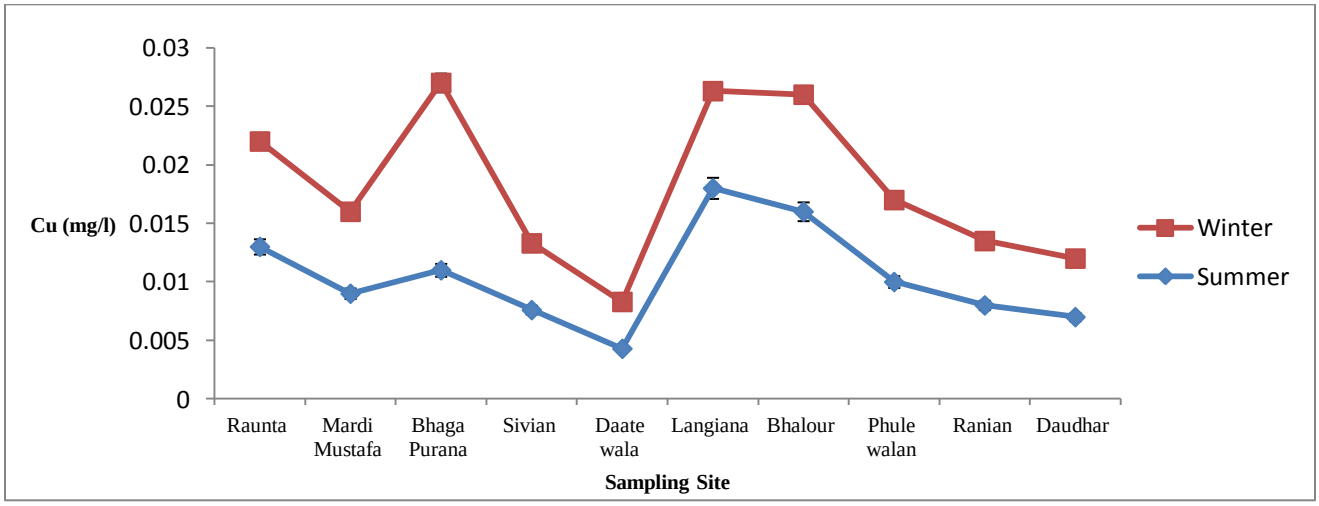

Figure 6: Seasonal Variations in Cu concentration in ten selected sites of Sirhind Canal, Moga, Punjab, India

In this study, Langian has shown highest Cu concentration followed by Bhalour, Raunta, Bhaga Purana in summer.. In winter, Bhaga Purana has shown the highest Cu concentration. Daatewal has shown minimum concentration in both the seasons.

Manganese (Mn): Mn is a vital micronutrient and contributes to the normal development of connective tissues, besides being necessary for respiratory enzymes. It is present in high concentrations in mitochondrial fraction of human kidney, liver, and pancreas. Manganese is used principally in the manufacture of iron and steel alloys and manganese compounds and as an ingredient in various products.

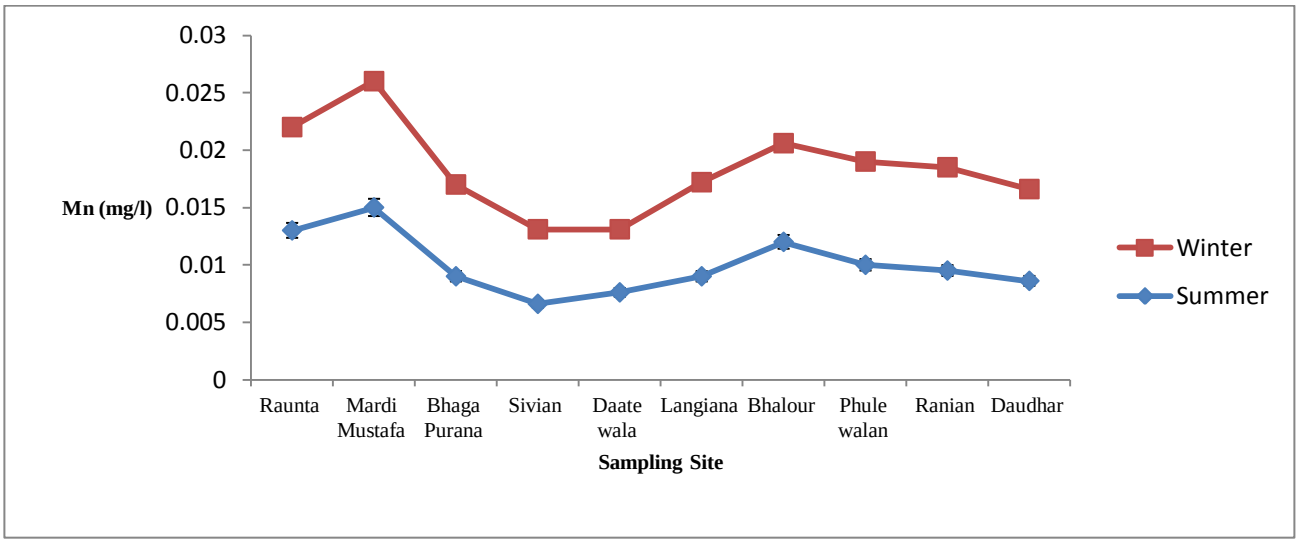

Figure 7: Seasonal Variations in Mn concentration in ten selected sites of Sirhind Canal, Moga, Punjab, India

In this study, Mn has shown highest concentration at Mardi Mustafa followed by Raunta, Phulewal in both the seasons. Mn concentration was minimum at Sivian in summer whereas in winter, it was minimum at Daate wala.

Nickel (Ni): Nickel is a compound that occurs in the environment only at very low levels. Humans use nickel for many different applications. The most common application of nickel is the use as an ingredient of steal and other metal products. It can be found in common metal products such as jewelry. Food items naturally contain small amounts of nickel. Chocolate and fats are known to contain severely high quantities. Smokers have a higher nickel uptake through their lungs. High level of nickel results in lung cancer, nose cancer, larynx cancer and prostate cancer, respiratory failure.

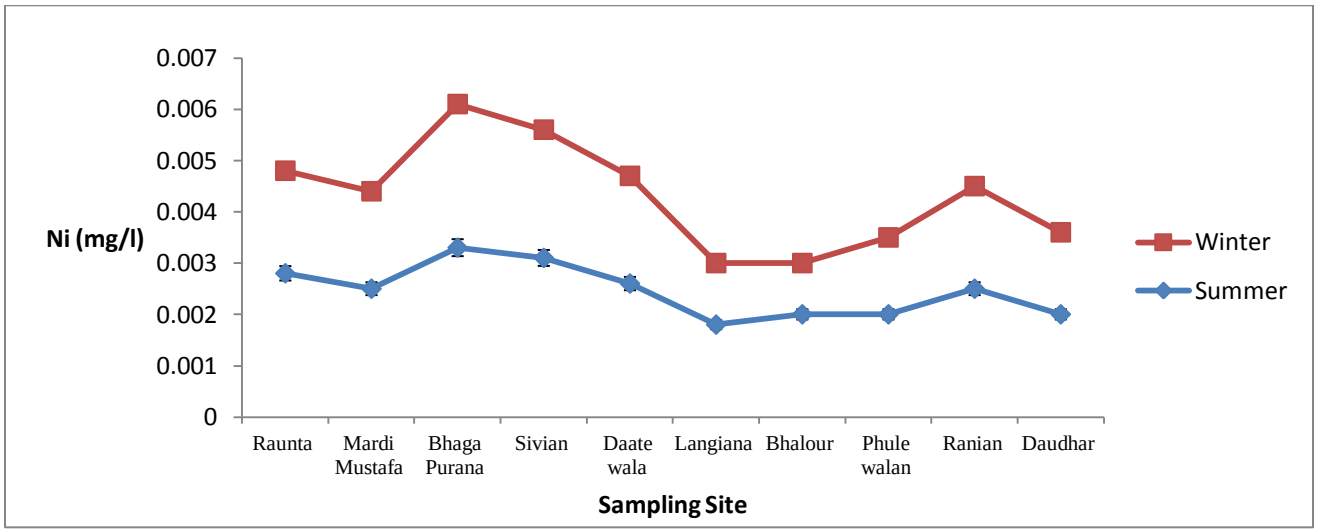

Figure-8: Seasonal Variations in Ni concentration in ten selected sites of Sirhind Canal, Moga, Punjab, India

In this study, maximum concentration of Ni was at Bhaga Purana followed by Sivian and Raunta in both the seasons but minimum concentration was at Langian in summer and at Bhalour in winter.

3.2 Discussion

During these investigations, results obtained were compared with the permissible limits given by [13-15].

Table 1: Permissible limits for heavy metals concentration in water

Standards	As	Pb	Zn	Mn	Fe	Co	Cu	Cr	Ni	Mn
ICMR(mg/l)	.05	0.1	5	0.1	0.3	NA	.05	.05	.02	.01
CPCB(mg/l)	.05	0.1	5	2	3	NA	3	2	3	2
WHO(µg/l)	NA	15	3000	100	300	40	2000	50	20	100

Therefore, in this study, significant variations were observed in the concentration of all heavy metals (As, Cr, Cu, Fe, Mn, Ni, Pb, Zn) at all the ten study sites with less accumulation during winter season and high during summers. As, Pb and Zn have shown little variations in their concentrations during summer and winters. Considerable variations were observed in the concentration of Fe, Cu & Cr during both seasons but the seasonal pattern for all the heavy metals was same i.e. high values during summer and low values during winter season [Figures1-8].

Fe has shown the highest concentration in both the seasons among all the heavy metals studied varied from 0.040-0.093 mg/l followed by Cr (0.019-0.058 mg/l), Cu (0.005-0.015 mg/l), Mn (.005-.015 mg/l), Zn (.0035-.0080 mg/l), Pb (.0046-.007 mg/l), As (.004-.0065 mg/l) & Ni (.001-.0031 mg/l). The maximum concentration of Fe, Zn & Mn was found at Raunta. Cr has shown maximum concentration at Daatewal but the concentration of Cu was low at this sampling spot. Concentration of Ni was highest at Bhaga Purana but Fe has shown low value at this spot. Likewise, Mn concentration was highest at Mardi Mustafa but Cr concentration has shown low value at this spot. Therefore, it can be said that all the heavy metals have shown significant variations ($p<0.05$) in its concentration at some points between summer & winter season. Also significant variations ($p<0.05$) have been observed among some study sites within the same season. Increased concentration of Fe, Cr & Cu is a matter of concern. Presence of Fe is responsible for brownish red colour of the water when allowed to stay for some time [16]. High concentration of Cr can be due to the presence Cr in detergents & soaps. Industrial waste can be one of the major reasons for increased Cu concentration. Increase in the concentration of heavy metals during summer seasons could be due to drought and decrease in water level. Also, increase in temperature during summer also increases toxicity due to depletion in dissolved oxygen, increase in energy demand causing rise in respiration rate in the organism, which leads to rapid assimilation of waste [17].

4. CONCLUSION

It has concluded that considerable variations have observed in the concentration of some heavy metals (Fe, Cr, Cu & Mn) in summer & winter seasons. These elevated levels of heavy metals can be attributed to industrial effluents, bathing, washing clothes along the River bank. Though all the parameters have shown values within permissible limits as given by WHO, still the increased concentration of these heavy metal may be threat to aquatic life, vegetation & man-kind because these heavy metals in water further contaminate the agricultural, enters into food chain & leads to the process of biomagnification. Therefore, steps should be taken to treat the effluent before discharging it in to any adjacent water body.

5. ACKNOWLEDGMENT

Authors are indebted to Punjab Agricultural University, Ludhiana, Punjab, India, for providing all the technical/practical support & friendly guidance for this experimentation.

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