# Seasonal Variations in Heavy Metal concentration in Groundwater of District Kangra, Himachal Pradesh, India

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*Abstract*: Research findings on Heavy metal analysis have shown seasonal variations in heavy metal concentration in groundwater of Kangra district, H.P., India, consecutively for both years (2014-2016). Groundwater samples were collected during Pre-monsoon, Rainy and Post-monsoon seasons for two years from 2014-15 & 2015-16 from the selected 17 sampling spots of kangra district. Heavy metals viz. B, Fe, Zn, Mn, Pb, Cu, Ni, Cr & Cd were estimated by using atomic absorption spectroscopy. Groundwater samples from seventeen prominent sampling spots of Kangra district were analysed for seasonal variations for two years. During these investigations, no traces of Copper (Cu), nickel (Ni), Chromium (Cr) and Cadmium (Cd) were found at selected sampling spots during all seasons. Significant variations were observed in concentration of B, Fe, Zn & Mn among most of the sampling spots during all the seasons at 5% level of significance (<0.05) consecutively for both years. Though the heavy metal concentration was found to be within permissible limits; yet increasing concentration of B, Fe & Zn in drinking groundwater could pose a serious threat on public health in the coming years. Correlation coefficient were also analysed to find out the correlation among various heavy metals studied.

# Index Terms—Seasonal variations, Heavy metals, Groundwater analysis, Boron, Iron, Zinc, Manganese, Lead

### I. INTRODUCTION

Groundwatercan be polluted by heavy metals leaching from industrial and consumer waste; this could be further aggregated by acid rain releasing heavy metals trapped in soils. Toxic heavy metals causebioaccumulation in organisms, as they are hard to metabolize. The concentration of these heavy metals increases at each level from producers to consumers and leads to the process of biomagnification. Heavy metal carries harmful effects on the living beings by distorting their biological functions [1].

A large number of studies have been done on heavy metal analysis of surface water and groundwater all over the worldby various researchers [2-11]; a very little work has been done on ground water analysis seasonal variations of Kangra district, Himachal Pradesh; considering these facts, current investigations were carried out to evaluate the groundwater quality of the region. Heavy metal toxicity has been aggregated by Modern agricultural and industrial practices [12]. Though heavy metals are essential for life when prsent in traces but it may pose serious health problems if taken in excess amounts.Increasing population, Industrialization & Urbanization has led to the introduction of heavy metals in to the environment that by agricultural run-off and leaching out, contaminate the soil & pollute the surface as well as groundwater [13-15].As metals are endocrine disruptors, they also disturb the synthesis, metabolism and transport of hormones or receptors [16-17].

# **II. MATERIALS AND METHODS**

Samples collected from the 17 selected sampling spots (S1-S17) of Kangra district, in high-grade polyethylene bottles, are given below:

S1=Shahpur, S-2=Samlana, Jawali, S-3=Indora, S-4=Mata Rani Chowk, Haripur,

S-5=Sukka Talab Chowk, Haripur, S-6=Garli, S-7=Sapadi, S-8=Jawalaji, S-9=Dehra,

S-10=Nagrota Bagwan, S-11=Dharamsala, S-12=Bod, S-13=Thural, S-14=Baijnath,

S-15=Chougan, Bir, S-16=Palampur, S-17=Main Bazar Kangra

Sampling spots were selected on the basis of accessibility in all seasons of the year and availability of facilities to take water samples. During these investigations, the entire chemicals used were of analytical grade. In the study, nine elements, B, Fe, Zn, Mn, Pb, Cu, Ni, Cr & Cd were studied for each groundwater sample during Pre-monsoon, Rainy & Post-monsoon season consecutively for two years.

Heavy metals were estimated by Atomic Absorption Spectrophotometery method. Absorbance was recorded for each sample. Standard solutions of metals were prepared for the calobration curve. Absorbance of the samples was then compared with the calibration curve to get the concentration of the heavy metals. Statistical analysis was done by using One-Way-ANOVA at 5% level of significance. Correlation coefficient was also calculated to understand the relationship among various haevy metals.

## **III. RESULTS AND DISCUSSION**

Heavy metal Analysis of groundwater of selected spots of Kangra district for two years (2014-2016) has given the following results:

### **3.1 Boron (B)**

Boron is very much essential in maintaining a good balance of sex hormones, estrogen and testosterone and helps our bodyto absorb magnesium in better way. Exposure to large amounts of boron over short periods of time can cause many health problems in human beings.





Figure 3.1 (a) shows that in 2014-15, boron concentration varied from 0.028 to 0.537 ppm during Pre-monsoon season. In rainy season, boron varied from 0.015 to 0.066 ppm whereas during Post-monsoon season it varied from 0.023 to 0.165 ppm. Boron concentration was found to be highest during Pre-monsoon season.

In 2014-15, boron concentration was found to be highest at Sampling spot S-5 (0.537 ppm) followed by S-1 (0.271 ppm) & S-4 (0.24 ppm) during Pre-monsoon. Boron concentration was found to be lowest at S-16 (0.028 ppm). During rainy season, boron concentration was found to be highest at Sampling spot S-8 (0.066 ppm) followed by S-14 (0.054 ppm) & S-6 (0.047 ppm). Boron concentration was found to be lowest at Sampling spot S-10 (0.015 ppm). During Post-monsoon, boron has shown maximum concentration at S-8 (0.165 ppm) followed by S-5 (0.1 ppm) & S-17 (0.097 ppm). Boron has shown minimum concentration at S-13 (0.023 ppm) during Post-monsoon. During these investigations, insignificant variations were found in boron concentration among sampling spots S-10, S-13 & S-16 during rainy season.



Figure-3.1 (b): Seasonal variations in B concentration of groundwater samples during Pre-monsoon, Rainy &Post-monsoon in district Kangra, H.P. (2015-16)

Figure 3.1 (b) shows that in 2015-16, boron concentration of groundwater samples varied from 0.066 to 0.541 ppm during Pre-monsoon season. Boron concentration varied from 0.018 to 0.74 ppm during Rainy season whereas during Post-

monsoon season it varied from 0.023 to 0.175 ppm.In 2015-16, boron concentration was observed maximum at Sampling spot S-5 (0.541 ppm) followed by S-1 (0.277 ppm), S-4 (0.248 ppm) during Pre-monsoon. Boron concentration was found to be lowest at S-10 (0.066 ppm). During rainy season, boron concentration was found to be highest at Sampling spot S-5 (0.74 ppm) followed by S-8 (0.068 ppm) & S-14 (0.057 ppm). Boron concentration was found to be lowest at Sampling spot S-10 (0.018 mg/l). During Post-monsoon, boron concentration has shown maximum concentration at S-8 (0.175 ppm) followed by S-5 (0.16 ppm) & S-17 (0.15 ppm). Minimum boron concentration was observed at S-15 (0.023 ppm).During these investigations, insignificant variations were found in boron concentration between sampling spots S-15 & S-16 during Post-monsoon season and sampling spots S-6 & S-17 during rainy season at 5% level of significance (p<0.005).

## 3.2 Iron (Fe)

Iron is an important component of haemoglobin; therefore plays very important role in supplying fresh oxygen to body tissues. The deficiency of iron can augment lead absorption and toxicity. At high concentration, iron can damage the blood vessels and affect the liver and kidneys.



Figure-3.2(a): Seasonal variations in Fe concentration of groundwater samples during Pre-monsoon, Rainy &Post-monsoon in district Kangra, H.P. (2014-15)

Figure 3.2 (a) signifies that in 2014-15, Fe concentration varied from 0.1 to 3.56 ppm during Pre-monsoon season. In rainy season, boron varied from 0.1 to 1.2 ppm whereas during Post-monsoon season it varied from 0.15 to 5.6 ppm. Fe concentration was found to be highest during Post-monsoon season. Sampling spots S-1, S-2, S-9, S-10, S-11 & S-14 have shown negligible Fe concentration during all the seasons. In 2014-15, Fe concentration was found to be highest at Sampling spot S-13 (3.56 ppm) followed by S-17 (1.3 ppm) & S-7 (0.54 ppm) during Pre-monsoon. Fe concentration was found to be lowest at S-16 (0.028 ppm). During rainy season, Fe concentration was found to be highest at Sampling spot S-13 (1.2 ppm) & S-4 (0.2 ppm). During Post-monsoon, Fe has shown maximum concentration at S-13 (5.6 ppm) followed by S-17 (2.1 ppm) & S-4 (1.97 ppm). During these investigations, significant variations were found in Fe concentration among most of the sampling spots during rainy season.



Figure-3.2(b): Seasonal variations in Fe concentration of groundwater samples during Pre-monsoon, Rainy &Post-monsoon in district Kangra, H.P. (2015-16)

Figure 3.2 (b) signifies that in 2015-16, Fe concentration varied from 0.047 to 4.5 ppm during Pre-monsoon season. Fe concentration varied from 0.01 to 1.8 ppm during Rainy season whereas during Post-monsoon season it varied from 0.064 to 6.3 ppm. In 2014-15, insignificant Fe concentration was observed at Sampling spot-10 but significant Fe concentration was found at this spot during all the seasons in 2015-16. In 2015-16, Fe concentration was observed maximum at Sampling spot S-13 (4.5 ppm) followed by S-17 (1.5 ppm), S-7 (0.57 ppm) & S-5 (0.47 ppm) during Pre-monsoon. During rainy season, Fe concentration was

found to be highest at Sampling spot S-13 (1.8 ppm) followed by S-7 (0.25 ppm) & S-15 (0.22 ppm). During Post-monsoon, Fe concentration has shown highest concentration at S-13 (6.3 ppm) followed by S-17 (2.4 ppm), S-4 (2.1 ppm) & S-15 (1.9 ppm). During these investigations, significant variations were found in Fe concentration among most of the sampling spots during Post-monsoon season at 5% level of significance (p<0.005).

## 3.3 Manganese (Mn)

Industrial waste, mining and acid mines are responsible for causing Manganese pollution. At higher concentration, it is more toxic to plants than animals.



Figure-3.3(a): Seasonal variations in Mn concentration of groundwater samples during Pre-monsoon, Rainy &Post-monsoon in district Kangra, H.P. (2014-15)

Figure 3.3 (a) represents that in 2014-15, Mn concentration varied from 0.03 to 0.26 ppm during Pre-monsoon season. In rainy season, Mn varied from 0.01 to 0.09 ppm whereas during Post-monsoon season it varied from 0.08 to 0.35 ppm. Mn concentration was found to be highest during Post-monsoon season. Mn was found only sampling spots S-6, S-9, S-12, S-13 & S-15; rest sampling spots have shown negligible Mn concentration during all the seasons. In 2014-15, Mn concentration was found to be highest at Sampling spot S-12 (0.26 ppm) followed by S-15 (0.05 ppm) & S-9 (0.042 ppm) during Pre-monsoon. During rainy season, Mn concentration was found to be highest at Sampling spot S-12 (0.26 ppm) followed by S-15 (0.09 ppm) followed by S-15 (0.025 ppm) & S-9 (0.024 ppm). During Post-monsoon, Mn has shown maximum concentration at S-12 (0.35 mg/l) followed by S-9 (0.16 ppm) & S-13 (0.11 ppm).





As shown in Figure 3.3 (b), in 2015-16, Mn concentration varied from 0.033 to 0.29 ppm during Pre-monsoon season. Mn concentration varied from 0.015 to 0.1 ppm during Rainy season whereas during Post-monsoon season it varied from 0.089 to 0.38 ppm. In 2015-16, Mn concentration was observed maximum at Sampling spot S-12 (0.29 ppm) followed by S-15 (0.055 ppm), S-6 (0.052 ppm) & S-9 (0.048 ppm) during Pre-monsoon. During rainy season, Mn concentration was found to be highest at Sampling spot S-12 (0.1 ppm) followed by S-15 (0.029 ppm) & S-9 (0.026 ppm). During Post-monsoon, Mn concentration has shown maximum concentration at S-12 (0.38 ppm) followed by S-9 (0.19 ppm) & S-6 (0.17 mg/l). Significant variations were found in Mn concentration all the seasons at 5% level of significance (p<0.005).

# **3.4 Lead (Pb)**

Mining activities, industrial effluents, coal and gasoline are main sources of lead pollution. Elevated concentration of lead carries adverse effects on aquatic life and nervous system of animals. Lead could bio-accumulate in humans when ingested with fish. Lead toxicity may cause osteoporosis, anaemia, reproductive disorders & behavioural problems.



Rainy &Post-monsoon in district Kangra, H.P. (2014-15)

Figure 3.4 (a) indicates that in 2014-15, Pb was observed at Sampling spots S-3 & S-8 only during Pre-monsoon, Rainy and Post-monsoon seasons. Highest concentration was observed at S-3 (0.22 ppm) followed by S-8 (0.1 ppm) during Pre-monsoon season. During rainy season, highest concentration was observed at S-3 (0.21 ppm) followed by S-8 (0.12 ppm). Likewise, highest concentration was observed at S-3 (0.26 ppm) followed by S-8 (0.15 ppm) during Post-monsoon season; rest of the spots have shown negligible Pb concentration.



Figure-3.4(b): Seasonal variations in Pb concentration of groundwater samples during Pre-monsoon, Rainy &Post-monsoon in district Kangra, H.P. (2015-16)

Figure 3.4 (b) indicates that in 2015-16,Pb was observed only at Sampling spots S-3 & S-8 only during Pre-monsoon, Rainy and Post-monsoon seasons. Highest concentration was observed at S-3 (0.24 ppm) followed by S-8 (0.17 ppm) during Premonsoon season. During rainy season, highest concentration was observed at S-3 (0.22 ppm) followed by S-8 (0.19 ppm). Likewise, highest concentration was observed at S-3 (0.28 ppm) followed by S-8 (0.21 ppm) during Post-monsoon season; rest of the spots have shown negligible Pb concentration. Permissible limit for Pb is 0.1 ppm for drinking water. In current observations, Pb has surpassed the drinking standards at sampling spots S-3 & S-8 that insists on water treatment technology before using this as drinking water.Data has shown insignificant variations in Pb concentration among all the seasons at 5% level of significance (p<0.005).

# 3.5 Zinc (Zn)

Zinc is one of the most common heavy metal pollutants found in surface & groundwater. Zn is very essential for many metallo-enzymes and toxic to plants at higher levels. At high concentration, Zinc causes structural & behaviour problem in fishes. Zn accumulation in fish causes hypoxia & haematological structures distortion [19-20].



Figure-3.5(a): Seasonal variations in Zn concentration of groundwater samples during Pre-monsoon, Rainy & Post-monsoon in district Kangra, H.P. (2014-15)

Figure 3.5 (a) implies that in 2014-15, Zn was observed at all the Sampling spots during Pre-monsoon, Rainy and Postmonsoon seasons. Highest concentration was observed at S-15 (8.16 ppm) followed by S-14 (2.08 ppm), S-13 (1.7 ppm) and S-5 (1.58 ppm) during Pre-monsoon season. Minimum Zn concentration was found at S-10 (0.03 ppm). During Rainy season, highest concentration was observed at S-15 (5.8 ppm) followed by S-14 (1.2 ppm), S-6 (1.1). Minimum Zn concentration was found at S-10 (0.017 ppm). Likewise, highest concentration was observed at S-15 (11.4 ppm) followed by S-14 (2.85 ppm) & S-13 (2.44 ppm) during Post-monsoon season. Minimum Zn concentration was found at S-10 (0.06 ppm).



Figure-3.5(b): Seasonal variations in Znconcentration of groundwater samples during Pre-monsoon, Rainy & Post-monsoon in district Kangra, H.P. (2015-16)

Figure 3.5 (b) implies that in 2015-16, Zn was observed at all the Sampling spots during Pre-monsoon, Rainy and Postmonsoon seasons. Highest concentration was observed at S-15 (8.2 ppm) followed by S-14 (2.2 ppm), S-13 (1.7 ppm) and S-13 (1.8 ppm) during Pre-monsoon season. Minimum Zn concentration was found at S-10 (0.035 ppm). During rainy season, highest concentration was observed at S-15 (5.9 ppm) followed by S-14 (1.5 ppm), S-6 (1.4). Minimum Zn concentration was found at S-10 (0.02 ppm). Likewise, highest concentration was observed at S-15 (11.8 ppm) followed by S-14 (2.9 ppm) & S-13 (2.5 ppm) during Post-monsoon season. Minimum Zn concentration was found at S-10 (0.06 ppm).

Zn concentration was found within permissible limits at all the sampling spots except at sampling spot S-15. Though it may be extended up to 10 ppm; still during post-monsoon, Zn exceeded the extended limit also.

Zn has shown significant variations in its concentration among all the sampling spots during all the seasons at 5% level of significance (p<0.005).

# 3.6 Cu, Ni, Cr & Cd

During these investigations, no traces of Copper (Cu), nickel (Ni), Chromium (Cr) and Cadmium (Cd) were found at selected sampling spots during all seasons consecutively for both years.

# 3.7 Correlation Matrix of heavy metals

Heavy metals are positively correlated with each other that shows that increase in the concentration of one heavy metal results in to increase in the concentration of another heavy metal except boron that is negatively correlated with Fe & Zn during all the seasons in 2014-15 as well as in 2015-16. Fe has shown positive correlation with PO<sub>4</sub>, K, COD and Zn during all the seasons & negative with all others parameters in 2014-15 as well as in 2015-16. Zn showed positive correlation with COD & Fe consecutively for both years (2014-16) during all the seasons and negative correlation with all other parameters.

# **IV. CONCLUSION**

It has been concluded from these studies that most of the heavy metal have shown their concentration within permissible limits only at most of the selected sampling spots but escalating levels of Fe, Zn, B at some sites is worrisome as the water is

being used for household activities and other domestic purposes; on the other side, negligible concentration of most toxic elements like Cu, Ni, Cr & Cd in groundwater is a sigh of relieve. Though, state pollution control board has set certain guidelines & laws to dispose of the waste in a proper way; these anti pollution laws become ineffective due to improper monitoring system on regular basis. Hence, it is very much advisable for the public living in that region to opt for filtration technique like reverse osmosis before using groundwater for drinking to avoid any deleterious effect on their health.

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