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# Pollution assessment of heavy metals in groundwater and agricultural soil in tailing of Zawar mines, Udaipur, Rajasthan

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## Abstract
Samples of groundwater and agriculture soil were collected from the surroundings of Kanpur Village situated near Zawar Mines, Udaipur to check Pollution Load Index of heavy metals. Kanpur Village is situated at a distance of 1.35 km from the Tailing Dam at Zawar Mines. Four samples each of groundwater and agriculture soil were collected from around the village and investigated for Pollution Load Index (PLI) for two seasons. In pre monsoon the PLI in water ranged between 0.119-0.420 while in post monsoon it ranged from 0.169-0.751. In agriculture soil maximum PLI in pre monsoon was 16.09 and minimum was 10.80 and in post monsoon maximum was 17.78 and minimum 15.0. The aim of the present study is to assess the impact of heavy metal pollution in the form of the Concentration Factor (CF), Pollution Load Index (PLI) and Translocation Factor in water and soil samples obtained from surrounding of Kanpur village and estimate the extent of magnification in food web of the surrounding environment.

**Keywords**
*heavy metal, groundwater pollution, soil pollution, pollution load index, Lead-Zinc mine*

## Introduction

Semi-arid regions of Rajasthan are largely dependent on ground water quality for domestic, irrigation and industrial requirement (Moncur et. al., 2005). Groundwater here is the major source of water supply in both urban and rural areas and its significance for the existence of human society cannot be over ruled (Shyamala et. al., 2008). Groundwater quality is mainly controlled and modified by natural as well as anthropogenic factors. These include point and non-point sources like waste disposal, mining activities, waste treatment works, site leaching, sanitation, cemeteries and many others (Kumar and James, 2013).

Drinking water containing high levels of toxic and essential trace metals like lead, (Pb), Cadmium (Cd), Iron (Fe), Manganese (Mn) and Zinc (Zn) can be hazardous to human health. The contamination of water is directly related to the degree of contamination within ambient environment (Chary *et. al.,* 2008).

Heavy metals in soil have been considered as powerful tracers for monitoring the impact of anthropogenic activities such as industrial emissions, mining activity (purification of mineral, waste deposition and chemicals), vehicular emissions and atmospheric deposition. These lead to accumulation of heavy metals in air and their subsequent deposition into soils (Guo *et. al.,* 2012; Lu *et. al.,* 2012; Soriano *et. al.,* 2012). Heavy metal is among the most dangerous pollutants of anthropogenic origin due to their toxicity and persistence in the environment (Guo *et. al.,* 2012; Koz *et. al,* 2012).

The objective of the present study was to highlight the significance of heavy metals being deposited over ground and soil causing deterioration of soil fertility and groundwater quality. Hence, determination of physiochemical parameters in water and soil along with Contamination Factor (CF) and Translocation Factor

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(TF) of heavy metal in soil and water for both seasons were carried out around Kanpur village. Based on the result, heavy metal assessment index (Pollution Load Index) was calculated to check the magnification of pollution load of heavy metals in soil and then to groundwater by Zn-Pb mine tailing dam. On the basis of this study improvement measures and guidance to environmental planners will be imparted to make an effective management plan in reducing the pollution load of Zawar Mines area of Udaipur.

## Materials and Methods

### Study Area

Kanpur Village, is situated at longitude 73º45'8.57"E and latitude 24º19'44.7"N. The village lies on SE of the tailing dam of Zawar Mines, the distance between tailing dam and the village being about 1.35 km. The difference in elevation between the tailing dam and Kanpur village being 50 m and the flow of leachate take place towards the village.

### Sample collection

Selected sampling points are situated in the area, which is mostly used for drinking, household purposes and irrigation. Before sample collection, the sampling bottles were rinsed 2 to 3 times. Samples were collected from different sites of tailing dam and residential area of Kanpur village. In total three groundwater samples (GW-1, GW-2 and GW-3) were collected from wells which are being used for drinking and agriculture purpose. Two from Kanpur village well-1(GW-2) and Kanpur village well-2(GW-3), one from hand pump (GW-1) and one surface water sample from tailing dam site (TD-1).

Three soil samples were collected from various agriculture fields of Kanpur village S-1, S-2, S-3 and last one (S-4) from near the residential area of village.

Collected samples were preserved at 4°C and taken to the laboratory for analysis. Electrical conductivity (EC) and pH were measured at the site itself by (Globe Digital Water analysis Kit, model 1024 G). Alkalinity, total hardness, total dissolved solids, chloride, calcium and magnesium hardness were determined by titration method. Sulphates were determined by $BaCl_2$ method (spectrophotometric method, Systronics), flame photometer was used in the analysis of Na and K (Flame photometry method, Systronics). Chemical parameters were determined by the standard methods recommended in IS 10500:2012 (Bureau of Indian Standard (2012) and American Public Health Association (APHA 22nd Ed., 2012).

Figure 1 is the map showing Google image of the Zawar Mines area where water and soil sampling stations are located. The map shows clear image of runoff drainage and the position of the Tailing Dam. The image reflects that due to the leachate of tailing in soil, the heavy metal content in soil samples had increased and is contaminated by their deposition. Tested samples show that in pre and post monsoon their concentration differed. Seasonal comparison show heavy metal concentration is high during post monsoon season.

**Figure 1a.** *Google image showing water and soil sampling stations.*

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***Figure 1b.*** *Google image showing drainage direction of leached runoff towards downstream.*

***For heavy metals detection in water samples.*** Water samples were collected in new screw cap, high density polythene bottles (1.5 litres) which were first rinsed two to three times with the water to be sampled and acidified with $HNO_3$ at point of collection. The samples were adequately labelled and were kept at 4°C prior to analysis. For analysis, in 100 ml water sample, 5ml con. HCL and 0.5ml $HNO_3$ was added and reduced to 20ml by heating. The solution was cooled, filtered and made up to 100 ml in standard flask. Absorbance was measured at different wavelengths for different metals. A reagent blank was also prepared and series of 100ml standards for different metals was made by diluting a suitable volume of the standard solution with $HNO_3$ and reading were taken on Atomic absorption spectrometer (Instrument: Varian, Model No.AA280FS). Heavy metals content was measured by using different cathode lamps like Iron (Fe), lead (Pb), Cadmium (Cd), Manganese (Mn) and Zinc (Zn). The analyses were carried out in accordance with the standard procedures specified in IS 10500: 2012 and APHA, 2012.

***For heavy metals detection in soil.*** DTPA-TEA solution (2:1) extractable method was used. Here 10gm of dried soil and 20 mL of extracting solution were shaken for 2 h. Soil extracts (2:1 soil ratio) were obtained with DTPA-TEA (0.005 mol $L^{-1}$ diethylene tri amine penta acetic acid + 0.1 mol $L^{-1}$ triethanolamine + 0.01 mol $L^{-1}$ $CaCl_2$) solution at pH 7.3, filtered and was taken for reading on AAS at different wavelengths as described by Lindsay & Norvell (1978).

***Data analysis.*** Contamination Factor was calculated to examine difference in concentrations of heavy metals. Transfer of heavy metal from water to soil was calculated (TF- Translocation factor) and load of pollution in water and soil was assessed using Pollution Load Index.

***Contamination Factor.*** This calculation is used to evaluate the potential risk of the heavy metals to the environment using the formula given below (Kumar and Edward, 2009):

$$C^i_f = C^i_{0-1}/C^i_n \quad [1]$$

where Ci is the mean concentration of heavy metal from the water samples of the Zawar Mines (at least five).

***Translocation Factor* (TF).** Translocation factor (TF) refers to the accumulation and transfer of heavy metal from water to soil. It was calculated using the equation given by Zacchini *et. al.,* 2009.

$$TF = Soil/Water*100\ (\%) \quad [2]$$

***Pollution Load Index.*** To estimate the water and soil quality, an integrated approach of seasonal pollution load index of the five metals was calculated accordingly to Ali *et. al.* (2016). The PLI is defined as the $n^{th}$ root of the multiplication of the contamination factor of metals:

$$PLI= (Cf_1*Cf_2*------Cfn)^{1/n} \quad [3]$$

where $Cf_1$= Conc. of 1st metal, $Cf_2$= Conc. of $2^{nd}$ metal, Cfn= Conc. of metal n and n= total no. of metals studied.

Therefor PLI value of 0 indicates excellent, a value of 1 indicates the presence of only baseline level pollution and value above 1 indicate progressive deterioration of the site (Tomilson *et. al.,* 1980).

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## Results

Table 1 shows physico-chemical analysis of pre and post monsoon groundwater samples taken from different locations at Kanpur village and tailing dam at the mine. Here most of the water samples values exceed the permissible limits. calcium was high in almost all samples.

| Sr. No. | Parameters | Pre Monsoon TD-1 Tailing Dam water | Pre Monsoon GW-1 Kanpur village HP | Pre Monsoon GW-2 Kanpur village Well-1 | Pre Monsoon GW-3 Kanpur village Well -2 | Post Monsoon TD-1 Tailing Dam water | Post Monsoon GW-1 Kanpur village HP | Post Monsoon GW-2 Kanpur village Well-1 | Post Monsoon GW-3 Kanpur village Well -2 | Mean ± SD (Pre monsoon) | Mean ± SD (Post monsoon) | Permissible Limit as per IS 10500:2012 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. | pH | 8.25 | 7.80 | 7.0 | 8.25 | 8.0 | 7.3 | 7.2 | 7.73 | 0.58±0.29 | 0.37±0.18 | Nr |
| 2. | Conductivity at 25°C | 1411 | 1655 | 2792 | 1574 | 1695 | 1690 | 590 | 3890 | 705±352.3 | 1384±692 | - |
| 3. | Total Hardness ($CaCO_3$) (mg/l) | 650 | 760 | 1520 | 770 | 775 | 900 | 1540 | 1090 | 400±200 | 400±200 | 600 |
| 4. | Total dissolved solids (mg/l) | 975 | 1170 | 2191 | 1123 | 1160 | 1318 | 2190 | 1557 | 703±352 | 453±226 | 2000 |
| 5. | Sulphates as $SO_4$ (mg/l) | 520 | 611 | 1187 | 480 | 620 | 624 | 1188 | 754 | 329.5±165 | 268±134 | 400 |
| 6. | Alkalinity as $CaCO_3$ (mg/l) | 160 | 230 | 400 | 320 | 190 | 330 | 360 | 340 | 105±52.3 | 78±39.0 | 600 |
| 7. | Magnesium as Mg (mg/l) | 108 | 127 | 202 | 120 | 128 | 106 | 182 | 129.6 | 43±21.2 | 33±16.2 | 200 |
| 8. | Calcium as Ca (mg/l) | 80 | 96 | 272 | 108 | 96 | 184 | 312 | 220 | 89.4±45 | 89.4±45 | 100 |
| 9. | Chlorides as Cl | 63 | 87 | 130 | 77 | 75 | 100 | 125 | 140 | 29±14.4 | 29±14.2 | 1000 |
| 10. | Fluoride as F (mg/l) | 0.1 | 0.25 | 0.8 | 0.5 | 0.40 | 0.9 | 1.6 | 1.2 | 0.30±0.15 | 0.50±0.25 | 1.5 |
| 11. | Nitrate as $NO_3$ (mg/l) | 23 | BDL | 4 | BDL | 27 | 10 | 28 | 10 | 11±5.49 | 10.1±5.0 | Nr |
| 12. | Sodium as Na | 59 | 95 | 150 | 80 | 70 | 90 | 133 | 93 | 39±19.4 | 26.3±13.1 | - |
| 13. | Potassium as K | 24.5 | 3.6 | 1.8 | 3.1 | 29 | 2.8 | 1.7 | 2.5 | 11±5.42 | 13.3±7 | - |

**Nr = no relaxation**

**Table 1.** *Physico-chemical analysis of Pre and Post Monsoon groundwater samples (values in Mean±SD)*

Magnesium was high in pre monsoon the value being 202 mg/l in GW-2 sample. Sulphate in all samples varied from 480-1187 mg/l for pre and 620-1188 mg/l for post monsoon almost exceeding permissible limits for both seasons. Total hardness of all the samples was high in both seasons 650-1520 mg/l in pre and 775-1540 mg/l in post. Similarly TDS of samples varies from 975-2191 mg/l in pre and 1318-2190 mg/l in post Table 2 emphasized on concentrations of heavy metals in ground water samples for both pre and post monsoon

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which vary a lot. Heavy metal content in water was high with respect to the permissible limits. Between seasons comparisons showed that the concentration of heavy metal were high during post monsoon.

| S. No | Station | Parameters | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Pre Monsoon | | | | | Post Monsoon | | | | |
| | | Zn | Mn | Cd | Fe | Pb | Zn | Mn | Cd | Fe | Pb |
| 1 | TD-1 | 0.073 | 0.095 | 0.021 | 0.066 | 0.042 | 0.095 | 0.098 | 0.039 | 0.088 | 0.056 |
| 2 | GW-1 | 0.01 | 0.011 | 0.031 | 0.028 | 0.01 | 0.042 | 0.01 | 0.006 | 0.046 | 0.049 |
| 3 | GW-2 | 0.059 | 0.336 | 0.029 | 0.03 | 0.031 | 0.085 | 0.434 | 0.006 | 1.1 | 0.04 |
| 4 | GW-3 | 0.02 | 0.046 | 0.039 | 0.042 | 0.03 | 0.025 | 0.017 | 0.009 | 0.051 | 0.07 |
| Permissible limits* (mg/l) | | 15 | 0.3 | 0.003 | 0.3 | 0.01 | 15 | 0.3 | 0.003 | 0.3 | 0.01 |
| Mean ± SD | | 0.03± 0.015 | 0.14 ±0.073 | 0.007 ±0.003 | 0.017 ±0.008 | 0.013 ±0.006 | 0.03 ±0.016 | 0.20 ±0.10 | 0.016 ±0.008 | 0.51 ±0.25 | 0.012 ±0.006 |

*Permissible limits as per IS 10500:2012

**Table 2.** *Heavy metal concentrations in groundwater samples for Pre & Post monsoon seasons.*

**Table 3** highlights the heavy metal concentrations in all four samples of soil where pre and post monsoon data indicate the values exceed permissible limits.

| S. No | Station | Parameters | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Pre Monsoon | | | | | Post Monsoon | | | | |
| | | Zn | Mn | Cd | Fe | Pb | Zn | Mn | Cd | Fe | Pb |
| 1 | S-1 | 5.96 | 43.9 | 0.17 | 3.2 | 41 | 6.7 | 44.3 | 0.19 | 3.8 | 45 |
| 2 | S-2 | 6.87 | 25.5 | 0.12 | 3 | 40 | 7.9 | 27.3 | 0.11 | 3.4 | 43 |
| 3 | S-3 | 6.05 | 22.5 | 0.12 | 3.3 | 30 | 6.8 | 24.8 | 0.17 | 4.1 | 35 |
| 4 | S-4 | 5.2 | 39 | 0.15 | 2.6 | 10 | 5.9 | 44 | 0.19 | 2.9 | 12 |
| Permissible limits* (mg/kg) | | 0.6 | 2 | 0.01 | 4.5 | 0.1 | 0.6 | 2 | 0.01 | 4.5 | 0.1 |
| Mean ± SD | | 0.68 ±0.34 | 10.3 ±5.17 | 0.02 ±0.01 | 0.30 ±0.15 | 14.3 ±7.19 | 0.82 ±0.41 | 10.5 ±5.25 | 0.03 ±0.01 | 0.51 ±0.25 | 15.1 ±7.56 |

**Station: S-1** = *Kanpur Village Agriculture field near well-1,* **S-2** = *Kanpur Village Agriculture field,* **S-3** = *Kanpur Village agriculture field near Well-2,* **S-4** = *Kanpur Village near Hand Pump*
*Permissible limits as per Method manual for soil testing, govt. of India

**Table 3.** *Heavy metal concentration in soil samples around Kanpur village*

**Table 4 and figure 2** shows comparison of heavy metals in water samples for pre and post monson seasons and graphical representation based of Contamination factor in water samples. Here Cd content in water is very high i.e above 6 in all the village samples in pre monsoon while Pb values is considerable in Tailing dam (TD-1) and Kanpur village HP (GW-1). Mn and Pb values are moderately contaminated (1-3) in Pre monsoon season. In post monsoon season Cd values in TD-1 and Pb values, GW-2 have high contamination (>6) factor whereas Pb and Fe in TD-1, GW-1 and GW-2 have considerably (3-6) been contaminated. Cd and Mn in GW-1, GW-2 and GW-3 are moderately contaminated and rest of heavy metal like Zn, Mn and Fe samples, were having low contamination (<1) factor.

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| Monitoring Station | | Zn | CF | Mn | CF | Cd | CF | Pb | CF | Fe | CF |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Pre Monsoon | TD-1 | 0.073 | **0.0049** | 0.095 | **0.3167** | 0.021 | **7.00** | 0.042 | **4.2** | 0.066 | **0.2200** |
| | GW-1 | 0.059 | **0.0039** | 0.336 | **1.1200** | 0.029 | **9.67** | 0.031 | **3.1** | 0.030 | **0.1000** |
| | GW-2 | 0.020 | **0.0031** | 0.046 | **0.1533** | 0.039 | **13.0** | 0.030 | **3.0** | 0.042 | **0.1400** |
| | GW-3 | 0.010 | **0.0007** | 0.011 | **0.0370** | 0.031 | **10.3** | 0.010 | **1.0** | 0.028 | **0.0930** |
| Post Monsoon | TD-1 | 0.095 | **0.0063** | 0.098 | **0.3267** | 0.039 | **13.0** | 0.056 | **5.6** | 0.088 | **0.2933** |
| | GW-1 | 0.085 | **0.0057** | 0.434 | **1.4467** | 0.006 | **2.00** | 0.040 | **4.0** | 1.100 | **3.6667** |
| | GW-2 | 0.025 | **0.0017** | 0.017 | **0.0567** | 0.009 | **3.00** | 0.070 | **7.0** | 0.051 | **0.1700** |
| | GW-3 | 0.042 | **0.0028** | 0.010 | **0.0333** | 0.006 | **2.00** | 0.049 | **4.9** | 0.046 | **0.1533** |
| Classes of contamination Factor (CF) | | **<1** *Low* | | **1-3** *Moderate* | | | **3-6** *Considerable* | | **>6** *Very high* | | |

**Table 4.** *Contamination Factor values of Water Samples for Pre & Post Monsoon season*

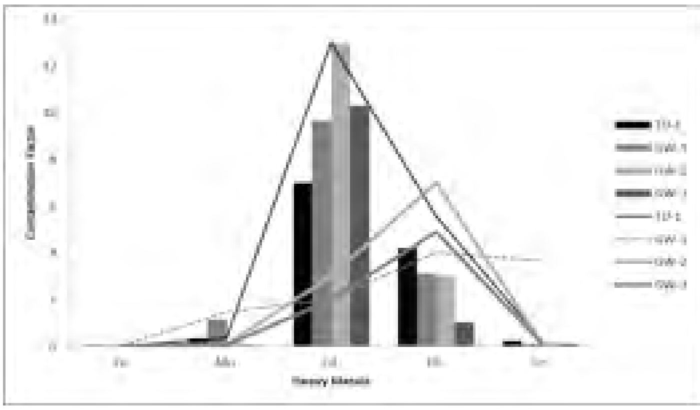

**Figure 2** *Contamination Factor of Pre & Post Monsoon groundwater samples.*
**Bar represent Pre monsoon and line shows post monsoon*

**Table 5 and figure 3** represent comparison of heavy metals in soil samples for pre and post monson seasons and graphical representation based of Contamination factor in soil samples.Here Zn, Cd, Mn and Pb content in soil is very high i.e above 6 in all the villages samples in pre and post monsoon season. While Fe content in soil sample is low contamination (<1) factor.

| Monitoring Station | | Zn | CF | Mn | CF | Cd | CF | Pb | CF | Fe | CF |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Pre Monsoon | S-1 | 5.96 | **9.93** | 43.9 | **22.0** | 0.17 | **17** | 41 | **410** | 3.2 | **0.71** |
| | S-2 | 6.87 | **11.5** | 25.5 | **12.8** | 0.12 | **12** | 40 | **400** | 3.0 | **0.67** |
| | S-3 | 6.05 | **10.1** | 22.5 | **11.3** | 0.12 | **12** | 30 | **300** | 3.3 | **0.73** |
| | S-4 | 5.20 | **8.67** | 39.0 | **19.5** | 0.15 | **15** | 10 | **100** | 2.6 | **0.58** |
| Post Monsoon | S-1 | 6.70 | **11.2** | 44.3 | **22.2** | 0.19 | **19** | 45 | **450** | 3.8 | **0.84** |
| | S-2 | 7.90 | **13.2** | 27.3 | **13.7** | 0.11 | **11** | 43 | **430** | 3.4 | **0.76** |
| | S-3 | 6.80 | **11.3** | 24.8 | **12.4** | 0.17 | **17** | 35 | **350** | 4.1 | **0.91** |
| | S-4 | 5.90 | **9.83** | 44.0 | **22.0** | 0.19 | **19** | 12 | **120** | 2.9 | **0.64** |
| Classes of Contamination Factor (CF) | | | **<1** *Low* | | **1-3** *Moderate* | | **3 - 6** *Considerable* | | **>6** *Very high* | | |

**Table 5.** *Contamination Factor of Soil samples for Pre & Post Monsoon seasons.*

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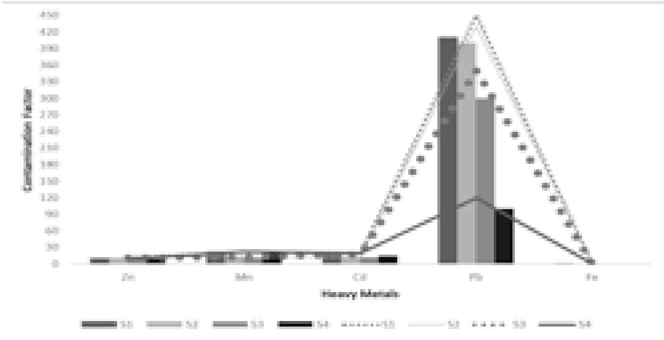


**Figure 3.** *Contamination Factor of Pre & Post Monsoon season of s oil samples.*
**Bar represent pre monsoon and line/dots shows post monsoon.*

**Table 6 and figure 4** shows Translocation Factor of Water and Soil Samples in pre and post monsoon season. As mentioned in Table highest recorded values were for Pb (Post monsoon) and Mn (Pre monsoon) which are 64200 and 27040 percent higher while the lowest translocation factor was recorded for Cd (Pre and Post season) and Fe (Pre and Post season) metal which were 500-1100% and 7400-1240% higher than permissible limits respectively.

| S. No. | Parameter | Water (mg/l) | | Soil (mg/kg) | | Translocation factor (TF) = Soil/Water*100 (%) | |
|---|---|---|---|---|---|---|---|
| | | Pre Monsoon | Post Monsoon | Pre Monsoon | Post Monsoon | Pre Monsoon | Post Monsoon |
| 1 | Zn | 0.040 | 0.061 | 6.02 | 7 | 15100 | 11500 |
| 2 | Mn | 0.122 | 0.139 | 33 | 35.1 | 27040 | 25300 |
| 3 | Cd | 0.03 | 0.015 | 0.14 | 0.16 | 500 | 1100 |
| 4 | Pb | 0.028 | 0.053 | 30.2 | 34 | 1079 | 64200 |
| 5 | Fe | 0.041 | 0.321 | 3.02 | 4 | 7400 | 1240 |

**Table 6.** *Average concentration of heavy metals in pre & post monsoon seasons in water and soil samples.*

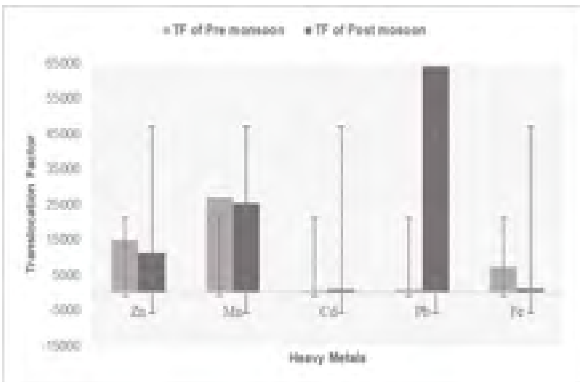


**Figure 4.** *Translocation factor of Pre & post season for water and soil samples.*

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**Table 7 and figure 5** represents Pollution Load index in pre and post monsoon season of Water samples. Pollution load index showed that groundwater samples have low pollution load, less than 1 due to translocation of metal through water to soil.

| Monitoring Station | PLI in Pre Monsoon | PLI in Post Monsoon |
|---|---|---|
| **TD-1** | 0.397 | 0.535 |
| **GW-1** | 0.420 | 0.751 |
| **GW-2** | 0.256 | 0.202 |
| **GW-3** | 0.119 | 0.169 |

**Table 7.** *Pollution Load Index in Water samples for Pre & Post monsoon season.*

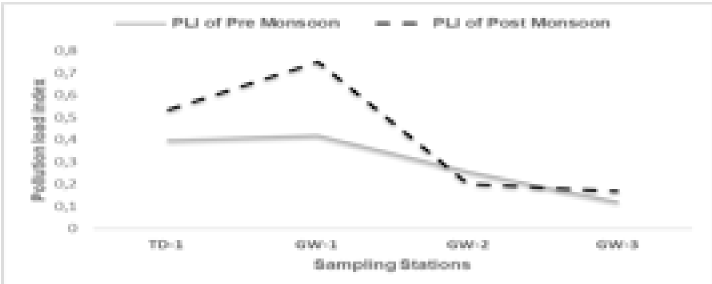


**Figure 5.** *Pollution load index of Pre & Post season for ground water.*

**Table 8 and figure 6** represented Pollution Load Index in soil samples for Pre & Post monsoon seasons.The metal content in water is less because soil absorbed the metal through ground and their PLI is above 1 indicating progressive deterioration of the soil by contamination and leaching.

| Monitoring Station | PLI in Pre Monsoon | PLI in Post Monsoon |
|---|---|---|
| **S-1** | 16.09 | 17.78 |
| **S-2** | 13.62 | 14.52 |
| **S-3** | 12.44 | 15.0 |
| **S-4** | 10.80 | 15.58 |

**Table 8.** *Pollution Load Index in Soil samples for Pre & Post monsoon season.*

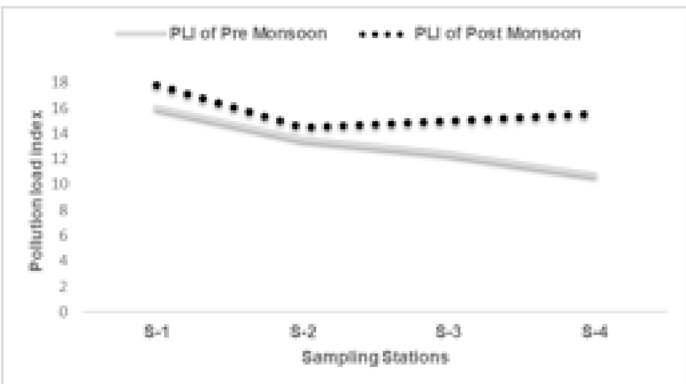


**Figure 6.** *Pollution load index of Pre & Post season for Soil samples.*

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**Discussion**

The physiochemical properties of groundwater shown in Table 1 indicate that calcium, magnesium and sulphate in underground water is exceeding permissible limits in one season monitoring. Increase in levels of Ca and Mg in water is due to weathering rock material which reacts with sulphuric acid present while processing of mineral ore (Zn-Pb) and forms calcium and magnesium sulphate in water, thereby increasing hardness in water. (Smith *et al*., 1994; Fernandez-Rubio *et al.,* 1986). So, the quality of groundwater has degraded. According to Motyka & Witkowski, (1999) sulphate concentration that the processes of oxidation of sulphide minerals taking place in the rocks are the most significant factors influencing these concentration.

Ground water conditions during seasonal monitoring varied a lot as shown in Table 2. Heavy metal content in water exceeded the permissible limits. Between seasons comparisons showed that the concentration of heavy metal were high during post monsoon. As shown in Table 2, high content of Cd was recorded from TD-1 and GW-3 at Kanpur village with concentration of 0.021-0.039 mg/l and 0.006-0.039 mg/l in pre and post monsoon respectively. These values are 7-13 times and 2-13 time more than the permissible limits. The average content of one season ranged between 0.03-0.015 mg/l for Cd which is 10-5 times above permissible limit. This high concentrations makes water dangerous for human consumption. High content of Pb was obtained in all the water samples ranging between 1-4.2 times above and in Post monsoon 4-7 times above permissible limits. As per the WHO limits, average per season requirement of Pb is 0.028-0.053 mg/l and in ground water samples it was 3 to 5.3 times higher. This was expected as local Zn-Pb mining was active in the area. This concentration renders water source risky for human consumption.

Cidu and Fanfani (2000) studied the impact of abandoned mines on water resources which showed pore water in dumps exhibited high contents of Pb, Cu, Co, Ni, Cd and Zn. This was also indicated in Humboldt Pb-Zn-Cu mines (N. Nevada) where the source of water were polluted by As, Cd, Cu, Mn, Pb and Zn from the mine dumps (Nash, 2003). In Trezebionka (Poland), where intensive mining activities were practiced, the mine water and ground water were reported to be characterized by higher content of heavy metals including Cd, Cu, Co, Ni, Pb, Zn and Mn. These polluting heavy metals initiated from mine excavation and extraction activities in the area (Gajowiec and Witkowski, 1993). The groundwater was naturally enriched in heavy metals but previous mining activities resulted in highly polluted and toxic groundwater within the vicinity of the mines, which is quiet similar to the present study.

Contamination Factor for Cd was very high i.e above 6 in all the village water samples for pre monsoon while Pb values were considerable in Tailing dam (TD-1) and Kanpur village HP samples (GW-1). Contamination Factor for Mn and Pb values was moderate (1-3) in Pre monsoon in GW-1 in Mn and GW-2 and GW-3 but showed towards higher end in post monsoon season in TD-1 probably due to untreated disposal of waste in the tailing dam. Similarly Pb values showed an increase in contamination factor for GW-2 (>6) whereas Pb and Fe in TD-1, GW-1 and GW-3 have considerably (3-6) been contaminated. Cd and Mn in GW-1, GW-2 and GW-3 are moderately contaminated and rest of heavy metal like Zn, Mn and Fe samples, were having low contamination (<1) factor. These may be due to their insoluble nature in water.

In Table 3, high content of Zn was found in soil samples of agricultural field at Kanpur village with concentration of 5.2-6.87 mg/kg in pre monsoon and in 5.9-7.9 mg/kg post season respectively. These values are 7-11 times and 10-13 time above the permissible limit. The average values of one season is 6.02-7.0 mg/kg of Zn in soil sample which is 10-12 times above permissible limit. These concentrations contaminate the soil meant for agriculture purpose and is harmful for human consumption. Similarly high content of Pb was obtained in all the soil samples with concentration of 10-41 and 12-45 mg/kg, making it 100-410 and 120-450 times beyond the permissible limits for pre and post monsoon respectively. The average content of Pb for one season is 30.2-34 mg/l in underground water which is 302-340 times above the permissible limit. Also it was observed that Cd content in soil was high 0.12-0.17 mg/kg in pre and 0.11-0.19 mg/kg in post season respectively. These values are 12-17 times and 11-19 time higher. Such increase in heavy metal concentration is due to leaching of metals in soil, as expected due to local Zn-Pb mining in the area.

Contamination factor as shown in Table 5 and Fig. 4 & 5 indicate that all the soil samples collected from agriculture fields have highly concentration of heavy metals in pre and post monsoon. The only exception is Fe in the soil having low contamination i.e less than 1 in both seasons. Increase in heavy metal concentration is due to leaching of metals in soil, as expected due to

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local Zn-Pb mining in the area. This concentration of metals deteriorate the fertility of the agriculture soil and the crops which are grown in the fields i.e. crop of maize and wheat might accumulate metal from soil and this will be harmful to the humans.

TF value was highest for Lead (Post monsoon) and Manganese (Pre monsoon) which is 64200 % and 27040% while the lowest TF value was recorded for Cadmium (Pre and Post season) and Iron (Pre and Post season) metal which although were 500-1100% and 7400-1240% higher than permissible limits respectively. TF for heavy metal in pre and post monsoon was of the order Mn>Zn>Fe>Pb>Cd and Pb>Mn>Zn>Fe>Cd respectively.

As expressed through Pollution load index, groundwater samples have low pollution load, less than 1 due to translocation of metal through water to soil (Table 6 and Fig. 6). The metal content in water is less because soil absorbs the metal through ground and their PLI is above 1 indicating progressive deterioration of the soil by contamination and leaching.

## Conclusions

Present study clearly indicates that water and soil samples contamination is directly related to mining activities in the study area. Pb and Zn are the main components extracted from the mines while Cd is a by-product in the smelting/ refining of the Pb-Zn-Cu ores and also a by-product of acid mine drainage. Soil content has high pollution load index as compared to groundwater due to translocation of heavy metal through water to soil. These leachate pollute surrounding areas and increase the extent of environmental pollution and health related problems.

In Zawar Mines, where untreated mining waste effluents have been discharged since a long time, soil and groundwater were found to be contaminated with alarmingly high concentrations of various heavy metals. As expected, the concentration of all metals present in soil was incredibly high in comparison to groundwater, owing to the fact that high concentrations of heavy metals is degrading the field crop and agriculture land in Kanpur village, Zawar Mines. The concentrations of heavy metals (Cd and Pb) in groundwater samples not only exceeded the recommended safe limits, rather these were 7-13 times higher than the drinking water quality standards. While in the soil (Zn, Fe, Cd, Mn and Pb) this limit exceeded11-19 times higher the soil quality standard, due to intensive Pb-Zn mining. Translocation factor established that the heavy metals in groundwater is accumulated by soil. So the PLI in groundwater is less as compared to soil. The contamination in the study area, particularly with Pb and Cd, requires an effective treatment strategy for remediation of the soil and groundwater. For minimizing this contamination of groundwater and soil, waste generated during refining of Zn-Pb ore, the acid content of the waste tailing should have been neutralized before its disposal and heavy plantation should be done that can accumulate heavy metal through soil and groundwater through phytoremediation. Main inference of the study is that the risk level of heavy metal leaching and groundwater contamination from the soil is very high with considerable likelihood of heavy metal transport by water percolating through the soils/mine waste due to the dumping. Frequent monitoring of groundwater and soil quality is necessary to determine the pollution levels and possibly initiate remedial measures.

The people of Zawar Mines who produce rice and maize in their agriculture fields will require a management plan against the bio magnification of metals into the ecosystem in order to alleviate the possible metal related health problems. This can be done by reducing the solubility and concentration of metals in the soil to restrict metal intake through the consumption of contaminated forages and soil (Paulinus, 2015). Increasing lime content in soil can change pH to 6.5 or above which will reduce metal availability to plants and decrease trace metal solubility at higher pH values. Additional measures such as deep flowing to reduce metal aggregation at the soil surface is required thereby reducing metal intake by crops during cultivation.

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