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# Heavy Metal Concentration in Groundwater of Kirana Hill Region, Rabwah, District Chiniot, Pakistan

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**Abstract:** The present study has been undertaken with an objective to evaluate the heavy metals concentration in groundwater of Rabwah town, Pakistan. The area is highly depending on groundwater sources for drinking purpose. Detailed analysis was carried out to understand the contamination level and distribution of heavy metals specifically lead, cadmium, zinc, nickel and transitional metal iron in drinking water during winter and summer. Twenty five surveyed private well sites located in Precambrian Kirana hills region were tested to map the groundwater quality and assess its suitability for drinking purpose. Detected amount of lead, cadmium and nickel were found higher than World Health Organization Standard maximum permissible limits, whereas the Ni levels were observed lower than the acceptable limit in some of the samples in summer. Generally, the mean metal concentration in sampled water sources have a descending order Ni>Pb>Cd>Zn>Cr in winter while Ni>Zn>Pb>Cr>Cd> Fe in summer. Water samples were highly enriched with Ni and Cr during summer and by Pb, Cd and Zn in winter. The quality of the drinking groundwater sources was observed unsafe for drinking; moreover, there is still need to take proactive measures to check the levels of heavy metals. The spatial analysis and distribution of groundwater quality in Rabwah town will make it easier for authorities and decision makers to determine the groundwater quality and recommend most suitable location for boring wells in future.

**Keywords:** Heavy metal, groundwater, Rabwah, atomic absorption spectrometer, GIS mapping, seasonal variation.

## Introduction

Most of rural and urban population is using groundwater without knowing its quality especially in under developing countries. According to WHO estimate, annually 842,000 deaths occur due to insecure water supply, sanitation and hygiene in developing countries (WHO, 2014) whereas 780 million population has no access to potable water due to bacteriological and chemical contaminants. The problem of ground water contamination owing to heavy metals has now raised concerns all over the world as toxic metals have no positive effect on health and long term exposure destroys the normal functioning of organ systems and some metals have carcinogenic effect (Anake et al., 2014).

The present study was conducted in Kirana hills region, District Chiniot, Pakistan.The purpose of present study is to determine concentration of heavy metals in ground water in vicinity of Kirana hills. The analyzed data of heavy metals areS spatially plotted on GIS based maps.Mostof the local population relies on private wells for drinking water and other household purpose. There is no record of private wells and no source for citizens to inform that S their bore wells water is fit for drinking purpose. If the water is contaminated due to leaching of heavy metals from hard rocks it will be the reason of health hazard. This study provides distribution map for heavy metals concentration which is useful for local population and munciple planners.

## Study area

The study area, Rabwah town in Chiniot District comprises of Precambrian rocks of Kirana hills in the north, agriculture fields in the west and River Chenab in the east. The Kirana hills consisted of isolated outcrops of volcanic and sedimentary origin from Chiniot to Sargodha (Shah, 1977). These volcanics are the leftovers of the extensive Precambrian igneous activity (Chaudhry et al., 1999) intruded by dykes and sills. Near Rabwah town, exposure of Kirana hills area belong to volcanic and meta-sediments of older Kirana Group which is successively covered by Taguwaliphyllites/slates and Asianwala quartzite. The surface area at shallow basement is made up of fine transported or weathered sediments, while harder parts are buried under the upper part.

## Materials and Methods

Clean polyethylene bottles were used to collect samples of drinking water from tube well bore wells and hand pump wells in winter (January, 2016) and summer (May, 2016) season. The location of water samples were recorded through GARMIN GPS receiver from eight administrative blocks of the town which were distributed on basis of their distance from hills (Fig.1). Zone 1 is most distant from hills and is prone to seasonal flooding whereas zones 2, 3 and 4 are to be found away from flood water of varying levels. Zones 7 and 8 extend adjacent to hills while 5 and 6 are enclosed with the area close to River Chenab.

The groundwater quality analysis has been carried out for the parameters of Zn, Cr, Ni, Cd Pb and Fe while attempts have been made to determine quality by using Arc GIS geo statistical analyst tools.

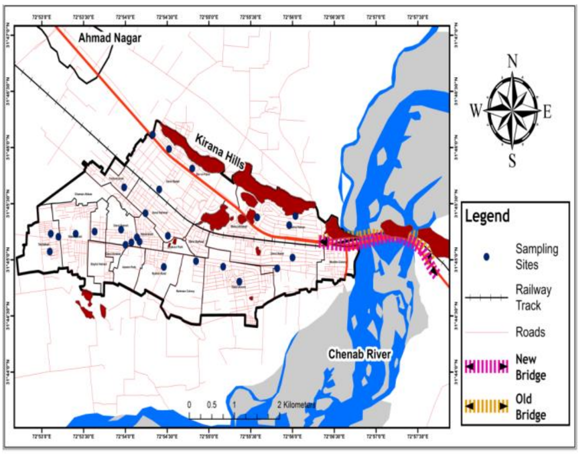


Fig. 1 Sampling locations of 25 samples analyzed for Zn, Cr, Ni, Cd and Pb.

## Metals analysis

The groundwater samples were collected from 25 private water wells of various depths located in the study area. The concentrations of parameters like Zn, Cr, Ni, Cd and Pb were analyzed through Atomic Absorption Spectroscopy (AAS) and Fe were determined with spectrophotometer. Later, the readings were compared with WHO and Pakistan Standards for heavy metals in drinking water.

## GIS mapping

The acquired values were then imported into ArcGIS for further analysis and spatial distribution maps were made to evaluate the results. In ArcGIS, each parameter was separately mapped by using geostatistical analytical tool Inverse Distance Weight (IDW). The Inverse Distance Weighted (IDW) interpolation is a mapping technique that develops the value of an unknown variable using values acquired from known locations (ESRI, 2005). It can be explained mathematically by following equations (Tomislav, 2009).

$$\lambda_i(S_o) = \frac{\frac{1}{d^{\beta}(S_o,S_i)}}{\sum_{i=0}^{n}\frac{1}{d^{\beta}(S_o,S_i)}} \; ; \; \beta > 1$$

Here, λi is representing the weight for neighbor i while d (so, si) is representing the distance from new point to a recognized sampled point. Meanwhile, β is working here as a coefficient to adjust the weights whereas 'n' is the total number of points in neighborhood analysis.

## Results and Discussion

The outcomes of heavy metals descriptive measurements including mean and standard deviation, in both summer and winter seasons are displayed in Table 1. As shown in Figures 2, 3, all water samples have lead (Pb) concentration higher in both seasons (January and May) than permissible limits of WHO standards (0.01 mg/L). It is observed that concentration of Pb is extremely high near hills in samples of zone 5, zone 8, and zone 6 in month January (i.e. 0.3918 mg/L). According to Jennings, *et al*. (1996) high concentrations of lead in the body can permanently damage the central nervous system, brain, and kidneys. Lead isone of the common elements found in the Earth's crust.

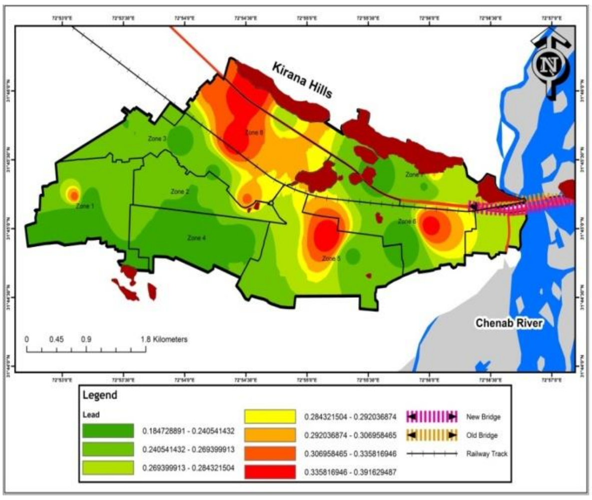


Fig. 2 IDW map, representing concentration of lead in water samples collected in winter season. High values were observed in zone 5 and zone 8.

Table 1 Results of analyzed water quality parameters.

| Parameter | Winter Season | | | | | Summer Season | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Pb mg/L | Zn mg/L | Cd mg/L | Ni mg/L | **Cr** mg/L | **pH** | Pb mg/L | Zn mg/L | Cd mg/L | Ni mg/L | **Cr** mg/L | TI mg/L |
| Min | 0.184 | 0.012 | 0.063 | 0.083 | 0.001 | 6.1 | 0.021 | 0.115 | 0.0005 | 0.0009 | 0.001 | 0.002 |
| Max | 0.391 | 0.574 | 0.251 | 1.255 | 0.009 | 8.2 | 0.548 | 0.400 | 0.006 | 0.188 | 0.079 | 0.304 |
| Average | 0.267 | 0.125 | 0.130 | 0.740 | 0.002 | 7.1 | 0.164 | 0.285 | 0.004 | 0.361 | 0.028 | 0.033 |
| Standard Deviation | 0.064 | 0.141 | 0.048 | 0.306 | 0.001 | 0.51 | 0.115 | 0.670 | 0.001 | 0.043 | 0.017 | 0.045 |
| WHO standards | 0.01 | 3 | 0.003 | 0.07 | 0.05 | 7 to 8.5 | 0.01 | 3 | 0.003 | 0.07 | 0.05 | 0.3 |
| Fit for use % | 0% | 100% | 0% | 4% | 100% | 100% | 0% | 100% | 0% | 76% | 89% | 95% |

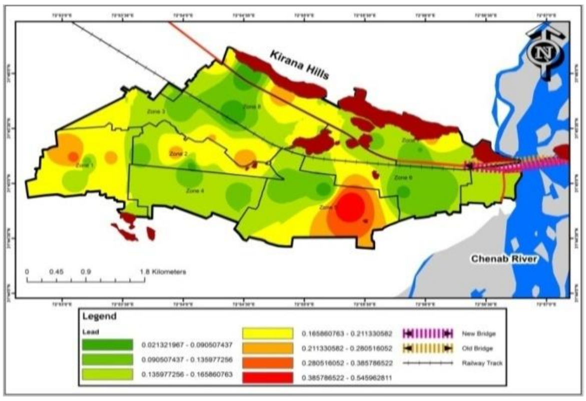


Fig. 3 IDW map of lead values analyzed in summer season. Relatively low lead concentration was recorded in some parts of town.

The possible cause of its presence in drinking water somewhat could be result of dissolution occurred from natural sources. Moreover, polyvinyl chloride (PVC) pipes also contain lead compounds which can be leached in drinking water but it depends on the presence of chloride, temperature, pH, and standing time of water in them (WHO, 2011).

High concentrations of Nickel (Ni) were observed in winter season. Only 4% water samples have Ni concentration within the permissible limit (0.07mg/L). In summer season, 76% water samples were within the WHO defined range. Comparatively highest concentration was observed in almost all parts of the town (1.2553 mg/L) in winter; however, this trend shifts towards northern and western parts in summer (Figs. 4,5). Higher concentration of nickel can increase the chances of cancer, lung embolism, birth defects, asthma and chronic bronchitis (WHO 2005). Nickel is hard, ferromagnetic metal of natural origin which also can be present in groundwater as a result of dissolution from nickel ore-bearing rocks. Nickel is found in the form of different salts, for example chloride, nitrate, and sulfate which are soluble in water (Morgan and Flint, 1989; Haudrechy et al., 1994).

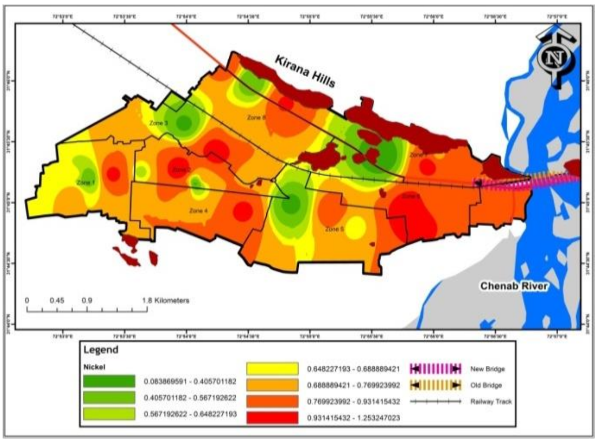


Fig. 4 IDW map of Nickel for 25 samples in winter season.

Highest concentrations of Cadmium (Cd) were noticed in samples, collected from areas close to hills in summer, mostly in central parts of the town.

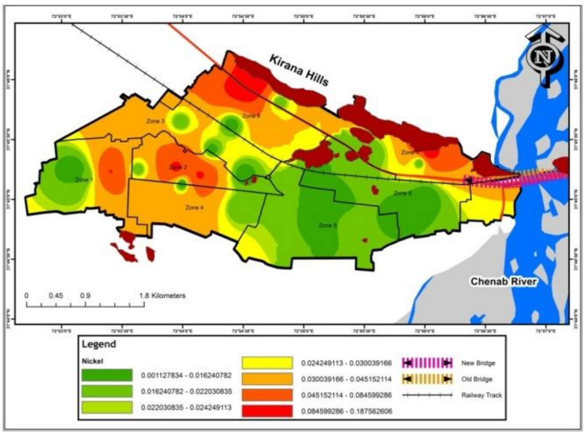


Fig. 5 IDW map of nickel in summer season.

All water samples (100%) exceed the WHO specified range (0.003 mg/L) in both seasons (Figs. 6, 7). Comparatively low values were witnessed in some parts of zone 4, zone 5 and zone 6 (0.0005 mg/L). Cadmium is naturally found with zinc and lead, in form of sulfide ores. High level of cadmium can critically affect the kidney (WHO 2011). According to Ros and Slooff (1987), increase in acidity can dissolve cadmium and it is mostly found in bottom sediments and suspended particles (Friberg et al., 1986).

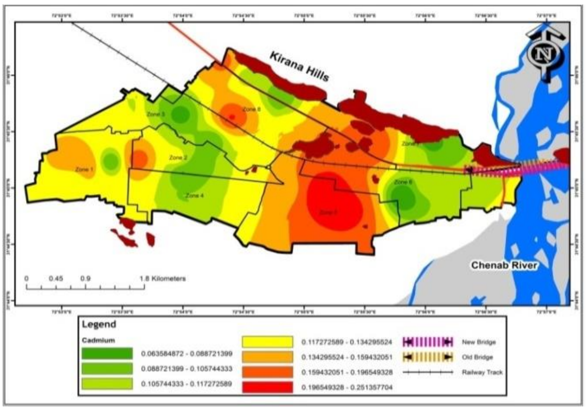


Fig. 6 IDW map of cadmium in winter season, high values were observed in some parts of zone 5, zone 6 and zone 7.

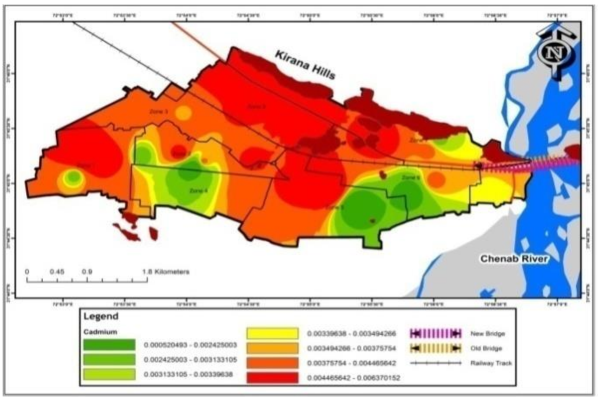


Fig. 7 IDW map of cadmium in summer season, high values were observed throughout the area.

The range of zinc in all water samples (100%) analyzed fell within the admissible limit of WHO (3 mg/L) in both seasons (Figs. 8, 9). However, comparatively very low values (0.012 mg/L) were also observed in summer (Figs. 8 and 9). Higher zinc concentration may be due to leaching of zinc from piping and fittings (WHO, 2003).

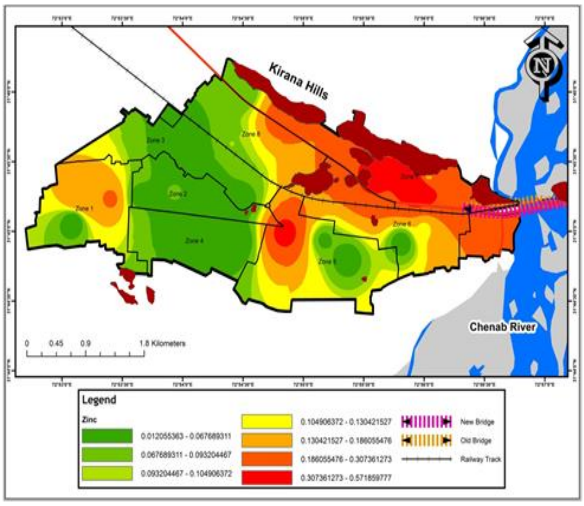


Fig. 8 Zinc IDW map in winter season.

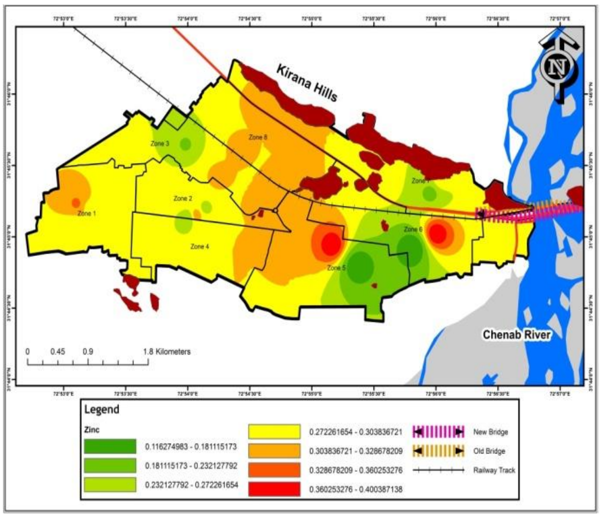


Fig. 9Representing concentration of zinc in water samples collected in summer season.

Some groundwater samples were also tested for chromium, all of them were found according to the WHO standards (0.05 mg/L) in winter season and 11% samples were observed exceeding the permissible limit in summer (Table 1). Chromium is extensively scattered in the earth's crust and found in rocks in the trivalent state. Its toxicology depends upon its oxidative stage. It affects gastrointestinal, respiratory, blood circulatory system if it is ingested in high doze (Guertin, 2004).

The transitional metals like iron content in the groundwater samples fell under the permissible limit of WHO, (0.3 mg/L) except two samples that slightly exceeds the desirable limits in zone 7(0.34 mg/L) near the hills (Figs. 10, 11). Chronic iron can cause depression, convulsions, respiratory failure, and cardiac arrest (WHO, 2008).

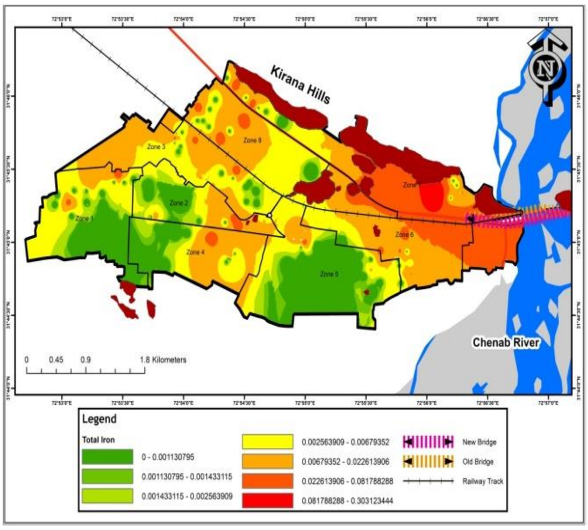


Fig. 10 IDW map of total iron with high concentration in eastern part of zone 7.

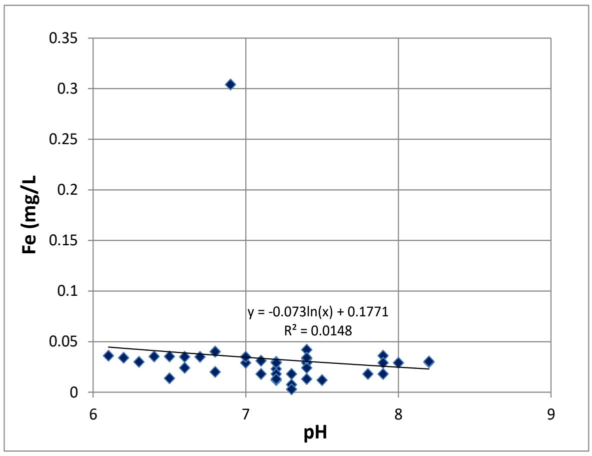


Fig. 11 Bivariate analysis between pH and Fe depths.

## Comparison of Metals Concentration due to Seasonal Variation

Comparatively slight increase in concentration was observed in zinc and chromium in summer while lead, cadmium and nickel are in lower concentrations in summer season. This slight variation may be due to several reasons. In soil solution, metals exist as free metal ions e.g. Cd ²+ and $Cr^3$. It can be linked with mobile inorganic and organic colloidal material. The mechanisms like adsorption and precipitation impede the movement of metals in groundwater. Metal and soil collaboration occurred if metals could be found at the soil surface. Downward transportation occurs only if capacity of soil is weighted down or metal contact with linked waste matrix increases its mobility (Joan *et al*., 1992). Lead and cadmium are less mobile and has tendency to form metallo-organic complexes at top soils while zinc is comparatively more mobile and leaches down (Olade, 1987).

The less concentration of some metals in groundwater is the outcome of high metal concentration in soils in winter. Since this is due to low precipitation in late autumn and winter. Consequently, the dying vegetation remains stored in soil, so to decrease the concentrate-ons of these constituents. Likewise, mostly the precipitation falls in summer which takes away the soluble metal matters from the soil to some extent (Naveeduallah et al., 2013) and leaches them down. Furthermore, the leaching trend variationin some metals could be as a result of climate change,high precipitation during winter, fewer precipitations during summer and greater air temperatures (Visser et al., 2011).

According to other studies, temperature had slightinfluence on lead (orthophosphate) and lead oxide solids dissolution. But, the presence of natural organic matter increases the lead oxide dissolution 36 times more at 20 °C in comparison with 4 °C as a result of faster reductive dissolution. Moreover, downward leaching of elemental lead and inorganic lead compounds from soil to groundwater is very common most natural situations except high acidity (Master et al., 2016).

The concentration of organic material and pH is inversely associated with presence of cadmium concentration in groundwater. It is because cadmium is found in water in +2 oxidation state. Sometimes, cadmium can form poorly soluble cadmium sulfide with a tendency to precipitate. Free cadmium could be toxic and widespread at low salinity. The soil of our studied area is highly saline. It was observed in an experiment that at low pH concentration of $CaCO_3$ increases that allows the adsorption of Ni, as this metal dissolves in water easily in this form therefore its mobility increases (Abigail et al., 2012)

## Conclusion

On account of the research, the values of Pb, Cd, Cr and Ni were extremely high in drinking water exceeding the permissible limits (WHO standards). Most of groundwater samples collected from populated zones which cannot be used for drinking purpose and in addition cause economic loss and health hazards among locals. The monitoring of geochemical parameters shows contamination levels of these toxic metals which are affecting a major portion of local population. Keeping in view this situation, an analysis of the groundwater quality and nature of the phenomenon associated will help in proper groundwater resource management. The GIS mapping helps to analyze complex spatial data and provides a generic overview of heavy metals concentration in the area. It is vital to treat these contaminations in groundwater to make it potable.

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