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Evaluation of the Heavy Metal in Soils of Kachwani Singaram Watershed of Musi River by X-Ray Fluorescence Spectrometry

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ABSTRACT

The main objective of research was to identify the heavy metal contaminated zones of soil and groundwater in the study area. Twenty five groundwater and ten soil samples collected from agriculture, residential and industrial areas and analysed by X-Ray Fluorescence Spectrometer. Due to anthropogenic activities in Kachwani Singaram watershed have deteriorated water and soil quality during the last few years due to over population and industrial development. Soil samples were analysed for Heavy metals using XRF or X-ray Fluorescence Spectrometry. Analysed data were compared with the national and international standards and subjected to factor analysis for six variables to assess and characterize hydro chemical process. Comparison of results with groundwater water samples and soil samples with WHO or BIS or Canadian guidelines show that most of groundwater samples are heavily contaminated with Heavy metals and toxic trace elements like lead, chromium, nickel, barium, aluminium, boron, and selenium, which was quantified and presented in the form of spatial variation Diagrams prepared using ArcGIS. The results reveal that the contamination is mainly due to anthropogenic activities in and around the study area due to high population density and industrial setup in the region being very close to Hyderabad city.

1. INTRODUCTION

Groundwater is recharged from, and eventually flows to, the surface naturally; natural discharge often occurs at springs and seeps, and can form oases or wetlands. The study of the distribution and movement of groundwater is hydrogeology, also called groundwater hydrology (Gagan et al, 2016).

At the end of centaury the world faced a number of challenges affecting the availability, accessibility, use and sustainability of its freshwater resources. Water is most vital of all natural resources; it has the power to promote economic and social advancement of all people (Koudstaal et al., 1992). The groundwater table generally is inclined toward the ocean, while a wedge of salt is inclined toward the land. Porosity is important, but, alone, it does not determine a rock's ability of being an aquifer. Areas of the Deccan Traps basaltic lava) in west central India are good examples of rock formations with high porosity but low permeability, which makes them poor aquifers. In some areas of uniform geology, such as certain alluvial deposits in valleys, wells can be constructed anywhere with equal success (Rubey et al., 1959). Around the World, groundwater pollution is a very serious and costly problem. If

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once contaminated found water, it is very expensive to clean-up and make usable again. Abundant resource that existed in oceans, seas, rivers, streams, lakes, reservoirs, glaciers, polar ice caps, shallow water bodies and groundwater is increasingly being wasted, misused or polluted. Due to increasing population, steady deterioration, disuse, and disappearance of traditional tanks, ponds and wells are the other causes of water crisis in India. In recent years the problem got aggravated due to extraction of groundwater using bore wells operated by electric, diesel or petrol (Janakarajan et al., 1999). The quality of irrigation water does not pose a problem in the state, salt effected soil occurs only in coastal areas and in areas of major irrigation projects where poor internal drainage conditions prevail (Tanji et al., 2002).

During the last few years, there have been reports of undesirable changes in groundwater quality by the people inhabiting the study area, which are due to an increase in urbanization, industrialization and agricultural activities; it is a well-known fact that a polluted environment has detrimental effect on the health of people, animal life and vegetation. In view of this, hydro geochemical investigations were carried out in the south-eastern part of the Ranga Reddy district, Hyderabad to assess the contamination of heavy metals and trace metals in Groundwater and soil for its suitability for domestic, industrial and as well as irrigation purpose.

1.1. Objectives of the Study

1. Determination of Heavy metals contamination in soil sample by XRF-analysis
2. To assess the impact of contamination in Musi river water on the groundwater, to know the health effects on the people living and using the water for different purposes.
3. Comparison with Standards as per World Health Organization WHO, (2006) and Bureau of Indian Standards (BIS, 1991).

2. Sampling and Chemical Analysis

The objective of the present investigation was to assess toxicity of trace metals and heavy metals contamination in soil, twenty five samples of soil were collected from bore-wells, dug wells, injection wells, hand pumps etc., in the month of November-December 2011 for registering the maximum effect of contamination. Selection of sampling site was based on potential areas prone to pollution viz., industrial units, habitation sites, industrial, sewage discharged areas and domestic areas etc. 25 samples of soil is collected to identify contamination level of heavy metals by using XRF (X-ray Fluorescence spectrometry) Model, type Philips Magi X PRO model PW 2440 XRF with Rh4KW tube.

2.1. Heavy Metals Contamination in Soil

Contamination of soil especially by heavy metals (atomic weight >100) appear to be virtually permanent, as heavy metals can be transformed from one chemical form to another through chemical and biochemical reactions but are not destroyed. The heavy metal (Ba, Co, Cr, Cu, Mo, Ni, Pb, Rb, Sr, V, Y, Zn, and Zr) concentrations of the study area are presented in table 4. To assess soil contamination in the study area, the concentrations of heavy metals and their spatial distribution was compared with heavy metal concentration in the earth's crust (Taylor and McLennan 1995) (table 5).Among the thirteen heavy metals detected in the soils of study area only Sr and Zn are with the permissible limit. The increased levels of barium, cobalt, chromium, copper, molybdenum, nickel, lead, rubidium, vanadium, yttrium and zirconium in the study area are major concern for the suitability in agricultural and other land management practices. The higher standard deviation observed for heavy metal Cr, V, Sr, Ba, Zr, Rb and Y in soil suggests that these metals are not uniformly distributed in the study area. Out of the twenty-five soil samples, five samples for Mo and one sample for Co were found to be below detectable limit. Metals associated with the aqueous phase of the soil are subject to movement with soil water and may be transported through the vadose zone to the ground (Nielsen et al., 1986). Metals unlike hazardous organic cannot be degraded. Some metals, such as Cr, As, Se and Hg can be transforming to other oxidation states in soil, reducing their mobility and toxicity. Immobilization of metals, by mechanisms of absorption and precipitation will prevent movement of the metals to ground water (Mulligan et al., 2001).

Metal –soil interaction such that when metals are introduced at the soil surface down ward transportation does not occur to any great extent unless the metal retention capacity of the soil is overloaded. Crops develop greater tolerance to sodium when irrigation water contained sufficient potassium. Changes in soil properties may occur with continuous use of irrigation water particularly when water is of poor quality. As the scarcity of clean potable drinking water has emerged in recent years as one of the critical problems facing India today even while the coverage of people with access to water supply in India has reached levels of over 80% .It has been increasingly realizing that while the approaches of the 1970 and 1980 have succeed in mitigating the immediate needs of water supply in rural areas (Rosegrant et al., 1999).

These may not be sustainable in view of the emerging problems.

Likewise the statistical summary given in the table 5 and the box plot in the figure 4 does not account for these samples for Mo and Co. Lead gives the least variation among the heavy metals while chromium and vanadium show highest variation in soil samples (table 5). Spatial variation maps (figure 5a-k) of the heavy metal contamination were prepared into three zones using I.D.W (inverse distance weighted) interpolation method in Arc GIS 9.3.1 for the heavy metals that exceed the desirable limit prescribed (Purushotham et al., 2012).

Although no measures are known that could be universally applied to choose the optimal set of parameters, cross-validation method is often used to select an interpolator from finite number of candidates (Tomczak et al., 1998).

The method is based on removing one data point at a time, performing the interpolation for the location of the removed point using the remaining samples (i.e., pretending that removed point does not exist), and calculating the difference (residual) between the actual value of the removed data point and the estimate for this point obtained from remaining samples. This scenario is repeated until every sample has been in turn removed. In this study the error estimation maps prepared by above said method show almost negligible deviation from actual value. Hence IDW interpolation method was found reliable for the present study.

The concentration of strontium and zinc is within the desirable limits; hence these elements are not discussed below.

2.2. Arsenic (As)

The concentration of Arsenic in the groundwater ranges from (0.7 – 4.8) ppb. The desirable limit of Arsenic is specified as 10 mg/l WHO (2006). A Spatial variation map has been generated (Fig 1) for the study area.

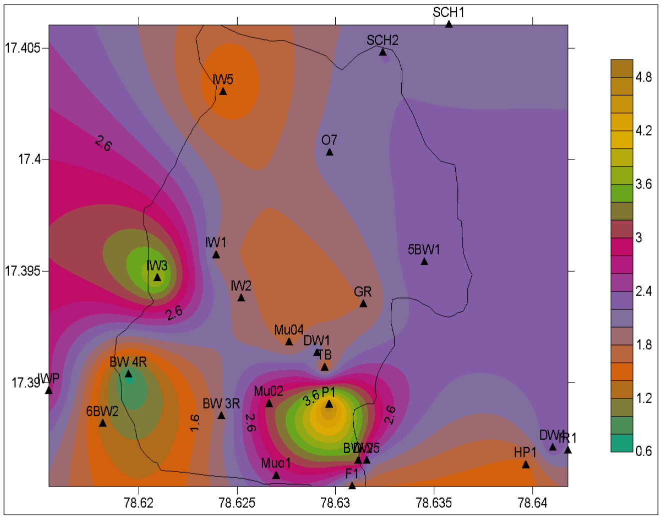

Figure 1. *Map showing the spatial distribution of Arsenic in the study area*

2.3. Barium

The main source of barium in the study area is predominant siliceous soils. Barium concentration in the soils of the study area ranges from 573-913mg/kg with an average of 743.4 mg/kg. Sixty-eight percent samples exceed the limit of 550 mg/kg. A Spatial variation map has been generated (Fig 2) for the study area.

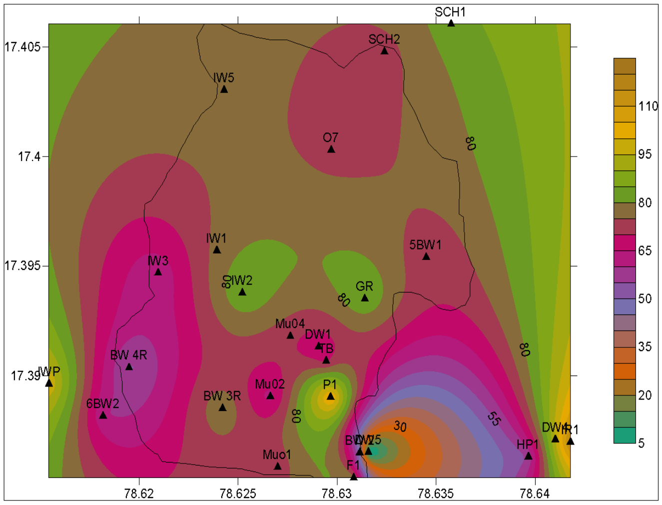

Figure 2. *Map showing the spatial distribution of Barium in the study area*

2.4. Cobalt

The cobalt concentration in the soils of the study area varies from 5.9-18.5mg/kg with an average of 12.2mg/kg. Sixty-six percent of cobalt samples exceed the desirable limit of 10 mg/kg. A Spatial variation map has been generated (Fig.3) for the study area.

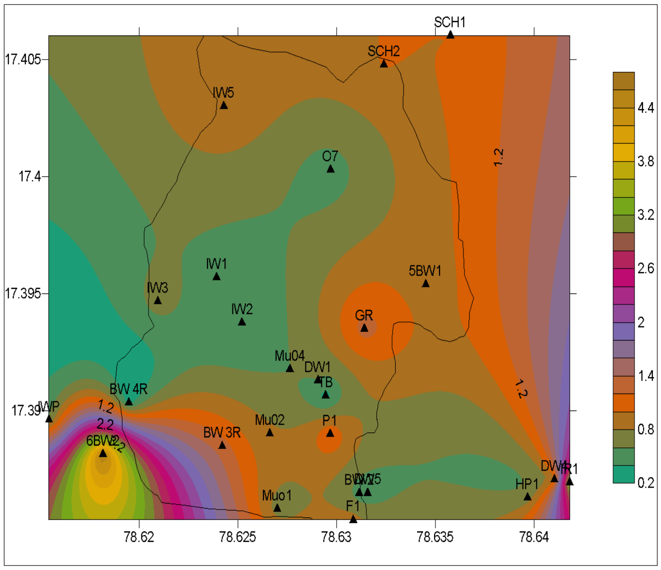

Figure 3. *Map showing the spatial distribution of Cobalt in the study area*

2.5. Chromium

Sixty-eight percent of chromium samples are beyond the desirable limit of 35 mg/kg. The concentration of chromium varies from 65.4mg/kg-126.2mg/kg with an average of 95.8mg/kg. A Spatial variation map has been generated (Fig.4) for the study area.

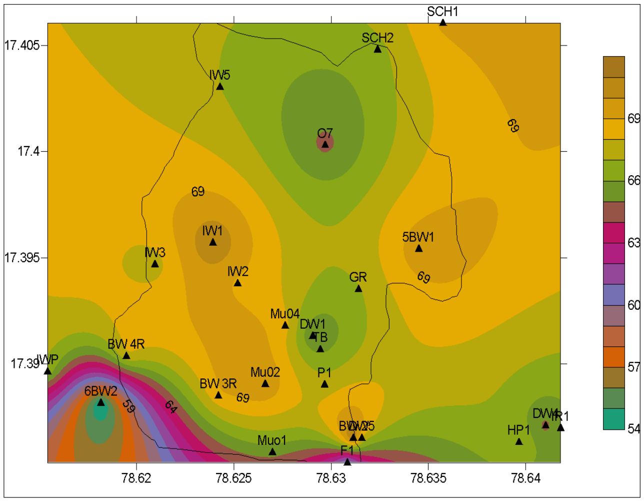

Figure 4. *Map showing the spatial distribution of Chromium in the study area*

2.6. Copper

Copper concentration varies from 9.6-118.1mg/kg with an average of 64.3mg/kg. Twenty-five percent of copper samples exceed the desirable limit of 25 mg/kg. A Spatial variation map has been generated (Fig 5) for the study area.

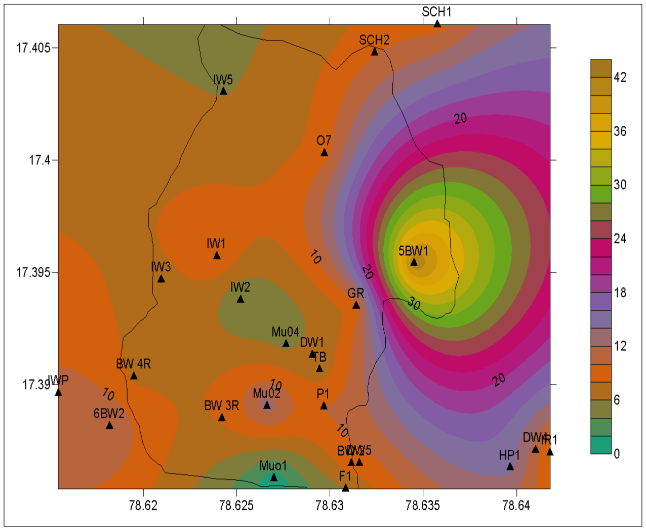

Figure 5. *Map showing the spatial distribution of Copper in the study area*

2.7. Molybdenum

The molybdenum concentration ranges from 1.0-4.1mg/kg with an average concentration of 2.5 mg/kg. A Spatial variation map has been generated (Fig.6) for the study area.

2.8. Nickel

The spatial distribution of nickel is given in the variation map (figure 7). Nickel concentration ranges from 2.5-7.8mg/kg with an average of 5.1mg/kg. Eighty-four percent of nickel samples are beyond the desirable limit of 20mg/kg.

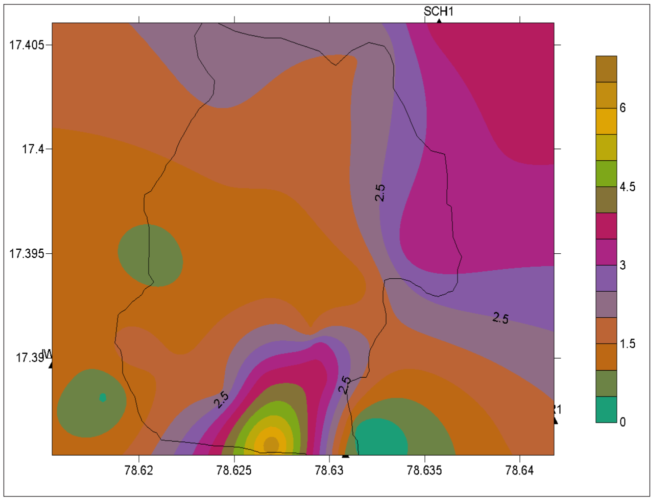

Figure 6. *Map showing the spatial distribution of Molybdenum in the study area*

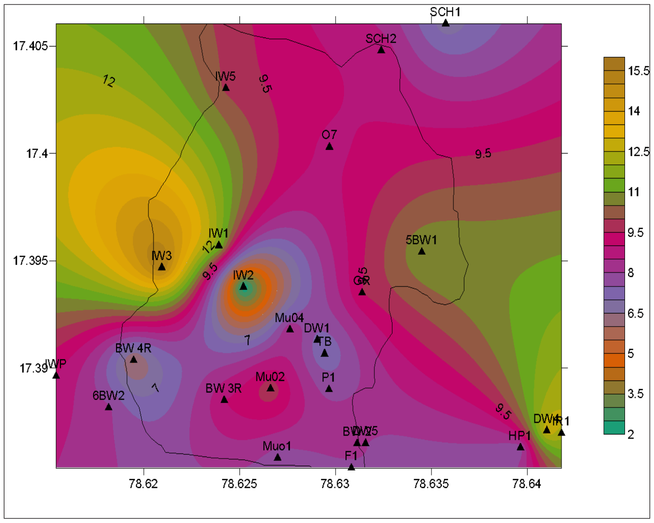

Figure 7. *Map showing the spatial distribution of Nickel in the study area*

2.9. Lead

The average concentration of lead in the study area is 35.9 mg/kg. The concentration of lead of the area ranges from 10.1-61.7mg/kg. Hundred percent of the lead samples are beyond the desirable limit of 20 mg/kg. A Spatial variation map has been generated (Fig.8) for the study area.

2.10. Rubidium

The concentration of rubidium in soils of the study area ranges from 77.3-154.7mg/kg. Hundred percent of rubidium samples are beyond desirable limit of 112 mg/kg. A Spatial variation map has been generated (Fig. 9) for the study area.

2.11. Vanadium

The concentration of vanadium in the soil of the study area ranges from 64.8-201.1mg/kg with an average of132.9 mg/kg. Eighty-eight percent of vanadium samples crossed the desirable limit of 60 mg/kg. A Spatial variation map has been generated (Fig. 10) for the study area.

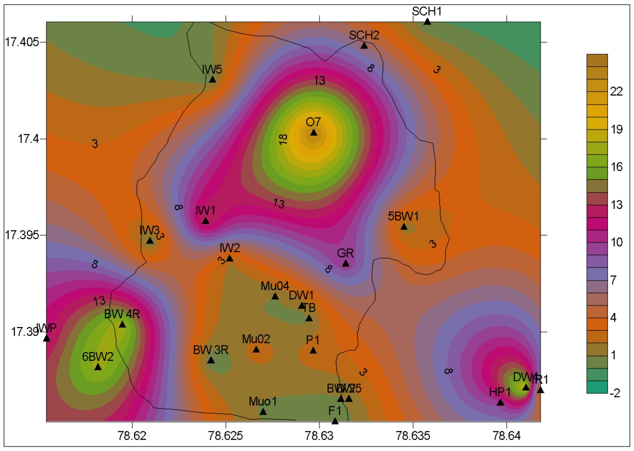

Figure 8. *Map showing the spatial distribution of Lead in the study area*

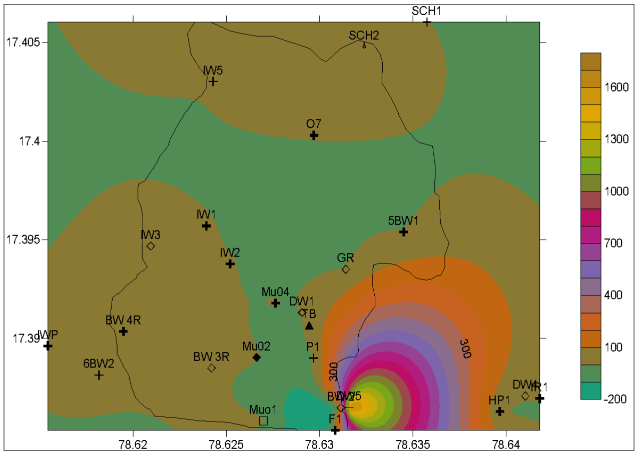

Figure 9. *Map showing the spatial distribution of Rubidium in the study area*

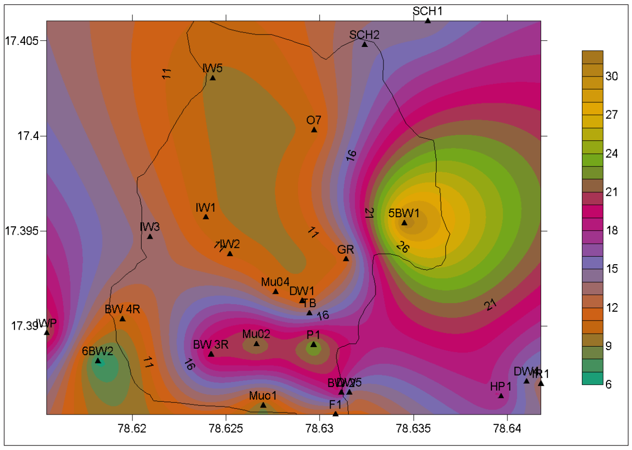

Figure 10. *Map showing the spatial distribution of Vanadium in the study area*

2.12. Yttrium

The concentration of Yttrium ranges from 34.9-70.2mg/kg. Hundred percent of yttrium samples crossed the limit of 52 mg/kg.

2.13. Zirconium

The concentration of zirconium ranges from 374.6-1028.6mg/kg. Ninety percent of zirconium samples crossed the limits of 70 mg/kg.

3. RESULTS AND DISCUSSION

The soil samples were analysed for their heavy metal content. The analytical status of heavy metals is discussed in the form of spatial variation maps (Fig. 4). Each map was interpolated to various zones ranging from low to high using Arc GIS 9.3.1. The results of this study were compared with WHO (2006), BIS (1991) and ISI (1983) standards for heavy metal concentration in the groundwater

3.1.Toxic Heavy Metals (Pb, As, Be, Cd and V)

The toxic heavy metals analysed include lead, arsenic, barium, cadmium and vanadium. The concentration of lead in samples varies from10.1-61.7µg/l with an average concentration of35.9µg/, which is beyond the desirable limit of10µg/l as recommended by BIS (1991) and W.H.O (2006). The main sources of lead contamination are industrial discharges from smelters, battery manufacturing units, runoff from contaminated land areas, atmospheric fallout and sewage effluents.

Arsenic concentration in the samples varies from 2.9-9.1µg/l with an average concentration of 6.02µg/l all the samples except smp-11 are within the acceptable limit10µg/l given by W.H.O (2006). Spatial variation map (Fig.1) shows low (0.7-3.110µg/l), moderate (3.1-5.210µg/l) and high (5.2-11.01µg/l) arsenic contamination zones. The high arsenic concentration is due to anthropogenic activities like poultry waste, brick making and agricultural practices.

Concentration of beryllium in the samples varies from µg/l, with an average concentration of0.210µg/l. BIS and WHO have not prescribed any guideline value for beryllium concentration in the groundwater. Concentration of cadmium in the samples ranges from 0.1 to 5.9 µg/with an average concentration of 3µg/l. The samples of cadmium are within the desirable limit of 3 µg /l as recommended by BIS (1991) and WHO (2006). Spatial variation map of cadmium shows low (0.1-1.1µg/l), moderate (1.1-3.0µg/l) and high (3.0-5.9 µg/l) contaminated areas. Fertilizers produced from phosphate ores constitute a major source of diffuse cadmium pollution. High level of cadmium concentration may also be due to discharge from industrial waste or by leaching from sewage laden landfills (Singh 2003).

Vanadium concentration ranges from 201.1-64.8µg/l, with an average concentration of 132.9µg/l. BIS and WHO has not prescribed any guideline value for vanadium concentration. The spatial variation map of vanadium concentration is given in Fig.10.

3.2. Transition Heavy Metals (Cr and Ni)

Chromium concentration varies from 126.2-65.4µg/l, with an average concentration of 95.8µg/l. all the values of chromium are beyond the desirable range of 50 µg/l given by WHO (2006) and BIS (1991). The spatial distribution of chromium (Fig.4) shows three zones low (11.6-97.0µg/l), moderate (97.0-130.0µg/l) and high (130-415µg/l). The concentration range of nickel in samples varies between from 7.8-2.5µg/l, with an average concentration of 5.1µg/l. All the values of nickel are beyond the acceptable limit of 20 µg/l given by WHO (2006) and BIS (1991).Spatial variation map of nickel (Fig 7) shows low (8.9-40.0µg/l), moderate (40.0-50.0µg/l) and high (50.0-180.0µg/l) contaminated areas.

3.3. Alkaline Heavy Metals (Sr and Ba)

The concentration of strontium varies from 503.6-212µg/l(Table 7),with an average concentration of 3578µg/l. Spatial distribution map of strontium is given in Fig. 4h. The main sources of strontium contamination are anthropogenic activities, industrial discharges and sewage effluents in the study area. BIS and WHO have not given any guideline value for strontium concentration.

The concentration of barium in the samples ranges from 573.0-913.8µg/, with average concentration of 743.4µg/l. Except one sample (smp-11), all the values of barium are within the desirable limit of 700 µg/l given by WHO (2006)and BIS (1991). Spatial variation map of barium is shown in (Fig. 2).

3.4. Alkali Heavy Metals (Li And Rb)

The concentration of lithium in the soil sample varies from 4.9 to 59.4 µg/l with an average concentration of 32 µg/l. The concentration of rubidium varies from 154.7-77.3µg/with an average concentration of 116µg/spatial distribution map of rubidium concentration of the study area is represented by Fig.9. BIS and WHO have not recommended any standard value for lithium and rubidium concentration.

4. Conclusions

Water quality in the area has deteriorated due to increased human population, rapid urbanization, and un-scientific disposal of waste and improper water management. Anthropogenic activities like poultry farms, various industries including chemical and pharmaceuticals, sewage release of reactive pollutants by chemical industries are the main cause for the degradation of water and soil quality in the watershed.

Trace element study indicates that during both pre and post monsoon, concentration of lead, strontium, chromium, nickel, boron, aluminium, selenium found to be high. The findings clearly indicate that the groundwater of the study area is heavily polluted besides high TDS and other inorganic major constituents. A periodical monitoring of the environment by adopting safe domestic and industrial waste disposal system can control the degradation of quality of the groundwater. Indiscriminate use of fertilizers/pesticides, sewage release of reactive pollutants into the atmosphere by chemical industries is the main cause for deterioration of air, water and soil quality in the watershed. The findings of the study also indicate the need for proper industrial planning and the safe disposal of industrial and urban waste, which would otherwise lead to severe environmental degradation. Usually, awareness programs can be conducted to the farmers' use of fertilizers/pesticides and changing of crop systems etc. and mitigate measures is implemented to avoid further deterioration of the Environment for Sustainable Development.

Soil quality degradation has been a major concern for last few decades due to increase in urbanization and industrialization. The main objective of his research was to identify the heavy metal contaminated zones in the study area. Ten soil samples collected throughout the agriculture, residential and industrial areas and were analysed by X-ray Fluorescence Spectrometer for 13 trace metals and ten major oxides. These metals can affect the quality of soil and infiltrate through the soil thereby causing groundwater pollution. Based on the chemical analysis of major oxides ($SiO_{2,}$ $Al_2O_{3,}$ $Fe_2O_{3,}$ MnO, MgO, CaO, Na_2O, K_2O, TiO_2, and P_2O_5) and their distribution; it is observed that, these soils are predominantly siliceous type with slight enrichment of alumina component in the study area.

Conflict of Interest: The authors declared no conflict of Interest

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