Water quality concern in the Amaravathi River Basin of Karur district: a view at heavy metal concentration and their interrelationships using geostatistical and multivariate analysis

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ABSTRACT

Several textile and bleaching industries in the city of Karur, discharge their effluent and was mixed with municipal sewage let into the river Amaravathi at different discharge points. Concentration of trace elements (Cd, Pb, and Ni) exceeded their permissible limits (.003, .01, and .02 ppm, respectively) prescribed by the World Health Organization. Cd (Degree of contamination) and HEI (Heavy metal evaluation index) values were calculated, Cd value of 50% samples have <4 indicates low degree of contamination and for groundwater samples only one-third samples were observed in low pollution and the remaining samples fall in medium to high degree of pollution. HEI value indicates that the average value (12.510, 12.514, and 12.164) of both the samples were above the low pollution range. Good positive correlations observed for Mn, Ni, and Fe with r value from .522 to .913. Principal component analysis (PCA) was used to analyze the data and to identify possible sources of these heavy metals. Three factors for surface water and two factors for groundwater were extracted, where the first three factors account for approximately 58.7% of the total variance of the data-set. The results of groundwater samples show that the factor 1 and 2 accounted for 74.508 and 71.261% of the total variance. The data thus obtained are a sign of anthropogenic and mineral source for these elements in river and groundwater. The spatial distribution map based on ordinary kriging showed that elevated concentrations of heavy metals were located in the upper and down streams of the Amaravathi River basin. The dominance of heavy metals in groundwater and surface water of the Amaravathi river followed the sequence as Pb > Fe > Zn > Cd > Cu > Ni > Mn; Pb > Zn > Cd > Fe > Cu > Ni > Mn, respectively.

Introduction

Water is extremely essential for all forms of lives. Over one billion people worldwide have no access to safe drinking water. The quality of water is a vital concern for mankind since it is directly linked to human welfare (Sehar, Naz, Ali, & Ahmed, 2011). Rivers are important resources, because they are directly used for drinking, bathing, agriculture, transportation, power generation, recreation, and other human activities including waste disposal. But river water is adversely affected due to the discharge of untreated or partially treated industrial effluents, municipal wastewater, as well as washing clothes and cattle bathing (Kumari, Tripathi, Pathak, & Tripathi, 2013). Heavy metals are elements having atomic weights ranging between 63.546 and 200.590 and a specific gravity greater than 4.0 i.e. at least five times that of water. These metals exist in water in colloidal, particulate, and dissolved phases with their occurrence in water bodies being either of natural sources like eroded minerals with sediments, leaching of ore deposits, and volcanism extruded products or of anthropogenic origin like solid waste disposal and industrial or domestic effluents (Momodu & Anyakora, 2010). Few transition elements at trace levels in human metabolism are important for good health. Heavy metals normally found in nature in average amounts do not pose a risk to the environment. However, if the levels of these metals increase, health hazards and risks correspondingly become serious. They produce toxicity by forming complexes with proteins, in which –COOH, –NH2, and –SH groups are engaged. The source of heavy metal ions directly is the meal and indirectly are the industrial activities and traffic (Tuzen & Soylak, 2006).

River water sometimes contains organic contaminations, discharged from agricultural and municipal drains, chemicals and metals, and run-off from land-based activities (Goldar & Banerjee, 2004). The assessment of water quality can be the first and the
most important step toward applying an appropriate quality management plan in order to eliminate water pollution (Mansouri, Salehi, Etebari, & Moghadam, 2012). There is thus the need to assess the quality of groundwater sources. Therefore, the objective of the present study is to explore the heavy metals concentration in the groundwater and surface water of the Amaravathi river belt of Karur region. With the assist of atomic absorption spectrophotometer, the presence and concentration of heavy metals like Cd, Pb, Cu, Zn, Mn, Ni, Fe, and Cr were determined and the findings were compared with the maximum contaminant limit specified by WHO (2005), BIS (2003), ICMR (1975), and USEPA (2009).

Description of the study area

Location

Amaravathi rises from Naimakad at an elevation of 2300 m above mean sea level in the Western Ghats in Idukki district of Kerala state. It flows toward northeast and finally merges with the river Cauvery on its right bank. Amaravathi River lies between the latitudes 11.20°N and 12.00°N and longitudes 77.28°E and 78.50°E in Karur district (Figure 2). It receives water from a number of small streams through the course of 282 km and covers a total area of 8280 km² mainly constituting four districts namely Coimbatore, Erode, Dindigul, and Karur in Tamilnadu. Amaravathi is a tributary of Shammuganadhi, Nankanchi, and Kodaganar Rivers, which join at 60, 40, and 20 km upstream of Karur town, respectively. Amaravathi enters into Karur district near Aravakurichi and merges with river Cauvery near Kattali village, and the flow in the river is seasonal from late October to early February (CGWB, 2008).

Drainage

Major part of Karur district is drained by Cauvery River. Amaravathi, Kodavanar, and Nanganji are the important rivers draining the western part of the district and the river Pungar drains in the eastern part of the district. The drainage pattern, in general, is dendritic. All the rivers are seasonal and carry substantial flows during the monsoon period (Jafar Ahamed, Loganathan, & Jayakumar, 2015).

Geomorphology and hydrogeology

The entire area of the district is a pediplain. The Rangamalai hills and Kadavur hills occurring in the southern side of the district constitute the remnants of the much denuded Eastern Ghats and rise to heights of over 1031 m above mean sea level. There are numerous small residual hills represented by Ayyarmalai, Thanthonimalai, and Velayuthampalayam hills. The general elevation of the area is ranging between 100 and 200 m above mean sea level. The prominent geomorphic units identified in the district are structural hill, pediments, shallow pediments, buried pediments, and alluvial plain. Karur district is underlain entirely by Archaean Crystalline formations with recent alluvial deposits occurring along the river and stream courses. The hard consolidated crystalline rocks of Archaean age represent weathered, fissured, and fractured formations of gneisses, granites, charnockites, and other associated rocks. Groundwater occurs under phreatic conditions, and the maximum saturated thickness of aquifer in hard rock formation varies from 15 to 35 m depending upon the topographic conditions. The groundwater level in the study area available from a depth of 70 to 200 m and water samples were collected from TWAD monitoring bore wells. The thickness of alluvium deposit is estimated to be around 10–12 m. The aquifer parameters for the formation of hard rock and alluvium are furnished in Table 1.

Table 1. Range of aquifer parameters.

| Formation     | Specific yield (%) | Transmissivity (m²/day) | Permeability (m/day) | Yield in LPS |
|---------------|--------------------|-------------------------|---------------------|-------------|
| Alluvium      | 6.8                | 45–205                  | 2–4.5               | 8.3–16.66   |
| Hard rock     | 7–2.3              | 28–75                   | 5–9                 | 1.66–2.5    |

Soil and vegetation

Red soil is the predominant one covering a major part of the district followed by thin red soil and red loam. The red soil is predominantly seen in Kadavur, Kulithalai, Krishnarayapuram, Thanthoni, and Thogamalai blocks. The thin red soils are seen in Aravakurichi and Paramathy blocks. A major portion of the Karur block is covered by red loam (Jafar Ahamed, Loganathan, & Jayakumar, 2015). The major crops under cultivation in this area are paddy (16.30%), groundnut (6.90%), sugar cane (6.40%), jowar (22.60%), and banana (5.30%). Total geographical area is 289557 ha of which area utilised for cultivation is 114554, 37264 ha land put into non-agricultural uses and remaining in other activities (Table 2).

Table 2. The ninefold lands-use/land-cover statistics for the district (CGWB, 2008).

| S. No. | Classification                      | Area (Ha) |
|--------|------------------------------------|-----------|
| 1      | Forests                            | 6187      |
| 2      | Barren and uncultivable lands       | 2901      |
| 3      | Land put to non-agricultural uses   | 37,264    |
| 4      | Cultivable waste                   | 67,831    |
| 5      | Permanent pastures and other grazing lands | 10,801 |
| 6      | Groves not included in the area sown | 1278     |
| 7      | Current fallows                     | 4774      |
| 8      | Other fallow lands                  | 46,802    |
| 9      | Net area sown                       | 111,719   |
| Total  |                                    | 289,557   |
Irrigation practices

The data available indicate that an area of about 54709 ha, which is about 18.89% of the total geographical area of the district is under irrigated agriculture. Dug wells are the major source of water for irrigation in the district, accounting for about 59.97% of the total area irrigated in the district (CGWB, 2008). Tube wells account for about 9.48% of the total area irrigated in the district. On the net area irrigation, the canal irrigates only 29.45% area. The area irrigated under the tank is 1.10%.

Rainfall and climate

Amaravathi River Basin has four distinct seasons, namely southwest monsoon from June to early September, northeast monsoon from October to December, winter season from January to February, and summer season from March to May. The district receives the rain under the influence of both southwest and northeast monsoons. The northeast monsoon chiefly contributes to the rainfall in the district. Most of the precipitation occurs in the form of cyclonic storms caused due to the depressions in Bay of Bengal. The southwest monsoon rainfall is highly erratic and summer rains are negligible. The normal annual rainfall over the district from 1901 to 2011 varies from about 620 to 745 mm, and in 2012, it was 527.6 mm, much less than the normal average of 652.20 mm (Renganathan, 2014), and it is the minimum around Aravakurichi (622.7 mm) in the western part of the district. It gradually increases toward eastwards and attains a maximum around Kulithalai (744.6 mm). The district enjoys a tropical climate, and the relative humidities are generally between 40 and 80%. The mean maximum temperature ranges from 26.7 to 38.56 °C, and the mean minimum temperature ranges from 18.7 to 29.3 °C. The daytime heat is tyrannical and the temperature is as high as 43.9 °C. The lowest temperature recorded is of the order of 13.9 °C (CGWB, 2008).

Experimental work

Sampling and analytical methods

About 12 surface water samples were collected in the month of November 2011 and 24 groundwater samples (Figure 1) were collected from the Amaravathi river belt during November 2012 and 2013 in a pre acid washed 250 ml plastic bottles. The water samples were filtered using a .45 μm Whatman filter paper. The samples were preserved by acidifying to pH ~2 with HNO₃ and kept at a temperature of 4 °C until analysis. Prior to any analysis, all the glassware and containers were soaked in deionised distilled water. The determination of Cd, Pb, Cu, Zn, Mn, Ni, Fe, and Cr (227, 281.5, 323, 212, 278, 231, 247.5, and 358 nm respective wavelength) in water samples were carried out by atomic absorption spectrophotometer (Perkin Elmer A analyst 400). The limit of detection for Cd was .0001 ppm for all other elements. The blank readings for all the metals were .00 ppm in deionised water with EC value lower than 5 μS/cm.

Pollution evaluation methods

Surface and groundwater samples suitability for agriculture and drinking purposes were determined by evaluating the heavy metal concentrations in terms of
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pollution evaluation indices, namely heavy metal evaluation index (HEI) and degree of contamination ($C_d$). These indices are calculated by using the monitored value of the desired parameters and maximum permissible limit of the individual parameters. HEI provides an overall quality of surface and groundwater with respect to trace metals and is expressed as (Prasanna, Praveena, Chidambaram, Nagarajan, & Elayaraja, 2012; Edet & Offiong, 2003):

\[
\text{HEI} = \frac{\sum_{i=1}^{n} H_i}{H_{mac}}
\]

where $H_i$ – monitored value and $H_{mac}$ – maximum permissible concentrations of the $i^{th}$ parameter.

The $C_d$ is designed discretely for all sample of water analyzed, and is calculated as a sum of the contamination factors of every component exceeding the upper permissible value. Thus, the $C_d$ sum up the combined effects of several quality parameters judged detrimental to household water. The contamination index is computed from the below equation

\[
C_d = \sum_{i=1}^{n} C_{fi}
\]

where

\[
C_{fi} = \frac{C_{Ai}}{C_{Ni}} - 1
\]

where $C_{fi}$ – contamination factor, $C_{Ai}$ – analytical value, and $C_{Ni}$ – upper permissible concentration of the $i^{th}$ component ($N$ represents the normative value).

**Multivariate and geostatistical analysis based on GIS**

The detection of pollutants sources was performed with the help of multivariate statistical analyses, such as principal component analysis (PCA), cluster analysis (CA), and Karl Pearson’s correlation coefficients. Multivariate statistical analyses of the data were obtained by using SPSS software for windows version 16.0. PCA was used to identify the potential sources of trace metals and to verify and quantify interrelationships among the real variables in a data-set (Chen, Jiao, Huang, & Huang, 2007). CA was used to determine the association between sampling sites because it provides an indication of similarities or dissimilarities between their trace metal contaminations (Yang et al., 2014). Pearson’s correlation coefficient provides the elemental relationships between the original variables, are presented in non-parametric form. GIS mapping techniques were employed to produce spatial distribution of heavy metals and Arc GIS 9.3 was used to create the spatial distribution and sampling location maps.

**Results and discussion**

**Groundwater chemistry**

Temperature is one of the significant parameters which judge the range of pH and dissolved oxygen content in water samples. Samples with temperature $>$32 °C make water unsuitable for drinking purposes. An increase in temperature leads to the reduced dissolution of ambient oxygen into water samples. The temperature of surface water samples was in the range of 27.1 to 27.8 °C with an average value of 27.4 °C corresponds to November 2011. The temperature in groundwater samples range from 26.7 to 27 °C from the Amaravathi River basin during November 2012, in November 2013 it ranged between 27.2 and 27.8 °C. pH in water samples represent the acidic or alkaline nature, in surface water sample pH ranging from 7.44 to 8.71 with an average value of 7.98. In groundwater samples, pH ranged between 7.26 to 8.45 and 7.42 to 8.32 during November 2012 and November 2013, respectively. For surface water, EC ranges from 615 to 1010 μS/cm with a mean value of 882 μS/cm for November 2011, and in groundwater samples it vary from 1320 to 6123 μS/cm and 1426 to 6672 μS/cm corresponds to November 2012 and November 2013. According to Langenegger (1990) classification, the majority of the samples fall under saline category (1500–10,000 μS/cm). TDS is regarded as one...
of the key factors which decide the use of groundwater for any purpose (Maiti et al., 2013). The TDS value of surface water (November 2011) and groundwater found during November 2012 and 2013 exceeds the acceptable limit of 500 mg/L. Davis and De Wiest (1966) proposed four classes of waters based on TDS for drinking but no one sample fall under desirable for drinking category (<500 mg/L). The DO concentration of surface water samples (November 2011) and groundwater during November 2012 and 2013 are found to be within the limit, i.e. >6 mg/L recommended by BIS (2003) and WHO (2005).

**Metals concentration**

The mean concentration and descriptive statistics of the metals in surface and groundwater of the Amaravathi river delta is given in Table 3 along with some of the national and international standards for drinking water. The analyzed results show that the levels of lead, cadmium, and nickel exceeded their threshold limits (.01, .003, and .02 ppm, respectively) set by the WHO health-based guideline for drinking water. But the Cr concentration in both surface and groundwater samples were below the detectable limit. River water bodies serve the local population for drinking water supply and sundry uses to the rural pupils, this could be warning to environmental and health hazards (WHO, 2008).

Cd occurs mostly in association with Zn and Ca. Cd may interfere with the metallothionein’s (protein) ability to maintain levels of Zn and Cu in the body. When Cd induces metallothionein’s activity, it bridges to Cu and Zn and thus disrupting the homeostasis level (Nduka & Orisakwe, 2011). Under the long-term environmental exposure, the impacts incorporate unsettling influences in the resorption in the proximal tubules, lung infections, and the skeletal structure disorders (Rajappa, Manjappa, & Puttaiah, 2010). Cd concentration in the surface water samples has a mean value of .057 ppm from range of .013 to .099 ppm, same value was observed for groundwater samples in November 2012, while in November 2013 the average Cd value was .056 ppm and values range from .012 to .101 ppm. The samples from lower belt of the Amaravathi River have high Cd content mainly arise from battery industries, industrial activities, widely used in electroplating and also from pigments. The average value shows that all the samples lies above the safe range i.e. .003 ppm recommended for drinking water.

The concentration of Pb ranged between .213 and .314 ppm for surface water samples with a mean value of .264 ppm, a minimum value of .142 and .127 ppm and maximum of .314 and .293 ppm with an average value of .231 and .227 ppm in groundwater samples for November 2012 and 2013, respectively. The average value shows that the samples exceeded the standard specification limit (Table 3). High concentration of Pb was relatively from the usage of unleaded petrol in the region several years ago and also the usage of pesticides for agricultural activities which contains Pb. It could be found naturally in rocks like galena (PbS), cerussite (PbCO3), minim (Pb3O4), and other minerals. Pb will impede with the functions of essential nutrients of similar features such as Ca and Zn, because of its magnitude and charge resemblance, it replaces Ca and gets included in bone. Pb in lower concentration is not harmful but if high levels of Ca are ingested, Pb in bone was replaced, the free Pd in the body system resulting in hypertension, nephrotoxicity, and neurotoxicity (Lewis & Cohen, 2004; Osmond et al., 1995).

Cu is one of the essential elements necessary for the metabolism but however in excess concentration cause adverse effects in the organism. The average Cu values in surface and groundwater samples were .050, .045, and .044 ppm, respectively. In surface water samples, the minimum recorded value was .023 and maximum .075 ppm and in groundwater samples the lower and higher values for November 2012 and 2013 were .022–.075 ppm and .019–.074 ppm, respectively. The ideal intake amount of Cu is 2 mg/day. Water with 3 ppm Cu is associated with gastrointestinal disturbance in adults (Chung, Chung, Liao, & Miaw, 2009; Saleshrani & Prabhahar, 2013). In the present study all the samples are in safe range.

Zn is an essential trace element for organisms and plays an important role in the physiological and metabolic processes of many organisms. The desirable limit of Zn in drinking water is specified as 3 ppm (WHO, 2008). Several studies suggest that excessive amount of Zn (3–5 ppm) can cause neuron death and toxicity resulting in diarrhea, vomiting and may appear opalescent and develop a greasy film on boiling vessel and produce bitter taste (Pizarro et al., 1999; WHO, 2006; Atapour, 2012). The analysis of surface water revealed

| Parameters | Cd | Pb | Cu | Zn | Mn | Ni | Fe |
|------------|----|----|----|----|----|----|----|
| **(a) Surface water** | Minimum | .013 | .213 | .023 | 0 | 0 | 0 | .017 |
| | Maximum | .099 | .314 | .075 | .766 | .057 | .051 | .07 |
| | Average | .057 | .264 | .050 | .159 | .023 | .026 | .050 |
| | Standard deviation | .037 | .026 | .021 | .239 | .019 | .017 | .014 |
| **(b) Groundwater samples – November 2012** | Minimum | .013 | .142 | .022 | 0 | 0 | 0 | .060 |
| | Maximum | .099 | .314 | .075 | .766 | .057 | .051 | .799 |
| | Average | .057 | .231 | .045 | .104 | .017 | .035 | .123 |
| | Standard deviation | .032 | .044 | .016 | .180 | .021 | .032 | .148 |
| **(c) Groundwater samples – November 2013** | Minimum | .012 | .172 | .019 | .002 | 0 | 0 | .052 |
| | Maximum | .101 | .293 | .074 | .682 | .059 | .083 | .764 |
| | Average | .056 | .227 | .044 | .096 | .015 | .032 | .116 |
| | Standard deviation | .032 | .044 | .016 | .164 | .017 | .028 | .142 |

Table 3. Descriptive statistics for metals in surface and groundwater samples (ppm).
that the concentration of surface water was lower than the prescribed standards. The minimum value recorded was from 0.015 ppm to 0.766 ppm with a mean value of 0.159 ppm. In groundwater samples for November 2012 and 2013 the values ranged from 0.02 to 0.090 ppm with an average value of 0.023 ppm. Average values of 0.017 and 0.015 ppm were observed for groundwater samples in November 2012 and 2013 and the values ranged between 0.015 and 0.059 ppm, respectively. Dobson, Erickson, and Aschner (2004) and Sehar et al. (2011) have reported that Mn exposure rivets both psychiatric indication and Parkinsonism skin texture. High concentration of Mn may lead to mitochondrial fraction of the human kidney, liver, and pancreas, however, high dosage of Mn results in some diseases, including liver damage. The highly recommended value in drinking water is 0.1 ppm and all the samples are in safe range.

Elevated level of Ni may cause diverse diseases like, vomiting, nausea, abdominal discomfort, headache, cough, and shortness of breath (WHO, 1997). The main source of nickel in drinking-water is (i) leakage from metals in contact with drinking water, such as pipes and fittings. Nickel is used generally in the fabrication of stainless steels, non-ferrous alloys, and super alloys. (ii) Use of nickel and nickel salts in electroplating, as catalysts, in nickel-cadmium batteries, in coins, in welding products, and in certain pigments and electronic products (Sekhon & Singh, 2013). Food is the dominant source of nickel exposure in the non-smoking, non-occupationally exposed population while water is generally a minor contributor to the total daily oral intake (WHO, 2003). The recorded Ni concentration in surface water samples are found between 0.017 and 0.057 ppm (mean: 0.026 ppm) and in groundwater samples concentration varies from 0.090 to 0.083 ppm with an average value of 0.035 and 0.032 ppm, respectively, for November 2012 and 2013. 90% of samples in upper belt of the river exceeded the recommended limit of 0.02 ppm.

Fe is an essential element in human nutrition; however, estimates of the minimum daily requirement for iron depend on age, sex, physiological status, and iron bioavailability and range from about 10 to 50 mg/day (WHO, 2003; Adeola Oketola, Seun Adelokun, & Osibanjo, 2013). Fe plays a number of bio-inorganic functions in living things (human, plants, animals, and bacteria), however, excessive intake may damage liver, heart, and endocrine glands and it may change the color of the water (Mansouri et al., 2012; Porter, 2001; Sivakumar & Dheenedayalan, 2012). Fe value in surface water varies between a minimum of 0.017 ppm and a maximum of 0.70 ppm, with an average value of 0.050 ppm. In November 2012 and 2013, the Fe content in groundwater samples varies from 0.060, 0.052 ppm and maximum of 0.799 and 0.764 ppm, respectively. Maximum concentration was observed in upper belt of Amaravathi river which may be mainly due to the weathering of deeper materials usually contain higher percentage Fe (silicates, feldspar, and biotite) and in downstream, it is owing to the mixing of industrial wastewater and also from the reaction of rainwater and groundwaters with siltstone, shale, limestones, and anthropogenic constructional basis.

**Trace metal pollution evaluation indices**

The results of $C_d$ and HEI for surface and groundwater samples are incorporated in Table 4 and 5. The extent of metal pollution was estimated using the degree of contamination ($C_d$) and was mainly classified into three categories (Prasanna et al., 2012; Edet & Offiong, 2003; Backman, Bodis, Lahermo, Rapant, & Tarvainen, 1997) as follows: $C_d < 4$ (low), $C_d = 4–8$ (medium), and $C_d > 8$ (high). $C_d$ value in surface water samples range from −9.793 to 9.793 with a mean value of 5.354. Table 6 indicates that 50% (S1, S2, S4, S5–S7) samples have low degree of contamination and remaining 50% (S3, S8, S9, S10, S11, and S12) samples exceed $C_d > 8$ (high), suggested that they are impaired highly. In groundwater samples for November 2012, the range and mean value of $C_d$ was 1.808–13.586 and 5.37. The classification Table 6 evidently shows that 58.33% (B, E–L, a, d, g–i) and 16.67% (c, j–l) samples belong to medium and high contamination and only 25.00% (A, C, D, b, e, and f) samples are found to be in safer zone. And in the year 2013, the average value of $C_d$ was 4.979 and ranged between .429 and 13.443, the mean deviation and percentage deviation were presented in Table 5. About 12.50% (c, h, k) samples are classified as high polluted zone, 50.00 (G–L, a, d, g–i) and 37.50% (A–E, b, e, f) samples fall within medium and low pollution zones. The $C_d$ value reflects that only one-third samples are in

| Sample id | Mean deviation | % deviation | HEI | Mean deviation | % deviation |
|-----------|----------------|-------------|-----|----------------|------------|
| S1 −.967  | 4.567          | 82.533      | 5.753 | −6.757        | 54.015     |
| S2 −.331  | 5.203          | 94.027      | 6.669 | −5.841        | 46.688     |
| S3 8.849  | 3.315          | 59.909      | 15.849 | 3.339         | 26.695     |
| S4 2.932  | −2.602         | −47.018     | 9.932 | −2.578        | −20.607    |
| S5 1.772  | −3.762         | −67.980     | 8.772 | −3.738        | −29.879    |
| S6 3.249  | −2.285         | −41.282     | 10.249 | −2.261        | −18.070    |
| S7 3.873  | −1.661         | −30.014     | 10.873 | −1.657        | −13.085    |
| S8 9.166  | 3.632          | 65.625      | 16.166 | 3.656         | 29.221     |
| S9 9.793  | 4.259          | 76.956      | 16.793 | 4.283         | 34.234     |
| S10 9.429 | 3.895          | 70.385      | 16.429 | 3.919         | 31.327     |
| S11 9.088 | 3.554          | 64.227      | 16.088 | 3.578         | 28.603     |
| S12 9.793 | 4.017          | 72.580      | 16.551 | 4.041         | 32.298     |

| Minimum | 5.534 | 12.510 |
low pollution zone, and the remaining were in median or in high pollution zone due to contamination by both geogenic and man-made activities.

Pollution indices for trace elements were identified significantly by means of heavy metal evaluation index. For better understanding, the pollution levels have been classified as low (HEI <10), medium (HEI = 10–20), and high (HEI >20). HEI value in surface water samples varies from 5.753 to 16.793 with a mean value of 12.510. Analyzed report shows that about 66.67% (S3, S6, S7, S8, S9, S10, S11, S12) samples fall in medium zone and 33.33% (S1, S2, S4, S5) fall in low zone. Fascinatingly, in the lower basin samples (S8–S12), HEI values were above the mean value of indices (Table 4), reflect the possible contamination by metal pollutants. In groundwater samples, HEI values range from 8.705 to 20.586 (mean: 12.514) for November 2012 and a minimum value of 7.334. Maximum values of 20.443 with an average value of 12.164 were recorded for samples in the year November 2013. The samples A, C, D:A–E, b (2012:2013) may be considered as less polluted, samples B, E–L, a, b, d–l:F–L, a, d–l (2012:2013) as moderately contaminated and sample c in both years was highly contaminated, nearby no industries were located and contamination is mainly due to the orientation of agricultural activities and weathering of deeper minerals. The variation trends of \( \text{Cd} \) and HEI at different sampling points are shown in Figure 2 which reveals similar deviation for surface and groundwater samples.

Table 5. Water pollution indices for groundwater samples.

| Sample id | November 2012 | November 2013 |
|-----------|---------------|---------------|
| \( C_d \) | \( \text{Cd} \) | \( \text{Cd} \) |
| Mean deviation | % deviation | HEI | Mean deviation | % deviation | HEI |
|----------------|-------------|-----|---------------|-------------|-----|
| A | 1.808 | −3.562 | −66.328 | 8.705 | −3.809 | −50.41 |
| B | 4.277 | −1.093 | −20.363 | 11.277 | −1.237 | −19.93 |
| C | 2.870 | −2.500 | −66.557 | 9.870 | −2.644 | −21.129 |
| D | 2.868 | −2.502 | −66.593 | 9.86 | −2.646 | −21.145 |
| E | 4.883 | −532 | −9.911 | 11.838 | −4.308 | −28.777 |
| F | 4.069 | −1.301 | −24.230 | 11.277 | −1.237 | −9.889 |
| G | 4.975 | −395 | −7.358 | 11.975 | −2.644 | −21.129 |
| H | 5.260 | −110 | −2.043 | 12.260 | −2.078 | −21.129 |
| I | 6.032 | .662 | 12.323 | 13.032 | .518 | 13.639 |
| J | 4.002 | −3.168 | −8.280 | 11.909 | −605 | −4.833 |
| K | 6.308 | .938 | 17.476 | 13.308 | .794 | 28.416 |
| L | 6.223 | .853 | 15.890 | 13.233 | .709 | 6.070 |
| a | 4.909 | −461 | −8.280 | 11.909 | −605 | −4.833 |
| b | 3.623 | −1.747 | −32.541 | 10.623 | −1.891 | −15.115 |
| c | 13.586 | 8.216 | 152.999 | 20.586 | 8.072 | 64.504 |
| d | 5.339 | −.031 | −583 | 12.333 | −175 | −1.401 |
| e | 3.302 | −2.068 | −35.510 | 10.302 | −2.212 | −17.676 |
| f | 3.846 | −1.524 | −28.378 | 10.846 | −1.668 | −13.328 |
| g | 4.650 | −.720 | −13.414 | 11.650 | −.864 | −6.907 |
| h | 7.636 | 2.266 | 42.192 | 14.636 | 2.122 | 16.955 |
| i | 7.349 | 1.979 | 36.861 | 14.349 | 1.835 | 14.667 |
| j | 8.058 | 2.688 | 50.052 | 15.058 | 2.544 | 20.328 |
| k | 8.518 | 3.148 | 58.628 | 15.518 | 3.004 | 24.008 |
| l | 8.094 | 2.724 | 50.724 | 15.094 | 2.580 | 20.616 |
| Minimum | 1.808 | 8.705 | .429 | 7.334 |
| Maximum | 13.586 | 20.586 | 13.443 |
| Mean | 5.370 | 12.514 | 4.979 |

Table 6. Categorisation of water samples based on pollution indices.

| Indices | Category | Degree of pollution | No. of samples | % | Samples |
|---------|----------|---------------------|----------------|-----|---------|
| Surface water samples | \( C_d \) | Low | 6 | 50.00 | S1, S2, S4, S5-S7 |
| | 4–8 | Medium | 6 | 50.00 | S3, S8, S9, S10, S11, S12 |
| | >8 | High | 6 | 50.00 | S3, S8, S9, S10, S11, S12 |
| HEI | <10 | Low | 4 | 33.33 | S1, S2, S4, S5 |
| | 10–20 | Medium | 8 | 66.67 | S3, S6, S7, S8, S9, S10, S11, S12 |
| | >20 | High | | | |
| Groundwater samples – November 2012 | \( C_d \) | Low | 6 | 25.00 | A, C, D, b, e, f |
| | 4–8 | Medium | 14 | 58.33 | B, E-L, a, d, g-i |
| | >8 | High | 4 | 16.67 | c-j, i |
| HEI | <10 | Low | 3 | 12.50 | A, C, D |
| | 10–20 | Medium | 20 | 83.33 | B, E-L, a, d, b-d-i |
| | >20 | High | 1 | 4.17 | c |
| Groundwater samples – November 2013 | \( C_d \) | Low | 9 | 37.50 | A-E, b, e, f |
| | 4–8 | Medium | 12 | 45.83 | G-L, a, d, g-i, j |
| | >8 | High | 3 | 16.67 | c-h, k |
| HEI | <10 | Low | 6 | 25.00 | A-E, b |
| | 10–20 | Medium | 17 | 70.83 | F-L, a, d-i |
| | >20 | High | 1 | 4.17 | c |
Multivariate statistical analysis

Karl Pearson’s correlation coefficient matrices were performed for analyzed parameters for both surface and groundwater samples and the values are presented in Table 7. In surface water samples, Zn, Mn, and Fe shows significant positive correlation, while inverse correlation were observed between Cu and Mn with Cd ($r = -.797$ and $-.635$). Mn have significant good correlation with Cu ($r = .913$) and moderate with Zn ($r = .672$). The pronounced positive correlation was exhibited between Fe and Ni ($r = .706$) and also with Pb ($r = .642$). A moderate correlation ($r = .540$ and .522) was observed between Zn and Pb and Cu also. The result suggests that these metals are not derived from same sources, but from different sources like wastewater mixing, high traffic load, and anthropogenic activities. Among the groundwater samples, Mn and Ni exhibit good positive correlation with Cu and Zn and negatively correlated with Mn and Ni in both the seasons. High positive correlation were observed for Ni vs. Mn ($r = .841$, .753), Ni vs. Cu ($r = .775$, .616), moderate correlation for Mn vs. Cu and Zn ($r = .650$, .570 and .604, .609), Ni vs. Zn ($r = .544$ and .536), Fe vs. Cu ($r = .552$), and negative correlation was exhibited by Cd with all other parameters except Pb for the season November 2012 and 2013.

Detection of pollution source

Factor analysis was used to look at the degree of metal pollution and for source identification (Singaraja, Chidambaram, Prasanna, Thivya, & Thilagavathi, 2014). Afterwards component loading, a measure of degree of proximity between the variables and factor score interpreted by Kaiser criterion called varimax rotation, a scheme that explains the possible groups/sources that influenced the water system for maximisation of the variance of factor with acceptable Eigen value $>1$ (Cloutier, Lefebvre, Therrien, & Savard, 2008; Shrestha & Kazama, 2007). PCA was classified into three categories thus value $>.75$ indicate strong loadings, $.75−.50$ have moderate loading, and $.50−.30$ indicate weak loadings (Liu et al., 2003). Component loadings, Eigen value, total percentage variance, and

Table 7. Correlation coefficient ($r$) between the metals in surface and groundwater samples.

| Parameters | Cd   | Pb   | Cu   | Zn   | Mn   | Ni   | Fe  |
|------------|------|------|------|------|------|------|-----|
| (a) Surface water |      |      |      |      |      |      |     |
| Cd         | 1    |      | -.797*** |      | .063 |      | .187 | .232 |
| Pb         |      | 1    | -.024 | .540 | .189 | .306 | .642*|
| Cu         |      |      | 1    | .522 | .913* | -.443 | -.254 |
| Zn         |      |      |      | 1    | .672** | -.400 | -.053 |
| Mn         |      |      |      |      | 1    | -.381 |-.107 |
| Ni         |      |      |      |      |      | 1    | .706* |
| Fe         |      |      |      |      |      |      | 1    |
| (b) November 2012 |      |      |      |      |      |      |     |
| Cd         | 1    |      | -.648** |      | -.076 | -.739*** | -.751*** | -.405* |
| Pb         |      | 1    | .123 | .441* | .202 | -.018 | .014 |
| Cu         |      |      | 1    | -.559*** | .650* | .775** | .494* |
| Zn         |      |      |      | 1    | -.604* | .544  | .114 |
| Mn         |      |      |      |      | 1    | .841** | .262 |
| Ni         |      |      |      |      |      | 1    | .360 |
| Fe         |      |      |      |      |      |      | 1    |
| (c) November 2013 |      |      |      |      |      |      |     |
| Cd         | 1    |      | -.559*** |      | -.024 | -.691*** | -.701*** | -.371 |
| Pb         |      | 1    | .200 | .405* | .203 | -.046 | .087 |
| Cu         |      |      | 1    | .442* | .570 | .616* | .552* |
| Zn         |      |      |      | 1    | .609** | .536** | .107 |
| Mn         |      |      |      |      | 1    | .753** | .170 |
| Ni         |      |      |      |      |      | 1    | .378 |
| Fe         |      |      |      |      |      |      | 1    |

*Correlation is significant at the .05 level (2-tailed); **Correlation is significant at the .01 level (2-tailed). Bold value indicates high significant correlation.
cumulative percentage of PCA for both the samples were listed in Table 8. For surface water samples, three PCs were isolated which explained 94.216% of the total variance with Eigen value >1.9 was shown in Scree plot (Figure 3). Factor 1 was dominated by Cd, Cu, and Mn accounted for 36.664% of the total variance with an Eigen value of 2.566 and input in the surface water was mainly originating from industrial wastes, rainwater runoff containing trace amount of elements from soil layer and also influence of pesticide activities. Factor 2 accounted for 29.503% of the total variance at an Eigen value of 2.065 and was represented by Pb, Ni, and Fe, mainly from automobile exhaust, mixing of agricultural runoff with river water and wastewater dominance. Factor 3 is mainly contributed by Pb and Zn with a variance 28.049%

Table 8. Varimax principle component analysis for surface and groundwater samples.

| Parameters | Surface water sample | Groundwater samples |
|------------|----------------------|---------------------|
|            | PC1 | PC2 | PC3 | PC1 | PC2 | PC1 | PC2 |
| Cd         | -0.936 | 0.080 | 0.322 | -0.905 | 0.185 | -0.889 | 0.313 |
| Pb         | -0.120 | 0.555 | 0.781 | -0.149 | 0.844 | -0.118 | 0.861 |
| Cu         | 0.924 | -0.227 | 0.267 | 0.832 | 0.302 | 0.779 | 0.287 |
| Zn         | 0.244 | -0.202 | 0.923 | 0.365 | 0.827 | 0.386 | 0.787 |
| Mn         | 0.845 | -0.122 | 0.479 | 0.814 | 0.398 | 0.796 | 0.367 |
| Ni         | -0.194 | 0.887 | -0.245 | 0.908 | 0.223 | 0.890 | 0.150 |
| Fe         | -0.099 | 0.925 | 0.190 | 0.571 | -0.079 | 0.550 | 0.005 |
| Eigen values | 2.566 | 2.065 | 1.963 | 3.48 | 1.735 | 3.29 | 1.699 |
| % of variance | 36.664 | 29.503 | 28.049 | 49.716 | 24.792 | 46.995 | 24.265 |
| Cumulative % | 36.664 | 66.167 | 94.216 | 49.716 | 74.508 | 46.995 | 71.261 |

Figure 5. (a–c) Dendogram showing relationship among metals in surface and groundwater samples.
and Eigen value of 1.963 representing the rock dominance (sulfide minerals) on the river bank, these on oxidation release trace metals like Cu, Zn, Pb, etc. in water which was evidently reported by Sahraei Parizi and Samani (2013). Loadings of component 1, 2, and 3 are shown in Figure 4. Positive loading in PCA point out that the water samples were polluted by individual parameters and negative scores indicate unlikely by those parameters.

For groundwater samples in both seasons (November 2012 and 2013), the parameters were grouped into two main components with the total variance percentage of 74.508 and 71.261, respectively. Scree plot of Eigen values were the most satisfactory method of PCA (Figure 3). In both the seasons, Factor 1 loaded by Cd, Cu, Mn, Ni, and Fe accounted for variance of 49.716 and 46.995 with an Eigen value of 3.48 and 3.29 and this contribution was mainly by

![Figure 6a. Spatial distribution of Cd in groundwater samples (November 2012 and 2013).](image-url)
anthropogenic toxic pollution by industrial effluents/metal activities and minor source by natural weathering processes. Factor 2 was contributed by Pb and Zn accounted for 24.792 and 24.265% of data variance and having Eigen value of 1.735 and 1.699. Scores of component 1 and 2 for groundwater samples are represented in Figure 4. It explains that Pb and Zn was derived into groundwater by non-point sources like agricultural fertilizers (Zn based) leaching process, usage of carbon waste to irrigation land from industries, toxic pesticides and fungicides and point sources from industries which located on the belt of the river basin. There are several textile industries located in and around Karur district; the government implemented the zero discharge effluents into river, big factories had even dug tube wells to a depth of

Figure 6b. Spatial distribution of Cu in groundwater samples (November 2012 and 2013).
Hierarchical cluster analysis was performed to understand and identify the natural groups both in samples (Q-mode) and variables (R-mode). R-mode HCA was done to classify the parameters into groups based on their similarity with each other, whereas the Q-mode was performed to classify the parameters into groups based on their dissimilarity with each other (Nagaraju, Sunil Kumar, Thejaswi, & Sharifi, 2014; Davis, 2002). R-mode CA was performed on the surface water samples constitute of three clusters, where as elements belong to same group was instigating from the same sources. Cluster 1 includes elements like Cu, Fe, Mn, Ni, and Cd (Figure 5a) reflects the influence of anthropogenic contribution and runoff 275 m and discharged effluents into these wells, leads to contamination of groundwater in the area. Owing to these reasons, the soil turned infertile, yield of the crops came down, slowly the farmlands became barren and 250 open wells get contaminated (Suchitra, 2014).

Cluster analysis

Hierarchical cluster analysis was performed to understand and identify the natural groups both in samples (Q-mode) and variables (R-mode). R-mode HCA was done to classify the parameters into groups based on their similarity with each other, whereas the Q-mode was performed to classify the parameters into groups based on their dissimilarity with each other (Nagaraju, Sunil Kumar, Thejaswi, & Sharifi, 2014; Davis, 2002). R-mode CA was performed on the surface water samples constitute of three clusters, where as elements belong to same group was instigating from the same sources. Cluster 1 includes elements like Cu, Fe, Mn, Ni, and Cd (Figure 5a) reflects the influence of anthropogenic contribution and runoff.
from township wastes. Cluster 2 is composed by Pb and cluster 3 consisting of Zn were mainly attributed by irrigation land runoff mingle with river water system. In groundwater system same clusters have been isolated for both seasons. Cu, Ni, and Mn were associated in cluster 1 resembles from the same sources and classified as low or minor pollutants to the water samples. Clusters 2–5 (Figure 5b and c) were individually assigned by Cd, Fe, Zn, and Pd, while its origins were from different sources at different sites seemingly outcome from the deeper hard rock and by man-made activities identified as moderate pollutants. Pb was clustered independently, considered as high pollutant in the samples derived from both point and non-point sources.

**Spatial distribution**

Figures 6a–g show the spatial distributions of different elements concentration in the groundwater samples using Kriging method. Cd was distributed

![Figure 6d. Spatial distribution of Mn in groundwater samples (November 2012 and 2013).](image)
evenly throughout the river basin except central locations (Figure 6a), while high concentration of Cu were extended from southern part of the river basin (right side of the river basin) to northwest of the study area (left side of the river basin) shown in distribution map (Figure 6b). Apparently, high Fe content was observed in upper and moderate in central part in sample a and samples b–g, respectively (Figure 6c). Mn and Ni were spread from upper part to middle part of the river basin and little governance of Ni in lower region (Figure 6d and e). Metal Zn (Figure 6f) was distributed crisscrossly covering the little part of upper basin and highly in lower basin. Pd was evenly distributed throughout the study basin which occurs as major element with concentration when compared to other metals. The sequence of metal concentration by average value as Pb > Zn > Cd > Fe > Cu > Ni > Mn for surface water samples and for groundwater samples the assemblage follows as Pb > Fe > Zn > Cd > Cu > Ni > Mn.
Principal component analysis revealed that two main factors controlling the metal groundwater chemistry namely man-made pollution, specifically sewage with wastewater and host rock weathering. Cluster 1 of surface water includes elements like Cu, Fe, Mn, Ni, and Cd derived from equivalent sources and cluster 2 and 3 likely from farming sources. Groundwater samples are

Conclusion

This study has provided some insights into the spatial distribution outline of trace elements at different sites from different water samples collected on the bank of Amaravathi River. The order of trace element concentration in surface water samples is Mn < Ni < Cu < Fe < Cd < Zn < Pb and for groundwater samples, the order is Pb > Fe > Zn > Cd > Cu > Ni > Mn. Degree of contamination (>4) and heavy metal evaluation index (>10) value highlights the semi-critical stage of water samples presented in medium contamination by metals. Principal component analysis revealed that two main factors controlling the metal groundwater chemistry namely man-made pollution, specifically sewage with wastewater and host rock weathering. Cluster 1 of surface water includes elements like Cu, Fe, Mn, Ni, and Cd derived from equivalent sources and cluster 2 and 3 likely from farming sources. Groundwater samples are
grouped into different clusters with non-like sources varied by different sampling sites. Spatial distribution maps provide the course of metal concentration covering the study region. These results are valuable in prospect actions in river and groundwater management for home government and policy-makers.

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Figure 6g. Spatial distribution of Pb in groundwater samples (November 2012 and 2013).
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