

Appraisal of Heavy Metals in Groundwater in Chennai City Using a HPI Model

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Abstract Heavy metal contamination in Chennai city was evaluated using a heavy metal pollution index (HPI) model in conjunction with the spatial distribution maps. Metals such as Cd, Cr, Cu, Pb and Zn in the groundwater were determined using standard methods and the resultant data was utilized in the development of a HPI model. The metal concentrations showed a dominance in the order of $Zn > Cu > Cr > Pb > Cd$ respectively. About 14.3 % of the samples ($n = 2$), exhibited high HPI (>38) and the highest value, $HPI = 97.55$, has been recorded from Thiruvannamiyur area. Statistical analysis revealed a positive correlation between metals such as Cd and Cr ($r = 0.606$), Cd and Cu ($r = 0.601$), Cr and Cu ($r = 0.464$) and Pb and Zn ($r = 0.416$), suggested their common origin. The spatial distribution maps of heavy metals and the HPI suggested that the SW region, especially Adyar and Thiruvannamiyur regions are highly contaminated with the metals. Industrialisation and improper waste dumping were identified as the major cause for the accumulation of metals in the groundwater of Chennai city.

Keywords Heavy metals · Heavy metal pollution Index (HPI) model · Spatial distribution · Chennai city

Groundwater contamination is one of the most important environmental issues in the present world (Vodola et al. 1997), in which metal contamination deserves major concern due to its high toxicity even at low concentration (Marcovecchio et al. 2007; Momodu and Anyakora 2010). Naturally metals enter into groundwater from a variety of sources, such as chemical weathering of rocks and soils, decomposing vegetation and animal matter and wet and dry fallout of atmospheric particulate matter (Reiners et al. 1975; Charles et al. 1994). However, manufacturing processes act as the major sources of metals in many industrial urban areas. Municipal solid wastes can also contribute considerable amount of metals to the groundwater through batteries, disposable household materials, plastics, paints and inks, body care products, medicines and household pesticides (Bardos 2004). Though metals such as zinc, chromium, manganese, cadmium, cobalt, etc. play a biochemical role in the aquatic life, their excess presence is toxic and also non-biodegradable (Nurnberg 1982).

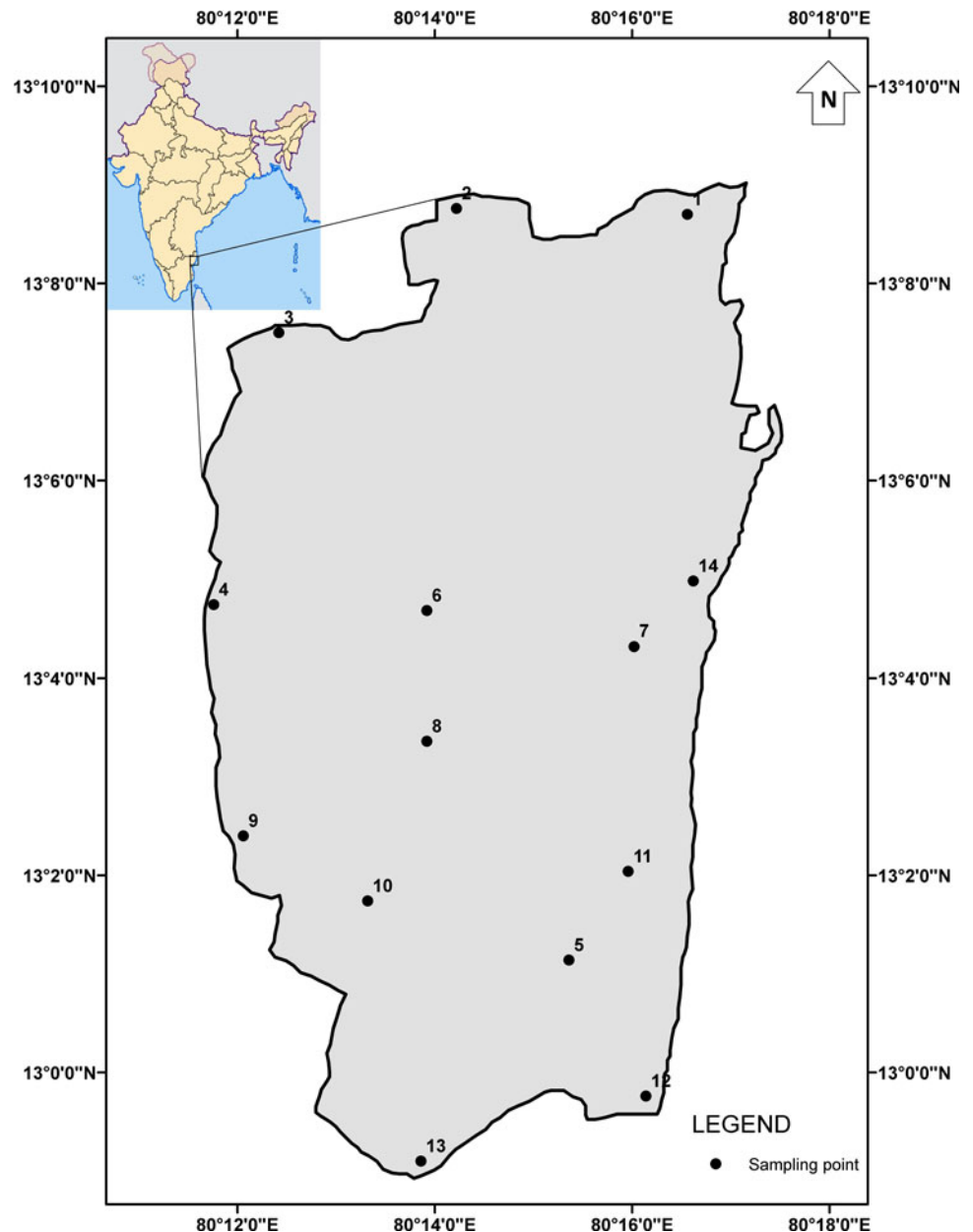
The present study was carried out in Chennai; the capital of Tamil Nadu located in the South-East coast of India (Fig. 1). As of 2011 census, the city had 4.6 million residents making it the sixth most populous city in India. Chennai city has numerous industries like leather tanneries, cotton textiles, chemical and chemical products, petrochemical, pesticides and fertilizer units. The climate is tropical and the average annual rainfall of the district is 1,200 mm (1978–2008). The temperature and humidity are in the range of 13.9–45°C and 65 %–84 % respectively. Major part of the study area has flat topography with very gentle slope towards east. The major geological formations are Achaean crystalline rocks, consolidated Gondwana and Tertiary sediments and the recent alluvium. Crystalline rocks of the district comprise chiefly of charnockites, gneisses and the associated basic and ultra basic intrusive.

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Fig. 1 Location map of the study area



Weathered and jointed/fractured crystalline rocks of varying thickness act as the deep aquifer for many regions of Chennai district. The alluvium, sand, silts and clay covers the major part of Chennai with varying thickness (CGWB 2008). Many researchers have studied the contamination due to metal contamination in both surface and groundwaters (Tanji and Valoppi 1989; Asubiojo et al. 1997; Klavins et al. 2000; Leung and Jiao 2006; Kaushik et al. 2009; Mansouri et al. 2012). A few studies were conducted in Chennai for assessing the metal contamination (Ramesh and Purvaja 1995; Kumaresan and Riyazuddin 2008; Jayaprakash et al. 2012). However, the rapid increase in the population as well as industries amplified the contamination load. Moreover, the adverse affect of metals on human

health asking for a thorough and routine monitoring of this contamination. The present study evaluates the heavy metal pollution and its distribution in the groundwater of Chennai city.

Materials and Methods

A total of 14 groundwater samples were collected from the study area during March 2008. Wells were pumped out at least 10 min prior to the sample collection. Polythene sampling bottles of 500 mL capacity were used as sample container. Bottles were washed with distilled water and acidified with conc. HNO_3 . Collected samples were

transported to the laboratory and analysed within 24 h. Many of the sampled wells were the main domestic source of water for the local people. The analyses of the metals were carried out using AAS (Perkin Elmer A Analyst 400). The AAS was calibrated for all the metals by running different concentrations of standard solutions. Only standards (above 1,000 µg/mL) were held in storage. Working standards were diluted from standard stock solutions only when needed. Standard addition solutions can be prepared containing all of the required elements. This will avoid multiple splitting of the sample for individual elements and reduce the amount of time spent in preparing standards. Average values of three replicates were taken for each determination. The detection limits for Pb, Cd, Zn, Cu and Cr were 3.0, 1.60, 1.60, 3.0 and 3.0 mg/L respectively. Statistical analysis was performed using SPSS 16 and Geostatistical tool of Arc GIS 9.3. Heavy metal pollution index (HPI) was calculated for the study area using the Eq. 1 (Mohan et al. 1996).

$$\text{HPI} = \left[\sum_{i=1}^n Q_i \times W_i \right] / \sum_{i=1}^n W_i \quad (1)$$

where Q_i is the Sub index of the i th parameter, W_i is the unit weight of the i th parameter and n is the number of parameters considered. The sub index (Q_i) of the parameter is calculated by the Eq. 2

$$Q_i = \sum_{i=1}^n [(M_i - I_i)] / [(S_i - I_i)] \times 100 \quad (2)$$

where M_i is the monitored value of heavy metal of the i th parameter, I_i is the ideal value of the i th parameter, S_i is the Standard value of i th parameter.

Results and Discussion

The summary statistics of metal concentration in the study area is presented in Table 1. A box plot was created for all the metals for the better visualization of statistical parameters (see Fig. 2). Chromium is a steel-like gray, odourless, tasteless, hard metal that takes a high polish and has a high melting point. Industrial activities such as electroplating, leather tanning, and wood preservation release large quantities of liquid and solid waste containing chromium

Table 1 Statistical summary of metal concentration in the groundwater (µg/L)

	Cd	Cr	Cu	Pb	Zn
Min.	0.8	5.2	26.023	1.67	35.02
Max.	2.6	88.36	531.85	24.83	1,142.70
Avg.	1.33	17.19	139.28	8.47	213.78

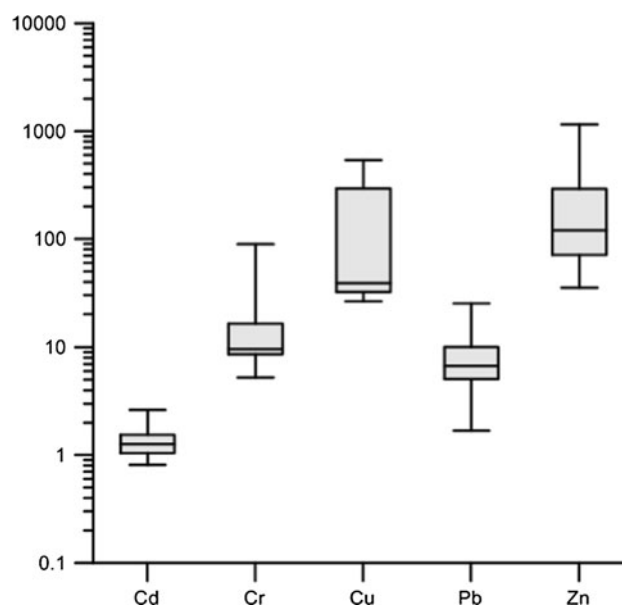


Fig. 2 Box-whisker plot showing the distribution of metals (in µg/L) in the groundwater

(Fetter 1993). Chromium compounds bind to soil and eventually contaminate the groundwater. The possible health hazards are skin irritation, ulceration, and liver and kidney damage. The concentration of Cr in the Chennai region is ranged between 5.2 and 88.36 µg/L. In which 8 % of the samples exceeded the permissible limit 50 µg/L (WHO 2011).

Cadmium is a minor metallic element naturally occurring in the earth's crust and waters. It is used as a pigment for corrosion resistant plating on steel and also used in stabilizing the plastic. Exposure to certain forms and concentrations of cadmium is known to produce toxic effect on humans. The maximum permissible limit of Cd in drinking water is 10 µg/L (WHO 1996). Result shows a range (0.8–2.6 µg/L) of cadmium with an average of 1.33 µg/L. All the samples contained below the permissible limit. Copper is a malleable metallic element used in large quantities as an electrical conductor such as brass and bronze. Industries such as steel, plastic and blast furnaces cause the accumulation of Cu in water. Agrochemicals and waste dumps also act as important sources. The accepted value of Cu in drinking water is 30 µg/L (USEPA 2003). In the present study, the concentration of copper ranged from 26.023 to 531.85 µg/L. Lead is a heavy metal, belonging to the carbon group, mostly used in the manufacture of lead-acid storage batteries. Lead is also released from smelting, motor-vehicle exhaust fumes and from corrosion of lead pipe work (Gowd and Govil 2008). A relatively high concentration Pb (1.67–24.83 µg/L), was recorded at the study area. 33 % of the samples exceeded the permissible limit 10 µg/L (WHO 2011). The concentration of zinc in

Table 2 Correlation matrix of the metals in the groundwater

	Cd	Cr	Cu	Pb	Zn
Cd	1.00				
Cr	0.60	1.00			
Cu	0.60	0.46	1.00		
Pb	0.07	−0.29	0.08	1.00	
Zn	−0.08	−0.11	−0.29	0.41	1.00

the study areas varied between 35.02 and 1,142.70 µg/L and 15 % of the samples exceeded the permissible limit 300 µg/L.

Correlation matrix created for the metals are presented in Table 2. Cadmium is strongly correlated with Cr ($r = 0.606$) and Cu ($r = 0.601$). A positive correlation was observed between Cr and Cu ($r = 0.464$) and Pb and Zn ($r = 0.416$). These relations suggest a common origin of these heavy metals. Heavy metals like Cd, Cr, Cu, Zn, Pb, and Fe are largely originated from the un-segregated solid waste containing steel scrap, lead batteries, tins, cans, etc. In the study area most of the surface water bodies were contaminated by domestic and industrial wastes. Interactions with the groundwater and polluted surface water contributed to majority of the contaminants in groundwater. The presence of sandy aquifer in most part of the study area increases the chances of this interaction.

The HPI represents the composite influence of metals on the overall quality of water (Sheykhi and Moore 2012). In this indexing, weights (W_i) between 0 and 1 were assigned for each metals. The rating is based on the relative importance of individual quality considerations and defined as inversely proportional to the recommended standard for each heavy metal (Mohan et al. 1996). In the present study metals such as Cd, Cr, Cu, Pb and Zn were considered. The HPI for the study area is determined by incorporating the average values of recorded heavy metals. The details of the calculation are presented in Table 3. The mean HPI resulted in this study was 31.29 and the individual values are given in the Table 4. Heavy metal pollution index (HPI) can be classified in to three categories like low (<19), medium (19–38) and high (>38) (see Table 5). Most

Table 4 HPI for the individual groundwater samples

S. No	HPI	Deviation
1	14.67	−16.62
2	14.23	−17.06
3	13.15	−18.14
4	17.65	−13.64
5	45.49	14.19
6	25.72	−5.57
7	16.23	−15.07
8	9.72	−21.58
9	16.84	−14.46
10	32.99	1.70
11	97.55	66.26
12	15.54	−15.76
13	14.30	−17.00
14	16.23	−15.07

Table 5 Classification of groundwater based on HPI

HPI class	Description	No. of samples	% of samples
<19	Low	9	64.28
19–38	Medium	3	21.42
>38	High	2	14.3

of the samples (64.28 %) fall in the low category and the rest of the samples belonged to were represented in the Medium and high categories. The highest value of 97.55 was recorded from the Thiruvannmiyur region of the study area. This suggested the effect of urbanisation and industrialization on groundwater quality.

Figure 3a–e shows the spatial distribution of metals in the groundwater of Chennai city. In general, higher concentrations are exhibited in the Southern part of the study area, especially SE regions including Thiruvannmiyur and Adyar. These areas are bounded by river Adyar and Buckingham canal. Both water bodies are extremely contaminated with the sewage as well as the industrial

Table 3 Calculation of HPI for the Chennai city

Heavy metals	Mean value (M_i) [µg/L]	Standard permissible value (S_i) [µg/L]	Highest desirable value (I_i) [µg/L]	Sub index (Q_i)	Unit weightage (W_i)	$Q_i \times W_i$
Cd	1.33	10	–	18.6	0.1	1.86
Cr	17.19	50	10	33.05	0.1	3.305
Cu	139.28	1,500	50	7.56	0.01	0.0756
Pb	8.47	50	10	84.7	0.025	2.1175
Zn	213.78	1,500	50	11.48	0.0002	0.002296

$$\sum Q_i W_i = 7.36; \sum W_i = 0.2352; \text{HPI} = 31.29$$

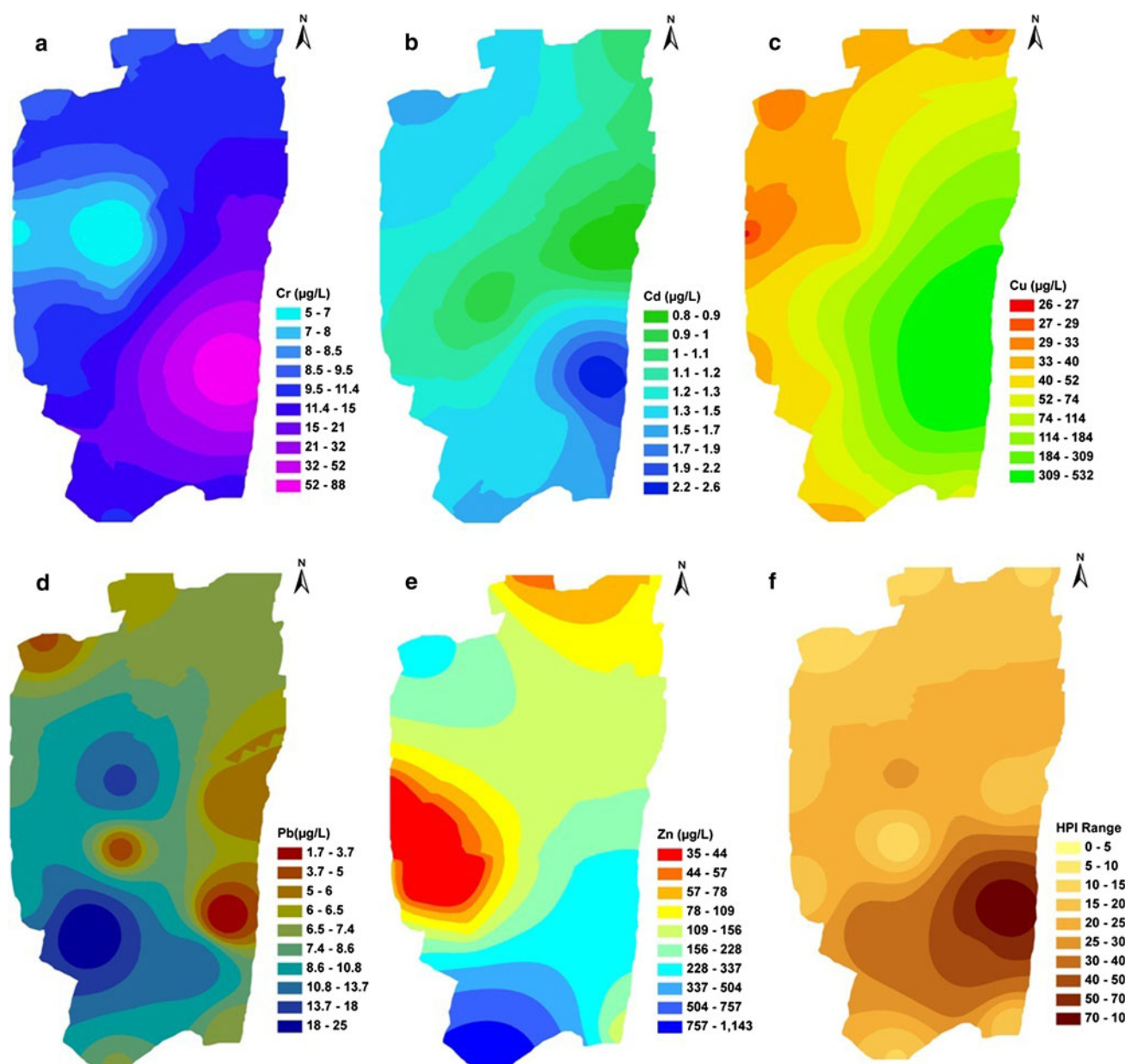


Fig. 3 Spatial distribution of metals and HPI in the groundwater of Chennai

effluents. This may be the reason for high concentration of Cu, Cr and Cd in this part of the study region. Pb shows a deviation from the normal trend, higher concentration is observed at the NW and SW regions. High concentration of Cr in this part of the area is largely controlled by the leather industries. This can also be attributed to the natural slope and groundwater flow directions towards the Bay of Bengal, located in the eastern boundary of the study area. Spatial distribution of HPI is plotted in Fig. 3f. This map well in agreement with the other metals, showed the high values at the SE region of the study area.

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