



Spectrophotometer-Based Analysis of Hexavalent Chromium in Various Water Bodies of Hyderabad City Reveals Large Anthropogenic Input

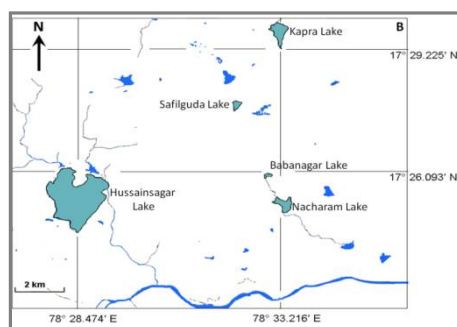
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ABSTRACT

In India the awareness about the environmental pollution and its adverse effect is extremely low. The public, in general, do not bother and allow indiscriminate anthropogenic dumping of heavy metal and other wastes. However, long-term human exposure to toxic heavy elements through various pathways leads to severe health hazard. It is widely known by the researchers that the toxic form of chromium, the hexavalent chromium, is extremely hazardous. However, its concentration in surface and groundwater bodies has not been estimated in most of the cases. Such a situation is valid for the Indian cities also. Therefore, here we report spectrophotometer-based estimation of hexavalent chromium ($57\text{--}268\ \mu\text{gL}^{-1}$) concentrations in different water bodies collected from various locations of Hyderabad city that include lakes and groundwater samples in their vicinity. Comparison of our data with the permissible safe limit for Cr(VI) in drinking water, set by the Italian authorities reveal that the studied water bodies and aquifers are contaminated to variable degrees and pose serious threat to the ecosystem. In view of low geochemical baseline value for chromium, the origin of hexavalent chromium contamination is inferred to be anthropogenic. Several medium and small scale industries in and around our study area appear to be responsible for hexavalent chromium contamination. An integration of toxic Cr(VI) data presented in this study together with health data indicates that there exists an impending health hazard, if proper mitigation measures are not taken up immediately. Some mitigation measures are therefore recommended.

Graphical Abstract



Existing water bodies in specified portion of Hyderabad city.

Keywords: Lakes, Groundwater, Hexavalent chromium, Mitigation.

INTRODUCTION

Chromium (Cr) is an interesting toxic heavy metal that occurs in nine different oxidation states, from -2 to +6. Out of these, only the trivalent (III) and hexavalent (VI) forms of Cr are of clinical significance. While Cr(III) is considered to be essential to mammals for the maintenance of glucose, lipid, and protein metabolism, Cr(VI) is known to have an adverse effect on the lungs, liver, and kidneys [1]. It is to be noted that the two forms of chromium (Cr^{3+} and Cr^{6+}) can convert back and forth in water and in the human body, depending upon the ambient environmental conditions. Contamination due to chromium can arise from both natural sources as well as human activities [1, 2]. Therefore an extensive literature survey was carried out to find out if there exist some publications which report the concentration of hexavalent chromium on water samples from Indian cities. Our survey revealed that the concentration of total chromium [Cr (total)] in surface and groundwater bodies from different parts of India were reported [3, 4], including the city of Hyderabad [5-7]. However, it is interesting to note that except for one recent report on the presence of Cr(VI) in groundwater samples from Kanpur [8], no attempt was made earlier to determine the concentration of Cr^{6+} in the natural water samples from Indian cities.

The toxicity of dissolved hexavalent chromium has become a matter of great concern in recent years [1, 9]. In this work we therefore report concentration of dissolved chromium (VI) in surface and groundwater samples collected from various sites of Hyderabad city using a spectrophotometer. The plausible origin of the dissolved toxic metal in water samples is evaluated. We then discuss the significance of our results in the light of impending health hazard, taking examples of studied clinical cases that were reported in the study area. Finally, suitable mitigation measures are briefly highlighted.

MATERIALS AND METHODS

Water samples were collected from different lakes (Figure 1) and adjacent groundwater sources (not shown) lying within 0.5 to 1.0 km of the lakes in the city of Hyderabad (Telangana). Poly-propylene bottles (1 litre) for sample collection were soaked in 5% HNO_3 for 24 h followed by rinsing them a number of times with deionised water. These bottles were dried and water samples were collected in duplicate after filtration. One of the bottles containing filtered water sample was acidified with 5 mL HNO_3 and the other was not acidified. These bottles were sealed properly to avoid loss due to evaporation. The pH of each sample was measured (7.1 to 7.9) in the laboratory using samples from those bottles that were not acidified with the help of a calibrated systronic pH-meter (Model 335). The calibration of the pH-meter was done using specific buffers. Analytical grade chemicals and double distilled water were used throughout the investigation. The concentration of metal in terms of absorbance was recorded by Elico-164 double beam spectrophotometer. In order to get maximum sensitivity of spectrophotometer, the wavelength for maximum absorbance was chosen for the calibration plot and subsequent sample analysis.

A standard Cr(VI) solution of $500 \mu\text{g mL}^{-1}$ was prepared from pure $\text{K}_2\text{Cr}_2\text{O}_7$. Reagent solutions such as hydroxylamine hydrochloride (0.2% w/v), 4,4'-sulfoxylbisbenzeneamine (Dapsone, 0.2% w/v) and N-(1-Naphthyl) ethylenediamine dihydrochloride (NEDA, 0.5% w/v) were prepared by dissolving the required amount of reagents in double distilled water. To a series of $\text{K}_2\text{Cr}_2\text{O}_7$ solution containing 0.2, 0.4, 0.6, 0.8 and 1 ml $\text{K}_2\text{Cr}_2\text{O}_7$ solution of strength $500 \mu\text{g mL}^{-1}$ taken in 10 mL volumetric flasks, 2 mL hydroxylamine hydrochloride, 2 mL Dapsone solutions were added and kept for 5 minutes to complete the reaction. The volumes were made up to the mark with double distilled water after adding 1 mL NEDA solution. The absorbance of each solution was measured at 540 nm against the corresponding reagent blank. The calibration curve was constructed by plotting [Cr(VI)] in $\mu\text{g mL}^{-1}$

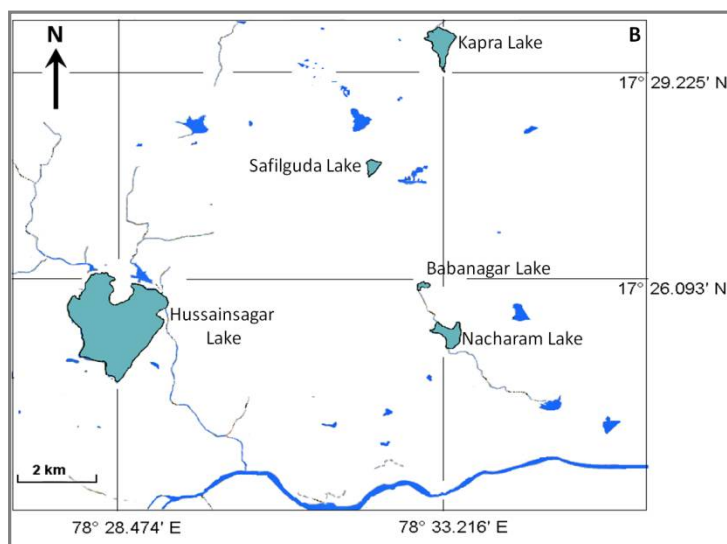


Figure 1. Existing water bodies in specified portion of Hyderabad city. Names of the studied lakes are mentioned. Groundwater samples were collected within 0.5-1.0 km of the studied lakes (not shown).

against absorbance, which was used subsequently to evaluate the dissolved Cr(VI) concentrations in water samples collected from various sites. The molar absorptivity obtained ($3.77 \times 10^4 \text{ mol L}^{-1} \text{ cm}^{-1}$) is in excellent agreement with that reported ($3.49 \times 10^4 \text{ mol L}^{-1} \text{ cm}^{-1}$) earlier [10].

The Cr(VI) content of natural water samples were measured in a similar way as was done during calibration. 2 mL of each water sample and the other reagent solutions were taken in 10 mL standard flask and the absorbance of the solutions were measured directly using the spectrophotometer. Two other sets of measurement were also carried out (Table 1) by adding known amounts (0.1 and 0.25 $\mu\text{g mL}^{-1}$) of Cr(VI), and these measurements are referred to as spiked Cr(VI). In both the cases the concentration of Cr(VI) was estimated using the standard calibration curve. For spiked samples, the amount of spike added was subtracted. The effect of foreign ions was examined by adding masking agent (1ml of 5% EDTA) to the reaction mixture.

RESULTS AND DISCUSSION

Water samples collected from various locations of Hyderabad city and analyzed for concentration of chromium (VI) is presented in table 1. A number of researchers have measured Cr (total) in the surface and groundwater samples collected from different locations of Hyderabad city. In order to have a better insight to the data that are obtained in this study, we prefer to discuss them in the backdrop of the previously reported dissolved Cr (total) concentrations. These values are therefore included in table 1. The concentration of Cr(VI) in different water bodies analyzed in this study is variable ranging from $57 \mu\text{g L}^{-1}$ to $268 \mu\text{g L}^{-1}$ (Table 1). Maximum concentration is noted in the groundwater sample near Babanagar Lake (Figure 1). In table 1 the guideline as well as desirable values of Cr (total) recommended for drinking water are also listed [11, 12]. Both recommend safe limit of Cr (total) in drinking water to be $50 \mu\text{g L}^{-1}$. However, these organizations do not list the safe limit for Cr(VI) in drinking water [13, 14]. In Italy, the maximum permissible limit of Cr(VI) in drinking water has been fixed at $5 \mu\text{g L}^{-1}$. Therefore if we take the maximum permissible limit as recommended by the Italian authorities, none of the samples from surface and groundwater sources that are analyzed in this study can be considered as safe for drinking purpose (Table 1). Following maximum permissible limit set by [13, 14], similar observation is also valid for pre-monsoon average surface waters from Katedan area, average groundwater of Maheshwaram area and some of the pre-monsoon groundwater samples from Bolaram, Patancheru and Katedan areas (Table 1). This obviously is a matter of great concern in a thickly populated city like Hyderabad.

All the samples analyzed in this study have high to extremely-high concentrations of Cr(VI). Therefore the obvious question that arises is, what is the relationship between Cr(VI) and Cr (total) in surface and groundwater sources? In two significant studies [15, 16], the total as well as hexavalent chromium occurrences in surface and groundwater sources collected at various locations in the United States were investigated. It was found that the surface water speciation is generally dominated by trivalent chromium [15, 16]. We therefore plotted Cr(VI) concentrations of lake water as well as groundwater in their vicinity pertaining to four locations of Hyderabad city (Figure 2). It is encouraging to note that the Cr(VI) content of groundwater is mostly higher when compared to the corresponding lake water, except for one location at Kapra (Figure 2). Therefore the general inference that the surface water speciation is dominated by trivalent chromium seems to be valid for Indian samples as well.

Table 1. Cr(VI) concentration of water samples from different sources of surface water, lakes and ground water from Hyderabad

| Source of Water | Cr(VI) content of water sample in $\mu\text{g L}^{-1}$ (this study) | | | | Source of Water | Cr (total) content of water sample in $\mu\text{g L}^{-1}$ [Published work] |
|------------------------|--|--|-----|----------------|---|--|
| | Cr(VI) measured on sample using | | | | | |
| | Unspiked sample | Spiked with Cr(VI) solution $\mu\text{g mL}^{-1}$ of | | Average Cr(VI) | | |
| 0.1 | | 0.25 | | | | |
| Nacharam Lake | 50 | 65 | 55 | 56.7 | GW at various sites of Hyderabad | 4.-6.5 [8] |
| GW near Nacharam Lake | 85 | 90 | 85 | 86.7 | GW at Maheswaram (South of Hyderabad) | 11.6-418.9 [9] |
| Babanagar Lake | 120 | 115 | 120 | 118.3 | Gw of Bollaeam and Patancheruvu (Hyderabad) | Pre monsoon 19-95 [30] Post monsoon 10-65 [33] |
| GW near Babanagar Lake | 255 | 280 | 270 | 268.3 | GW at Katedan (Hyderabad) | Pre monsoon 6.4-217.4 [31] Post monsoon 047-10.4 [31] |
| Safilguda Lake | 155 | 155 | 150 | 153.3 | SW at Katedan (Hyderabad) | Pre monsoon 5.3-770.8 [31] Post monsoon 6.7-107.1 [31] |
| GW near Safilguda | 155 | 170 | 170 | 165.0 | Guidelines and desirable value of Cr(total) | 50 [13, 14] |
| Kapra Lake | 195 | 210 | 190 | 198.3 | Italian permissible limit of Cr(VI) | 5 [32] |
| GW near Kapra Lake | 75 | 85 | 70 | 76.7 | -- | -- |
| Hussansagar Lake | 105 | 100 | 105 | 103 | -- | 72.3 [7], 93-105 [29] |

Presence of Cr in water bodies may arise either from natural sources or due to anthropogenic activities. Therefore evaluation of source of high Cr(VI) in terms of geogenic (natural) versus anthropogenic (human-induced) is necessary so that suitable mitigation measures can be adopted. We would examine first whether high hexavalent chromium documented in the water samples of present study could result from any natural source. The natural source includes weathering of Cr-bearing minerals in soils and rocks. There are a large number of studies, which have shown presence of naturally occurring dissolved hexavalent chromium in high concentrations both in surface and groundwater bodies. In all such studied cases, there exists a close association of water bodies with serpentine soils, chromite ores and ultramafic rocks [3, 4, 17]. However, such a geogenic origin for the presence of hexavalent chromium is ruled out for the water samples of present study. This inference gets support from the geochemical baseline mapping using top and bottom soils of the city. It has been observed that the average background values of Cr(total) range from 50 to 80 ppm [18], which is not significantly different from that of the average earth crust [19]. Therefore the observed high values of dissolved Cr^{6+} documented in surface and groundwater samples owe their origin to anthropogenic pathways. In general, anthropogenic nature of chromium contamination for surface and groundwater bodies originates from presence of chrome plating factories, leather tanneries and textile manufacturing facilities [2]. Moreover, solid wastes from chromate-processing facilities, when disposed of improperly, can be sources of contamination for water bodies [17]. Cr(VI) compounds are

also used as pigments in dyes, paints, inks etc. Therefore the high levels of Cr(VI) documented in the surface and groundwater bodies of Hyderabad city owe its origin to several industries in and around our study area. The industries include textile, engineering products, chemicals and pharmaceuticals, steel and other metal products, communication equipments, paper and paper products, printing and paint industries, tanneries and leather products, dyeing of saris etc [20]. Furthermore, high degree of Cr(VI) contamination in many surface water bodies and groundwater in their vicinity could also be attributed to direct entry of untreated or partially treated industrial effluents that flow to the lakes directly [21]. Besides the plausible sources mentioned above for the city of Hyderabad, another

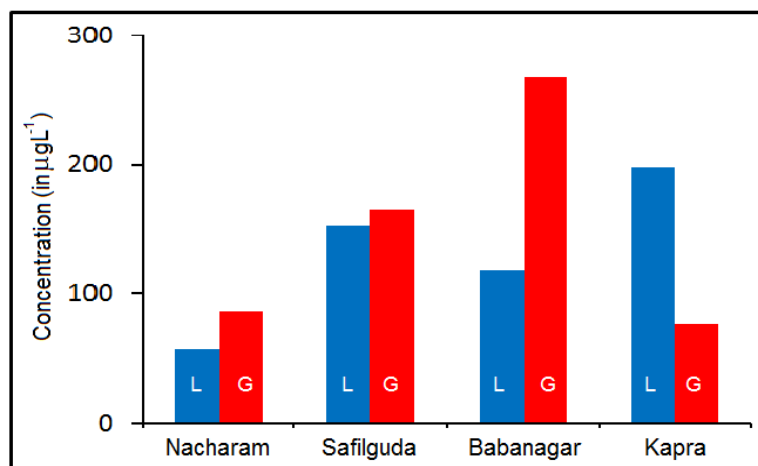


Figure 2. Histogram showing hexavalent chromium concentration. The groundwater (G) speciation of hexavalent chromium (Cr^{6+}) is more than the lake water (L), except for Kapra Lake.

significant source of Cr(VI) contamination, which has not been cited or discussed by any researchers so far, is the use of chromate and dichromate salts by a large number of research laboratories and educational institutions in the city. This is a potential anthropogenic source for a city like Hyderabad, where a large number of intermediate, degree and post-graduate colleges are present. Utmost care should therefore be exercised by these institutes and organizations so that the ecosystem is maintained clean and safe [22].

There are several studies which show the toxic effects of hexavalent chromium in humans. Severe skin diseases and skin ulcers among the users of chromium-contaminated water in Sukinda mines of Orissa was documented [23]. Indigestion and diarrhoea are common in human population who are chronically exposed to hexavalent chromium [24]. Dermal exposure to hexavalent chromium leading to prolonged acute renal failure is reported recently [25].

High Cr(VI) content in water bodies of Hyderabad and the associated health hazard among the city population was never attempted directly. In fact, Cr(VI) data on surface and groundwater bodies of Hyderabad was not available prior to this study. However, in a noteworthy study conducted by the Indian Institute of Health and Family Welfare, the effect of industrial pollution to the citizens living in and around Hyderabad city was addressed [26]. The outcome of this interesting study is as follows: (i) acute diseases were noted in 24.6 per cent of the study population, (ii) chronic diseases were documented in 7.6 per cent population. Acute diseases were found to occur at higher incidence to those who live close to industrial points (27.8 per cent). Acute renal impairment (ARI), skin diseases, diarrhoea and malaria constituted major illnesses. Taking a cue from the studies on exposure of hexavalent chromium vis-a-vis human health [25] and integrating the results of our study with that conducted by IIHFW [26], we speculate that the reported skin diseases, diarrhoea and ARI within the population of Hyderabad city might be a result of Cr^{6+} ingestion.

In view of the results documented in our study and the discussion made thereof, it is necessary to recommend some mitigation measures. An exorbitant cost is involved to clean up the mess arising from heavy metal contamination [17]. Therefore the best way to eliminate the effect of heavy metal pollution is to make people aware about the impending danger, so that the problem is tackled at the initial stage. Coming to the specific problem of chromium-contamination of soil, surface and groundwater sources, it is recognized as a potential threat. Since it can originate from both natural as well as anthropogenic sources, the threat is common to many nations including the developed ones. Therefore over the past few decades several new methodologies and treatment approaches have been developed to mitigate the adverse effects of Cr-contaminated soils and water bodies. However, before taking up the *in situ* remediation of highly contaminated soil and water bodies, it may be a good idea to take up some interim remedial measures such as covering or fencing the contaminated sites, thereby restricting the access. This ensures no direct contact and temporarily reduces migration of chromium contamination. Simultaneously as a follow-up step, the common public should be educated about the menace of hexavalent chromium, so that no industry/agency is allowed to dump the waste materials in an indiscriminate manner. This should be followed by proper mitigation measures. There are many innovative technologies that can potentially be used for *in situ* remediation of Cr-contaminated soil and water bodies. Some of the widely used technologies include: (i) geochemical fixation [27], (ii) permeable reactive barriers-PRBs [28] (iii) reactive zones [29] and (iv) natural attenuation [30]. Therefore it is necessary to have an in-depth understanding of the chromium cycle together with site characterization so that the most suitable and cost-effective technology can be adopted as the remedial measure.

APPLICATION

This study is conducted with an aim to impart hands-on training and generate awareness to the student members of St. Pious Undergraduate Environment Research (SPUGER) group. The study and the discussion on the results presented here have been found to be extremely useful to the students. Further, they have become alert about the menace of heavy metal pollution. Based on the results of this study, they also organized awareness program for the local residents.

CONCLUSION

The present study reveals that the concentrations of dissolved hexavalent chromium in the surface water bodies (lakes) as well as groundwater in their vicinity are high in the Hyderabad city. Higher incidences of ailments such as chronic skin diseases, diarrhoea and acute renal failure amongst the city population are perhaps indicative of Cr⁶⁺ ingestion originating from anthropogenic activities. We recommend that besides undertaking proper mitigation measures, public awareness is mandatory to tackle such a grim situation.

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