Evaluation of Heavy Metal Contamination in Ground Water of Ambad Industrial Area of Nashik, Maharashtra, India

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Abstract: For the present study, twenty one groundwater samples were collected from various sources (10dug wells, 8handpumps and 3bore wells) of Ambad industrial area. To compare the data with surface water, 4 nalla samples were also collected from the same region. The study presents the comparison between concentrations of various heavy metals during pre monsoon and post monsoon seasons for 2 consecutive years. The analytical data shows that the concentration of heavy metals namely total Cr, Cr⁶⁺, Fe and Znare beyond the acceptable limits of Bureau of Indian Standards, 2012 (BIS) in most of the collected water samples. However, among all these metals, concentration of Cr^{6+} was found highest in both type of water samples i.e. in nalla (90mg/l) as well as in groundwater (218mg/l). Being carcinogenic in nature, hexavalent chromium may be fatal if ingested for a long time. Hence, the present study indicates that the groundwater as well as surface water of Ambad area is getting contaminated with various harmful metals which may be due to untreated industrial wastewater discharge into various water streams or land in their vicinity. Therefore, an immediate check *and necessary action is recommended to rectify the problem.*

Keywords: groundwater, heavy metals, hexavalent chromium, waste water, carcinogenic

1. Introduction

In India, groundwater is the major source which is used to meet the domestic, agricultural and industrial needs and in Maharashtra state its dependence is reaching upto 65% [1]. According to a UNESCO report, majority of Indian population has no access to safe drinking water and about 66 million people rely on unsafe ground water for consumption [2].Besides, significant changes in land use due to rapid increase in population and urbanisation, resulting in more demand of water and decline in water table. Also, the quality of water is another major concern in many parts of the country.

Due to increase in anthropogenic activities, the composition of different kinds of micronutrients and heavy metals are changing, which affects soil fertility and ultimately the quality of ground water[3]. Heavy metals are stable and persistent environmental contaminants since they cannot be degraded or destroyed. Therefore, they tend to accumulate in soils and sediments [4]. Elevated concentrations of heavy metals in soils may cause phytotoxicity, direct hazard to human health, indirect effects due to transmission through the food chain or contamination of ground or surface waters [5]. Environmental Protection Agency (EPA) has declared Cr (VI)as carcinogenic metal and its exposure via inhalation route can be fatal [6].

The monitoring of water quality is one of the important tools for sustainable development and provides important information for water management. Hence, in the current study, an industrial area is covered for the investigation of its water quality. Although, a lot of studies have been done and published in the past in reference to the heavy metal contents in surface water, but this may be the first study with emphasis of Chromium (VI) contamination in groundwater of Nashik City. In the present study, analytical data concerning the contamination of the groundwater as well as surface water at the Ambad industrial area of Nashik is discussed.

2. Materials and methods

2.1 Study Area

Nashik is an important ancient city of Maharashtra. It is located on the banks of River Godavari at a distance of about 565 m above mean sea level. It lies between 19° -33' and 20° -53' North latitude and 73^0 -16' and 75^0 -6' East longitude. It is spread on an area of 259.13 km^2 . The climate is dry except during south-west monsoon. The average rainfall is 1034 mm, July being the rainiest month. The hottest month is May having average daily maximum temperature of 41° C and coldest month being December with mean daily temperature of 10.2^oC *(Source: Report on Environmental Status of Nashik region, Maharashtra by MPCB).*

Nashik district gets its water supply from wells, lakes, rivers and percolation tanks. The Darna, Gangapur, Chanakapur and Waghad lakes have been formed by constructing dams across rivers. The main source of water to Nashik city is Gangapur Dam. Ground water is used as secondary source of water and used to a maximum extent in summers as dam water supply gets depleted. The studied locations fall under Ambad area, which is surrounded by industries, mainly electroplating.

2.2 Sampling and Analytical methods

For the present study, a total of 25 water samples were collected from the Ambad area in the month of December and May as pre and post monsoon representatives. The samples were collected for 2 consecutive years. Among all 25 samples, 4 surface water samples were collected from major nallas of the region (N1-N4) and 21 ground water samples were collected from 10 dugwells (D1-D10), 8 handpumps (H1-H8) and 3 borewells (B1-B3) of the region (Table1). The samples were stored in the air tight precleaned plastic can. Collected samples were transported to laboratory immediately. The samples were analyzed for Cd, Total Cr, Cr^{6+} , Mn, Fe, Ni, Cu, Pb and Zn using Inductively Coupled Plasma Spectrophotometer (Thermo Scientific – iCAP 6000 series) as per the standard methods [7] and the values obtained are compared with the drinking water standards [8].The precise locations of sampling points were determined in field through GPS (Global Positioning System) GARMIN that gave exact latitude and longitude.

Table 1: Details of locations under study

No.	S. Location no.	Source	Latitude	Longitude	Use of Water
1.	D1	Dug well	N 19°57.550'	E 73°43.889'	Washing & Cleaning
2.	D ₂	Dug well	N 19°57.631'	E 73°43.822	Washing & Cleaning
3.	D3	Dug well	N 19°57.708'	E 73°43.903	Washing $\&$ Cleaning
4.	D4	Dug well	N 19°57.418'	E 73°43.881	Washing & Cleaning
5.	D5	Dug well	N 19°57.508'	E 73°43.927	Washing & Cleaning
6.	D6	Dug well	N 19°57.593'	E 73°43.914'	Washing & Cleaning
7.	D7	Dug well	N 19°57.587'	E 73°43.974'	Washing & Cleaning
8.	D ₈	Dug well	N 19°57.686'	E 73°43.946'	Washing & Cleaning
9.	D ₉	Dug well	N 19°57.668'	E 73°43.951	Washing & Cleaning
10.	D10	Dug well	N 19°57.705'	E 73°43.903	Washing & Cleaning
11.	H1	Hand pump	N 19°57.478'	E 73°43.826	Washing & Cleaning
12.	H ₂	Hand pump	N 19°57.356'	E 73°43.765	Washing $\&$ Cleaning
13.	H3		Hand pump N 19°57.373'	E 73°43.757	Washing & Cleaning
14.	H ₄	Hand pump	N 19°57.737'	E 73°43.660'	Washing & Cleaning
15.	H ₅		Hand pump N 19°57.685'	E 73°43.773	Washing & Cleaning
16.	H ₆	Hand pump	N 19°57.338'	E 73°43.682	Washing $\&$ Cleaning
17.	Η7		Hand pump N 19°57.183'	E 73°43.509'	Washing & Cleaning
18.	H8	Hand pump	N 19°57.460'	E 73°43.603	Washing & Cleaning
19.	B1	Bore well	N 19°57.616'	E 73°43.868	Washing & Cleaning
20.	B ₂	Bore well	N 19°58.201'	E 73°46.089	Washing & Cleaning
21.	B3	Bore well	N 19°58.716'	E 73°46.782	Washing & Cleaning
22.	N1	Nalla	N 19°57.801' E 73°43.911'		Effluent

3. Results and discussion

The analysis results of the present study are shown in Table 2-5. Table 2 shows the data obtained from the dug well samples, Table 3 shows the hand pump samples, Table 4 shows the bore well samples and Table 5 shows the nalla samples. The results also represent the data obtained in the samples of two different seasons i.e. pre and post monsoon seasons of two consecutive years i.e. year 1 and year 2. To investigate the seasonal variations of the heavy metal contents in groundwater and surface water, the data was exposed to the several statistical treatments (Table 6).

a) Cd

Cadmium (Cd) is not an essential, non-beneficial element known to have a toxic potential. The Cd occurs due to the natural and anthropogenic sources in the environment. Industries such as electroplating, pigments, plastic, stabilizers and battery, use cadmium as a metal source in their activities. It is highly toxic and can cause food poisoning. It replaces zinc biochemically and causes high blood pressure, kidney damage etc. It causes a painful disease called Itai-itai, which interferes in enzymatic activities in humans[9].

The present study shows that, in year 1, the post monsoon values of Cadmium (Cd) varied from 0.005 to 0.174 mg/l while in pre monsoon it was found Below Detection Limit (BDL) in all the ground water samples. In surface water (nalla) samples, Cd concentration was found BDL during year 1 pre monsoon, while during post monsoon it ranged from BDL to 0.085mg/l.

While in post monsoon of year 2, Cd concentration was found in detectable range at two locations i.e. at D10 (0.006 mg/l) and H2 (0.01mg/l). In pre monsoon of year 2, it was observed in the range of 0.008 to 0.04mg/l. However in surface water, Cd was observed BDL in all the samples during year 1 pre monsoon, while during post monsoon, it was observed only in N2 i.e. 0.66mg/l which was very much higher than the acceptable limit of 0.003mg/l [8], all other samples have BDL Cd content. Hence, it may be predicted that more samples of the year2were contaminated with Cd as compared to the samples collected in year1. Interestingly, most of the samples having Cd content above acceptable limit of 0.003 mg/l [10]were detected at handpumps and dug wells.

b) Total Cr

Chromium (Cr) is a metallic chemical that originates as a contaminant in the environment from the discharges of dye and paint pigments, wood preservatives, chrome-plating liquid wastes and leaching from hazardous waste sites[11].Chromium exists in the environment in several diverse forms such as trivalent [Cr (III)] and hexavalent [Cr (VI)], of which hexavalent chromium is a so-called carcinogen and a potential soil, surface water and ground water contaminant. Chromium enters the environment

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mostly in the chromium (III) and chromium (VI) forms as a result of natural processes and human activities [12].

Table 3: Concentration of various heavy metals in the water sample of hand pumps

In the present study, total chromium (Cr) content was observed in most of the samples of dug wells during both years of study. Also, it was found beyond acceptable limit (0.05mg/l) in most of the samples of hand pumps in year 2 during both the seasons.

The total Cr concentration in ground water samples of year1 ranged from BDL to 199mg/l in pre monsoon while in post monsoon it ranged from BDL to 326.6mg/l. It was also observed in all the surface water (nalla) samples. In pre monsoon it ranged from 0.77 at N2 to 56.3mg/l at N4 and in post monsoon it ranged from 2.58 at N2 to 33.2mg/l at N4.

However, in year 2, Cr concentration of groundwater in pre monsoon was observed minimum (BDL) in 3 samples of hand pump and at one dug well sample atD7 and maximum (473mg/l) at H2. In post monsoon, minimum of BDLwas observed in 2 samples of hand pumps, 5 dugwells and 1 sample of borewell. Maximum concentration was found at H2 i.e. 123mg/l. In surface water (nalla) samples, Cr concentration was found in the range of 0.27 at N2 to 142 mg/l at N4 in pre monsoon and in post monsoon it ranged from BDL at N2 to 46.8mg/l at N4.

c) Cr6+

Hexavalent chromium (Cr^{6+}) is known to cause cancer in humans. When swallowed, hexavalent chromium can upset the gastrointestinal tract and damage the liver and kidneys. It is readily soluble in water. Under high energy(oxidizing) and alkaline (pH above 7) conditions, hexavalent chromium can be predominant in groundwater [10].

In ground water samples of year 1, pre monsoon readings ranged from BDL to 139mg/l, while in post monsoon it got lowered and ranged from BDL to 4.25mg/l. In surface water samples, during pre monsoon, minimum i.e. BDL was observed at N1 and maximum i.e. 17.9mg/l at N4, while

during post monsoon, minimum i.e. BDL was observed at N2 and maximum i.e. 3.2mg/l at N4.

During pre monsoon of year 2, $Cr⁶⁺$ content in groundwater samples was observed from BDL to 218mg/l (at H2), however in post monsoon of year 2, the Cr^{6+} content remarkably decreased and observed in the range of BDL to 3.05mg/l (at H1). While in surface water samples, during pre monsoon, minimum (0.005mg/l) was observed at N2 and maximum (90mg/l) at N4 and during post monsoon season, the maximum concentration of pre monsoon at N4 got decreased to 1.79mg/l. However, the Cr^{6+} content ranged from BDL to 2.86mg/l.

d) Cu

Copper (Cu) is an essential micronutrient. In aquatic environment, it exists in three forms namely soluble, colloidal and particulate. High concentration of Cu may cause physiological effects in human such as hypertension and produces pathological changes in brain tissues. It may be responsible for specific disease of the bone, if ingested in

excessive concentration[13]. Intrusion of industrial and domestic wastes, corrosion of brass and copper pipes are main source of Copper contamination in water [14].

In the present study, the copper content in ground water samples varied from a minimum of BDL to a maximum of 0.23mg/l. The values of Cu were found within the acceptable limit of BIS drinking water standards in all the samples of both the years, except at one location (H4), where it was found 0.23mg/l. The BIS acceptable limit for Cu was 0.05 mg/l [8].

However in surface water samples, during pre monsoon of year 1, Cu content varied from 0.145mg/l to 0.39mg/l and in post monsoon, it varied in the range of 0.02mg/l to 2.32mg/l. In year 2 pre monsoon, it varied from minima of 0.09mg/l to maxima of 0.52mg/l and during post monsoon, it was observed as BDL in all samples except at N4 where it was found as 0.03mg/l.

Table 4: Concentration of various heavy metals in the water sample of bore wells

Location Year		Cd							Сu	Fe		Ph		Мn		Ni		Zn	
		Pre	Post	Pre	Post	Pre	Post	Pre	Post Pre		Post	Pre	Post	Pre	Post Pre		Post Pre		Post
B ₁					BDL 0.019 1.19 0.521	5.6													1.29 BDL
			BDL BDL		1.01 ± 0.29	3.2	0.32												0.02 BDL 0.3 BDL BDL BDL 0.024 BDL BDL BDL 0.08 BDL
B ₂																			BDL 0.136 0.392
																			N.A. N.A.
B ₃																			BDL 0.021 BDL BDL BDL BDL BDL BDL BDL
																			BDL BDL 0.03 BDL 0.1 BDL BDL BDL BDL BDL BDL BDL BDL 0.06 0.017 BDL BDL BDL
	\mathbf{I} and \mathbf{I} and \mathbf{I} and \mathbf{I}																		

N.A: Sample not available

Table 5: Concentration of various heavy metals in the water sample of nallas (surface water)

Location Year	Cd						Сu		Fe		Pb		Mn		Ni		Zn	
	Pre l	Post	Pre	Post	Pre	Post	Pre	Post	Pre l	Post	Pre	Post	Pre	Post	Pre	Post	Pre	Post
N1	BDL	BDL.	BDL	$2.53 \perp$	6.86	2.67	0.24	0.02	12.6	0.11	0.067	BDL	0.367	0.26	0.917		.69	BDL
	BDI.		BDL 0.009	2.86	2.34	3.13	0.09	BDL	3.59	0.36	BDL	BDL	0.83	0.17	2.79	0.08	BDL	BDL
N ₂	BDI.	0.085	0.02	BDL	0.77	2.58	0.39	2.29		17.6 89.39	BDL	1.62	0.058	10.5		0.057 0.136		84.11
	BDL	0.66	0.005	BDL	0.27	BDL	0.2	BDL	42.3	90.9	0.19	0.01	1.02	0.77	0.03	0.04		2.17
N ₃	BDL	0.026	BDL	1.81	20.9	2.75	0.263	0.26	9.27	12.5	BDL	BDL	0.267	0.33	4.28	0.025	0.71	BDL
	BDL	BDL	11.7	2.54	19.6	2.8	0.15	BDL	1.94	0.32	0.01	BDL	0.47	0.23	L.93	0.03	BDL	BDL
N4	BDL	BDL.	17.9	3.2	56.3	33.2	0.145	2.32	0.34	1.99	BDL	BDL	1.28	0.45	0.191	0.069	0.97	BDL
	BDL	BDL	90	. .79	142	46.8	0.52	0.03	1.08	0.24	0.02	BDL	1.7	0.16	l.24	0.23	0.23	BDL

Table 6: Comparison of statistical data of different metals in pre monsoon season in ground water (dug wells, handpumps and borewells)

e) Fe

Iron (Fe) is the fourth most abundant element by mass in the earth's crust. In surface water, it is generally present in ferric state and in ground water is in the form of ferric hydroxide. Presence of iron in water and soil environment is due to its release as corrosion product[15].Prolonged consumption of drinking water with high concentration of iron may lead to liver disease called as haermosiderosis and its shortage causes anaemia in human body [16].

The iron concentration in ground water samples of year1 ranged from 0.06 to 1.69mg/l in pre monsoon while in post monsoon it ranged from 0.06 to 3.04mg/l. It was also observed in all the surface water (nalla) samples. In pre monsoon it ranged from 0.34 to 17.6mg/l and in post monsoon it ranged from 0.11 to 89.39mg/l.

However, in the second year (year 2), Fe concentration of groundwater in pre monsoon was observed minimum (BDL) in bore well sample (B3) and maximum (2.56mg/l) in a handpump water sample (H7). In post monsoon, minimum of BDL and maximum of 1.73mg/l (in H7) was observed. In surface water (nalla) samples, Fe concentration was found in the range of 1.08 to 42.3 mg/l in pre monsoon and in post monsoon it ranged from 0.24 to 90.9mg/l. Hence, it was found that most of the water samples had Fe concentration beyond the acceptable limit of 0.3mg/l [8].

f) Pb

Lead (Pb) is a serious body poison. Its presence in the body inhibits several key enzymes involved in the overall process of haemo-synthesis [17].Its adverse effects are mostly seen in children up to the age of 6 years and pregnant women[18]. In the first year (year 1), the lead in the ground water samples ranged from BDL to 0.1 mg/l in post monsoon season while it was BDL in the pre monsoon. However in surface water samples it was observed BDL to 0.67mg/l in pre monsoon, while in post monsoon it was found BDL to 1.62mg/l.

The study revealed that the concentration of lead was below the detectable level (BDL) in most of the ground water samples in the year2 during pre monsoon as well as post monsoon season. However in surface water, it ranged from BDL to 0.19mg/l during pre monsoon, while during post monsoon, it ranged from BDL to 0.01mg/l. However the concentration of lead in most of the water samples was observed within the safe limit of BIS (year 2), but few were found beyond acceptable limit 0.01 mg/l [8, 9]. Industrial effluents, old plumbing, household sewages, agricultural runoff containing phosphatic fertilizers and human and animal excreta are considered as prime sources of lead contamination in ground water[19].

g) Mn

In the year1, the values of Manganese (Mn) concentration in ground water samples ranged from BDL to 0.313 mg/l in pre monsoon season, for post monsoon it was from BDL to 0.24 mg/l. Infact, in most of the ground water samples it was found below detection limit (BDL). However, it was observed above acceptable limit (0.1mg/l) in all the surface water samples in post monsoon season $(0.26 - 10.51 \text{mg/l})$, while in pre monsoon, minimum of 0.058 and maximum of 1.28mg/l Manganese was observed.

In the second year (year 2), the concentration of Mn was detected in most of the ground water samples, although the detected concentration was below acceptable limit (0.1mg/l). In premonsoon, it ranged from BDL to 1.12mg/l, while in post monsoon from BDL to 0.172mg/l. In surface water nalla samples, during pre monsoon it ranged from 0.47 to 1.7 mg/l while in post monsoon it ranged from 0.16 to 0.77mg/l.

Manganese pollution is mainly contributed by traffic and unsanitary deposits. Sometimes manganese containing water is not suitable for domestic purpose even [20].

h) Ni

Nickel (Ni) is associated with nickel alloys, electroplating, machinery parts, stainless steel, spark plugs and also as catalysts. It may cause dermatitis, which may results in itching of the fingers, hands and forearms.

In this study, during pre and post monsoon ofyear 1, the Nickel (Ni) content in the groundwater samples was estimated to be the below detection limit in all the samples, except three exceptions of D8 (0.08 mg/l), D9(0.011mg/l) in pre monsoon and D8 (0.28mg/l) in post monsoon. Out of them, sample from D8was found beyond acceptable limit of 0.02mg/l [8]. However, in surface water samples, during pre monsoon it ranged from 0.057 to 4.28 mg/l while in post monsoon it ranged from 0.025 to 0.136mg/l.

During second year (year 2), Ni followed the similar trend as observed in the case of Mn i.e. concentration of Ni was detected in most of the ground water samples, although the detected concentration was below acceptable limit (0.02mg/l). In pre monsoon of year 2, it was found with minimum of BDL and maximum of 0.27mg/l, while in post monsoon, minimum of BDL and maximum of 0.252mg/l. However, in surface water samples it was observed in the range of 0.03 to 2.79mg/l in pre monsoon, while in post monsoon it was found in the range of 0.03 to 0.23mg/l.

i) **Zn**

Zinc (Zn) is an essential nutrient which is necessary for growth and several physiological functions. It also plays an important role in protein synthesis. It can also be toxic to the organisms, if ingested above higher concentration. Due to its restricted mobility from the place of rock weathering or from the natural sources, it shows fairly low concentration in surface water.

During pre monsoon of year 1, the Zinc (Zn) content in the ground water samples recorded the highest value of 1.29 mg/l at B1 and minimum of BDL. During post monsoon of year 1, the highest level of Zn was found to be 0.797mg/l at H2 and with a minimum of 0.052mg/l at H6. However, in surface water samples during pre monsoon, minimum of 0.71mg/l at N3 and maximum of 2.27mg/l at N2 was observed. During post monsoon, all the samples were detected with BDL concentration except at N2, where it was found to be 81.11mg/l, which is quiet higher than the acceptable limit of Zn (5.0mg/l) given by BIS[8].

In pre monsoon of year 2, it was found with minimum of BDL and maximum of 3.36 mg/l (at H4), while in post monsoon, all the samples were detected with BDL concentration except one i.e. at H8 with 0.29mg/l concentration of Zn in ground water samples. However in surface water samples, it was observed BDL to 3.37mg/l in pre monsoon, while in post monsoon it was found BDL in all the samples except the sample of N2 which has 2.17 mg/l of Zn. Hence, it was observed that in year 2, the concentration of Zn got lowered at all the sampling locations as compared to the previous year.

4. Conclusions

The present study reveals the fact that most of the surface and ground water samples in the area were significantly contaminated by the heavy metals. The detected concentrations of most of the heavy metals were far beyond the acceptable limits mentioned by BIS. Among all these, high concentration of total Cr and $Cr⁶⁺$ in most of the water samples is of great concern, because hexavalent chromium is extremely toxic and is considered by the World Health Organization and the United States Environmental Protection Agency to be a human carcinogen. Detected concentration of heavy metals suggests that the surface water samples were comparatively more contaminated than the ground water samples. However, the intensity of contamination was found more in groundwater samples. Among all the ground water samples, water collected from handpumps were found to be more contaminated, as these samples had heavy metal content beyond the drinking water standards [8].

However, among all the heavy metals analysed, total Cr, Cr⁶⁺, Fe and Zn were observed in most of the collected water samples. Iron was observed in all the samples in post monsoon season and some samples in pre monsoon which may occur due to the industrial and municipal discharge. Zinc was observed in both seasons in most of the samples but below the acceptable limit. High concentration of total Cr and Cr^{6+} in water was also of great concern. This was because chromium VI compounds are [genotoxiccarcinogens](http://en.wikipedia.org/wiki/Genotoxicity) Ingestion of chromium VI can also cause irritation or ulcers in the stomach and intestines. Presence of chromium VI in this area may be due to anthropogenic influences, plating industry, agrochemical industry and discharges of untreated waste. Hence, study clearly indicates that the aquifers of Ambad industrial area of Nashik district are getting contaminated due to increase in concentration of the metal ions at an alarming rate. This may be possibly due of discharge of untreated water from the industries to the land and water sources in their vicinity. Hence any delay in delay in awareness and response by government agencies may lead to the possibility of risk on human health. However, to rectify this problem many conventional and nonconventional sources are suggested now a days. Apart from conventional sources of effluent treatment, unconventional source like microorganisms producing biosurfactants is highly recommended. This technique is cost effective as well as environmental friendly [21].

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