Industrial Impact of Chromium, Fluoride & Salinity in Unnao UPSIDC Area, Unnao, Uttar Pradesh

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Abstract--- Industrialization of newly developed areas of Unnao District, Uttar Pradesh by leather tanning Industries has affected the surface and ground water quality area due to solid/ liquid waste disposal to the surface. In the tanning of leather, Chromium salts, especially chrome alum and Chromium sulfate are used. The Chromium (III) stabilizes the leather by cross linking the collagen fibers. The study identified the areas with high Chromium, Fluoride and salinity in Ground / Surface water bodies, which are the major health affecting parameters to the inhabitant using this water for drinking purposes.

The Effluent samples near CEPT at Dahi Chowki has been recorded the total Chromium as 4285 micro gram/l. Mirza tannery drain, recorded total Chromium as 6578 micro gram/l. In ground water samples high values of Hexavalent Chromium have been found near J R Inter College, Dharamkanta (2876 µg/l); Shivnagar (13 µg/l); Masnagar (8 µg/l); areas in Unnao. It has been observed that in Dharamkanta area, fresh dumping of industrial solid waste containing Chromium salts is being done. High salinity in ground water has also been found in Laukhera, Dakari and Madhuwasi area of industrial pocket of Unnao district. The values of electrical conductivity and fluoride have been recorded as high as 24385 micro s/cm and 7.82 mg/L respectively. The presence of Chromium (total), fluoride and salinity in surface as well as in ground water indicates that surface water is polluting ground water, however the quantum and area at present is very small but it has started polluting the ground water. Disposal of solid and liquid wastes should be properly managed as per Central Pollution Control Board guidelines. Remedial measures should be under taken for the people of the areas to protect from harmful health effects of parameters.

I. INTRODUCTION

Hexavalent Chromium is a form of the metallic element Chromium. Chromium naturally occurs in rocks, animals, plants, soil, and in volcanic dust and gases. It comes in several different forms including trivalent Chromium and hexavalent Chromium. Trivalent Chromium is often referred to as Chromium (III) and is an essential nutrient for the body. Hexavalent Chromium, or Chromium (VI), is generally used or produced in industrial processes and has been demonstrated to be a human carcinogen when inhaled [1,2].

Fluoride is an ion of the chemical element fluorine which belongs to the halogen group. Fluoride has a significant mitigating effect against dental caries if the concentration is approximately 1 mg/l. However, continuing consumption of higher concentrations can cause dental fluorosis and in extreme cases even skeletal fluorosis.

A. Occurrence

Chromium is the 21st most abundant element in Earth's crust with an average concentration of 100 ppm Chromium compounds are found in the environment, due to erosion of Chromium-containing rocks and can be distributed by volcanic eruptions. The concentrations range in soil is between 1 and 3000 mg/kg, in sea water 5 to 800 µg/liter, and in rivers and lakes 26 µg/liter to 5.2 mg/liter [3].

B. Different Forms of Chromium Compounds

Chromium forms many different oxides that exhibit general acid-base behavior as well as displaying a range of different colors [13]. Chromium (II) oxide, CrO, is basic. It is found in the form of an insoluble black powder. Chromium (III) oxide, Cr_2O_3 is the main oxide of chromium. It is amphoteric and while it is insoluble in water, it will dissolve in acid. It is found in nature in the form of a rare mineral, eskolaite. It is used as a pigment, producing a dark green color. Chromium trioxide or chromium (VI) oxide, CrO_3 dark red-orange granular complex. Chromate, CrO_4^{2-}, is a salt of chromic acid. This salt is associated with a yellow color and orange color in acidic conditions.

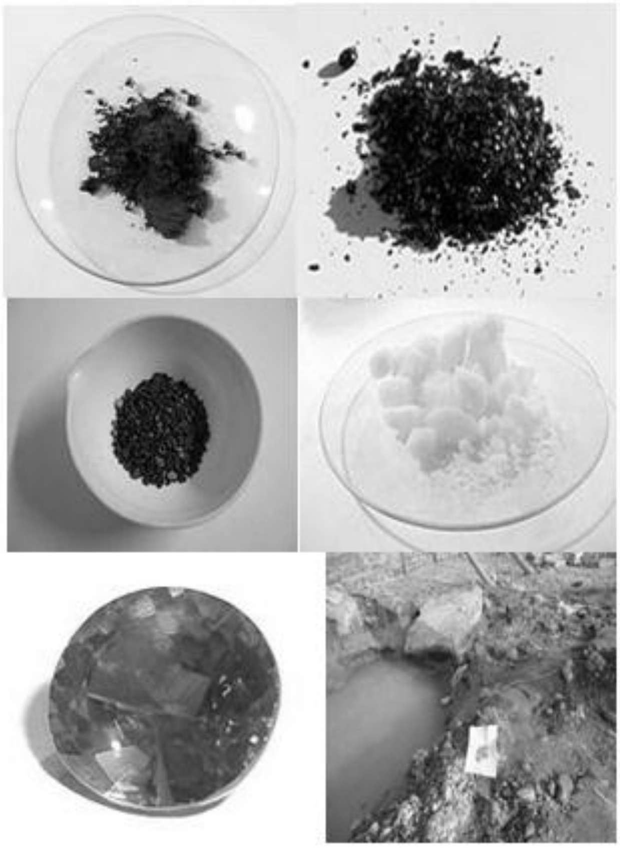


Fig. 1: Different forms of Chromium

C. Study Area

The area of study was selected the four different sites of Uttar Pradesh State, Industrial Development Corporation in Unnao District, U.P., where most of the tanneries are shifted from Kanpur city area of Uttar Pradesh. (The district map is shown in Fig-2). The solid waste disposed of by the industries is being used for filling the land which contains mainly basic chrome sulphate as a toxic hexavalent chromium pollutant to surface and ground water. (Fig-3)

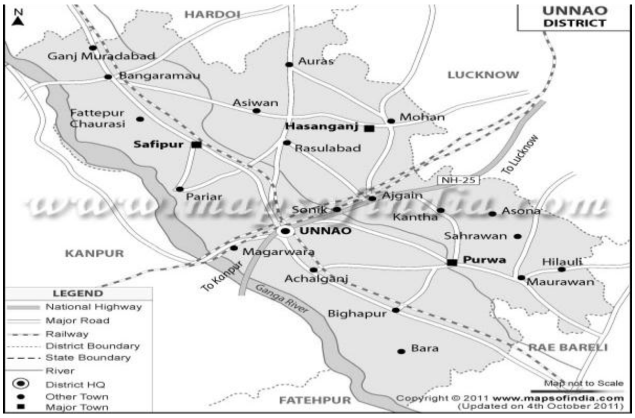


Fig. 2: District map of Unnao, Uttar Pradesh

D. Health Impact

The dissolved metals and ions play a very important role in various physiological processes in the flora and fauna of the habitat. If present in higher or low concentration than the required causes, unavoidable effects or diseases. The health effects of Chromium to toxicity, dermatitis, ulcer; copper to liver damage, CNS irritation; iron to haemochromatosis, lead to paralysis, toxicity, anemia, mental disorders; zinc to syndromes, retarded growth, immunity, anemia; manganese to manganism are well reported [4,5].

E. Chromium toxicity

Water insoluble Chromium (III) compounds and Chromium metal are not considered a health hazard, while the toxicity and carcinogenic properties of Chromium (VI) have been known for a long time.

Because of the specific transport mechanisms, only limited amounts of Chromium (III) enter the cells. Several *in vitro* studies indicated that high concentrations of Chromium (III) in the cell can lead to DNA damage. Acute oral toxicity ranges between 1.5 and 3.3 mg/kg. The proposed beneficial effects of Chromium(III) and the use as dietary supplements yielded some controversial results, but recent reviews suggest that moderate uptake of Chromium(III) through dietary supplements poses no risk.

The acute oral toxicity for Chromium(VI) ranges between 50 and 150 µg/kg. In the body, Chromium(VI) is reduced by several mechanisms to Chromium(III) already in the blood before it enters the cells [6]. The Chromium (III) is excreted from the body, whereas the chromate ion is transferred into the cell by a transport mechanism, by which also sulfate and phosphate ions enter the cell. The acute toxicity of Chromium(VI) is due to its strong oxidation properties. After it reaches the blood stream, it damages the kidneys, the liver and blood cells through oxidation reactions. Hemolytic, renal and liver failures are the results of these damages. Aggressive dialysis can improve the situation.

The carcinogenetic of chromate dust is known for a long time, and in 1890 the first publication described the elevated cancer risk of workers in a chromate dye company. Three mechanisms have been proposed to describe the genotoxicity of Chromium (VI) [7]. The first mechanism includes highly reactive hydroxyl radicals and other reactive radicals which are by products of the reduction of Chromium (VI) to Chromium (III). The second process includes the direct binding of Chromium (V), produced by reduction in the cell, and Chromium (IV) compounds to the DNA. The last mechanism attributed the genotoxicity to the binding to the DNA of the end product of the Chromium (III) reduction.

Chromium salts (chromates) are also the cause of allergic reactions in some people. Chromates are often used to manufacture, amongst other things, leather products, paints, cement, mortar and anti-corrosives. Contact with products containing chromates can lead to allergic contact dermatitis and irritant dermatitis, resulting in ulceration of the skin, sometimes referred to as "chrome ulcers". This condition is often found in workers that have been exposed to strong chromate solutions in electroplating, tanning and chrome-producing manufacturers.

F. Effect of High Fluoride on Human Health

The maximum permissible limit of fluoride in drinking water specified by WHO, 1984 and BIS, 2001 is 1.5 mg/l. However, BIS (IS: 10500:2001) has suggested the desirable limit of 1.0 mg/l with the recommendation that fluoride may be kept as low as possible. Ingestion of water with fluoride contents above 1.5 mg/l results in dental fluorosis characterized by opaque white patches, staining, mottling and pitting of teeth. Skeletal fluorosis may occur when fluoride concentrations in drinking water exceeds 4 – 8 mg/l, which leads to an increase in bone density, calcification of ligaments, rheumatic or arthritic pain in joints and muscles along with stiffness and rigidity of the joints, bending of the vertebral column, and so on.

G. Hydrochemistry of fluoride

Even though food items like tea sometimes contribute substantially, ground water is the major source of human intake of fluoride and in India people are at risk of developing fluorosis from drinking high F^- water. The house to house epidemiological surveys have shown that there are villages where nearly 75 percent of the population is seriously affected by fluorosis and a great majority is crippled [3].

Fluoride occurs mostly as free fluoride ions in natural waters, although its complexes with Al, Be, B, and Si are also encountered under specific. Fluoride is mainly derived from weathering, although atmospheric deposition from soil dust and industrial emission may also contribute. Recently published measurements of dry deposition near Agra indicate even larger amounts of F^- derived by atmospheric deposition.

The primary sources of F^- in natural waters are apatite and fluorite, besides the replacement of OH^- by F^- ion in mica, hornblende and soil consisting of clay minerals [8,9]. The solubility of CaF_2 increases with the increase in alkalinity in ground waters, according to the following reactions:

$$CaF_2 + CO_3^{--} \rightarrow CaCO_3 + 2F^-$$

$$CaF_2 + 2HCO_3^- \rightarrow CaCO_3 + 2F^- + H_2O + CO_2$$

Thus, a positive relationship of fluoride with alkalinity suggests the dissolution of F^- bearing minerals in the ground waters. In these reactions, the concentration of dissolved ionic species and pH of water play important roles [10, 11]. The presence of $CaCO_3$ also favors the dissolution of F- from F- containing minerals as shown below:

$CaCO_3 + H + 2F^- \rightarrow CaF_2 + HCO3^-$

$CaF_2 \rightarrow Ca^{++} + 2F^-$

H. Drinking Water Standards

In India BIS 1991 has recommended 0.05 mg/l Chromium in drinking water in view of its severe toxicity. Fluoride limit in drinking water is 1.5 mg/l considering its health impact on human body [4, 5].

II. METHODOLOGY

The samples were collected from the ground water, surface water and Effluents in the area in pretreated 1 lt. Polypropylene (TORSON) bottles and were treated with analytical grade Hydrochloric acid for total Chromium. The samples for basic analysis like Electrical conductivity and fluoride were collected in another bottle without any treatment. The samples for hexavalent chromium were collected in 125 ml Tarson bottle with preservation in ice box. These samples were analyzed for the estimation of total & hexavalent Chromium, pH, Conductivity & Fluoride following the methodology laid down in Standard Methods for Water and Waste Water Analysis (APHA 19th. edition) [12]. The analytical data is given in table.

III. RESULTS & DISCUSSIONS

The chemical analysis results have been summarized in Table-1 and maps. It has been found that the concentrations of Chromium, Electrical Conductivity & Fluoride content in some samples of ground / surface water are given in Table-1. The perusal of analysis of data indicates –

1. Chromium (total) has been found in ground & surface water at few places in study area of Unnao district. The Effluent samples near CEPT at Dahi Chowki has been recorded total Chromium as 4285 micro gram/l. Mirza tannery drain, recorded total Chromium as 6578 micro gram/l. Locations of high Chromium content from various surface and ground water samples are depicted in Figure-3.

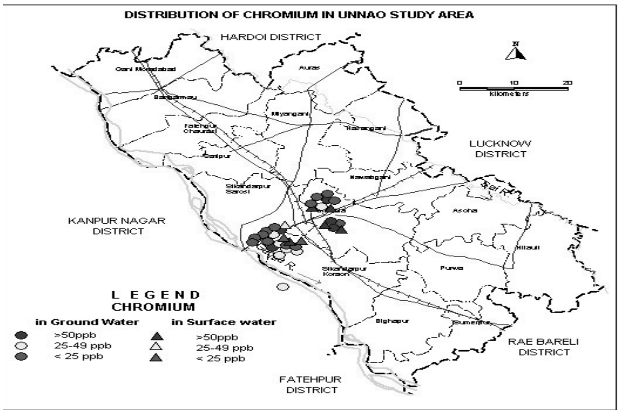


Fig. 3: High Chromium locations in the area

2. In ground water samples high values of Hexavalent Chromium have been found near J R Inter College, Dharamkanta (2876 µg/l); Shivnagar (13 µg/l areas in Unnao. It has been observed that in Dharamkata area, fresh dumping of industrial solid waste containing Chromium salts is being done.

3. High salinity in ground water has been found in Laukhera, Dakari, Banther, Madhuwasi, Dahi Chowki areas of industrial pocket of Unnao district.

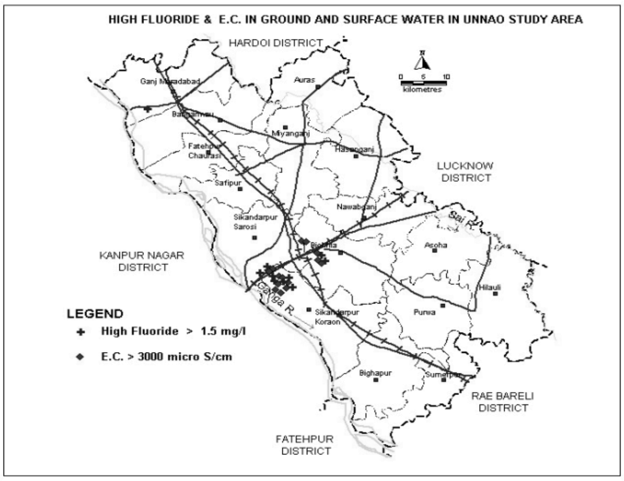


Fig. 4: High Fluoride and EC locations in the area

4. At few locations having high Fluoride has been detected (more than 1.5 mg/l as per BIS) in the surface effluent water samples, which might be the reason for occurrence of high fluoride in ground water in the area. (Table-1).

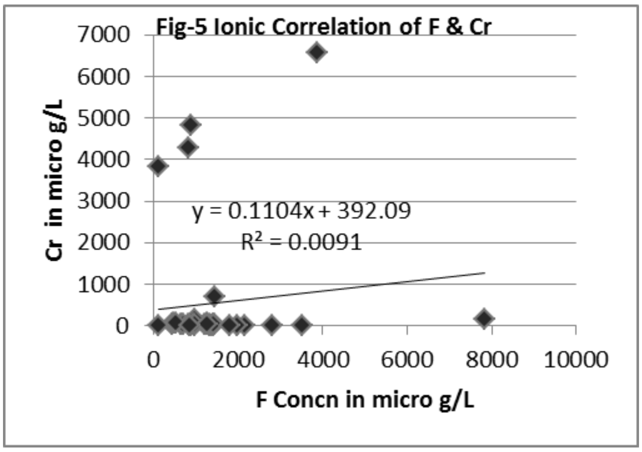
SN	Location	Type	EC in µs/cm	Cr VI	Cr	F in mg/l
1	Effluent Benther	S	1380	ND	4	1.35
2	Right Effluent Benther	S	4208	ND	12	2.81
5	J S slaughter house	S	905	ND	19	2.17
6	Benthar	G	804	ND	11	1.36
7	Lauikhera	G	6360	ND	56	1.28
8	Gaya prasad, laukhera	G	4850	ND	41	0.98
9	Sambhu, Laukhera	G	808	ND	0	0.88
10	Manglal, Laukhera	G	1040	2.39	4	0.99
11	Sushil, laukhera	G	890	ND	18	3.51
12	Jagannath Jalimkhera	G	2250	ND	34	1.42
13	Ramkumar Jalimkhera	G	1760	ND	36	0.90
14	JagawathJalimkhera	G	1540	ND	32	1.34
15	Raj bhadur,	G	6420	ND	40	1.21

	Dakari					
16	Horilal,Maduwasi	G	1950	ND	152	0.97
17	Kanya vidyalay,Maduwasi	G	4680	ND	8	1.34
18	Mirza tannery drain, unnao	S	1820	ND	6578	3.88
19	Unnao distillery	S	890	ND	39	0.95
20	Munna Awasthi, Rishinagar	G	1724	ND	23	0.65
21	New Krishna sweet	G	940	ND	45	0.44
22	DC Dwedi, Risinagar	G	1234	ND	12	1.43
23	JL Dwedi, Risinagar	G	1488	ND	28	1.45
24	Pal Traders,Subasnagar	G	1278	ND	36	0.68
25	Hanuman Temple Ambikapuram	G	668	ND	26	0.45
26	Vinod Rathor,Suklaganj	G	1688	ND	24	0.72
27	JHS Singrausi, Darmkanta	G	905	ND	18	1.98
28	JAR Inter college, Daramkanta	S	3854	2876	4812	0.88
29	JAR Inter college, Daramkanta	G	3012	388	698	1.45
30	Pintu Gupta, Shivnagar	G	3612	13	162	7.82
31	Eff CEPT, Dahi Chowki	S	7946	45	4285	0.84
32	Eff CEPT, Dahi Chowki	S	19988	65	3820	0.11
33	CEPT, Dahi Chowki	G	1842	5	28	1.41
34	Garhi, Nr tower	G	1158	4	22	0.99
35	Jhanjhari	G	2836	7	28	0.82
36	Central School	G	688	12	56	0.48
37	Masnagar	G	1345	5	55	0.54
38	Masnagar invillage	G	2822	8	32	1.28
39	Masnagar	G	1010	6	18	0.85
	onroad					
40	CEPT, Banther	S	24385	ND	_	0.11
41	J S slaughter house	S	1856	ND	_	1.81

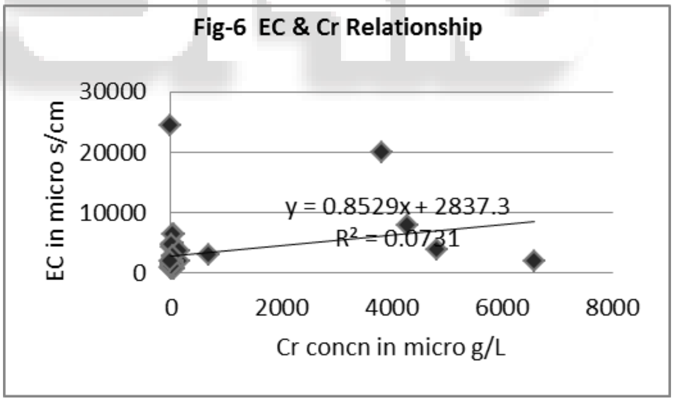
Table 1: Surface / Ground Water Quality of Study Area in Unnao Distt, UP

S= Surface Water; G= Ground Water; Cr in µg/L

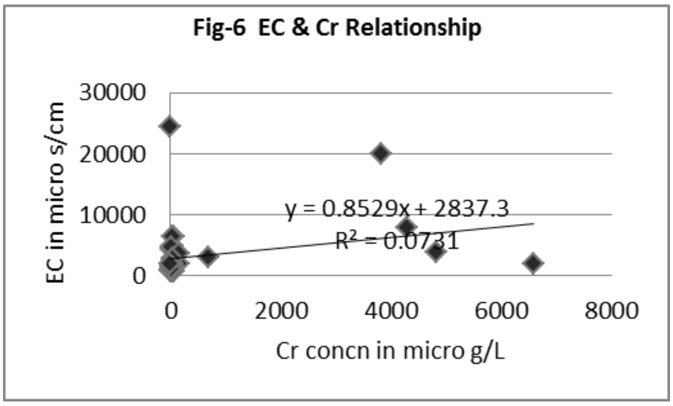
5. Relationship Chromium & Fluoride –
The relationship of Cr and F is given in figure – 5, which shows a positive correlation for surface effluent samples and poor relationship for ground water samples.



6. Relationship Chromium & EC – The relationship of Cr and EC is given in figure – 6, which shows a positive correlation for surface effluent samples as well as ground water samples.



7. Relationship EC & Fluoride –



The relationship of Cr and F is given in figure – 5, which shows a poor correlation for surface effluent samples and ground water samples. The fluoride is generally independent on conductivity of water samples particularly in ground water due to its less solubility.

IV. COCLUSIONS AND RECOMMENDATIONS

1. The presence of Chromium (total) in surface as well as in ground water indicates that surface water is polluting ground water, however the quantum and area at present is very small but it has started polluting the ground water.
2. Hexavalent Chromium has been recorded in Dharmkanta, near Unnao bypass area, where industrial solid waste is being dumped on the road which should be stopped immediately by the concerned authorities.
3. Effluent treatment plants should be in proper working condition as effluent near Dahi Chowki has been found to contain Chromium in significant amount.
4. Disposal of solid and liquid wastes should be properly managed as per Central Pollution Control Board guidelines. The CPCB should be asked to look into this matter and a detailed study should be undertaken.
5. Deeper aquifers, which are safe from contaminants, can be used for drinking purposes.
6. Remedial measures should be under taken for the people of the areas.

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