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Review Article

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Analysis of health risk effects of hexavalent chromium in tannery water affected areas of Kasur, Pakistan

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Abstract

Chromium is widely used in leather industries and can accumulate in animal bodies, adversely affecting various bodily structures, includes reproductive organs. Kasur District in Pakistan is renowned for its leather tanneries, with over 270 individual tanneries currently operating. Water samples were collected from areas affected by tannery effluents and analyzed using Atomic Absorption Spectroscopy. Additionally, health department data on patients from selected union councils were gathered to examine diseases linked to chromium toxicity. The analysis revealed significantly increased concentration of chromium in water samples compared to control samples, posing a potential threat to local organisms. The USEPA sets permissible limits for industrial wastewater discharge at less than 0.5 µg/ml and for drinking water at 0.1 µg/ml. However, untreated chromium from tanning activities is discharged directly into the environment, contaminating adjacent water channels and the habitat. Consequently, groundwater becomes polluted, impacting public health as chromium is ingested through drinking water and the food chain. Various diseases were observed among residents in nearby areas. In conclusion, chromium discharged from tanneries into the Kasur environment contaminates water and crops consumed by humans, leading to diseases such as kidney, bone, and gastrointestinal disorders.

Keywords: Health, Chromium, Disease, Human, Pakistan

Introduction

Pakistan boasts a robust leather industry, contributing approximately 17.61% to the nation's total exports. Over one million individuals are employed in this sector, with major industrial hubs located in cities such as Faisalabad, Gujranwala, Karachi, Kasur, Lahore, Multan, Peshawar, and Sialkot. Annually, these regions produce about 35 million sheep and goat skins, along with over 7.8 million cattle hides. However, the leather industry significantly contributes to environmental degradation, underscoring the need for ecological sustainability to protect living organisms that are directly exposed to this compromised environment (Andleeb, Mahmood et al. 2018). In the Dingarh area, Rohi Nallah was traditionally used for tanning with tree bark, and all activities were performed manually. Tannery operations have since expanded south of the river to areas including Niaz Nagar, Abdul Qadir, Younus Nagar, and Kot Molvi. Despite being essential for economic purposes, the tanning industry is often deemed a "noxious" industry worldwide due to its adverse effect on humans and animals health, plants, and the environment. Currently, tanning activities in this region discharge approximately 150 tons of solid waste and around 9,000 cubic meter of polluted wastewater daily into main streams. This has led to significant pollution of the natural environment, causing serious health hazards for local communities, including both humans and animals, who are openly exposed to polluted groundwater, crops, and polluted conditions.

Chromium is a shiny, and hard metal with a silver-gray hue that can be refined to a high gloss. It does not tarnish when exposed to air but form green chromic oxide when heated. Although unstable in oxygen, chromium quickly develops a thin oxide layer that is resistant to oxygen, protecting underlying metal. Due to its inherent brittleness, commercial alloys typically contain no more than 30-40% chromium by weight. It has melting point of $1857\pm 20^{\circ}\text{C}$, a boiling point of 2672°C , a specific gravity of 7.187 at 20°C , and common valences of 2, 3, or 6. All chromium compounds are colored and toxic. Trivalent chromium cannot penetrate cell membranes, which makes it less dangerous to living cells. This form of chromium is essential for glucose and lipid metabolism (Gomez and Callao 2006, Mohan and Pittman Jr 2006). Cell membranes are penetrable to the hexavalent form of chromium (Cr-VI), making it hazardous to cell membrane, the surrounding environment, and living organisms (Decorosi, Lori et al. 2011). Both Cr-VI and trivalent chromium (Cr-III) can form chromium-protein and chromium-DNA complexes, which cause mutagenicity and alter the form and function of enzymes (Poljsak, Pócsi et al. 2011).

The main ore of Cr is chromite (FeCr_2O_4), and the metal can be obtained by reducing its oxide with aluminum. Environmental sources of Cr include chemical plant wastes, aerial particles from tobacco burn, road dust from catalytic converter wear, polluted landfills, asbestos brake and lining erosion, and emissions from incineration services. Occupational exposure to chromium occurs in various industries, including wood preservatives, high-fidelity magnetic tape production, alloy or steel welding, textile, porcelain and ceramics, cement manufacturing, and the use of antifreeze and anti-algae agents (Nriagu and Nieboer 1988). Recently, heavy metal chromium has become a significant concern for environmental contamination and biological toxicity, ranking seventh among all elements on Earth in terms of its impact. This study investigates the effects of chromium toxicity on the human population residing near the tanneries in Kasur.

Material and Methods

Area of study

The research was conducted in the Kasur district of Punjab province, eastern Pakistan, near the Indian border. Key locations within the study area include the tannery zone (Din Garh), Kamal Chishti Mazar, Kamal Chishti Chok, Basti Kambohan Wali, Dole Wala, and Faqire Walla, as

well as a wastewater treatment plant and various sampling sites. The region primarily consists of small villages and agricultural land watered by river and groundwater. The main crops grown in the area are wheat, rice, sugarcane, and cotton.

Location of study

District Kasur, located in Pakistan at latitude $31^{\circ} 05'$ north and longitude $74^{\circ} 31'$ east, covers an approximate area of 3995 square kilometers. Positioned along the Lahore Ferozepur Road, it is situated 55km away from Lahore city (Fig.1). Geologically, District Kasur shares borders with Lahore district to the north, Sheikhpura district to the northwest, and Okara district to the southwest, with Indian Territory to the southeast. The district is composed of four Tehsils: Kasur, Pattoki, Chunian, and Kot Radha Kishan (Ali, Saeed et al. 2021). District Kasur experiences extreme climatic conditions. The summer season typically extends from April to September, with June being the hottest month. During this time, the average maximum and minimum temperatures are approximately 40 and 27 degrees Celsius, respectively. The winter season spans from November to March, with January being the coldest month. In January, the average maximum and minimum temperatures are around 20 and 6 degrees Celsius, respectively.

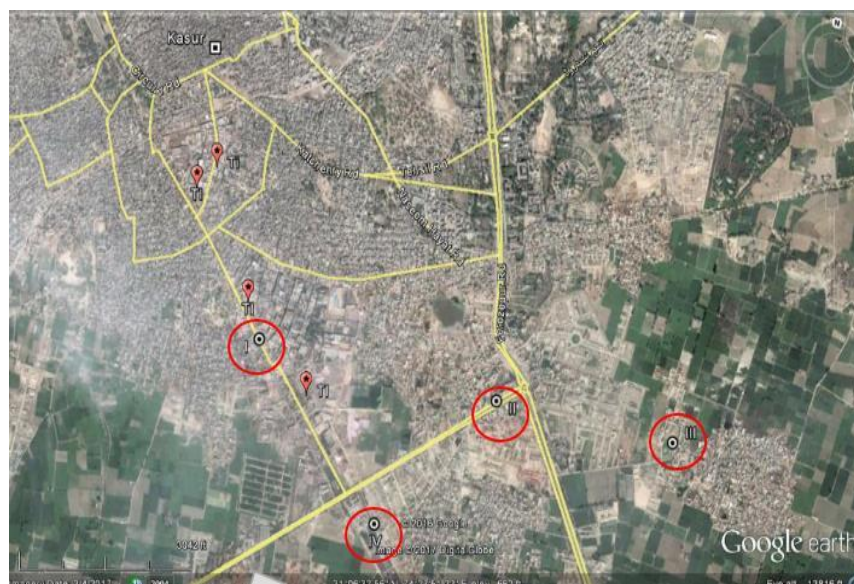


Figure 1: Indicates sampling areas and tanneries in District Kasur

Water Sampling

Four water samples were gathered from study area during the month of December, using airtight sterilized water bottles. To prevent contamination and degradation, these bottles were stored in an icebox during transportation. Subsequently, they were brought to the water and soil testing laboratory for research located at Thokar Niaz Baig in Lahore. The process of water collection has been illustrated in Figure 2.



Figure 2: Shows the water sample collection

Patient's data collection

Six villages were randomly selected in District Kasur: Bahadarpur, Shamsपुरa, Dhoolay wala, Shaikh Ummad Kohna, Roshan Bheela, and Noorpur. These villages were chosen because of their geographical proximity to the tanneries of Kasur. Waste water from leather factories flows through these villages via a drain called Rohi Nala, and after passing through an effluent treatment plant, it eventually empties into the Satluj River. Surveillance was conducted for this purpose.

During the survey, fifty houses were surveyed in each village. Data was collected from houses located within a radius of 1km, 4km, and 7km from the tanneries' wastewater outlet (Rohi Nala). This area was selected due to the seepage of polluted water. MS Excel was utilized for calculation and analysis. The study investigated various diseases including skin diseases, gastrointestinal diseases, liver cancer, and kidney diseases, among others.

Permission and consent of participation

This study was conducted according to the Declaration of Helsinki. Patient consent was obtained prior to commencing the work. Additionally, the research was permitted by university's ethical review board to ensure compliance with regulations governing human studies.

Estimation of chromium in water samples

Digestion of Water Samples

The water samples underwent digestion using a combination of nitric acid and perchloric acid, by the procedure (Enamorado-Báez, Abril et al. 2013). For digestion, 0.5 milliliters of the water samples were transferred into a 25ml digestion tube. Subsequently, 0.5 milliliters of (HNO₃) were included to the tube, and the mixture was slightly mixed. The resulting mixture was heated to 60°C for duration of 30 to 45 minutes to ensure the oxidation of all oxidizable materials, after which it was allowed to cool at 37°.

Once cooled, 2.5 milliliters of 70% perchloric acid were added to mixture, and it was slightly boiled till dense white fumes appeared. The mixture was then cooled once more to room temperature. Following this, 0.5ml of double distilled water (ddH₂O) was added to the mixture, and it was further boiled to release any remaining fumes. After cooling to room temperature, the solution was filtered until only 1 milliliter of the final concentrated solution remained. After cooling, it was filtered by filter paper, using both <0.45 µm Millipore filter paper and Whatman No. 42 filter paper. Subsequently, the filtrate was transferred to a 25 milliliter volumetric flask by adding (ddH₂O), thereby adjusting the final volume to 250 ml .

Solutions preparation

To prepare the chromium stock solutions up to 1000 mg/L, 2.8 grams of potassium dichromate was added in 1000 mL of (ddH₂O). Subsequently, to prepare a 20 mg/L chromium stock solution, 20 mL of this stock solution was diluted in 1000 mL of distilled water (dH₂O). Additionally, solutions with metal concentrations of 50, 100, 150, and 200 mg/L were prepared accordingly (Chekri, Noël et al. 2010).

Cr detection by Atomic Absorption Spectrophotometer (AAS)

The chromium metal concentration in final filtered sample solution of water was measured using an (AAS), specifically the GBC 932 plus model (Saha and Gilbreath 1991).

To calculate Cr concentration formulae used as follows,

Cr concentration = AAS reading \times Dilution factor / weight or volume of the sample

Dilution factor was calculated as,

$$\text{Dilution factor} = \text{final volume} / \text{initial volume}$$

Statistical investigation

The data were analyzed by IBM-SPSS Statistics 20 software and Microsoft Excel. Differences between control and experimental samples were assessed using Student's paired t-test. The means \pm standard error, and p-values were obtained. Furthermore, means of soil and water samples from experimental and control areas were compared using the Welch Two Sample t-test, employing the R-software program (Andleeb, Mahmood et al. 2018).

Results

This study explores the chromium concentration in tannery water and its effect on human disease.

Chromium Concentration

The average Cr concentration in water samples were notably elevated ($595.4 \pm 114.6 \mu\text{g/ml}$), with the highest level observed at site-1 ($973 \pm 95 \mu\text{g/ml}$) and the lowest at site-2 ($862 \pm 131 \mu\text{g/ml}$) (Table 4.1). This discrepancy was deemed statistically significant ($t = 10.44$, $df = 10$, $p < 0.0001$). Furthermore, the significantly higher chromium concentration in water samples from the experimental area compared to the control area ($t = 11.3963$, $df = 11$, $p\text{-value} < 0.0001$) was obtained.

Table 1: Chromium concentrations in water samples

Sample	Control group	Site 1	Site 2	Site 3	Site 4	Site 5
	Mean \pm Stdev	Mean \pm Stdev	Mean \pm Stdev	Mean \pm Stdev	Mean \pm Stdev	Mean \pm Stdev
	Kasur	Bahadar Pura	Shams Pura	Adda Doallay Wala	Shaikh ummad kohna	Noor poor
Water(μ g/l)	0.3 \pm 0.08	906 \pm 121	937 \pm 131	535 \pm 95	411 \pm 110	203 \pm 116

Disease surveillance

Out of a total of 1834 individuals surveyed, 153 individuals were diagnosed with skin diseases, comprising 64 males and 69 females. This represents 54.9% of males and 45.09% of females affected by various skin ailments. Additionally, 122 individuals were found to have kidney diseases, with 57.37% being male and 42.62% female. Furthermore, 342 individuals were recorded with gastro and abdominal diseases, with 42.1% males and 57.89% females affected. For liver diseases, the proportion was 47.82% males and 51.3% females, with a total of 115 cases reported. Additionally, there were 69 cases of cancer, with 43.47% males and 56.52% females affected. These findings are depicted in Figure 3. Table 2 contains details of the population observed during the survey.

Table 2: Total surveyed population village wise and gender wise

Sr.No	Village Name	Distance from Rohi nala	Male	%age	Female	%age	Total
1	Bahadarpura	1Km	165	47.14	185	52.85	350
2	Shampur	1Km	176	58.66	124	41.33	300
3	Sheikhummad Kohna	4Km	188	52.36	171	47.63	359

4	Dolay wala	4Km	133	47.5	147	52.5	280
5	Roshan Bhella	7Km	203	59.7	137	34.41	340
6	Noorpur	7Km	123	60	82	40	205
7	Average		164.666	54.226	141	44.786	305.666
8	Variance		976.266	36.379	1331.6	55.026	3362.67
9	Standard deviation		31.2452	6.03152	36.491	7.4179	57.9885
10	Total		988	53.87	846	46.12	1834

The table 3 comprises of skin disease patients observed during the study.

Table 3: Skin Diseases patients

Sr.No	Village name	Distance from Rohi nala	Male	%age	Female	%age	Total
1	Bahadr Pura	1Km	15	45.45	18	54.54	33
2	Shampur	1Km	22	59.45	15	40.54	37
3	Sheikh ummad kohna	4Km	18	56.25	14	43.75	32
4	Daulay wala	4Km	16	61.53	10	38.46	26
5	Roshan Bhela	7Km	8	57.14	6	42.85	14
6	Noor pur	7Km	5	45.45	6	54.54	11
7	Average		14	54.211	11.5	45.78	25.5
8	Variance		40.4	49.452	24.7	49.444	114.7
9	Standard deviation		6.356	7.032	4.969	7.0316	10.709
	Total		84	54.9	69	45.09	153

The table 4 comprises of kidney disease patients observed during the study

Table 4: Kidney Diseases patients

Sr.No	Village name	Distance from Rohi nala	Male	%age	Female	%age	Total
1	Bahadr Pura	1Km	18	60	12	40	30
2	Shampur	1Km	14	60.86	9	39.13	23
3	Sheikh ummad kohna	4Km	12	57.14	9	42.85	21
4	Daulay wala	4Km	11	57.89	8	42.1	19
5	Roshan Bhela	7Km	9	56.25	7	43.75	16
6	Noor pur	7Km	6	46.15	7	53.84	13
7	Average		11.666	56.381	8.666	43.611	20.333
8	Variance		17.066	28.14	3.466	28.126	35.066
9	Standard deviation		4.131	5.304	1.861	5.303	5.921
10	Total		70	57.37	52	42.62	122

The table 5 comprises of kidney disease patients observed during the study

Table 5: Liver Diseases patients

Sr.No	Village name	Distance from Rohi nala	Male	%age	Female	%age	Total
1	Bahadr Pura	1Km	13	59.09	9	40.9	22
2	Shampur	1Km	12	54.54	10	45.45	22
3	Sheikh ummad kohna	4Km	7	43.75	9	56.25	16
4	Daulay wala	4Km	7	41.17	10	58.82	17
5	Roshan Bhela	7Km	8	42.1	11	57.89	19
6	Noor pur	7Km	9	47.36	10	52.63	19

7	Average		27.665	32.247	26.996	35.578	19.166
8	Variance		6.666	53.138	0.566	53.155	6.166
9	Standard deviation		2.5819	7.289	0.752	7.29	2.483
10	Total		55	47.82	59	51.3	115

The table 6 comprises of cancer disease patients observed during the study

Table 6: Cancer Diseases patients

Sr.No	Village name	Distance from Rohi nala	Male	%age	Female	%age	Total
1	Bahadr Pura	1Km	6	35.29	11	64.7	17
2	Shamspura	1Km	7	36.84	12	63.15	19
3	Sheikh ummad kohna	4Km	6	54.54	5	45.45	11
4	Daulay wala	4Km	4	44.44	5	55.55	9
5	Roshan Bhela	7Km	4	50	4	50	8
6	Noor pur	7Km	3	60	2	40	5
7	Average		5	46.851	6.5	53.141	11.5
8	Variance		2.4	96.324	16.3	96.259	29.5
9	Standard deviation		1.549	9.814	4.037	9.811	5.431
10	Total		30	43.47	39	56.52	69

The table 7 comprises of gastrointestinal disease patients observed during the study

Table 7: Gastrointestinal diseases patients

Sr.No	Village name	Distance from Rohi nala	Male	%age	Female	%age	Total
1	Bahadr Pura	1Km	36	48	39	52	75

2	Shampura	1Km	29	41.42	41	58.57	70
3	Sheikh ummad kohna	4Km	30	40	45	60	75
4	Daulay wala	4Km	21	35.59	38	64.4	59
5	Roshan Bhela	7Km	16	47.05	18	52.94	34
6	Noor pur	7Km	12	41.37	17	58.62	29
7	Average		24	42.238	33	57.755	57
8	Variance		84.4	21.396	150	21.382	426.8
9	Standard deviation		9.186	4.625	12.247	4.624	20.65
10	Total		144	42.1	198	57.89	342

The figure 3 comprises of patients observed during the study.

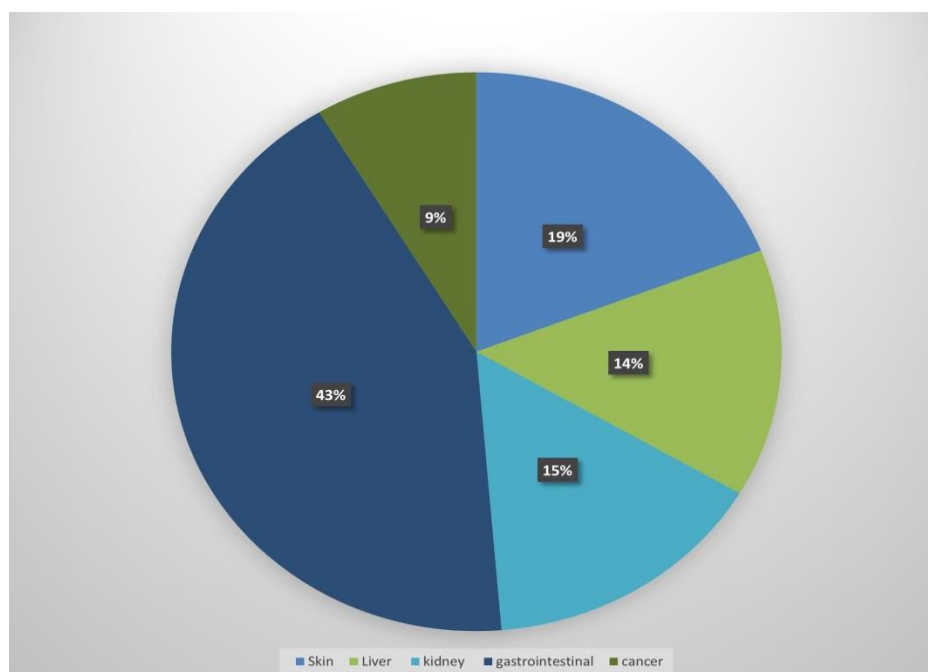


Fig 3: Percentage of people affected by diseases

Discussion

The study concluded that the elevated levels of chromium and other metals in water lead to reduced biomass in plants, indicating toxicity. Consequently, these metals are causing disturbances in human lives as well (Bareen and Tahira 2011).

The role of heavy metals is indispensable in daily life; however, they also serve as a significant source of environmental pollution and pose risks to humans and animals health. Heavy metals characterized by their density, persist in environment and can either be important trace elements, inert, or toxic when present in excessive amounts. The removal of metals in environment from industrial activities than controls, as observed in the current study. In the five various sampling areas, the highest chromium levels were detected at site-3, attributed to natural rather than anthropogenic sources. Notably, significant man-made sources include mineral processing and combustion processes raising concerns about occupational health hazards. Due to metals transportation by water, food, or air, contamination can extend to distant areas, resulting in exposure to the general population (Fendorf, Michael et al. 2010). In this study, the heavy metal chromium from all sites under study, play important role in the spreading of disease to people and other living organisms.

For tanning purposes, chromium salts are extensively utilized, with approximately 60% to 70% of all chromium salts reacting with animal skins. However, around 30% to 40% of the applied chromium quantity remains in liquid and solid wastes within the spent tanning solutions. It's estimated that more than 50 m³ of wastewater is produced during the production of 200 kg of leather through the application of 1 ton of wet Cr salt (Abas, Kalair et al. 2015).

About 50,000 tannery workers and inhabitants residing in the area of industrial sector of the tannery areas in Kasur District are highly vulnerable to long-lasting infections and cancers. According to a health valuation directed in 2016 in Kasur, out of 6,460 households surveyed, it was found that 62% of population suffered from more than one disease related to air and groundwater contamination in the area (Rehman and Alharthi 2016). In this study, it was found that the increasing level of chromium show hazardous effect on humans. Out of 1834 people surveyed, 153 people were diagnosed with skin diseases, consisting of 64 males and 69 females. This represents 54.9% of males and 45.09% of females affected by various skin ailments. Moreover, its control is necessary to avoid from harmful diseases.

Conclusion

To conclude, the average chromium concentrations in water sample is significantly higher in the tannery areas, posing a highly dangerous situation for biological systems in the region. The life

was observed poor, due to chromium contamination. Furthermore, the overall morbidity rate of all diseases in tannery-affected areas is very high, which raises concerns for both the health department and the general public. Moreover, there exists a strong relationship between pure and clean water and disease morbidity rate. Access to clean water is essential in mitigating the risk of various diseases, including skin ailments, bone disorders, gastrointestinal issues, cancer, and liver diseases, as indicated by previous studies.

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