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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.

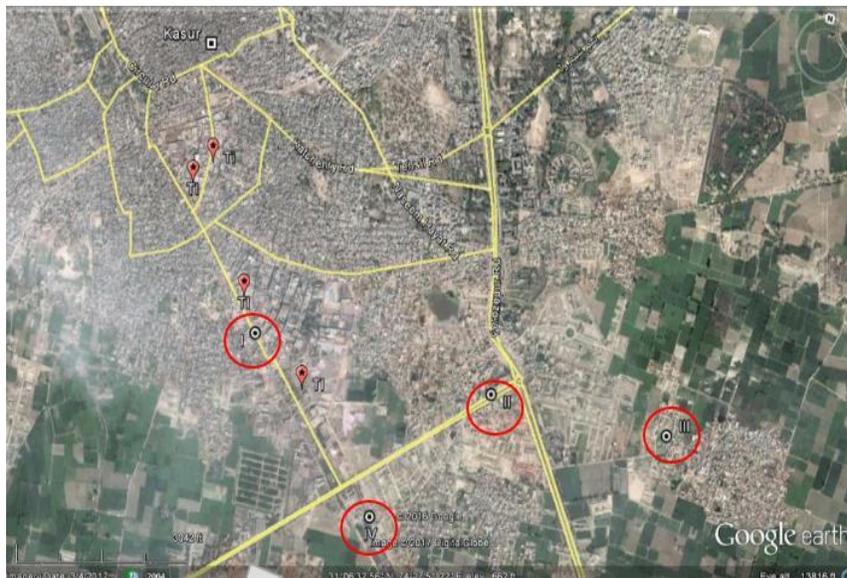


Figure 1: Indicates sampling areas and tanneries in District Kasur

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, Shampur, 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.

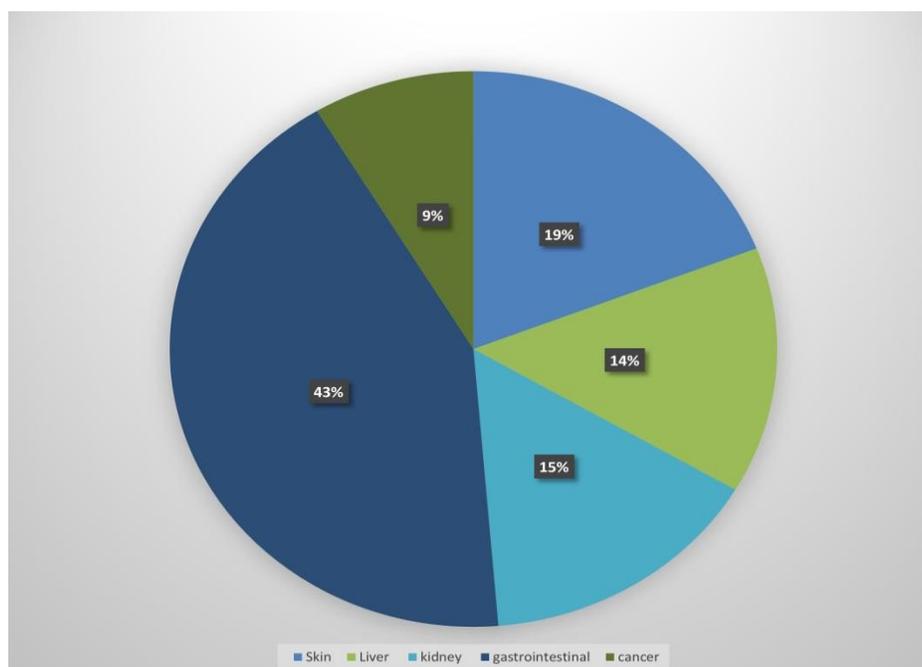


Fig 3: Percentage of people affected by diseases

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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