ASSESSMENT OF GROUNDWATER CONTAMINATION IN DHAKA CITY FROM TANNERY WASTE

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A thesis submitted to the Department of Civil Engineering of Bangladesh University of Engineering and Technology, Dhaka, in partial fulfillment of the requirements for the degree
of

MASTER OF SCIENCE IN CIVIL ENGINEERING

JULY, 2001

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DECLARATION

I hereby certify that the research work reported in this thesis has been performed by me and this work has not been submitted elsewhere for any other purpose (except for publication).

July, 2001

Saha

Ganesh Chandra Saha

DEDICATED

TO

MY MOTHER

ACKNOWLEDGEMENT

The author wishes to express his deepest gratitude to Dr. M. Ashraf Ali, Associate Professor, Department of Civil Engineering, BUET for his constant support and guidance during the course of this research work starting from, development of the research proposal till writing of this thesis. His careful reading of the draft, valuable comments, criticism and constructive suggestions immensely contributed to the improvement of the thesis.

The author expresses his profound gratitude to Dr. A. B. M. Badruzzaman, Professor of Civil Engineering Department, BUET, for his advice and co-operation. The author is also grateful to the Civil Engineering Department, BUET, for having provided him with all the facilities and equipment, which enabled him to carry out the research work.

The author wishes to thank the Dhaka Water Supply and Sewerage Authority (DWASA) for assisting in collection of water samples from Deep Tubewells from different Zones of Dhaka city.

The author also expresses his sincere thanks and indebtedness to Dr. B. C. Basak, Professor and Head, Mr. Md. Nuruzzaman, Professor, Dr. Md. Showkat Osman, Professor, Dr. N. C. Das, Associate Professor, Department of Civil Engineering, BIT Dhaka for their valuable suggestion regarding this research work.

The author is grateful to his family members, colleagues and friends for their co-operation and companionship extended to him during this study.

The author also expresses his sincere thanks to Mr. Abdul Ali for drawing some of the figures contained in this thesis. The author also expresses his sincere thanks to Mr. A. B. M. Abdur Rahman and Mr. Abbasuddin of Environmental Engineering laboratory for their services and support during the course of this research work.

ABSTRACT

The Tannery industries located at Hazaribagh are one of the major polluting industries in Dhaka. The tanning process requires a huge amount of chromium especially in blue green section of the industry. At present wastewater from the tannery industries is discharged through open drains into a wastewater pond/lagoon, which finally flows into the Buriganga River though three outfalls. The stagnant pond area serves to retain the tannery wastewater for prolonged periods of time, allowing dissolved constituents including chromium to percolate into the subsurface and possibly contaminate the aquifer below. The present study aims at assessing the groundwater contamination, particularly chromium contamination, from tannery waste in Dhaka.

Groundwater samples were collected from 21 DTW stations from the six Zones of DWASA, including all seven stations located in Zone 2 covering Hazaribagh area, and analyzed for a wide range of parameters including chromium. Chromium concentrations in the groundwater samples from Zone 2 were found to be significantly higher than those from the other DWASA zones. Speciation data suggest that only a small fraction of chromium is present in Cr(VI) form and majority of dissolved chromium in groundwater is present in less toxic Cr(III) form. Out of the 14 groundwater samples from Zone 2, two exceeded the Bangladesh drinking water standard of 0.05 mg/l. Average chromium concentration in groundwater from the seven tubewells of Zone 2 is about 0.036 mg/l, about ten times higher than the average chromium concentration of 0.004 mg/l in water samples from 14 tubewells from 5 other zones. In the absence of any natural source of chromium and the presence of a large number of tanneries in the Hazaribagh area, it appears that chromium from tannery wastewater is already contaminating the groundwater in and around Hazaribagh area. Concentration of sulfide was also found to be higher in the groundwater samples from Zone 2, which also appears to suggest that the groundwater in the Hazaribagh area is being contaminated by the tannery wastewater. Apart from chromium, alarmingly high lead concentrations, varying from 0.001 to 0.14 mg/l, were also detected in many of the DWASA groundwater samples. Among the 21 samples analyzed, 17 exceeded the WHO guideline value (for drinking water) of 0.01 mg/l and two exceeded the Bangladesh drinking water standard of 0.05 mg/l.

Sediment samples were collected from two boreholes at the effluent discharge area and were analyzed for pH, lead and chromium. Very high accumulation of chromium (reaching close to 15,000 mg/kg of sediment) was detected in the top layer of sediment. The accumulation of chromium appears to be restricted primarily to the first 10 feet of soil. This is probably due to the fact that most of the chromium in the tannery wastewater is present in Cr(III) form and Cr(III) generally is not transported to great distance by groundwater because of its low solubility. However, groundwater with low levels of Cr(III), leached from the heavily contaminated sediments, can still move downward and slowly contaminate the aquifer below. Results from this research work suggest that a huge quantity of chromium has accumulated in the sediment at the effluent discharge area at Hazaribagh, which can potentially contaminate the groundwater aquifer and thus endanger the water supply of the Dhaka city dwellers.

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Chapter 1

INTRODUCTION

1.1 GENERAL

The important industries in Bangladesh include leather tanning, textile, paper and pulp, fertilizer, sugar, steel, oil refining, chemical, pharmaceutical, and other small scale agro-based and agro-allied industries. In terms of waste load generation, the principal polluting industries are paper and pulp, textile (dyeing and printing) and the tanneries. In Dhaka, environmental pollution from tannery industries is a particular concern.

Majority of the tannery industries is located in the Hazaribagh area in Dhaka near the Buriganga River. About 200 tanneries are processing leather in these industries, which account for most of the processed leather in Bangladesh. The tanning process requires a huge amount of chromium especially in blue green section of the industry. A significant fraction of this chromium is discharged along with the effluent from the industry. An estimated 15,800 m^3/day of wastewater with a BOD load of 17600 kg/day and high chromium concentration is discharged from the tannery industries at Hazaribagh (BKH, 1995). Wastewater from tannery industry typically contains chromium, dissolved lime, hydrogen sulfide, dyes, oils, organic matter, and suspended solids. Chromium is a toxic heavy metal and its presence in tannery waste is cause of great concern. Very high chromium concentrations, reaching close to 4000 mg/l, have been detected in tannery wastewater.

After the devastating flood of 1988, a dike was constructed in the flood plain between the Buriganga River and Hazaribagh area. At present wastewater from the tannery industries is discharged through open drains into the stagnant pond that now exists between the dike and Hazaribagh area and finally into the Buriganga River through three outfalls. The stagnant pond area serves to retain the tannery wastewater for prolonged periods of time, allowing dissolved constituents (e.g., chromium) from the wastewater to percolate into the subsurface. Depending on the subsurface geology, hydrogeology and geochemistry, dissolved contaminants such as chromium may eventually reach the aquifer, contaminating the precious groundwater resource. Wastewater containing chromium that is eventually discharged into the Buriganga River pollutes the river water as well and the pollutants may in turn find their way into the aquifer as a result of recharge.

In Dhaka, groundwater is the principal source of water supply. Groundwater is extracted through a network of about 300 deep tubewells (DTWs) and distributed to the city dwellers through a distribution system. Any contamination of groundwater would endanger the entire water supply system in Dhaka. Chromium is a toxic heavy metal and it has significant adverse health effects. The World Health Organization has set a guideline value of 0.05 mg/l for maximum concentration of chromium in drinking water. The Bangladesh standard for chromium is also 0.05 mg/l (GOB, 1997). For a long time, people have been expressing concern about the possibility of groundwater contamination by chromium from tannery waste. In recent years, this topic has attracted considerable media attention. However, there appears to be a lack of data on chromium concentration in groundwater samples and migration of chromium from tannery wastewater into the groundwater aquifer. There appears to be no monitoring of chromium concentration in the groundwater samples from DTWs, particularly those located in the Hazaribagh area. Very limited work has been done to date to determine the state of chromium concentration in the subsurface environment and to develop a better understanding of the processes that may lead to chromium contamination of groundwater. It should be mentioned that chromium can exist in water/wastewater either as Cr(III) or Cr(VI) and Cr(VI) is considerably more toxic than Cr(III). Thus speciation of chromium in groundwater (as well as in the effluent) is very important. But so far there is no data on speciation of chromium in groundwater or in the tannery effluent.

1.2 OBJECTIVES OF THE PRESENT RESEARCH

The overall objective of this study was to evaluate possible groundwater contamination in Dhaka (particularly in Hazaribagh area) by the effluents from the tannery industries located at Hazaribagh. Specific objectives of this research work were:

(i) To determine the concentrations of total chromium, Cr(III), Cr(VI) and a number of other water quality parameters in the DTW water in and around Hazaribagh area, as well as other areas of Dhaka city.

(ii) To determine possible co-relation between chromium concentration and other water quality parameters in the groundwater samples.

(iii) To determine the speciation of chromium in the effluent from tannery industries.

(iv) To determine the concentration of chromium and a number of other parameters (such as pH, salinity, iron) as a function of depth in the sediment samples at different locations at the tannery effluent discharge area.

(v) To determine possible co-relation between chromium concentration and other geo-chemical parameters (e.g., pH, iron content) of soil samples.

(vi) To develop a better understanding of the mobilization process of chromium in the sub-surface environment.

1.3 SCOPE OF THE STUDY

A major objective of this study was to evaluate whether groundwater in Dhaka has already been contaminated by chromium from the untreated tannery wastewater that are discharged in the low-lying area at Hazaribagh. This objective was accomplished through analysis of groundwater samples collected from DWASA deep tubewell pump stations from different zones of Dhaka city, including those at Hazaribagh. The collected groundwater samples were analyzed for chromium and a number of other water quality parameters in order to determine whether the groundwater samples from Hazaribagh area show any sign of contamination from tannery wastewater. No attempt was made to assess chromium concentration in the Buriganga river where the tannery wastewaters are eventually discharged.

Another major objective of this research work was to assess the potential for groundwater contamination from tannery wastewater. For this purpose, wastewater samples were collected from a number of locations in the Hazaribagh area and analyzed for detailed characterization in order to estimate their pollution load. In addition, previous data on tannery wastewater characteristics was also evaluated. Accumulation and downward migration of chromium in the wastewater discharge area at Hazaribagh was evaluated through collection and analysis of borehole sediment samples. The sediment samples were analyzed for total chromium, total lead and pH. These data were then analyzed to assess the groundwater contamination potential of tannery wastewater. Assessment of different chemical forms of chromium in the sediment samples and their relative mobilities, though important, were beyond the scope of this study. Due to lack of geochemical data, no attempt has been made to predict or model movement of chromium in the subsurface environment.

1.4 METHODOLOGY

In order to determine possible contamination of groundwater by tannery wastewater, groundwater samples were collected from 21 DTW pump stations including all seven located in and around Hazaribagh area in DWASA Zone 2 and were analyzed for total chromium, Cr(III), Cr(VI) and a number of other water quality parameters including BOD_5, COD, sulfide, chloride and lead. Data from these analyses were used to assess the characteristics of groundwater in Dhaka and possible contamination of groundwater in and around Hazaribagh by tannery wastewater.

Pollution potential of tannery wastewater was evaluated through careful characterization of tannery wastewater samples from different locations; and also through analysis of available data on tannery effluent characteristics. Accumulation and downward migration of chromium in the sediments at the tannery effluent discharge area at Hazaribagh were evaluated through collection and analysis of borehole sediment samples, as well as groundwater samples from the boreholes. For this purpose two boreholes, each upto a depth of about 100 feet, was constructed at the effluent discharge area at Hazaribagh. The sediment samples were analyzed for total chromium, lead and pH. Groundwater samples were collected from three different depths of the boreholes and were analyzed for total chromium and a number of other water quality parameters.

Dáta generated through these laboratory investigations were then analyzed to assess the groundwater contamination potential of tannery wastewater. In order to compare the characteristics of sediment samples from Hazaribagh effluent discharge area and that from an uncontaminated area, bore hole samples were also collected from the premises of Janata Housing Ltd. located at Shar-E-Bangla Nagar, Dhaka.

Total chromium and lManganeead concentrations were determined using an Atomic Absorption Spectrophotometer (Shimadzu Mode AA680). Concentration of chromium (VI) was measured following the 1,5-Diphenylcarbohydrazide Method using a spectrophotometer (HACH, DR4000U). Chromium (III) concentration was calculated by subtraction from total chromium concentration. Manganese concentration was measured using the PAN method with a spectrophotometer (HACH, DR4000U), and iron concentration was measured using the thiocyanate colorimetric method. Arsenic concentration was determined using the Silver-diethyl-dithiocarbamate method (AWWA, 1985); absorbance was measured using a spectrophotometer (HACH, DR/EL4). Color, ammonium, nitrate, fluoride, sulfate, sulfide, and phosphate concentrations were determined with a spectrophotometer (HACH, DR4000U). Ammonium was determined using Nessler method, nitrate by the cadmium reduction method, and phosphate by the molybdenum blue method. Chloride, alkalinity, hardness, carbon-di-oxide, and total and dissolved solids were determined by volumetric methods following Standard Methods (AWWA, 2000). The pH was measured using a pH meter (HACH), conductivity was measured using a conductivity meter, and turbidity was measured using a standard turbidity meter.

1.5 ORGANIZATION OF THE THESIS

Apart from this chapter, the remainder of the thesis has been divided into four chapters. Chapter 2 titled "Literature Review" presents an overview of the tannery industry in Bangladesh. The processes used and the types of wastewater generated have been described. This chapter also provides an overview of the occurrence of chromium in the environment including its health effects and its chemistry and mobilization in water and soil environments.

Chapter 3 titled "Water Quality of Dhaka City", provides detailed characterization of groundwater extracted by DWASA deep tubewells. This Chapter also provides a brief description of water supply services in Dhaka City provided by the DWASA. Groundwater samples from 21 deep tubewell pump stations (including all seven stations located in the Hazaribagh area) belonging to the six DWASA Zones have been analyzed. These results have been analyzed to assess possible contamination of groundwater in Dhaka by tannery wastewater.

Chapter 4 titled "Sediment and Groundwater Contamination by Tannery Effluents" provides detailed characterization of wastewater from the tannery industries located at Hazaribagh. Characteristics of sediment samples from two boreholes constructed at the wastewater discharge site at Hazaribagh have been presented in this Chapter. In addition characteristics of groundwater samples collected from the boreholes have been presented. The results of these laboratory tests have been analyzed to assess the potential for groundwater contamination by the tannery wastewater in Hazaribagh area.

Finally, Chapter 5 presents major conclusions of the study and also provides recommendations for future study.

Chapter 2

LITERATURE REVIEW

2.1 INTRODUCTION

The primary objective of this research work is to assess possible groundwater contamination in Dhaka from effluents of tannery industries located at Hazaribagh. Among the various contaminants present in the tannery effluent, chromium is of primary concern, especially from the point of view of groundwater contamination. This chapter provides an overview of the tannery industry in Bangladesh. The processes used and the types of wastewater generated have been described. Since chromium in tannery wastewater is of prime concern, this chapter provides an overview of the occurrence of chromium in the environment including its health effects and its chemistry and mobilization in water and soil environments.

2.2 TANNERY INDUSTRIES IN BANGLADESH

The migration of leather tanning activity from developed to developing countries over the past four decades has helped the leather industry in Bangladesh register an impressive growth rate in the last two decades. Being an exporter of wet blue in the seventies, Bangladesh now exports crust and finished leathers and leather products. Currently, leather industry is the fourth largest foreign exchange earner for the country. Special attention is given to development of infrastructure aimed at modernization and self-sustenance and for maximizing the foreign exchange earning potential of the Bangladesh Leather Industry.

Before the birth of Bangladesh in 1971, the leather industry in the erstwhile East Pakistan consisted of only about 35 medium-to-large and 25 cottage-to-small-scale tanneries and they were mainly engaged in the production of wet blue for export. The cottage and small-scale units were also making some kind of low-grade finished leathers for domestic consumption. With the emergence of Bangladesh in 1971, the non-Bengali tanners disappeared as a result of which the leather making activity in the country came to a virtual stand still. The Government came to the rescue and formed Tanneries Corporation under which all the existing tanneries were nationalized. Later on, the nationalized tanneries were disinvested to private entrepreneurs during the late seventies and early eighties.

Wet blue remained the main exported commodity until the Government imposed an export duty on wet blue in 1977-78. To encourage the export of crust and finished leather, Government introduced in 1980-81 many incentives in the form of duty drawback, export performance benefit, income tax holiday including reduced import duty on leather machinery. Further, to promote rapid development of leather sector, Government imposed a ban on export of wet blue leather in 1990. Simultaneously, efforts were initiated by the Government for modernizing the leather industry through up gradation of infrastructure for making finished leather through BMRE (Balancing, Modernization, Rehabilitation and Expansion) and offering fiscal and non-fiscal assistance. This has really enabled many units to upgrade their leather processing facility and for the installation of modern machinery for the production of crust and finished leather of international quality.

In early nineties, some firms have taken the step in the right direction and ventured into producing some types of leather goods like wallets, belts, ladies' hand bags and gloves and started exporting them in a limited way. In the middle of nineties, leather shoe manufacturing with modern machinery began export of quality shoes.

Leather industry is one of the leading export earning sectors of the country. Export earning of the sector was US$ 233.75 million in 1997-98 and the main importers were countries in European Union, USA, Japan, Taiwan, Korea, Brazil, Australia, Hong Kong, Mexico, China, Russia, India, Singapore, Malaysia, South Africa etc. The leather sector provides direct employment to about 50,000 people.

Bangladesh being a beef consuming agricultural country has a sizable livestock population and hence assured supply of hides and skins to sustain the leather industry in the country. The main raw materials are cowhides and goatskins. Only about 20% of the leathers are consumed locally and large surplus is exported in the form of crust and finished leathers and leathers and leather products. The export performance of the leather industry during 1990-97 has been shown in Table 2.1.

Table 2.1 Export of Leather and Leather Products (1990-91 TO 1997-98, in Million US Dollars)

Year	Leather	Leather bags and purse	Leather Footwear	Total
1990-91	131.29	--	--	137.13
1991-92	144.46	--	--	148.85
193-94	168.17	4.33	14.94	187.14
1994-95	202.08	6.33	12.54	220.95
1995-96	211.70	6.96	19.13	237.79
1996-97	195.26	3.81	17.78	216.85
1997-98	190.26	5.47	38.02	233.75

Source: Export Promotion Bureau of Bangladesh (1999)

Hides and skins available in Bangladesh, though smaller in size and thinner in substance, enjoy a good demand in the international market for their fine fiber structure and good grain pattern. The leathers produced from them are used mainly for making high quality leather shoes and other goods. Kushtia and Dhaka Goat skins are well known in leather world for their fiber structure and unique grain pattern and are considered the ideal material for the famous glace kid leathers. Apart from goatskins and cowhides, small quantities of sheep skins and buffalo hides are also processed by the Bangladesh leather industry.

About 30 units are well equipped for processing crust and finished leather and their total processing capacity is about 85.5 million square feet. Though the Bangladesh leather industry enjoys sufficient capacity to produce good quality crust leather, capacity to produce export quality finished leather are still to be improved. It is to be noted that only 3 or 4 tanneries are exporting finished leather on a regular basis. There exists a need to increase the range of finished leather made in the country to make a greater impact in the global leather market.

Many of the chemicals needed for leather processing are imported from other countries and there are many multinational companies offering their entire range of chemicals/auxiliaries. These companies act as the main source of technologies for the processing of crust and finished leathers.

The development of leather product industry has been given due importance in the last couple of years. The leather goods industry has registered satisfactory progress in recent years and is expected to make greater contribution to foreign exchange earning capacity of the leather sector in the years to come. Some firms mainly catering to developed countries produce high quality leather jackets. Leather footwear industry came into being with the setting up of a few modern shoe units in the middle of this decade. Now, there are approximately 15 export oriented shoe manufacturing units located in and around Dhaka City and these units are making men's and ladies' shoes, shoe uppers, moccasins etc. There are many small footwear units spread all over the country catering to domestic market.

2.3 PROCESSES AND CHEMICALS USED IN TANNERY INDUSTRIES

Tanning of hides and skins to convert them into "leather" has been an important industrial activity since antiquity. In the case of tannery industry the main concern of pollution is due to the excessive use of chemicals, use of inefficient and old technology for the manufacturing processes, the excessive generation of waste, difficulty in treating the waste and overuse of scare resources. This section mainly focuses on the common processes of leather production, alternatives and options with respect to environmental implications, water and energy consumption, process efficiencies, etc. This section has been compiled mainly from DOE (1992).

2.3.1 The Tanning Process

Tanning consists of transforming animal hides and skins into leather. The hides, after removal of flesh and fat, are treated with chemicals, which cross-link the microscopic collagen fibers to form a stable, durable material. The chemicals used in the process may be natural-extract from vegetable matter or may be produced synthetically. The overall tanning operation mainly involves trimming, dying, buffing, surface coating and a number of others operations.

There is no single process for the production of leather. Different option and unit operations are being used depending on the various factors such as final product, national and international market demand, economic situation and trade policy and availability of the latest technology. Accordingly different wastes are generated and as such treatment and reuse/recycle options of the generated waste also vary.

The following section describes the structure of the skin of hides to be tanned, as well conservation of hides and the major stages of the tanning process, with a view to identifying the significant chemical inputs and waste outputs.

Structure of Skin

The skin is divided into three layers: epidermis, dermis and flesh. The "epidermis" located on the grain side has different layers of cells. Keratin, a protein containing many sulphides is the main element of this layer. The epidermis is insoluble in water, organic solvents, diluted acids and bases but can be easily dissolved in concentrated basic solutions or concentrated reducing solutions. "Dermis", the thicker layer that consists of a great number of collagen fibers and some of elastic fibers, is called the dermis part of the skin. It has two areas, the grain side and the flesh side. Elastic fibers are scattered and dispersed and the collagen fibers are close together. The elastic fibers are easily dissolved in trypsin-an enzyme and insoluble in water, acid or alkali diluted cold solutions. The "flesh" consists of fibers and is very fatty. It has no pronounced barrier with dermis layer.

Conservation/Curing of Hides and Skins

The skin tends to putrefy after the animal as been killed. As the tanneries are often far from the slaughterhouses and also hides are collected from all parts of the country, the skins and hides have to be conserved or cured before they are taken up to the tannery industry for the leather production. Conservation is usually done by refrigeration. The curing operation is done by the following two methods.

Curing by salt: In this method, first a layer of hides is spread out and packed by the flesh side up and covered with a layer of salt. Then another layer of hides is spread and covered by a layer of salt. This process is continued until a considerable stack height is obtained. Over the top of this stack a heavy layer of salt is spread. Through osmosis process the salt dissolves in all the hides thus reducing the moisture content of the hide preventing it from putrefaction. Skins stay in a stack for approximately one month.

Curing by brine solution: The fresh hides are agitated in a saturated solution of brine until the expected amount of moisture within the hide is replaced y the salt solution. They are then removed from the brine solution, drained and packed for shipment. Solid salt is usually sprinkled before the shipment. The amount of salt transported through hides is the same in both the processes.

2.3.2 Tanning Operations

For different type of animal hides (cowhides, sheep and goad skins) the tanning operations applied such as concentration time, temperature, chemicals, pH etc. are different. A brief step-by-step description for the most representative manufacturing processes i.e., cowhides and sheepskins is given below: Table 2.2 represents the schematic overview of the tanning process.

2.3.2.1 Beamhouse Process

The beamhouse process prepares the skin for the tanning operation. At this stage the hide is prepared for tanning by cleaning and conditioning, and by ensuring the correct moisture content. The hair, epidermis, inter-fiber proteins, and flesh are eliminated at this stage. Collagen and elastic fibers, which are the basis of leather, are treated to improve their reactivity towards tanning agents. The steps, which comprise the beamhouse operation, are the following:

A. Soaking: Hides must regain their original moisture. At this step hides are placed in special containers named paddle-vats or vats filled with water, from a few hours to one day to re-hydrate the skin and reverse the cure process. In the process, dirt, salt and blood are removed from the hides.

***B. Unhairing*:** In this step, after soaking, the hides are placed in an alkali bath composed of lime, sodium sulfide and sodium sulphydrate. The reaction is left to work for half a day. The process is traditionally used to loosen wool and hair, or dissolve these into pulp. The epidermis is eliminated by a chemical attack of the keratin.

Additionally the process opens the fiber structure and 'plumps' the hide. This process is responsible for the major part of the COD load from a tannery. Limed hides (pelts) are fleshed by mechanically removing the adipose tissue from the flesh side of the hide. In some cases fleshing is carried out immediately after soaking called green fleshing.

***C. Liming*:** At this step hides are split in the limed condition, allowing the subsequent processing to be rapid and economical. The main purpose of this stage is to make the hide swell to make the fiber releasing process easier. The hides are soaked in a slurry bath for about 24 hours. At this stage, hides are called limed hides.

***D. Deliming*:** Limed hides are full of alkali reactive reagents. For proper and efficient tanning process the pH should have a neutral value. At this step the hides are first thoroughly washed and neutralized with chemicals. For the washing enormous quantity of water is required. At this step, in most of the cases, the water valve is left open for set of period without accounting of the actual volume of water used. The major chemicals used in this step are 0.5-0.2% acids such as sulfuric, hydrochloric, lactic, formic, boric and mixtures, acidic salts, ammonium chloride or sulfate, hydrogen peroxide. In a rotating drum the total operation takes place for one hour with the subsequent washing with water.

***E. Bating*:** To have an effect on the grain of the pelt, and on the general run, and on the stretch of subsequent leathers, some strong chemicals - enzymes are used. They operate under narrow physical - chemical condition. The process is called enzymatic process. This operation finishes the elimination of the residues. The bating process time is 30 minutes to 12 hours. The hides are rinsed and cooled. The bating material is typically composed of 50% wood flour or other carrier, 30% deliming agent (ammonium chloride), 1-5% pancreatic enzyme.

***F. Pickling*:** The adjustment of the pH of the pelts is the final beamhouse operation. In this step the skins are sterilized, ending the bating action, and improving the penetration of the subsequent tanning material. A number of organic and inorganic chemicals are used in this step. To bring the hides to an acidic condition they are immersed in a brine and acid solution. The brine solution is added to prevent the hides from swelling. The process takes about three hours. At this stage, unless it is a special hide (e.g. sheep skin), the hide is ready for the tanning.

*G. **Degreasing***: The process to improve the quality of the final leather is the degreasing of the hides. The step is also necessary for the sheepskins where the wool needs to be recovered. Solvent recovery process is usually used for the degreasing. Organic solvents are used for the degreasing.

2.3.2.2 Tanning

The process to stabilize the collagen structure of the hide by blocking the reactive functions, using natural or synthetic chemicals is called tanning. Also tanning imparts a particular 'feel' to the resulting leather. For hide tanning a number of chemicals are available, but chrome being the most commonly used.

A number of tanning processes are available that can be used alone, or in combination with each other. In the tanning process no direct solid wastes are generated but since only a part of the chemicals is taken up by the hide, acidic effluents containing unused chemicals will be generated. Subsequent washings of the hides will generate the unfixed chemicals from the hides. Treatment of the effluents in this operation will generate sludge, which may create secondary form of pollution.

*A. **Chrome Tanning***: Majority of the tanning process presently uses the chrome tanning. This is done by immersion of the hides in a bath containing chromium salts and brine and a number of other chemicals. The equipment used is a drum. The process of the rotation of the drum takes about 4-24 hours.

*B. **Vegetable Tanning***: For the production of some special leather and for sole and saddlery the tanning process used is called 'Vegetable Tanning". Substance used for this type of tanning are typically 15-30% of commercial tanning extract (bark or wood of tree, aqueous extract), often sulfated, then spray dried and concentrated. Vegetable tanning is also used in combination with chrome tanning.

C. Syntans: Syntans are used in combination with chrome and vegetable tannins, either to re-tannage or as a principal tanning agents for certain special leathers. Sulphonated products of phenol, cresol, and naphthalene are generally used.

2.3.2.3 Post Tanning Activities

The hide after the tanning operation is called the 'Wet Blue' leather, which has a blue color due to the chrome salts. The wet blue hides are classified according to the thickens, surface smoothness, appearance, presence of scars etc. The steps of the operations are as follows:

A. Sammying: To remove the excess moisture, the tanned leathers are treated by pressurized rollers. In this operation the residual tanning solutions are also removed.

B. Splitting: To have a constant thickness on the external grain side and variable thickness on the internal flesh side, the tanned hide is split with a special machine.

C. Shaving: The process to adjust the thickness with more precision using a plane after the splitting operation is called the shaving. In this operation the tanned hide is leveled, the surplus material yielding a waste of small fragments.

D. Currying: The process is called the 'Post-tanning Wet Work'. Here the main operations are retan, dyeing, and fat-liqoring. The operations here taking place one after the other in a drum. Those operations are needed to stabilize further the collagen network of the tanned leather, which imparts further tannage with the combinations of chrome, vegetable, glutarldehyde or syntan agent. The purpose of those operations are:

- to give special characteristics such as perspiration resistance to the hide;
- to bring the hide to a neutral level by eliminating residual tannin agents ;
- to dye the fibers with synthetic or natural dyes ;
- to adjust the quality of the fibers of the hide such as solidity, elasticity, density,
- swelling and how their connections are fixed in the hide.
- to make the leather pliable by lubricating ;
- to make leather soft.

Few solid wastes are produced, and the aqueous effluents do not generally contribute significantly to the overall load of pollutants from the tannery.

Table 2.2 Represents the Schematic Overview of the Tanning Process

Raw Cow / Buff hides / Goat skins

Chemical	%	Process	Parameter	*ppm*	EL. kg/t
Water	500	Pre Soaking Drum	BOD	412	2.06
			COD	1011	5.06
			TDS	10800	54
			TSS	1810	9.05
			TS	12610	63.05
			CO	6403	32.02
			SO_4	84	0.42
Water	500	Main Soaking Drum	BOD	5625	28.13
Preservative	0.1-0.15		COD	16757	83.79
Wetting Agent	05		TDS	38450	192.25
Soda Ash	0.25		TSS	5080	25.40
			TS	43530	217.65
			CO	20396	101.02
			SO_4	156	0.78
Water	500	Washing Drum			
Water	450	Liming Drum	BOD	15825	71.21
Sod. Sulfide	3.5		COD	31156	140.20
Lime	3-5		TDS	27770	124.97
Liming Auxiliary	1-2		TSS	16130	72.59
			TS	43900	197.55
			CO	3166	14.25
			Sul	3600	16.20
			SO_4	232	1.04
Water	300	Washing Drum			
Water	125	Fleshing Machine			

Contd.

Cont'd

Chemical	%	Process	Output
		Lime * Splitting M/c	*Split*
Water	300	Washing Drum	
Water	50	Deliming Drum	see effluent data
Amm. Sulfate	2-3		
Sod. Metabisulfite	0.5-1		
Bating Agent	0.5-1		
Wetting Agent	0.3		
Water	500	Washing Drum	
Water	80	Pickling Drum	see effluent data
Salt	8-10		
Formic Acid	0.25-0.5		
Sulfuric Acid	1-1.5		
Full Pickle Bath	80	Cr-Tanning Machine	see effluent data
Water	100		
BCS	8		
Tanbase (Hodgson)	0.3-0.4		
Preservative	0.05-0.1		
Water	150	Washing Drum	
Wetting Agent	0.1		
Water	250	Acid Wash Drum	
Formic/Acetic Acid	0.25-0.5		

Contd.

Deliming Drum effluent:

	ppm	EL. kg/t
BOD	5250	2.63
COD	10203	5.40
TDS	20970	10.49
TSS	4690	2.35
TS	25660	12.83
Sul	435	0.22
SO_4	8137	4.07
N	2050	1.03

Pickling Drum effluent:

	ppm	EL. kg/t
BOD	990	0.79
COD	3099	20.48
TDS	53540	42.83
TSS	1755	1.40
TS	55295	44.24
Cl	25020	20.02
SO_4	86378	6.91

Cr-Tanning Machine effluent:

	ppm	EL. kg/t
BOD	544	0.98
COD	5572	10.03
TDS	89240	160.63
TSS	2240	4.03
TS	91480	164.66
Cl	25218	45.39
Cr	3861	6.95
SO_4	23462	42.23

Cont'd

Chemical	%	Process		ppm	EL. kg/t
Water	250	Rechroming Drum	BOD	581	1.45
Chrome	6		COD	5221	13.05
(Chromosol B)	1		TDS	13685	34.21
Sod. Formate	1		TSS	1095	2.74
Sod. Bicarbonate			TS	4780	36.95
			Cl	1304	3.26
			Cr	1248	3.12
			SO_4	5815	14.54
Water	400	Washing Drum			
Water		Neutralisation Drum	BOD	620	1.55
Neutralising Syntan			COD	2442	6.11
Sod. Formate			TDS	10270	25.68
Sod. Bicarbonate			TSS	960	2.40
			TS	11230	28.08
			Cl	632	1.58
			Cr	338	0.85
			SO_4	2861	7.15

Composition

Chemical	%	Process		ppm	EL. kg/t
Water	400	Washing Drum	BOD	1531	80.84
			COD	3671	193.83
			TDS	9098	480.37
			TSS	1637	86.43
Water	400	Washing Drum	TS	10735	566.81
			Cl	280	152.06
			Sul	206	10.88
			Cr	158	8.34
			SO_4	1323	69.85
			N	62	3.27
Water	225	Retanning & Fatliquoring Machine	BOD	2025	4.56
Acrylic resin	2-3		COD	505	10.14
Syntan. Phenolic	5-8		TDS	3490	7.85
Syntan. Metamine	4-6		TSS	760	1.71
Mimosa	4-16		TS	4250	9.56
Dye	2-3		Cl	435	0.98
Fatliquor (mixture)	10-20		SO_4	152	3.47
Formic Acid	1				
Water	350	Rinse Drum			
Water	200	Top Dyeing (optional) Drum			

Leather

2.3.2.4 Drying and Finishing

The operation for definitive commercial look to the leather is called the drying tanned finishing. The operation includes drying, buffing and finishing.

A. Drying: The purpose of this step is remove moisture. The process is carried out by vaporization.

B. Buffing: This operation is carried out by the action of abrasive papers installed on rolls.

C. Finishing: The final finishing process includes mechanical treatment of grain and flesh followed y application of surface finish. The surface coatings consist of dyes of pigments dispersed in a binder, typically casin or an acrylic or polyurethane polymer. It also presents the main waste steams resulting from the different steps in tanning as will discussed in the next section.

2.4 WASTEWATER FROM TANNERY INDUSTRY

Tanning operations require a large volume of water mainly for washing after each of the steps. The average volume of water required for the processing of one ton of hide is about 50 m^3 (WHO, 1982). This water is discharged as liquid effluents by the tannery industries. Table 2.3 shows the distribution of the pollution parameter from the different steps of leather production process.

Table 2.3 Percent distribution of pollution load at different step of leather Processing per Ton of Hide Processed (Source: DOE, 1992)

Parameters	Total in Effluent	Soaking	Liming	Deliming Bating	Pickling Tanning	Subsequent Operations
BOD_5	75-90 kg/t (100%)	7.5-9.0 kg/t (10%)	52-63 kg/t (70%)	2.5 kg/t (3%)	1 kg/t (1.2%)	1.5-14.5 kg/t (15%)
COD (%)	220-200 kg/t (100%)	30-33 kg/t (15%)	110-120 kg/t (55%)	6 kg/t (3%)	2 kg/t (1%)	50-58 kg/t (25%)
Oxidisable matter (%)	110-130 kg/t (100%)	30-33 kg/t (13%)	7-82 (64%)	--	--	14-17 kg/t (23%)
Suspended Solids (%)	140 kg/t (100%)	7 kg/t (5%)	77 kg/t (55%)	--	--	56 kg/t (40%)
Salinity (%)	230-350 kg/t (100%)	150-210 kg/t (60%)	--	20-3 kg/t (8%)	60-90 kg/t (25%)	17-25 kg/t (7%)
Toxicity	2.5 k Eq/t (100%)	--	1.9 k Eq/t (76%)	--	0.6 k Eq/t (24%)	--

The above table shows that soaking is the main source of salinity (60%), while liming is responsible for half of the total pollution. For the tanning of one ton of hide, about 60 to 90 kg of various salt are required and the input of chromium salt is 25 kg. In total 20 to 25% of chromium salts will remain unused and is discharged with the effluent.

2.5 ENVIRONMENTAL IMPACT OF TANNERY INDUSTRIES

Reviewing the waste streams described in the previous sections it is evident that tannery waste can cause severe damage not only to human beings but to the environment and ecology, if the waste is discharged without any treatment. The tannery industries discharge their total emission to the surrounding environment including the river Buriganga, nearby land and in the surrounding air without any treatment or taking any preventive measure to abate or reduce the adverse effects. The waste streams of all the tanneries have a significant contribution to the destruction of the environment around Hazaribagh. The following section describes the adverse environmental effects of tannery waste.

Effect on Surface Water

The wet land and surface water bodies on the south-west, west and west-north of the tannery industrial area at Hazaribagh are already polluted and has been turned into tannery waste lagoon, and is unacceptable for any kind of use. The wastewater from the lagoon was collected during a survey by the DOE and analyzed in the DOE laboratory. High level of pollution load detected in the wastewater samples from the lagoon. The most important surface water body outside the embankment is the river Buriganga. The regular monitoring results of the DOE proved that the river is highly polluted. And the chromium concentration at the drinking water intake point is also alarming. An investigation was conducted to assess the effects of tannery waste on the dissolve oxygen (DO) of the river. The DO found was 0.15-3.00 mg/l, which is far below the BEQS 6 mg/l (DOE, 1992).

Effects on Land

In the tannery industrial area at Hazaribagh, the soil on both sides of the flood protection embankment is highly contaminated with tannery waste. The soil has significantly increased concentration of different organic and inorganic pollutants and heavy metals

(DOE, 1992). Chloride concentration is very high. There is also increased concentrations nitrogen, NH_4-N, NH_3-N, Phosphorus and Sulfur on the surface of soil (DOE, 1992). Even at a depth of 1.2 meter accumulation of nitrogen was found. It was also found that the tannery industries are not only discharging chromium as heavy metal, which is inherent to the tanning process, but significant amounts of Zn, Mn, Cu and Pb as well. The concentration of chromium found in the Hazaribagh soil is 2942 ppm (DOE, 1992). More or less uniform chromium distribution within the soil profile down to 1.2 meter was found and it can be concluded the tannery waste has severely contaminated of soils with chromium. Other heavy metals such as Zn, Cu and Pb have also been found at high concentrations. Phenols, hydrocarbons, available N (NH_4^+, NO_3), Chloride, SO_4, TOC (Total Organic Carbon) and EC have also been found exceeding critical limits in soils for agricultural production and general use (Nuruzzaman,1995).

Effects on Groundwater

According to Bangladesh EQS, the standard for chromium in the ground water is .05 mg/l. A survey conducted by DOE, found the concentration of chromium in groundwater in DWASA water in and around Hazaribagh area between 0.02 - 0.04 mg/l (DOE, 1993-94). Although the groundwater pollution by chromium still has not exceeded the EQS, but it is very close to the limit and the situation is very alarming.

Effect on Air Quality

Biological decomposition of organic materials as well as sulfide emissions from wastewater, are responsible for the characteristics objectionable odors from the tanneries and their wastes. The following are important sources of odors:

- sulfide emissions from de-hair and waste treatment;
- ammonia emissions from deliming ; and
- fleshing

Effects on Human Health

A study about the prevailing health problems of the workers of tannery industries found that, continuous handling of chemicals cause cumulative effect in the human body. The study (Ali, 1994) found that, clinical manifestations similar to chromium toxicity like abdominal discomfort/gastritis, skin ulcer, dermatitis, nausea, ulcer/loss of smell, erosion and discoloration of teeth and asthma were found among the people who worked in the tannery industry and also those who lived in and around the tannery industrial area for more that 10 years.

Effect on Vegetation and Structure

Hazaribagh is a densely populated area with a lot of residential holdings. There are homestead gardens and residential holdings where seasonal vegetables are grown besides permanent plantation. It was gathered from the inhabitants of the area that decades ago the quality and quantity of fruits, vegetables etc. grown in the homestead gardens were much higher compared to the present condition. According to the inhabitants, this deterioration has taken place gradually and at present many of the fruit plants do not bear any fruit at all. It is important to ascertain whether the vegetables grown here contain any constituents, which are harmful for human health. During a visit to the Hazaribagh area, the leaves of some of the trees were observed to be yellowish and some of the rooftop CI sheets were found to be rusted. Some buildings located close to the tanneries were found to have blue stains on them.

2.6 OCCURRENCE OF CHROMIUM

2.6.1 Chromium in Aquatic System

The chemical pollutants in aquatic environment are characterized by (i) longitudinal variations in suspended solids, colloidal particles, and natural and synthetic ligands and (ii) variations in redox conditions, degree of mixing, and densities of living organisms. The fate of metal in natural waters is heavily depended upon these variables. Transformations such as methylation and reduction to the metallic form constitute effects of the environment on metals. Similarly, downward movement of metals to the bottom of natural water bodies results from scavenging by suspended solids and concomitant sedimentation. Organic ligands (natural/synthetic) and chlorides complex metals, reducing the sorption process and increasing residence time in water. In essence, speciation of metals is determined by the aquatic environment, and changes in speciation are responses to alterations. Distribution and transport of metals in aquatic environment are primarily controlled by the sediment and the water column, respectively. Mobilization of metals, or lack of it, from bed sediments depends upon the physical texture and chemical nature of sediments, which in turn determine the amount and strength of metal binding (Moore, 1984)

Because of the low solubility of chromium generally, the levels found in water are usually low (9.7 μg/L) (NRC 1974). However, there are examples of contamination or water, in some cases serious, in which effluents containing chromium compounds have been discharged to rivers. The chromium may be in the trivalent or hexavalent form, either as a soluble salt or as insoluble particles and often as a chemical complex. The valency of the chemical form in natural waters is influenced by the acidity of the water. Trivalent chromium is converted to the insoluble hydroxide at neutral pH (NRC 1977). Total chromium levels in raw water are usually 10 μg/L or less; rarely do levels exceed 25 μg/L except in highly contaminated situations (Towill, 1978). There is a tendency for the naturally occurring higher levels of chromium to be associated with waters of high hardness (CEC 1979).

2.6.2 Chromium in Soils and Bed Sediments

Soils generally have a considerable capacity to retain heavy metals. The retention of added heavy metals to soils is often well correlated with soil organic matter. The organic component of the soil constituents has a high affinity for heavy metals because of the presence of ligands or carboxyl, phenolic, alcoholic and carbonyl groups which can from chelates with these metals. The formation of organic complexes with divalent metal ions is of considerable environmental importance as it may render them relatively unavailable to plants and to subsequent leaching (Merrington, 1996)
Most rocks and soils contain small amounts of chromium. The most common ore is chromite in which the metal exists in the trivalent from. The ore is present in commercial quantities only in a few countries. Hexavalent chromium also exists naturally but infrequently. Chromium in its naturally occurring state is in a highly insoluble form. However, weathering, oxidation and bacterial action can convert it into a slightly more soluble form. Most of the more soluble forms in soil, especially any hexavalent chromium, are mainly the result of contamination by industrial emissions (WHO, 1984)

2.7 TOXICITY OF CHROMIUM

Chromium is not acutely toxic to humans. This is due to the high stability of natural chromium complexes in abiotic matrices. In addition, the hard acid nature of chromium imparts strong affinity for oxygen donors rather than sulfur donors present in bio-molecules. However, Cr (+6) is more toxic than Cr (+3) because of its high rate of adsorption through intestinal tracts. In the natural environment, Cr (+6) is likely to be reduced to Cr (+3), thereby reducing the toxic impact of chromium discharges.

Chromium and dichromate were frame shift mutagens in the *Salmonella* plate incorporation test, through trivalent chromium did not cause an increase in reversion frequency (Lofroth and Ames, 1978). It appears, based on experimental evidence, that hexavalent chromium also has mutagenic properties. Although the case for trivalent chromium is not as strong, its mutagenicity must be considered a possibility.

Epidemiological studies have shown a positive relationship between occupational exposure to chromates and cancer incidence (Sittig, 1980). Risk of lung cancer appears greatest among ferrochromium, chromate and chrome pigment workers. Slightly soluble hexavalent chromium salts, specifically calcium chromate, are the most potent carcinogens. These compounds have induced high levels of chromosomal aberrations in cultures of mammalian cells.

Hexavalent chromium at 10 mg/kg of body weight will result in liver necrosis nephritis, and death in man; lower doses will cause irritation of the gastrointestinal mucosa. Hexavalent chromium has been implicated as the cause of digestive tract cancers in man and there is firm evidence that there is an increased risk of lung cancer for workers who are exposed to high levels of chromium. Exposure to a mixture of chromium (VI) compounds of different solubility (astound in the chromate production industry) carries the greatest risk of human beings.

2.7.1 Health Aspects Of Chromium

Chromium appears to be necessary for glucose and lipid metabolism and for utilization of amino acids in several systems. It also appears to be important in the prevention of mild diabetes and arteriosclerosis in humans (Towill, 1978). The harmful effects of waterborne chromium in man are associated with hexavalent chromium; trivalent chromium, which is regarded as a form of chromium essential to man, is considered practically non-toxic and no local or systemic effects appear to have been reported. People living in areas of the world where arteriosclerosis is virtually absent tend to have higher chromium levels in tissues than people from areas where the disease is endemic (Schroeder, 1968).

Hexavalent chromium at 10 mg/kg of body weight will result in liver cero sis, nephritis, and death in man; lower doses will cause irritation of the gastrointestinal mucosa (Kaufmam, 1970). Hexavalent chromium has been implicated as the cause of digestive tract cancers in man, and there is firm evidence that there is an increased risk of lung cancer for workers who are exposed to high levels of chromium (CEC 1979). Exposure to a mixture of chromium (VI) compounds of different solubilities (astound in the chromate production industry) carries the greatest risk of human beings.

2.8 FATE OF CHORMIUM IN WATER AND SOIL

2.8.1 General

Chromium ($[Kr]4s^1 3d^5$) is a first-series transition element from group VIB. In its elemental from, it is a white, hard, lustrous, and brittle metal with a fairly high melting point (approximating 2000 ^{0}C). It can exist in oxidation states ranging from -2 to +6, but only the 0, +2, +3 and +6 forms are commonly encountered. The critical chemistry of chromium in respect to plant accumulation from the environment revolve around the reduction of Cr(VI) to Cr(III), the oxidation of Cr(III) to Cr(VI) and the relative stability of Cr(III) compounds once formed.

In acid solution Cr^{2+} (chromous), Cr^{3+} (chromic), and $Cr^2O_7^{-2}$ (dichromate) are representative and in basic solution $Cr(OH)_2$, CrO_2, CrO_2^{-1} (chromite), and CrO_4^{-2} (chromate) are representative. The chromous ion is rapidly oxidized to Cr(III) by air and slowly by H^+. In its highest oxidation state chromium forms exclusively oxy-compounds and all are potent oxidizing agents.

2.8.2 Soil Chromium Chemistry

The naturally occurring concentration of chromium in soil depends on the chromium concentration of the parent material. Chromium will generally be present in the trivalent oxidation state but can also exist in the hexavalent oxidation state. This oxidation state is fairly stable in low organic matter soils and is water-soluble. Movement of chromium through soil is dependent on soil texture, pH, and organic matter type and content. Most trivalent chromium added to soils is quickly immobilized, but small quantities can be oxidized. Hexavalent chromium added to soils may be reduced or absorbed or may remain in solution depending on the organic matter content, pH, and texture of the soil. Chromium will be more available to plants growing in a neutral to basic soil than in an acidic soil. This is probably due to the mobility of Cr(VI).

Figure 2.1 shows chromium cycle in soil and water. Like any circle, this cycle has no beginning and no ending. A logical starting place might be Cr(VI), the thermodynamically stable chromium form in a system in equilibrium with the air. But we know that in real soils, Cr(VI) is the least stable form, and this tells us something about soils. The $HCrO_4^-$ anion can temporarily depart from the cycle by being adsorbed or precipitated, leached into streams or groundwater, or taken up by living organisms. Eventually the sidetracked chromium should find its way back to the circle, probably in a reduced form.

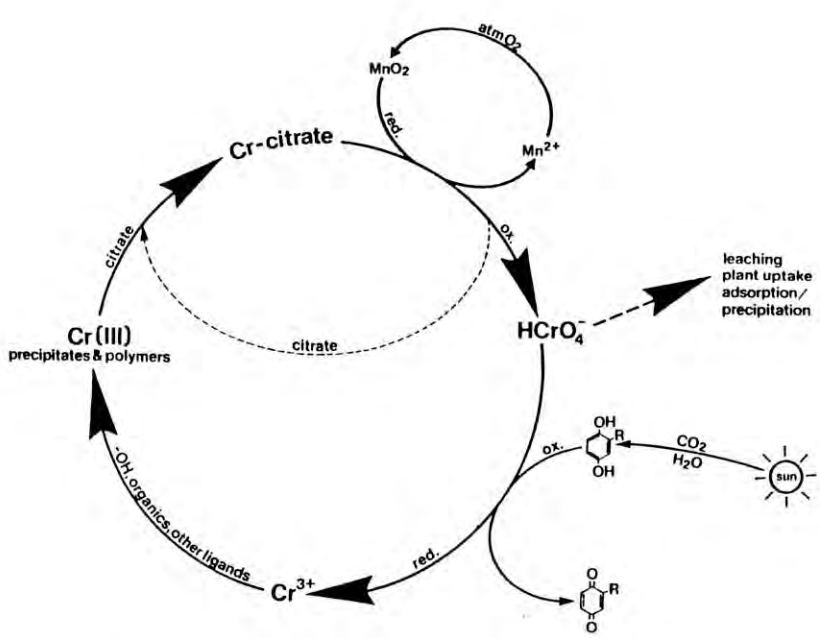

Figure 2.1 The Chromium Cycle in Soils and Water

The next steps is "dechromification", or Cr(VI) reduction by carbon reduced by the sun's energy through photosynthesis. An intermediate species, such as Fe^{2+} or S^{2-}, reduced by carbon, can serve as the direct electron donor. Analogous to denitrification, the most important part of the nitrogen cycle because it preserves O_2, "dechromification" is the vital segment of the chromium cycle. Without it, all atmospheric O_2 theoretically could end up as chromate, even if each chromium in the earth's crust only took on one more oxygen. However, all life probably would be poisoned by Cr(VI) long before all of the crust's chromite could meet with manganese. Indeed, oxidation processes are a threat to life on earth.

Following reduction of Cr(VI), Cr(III) is bound by a variety of ligands that render it insoluble, immobile, and unreactive, and chromium reciprocates by stabilizing the ligand matrices, for example, leather, or soil humus. Mobile ligands, such as citrate, extract Cr(III) and deliver it to manganese oxide surfaces where both the organic and the chromium become oxidized. Sometimes the ligands is recycled because the Mn(III) formed by reverse dismutation picks up its electrons from the Cr(III) in "preference" to those from the organic ligand, and only the chromium is oxidized. When organic ligands are excessive in relation to small amounts of Cr(III) held, the surplus organic sites tend to induce reverse dismutation of MnO_2 by binding the Mn(III). The Mn(III)-organic may prevent formation of Cr(VI) or reduce it as fast it forms, short-circuiting the cycle of speeding up the cycling gyrations.

2.8.3 Water Chromium Chemistry

Surface Water: Naturally occurring levels of chromium in water can be very low, in the picogram per milliliter range. Chromium will be present in rivers as soluble and insoluble forms. Most of the soluble chromium is present as hexavalent chromium but this generally accounts for only a few percent of the total chromium. Chromium(III) will be present in solids suspended in the water as minerals, organics and occluded oxides. The actual concentration of chromium in water will depend on the source of the water and materials it passes through and carries with it.

The importance of total chromium concentrations in water is not known. However, in many waters there is the possibility of oxidation of Cr(III) to Cr(VI). Very little is known about the behavior of soluble organic chromium in aqueous and biological systems and there have been few studies on the importance of different phases in the transport of chromium in rivers. Schroeder and Lee (1975) have shown in simulated natural water systems that Cr(III) can be oxidized by manganese dioxide and slowly by oxygen. The oxidation can be inhibited by substances in natural water.

Hexavalent chromium is reduced by ferrous iron, dissolved sulfide, and organic sulfhydryl groups. Benes and Steinnes (1975) and Lovett and Lee (1976) suggested that organic matter is important in the reduction of Cr(VI) and that some of the chromium in river water is organically bound. Yamazaki (1980) gave evidence of the formation of anionic and neutral charged organic Cr(VIII) complexes in aqueous systems. The complexes formed remained soluble for at least 10 days. The rate of formation of Cr(III) complexes will be relatively slow if only Cr(III) is present but might be much more rapid if Cr(VI) is reduced.

Groundwater: Groundwater contamination by chromium is major problem in industrialized areas, particularly those that have large metal-plating industries. Other important industrial sources of chromium are wood treatment and tannery facilities, as well as chromium mining and milling operations. Typically, chromium-containing wastes have been disposed of by discharging them to surface impoundments or lagoons. Leakage from these lagoons into groundwater has been relatively common. Almost all reported incidences of chromium-related groundwater contamination are of industrial origin. Naturally occurring chromium also occurs at potentially harmful concentrations (Robertson, 1975).

Groundwater contamination by chromium can be extensive in sand and gravel and fractured rock aquifers because groundwater velocities in these materials typically are between about 0.1 and 5m per day. At the other extreme, groundwater velocities in clayey materials tend to be low, on the order of a few centimeters or less per year, so chromium-contaminated groundwater cannot extend far from the source.

The mobility of chromium in groundwater depends also on its solubility and its tendency to be adsorbed by soil or aquifer materials. These factors, in turn, depend on the groundwater chemistry and the characteristics of soil or aquifer material in contact with the chromium-containing groundwater.

Solubility of Chromium: There are no significant solubility constraints on the concentrations of Cr(VI) in groundwater. Solubility can, however, significantly limit the concentration of Cr(III) in groundwater at a pH above 4 or 5. The low solubility of the Cr(III) solid phases Cr_2O_3 (Hem, 1977) is likely the major reason why Cr(III) generally makes up a small percentage of the total chromium concentration in natural or polluted groundwater and why it rarely occurs at concentrations above the drinking water standard of 0.05 mg L^{-1}. Chromium (III) tends to be essentially immobile in most groundwater because of its low solubility.

Chromium (III) solution concentrations in equilibrium with Cr_2O_3 are less than 0.005 mg L^{-1} above a pH of 4, whereas Cr (III) solution concentrations in equilibrium with $Cr(OH)_3$ vary from approximately 0.05 to 500 mg L^{-1}, between a pH of 5 and 9 (Hem,1977). Although the theoretical solubility of Cr_2O_3 is much lower than that of Cr $(OH)_3$, Hem(1977) suggests that chromium is more likely to precipitate as $Cr(OH)_3$ in natural aqueous systems where waste has been introduced as Cr(VI) and subsequently been reduced to Cr(III).

When Cr (VI) is transported by groundwater, it may be transformed to and precipitated as Cr(III) if the groundwater enters a low redox zone. Laboratory studies have shown that Cr(VI) can be reduced readily to Cr(III) in the presence of organic matter, especially at low pH (Bartlett and Kimble, 1976b; Bloommfield and pruden, 1980; Schroeder and Lee, 1975) found that Cr(VI) could also be reduced by Fe(II) and dissolved sulfides.

Chromium (III) generally is not transported to great distances by groundwater because of its low solubility. However, Cr(III) could be converted to the more soluble Cr(VI) if the redox state at a particular location were to change with time from reducing to oxidizing. Chromium (III) has been found to be oxidized by manganese under natural conditions (Bartlett and James, 1976; Schroeder and Lee, 1975).

Chromium (III) can form highly soluble organic complexes in the laboratory, particularly under acid conditions (Bartlett and Kimble, 1976a; James and Bartlett, 1983a). Thus, if it is in a complexed form, Cr(III) may exist at much higher concentrations in groundwater than if it is uncompelxed. The existence of Cr(III) complexes has not been documented under field conditions.

2.8.4 Chemical Speciation, Oxidation and Reduction

Chromium speciation is affected by Pe (redox) and pH conditions. Chromium (VI) predominates under oxidizing (high redox) conditions, whereas Cr(III) predominates under more reducing (low redox) conditions. Oxidizing conditions generally are found in shallow aquifers within a few meters of the water table, where there is a continual replenishment of oxygen from the atmosphere via the unsaturated zone. Oxygen in groundwater tends to be consumed by hydro chemical and biochemical oxidation reactions, usually involving organic matter. In shallow groundwater, this oxygen is replaced from the atmosphere. In deeper groundwater that are isolated from the atmosphere, no replenishment of oxygen occurs, and reducing conditions develop (See Fig. 2.2).

Chromium (VI) is extensively hydrolyzed in water. At total chromium concentrations below 500 mg L^{-1} (0.01 *M*), the dominant Cr(VI) species are the oxyanions $HCrO_4^-$ and CrO_4^{2-} Equilibrium between the two species is dependent on pH:

$$HCrO_4^- \rightarrow CrO_4^{2-} + H^+$$

At low pH, the concentration of H^+ ions is high, so the reaction tends to the left, and $HCrO^-_4$ is the dominant species. At higher pH, where the H^+ concentration is lower, the reaction tends to the right, and CrO_4^{2-} predominates, In natural groundwater, the pH is typically between 6 and 8, so the CrO_4^{2-} ion is the dominant species. At Cr(VI) concentrations above 500 mg L^{-1}, the $Cr_2O_7^{2-}$ ion predominates in acidic environments (Baes and Mesmer, 1977). However, Cr(VI) at concentrations on the order of 10 mg L^{-1} imparts a characteristic yellow color to water (Deutsch, 1972). Chromium (VI) does not commonly form complexes with inorganic or organic ligands (Langard, 1980; NAS, 1974).

The dominant Cr(III) species occurring in groundwater also depend on pH.

$Cr^{3+} + H_2O \leftrightarrow CrOH^{2+} + H^+$

$CrOH^{2+} + H_2O \leftrightarrow Cr(OH)^+_2 + H^+$

$Cr(OH)^+_2 + H_2O \leftrightarrow Cr(OH)^0_3 + H^+$

$Cr(OH)^0_3 + H_2O \leftrightarrow Cr(OH)^-_4 + H^+$

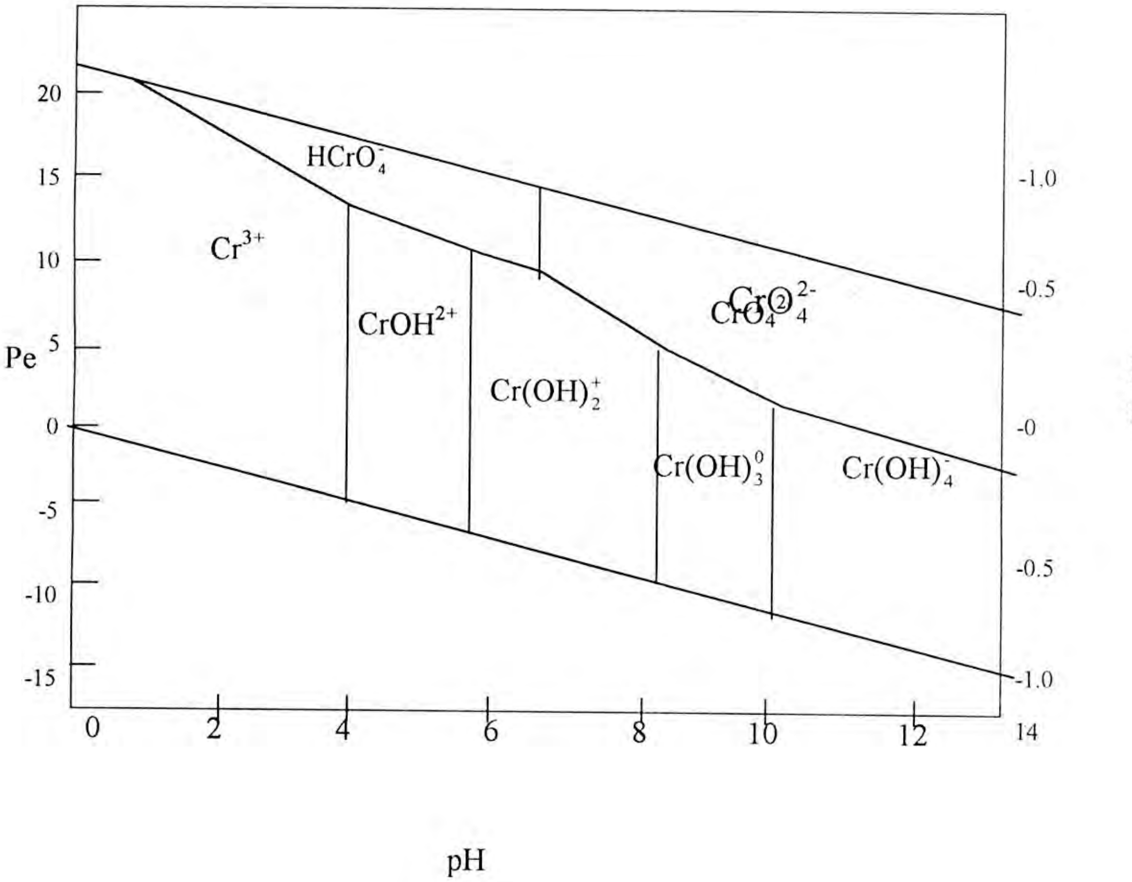

Figure 2.2 Areas of dominance of dissolved chromium species at equilibrium in the system Cr + H_2O + O_2 at 25^{0}C and 1 atm. (Data from Baes and Mesmer, 1977; Hem. 1977)

$Cr(OH)_2^+$ is the document species in natural groundwater with a pH between 6 and 8. $CrOH^{2+}$ predominate in more acidic waters and $Cr(OH)_3^0$ and Cr $(OH)_4^-$ predominate in more alkaline waters. Chromium (III) complexes with many organic ligands, as well as fluoride, ammonia, cyanide, thiocyanate, oxalate, and sulfate (Baes and Mesmer, 1977).

Reduction strategies for Cr(VI) in soils are based on the concept that Cr(III) has negligible toxicity and minimal mobility compared with Cr(VI) and, therefore, reduction of Cr(VI) to Cr(III) is a means of eliminating the hazard associated with Cr contamination in a soil without changing its total Cr concentration. Successful strategies for effecting such remediation must satisfy three criteria: (1) newly reduced Cr(III) is in a form that is inert to reoxidation, (2) extraneous or objectionable byproducts of the Cr(VI) reduction reaction are not released (e.g., nitrate, Fe(III) oxide crusts, or partially oxidized S-containing compounds), and (3) oxidation-reduction and acidity conditions of the soil are controlled so that Cr(III), other metals or soil pollutants are not solubilized. In addition, marked changes in these conditions could inhibit the desired Cr(VI) reduction reaction.

Element Fe (e.g., steel wool) reduces Cr(VI) to Cr(III) in chromites processing residue-enriched soils and other aqueous environments (James, 1994; Powell et al., 1995), and in the process, alkalinity is generated. The Fe(III) and Cr(III) formed by the redox reaction may create a mixed oxide with low solubility, thereby minimizing the chances for reoxidation of Cr(III). In contrast, reduction of Cr (VI) coupled to oxidation of Fe(II) compounds may generate net acidity, and the soil pH may decrease markedly, depending on the pH buffer capacity to the soil (James, 1994). Similar mixed Cr(III)-Fe(III) oxides may form, however. The reduction of Cr(VI) by organic compounds (e.g., hydroquinone) will also generate alkalinity, and newly formed Cr(III) may be complexed with organic materials, such as humic acids in soils. Such complexation in insoluble forms will inhibit reoxidation if Cr(III) is bound in insoluble organic complexes (e.g., with humic acids). In contrast, solubilization of Cr(III) by organic acids may increase oxidation of Cr(III), depending on the form of Cr, pH, and the organic acid involved (James and Bartlett, 1983a). The most efficacious methods for remediating Cr(VI)-contaminated soils will depend on native soil pH, the presence of natural reducing agents, forms of Cr(VI) present (e.g., their solubility), the pH buffer capacity of the soil, and the ease with which the reducing agents may be incorporated into depths soil where Cr(VI) is found.

Chromium Reduction Reactions:

Reduction by Elemental Iron [With formation of Fe(III)]

$$Fe + CrO_4^{2} + 0.5\ H_2O + 2H^+ \rightarrow Fe\ (OH)_3 + 0.5\ Cr_2O_3$$

Reduction by divalent Iron [With formation of Fe(III)]

$$6\ Fe^{2+} + 2CrO_4^{2} + 13\ H_2O \rightarrow 6\ Fe\ (OH)_3 + Cr_2O_3 + 8\ H^+$$

Reduction by organic compounds (e.g., hydroquinone, with formation of quinone)

$$1.5\ C_6H_6O_2 + CrO_4^{2} + 2\ H^+ \rightarrow\ 0.5\ Cr_2\ O_3\ +\ 1.5\ C_6H_4O_2\ +\ 2.5\ H_2O$$

2.8.5 Adsorption and Precipitation

Soil pH will determine both the speciation of Cr(VI) and the change characteristic of the colloidal surface with which it reacts. Above pH 6.4, $HCrO_4^-$ dissociates to $CrO_4^=$ as the dominant form of Cr(VI) in dilute aqueous systems (Deltombe et al., 1966). Divalent $CrO_4^=$ may be adsorbed in similar fashion to $SO_4^=$ and $HPO_4^=$, forming binuclear binuclear bridged complexes on goethite or on aluminum oxides and other soil colloids with positively charged surfaces. Chromate also may be adsorbed by ligand exchange on Fe(III) and Al(III) oxides (Russell, 1973; Parfitt, 1978). Depending on the colloid, $HCrO_4^-$ may be similar to $H_2PO_4^-$ and be tightly held in soils, or it may be similar to HCO_3^-, Cl^- and NO_3 and remain soluble.

Soil pH also affects the quantities of positive and negative charge on soil colloids, especially on organic matter and on Fe(III), Al(III), and Mn(III, IV) oxides (McKenzie, 1977; Parfitt, 1978). Binding of Cr(VI) species in soils will depend on soil mineralogy and on the relation of soil pH to the pH of zero point of charge of the colloids involved. Bartlett and Kimble, (1976a) showed that orthophosphate prevented adsorption of chromate, presumably by competition for the same sites, and that adsorption and desorption behavior of chromate was analogous to that of phosphate.

2.8.6 Mobility of Chromium in Soil

Chromium (VI) tends to be moderately to highly mobile in most shallow groundwater due to the lack of solubility constraints and the low to moderate adsorption of Cr(VI) anionic species by iron and other metal oxides and hydroxides in neutral to alkaline waters. Chromium (III) tends to be relatively immobile in most groundwater because of the precipitation of low solubility Cr(III) compounds above a pH of 4 and because of the high adsorption of the Cr^{3+} ion by soil clays below a pH of 4.

To continue the analogy with aluminum, it seems safe to assume the ionic trivalent chromium in solution or on acid soil exchange sites (below pH 5) will be the most available form of inorganic Cr(III), chemically and biologically, even though exchangeable chromium would be held tightly compared with other cations. However, the most mobile Cr(III), by diffusion or mass flow, will be soluble organic (and some fluoride) complexes and dispersable colloidal sized inorganic hydroxy-polymers, silicates, carbonates, and crystalline $FeCr_2O_4$ and clay minerals. Dispersability will depend on wetting and drying, freezing and thawing, ionic strength of soil solution, and biologically mediated surface interactions of cations, anions, H_2O, and organic substances.

2.8.7 Sediment Chromium Chemistry

Elevated chromium levels from anthropogenic sources have been reported in sediments. Sediment enrichment is correlated with fluxes of charcoal from different combustion processes e.g., oil, coal, and wood burning. Sediments of the lower Saddle River (New York), receiving heavy urban discharge, showed a chromium enrichment of 510% (35mg kg^{-1}) compared to control areas (Wilber and Hunter, 1979). Sequential extraction produced the following chromium fractionation: 0.5% in river water soluble fraction, 0.6% in ion-exchangeable fraction, 2.7% in easily reducible manganese oxide fraction, 28.3% in organic fraction bound to humic materials and 67.9% in easily reducible iron oxides. Only the first two fractions were determined to be bio-available under aerobic conditions. For the total chromium of sediment levels of 2.90 mg kg^{-1}, this represented only 0.03 mg kg^{-1} of available chromium.

Total chromium levels of 8 – 241 mg kg^{-1} were reported for the sediments of the estuary and Gulf of St. Lawrence, Canada (Loring, 1979). About 2 –11% of the total chromium was in the non-detrital fraction and potentially bio-available. The remainder was held in the acetic acid insoluble detrital fraction, not readily bio-available. Organic matter, mostly of terrestrial origin and Fe-Mn oxide grain coatings transport the non-detrital-chromium to bottom sediments. Chromium in Lake Ontario sediments was enriched in the humic and fulvic acids compared to the entrapping sediments (Nrigau and Coker, 1980). The enrichment factor was approximately 2. About 8-11% of total chromium in sediment was associated with the organic matter. In the sediments samples of Dhanmondi lake in Dhaka, concentrations of chromium at different locations varied from 21 mg/kg to 170 mg/kg (Ashfaque, 1999). Chromium concentrations were found to vary with particle sizes.

Chapter 3

WATER QULITY OF DHAKA CITY

3.1 INTRODUCTION

In Dhaka, groundwater is the principal source of water supply. Dhaka Water Supply and Sewerage Authority (DWASA) is entrusted with the task of water supply in Dhaka City. Groundwater is extracted through a network of about 300 deep tube wells (DTWs) and distributed to the city dwellers through a distribution system. Any contamination of groundwater would endanger the entire water supply system in Dhaka.

For a long time, people have been expressing concerns about the possibility of groundwater contamination by chromium from tannery wastewater. At present wastewater from the tannery industries is discharged through open drains into a stagnant pond and finally into the Buriganga River through three outfalls. The stagnant pond area serves to retain the tannery wastewater for prolonged periods of time, allowing dissolved constituents (e.g., chromium) from the wastewater to percolate into the subsurface. Wastewater from tannery industry typically contains high concentrations of chromium (reaching as high as 4000 mg/l), BOD_5, dissolved lime, hydrogen sulfide, dyes, oils, organic matter, and suspended solids. Thus, wastewater from tannery industries can potentially contaminate the groundwater, particularly in the Hazaribagh area where the tanneries and wastewater discharge area are located. In this regard, contamination of groundwater by chromium is of particular concern.

Although concerns have been expressed about possible contamination of groundwater by wastewater from tannery industries, there appears to be a lack of systematic data on quality of groundwater extracted from DWASA deep tubewells. In order to detect possible contamination of groundwater by tannery wastewater, there is an urgent need to assess the quality of groundwater extracted from DWASA deep tubewells, particularly those located in the Hazaribagh area.

This Chapter provides detailed characterization of groundwater extracted by DWASA deep tubewells. Groundwater samples from 21 deep tubewell pump stations (including all seven stations located in the Hazaribagh area) belonging to the six DWASA zones, have been analyzed. Analysis has been done for a wide range of parameters, especially those having high concentrations in tannery wastewater (e.g., chromium, chloride, sulfide). Analysis of these test results provides very useful information on the quality of DWASA water supply and on possible contamination of groundwater by tannery wastewater. This Chapter also provides a brief description of water supply services in Dhaka City provided by the DWASA.

3.2 DHAKA WATER SUPPLY AND SEWERAGE AUTHORITY

3.2.1 Background, Administration and Responsibilities

Dhaka Water Supply and Sewerage Authority (DWASA) was established under the water Supply and Sewerage Ordinance, 1963. It looks after construction, expansion, operation and maintenance of water supply, sanitary sewerage works and drainage system in Dhaka. According to the Ordinance of 1963, DWASA was supposed to look after solid waste collection and disposal but the Authority did not take it up and this component has been excluded in the amended Act of 1996. As a result this activity remained with the Dhaka City Corporation (DCC). However, the storm water drainage which was looked after by Department of Public Health Engineering was transferred to DWASA by a Government order in 1989. The responsibility for supply of Narayanganj Pourashava was placed under DWASA in 1990. The WASA ordinance, 1965 has been repealed and replaced by Act 6 of 1996. Under this Act the power of the Authority is vested on a 12 member Board. Only 2 members are from the Government and the rest are from water users, city corporation/pourashava, trade bodies and professional bodies. The Chairman of the Board is appointed by the Government from among the members of the Board.

As per the new Act, a Managing Director (MD) looks after the day to day activities of the Authority. He is supported by three Deputy Managing Directors (DMDs). The functions of these DMDs involve financial, administrative, technical, planning and development activities. They are supported by officers and employees posted at the head office, six zonal offices and the treatment plant at Pagla. According to Management Information Report of August 1997, the total manpower of DWASA is 3265 against sanctioned posts of 3137. The department-wise breakdown is as follows:

Engineering Department	: 2105
Commercial Department	: 598
Secretarial (including Computer)	: 562
Total	: 3265

The primary responsibilities of the DWASA are: (1) To construct, operate, develop and maintain the necessary infrastructure to extract, treat and reserve water in order to supply pure water to the people, industries and the commercial organizations; (2) To construct, operate, maintain and develop waste treatment and disposal system; and (3) To construct, operate, maintain and develop storm sewer in order to remove the water-logging problem of Dhaka City.

3.2.2 Water Supply Activities

The DWASA service area has been divided into seven zones of which six are in Dhaka and one in Narayangonj. Figure 3.1 shows different zones of DWASA in Dhaka City and Table 3.1 presents recent statistics on DWASA services.

Table 3.1 Water Service Provided by the DWASA

Sl No.	Description	Unit	June 1998	June 1999	% Increase	September 1999
1	Deep Tubewell	Number	237	277	16.9	277
2	Water Production	Million liter	930	1,070	15.1	1,028
3	Water Demand	Million liter	1,400	1,440	2.8	1,440
4	Water Line	km	1,610	1,643	2.0	1,646
5	Water Connection	Number	171,855	178,377	3.8	180,129
6	WTP	Number	3	3	0	3

Source : DWASA (2000a), DWASA (2000b)

As of September 1999, the DWASA has installed 277 DTW along with 3 water treatment plants (WTP), 1 in Dhaka and 2 in Narayangonj, to meet the water demand in its service area. Although the combined capacity of the DTWs and the WTPs meet 80% of the current daily demand, the actual production (Table3.2) of water from these facilities is only about 70% of the current daily demand. Table 3.2 shows the DWASA water supply is heavily dependent on groundwater with more than 96 percent of total water production coming from groundwater source. It should be noted that besides domestic water demand, industrial and commercial institutions exert a significant demand on DWASA water.

Table 3.2 Source-wise Water Production

Production	Total (MLD)	Groundwater Source (MLD)	Surface Water Source (MLD)
Production Capacity	1,152.5	1,067.3	85.2
Actual Production	1,028.5	990.3	38.2

3.2.3 Water Quality Assessment by DWASA

According to DWASA sources, the groundwater and surface water extracted by the WASA are monitored regularly through the its own Quality Control and Research Division. According to DWASA the quality of the groundwater supplied is, in most cases, within the acceptable limits set by the WHO guidelines (DWASA, 2000). There is provision for chlorination to prevent contamination in the supply line. Like groundwater, the surface water is also chlorinated before it is delivered into the supply line. Color, pH, turbidity, odor, temperature, dissolved oxygen, alkalinity, hardness, chloride, residual chlorine, calcium, total coliform and fecal coliform are usually tested at the Organization's quality control and research laboratory. In addition, groundwater samples from the DTWs are also tested for arsenic every three months and river water samples are tested for chromium and aluminum every six months. Water samples are also collected from the supply lines by the DWASA Quality Control and Research Division and the parameters listed above are tested (DWASA, 2000a). According to DWASA, necessary mitigation measures are adopted if there is any change in the quality of the water.

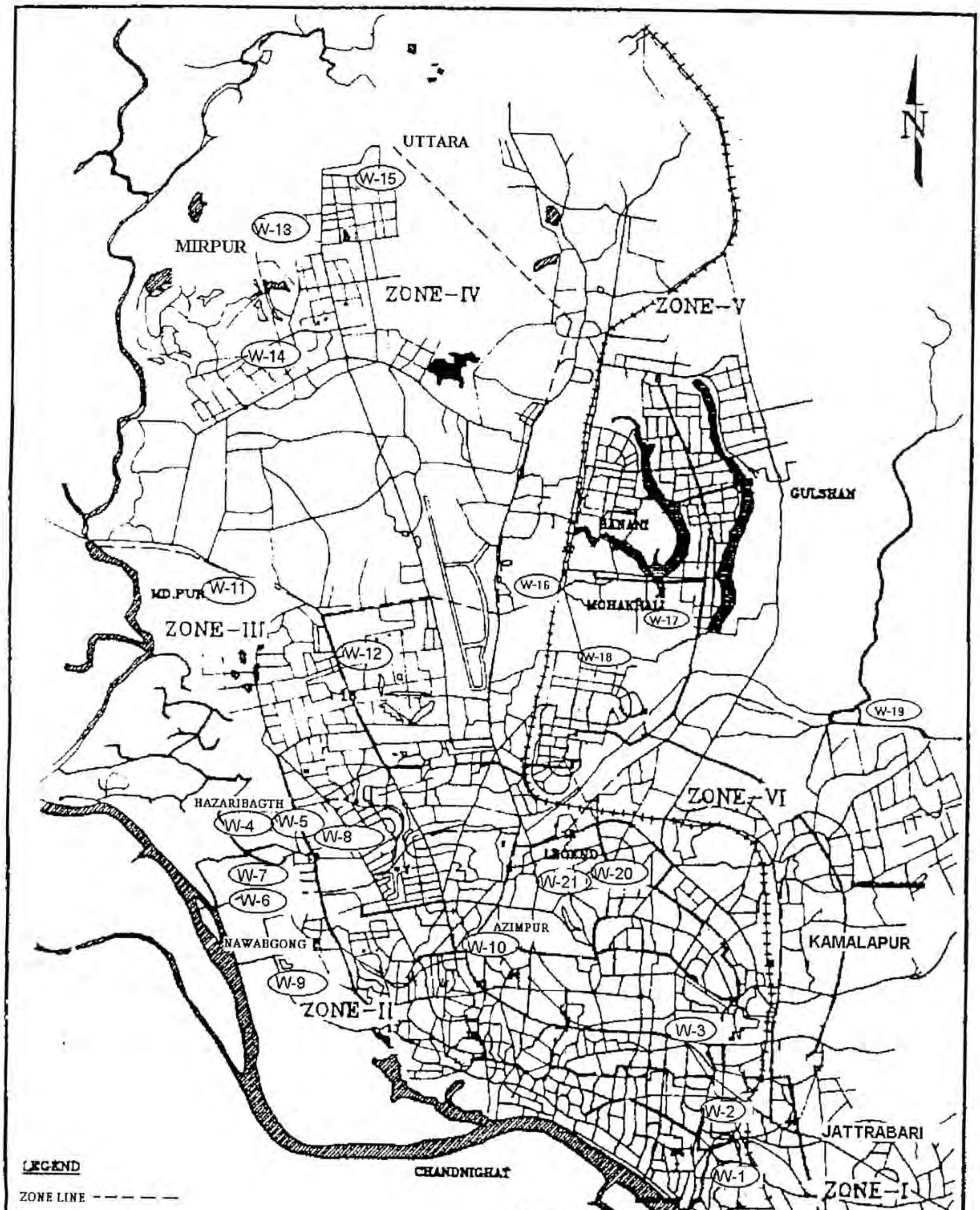

Figure 3.1 Different Zone of DWASA in Dhaka City and Approximate location of DTW Stations from which water sample were collected

It should be noted that according to available information, DWASA does not test its extracted groundwater samples for chromium. Thus there is no data on chromium concentration in groundwater extracted by DWASA tubewells.

3.2.4 Sewerage Activities

DWASA has 624 km of sewer lines (as on July, 1997), out of which 93 km in Zone IV consists of small-bore system and is not in operation. A total of 43,626 sewer connections have been given during the year upto August 1997. Zone-wise breakdown of sewer line is as follows:

Zone I	: 150 km
Zone II	: 110 km
Zone III	: 90 km
Zone IV	: 93 km*
Zone V	: 61 km
Zone VI	: 120 km
Total	: 624 km

* 93 km of sewer line in Zone IV is small-bore system and is not in operation.

DWASA has 21 sewer lift pump stations in different zones and a sewage treatment plant at Pagla.

3.3 MATERIALS AND METHODS

In order to assess the quality of water extracted by deep tubewells of DWASA, water samples were collected from 21 deep tubewell pump (DTW) stations located in six DWASA zones. The Hazaribagh area belongs to Zone 2 of DWASA and water samples were collected from all seven DTW stations located in this zone. For each of the Zones 1, 4, 5 and 6, water samples from three DTW pump stations; while for Zone 3, water samples were collected from two DTW stations. Table 3.3 lists the DTW stations from which samples were collected along with sampling dates. As shown in Table 3.3 water samples from DTW stations located in Zone 2 were collected at two different times, first in March 2000 and in June 2001. Figure 3.1 shows the different DWASA zones on a map of Dhaka city.

For each DTW station, water samples were collected in two plastic containers, a 1-L and a 2-L container. Prior to sampling, the plastic containers were acid-washed and rinsed with de-ionized water. After sampling, the 1-L container was acidified with 1 ml of concentrated hydrochloric acid. Water from this acidified container was later used in the laboratory for analysis of chromium and other heavy metals (iron, lead, manganese and arsenic). Water from the 2-L (i.e., non-acidified) container was used for analysis of a wide range of water quality parameters (e.g., pH, color, turbidity, conductivity, carbon-di-oxide, alkalinity, hardness, chloride, sulfide, sulfate, ammonia, nitrate, fluoride, phosphate, and dissolved solids).

Table 3.3 Location of DWASA Water Pump

Zone	Well No.	Location	Date of Sampling
1	1	Baldha garden pump, Narinda Dhaka.	03-06-2000
	2	Kaptan Bazar Pump, Kaptan Bazar, Dhaka.	03-06-2000
	3	Bangabhaban Park Pump, Bangabhaban, Dhaka.	03-06-2000
2	4	Hazaribagh Park Pump, Hazaribagh, Dhaka.	15-03-2000 06-06-2001
	5	Badda Nagar Pump, Hazaribagh, Dhaka.	15-03-2000 06-06-2001
	6	College of Leather Technology, Hazaribagh, Dhaka.	15-03-2000 06-06-2001
	7	Tannery Area Pump, Hazaribagh, Dhaka.	15-03-2000 06-06-2001
	8	BDR Gate-1 Pump, Pilkhana, Dhaka.	15-03-2000 06-06-2001
	9	Nawabgong Pump, Nawabgong, Dhaka.	15-03-2000 06-06-2001
	10	Azimpur Shishupark Pump, Azimpur, Dhaka.	15-03-2000 06-06-2001
3	11	Bashbari Water Pump, Mohammadpur, Dhaka.	23-05-2000
	12	Road No.- 8 ,Dhamondi , Dhaka.	02-05-2000
4	13	Dawan Para Pump. Mirpur, Dhaka	20-05-2000
	14	Block-C, Mirpur-10, Dhaka	20-05-2000
	15	Pallabi Water Pump, Mirpur, Dhaka.	03-06-2000
5	16	Tejkunipara Water Pump, Tejkunipara, Firmgate, Dhaka.	30-05-2000
	17	Mohakhali Lab. Pump, Mohakhali, Dhaka.	03-06-2000
	18	Tibbet Water Pump, Tejgaon, Dhaka	03-06-2000
6	19	Banasree Housing Ltd. Rampura, Dhaka.	23-05-2000
	20	Osmani Uddan Pump, Osmani Uddan, Dhaka	03-06-2000
	21	High Court Water Pump, High Court, Dhaka.	06-06-2000

Chromium concentrations in the water samples were measured with an atomic absorption (flame) spectrophotometer (Shimadzu, Model 680). A sample "standard curve" for chromium is given in Appendix A. In order to determine speciation of chromium, concentration of Cr^{6+} was measured (in groundwater samples from Zone 2) following the 1,5-Diphenylcarbohydrazide Method using a spectrophotometer (HACH, DR4000U). Lead concentration was also measured with the atomic absorption spectrophotometer. Manganese concentration was measured using the PAN method with a spectrophotometer (HACH, DR4000U), and iron concentration was measured using the thiocyanate colorimetric method. Arsenic concentration was determined using the Silver-diethyl-dithiocarbamate method (AWWA, 1985); absorbance was measured using a spectrophotometer (HACH, DR/EL4).

In this study, pH was measured using a pH meter (HACH), conductivity was measured using a conductivity meter, and turbidity was measured using a standard turbidity meter. Hardness was measured using EDTA titrimetric method and chloride was measured using $AgNO_3$ titrimetric method. Color, ammonium, nitrate, fluoride, sulfate, sulfide, and phosphate concentrations were determined with a spectrophotometer (HACH, DR4000U). Ammonium was determined using Nessler method, nitrate by the cadmium reduction method, and phosphate by the molybdenum blue method. Alkalinity, carbon-di-oxide, and total and dissolved solids were determined by volumetric methods following Standard Methods (AWWA, 2000).

3.4 RESULTS AND DISCUSSION

3.4.1 Chromium in DWASA Deep Tubewell Water

Total chromium concentration of water samples from 21 DTW pump stations is presented in Table 3.4. Chromium concentration in the 21 water samples varied from 0.002 mg/l to 0.12 mg/l. It is clear from Table 3.4 that chromium concentrations in water samples from Zone 2 are significantly higher than those from the other DWASA zones. Out of seven water samples from Zone 2, two exceeded the Bangladesh drinking water standard and WHO guideline value of 0.05 mg/l (GOB, 1997). It should be noted that water samples from the seven DTW stations in Zone 2 were collected on two different occasions and there are significant variations in chromium concentrations in these two samples. Except for one DTW station (Well No. 4), chromium concentration in all water samples collected in June 2001 were lower than those in water samples collected in March 2000. This may be due to the fact that the second sampling operation was carried during early monsoon (in June) and possible higher recharge during this time may be responsible for lowering of chromium concentration due to dilution. This suggests that regular monitoring of chromium concentration in the water samples from these DTW stations is needed to ascertain the level as well as variation in chromium concentration.

Chromium concentrations in none of the water samples from the 14 DTW stations from other zones exceeded the Bangladesh standard. Average chromium concentration in 14 water samples from the seven tubewells of Zone 2 is about 0.036 mg/l; while average chromium concentration in water samples from the 14 tubewells from 5 other zones is about 0.004 mg/l, about ten times less than that for Zone 2.

Table 3.4 Chromium Concentration in DWASA Water

Zone	Well No.	Total Cr (mg/l)	Zone	Well No.	Total Cr (mg/l)
1	1	0.003	3	11	0.003
	2	0.003		12	0.003
	3	0.003	4	13	0.004
2	4	0.0020[a] 0.0205[b]		14	0.004
	5	0.0300[a] 0.0147[b]		15	0.003
	6	0.1100[a] 0.0142[b]	5	16	0.011
	7	0.1200[a] 0.0169[b]		17	0.004
	8	0.0300[a] 0.0088[b]		18	0.005
	9	0.0400[a] 0.0120[b]	6	19	0.006
	10	0.0500[a] 0.0327[b]		20	0.002
	-	-		21	0.004

[a] Sample collected on 15-03-2000
[b] Sample collected on 06-06-2001

Thus, results from this study suggest that chromium concentration in water samples from DWASA deep tubewell pump stations located in and around Hazaribagh area are significantly higher than those from other areas of the Dhaka city. In the absence of any natural source of chromium and the presence of a large number of tanneries in the

Hazaribagh area, it appears that tannery wastes are responsible for the higher chromium concentrations in DTW water samples from Zone 2. In other word, it strongly suggests that tannery wastes have already contaminated the groundwater aquifer in the Hazaribagh area.

3.4.2 Speciation of Chromium in Groundwater

Table 3.5 shows speciation that is chemical form of chromium in groundwater samples collected from seven DTW pump stations located in Zone 2 of DWASA. It shows that very little chromium is present in the more toxic Cr^{6+} form. In fact, most of the values are below the detection limit of 0.006 mg/l. Thus, majority of dissolved chromium in groundwater is present in less toxic Cr^{3+} form.

Table 3.5 Speciation of Chromium of Groundwater Samples from DWASA Zone 2

Zone	Well No.	Total Cr (mg/l)[a]	Chromium(VI) Cr^{6+} (mg/l)[a]
2	4	0.0205	0.006
	5	0.0147	0.006
	6	0.0142	0.001[b]
	7	0.0169	0.003[b]
	8	0.0088	0.000[b]
	9	0.0120	0.000[b]
	10	0.0327	0.006

[a] Sample collected on 06-06-2001
[b] Detection limit of the instrument for Cr(VI) is 0.006 mg/l; values below this limit are not reliable

3.4.3 Iron, Lead, Manganese and Arsenic in DWASA Deep Tubewell Water

Iron

Iron concentrations in water samples from 21 DTW pump stations were found to vary from negligible to 1.5 mg/l (see Table 3.6). Only one sample from Zone 6 exceeded the Bangladesh drinking water standard of 1.0 mg/l. The calculated average concentrations of iron in the six zones are 0.07, 0.21, 0.06, 0.08, 0.01, and 0.52 mg/l, respectively. Very high concentration of iron (1.5 mg/l) in one tubewell (# 19) is responsible for the high average of Zone 6. Among the other five zones, iron concentration in Zone 2 (which includes the Hazaribagh area) is the highest. In fact, average iron concentration for this zone is 3 to 20 times higher than the average value in the other four zones. Thus, iron concentration in water samples from Zone 2 appears to be higher compared to that in most of the other zones.

Lead

Lead concentrations in water samples from 21 DTW pump stations were found to vary from 0.001 to 0.14 mg/l (see Table 3.6). Among the 21 samples, 17 exceeded the WHO guideline value (for drinking water) of 0.01 mg/l and two exceeded the Bangladesh drinking water standard of 0.05 mg/l. Of the two DTWs exceeding the Bangladesh standard, one is located in Zone 5 and the other in Zone 6. However, no clear zone-wise trend of lead concentration could be observed. The fact that more than 80% of the tubewell water tested in this study exceeded WHO guideline value for lead is very alarming.

Table 3.6 Iron, Lead, Manganese and Arsenic Concentration in DWASA Water

Zone	Well No.	Iron (mg/l)	Lead (mg/l)	Manganese (mg/l)	Arsenic (µg/L)
1	1	0.02	0.02	0.031	< 5
	2	0.04	0.01	0.037	< 5
	3	0.15	0.04	0.070	< 5
2	4	0.35	0.001	0.095	10
	5	0.10	0.008	0.078	< 5
	6	0.50	0.015	0.140	< 5
	7	0.08	0.012	0.058	< 5
	8	0.05	0.021	0.031	< 5
	9	0.20	0.023	0.107	< 5
	10	0.20	0.01	0.098	< 5
3	11	0.1	0.03	0.002	< 5
	12	< 0.02	0.02	0.027	< 5
4	13	< 0.02	0.026	0.023	12
	14	0.15	0.018	0.046	< 5
	15	0.08	0.012	0.036	< 5
5	16	< 0.02	0.14	0.032	< 5
	17	< 0.02	0.02	0.039	< 5
	18	< 0.02	0.04	0.036	< 5
6	19	1.5	0.08	0.001	< 5
	20	< 0.02	0.02	0.057	< 5
	21	0.05	0.03	0.057	< 5

Manganese

Manganese concentrations in water samples from 21 DTW pump stations were found to vary from 0.001 to 0.14 mg/l (see Table 3.6). Among the 21 samples, two exceeded the Bangladesh drinking water standard of 0.1 mg/l; and none exceeded the WHO guideline value of 0.5 mg/l. Both the samples exceeding the Bangladesh drinking water standard are from Zone 2 where the tanneries are located. The calculated average concentrations of manganese in the six zones are 0.046, 0.087, 0.015, 0.035, 0.036, and 0.038 mg/l, respectively. Thus, manganese concentrations in water samples from Zone 2 appear to be significantly higher than those from the other zones, although most samples satisfy the Bangladesh drinking water standard for manganese.

Arsenic

Except for two samples, arsenic concentrations of all the water samples were below the detection limit of 5 μg/L (Table 3.6). Only two samples showed arsenic concentration above the detection limit; but even in these samples arsenic concentrations were very low (10 and 12 μg/L). Thus with respect to arsenic, DWASA deep tubewell waters appear to be quite safe.

3.4.4 Other Water Quality Parameters

pH

pH values in water samples from 21 DTW pump stations were found to vary within a narrow range, from 5.8 to 6.6 (see Table 3.7). The lowest value (5.8) was recorded for the well # 3 and well # 20 in Zone 1 and Zone 6, respectively. The highest value (6.6) was recorded for well # 4 in zone 2. Although no clear zone-wise trend could be observed, pH values of Zones 1, 5 and 6 appear to be lower (averaging close to or below 6.0), compared to the other three zones where average values varied from about 6.3 to 6.5.

Carbon-di-oxide

Carbon-di-oxide concentration in water samples from 21 DTW pump stations are listed in Table 3.7. Except for one, all samples showed high carbon-di-oxide concentration, typical of any groundwater. The lowest value of 22 mg/l probably resulted either from an experimental error or from improper storage of sample (resulting in escape of CO_2

from the sample). No clear zone-wise trend of carbon-di-oxide value could be observed. However, as expected, higher carbon-di-oxide values in general could be associated with lower pH values.

Chloride

Chloride concentrations of water samples from 21 DTW pump stations were found to vary from 18 mg/l to 110 mg/l (see Table 3.7). All values satisfy the Bangladesh standard as well as the WHO guideline value for drinking water. The lowest concentration of 18 mg/l was recorded for well # 19 in Zone 6 and the highest concentration was recorded for well # 2 in Zone 1. Chloride concentrations of water samples (averaging over 100 mg/l) from Zone 1 are clearly higher than those of the other zones. Chloride concentrations of samples from Zones 3, 4, and 5 were relatively low, averaging from about 30 to 42 mg/l. Chloride concentrations of water samples from Zones 2 and 6 were close to 50 and 70 mg/l, respectively. Since tannery wastes contain high concentrations of chloride and since chloride is a conservative solute, higher concentration of chloride was expected in water samples from Zone 2. However, water samples from Zone 1 were found to contain the highest concentrations of chloride.

Total Dissolved Solids (TDS)

Total dissolved solids concentrations of water samples from the 21 DTW pump stations varied from 194 to 502 mg/l. The lowest concentration was recorded for the well # 19 in Zone 6 and the highest concentration was recorded for well # 20, also in Zone 6 (see Table 3.7). The trend in TDS concentration closely followed the trend observed in chloride concentration (discussed above) with highest concentrations in Zone 1, followed by those in Zones 2 and 6, and with relatively lower concentrations in Zones 3, 4 and 5.

Conductivity

Conductivity values of water samples from 21 DTW pump stations varied from 114 μs/cm to 328μs/cm. The lowest concentration was recorded for the well # 13 in Zone 4 and the highest concentration was recorded for well # 2 in Zone 1 (see Table 3.7). As expected, conductivity values followed the trend observed for TDS and chloride (discussed above).

Color

Color concentrations in water sample from all the 21 DTW pump stations were found to be low, varying from 0 to 8 Pt.-Co. unit (Table 3.7). All values satisfy the Bangladesh standard as well as WHO guideline value for drinking water. No clear zone-wise trend for color concentration could be observed.

Table 3.7 Characteristics of DWASA Water

Zone	Well No.	pH	CO_2 (mg/l)	Chloride (mg/l)	TDS (mg/l)	Conductivity (μS/cm)	Color Pt-Co	Turbidity (NTU)
1	1	6.0	97	105	413	311	Trace	0.36
	2	5.9	74	110	483	328	Trace	1.02
	3	5.8	95	105	459	306	Trace	1.35
2	4	6.6	52	34	291	194	1	2.80
	5	6.5	74	57	359	281	1	0.55
	6	6.5	69	48	299	203	1	3.70
	7	6.4	75	58	315	218	1	0.61
	8	6.4	108	54	333	247	1	0.30
	9	6.5	55	43	308	202	8	3.00
	10	6.4	92	54	331	214	2	2.40
3	11	6.5	51	26	231	149	1	0.14
	12	6.1	110	58	221	135	5	0.32
4	13	6.4	63	26	280	114	1	0.22
	14	6.5	80	29	294	130	7	2.20
	15	6.4	71	33	215	120	2	0.41
5	16	6.1	86	26	224	130	1	0.20
	17	5.9	71	38	225	156	2	0.60
	18	6.0	76	29	228	158	2	0.24
6	19	6.5	22	18	194	136	6	2.70
	20	5.8	118	100	502	326	Trace	0.36
	21	5.9	99	90	459	306	1	0.42

Turbidity

Turbidity values of water samples from 21 DTW pump stations were found to be low, varying from 0.14 NTU to 3.7 NTU (Table 3.7) and all satisfying the Bangladesh standard as well as WHO guideline value for drinking water. Although no clear trend could be observed, turbidity values of water samples of Zones 1, 2 and 6 are marginally higher than those of the other zones.

Alkalinity

Alkalinity (as $CaCO_3$) of water samples from 21 DTW pump stations was found to vary from 98 to 211 mg/l (see Table 3.8). The lowest value was recorded for the well # 17 in Zone 5 and highest value was recorded for well # 5 in Zone 2. It can be seen from Table 3.8 that alkalinity values of water samples from Zone 2 higher compared to those from other zones. Average alkalinity of water samples from Zone 2 was over 180 mg/l while average values for the other five zones varies from about 110 to 147 mg/l.

Table 3.8 Characteristics of DWASA Water

Zone	Well no.	Alkalinity (as $CaCO_3$) (mg/l)	Hardness (as $CaCO_3$) (mg/l)	Carbonate Hardness[1] (mg/l)	Non-carbonate Hardness (mg/l)	F mg/l	NO_3-N mg/l
1	1	150	180	150	30	0.25	4.6
	2	135	188	135	53	0.31	3.1
	3	137	194	137	57	0.00	2.5
2	4	178	142	142	Nil	0.04	0.10
	5	211	186	186	Nil	0.30	0.20
	6	165	126	126	Nil	0.24	0.10
	7	167	134	134	Nil	0.23	0.50
	8	201	164	164	Nil	0.17	0.50
	9	188	172	172	Nil	0.22	0.20
	10	160	148	148	Nil	0.21	0.60
3	11	153	40	40	Nil	0.07	0.20
	12	128	132	128	4	0.01	2.5
4	13	120	76	76	Nil	0.10	0.50
	14	181	140	140	Nil	0.13	0.80
	15	142	115	115	Nil	0.15	0.67
5	16	130	106	106	Nil	0.04	0.60
	17	98	78	78	Nil	0.00	1.7
	18	103	72	72	Nil	0.03	0.90
6	19	153	32	32	Nil	0.16	0.10
	20	116	204	116	88	0.12	2.9
	21	169	206	169	37	0.03	2.3

Hardness

Hardness (as $CaCO_3$) of water samples from 21 DTW pump stations was found to vary from 40 mg/l to 206 mg/l (see Table 3.8). These values satisfy the Bangladesh standard (GOB, 1997) as well WHO guideline value for drinking water. The lowest value was recorded for the well # 11 in Zone 3 and highest value was recorded for well # 21 in Zone 6. However, no clear zone-wise trend of hardness values could be observed. Non-carbonate hardness (calculated) was found only at five stations out of twenty-one DTW pump stations. These five stations are located at Zone 1 and Zone 6.

Fluoride

Fluoride concentrations of water samples from 21 DTW pump stations varied from 0 mg/l to 0.30 mg/l, all satisfying the Bangladesh and the WHO guideline value for drinking water. The lowest concentration was recorded for the well # 3 in Zone no.1 and the highest concentration was recorded for well # 5 in Zone 2 (see Table 3.8). No clear zone-wise trend of fluoride could be observed.

Nitrate

Nitrate (NO_3) concentration in water samples from the 21 DTW pump stations varied from 0.1 mg/l to 4.6 mg/l, all satisfying the Bangladesh standard as well as the WHO guideline value for drinking water. The lowest concentration was recorded for well # 4 in Zone 2 and highest concentration was recorded for well # 1 in Zone 2 (see Table 3.8). Nitrate concentrations in water samples from Zone 1 appear to be significantly higher than those in the other water samples.

Phosphate

Phosphate (PO_4) concentration in water samples from the 21 DTW pump stations varied from 0.416 mg/l to 0.783 mg/l, all satisfying the Bangladesh standard for drinking water. The lowest concentration was recorded for the well # 4 in Zone 2 and the highest concentration was recorded for well # 19 Zone 6 (see Table 3.9). No clear zone-wise trend of phosphate concentration could be observed.

Sulfate

Sulfate concentrations in water samples from 21 DTW pump stations varied from trace quantity to 48.9 mg/l, all satisfying the Bangladesh standard as well as WHO guideline value for sulfate. The lowest concentration was recorded for well # 16 in Zone 5 and the highest concentration was recorded for well # 20 in Zone 6 (see Table 3.9). Sulfate concentrations in water samples from Zone 1 and Zone 2 were the highest, averaging about 44 and 21 mg/l, respectively. For Zone 6, two out of three wells showed sulfate concentrations comparable with those found for Zone 1. It should be mentioned that tanneries at Hazaribagh are located in Zone 2 and that tannery wastewater contains significant concentration of sulfate.

Table 3.9 Characteristics of DWASA Water

Zone	Well No.	PO_4 mg/l	SO_4 mg/l	Sulfide µg/L	NH_3-N (mg/l)
1	1	0.588	43.4	Nil	0.137
	2	0.586	47.8	Nil	0.320
	3	0.601	41.7	Nil	0.331
2	4	0.416	21.8	3	0.188
	5	0.547	29.0	3	0.187
	6	0.431	17.7	2	0.073
	7	0.428	13.4	3	0.021
	8	0.387	22.2	3	0.475
	9	0.419	18.5	1	0.250
	10	0.483	27.0	2	0.195
3	11	0.728	1.0	Nil	0.795
	12	0.625	22.8	Nil	0.610
4	13	0.425	2.7	2	0.102
	14	0.620	0.8	1	0.212
	15	0.552	2.6	1	0.107
5	16	0.668	Nil	Nil	0.207
	17	0.506	6.4	Nil	0.125
	18	0.521	3.4	Nil	0.141
6	19	0.783	0.8	Nil	0.658
	20	0.584	48.9	Nil	0.238
	21	0.519	44.3	Nil	0.301

Sulfide

As shown in Table 3.9, sulfide concentrations in water sample from 21 DTW pump stations varied from 0 to 3 µg/L. It is interesting to note that sulfide was detected in all the seven wells located in Zone 2. Among the other samples, only those from Zone 4 showed presence of sulfide. According to Bangladesh standard (GOB, 1997), there should not be any sulfide in drinking water. So none of the water samples from Zones 2 and 4 satisfy the Bangladesh drinking water standard for sulfide. It may be mentioned that tanneries at Hazaribagh are located in Zone 2. Since tannery wastewater contain significant concentration of sulfide (see Chapter 4), sulfide in well waters from Zone 2 may result from discharge and subsequent leaching of tannery waste in the subsurface.

Ammonia

Ammonia (NH_4^+-NH_3) concentrations in water samples from 21 DTW pump stations varied from 0.021 mg/l to 0.795 mg/l. The lowest concentration was recorded for the well # 7 in Zone 2 and the highest concentration was recorded for well # 11 in Zone 3 (see Table 3.4). Ammonia concentrations were relatively higher in water samples from Zones 1, 3 and 6. In fact, two water samples from Zone 3 and one from Zone 6 exceeded the Bangladesh standard for drinking water.

3.5 CONCLUSIONS

Groundwater samples from 21 deep tubewell pump stations in six DWASA Zones, including the seven stations located in Hazaribagh area (Zone 2), were analyzed for detailed characterization.

Chromium concentrations in water samples from Zone 2 were found to be significantly higher than those from the other DWASA zones. Speciation data suggest that very little chromium is present in Cr^{6+} form and majority of dissolved chromium in groundwater is present in less toxic Cr^{3+} form. Out of 14 water samples from Zone 2, two exceeded the Bangladesh drinking water standard and WHO guideline value of 0.05 mg/l. Among the 14 water samples from other zones, none exceeded the Bangladesh standard. Average chromium concentration in water from the seven tubewells of Zone 2 is about 0.036 mg/l, about ten times higher than the average chromium concentration of 0.004 mg/l in water samples from 14 tubewells from 5 other zones. In the absence of any natural source of chromium and the presence of a large number of tanneries in the Hazaribagh area, it appears that chromium from tannery wastewater is already contaminating the groundwater in and around Hazaribagh area.

Besides chromium, concentration of sulfide was also found to be higher in the groundwater samples from Zone 2. Since tannery wastewater contains very high concentration of sulfide, presence of sulfide also appears to suggest the contamination of groundwater in Hazaribagh area from tannery wastewater.

Apart from chromium, alarmingly high lead concentrations were also detected in many of the DWASA groundwater samples. Lead concentrations in the tested groundwater samples were found to vary from 0.001 to 0.14 mg/l. Among the 21 samples, 17 exceeded the WHO guideline value (for drinking water) of 0.01 mg/l and two exceeded the Bangladesh drinking water standard of 0.05 mg/l.

Relatively higher concentrations of iron and manganese were detected in the water samples from Zone 2 (compared to the other DWASA zones), although most of these values satisfied the WHO and Bangladesh drinking water standards. Arsenic concentrations in DWASA groundwater samples were found to be negligible.

Except for ammonia, the 21 DWASA groundwater samples mostly satisfied the WHO and Bangladesh drinking water standards for the other parameters tested in this study (pH, chloride, TDS, color, turbidity, hardness, fluoride, nitrate, phosphate, and sulfate). Ammonia concentrations in the tested groundwater samples varied from 0.021 mg/l to 0.795 mg/l. Ammonia concentrations were relatively higher in water samples from Zones 1, 3 and 6; two water samples from Zone 3 and one from Zone 6 exceeded the Bangladesh standard for drinking water.

Chapter 4

SEDIMENT AND GROUNDWATER CONTAMINATION BY TANNERY EFFLUENTS

4.1 INTRODUCTION

Majority of the tannery industries is located in the Hazaribagh area in Dhaka near the Buriganga River. About 200 tanneries are processing leather in these industries, which account for most of the processed leather in Bangladesh. At present untreated wastewater from the tannery industries is discharged through open drains into a stagnant pond and finally into the Buriganga River through three outfalls. The stagnant pond area serves to retain the tannery wastewater for prolonged periods of time, allowing dissolved constituents (e.g., chromium) from the wastewater to percolate into the subsurface. Thus, wastewater from tannery industries can potentially contaminate the groundwater, particularly in the Hazaribagh area where the tanneries and wastewater discharge area are located. Wastewater from different industrial and commercial activities in the area also appears to mix with the tannery effluent before falling into the low-lying area. So wastewater falling into the low-lying area is a mixture of tannery effluent and wastewater from other industrial and commercial activities in the Hazaribagh area.

In order to assess the pollution potential of tannery wastewater, careful characterization of tannery wastewater is needed. Since the tannery wastewaters have been accumulating in the discharge area for a long time, characterization of the sediment samples in the discharge area would give an indication of the level of sediment contamination (particularly with chromium) in the discharge area. Characterization of sediment samples and groundwater samples in the discharge area would also give an indication of the vertical movement of chromium and other contaminants in the discharge area.

This chapter provides detailed characterization of wastewater from the tannery industries located at Hazaribagh. Variation in characteristics of wastewater samples collected from different locations has also been discussed. Sediment samples from two boreholes constructed at the wastewater discharge site have been analyzed for total chromium (and a number of other parameters) in order to assess the accumulation of chromium in the sediments at the discharge area. In addition groundwater samples collected from the boreholes have been analyzed for chromium and a wide range of other parameters for assessing possible contamination of groundwater from tannery wastewater. Results of these analysis reveals the present level of contamination and potential for future contamination of sediment and groundwater by tannery wastewater.

4.2 MATERIALS AND METHODS

4.2.1 Collection of Wastewater Samples

The wastewater generated from the tanneries at Hazaribagh area is discharged into the low-lying area located to the west of tannery industries (see Fig. 4.1 and Fig. 4.2). Wastewater generated from different industrial and commercial activities in the area also appears to mix with the tannery effluent before falling into the low-lying area. The wastewater accumulates in the low-lying area and finally flows through the Sluice Gate No. 7 (Fig. 4.3) of the flood protection embankment (near Z.H. Sikdar Women Medical College and Hospital), falls into the natural drainage outlet and eventually flows into the river Buriganga (Fig. 4.3).

In order to characterize the wastewater from the tannery industries, wastewater samples were collected from three different locations, as listed in Table 4.1. Wastewater sample collected from the first location (i.e., Hazaribagh Bazar outfall) represents the combined wastewater flow that fall into the low-lying area. Wastewater sample collected from second site (i.e., Gazmahal shikaritala) represents mainly wastewater coming from Chowdhury Leather Complex and partly coming from different industrial and commercial activities. Wastewater sample from the third site primarily represents wastewater coming from the Bengal Leather Complex.

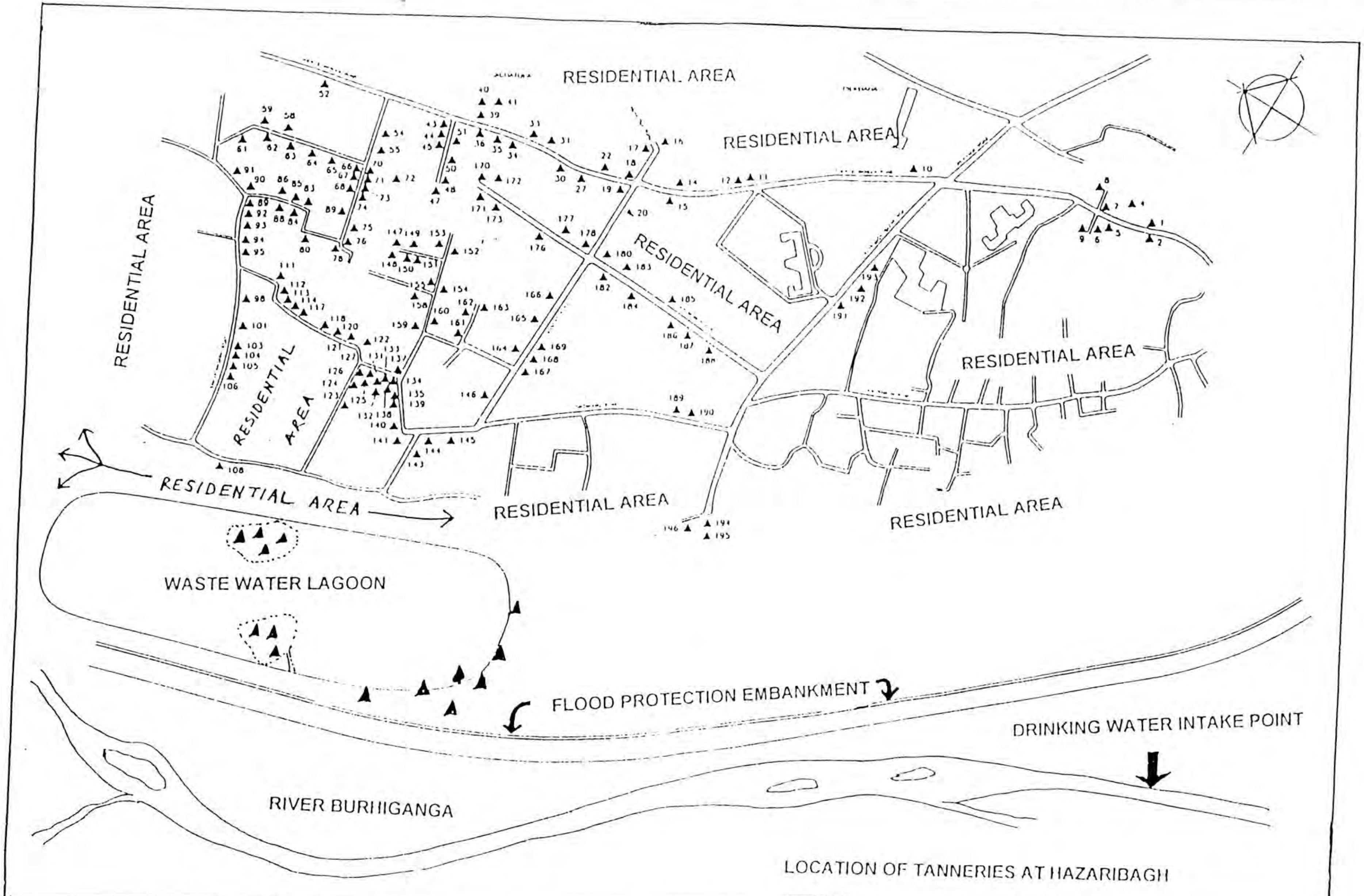

Figure 4.1 General Location of Tannery Industries and Wastewater Discharge Area at Hazaribagh

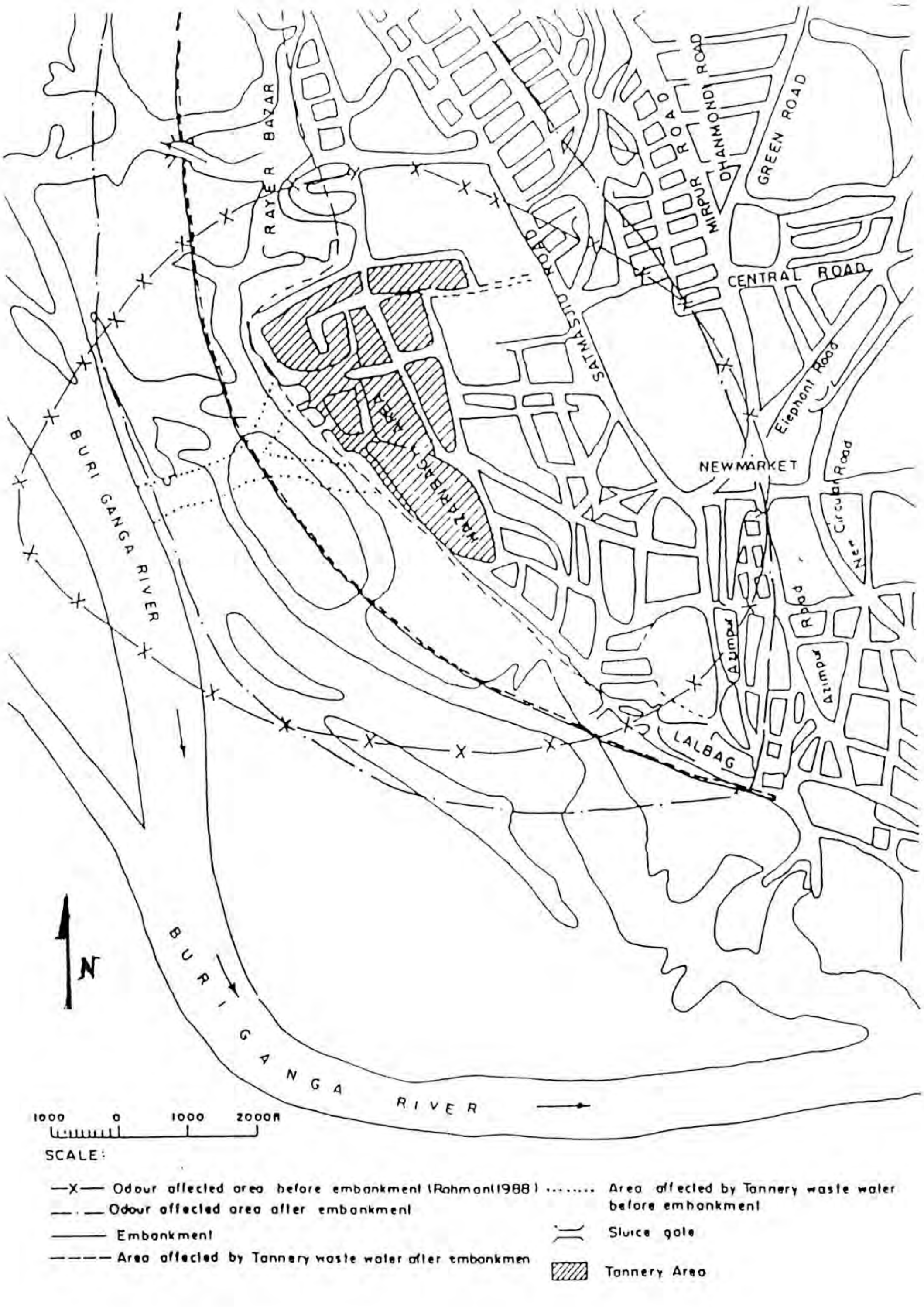

Figure 4.2 Map showing general location of Hazaribagh areas affected by tannery industries.

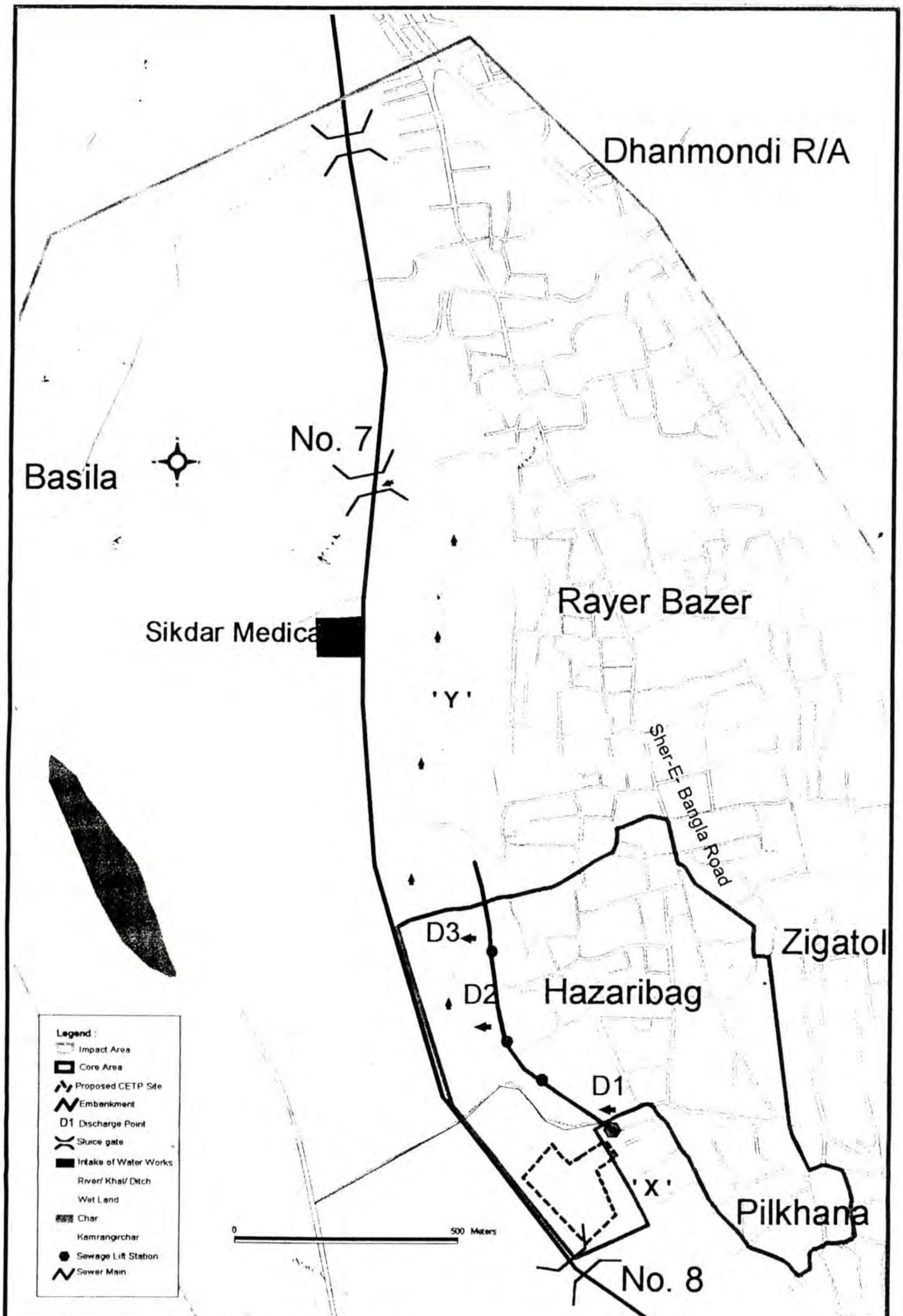

Figure 4.3 **Map showing flow path of tannery wastewater from the low-lying area at Hazaribagh through sluice gate No. 07**

Table 4.1 Locations of wastewater sampling points

Sample No.	Location	Date of Sampling
Sample No. 1	Hazaribagh Bazar outfall (N-23° 43.930", E-90° 21.949')	20-08-2000
Sample No. 2	Gazmahal, Shikaritala, Hazaribagh (N-23° 44.103', E-90° 21.707')	20-08-2000
Sample No. 3	Bengal Leather Complex Hazaribagh tannery More (N-23° 44.048', E-90° 22.042')	20-08-2000

Note : GPS used for measuring Latitude and Longitude.

4.2.2 Collection of Borehole Samples

As noted earlier, wastewater from tannery industries accumulate in the low-lying area, which serves to retain it for prolonged periods of time, allowing dissolved constituents (e.g., chromium) from the wastewater to percolate into the subsurface. In order to assess the accumulation of chromium in the sediment, two boreholes were constructed using wash boring method (see Table 4.2 for location) in the low-lying effluent discharge area at Hazaribagh. Both of these boreholes were constructed up to a depth of 100 feet and sediment samples were collected at 5 feet intervals. Boring operations conducted at the effluent discharge site at Hazaribagh have been shown in Figure 4.4 to 4.6. After collection, the sediment samples were immediately sealed in plastic bags (Fig. 4.7) and transported to the Environmental Engineering Laboratory for analysis.

It should be noted that boring operation in the effluent discharge area was extremely difficult. Most of the low-lying area was under a few feet of wastewater, which had accumulated over a few feet of sludge from the tannery effluent (see Fig. 4.8 & Fig. 4.9). Obnoxious smell of the tannery effluent was almost unbearable.

In order to compare the characteristics of sediment samples from Hazaribagh effluent discharge area and that from an uncontaminated area, borehole samples were also collected from the premises of Janata Housing Ltd. located at Shar-E-Bangla Nagar, Dhaka. At this location, borehole was constructed using wash boring method up to a depth of 90 feet.

Table 4.2 Locations of boreholes

Borehole Identification	Location of Borehole
Bore hole No.1	Hazaribagh bazar outfall
Bore hole No.2	Near flood protection dam
Bore hole No.3	Janata Housing Ltd. Shar-E-Bangla Nagar, Dhaka.

4.2.3 Collection of Groundwater Samples from Bore-holes

Efforts were made to collect groundwater samples from different depths of the two boreholes constructed at Hazaribagh. After drilling up to a particular depth, drilling operation was stopped for sometime for groundwater to accumulate at the bottom of the borehole. This water was then collected by pumping it to ground level (Fig. 4.10). However, this collected water was a mixture of groundwater (from that depth and the depths above it) and some of the water used by the drillers during the boring operation. Drillers used fresh water from Well No. 7 of Zone-2 (see Table 3.3) during boring operation. As a result, the groundwater samples do not represent the actual groundwater from the stated depths. However, groundwater sample collected from a particular depth is likely to consist of water mostly from that depth and as such is likely to provide a composition somewhat representative of that depth. In this study, groundwater samples were collected from three different depths (30, 60 and 90 feet) of the two boreholes constructed at Hazaribagh.

It should be noted that in order to collect groundwater from different specific depths, the ideal procedure is to construct peizometers, one for each depth. However, due to resource and time constraints, this could not be done as part of this research work.

4.2.4 Laboratory Analysis of Wastewater, Sediment and Groundwater Samples

Analysis of Wastewater Samples: Wastewater samples collected from the three locations were analyzed for a wide range of parameters including chromium, iron, lead, manganese, cadmium, copper, pH, color, turbidity, carbon-di-oxide, alkalinity, chloride, sulfide, sulfate, ammonia, nitrate, nitrite, phosphate, BOD_5, COD, total solids, total dissolved solids and total suspended solids.

Figure 4.4 **Photographs showing boring operation in the tannery wastewater disposal area at Hazaribagh (BH-1)**

Figure 4.5 Photographs showing boring operation in the tannery wastewater disposal area at Hazaribagh (BH-1)

Figure 4.6 **Photographs showing boring operation in the tannery wastewater disposal area at Hazaribagh (BH-2)**

Figure 4.7 Photographs showing collection of the sediment sample

Figure 4.8 **Photographs showing effluent discharge area (from Hazaribagh Bazar outfall side)**

Figure 4.9 Photographs showing effluent discharge area (from embankment side)

Figure 4.10 Photographs showing collection of ground water sample

To analyze for heavy metals (chromium, lead, cadmium, copper), wastewater samples were digested in order to convert all the metallic forms into dissolved ionic state. For digesting, 2.5 ml of diluted nitric acid (1:3) and 7.5 ml of diluted hydrochloric acid (1:3) were added to100 ml sample. The acidified samples were kept overnight and then digested for two hours under reflux conditions. Afterwards the cooled samples were filtered, and the volume of the filtrate was adjusted to 100 ml with de-ionized water. The sample was then ready for analysis using AAS (Atomic Adsorption Spectrophotometer).

Chromium concentrations in the water samples were measured with an atomic absorption (flame) spectrophotometer (Shimadzu Corporation Model No. AA 680). A sample "standard curve" for chromium is given in Appendix A (Fig. A1). Lead, Cadmium and Copper concentration was also measured with the atomic absorption spectrophotometer. Manganese concentration was measured using the PAN method using a spectrophotometer (HACH, DR4000U), and iron concentration was measured using the thiocyanate colorimetric method.

In this study, pH of the wastewater samples was measured using a pH meter (HACH). Turbidity was measured using a standard turbidity meter. Alkalinity, carbon-di-oxide, total solids, total dissolved solids, total suspended solids, BOD_5 and COD were determined by volumetric methods following Standard Methods (AWWA, 2000). Chloride concentration was measured using silver nitrate titrimetric method. Color, ammonium, nitrate, nitrite, fluoride, sulfate, sulfide, and phosphate concentrations were determined with a spectrophotometer (HACH, DR4000U). Ammonium was determined using Nessler method, manganese concentration by PAN method, nitrate by the cadmium reduction method, and phosphate by the molybdenum blue method. Filtered samples were used in this study for analysis of nitrate, nitrite, ammonia, sulfate, manganese, and phosphate.

Analysis of Sediment Samples: Sediment samples collected from the three boreholes were analyzed for pH, total chromium, and lead. The pH values were measured using the pH indicator paper (Universal Indicator pH 1-10, MERCK). Total chromium and lead concentrations of the sediment samples were determined by extracting these metals from the sediments and then analyzing the extractants for chromium and lead using an

Atomic Absorption Spectrophotometer (Shimadzu Model No. AA 680). The extraction procedure used in this study is summarized below.

Extraction of metal from sediment samples: Sediment samples from different specific depths were digested in order to convert all the metallic forms into dissolved ionic state. For digesting, a particular sediment sample was first dried in an oven at 105 °C for 24 hours and then grinded to get a uniform mixture of sediment. Then nitric acid (2.5 ml) and hydrochloric acid (7.5 ml), mixed in a ratio of one to three, were added to 1 gm of well-mixed oven-dried sediment sample. The sediment sample was kept in this condition overnight and then it was digested for two hours under reflux conditions. Afterwards the cooled sample was filtered, the residue was washed with warm nitric acid and the filtrate was made upto the mark of 100ml with de-ionized water. The sample was then ready for analysis using AAS (Atomic Adsorption Spectrophotometer). The metal content of the sediment sample in mg/kg of dry weight was then calculated according to the following relationship:

$$M_s = C_s \times (L_s / W_s) \times 1000$$

where,

M_s = Metal concentration in mg/kg in soil sample of sediment column

C_s = Metal concentration in ppm (or mg/l) found using AAS

L_s = Volume of sample in liter (0.10 liter in this case)

W_s = Mass of sediment in gm (1.0 gm in this case)

Analysis of Groundwater Samples: Groundwater samples were collected from three different depths (30, 60 and 90 feet) from each of the two boreholes constructed at the effluent discharge area at Hazaribagh. Six groundwater samples collected from the two bore-holes were analyzed for a wide range of parameters including, chromium, iron, lead, manganese, cadmium, copper, pH, color, turbidity, carbon-di-oxide, alkalinity, chloride, sulfide, sulfate, ammonia, nitrate, nitrite, phosphate, BOD_5, COD, total solids, total dissolved solids and total suspended solids.

Chromium concentrations in the water samples were measured with an atomic absorption (flame) spectrophotometer (Shimadzu Model No. AA 680). A sample "standard curve" for chromium is given in Appendix A (Fig. A1). Lead, Cadmium and

Copper concentration was also measured with the atomic absorption spectrophotometer. Manganese concentration was measured using the PAN method using a spectrophotometer (HACH, DR4000U), and iron concentration was measured using the thiocyanate colorimetric method.

The pH values were measured using a pH meter (Hach) and turbidity was measured using a standard turbidity meter. Alkalinity, carbon-di-oxide, total solids, total suspended solids, total dissolved solids, BOD_5 and COD were determined by volumetric methods following Standard Methods (AWWA, 2000). Chloride was measured using silver nitrate titrimetric method. Color, ammonium, nitrate, nitrite, fluoride, sulfate, sulfide, and phosphate concentrations were determined with a spectrophotometer (HACH, DR4000U). Ammonium was determined using Nessler method, nitrate by the cadmium reduction method, and phosphate by the molybdenum blue method.

4.3 RESULTS AND DISCUSSION

4.3.1 Characteristics of Tannery Effluent and its Pollution Potential

Table 4.3 shows characteristics of tannery effluent collected from three different sampling locations. Variation in wastewater characteristics presented in Table 4.3 probably represents the variation in sampling locations. As mentioned earlier, Wastewater Sample-1 collected from the first Hazaribagh Bazar outfall represents the mixture of wastewater (from tannery industries and other industrial/commercial activities) flow that falls into the low-lying area. Wastewater Sample-2 collected from Gazmahal Shikaritala represents mainly wastewater coming from Chowdhury Leather Complex and partly coming from different industrial and commercial activities; while Wastewater Sample-3 primarily represents wastewater coming from the Bengal Leather Complex.

With a few exceptions (e.g., chloride, sulfide, TDS, ammonia, lead and phosphate), concentrations of most of the parameters in Sample-1 are lower compared to those in the other two wastewater samples. This is probably due to the fact that Sample-1 represents the combined wastewater flow while the other two represent primarily those coming out from two tannery industries. In Sample-2, concentrations of BOD_5, COD, chromium,

NO_3, TS, alkalinity, cadmium, copper and manganese are higher than those in Sample-1 and Sample-3. On the other hand, in Sample-3, concentration of Sulfide, TSS, NH_3, SO_4 and Fe are higher than those in the other two samples.

Table 4.3 Characteristics of Tannery Effluent

Parameters	Unit	Sample-1 Hazaribagh Bazar Outfall	Sample-2 Gazmahal, Shikaritala, Hazaribagh	Sample-3 Bengal Leather Complex	Criteria for discharge into surface water body (ECR,1997)
BOD_5	mg/l	1080	22400	10400	50
COD	mg/l	1560	24800	15800	200
Chloride	mg/l	1300	1620	960	600
Total Chromium	mg/l	11.195	74.157	18.981	0.5
Chromium (VI)	mg/l	0.100 (*) 0.111 (*)	--	--	--
Sulfide	mg/l	180	46	5040	1
Total Solids	mg/l	6013	11374	7721	-
TSS	mg/l	1078	23.06	5010	150
TDS	mg/l	4935	9068	2711	2100
NO_2-N	mg/l	0.182	0.384	0.36	-
NO_3-N	mg/l	10	15	20	10
NH_3-N	mg/l	86.2	170.7	1003.2	50
Sulfate	mg/l	770	1142	4648	
pH	mg/l	7.6	8.6	5.4	6.9
Alkalinity as $CaCO_3$	mg/l	754	1358	820	-
Cadmium	mg/l	0.0119	0.022	0.0152	0.05
Lead (Pb)	mg/l	0.1091	0.1529	0.1051	0.1
Iron (Fe)	mg/l	1.9708	2.3235	8.4914	2
Copper (Cu)	mg/l	0.1829	0.2265	0.2177	0.5
Manganese	mg/l	0.07	0.08	0.08	5
CO_2	mg/l	Nil	Nil	Nil	-
Phosphate	mg/l	2.28	2.01	1.79	8.0
Color	Pt.-Co.	800	1120	792	-
Turbidity	NTU	26.8	28.6	792	-

(*) Samples collected on a different date.

Very high chromium concentration was detected in the wastewater samples, varying from 11.2 to 74.2 mg/l. It should be noted that Rahman (1997) reported characteristics of wastewater (collected directly from industries and not from wastewater drains) from 47 tannery industries (data provided in Appendix B). Chromium concentrations reported by Rahman (1997) appears to be significantly higher (reaching as high as 4043 mg/l for one industry) compared to those found in this study. This is primarily due to the fact that data reported by Rahman (1997) represent characteristics of wastewater collected directly from tannery industries, whereas in this study wastewater samples were collected from open drains carrying the combined flow of tannery effluent and water/wastewater from a variety of other sources. The same is also true for chloride; data reported by Rahman (1997) show significantly higher chloride concentration compared to those found in this study. The differences are not as dramatic for other parameters. This probably suggests that these other constituents in the wastewater are also contributed by other industrial and commercial activities in the area; whereas chromium and chloride are primarily contributed by the tannery effluents.

As shown in Table 4.3, two wastewater samples were also analyzed for chromium (VI) and the results suggest that very little chromium is present in Cr(VI) form and most of the chromium in the wastewater samples are present in Cr(III) form.

As shown in Table 4.3, with a few exceptions (e.g., chloride, nitrate, iron), concentrations of most of the parameters in all three wastewater samples exceed the criteria set by Bangladesh Environment Conservation Regulation (ECR) 1997 for discharge into surface water bodies. This is particularly true for BOD_5, COD, Chromium and Sulfide. Therefore, results from this study as well as previous studies clearly suggest that the tannery effluents have high pollution potential and must be treated before disposal.

4.3.2 Chromium in the Sediments at the Discharge Site

As described above, two boreholes were constructed at the tannery wastewater discharge site at Hazaribagh. Table 4.4 shows concentration of chromium in sediment samples collected from these two boreholes as a function of depth. Figure 4.11 & 4.12 also shows the distribution of chromium in the sediment samples as a function of depth. Table 4.4, Figure 4.11 & 4.12 clearly show very high accumulation of chromium of the top sediment at the wastewater discharge site at Hazaribagh. The sediment samples from borehole-1 located near Hazaribagh Bazar outfall showed significantly higher levels of chromium compared to the samples from borehole-2. This is probably due to the fact that borehole-1 is located very close to the point where wastewater first fall (from the open drains that carry tannery wastewater) in the low-lying area; while borehole-2 is located about a kilometer away from this site. Table 4.4 also shows chromium concentration in borehole samples from an uncontaminated area in Dhaka. It shows that the top sediment from Hazaribagh wastewater discharge area contain chromium almost two orders of magnitude higher than this uncontaminated area.

At borehole-1, the first 10 feet appears to be most contaminated, with chromium concentration in the sediment reaching close to 15,000 mg/kg of sediment. There appears to be a sharp drop of chromium concentration in the sediment below 10 feet depth. At borehole-2, the top ten feet also appears to be the most contaminated, although the chromium levels here are significantly lower that those at borehole-1. Similar to borehole-1, there appears to be sharp drop in chromium concentration in sediments below 10 feet depth.

Table 4.4 Chromium Concentration in Borehole Sediment Samples

Depth (ft)	Chromium in Borehole-1[a] (mg/kg)	Chromium in Borehole-2[b] (mg/kg)	Depth (ft)	Chromium in Borehole-3[c] (mg/kg)
0	8267.5	2505.10	0	67.49
2	14265.5	2404.0	5	52.34
4	14848.75	125.3	10	41.04
6	4349.10	138.4	15	37.29
8	4482.25	177.6	25	34.52
10	4467.25	235.0	30	30.27
15	75.20	45.5	35	50.83
20	74.43	42.7	40	54.59
25	39.72	38.8	50	42.09
30	35.32	38.0	55	28.77
40	56.53	42.0	70	53.13
50	37.57	41.6	80	19.30
60	50.16	33.0	90	18.20
70	33.42	30.0	-	-
80	23.11	42.5	-	-
90	27.5	44.1	-	-
100	34.48	45.8	-	-

[a] Located near Hazaribagh bazar outfall
[b] Located near flood protection dam
[c] Located at Sher-e-Bangla Nagar (uncontaminated area)

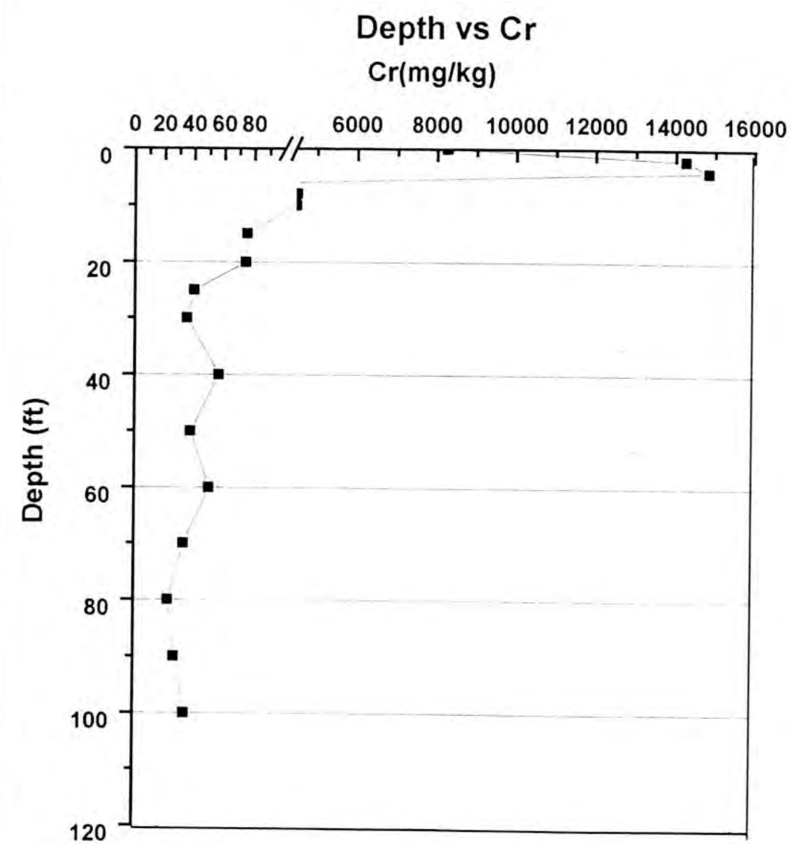

Figure 4.11 Distribution of Chromium in Borehole Sediment Samples Collected from Hazaribagh (BH-1)

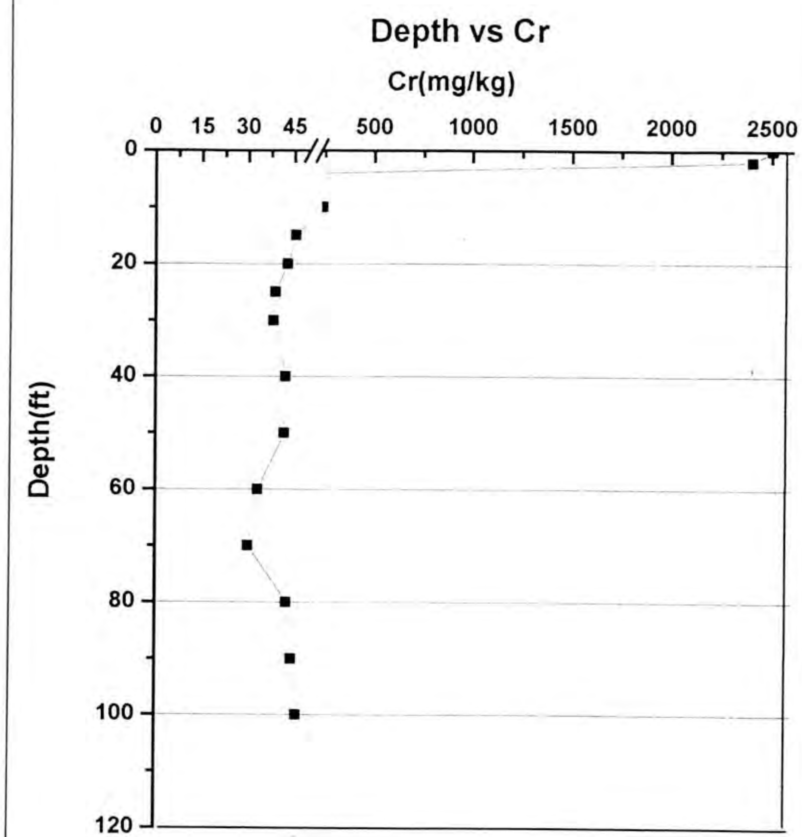

Figure 4.12 Distribution of Chromium in Borehole Sediment Samples Collected from Hazaribagh (BH-2)

It should be noted that at borehole-1, sediment samples from surface to a depth of about 4 feet were basically accumulated sludge; while at borehole-2 sediment samples of the first two to three feet represented accumulated sludge. Table 4.4, Figure 4.11 & 4.12 thus suggest that chromium from accumulated sludge and wastewater has penetrated into the soil below. However, the accumulation of chromium in the sediments appears to be restricted primarily to the first 10 feet of soil. This is not surprising because, as discussed earlier, most of the chromium in the tannery wastewater is present in Cr(III) form and Cr(III) generally is not transported to great distances by groundwater because of its low solubility. The low solubility of the Cr(III) solid phases [e.g., $Cr_2O_3(s)$] is the major reason why Cr(III) rarely occurs at concentrations above the drinking water standard of 0.05 mg/l (Hem, 1977). In addition, Cr(III) is also bound by a variety of ligands (e.g., soil organic matter) that render it insoluble, immobile, and un-reactive. Cr(III), as well as Cr(VI), can also be rendered immobile by adsorption on iron oxy-hydroxides in the sediment. However, groundwater with low levels of Cr(III), leached from chromium contaminated sediments, can still move downward and slowly contaminate the aquifer below. Detection of higher levels of chromium in groundwater samples (from DTWs) located in the Hazaribagh area probably suggests that such a process is actually taking place. It may be possible to estimate how much chromium in the sediment samples are present in easily-mobilized form through sequential extraction of chromium from the sediments with different extractants, but such an analysis was beyond the scope of the study.

It should be noted that chromium (III) can form highly soluble organic complexes in the laboratory, particularly under acidic conditions (Bartlett and Kimble, 1976a; James and Bartlett, 1983a). Thus, if it is in a complexed form, Cr(III) may exist at much higher concentrations in groundwater than if it is uncompelxed. However, the existence of Cr(III) complexes has not been documented under field conditions.

The small amount of Cr(VI) present in tannery wastewater is also likely to be quickly reduced to Cr(III) after discharge. Chromium(VI) transported by groundwater is transformed to and precipitated as Cr(III) if the groundwater enters a low redox zone. Laboratory studies have shown that Cr(VI) can be reduced readily to Cr(III) in the presence of organic matter, especially at low pH (Bartlett and Kimble, 1976b; Bloommfield and pruden, 1980). Schroeder and Lee (1975) found that Cr(VI) could also be reduced by Fe(II) and dissolved sulfides. High concentration of organic matter in tannery wastewater and presence of dissolved iron [Fe(II)] and sulfide suggest that Cr(VI) present in groundwater would be quickly be reduced to Cr(III).

It is possible for Cr(III) to be converted to the more soluble Cr(VI) if the redox state at a particular region in the subsurface becomes oxidizing. Chromium (III) has been found to be oxidized by manganese under natural conditions (Bartlett and James, 1979; Schroeder and Lee, 1975). However, there is no evidence that such oxidation is taking place in the subsurface at Hazaribagh site.

4.3.3 Lead and pH of Sediments at the Discharge Site

Table 4.5 shows pH values and concentration of lead in the borehole sediments samples from the two boreholes at Hazaribagh site. Figure 4.13 & 4.14 also shows lead concentration in the borehole samples. Table 4.6 shows pH and lead concentration is sediment samples from an uncontaminated site in Dhaka. As shown in Table 4.5 and Figure 4.13, very high concentration of lead was found in the top sediments at borehole-1. As was the case for chromium, high concentration of lead was restricted to the first ten feet of sediment where chromium concentration varied from about 105 to 211 mg/kg of soil. Unlike borehole-1, sediment samples from borehole-2 did not show presence of high levels of lead. In fact, lead concentrations in sediments from borehole-2 were comparable to those found in the uncontaminated sediments from borehole-3. As explained earlier, the lower level of lead in sediments from borehole-2 is probably due to the fact that it is located far away from the point where wastewater first fall (from the open drains that carry tannery wastewater) in the low-lying area, about a kilometer away from borehole-1. It appears that majority of the lead is either adsorbed or precipitated before reaching the location around borehole-2. In the Hazaribagh area, two paint industries (Roxy Paint and Pailac Paint), one Glue industry (Brothers Chemical Ltd.) and about 70 manually operated glue factories were identified. These industries are likely to contribute to the pollution problem at Hazaribagh. For example, the paint industries may be responsible for higher lead in combined wastewater and groundwater in the area.

Table 4.5 Lead Concentration and pH of Borehole Sediment Samples from Hazaribagh

Depth (ft)	pH in Borehole-1[a]	Lead in Borehole-1[a] (mg/kg)	pH in Borehole-2[b]	Lead in Borehole-2[b] (mg/kg)
0	8.5	210.93	--	--
2	7.5	180.69	8.0	31.82
4	7.5	174.65	7.5	30.48
6	6.0	186.05	8.0	30.68
8	6.5	136.47	7.5	25.96
10	7.5	105.49	7.5	13.50
15	--	--	6.0	15.29
20	6.5	22.48	6.0	15.87
25	6.5	14.35	6.0	20.31
30	6.5	30.35	6.0	20.56
40	7.0	11.43	6.5	12.29
50	6.5	25.16	6.0	20.77
60	6.0	40.74	5.5	16.21
70	6.0	23.56	5.5	13.55
80	6.5	10.28	7.0	13.71
90	6.5	12.13	7.0	12.80
100	6.5	8.65	7.5	28.61

[a] Located near Hazaribagh bazar outfall
[b] Located near flood protection dam

As discussed earlier, the tannery wastewater contains relatively high concentrations of lead. In addition, lead may also be present in the wastewater coming from other industrial activities in the Hazaribagh area. Thus high level of lead accumulated in the sediments also appears to be coming from the wastewater, which is being discharged in the low-lying area of Hazaribagh.

Table 4.5 shows pH values of sediment samples from Hazaribagh area, while Table 4.6 shows pH values of sediment samples from an uncontaminated site in Dhaka. From these data it appears higher levels of chromium in the sediments are, in general, associated with somewhat higher pH values.

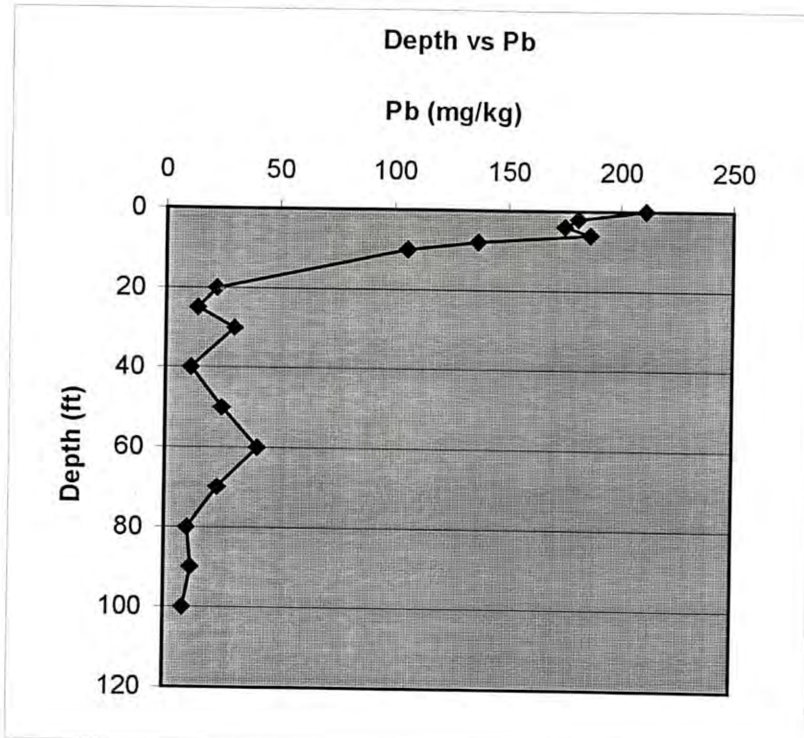

Figure 4.13 Distribution of Lead in Borehole Sediment Samples Collected from Hazaribagh (BH-1)

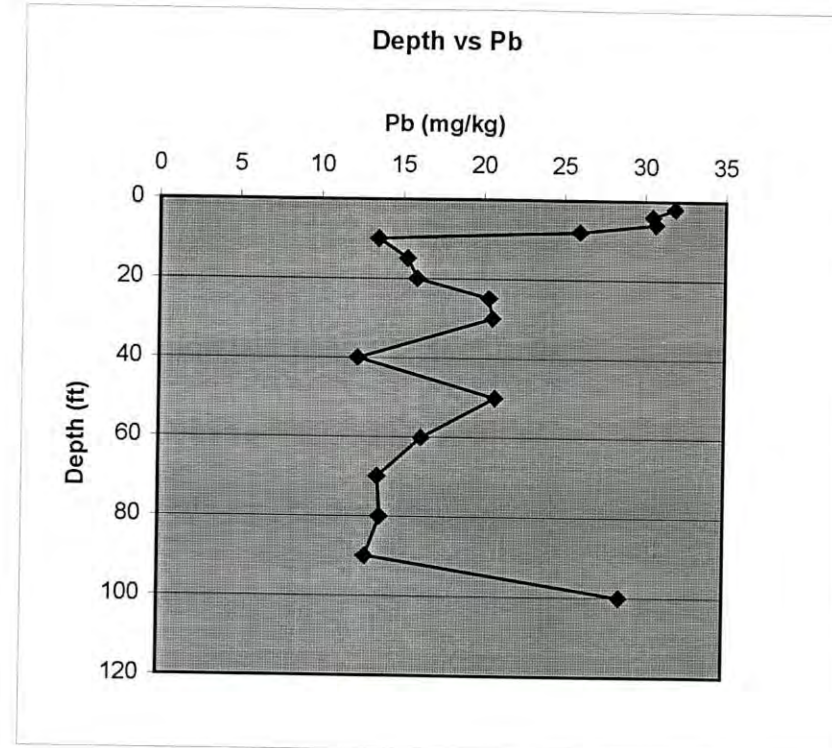

Figure 4.14 Distribution of Lead in Borehole Sediment Samples Collected from Hazaribagh (BH-2)

Table 4.6 Lead Concentration and pH of Borehole Sediment Samples from an Uncontaminated Site in Dhaka

Depth (ft)	pH in Borehole-3[c]	Lead in Borehole-3[c] (mg/kg)
0	6.0	46.10
5	6.0	42.27
10	6.0	41.96
15	6.0	35.05
25	5.5	39.20
30	6.0	33.44
35	5.5	18.37
40	5.5	14.20
50	6.0	16.28
55	6.5	18.92
70	6.0	9.58
80	6.5	19.28
90	6.5	17.39

[c] Located at Sher-e-Bangla Nagar (uncontaminated area)

4.3.4 Characteristics of Groundwater

As mentioned earlier, groundwater collected from the boreholes at the Hazaribagh site were actually mixture of groundwater (from that depth and the depths above it) and some of the water used by the drillers during the boring operation. As a result, the groundwater samples do not represent the actual groundwater from the stated depths. However, groundwater sample collected from a particular depth is likely to consist of water mostly from that depth and as such is likely to provide a composition somewhat representative of that depth.

Table 4.7 shows characteristics of groundwater collected from the borehole samples at the Hazaribagh site. High levels of chromium exceeding the drinking water standard of 0.05 mg/l were detected in the groundwater samples from 30 feet and 60 feet depths at borehole-1. Except for one sample (90 feet depth in borehole-2), lead concentration in all the groundwater samples exceeded the WHO guideline value of 0.01 mg/l. Thus groundwater in shallow depths at the Hazaribagh wastewater discharge area appears to be contaminated with high levels of chromium as well as lead. However, more careful sampling is needed to ascertain the concentrations of chromium, lead and other water quality parameters in the groundwater.

Table 4.7 Characteristics of Groundwater Samples Collected from Boreholes at Hazaribagh

Parameter	Unit	BH-1[a] (30 ft)	BH-1[a] (60 ft)	BH-1[a] (90 ft)	BH-2[b] (30 ft)	BH-2[b] (60 ft)	BH-2[b] (90 ft)
pH	--	7.30	8.0	7.7	8.0	8.0	7.8
Colour	Pt-Co	45.0	520	73	348	199	13
Turbidity	NTU	308.0	135	84	800	600	610
CO_2	mg/l	5.00	14.3	5.5	6.9	5	1.8
Chloride	mg/l	20.5	116	6.8	118	5	4
Alkalinity	mg/l	43.9	42.3	28.9	110.8	69.8	6.1
Hardness	mg/l	621.0	185	77	147	112	96
Iron	mg/l	0.08	2.00	0.20	0.08	0.40	0.20
NO_3	mg/l	0.20	0.20	0.30	0.30	0.50	0.20
F	mg/l	0.50	0.40	0.27	0.83	Nil	0.15
PO_4	mg/l	0.291	2.044	0.425	0.351	0.287	0.501
Mn	mg/l	0.102	0.344	0.307	0.585	0.166	-
Total Cr	mg/l	0.076	0.057	0.003	0.017	0.027	0.006
Lead (Pb)	mg/l	0.013	0.035	0.044	0.027	0.017	0.007
Arsenic (As)	µg/L	8.474	12.06	7.17	11.73	9.29	10.43

[a] Borehole-1 located near Hazaribagh Bazar outfall
[b] Borehole-2 located near flood protection dam

4.4 CONCLUSIONS

In order to characterize the wastewater from the tannery industries, wastewater samples were collected from three different locations and analyzed for a wide range of parameters including Chromium, BOD_5, COD, Sulfide and Chloride. Variation in characteristics among these wastewater samples probably resulted from the variation in sampling locations. Very high chromium concentration [mostly present as Cr(III)] was detected in the wastewater samples, varying from 11.2 to 74.2 mg/l. However, these values were relatively low compared to those reported by Rahman (1997). This is primarily due to the fact that data reported by Rahman (1997) represent characteristics of wastewater collected directly from tannery industries, whereas in this study wastewater samples were collected from open drains carrying the combined flow of tannery effluent and water/wastewater from a variety of other sources. Besides chromium, the wastewater samples contained very high concentration of BOD_5, COD, Sulfide, TS, TSS, and Ammonia. With a few exceptions, concentrations of most of the parameters in all three wastewater samples exceeded the criteria set by Bangladesh Environment Conservation Regulation (ECR) 1997 for discharge into surface water bodies. Therefore, results from this study as well as previous studies clearly suggest that the tannery effluents have high pollution potential and must be treated before disposal.

Two boreholes were constructed at the tannery wastewater discharge site at Hazaribagh and the borehole samples were analyzed for chromium, lead and pH. Very high accumulation of chromium (reaching close to 15,000 mg/kg of sediment) was detected of the top layers of sediment. The sediment samples from the borehole located near Hazaribagh Bazar outfall showed significantly higher levels of chromium, probably due to the fact that this borehole was located very close to the point where wastewater fist fall in the low-lying area; while the other borehole was located about a kilometer away from this site.

Results from this study suggest that chromium from accumulated sludge and wastewater has penetrated into the soil below. However, the accumulation appears to be restricted primarily to the first 10 feet of soil. This is not surprising because, as discussed earlier, most of the chromium in the tannery wastewater is present in Cr(III) form and Cr(III) generally is not transported to great distances by groundwater because of its low solubility. In addition, Cr(III) is also bound by a variety of ligands (e.g., soil organic matter) that render it insoluble, immobile, and un-reactive. Cr(III), as well as Cr(VI), can also be rendered immobile by adsorption on iron oxy-hydroxides in the sediment. However, groundwater with low levels of Cr(III), leached from chromium contaminated sediments, can still move downward and slowly contaminate the aquifer below. Detection of higher levels of chromium in groundwater samples (from DTWs) located in the Hazaribagh area probably suggests that such a process is actually taking place. It may be possible to estimate how much chromium in the sediment samples are present in easily-mobilized form through sequential extraction of chromium from the sediments with different extractants, but such an analysis was beyond the scope of the study.

The small amount of Cr(VI) present in tannery wastewater is also likely to be quickly reduced to Cr(III) after discharge. Laboratory studies have shown that Cr(VI) can be reduced readily to Cr(III) in the presence of organic matter, especially at low pH; Cr(VI) could also be reduced by Fe(II) and dissolved sulfides. High concentration of organic matter in tannery wastewater and presence of dissolved iron [Fe(II)] and sulfide suggest that Cr(VI) present in groundwater would be quickly be reduced to Cr(III). It is possible for Cr(III) to be converted to the more soluble Cr(VI) if the redox state at a particular region in the subsurface becomes oxidizing. However, there is no evidence that such oxidation is taking place in the subsurface at Hazaribagh site.

Very high concentration of lead was found in the top sediment samples from the borehole located close to the first point of discharge. This lead may come from the tannery effluents as well as from other industrial and commercial activities in the Hazaribagh area. Thus high level of lead accumulated in the sediments also appears to be coming from the wastewater, which is being discharged in the low-lying area of Hazaribagh.

High levels of chromium exceeding the drinking water standard of 0.05 mg/l were detected in the groundwater samples collected from the boreholes. In addition, lead concentration in four out of five groundwater samples exceeded the WHO guideline value of 0.01 mg/l. Thus groundwater in shallow depths at the Hazaribagh wastewater discharge area appears to be contaminated with high levels of chromium as well as lead. However, more careful sampling is needed to ascertain the concentrations of chromium, lead and other water quality parameters in the groundwater.

Chapter 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

The major objective of this thesis was to assess the ground water contamination in Dhaka City from untreated tannery wastewater containing high concentrations of chromium and other pollutants. In order to assess the quality of groundwater extracted by DWASA and to detect possible contamination by tannery wastewater, groundwater samples from 21 deep tubewell pump stations in six DWASA Zones, including the seven stations located in Hazaribagh area (Zone 2), were collected and analyzed for detailed characterization. Major conclusions derived from the analysis of these results are summarized below.

- Chromium concentrations in water samples from Zone 2 were found to be significantly higher than those from the other DWASA zones. Out of 14 water samples from Zone 2, two exceeded the Bangladesh drinking water standard and WHO guideline value of 0.05 mg/l. Average chromium concentration in water from the seven tubewells of Zone 2 is 0.036 mg/l, about ten times higher than the average chromium concentration of 0.004 mg/l in water samples from 14 tubewells from 5 other zones.

- In the absence of any natural source of chromium and the presence of a large number of tanneries in the Hazaribagh area, it appears that chromium from tannery wastewater is already contaminating the groundwater in and around Hazaribagh area.

- Little chromium is present in hexavalent (Cr^{6+}) form and majority of dissolved chromium in groundwater is present in less toxic trivalent (Cr^{3+}) form.

- Sulfide was detected in all the 7 groundwater samples collected from Zone 2. Since tannery wastewater contains very high concentration of sulfide, presence of sulfide also appears to suggest contamination of groundwater in Hazaribagh area from tannery wastewater.

- Apart from chromium, alarmingly high lead concentrations were also detected in many of the DWASA groundwater samples. Among the 21 samples, 17 exceeded the WHO guideline value (for drinking water) of 0.01 mg/l and two exceeded the Bangladesh drinking water standard of 0.05 mg/l.

In order to assess the pollution potential of tannery effluent, wastewater samples were collected from three different locations and analyzed for a wide range of parameters.

- Characteristics of wastewater vary significantly depending on the location of sampling (as well as time of sampling). The combined wastewater that is discharged into the low-lying area at Hazaribagh comprises of tannery wastewater as well as wastewater from a number of other industrial/commercial activities in the area. In general, the wastewater samples collected in this study primarily represent the combined wastewater (as opposed to wastewater from a particular tannery industry). Major findings are summarized below.

- Very high chromium concentration [mostly present as Cr(III)] was detected in the wastewater samples, varying from 11.2 to 74.2 mg/l.

- Besides chromium, the wastewater samples contained very high concentration of BOD_5, COD, Sulfide, TS, TSS and Ammonia.

- Concentrations of most of the parameters in all three wastewater samples exceeded the criteria set by Bangladesh Environment Conservation Regulation (ECR) 1997 for discharge into surface water bodies.

- Results from this study as well as previous studies clearly suggest that the tannery effluents have high pollution potential and must be treated before disposal.

Two boreholes were constructed at the tannery wastewater discharge site at Hazaribagh and the borehole samples were analyzed for chromium, lead and pH. Major findings derived from the analysis of borehole sediment samples are summarized below.

- Very high accumulation of chromium (reaching close to 15,000 mg/kg of sediment) was detected in the top layers of sediment. The sediment samples from the borehole located near Hazaribagh Bazar outfall showed significantly higher levels of chromium, probably due to the fact that this borehole was located very close to the point where wastewater fist fall in the low-lying area; while the other borehole was located about a kilometer away from this site.

- The accumulation of chromium appears to be restricted primarily to the first 10 feet of soil. This is probably due to the fact that most of the chromium in the tannery wastewater is present in Cr(III) form and Cr(III) generally is not transported to great distances by groundwater because of its low solubility. However, groundwater with low levels of Cr(III), leached from chromium contaminated sediments, can still move downward and slowly contaminate the aquifer below. Detection of higher levels of chromium in groundwater samples (from DTWs) located in the Hazaribagh area probably suggests that such a process is actually taking place.

- The small amount of Cr(VI) present in tannery wastewater is also likely to be quickly reduced to Cr(III) after discharge. Cr(VI) can also be rendered immobile by adsorption on iron oxy-hydroxides in the sediment.

- Very high concentration of lead was found in the top sediment samples from the borehole located close to the first point of discharge. This lead may come from the tannery effluents as well as from other industrial and commercial activities in the Hazaribagh area.

Groundwater samples from the boreholes were collected for detailed characterization. These samples were actually mixture of groundwater (from that depth and the depths above it) and some of the water used by the drillers during the boring operation.

- High levels of chromium exceeding the drinking water standard of 0.05 mg/l were detected in the groundwater samples collected from the boreholes.

- Lead concentration in four out of five groundwater samples exceeded the WHO guideline value of 0.01 mg/l.

- Thus groundwater in shallow depths at the Hazaribagh wastewater discharge area appears to be contaminated with high levels of chromium as well as lead. However, more careful sampling is needed to ascertain the concentrations of chromium, lead and other water quality parameters in the groundwater.

5.2 RECOMMENDATIONS

The major focus of this study was to assess groundwater contamination in Dhaka city from untreated tannery wastewater. From the results of this study, it appears that groundwater in Hazaribagh area is already contaminated with chromium from tannery wastewater. However, this study also suggests that long-term monitoring is required in order to ascertain the level of contamination. While this study focused on tannery wastewater, it appears that other industrial/commercial activities in Hazaribagh area may also contribute to the pollution problem in the area. This issue needs to be assessed in future study. Analysis of borehole samples conducted in this study revealed very useful information regarding the movement of chromium in the subsurface. However, more work is needed in order to have a better understanding of the processes affecting the fate and mobilization of chromium in the subsurface.

Major recommendations for continuation of the present work in the future are summarized below.

- Water samples from the seven DTW stations in Zone 2 were collected on two different occasions and there are significant variations in chromium concentrations in these two samples. Thus regular monitoring of groundwater quality from these as well as other DTW stations is needed to ascertain the level as well as variation in chromium concentration. In addition to chromium some other water quality parameters (e.g., sulfide) should also be monitored.

- The collected groundwater samples from boreholes were a mixture of groundwater (from that depth and the depths above it) and some of the water used by the drillers during the boring operation. Thus actual groundwater quality at shallow depths at Hazaribagh area could not be determined accurately. In order to collect groundwater from different specific depths, the ideal procedure is to construct peizometers, one for each depth. So in future study, construction of peizometer is needed to assess the groundwater at shallow depths at Hazaribagh.

- Detection of higher levels of chromium in groundwater samples (from DTWs) located in the Hazaribagh area probably suggests that chromium is being transported to the aquifer below. However, more work is needed to have a better understanding of the fate and transport of chromium in the subsurface. For example, it may be possible to estimate how much chromium in the sediment samples are present in easily-mobilized form through sequential extraction of chromium from the sediments with different extractants. Future investigations should carry out such analysis of sediment samples.

- From a quick survey in the Hazaribagh area, two paint industries (Roxy Paint and Pailac Paint), one Glue industry (Brothers Chemical Ltd.) and about 70 manually operated glue factories were identified. These industries are likely to contribute to the pollution problem at Hazaribagh. For example, the paint industries may be responsible for higher lead in combined wastewater and groundwater in the area. This issue should be assessed in any future study.

- Apart from chromium, alarmingly high lead concentrations were also detected in many of the DWASA groundwater samples. Among the 21 samples, 17 exceeded the WHO guideline value (for drinking water) of 0.01 mg/l and two exceeded the Bangladesh drinking water standard of 0.05 mg/l. This is a serious health concern and this issue should be assessed immediately. Along with chromium, lead concentration in DWASA water samples should be regularly monitored.

- In order to stop further deterioration of the environmental condition at the effluent discharge area at Hazaribagh, immediate steps should be taken for treatment of tannery wastewater before discharge into the environment.

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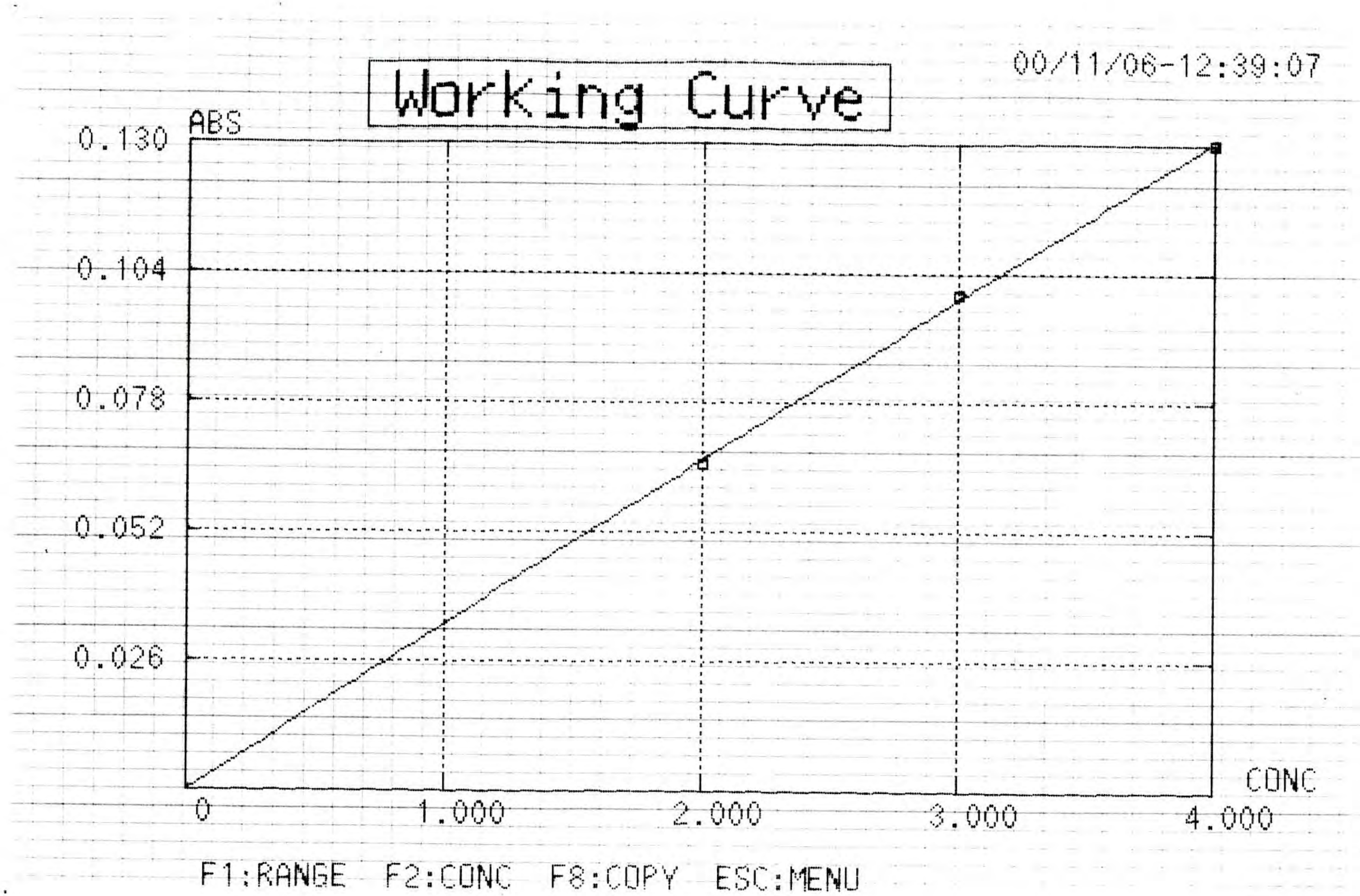
APPENDIX A

(Standard curve for chromium analysis using AAS)



Standard Curve of Chromium Analysis

APPENDIX B

Characteristics of Tannery Waste Water
(Source: Rahman, 1997)

ANALYSIS OF INDUSTRIAL WASTE WATER

TYPE OF INDUSTRY : *TANNERY*

TEST RESULT

SL. NO.	NAME OF INDUSTRY	LOCATION	Date of Sampling	Sample Received At BRTC	PARAMETER AND CONCENTRATION PRESENT							
					pH	BOD_5 mg/L	COD mg/L	Suspended Solids Mg/L	Sulphate (SO_4) mg/L	Sulphide mg/L	Nitrate (N) mg/L	Kjeldahl-N mg/L
1	Value tannery Ltd.	Dhaka	27/6/94	27/6/94	8.70	4200	8500	7525	446.40	40	---	---
2	Kalam Brothers Ltd.	Dhaka	27/6/95	27/6/94	11.30	9000	18200	22822	---	1500	---	---
3	Shahjalal Leather	Dhaka	25/6/94	25/6/94	8.90	600	13750	9068	298	65	---	---
4	Yusuf Leather Corp.	Dhaka	22/6/94	22/6/94	8.10	10800	16000	11489	806	400	---	---
5	Bay Tannery Ltd.	Dhaka	2/7/94	2/7/94	7.45	34800	49200	23081	3360	15	67.50	435
6	Bay Tannery Ltd.	Dhaka	17/7/94	17/7/94	4.50	0	300	4015	---	---	--	---
7	Bay Tannery Ltd.	Dhaka	17/7/94	17/7/94	8.40	1750	2400	6275	2947.50	---	---	1770
8	Bay Tannery Ltd.	Dhaka	18/7/94	18/7/94	7.70	2450	4800	5547	---	---	---	---
9	Bay Tannery Ltd.	Dhaka	18/7/94	18/7/94	11.00	3330	4100	6430	---	230	---	---
10	Bay Tannery Ltd.	Dhaka	17/7/94	17/7/94	4.50	350	2820	11269	1718.40	---	---	---
11	Apex Tannery	Dhaka	19/7/94	19/7/94	4.60	800	1320	4896	---	---	---	---
12	Apex Tannery	Dhaka	17/7/94	17/7/94	8.30	2400	3250	5406	2323.20	---	---	1350
13	Apex Tannery	Dhaka	19/7/94	19/7/94	3.90	1100	1500	4523	---	---	---	---
14	Apex Tannery	Dhaka	19/7/94	19/7/94	3.80	2200	5400	7498	---	---	---	---
15	Apex Tannery	Dhaka	9/7/94	19/7/94	4.50	10500	16500	8905	---	---	---	---
16	Apex Tannery	Dhaka	19/7/94	18/7/94	3.90	640	890	12408	2820	---	---	---

Contd......

ANALYSIS OF INDUSTRIAL WASTE WATER

TYPE OF INDUSTRY : *TANNERY*

TEST RESULT

SL. NO.	NAME OF INDUSTRY	LOCATION	Date of Sampling	Sample Received At BRTC	PARAMETER AND CONCENTRATION PRESENT							
					Kjeldahi-N (mg/L	Chloride (Cl) mg/L	Chromium (Cr) mg/L	Lead (pb) mg/L	Zinc (Zn) gm/L	Turbidity NTU	Colour TCU	Total Solids mg/L
1	Value tannery Ltd.	Dhaka	27/6/94	27/6/94	---	14500	7.70	0.09	0.56	---	---	---
2	Kalam Brothers Ltd.	Dhaka	27/6/94	27/6/94	---	30500	---	---	---	---	---	---
3	Shahjalal Leather	Dhaka	25/6/94	25/6/94	--	18750	101.60	0.57	1.02	---	---	---
4	Yusuf Leather Corp.	Dhaka	22/6/94	22/6/94	---	21000	2558	1.16	0.86	---	---	---
5	Bay Tannery Ltd.	Dhaka	2/7/94	2/7/94	435	41350	2865	0.758	0.728	---	---	---
6	Bay Tannery Ltd.	Dhaka	17/7/94	17/7/94	---	---	---	---	---	---	---	---
7	Bay Tannery Ltd.	Dhaka	17/7/94	17/7/94	1770	---	---	---	---	---	---	---
8	Bay Tannery Ltd.	Dhaka	18/7/94	18/7/94	---	13750	---	---	---	---	---	---
9	Bay Tannery Ltd.	Dhaka	18/7/94	18/7/94	---	---	---	---	---	---	---	22331
10	Bay Tannery Ltd.	Dhaka	17/7/94	17/7/94	---	---	3382	---	---	---	---	---
11	Apex Tannery	Dhaka	19/7/94	19/7/94	---	---	---	---	---	420	6000	14316
12	Apex Tannery	Dhaka	17/7/94	17/7/94	1350	---	---	---	---	---	---	---
13	Apex Tannery	Dhaka	19/7/94	19/7/94	---	---	---	---	---	195	7200	12389
14	Apex Tannery	Dhaka	19/7/94	19/7/94	---	---	---	---	---	1685	27500	23808
15	Apex Tannery	Dhaka	19/7/94	19/7/94	---	---	---	---	---	---	---	---
16	Apex Tannery	Dhaka	18/7/94	18/7/94	---	12500	3324	---	---	---	---	---

contd.....

ANALYSIS OF INDUSTRIAL WASTE WATER

TYPE OF INDUSTRY : *TANNERY*

TEST RESULT

SL. NO.	NAME OF INDUSTRY	LOCATION	Date of Sampling	Sample Received At BRTC	PARAMETER AND CONCENTRATION PRESENT							
					pH	BOD_5 mg/L	COD mg/L	Suspended Solids Mg/L	Sulphate (SO_4) mg/L	Sulphide mg/L	Nitrate (N) mg/L	Kjeldahl-N mg/L
17	Apex Tannery	Dhaka	17/7/94	17/7/94	6.80	150	370	3845	---	---	---	---
18	Apex Tannery	Dhaka	18/7/94	18/7/94	11.0	10500	12800	5609	---	150	---	---
19	Reliance Tanneries	Dhaka	2/7/94	2/7/94	4.1	1200	16800	24877	---	---	---	---
20	Orient Tanneries	Dhaka	---	2/7/94	4.9	8400	12500	23945	384	2	46	66
21	B. S. Leather	Dhaka	2/7/94	2/7/94	4.0	31200	38400	33637	---	---	---	---
22	Abul Khaer Tannery	Dhaka	4/7/94	4/7/94	9.8	28200	42200	25345	---	---	---	---
23	Amin Tannery	Dhaka	28/6/94	28/6/94	9.1	5100	14000	3344	432	500	700	---
24	Dhaka Hides & Skins	Dhaka	2/7/94	2/7/94	4.2	28800	51600	22535	---	---	---	---
25	Karim Tannery	Dhaka	3/7/94	3/7/94	9.5	36000	5640	20957	---	---	39.5	92
26	Noakhali Tannery	Dhaka	4/7/94	4/7/94	11.8	26400	40500	20267	---	---	---	---
27	Modina Tannery	Dhaka	3/7/94	3/7/94	11.2	10200	15000	9750	1017.6	350	49.5	72
28	Dhaka Tanneries Ltd.	Dhaka	3/7/94	3/7/94	8.3	32800	49500	16851	---	---	---	---
29	Gulshan Tannery	Dhaka	4/7/94	4/7/94	7.1	27000	40500	19360	---	---	---	95
30	Mohin Tannery	Dhaka	28/6/94	28/6/94	9.6	1500	6500	5992	220.8	85	550	---
31	Kid Tannery	Dhaka	29/6/94	29/6/94	10.9	3600	9300	5427	38.4	145	140	510
32	Helal Tannery	Dhaka	28/6/94	28/6/94	10.8	2100	7500	15746	739.2	450	650	---

Contd......

ANALYSIS OF INDUSTRIAL WASTE WATER

TYPE OF INDUSTRY : *TANNERY*

TEST RESULT

SL. NO.	NAME OF INDUSTRY	LOCATION	Date of Sampling	Sample Received At BRTC	PARAMETER AND CONCENTRATION PRESENT							
					Kjeldahi-N (mg/L	Chloride (Cl) mg/L	Chromium (Cr) mg/L	Lead (pb) mg/L	Zinc (Zn) gm/L	Turbidity NTU	Colour TCU	Total Solids mg/L
17	Apex Tannery	Dhaka	17/7/94	17/7/94	---	12500	---	---	---	---	---	---
18	Apex Tannery	Dhaka	18/7/94	18/7/94	---	---	---	---	---	---	---	---
19	Reliance Tanneries	Dhaka	2/7/94	2/7/94	---	32000	---	---	---	---	---	---
20	Orient Tanneries	Dhaka	---	2/7/94	66	24000	43.8	0.244	6.069	---	---	---
21	B. S. Leather	Dhaka	2/7/94	2/7/94	---	41500	---	---	---	---	---	---
22	Abul Khaer Tannery	Dhaka	4/7/94	4/7/94	---	28500	---	---	---	---	---	---
23	Amin Tannery	Dhaka	28/6/94	28/6/94	---	23000	1603	0.7	0.621	---	---	---
24	Dhaka Hides & Skins	Dhaka	2/7/94	2/7/94	---	40000	---	---	---	---	---	---
25	Karim Tannery	Dhaka	3/7/94	3/7/94	92	36500	---	---	---	---	---	---
26	Noakhali Tannery	Dhaka	4/7/94	4/7/94	---	37000	---	---	---	---	---	---
27	Modina Tannery	Dhaka	3/7/94	3/7/94	72	26500	531.3	0.487	0.794	---	---	---
28	Dhaka Tanneries Ltd.	Dhaka	3/7/94	3/7/94	---	36000	---	---	---	---	---	---
29	Gulshan Tannery	Dhaka	4/7/94	4/7/94	95	45500	---	---	---	---	---	---
30	Mohin Tannery	Dhaka	28/6/94	28/6/94	---	16000	361.3	0.273	0.483	---	---	---
31	Kid Tannery	Dhaka	29/6/94	29/6/94	510	45000	4043	1.944	0.736	---	---	---
32	Helal Tannery	Dhaka	28/6/94	28/6/94	---	23000	2232	0.983	0.571	---	---	---

contd.....

ANALYSIS OF INDUSTRIAL WASTE WATER

TYPE OF INDUSTRY : *TANNERY*

TEST RESULT

SL. NO.	NAME OF INDUSTRY	LOCATION	Date of Sampling	Sample Received At BRTC	PARAMETER AND CONCENTRATION PRESENT							
					pH	BOD_5 mg/L	COD mg/L	Suspended Solids Mg/L	Sulphate (SO_4) mg/L	Sulphide mg/L	Nitrate (N) mg/L	Kjeldahl-N mg/L
33	Millat Tannery	Dhaka	28/6/94	28/6/94	3.5	3300	4500	16486	2380.8	80	50	610
34	East Asia Tannery	Dhaka	29/6/94	29/6/94	10.8	6000	16500	6109	124.8	90	27.5	142.5
35	H & H Leather Ind.	Dhaka	29/6/94	29/6/94	9.8	7200	21000	11393	624	65	525	230
36	Rupali Tannery	Dhaka	29/6/94	29/6/94	8.4	4500	4950	8492	289.6	75	650	205
37	Arafat Tannery	Dhaka	29/6/94	29/6/94	8.6	2400	3000	9317	2515	60	137.5	650
38	Rowshan Tannery	Dhaka	28/6/94	28/6/94	9.5	5400	8600	7292	672	70	40	800
39	Rift Leather Complex	Chittagong	---	2/7/94	9	12000	13800	25886	1142.4	150	16	82
40	Cresent Tannery Ltd.	Dhaka	4/7/94	4/7/94	8.7	24600	937900	25244	---	---	---	---
41	Diamond Tannery	Dhaka	28/6/94	28/6/94	10.8	5400	10500	6912	105.6	360	130	152.5
42	Praxis Tannery	Chittagong	5/7/94	5/7/94	8.8	11400	17500	9003	652.8	10	25	34
43	Yousuf Leather Corp.	Dhaka	17/7/94	17/7/94	11.7	1050	1540	4323	---	175	--	--
44	Yousuf Leather Corp.	Dhaka	18/7/94	18/7/94	4.3	2550	310	7730	---	--	---	---
45	Yousuf Leather Corp.	Dhaka	19/7/94	19/7/94	7	4110	6500	8965	---	---	---	---
46	Yousuf Leather Corp.	Dhaka	18/7/94	18/7/94	3.5	1100	2250	15868	3868.8	---	---	---
47	Yousuf Leather Corp.	Dhaka	18/794	18/794	8.7	2200	3 800	6856	2736	---	---	1650

Contd......

ANALYSIS OF INDUSTRIAL WASTE WATER

TYPE OF INDUSTRY : *TANNERY*

TEST RESULT

SL. NO.	NAME OF INDUSTRY	LOCATION	Date of Sampling	Sample Received At BRTC	PARAMETER AND CONCENTRATION PRESENT							
					Kjeldahi-N (mg/L	Chloride (Cl) mg/L	Chromium (Cr) mg/L	Lead (pb) mg/L	Zinc (Zn) gm/L	Turbidity NTU	Colour TCU	Total Solids mg/L
33	Millat Tannery	Dhaka	28/6/94	28/6/94	610	3100	677.2	1.202	---	---	---	---
34	East Asia Tannery	Dhaka	29/6/94	29/6/94	142.5	53500	350	0.333	---	---	---	---
35	H & H Leather Ind.	Dhaka	29/6/94	29/6/94	230	57500	501.9	0.73	---	---	---	---
36	Rupali Tannery	Dhaka	29/6/94	29/6/94	205	4450	1721	0.899	---	---	---	---
37	Arafat Tannery	Dhaka	29/6/94	29/6/94	650	47500	73.8	0.488	--	--	--	--
38	Rowshan Tannery	Dhaka	28/6/94	28/6/94	800	22000	932	0.8	---	---	---	---
39	Rift Leather Complex	Chittagong	---	2/7/94	82	32000	479.1	0.546	---	---	---	---
40	Cresent Tannery Ltd.	Dhaka	4/7/94	4/7/94	---	32000	---	---	---	---	---	---
41	Diamond Tannery	Dhaka	28/6/94	28/6/94	152.5	21500	---	0.54	---	---	---	---
42	Praxis Tannery	Chittagong	5/7/94	5/7/94	34	62500	80.6	0.308	--	--	--	--
43	Yousuf Leather Corp.	Dhaka	17/7/94	17/7/94	---	---	--	---	---	---	---	---
44	Yousuf Leather Corp.	Dhaka	18/7/94	18/7/94	--	---	---	---	---	---	---	---
45	Yousuf Leather Corp.	Dhaka	19/7/94	19/7/94	---	17250	--	---	---	---	---	---
46	Yousuf Leather Corp.	Dhaka	18/7/94	18/7/94	---	---	3818	---	---	---	---	---
47	Yousuf Leather Corp.	Dhaka	18/794	18/794	1650	---	---	--	--	--	--	--